COOLING RAPIDLY AND RELAXING

SLOWLY WITH 4f IONS

A THESIS SUBMITTED TO THE UNIVERSITY OF MANCHESTER FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

JOSEPH WILLIAM SHARPLES

2013
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<td>[Fe^{III}d(bta)<em>{6}O</em>{6}(OMe)<em>{15}Cl</em>{6}]: a [Cs^{I}Ln^{III}(Ph_{2}acac)]<em>{n} chain: a [Mn^{II}(N</em>{3})<em>{2}(pyz)] layer; and the [Gd^{III}(HCOO)]</em>{n} network.</td>
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<td>The Zeeman effect removes the degeneracy of the $S = \frac{1}{2}$ state, splitting it into $(2S+1) m_s$ states, upon application of a magnetic field, $H$.</td>
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Hysteresis loops for $\{\text{Mn}_{12}\}$.  

Arrhenius plot of $\ln \tau$ versus $1/T$ for $[[\text{Dy}^{\text{III}}\text{Cp}^\prime_2(\mu-\text{SSiPh}_3)]_2]$. 

$\chi'$ (upper) and $\chi''$ (lower) versus $T$ plots for $[\text{Mn}_{8}^{\text{III}}\text{Mn}_{4}^{\text{IV}}\text{O}_{12}(\text{O}_{2}\text{CCH}_{2}\text{Br})_{16} (\text{H}_2\text{O})_4]$. 

Left: The torus-wheel $[\text{Mn}^{\text{III}}_{84}\text{O}_{72}(\text{O}_{2}\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{12}(\text{OH})_6]\cdot x\text{H}_2\text{O}\cdot y\text{CHCl}_3$. 

The vertex-sharing supertetrahedron $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_{7}\text{O}_{8}(\text{N}_3)_{8}(\text{L}_3)_{12}(\text{MeCN})_6]\text{Cl}_2\cdot 10\text{MeOH}\cdot \text{MeCN}$. 

The lanthanide elements from Ce ($4f^1$) to Lu ($4f^{14}$) and including La and Y along with their atomic numbers. 

Representation of the $4f$ orbitals by a general set, from top to bottom, left to right: $4f_{z^2}$; $4f_{x^2-y^2}$; $4f_{xy}$; $4f_{x^2-3y^2}$; $4f_{y^2-3x^2}$; $4f_{x^2}$ and $4f_{y^2}$. 

Electronic configuration of the $4f$ electrons of samarium(III) and terbium(III) and the orbital angular momentum of each orbital. 

From left to right, the energy level diagram of the electronic states in dysprosium(III) when electronic repulsion, spin-orbit coupling, and the crystal field are taken into account. 

Energy level diagram for the paired $m_J$ states of $\text{TBA}^+[[\text{Tb}^{\text{III}}\text{Pc}_2]]^-$ and $\text{TBA}^+[[\text{Dy}^{\text{III}}\text{Pc}_2]]^-$. 

The quadrupole-approximations of electron density for the ground terms of the lanthanide(III) series, from cerium(III) to
The angular dependence of the 4f electron density for the lanthanide(III) series, from cerium(III) to ytterbium(III), omitting europium(III) and gadolinium(III).

Structure of TBA$^+$[Ln$^{III}$Pc$_2$]$^-$.  

Left: [Ln$^{III}$$_2$({Me$_3$Si}$_2$N)$_4$(THF)$_2$(µ-$η^3$:$η^2$-N$_2$)]$. Centre: $χM$ versus $T$ for {Gd$^{III}$$_2$(N$_2$)} and {Gd$^{III}$$_2$(N$_2$)'}, the latter showing much stronger coupling. Right: $χM$ versus $T$ for {Dy$^{III}$$_2$(N$_2$)} and {Dy$^{III}$$_2$(N$_2$)'}, showing qualitatively similar behaviour to the gadolinium(III) analogue.

Arrhenius plot of $\ln \tau$ versus $1/T$ for {Dy$^{III}$$_2$(N$_2$)'}$-$ and {Dy$^{III}$$_2$(N$_2$)}.

Hysteresis loops between 11 and 15 K for {Tb$^{III}$$_2$(N$_2$)'}$^-$.  

The square-based pyramid [Dy$^{III}$$_5$O(O'tBu)$_12$].

$χ''$ versus $T$ for [Dy$^{III}$$_5$O(O'Pr)$_{13}$].

The octahedral [Dy$^{III}$$_4$K$_2$O(O'Bu)$_{12}$].

Left: [Dy$^{III}$$_3$($μ$$_3$-OH)$_2$(L)$_3$Cl(H$_2$O)$_2$]. Right: A representation of the orientation of three dysprosium(III) spins in a toroidal arrangement.

Main: magnetisation versus field for both isomers of {Dy$^{III}$$_3$}, water solvate, in a 0-7 T field: $□$ and acetonitrile / methanol solvate: ●. Inset: Hysteresis of magnetisation loops for the latter version in a 0±1 T a.c. field.
Left to Right, \[\text{[U}^{\text{III}}\text{I}_3(\text{THF})_2],\] \[\text{[U}^{\text{III}}\text{I}_3\text{N(SiMe}_3)_2]\] and \[\text{[U}^{\text{III}}\text{I}_3\text{CH(PPh}_3\text{NSiMe}_3)_2]\].

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<td>(E (m_s) = m_s g \beta H)</td>
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<tr>
<td>2</td>
<td>(M_{\text{sat}} = g S)</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>(\chi = M / H)</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>(\chi_M = \chi_{\text{Para}} + \chi_D)</td>
<td>25</td>
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<tr>
<td>5</td>
<td>(\chi_M = \frac{N g^2 \beta^2}{3 k_B T} S(S + 1))</td>
<td>25</td>
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<td>6</td>
<td>(\chi_M T = C)</td>
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</tr>
<tr>
<td>7</td>
<td>(\chi_M T = \frac{g^2}{8} S(S + 1))</td>
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<td>8</td>
<td>(\chi_M = \frac{C}{T - \theta})</td>
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<td>9</td>
<td>(\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2)</td>
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<tr>
<td>10</td>
<td>(J = 0.0123 \varphi - 1.364 \text{ cm}^{-1})</td>
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<tr>
<td>11</td>
<td>(\chi_M = \frac{(\chi_x + \chi_y + \chi_2)}{3})</td>
<td>29</td>
</tr>
<tr>
<td>12</td>
<td>(\chi_M = \frac{(\chi_x^2 + \chi_y^2 + \chi_2^2)^{1/2}}{3})</td>
<td>29</td>
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</table>
\[ E(m_s) = D \frac{m_s^2 - 5(S + 1)}{3} \]

\[ U = |D|S^2 \]

\[ \tau = \frac{1}{2\pi v} \]

\[ \tau = \tau_0 e^{\frac{U_{\text{eff}}}{k_B T}} \]

\[ D \propto -\frac{1}{S^2} \]

\[ J = L+S, L+S-1 \ldots L-S \]

\[ \hat{H} = -2J \hat{S}_{\text{radical}} \cdot (\hat{S}_{\text{Gd1}} + \hat{S}_{\text{Gd2}}) - z' <S_z> S_z \]

**List of Abbreviations and Symbols**

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<td>Alternating current</td>
<td>a.c.</td>
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<td>Anisotropy barrier</td>
<td>( U_{\text{eff}} )</td>
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<tr>
<td>Avogadro’s number</td>
<td>N</td>
</tr>
<tr>
<td>Blocking temperature</td>
<td>( T_B )</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>( k_B )</td>
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<tr>
<td>Curie constant</td>
<td>C</td>
</tr>
<tr>
<td>Curie temperature</td>
<td>( T_C )</td>
</tr>
<tr>
<td>Diamagnetic susceptibility</td>
<td>( \chi_D )</td>
</tr>
<tr>
<td>Direct current</td>
<td>d.c.</td>
</tr>
<tr>
<td>Electronic Bohr magneton</td>
<td>( \beta )</td>
</tr>
<tr>
<td>Frequency</td>
<td>( \nu )</td>
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Hamiltonian operator \( \hat{H} \)

In-phase susceptibility \( \chi' \)

Isotropic exchange constant \( J \)

Jahn-Teller \( J_{\text{JT}} \)

Landé g-factor \( g \)

Magnetic Field \( H \)

Mean value of the Z-component of the spin operator \( \langle S_z \rangle \)

Molar magnetic susceptibility \( \chi_M \)

Néel temperature \( T_N \)

Nuclear spin \( I \)

One, two and three-dimensional \( 1\text{-D, } 2\text{-D and } 3\text{-D} \)

Orbital angular momentum \( L \)

Out-of-phase susceptibility \( \chi'' \)

Overall angular momentum \( J \)

Paramagnetic susceptibility \( \chi_{\text{Para}} \)

Polyoxometallates \( \text{POMs} \)

Quantum tunnelling \( \text{QT} \)

Quantum tunnelling of magnetisation \( \text{QTM} \)

Radius \( r \)

Relaxation time \( \tau \)

Saturation magnetisation \( M_{\text{sat}} \)

Second order Steven’s constant \( \alpha \)

Single-ion zero-field splitting parameter \( d \)

Single-molecule magnets \( \text{SMMs} \)

Spin angular momentum \( S \)

Spin operator \( \hat{S}_n \)
<table>
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<td>Spin-Orbit Coupling</td>
<td>SOC</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
</tr>
<tr>
<td>Thermally assisted quantum tunnelling</td>
<td>TA-QT</td>
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<tr>
<td>Time constant</td>
<td>$\tau_0$</td>
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<tr>
<td>Volume susceptibility</td>
<td>$\chi$</td>
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<td>Weiss constant</td>
<td>$\theta$</td>
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<tr>
<td>$Z$-component of the spin operator</td>
<td>$S_Z$</td>
</tr>
<tr>
<td>Zero-dimensional</td>
<td>0-D</td>
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<tr>
<td>Zero-field splitting parameter</td>
<td>$D$</td>
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Abstract

Cooling Rapidly and Relaxing Slowly with 4f Ions: A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences.

Anisotropic magnetic materials have been proposed over the past twenty years or so as candidates for high density storage, so-called Single-Molecule Magnets (SMMs). These may in future be used to store data at the level of an individual molecule. Separately, isotropic materials may be harnessed for their large magnetocaloric effect which enables them to be used as refrigerants. These can potentially replace the increasingly rare and therefore expensive $^3$He and $^4$He currently employed either separately or in $^3$He-$^4$He dilution refrigerators.

This thesis examines the use of lanthanide(III) ions for these applications, by detailing the synthesis, characterisation and performance of three new classes of zero-dimensional compounds, $\{\text{Ln}^{III}\}_2$, $\{\text{Ln}^{III}\}_2\text{Zn}^{II}_4$ and $\{\text{Ln}^{III}\}_7$. These are assessed by several techniques including SQUID magnetometry, heat capacity measurements, luminescence spectroscopy, Electron Paramagnetic Resonance spectroscopy and *ab initio* calculations. In doing so we extended the use of a tripodal ligand widely employed in 3$d$ chemistry to 4$f$ ions, and found only the second 3$d$-4$f$ phosphonate SMM.

Investigating several members of a known three-dimensional lanthanide(III) polymer, $\{\text{Ln}^{III}\}_n$, showed the isotropic gadolinium(III) analogue is one of the very best of all known magnetic refrigerants in the low-temperature regime.

Joseph W. Sharples
September 2013
Declaration

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Acknowledgements and Messages

First of all, a huge “thank you” to my supervisor for these past, nearly four, years, Professor David Collison, for his unflagging support and advice of one sort and another. Hopefully all those train journeys at ungodly hours paid off.

Also, thanks to Mark Whiteley, one of the nicest and most helpful people imaginable, who supervised my 3rd-year and MChem projects, for setting me off on further roads, and to both Emma and Hannah for their good influence then and since.

To Professors Eric McInnes and Richard Winpenny for advice and inspiration. Sorry this took so long Richard, it wasn’t deliberate, honest!

To Iain May for what seems to have been a career defining chat a long, long time ago...

In the Magnets Group and beyond, thanks to Floriana Tuna for her expertise with EPR and SQUID.

To Stephen Sproules for help with EPR and being so knowledgeable about almost everything, danke sehr. Thanks to Asad for everything over the past eight (help!) years. Won’t forget seeing England keep The Ashes at Old Trafford, rain and all. To Eufemio, Panama’s greatest scientist! One day, maybe, I’ll get there... Thanks to Luke and Tom for being magnets-heroes to worship. To all those past and present members who’ve offered up some help or advice, you’re all wonderful. A special thanks to those who had to endure my tortuous writing up and for their (unwitting or otherwise) support through it, especially James, Sam and Claire.

For the newer Magnets Group members at Manchester and those venturing abroad (Scotland), best wishes! Keep your enthusiasm if possible. And good luck to all MChem students who passed through my orbit. I noticed not many of you stuck with chemistry though... To the latest project students Tom (Prodigy) and Hatty, I hope you get what you want!

Even more recently I made the geographically short move to the National EPR Service. I’m so grateful to know the wonderful people Chloe, Simon and Dan who haunt the Alan Turing Building. Thanks for keeping me at least slightly sane whilst figuring things out over there!
To my brothers John and Ben: Hurrah, made it this far! Thanks for all the things that have made this more bearable. Maybe all those weird side-projects can get done now... rockets, weather balloons, rail-guns, prog-rock albums??? So much to catch up with...

Lastly, thanks to my parents for all the moral support and the amazing chances they’ve given me over the years (not to mention living in the same house as me and John for the past few years in particular).
The Golden Age is before us, not behind us

Sallust
Chapter 1: Introduction
Chapter One: Introduction

Rationale for submitting this thesis in the alternative format

The alternative format thesis is suitable for this thesis as it concerns a number of well defined, though closely related, sections, namely the four sets of compounds which have been investigated. Chapter Four is a good example of why publication is beneficial; herein there are described novel compounds which at the time showed a large $U_{\text{eff}}$ energy barrier and magnetocaloric effect. Delaying publication would significantly diminish the impact of this work, as further advances are made in a rapidly expanding field. For all those contributing publication is thus desirable, particularly for those facilities whose only exposure is by their work in journals, such as the National EPR Facility utilised in Chapter Seven. As the thesis author’s work is exemplified by the manuscripts and publications presented here, the alternative format is deemed appropriate. The thesis author was also invited to publish a review article included as Chapter Three.

Organisation of this thesis

Chapter One is a general introduction to the field of magnetism, lanthanides and single-molecule magnetism. Chapter Two sets out the aims of this project. Chapter Three is a Review Paper discussing materials reported to show a large magnetocaloric effect over the past twenty-or-so years. Chapter Seven is a Review Paper in manuscript form discussing $3d$-$4f$ and $4f$ amino-polyalcohol compounds and their magnetic properties. Chapters Four, Five, Six and Eight are original research articles published, submitted or in the form of journal articles.

Contributing Authors

Chapter 3, Paper 1, “Coordination compounds and the magnetocaloric effect” is a review paper written by the thesis author with contributions from Professor David Collison concerning research published over the past twenty years in the field of magnetocaloric materials.
Chapter 4, Paper 2, “Lanthanide discs chill well and relax slowly” is an original research communication written by the thesis author with contributions from all listed authors. Synthesis was performed by the thesis author; X-ray crystallography by Yan-Zhen Zheng; SQUID measurements by Floriana Tuna; and analysis by the thesis author, Floriana Tuna, Eric McInnes and David Collison.

Chapter 5, Paper 3, “Using heat capacity measurements to probe magnetocaloric materials” is an original research article written by the thesis author. Synthesis and X-ray crystallography were performed by the thesis author and SQUID magnetometry by the thesis author and Floriana Tuna. Heat capacity measurements were performed by Marco Evangelisti and computer simulations by Jürgen Schnack. Analysis was by the thesis author, Marco Evangelisti and Floriana Tuna.

Chapter 6, Paper 4, “Investigations into the magnetocaloric and single-molecule magnet behaviour of \([\text{Ln}^{III}_2\text{Zn}^{II}_4]\) bicapped butterflies” is an original research article written by the thesis author. Synthesis and X-ray crystallography were performed by the thesis author. SQUID magnetometry was performed by the thesis author and Floriana Tuna, EPR was performed by the thesis author and Stephen Sproules, luminescence spectroscopy was performed by the thesis author and Adam Swinburne. Calculations were carried out by Nicholas Chilton. Analysis was performed by the thesis author.

Chapter 7, Paper 5, “The coordination chemistry and magnetism of some 3d-4f and 4f amino-polyalcohol compounds” is a review paper written by the thesis author with contributions from Professor David Collison concerning those 3d-4f and 4f molecules reported using triethanolamine and diethanolamine ligands.

Chapter 8, Paper 6, “Lanthanide(III) triethanolamine dimetallic compounds with bulky carboxylate ligands and the magnetocaloric effect” is an original research article written by the thesis author. Synthesis and X-ray crystallography were performed by the thesis author, with additional synthesis...
from Lois Lindley, an MChem student at The University of Manchester. SQUID magnetometry was performed by the thesis author and Floriana Tuna, luminescence spectroscopy was performed by the thesis author and Adam Swinburne. Simulations into the magnetocaloric effect were performed by the thesis author. Analysis was performed by the thesis author.

Appendix, Paper 7, “A Dense Metal-Organic Framework for Enhanced Magnetic Refrigeration” is an original research article written by Marco Evangelisti and international collaborators. SQUID magnetometry was performed by the author, Floriana Tuna and Marco Evangelisti. Synthesis was performed by the thesis author. Interpretation of magnetic and magnetocaloric data from SQUID magnetometry was performed by the thesis author, Marco Evangelisti and other authors. X-ray Crystallography was performed by Euan K. Brechin. This covers content included in Chapter 5, Paper 3 “Using heat capacity measurements to probe magnetocaloric materials.”
Chapter 2: Magnetism, Lanthanides and Single-Molecule Magnets
1. Metal co-ordination complexes, lanthanides, and general principles of magnetism

1.01 Paramagnetic metal co-ordination complexes

Paramagnetic metal co-ordination complexes have at least one metal ion bonded to, or connected by, ligands with at least one of these parts possessing an unpaired electron. Zero-dimensional (0-D) compounds, such as simple monometallic species or polymetallic “cages”, infinite 1-D chains, 2-D layers and 3-D networks, are known, as shown in Figure 1(a-d) in turn.

Fig. 1. Left to right 0→3D compounds: a) Core of \([\text{Fe}^{III}]_{14}(\text{bta})_{6}\text{O}_{6}\text{(OMe)}_{18}\text{Cl}_{6}\), where bta is benzotriazolate; b) \([\text{CsI}^{I}\text{Ln}^{III}(\text{Ph}_{2}\text{acac})_{4}]_{n}\) chain; c) \([\text{Mn}^{II}(\text{N}_{3})_{2}(\text{pyz})]_{n}\) layer, where pyz is pyrazine; and d) \([\text{Sm}^{III}(\text{HCOO})_{3}]_{n}\) network. Key: Fe\(^{III}\), orange; O, red; N, light blue; Ln\(^{III}\), deep purple; Cs, blue; Mn\(^{II}\), pale pink; C, light grey; no H atoms are shown for clarity.

These materials have myriad current and proposed applications such as contrast agents in magnetic resonance imaging, quantum bits in powerful new types of computers, luminescent light sources, high density memory in storage devices using single-molecule magnets (SMMs), and low temperature refrigerants. SMMs make up most research in the field of “Molecular Magnetism”, which until recently focussed on 0-D 3d metal cages. In fact, for SMMs, the large single-ion anisotropies of ions such as Dy\(^{III}\) can be an improvement upon conventionally employed ions such as Co\(^{II}\) and Mn\(^{III}\). Similarly the large and isotropic single-ion spin of Gd\(^{III}\) can result in superior magnetic refrigerants compared to Fe\(^{III}\). This chapter examines the most significant research since the first SMM-behaviour was discovered more than twenty years ago after a general introduction to magnetism, before discussing how lanthanide ions have revolutionised this area of research.
1.02 Electron spin and magnetisation

An electron in motion generates a magnetic moment from the combination of its spin, $S$, and orbital angular momentum, $L$, classically due to its spinning on its axis and by orbiting the nucleus, respectively.\textsuperscript{14} The electron has a spin, $S$, of $\frac{1}{2}$, composed of $(2S+1)$ $m_s$ microstates (= 2), labelled as $\pm \frac{1}{2}$, which denote two orientations of the electron with respect to the magnetic field, $H$. The paired $m_s$ states split, i.e. their degeneracy is removed, in a process called the Zeeman effect, shown in Figure 2, upon application of a magnetic field.

$$m_s = \pm \frac{1}{2}$$

\textbf{H}

*Fig. 2. The Zeeman effect removes the degeneracy of the $S = \frac{1}{2}$ state, splitting it into $(2S+1)$ $m_s$ states, upon application of a magnetic field, $H$.}

The energies of these states are given by Equation 1, where $g$ is the Landé g-factor, $\beta$ the electronic Bohr Magneton and $H$ the magnetic field strength. With unpaired electrons in an orbital the population of the lower energy (ground) state is increased when a magnetic field is applied as Maxwell-Boltzmann statistics imply, as one state is lowered in energy relative to the degenerate pair and the other raised. Lowering the temperature or increasing the magnetic field strength increases this ground state population.\textsuperscript{15,16}

$$E(m_s) = m_s g \beta H \textbf{ Equation 1}$$

Classically, spins are aligning with the field and the sample is magnetised. Saturating the material with a large enough field leaves only the ground ($m_s$) state populated where the saturation magnetisation, $M_{\text{sat}}$, is given by Equation 2 (in Bohr magnetons units), and $S$ is the ground spin state.

$$M_{\text{sat}} = g S \textbf{ Equation 2}$$

It should be remembered that $S$ and $L$ are simply labels, retained from this classical picture and in reality are quantised, taking only certain values.
1.03 Magnetic susceptibility and the Curie Law

The magnetic susceptibility of a compound describes how readily it can be magnetised in a magnetic field and is given by Equation 3, where $\chi$ is the volume susceptibility.\textsuperscript{15,16}

$$\chi = M / H \text{ Equation 3}$$

This can be converted to the more useful molar susceptibility, $\chi_M$, which is composed of the diamagnetic and paramagnetic susceptibilities, $\chi_D$, and $\chi_{\text{Para}}$. The former is due to electron pairs interacting with the magnetic field, and the latter to unpaired electrons. Paramagnetic species will have a diamagnetic contribution, opposite in direction, from their own filled orbital shells, which is almost always swamped in magnitude by the paramagnetism. Exceptions arise in $S = 1/2$ systems with large organic ligands. In general this behaviour is given by Equation 4.

$$\chi_M = \chi_{\text{Para}} + \chi_D \text{ Equation 4}$$

Accounting for the diamagnetism of a compound, often performed using Pascal’s Constants, gives the corrected $\chi_M$, hereafter magnetic susceptibility.

The Curie law, given in Equation 5, relates the magnetic susceptibility to temperature:

$$\chi_M = \frac{N g^2 \beta^2}{3 k_B T} S(S + 1) \text{ Equation 5}$$

where $N$ is Avogadro’s number, $k$ the Boltzmann constant, $T$ temperature and $S$ the ground state spin. Collecting terms gives the Curie constant $C$, defined as $N g^2 \beta^2 / 3 k \cdot S(S+1)$.

$$\chi_M T = C \text{ Equation 6}$$

Equation 7 is a useful approximation of Equation 5, where $\chi_M T$ values can be easily related to ground state spin values.

$$\chi_M T = \frac{g^2}{8} S(S + 1) \text{ Equation 7}$$

The variation of $\chi_M T$, or $\chi_M$, with temperature gives information on the interactions between metals when a deviation from Curie behaviour is seen. Curie behaviour implies a constant value of $\chi_M T$ with varying temperature due to non-interacting spins and using the Curie-Weiss law, given by Equation 8, relates the sign of the Weiss constant, $\theta$, to the nature of this interaction. A negative Weiss constant usually indicates an antiferromagnetic interaction and a positive Weiss constant
ferromagnetic interactions, \(^{16}\) although discrepancies can arise due to other factors such as an orbital contribution to the magnetisation.

\[
\chi_M = \frac{c}{T-\theta} \quad \text{Equation 8}
\]

A better characterisation would use a model of magnetic exchange interactions in conjunction with experimental magnetisation or susceptibility data to obtain coupling constants, which quantify the strength and nature of such effects, as discussed below.

### 1.04 Ferromagnetic and antiferromagnetic exchange

The magnetic moments (spins) on individual metals or ligands can interact, illustrated here with a hypothetical dimer of two \(S = \frac{1}{2}\) spins, which align in parallel or antiparallel fashion. The first case, known as ferromagnetic coupling, generates an \(S = 1\) ground state (Figure 3, left), by addition of the magnetic moment vectors. The second case, by their subtraction, gives an \(S = 0\) (diamagnetic) ground state (Figure 3, right) and is termed antiferromagnetic coupling. \(^{16}\)

Fig. 3. Left: An \(S = 1\) ground state by ferromagnetic coupling between two \(S = \frac{1}{2}\) spins. Right: An \(S = 0\) ground state from antiferromagnetic coupling of the same spins. The excited states are separated from the ground state by the exchange interaction, \(-2J\). Adapted. \(^{16}\)

Both states occur with a separation given by one commonly used convention as \(-2J\), called the isotropic exchange constant, where a stronger coupling gives a larger separation. A negative \(J\) signifies antiferromagnetic coupling, and a positive \(J\) ferromagnetic coupling, with units typically in \(\text{cm}^{-1}\) or K. Again, different conventions are used, which give different signs to the same interaction depending on the form of the Hamiltonian.
1.05 Modelling exchange interactions

For interacting spins we can define the simplest spin Hamiltonian by Equation 9, where $\hat{H}$ is the Hamiltonian operator, $-2J$ is the isotropic exchange constant and $\hat{S}_n$ is the spin operator for each spin.\(^{17}\)

$$\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2 \text{Equation 9}$$

Other forms are in common usage with $J$ (not $2J$) terms or varying sign conventions, for example, so care is needed to compare parameters obtained from different sources. Factors such as Zeeman splitting, spin-orbit coupling, the crystal field and the nuclear hyperfine interaction can also be taken into account by extending the Hamiltonian, which may account for differing values of $g$ (in anisotropic systems), or multiple exchange interactions in larger complexes, where more than one $J$ may be required. Modelling the magnetisation of a compound as a function of temperature and comparing the fit against experimental data can then confirm the nature and strength of coupling, anisotropy and ground state spin.

1.06 Super-exchange

The super-exchange pathway dominates the interaction between spins and occurs by overlap of the spin containing orbitals with intervening ligand orbitals. In $d$-transition chemistry simple relationships have been found which relate ferromagnetic or antiferromagnetic coupling to the bridging angles between metal or radical orbitals.\(^{16}\)

Although the mechanism of this process is less obvious for the lanthanides, owing to the relative lack of concerted studies, an empirical equation was established for gadolinium(III) by comparing the fitted $J$ values of more than twenty gadolinium compounds with a GdO$_2$Gd unit and a Gd-O-Gd bridge.\(^{18}\) This study found $J$ varies with the bridging angle by Equation 10, where $\phi$ is the bridging angle in degrees, and accounts for all but one of the measured compounds.

$$J = 0.0123\phi - 1.364 \text{ cm}^{-1} \text{Equation 10}$$

From this it is shown that ferromagnetic coupling occurs when $\phi$ is more than 110.9 °. Whilst limited and not universal across the lanthanide elements, the results could inform studies using strongly directing ligands to fix angles between metal ions to control the exchange, which is not always currently possible. The lack of control available may have influenced the development of single-ion SMMs, vide infra\(^{e,8,19}\).
1.07 The Curie Law, $\chi_M T$ and exchange coupling

The magnetic behaviour of compounds with magnetically non-interacting ions, where the orbital angular momentum is also quenched, follows the Curie law, giving a constant value of $\chi_M T$, recalling the Curie constant in Equation 6. Deviations from this can indicate an exchange interaction between spins. A useful way to assess these interactions is to calculate $\chi_M T$ values at room temperature and compare them to experimental results. For example, for a gadolinium(III) dimetallic with two $S = \frac{7}{2}$ spins, Equation 7 gives $\chi_M T$ as 15.75 cm$^3$ K mol$^{-1}$. If the experimental room-temperature value is larger, or smaller, this can indicate ferromagnetic, or antiferromagnetic interactions, respectively, between spins.

With weak exchange then only at low temperatures would differences compared to a non-interacting system be apparent: when the exchange interaction becomes significant compared to the thermal energy available, an increase or decrease in $\chi_M T$ is seen.

Antiferromagnetic exchange occurs below the Néel temperature, $T_N$, giving a decrease in magnetic susceptibility (and $\chi_M T$), whilst ferromagnetic exchange occurs below the Curie temperature, $T_C$, where $\chi_M$ (and $\chi_M T$) increases. Above these two temperature limits the behaviour is paramagnetic, the magnetic susceptibility decreases with increasing temperature as thermal energy randomises the spins, and $\chi_M T$ is constant. These observations are summarised in Figure 4 ($\chi_M T$ versus $T$, left and $\chi_M$ versus $T$, right, for ferromagnetically- (red), antiferromagnetically- coupled (blue), and uncoupled- (black) spins).

Fig. 4. Left: $\chi_M T$ versus $T$ and plots for idealised ferromagnetically-, antiferromagnetically-, and non-, coupled spins, shown as black, blue and red symbols respectively. Right: The same for $\chi_M$ versus $T$. 
1.08 Zero-field splitting and anisotropy

$\chi_M$ is an average susceptibility, obtained when measuring a powdered sample. It is composed of three parts as given by Equation 11, where $\chi_x$, $\chi_y$ and $\chi_z$ are susceptibilities measured by applying a field along one axis of a crystal of the desired compound.\(^{15}\)

$$\chi_M = \frac{(\chi_x + \chi_y + \chi_z)}{3} \text{ Equation 11}$$

A more anisotropic sample is better described with Equation 12:

$$\chi_M = \frac{(\chi_x^2 + \chi_y^2 + \chi_z^2)^{1/2}}{3} \text{ Equation 12}$$

One result of anisotropy is that, in systems with $S > \frac{1}{2}$, $S$ states are split into their constituent $m_s$ states in zero-field by an amount proportional to $D$, the zero-field splitting parameter, which has important consequences for SMM behaviour. Second order SOC also contributes to introducing this zero-field splitting in a spin state and a negative $D$ value is a pre-requisite in SMMs as will be discussed below.\(^{16}\)

1.09 The first single-molecule magnets: anisotropy barriers and blocking temperatures

A single-molecule magnet is a coordination compound that retains a magnetisation, $M$, in the absence of an applied magnetic field, $H$. Applying $H$ in the opposite direction gives $-M$. These two distinct magnetised states led to SMMs being proposed as candidates for magnetic data storage at much higher densities than current technologies.\(^{8}\) These two states ($+M$, $-M$) correspond to the 0 and 1 states of conventional “bits”, or pits and troughs in discs.

An SMM has $S$ and a negative $D$. Here the first SMM and its derivatives, with $S = 10$, are used to illustrate how SMMs work and why these conditions are required. Then possible ways to improve SMM performance will be discussed. Although this directly relates to $d$-block SMMs, most of the terminology is common to $3d$-$4f$ and $4f$ SMMs, which are introduced and compared in Section 2.

1.10 The first SMM: $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O} \cdot 2\text{CH}_3\text{CO}_2\text{H}$

The first and most studied SMM was discovered more than twenty years ago, namely $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O} \cdot 2\text{CH}_3\text{CO}_2\text{H}$\(^{20,21}\) abbreviated here as $\{\text{Mn}_{12}\}$. This is composed of a central $\{\text{Mn}^{\text{IV}}\text{O}_4\}$ cubane and outer $\{\text{Mn}^{\text{III}}\}$ ring, linked by $\text{O}^2-$ and $\text{O}_2\text{CCH}_3$.
The antiferromagnetic coupling between the Mn$^{\text{III}}$ and Mn$^{\text{IV}}$ ions gives an $S = 10$ ground state (Figure 5, right).

For an $S = 10$ system, the $m_s = 0, \pm 1, \pm 2, \pm 3... \pm 10$ states are degenerate in the absence of zero-field splitting. Arbitrarily introducing this splitting will remove their degeneracy according to $D$, with the energy of each $m_s$ doublet and the $m_s = 0$ singlet in a system of appropriate (axial) symmetry given by Equation 13.

$$E (m_s) = D \frac{m_s^2 - S(S+1)}{3} \text{ Equation 13}$$

With $-D$ the largest magnitude $|m_s|$ states are lowest in energy. These are equally populated, as denoted in the simplified picture, Figure 6, left, by the “Z” symbols.
Fig. 6. Left: $-D$ split energy levels for $S = 10$ ($H = 0$). Centre: Paired $m_S$ states are further split by the Zeeman effect ($H > 0$). Right: These states return to their paired multiplets ($H = 0$), leaving only one ($m_s = -10$) populated. Spin population is represented by $Z$. Adapted.16

In an applied field (Figure 6, centre) Zeeman splitting rearranges these states. Recalling Equation 1 which relates the energy of each $m_s$ state to the magnitude of $^s*$, in a large enough field, termed the high field limit, this order will be $m_s = -10, -9, -8, -7, -6, -5, -4, -3, -2, -1, 0, +1, +2, +3, +4, +5, +6, +7, +8, +9, +10$ from lowest to highest energy. In Figure 6, centre, we only approach this case, but this shows how states can move in energy.

The $m_s = -10$ state is now most stable and at low temperatures is exclusively populated, as the “Z” symbols indicate. Equation 2 which relates the $M_{sat}$ with the populated spin state says that, if we populate only one spin state, we will have a finite magnetisation, remembering that if each of a $\pm m_s$ state is populated then the resultant magnetisation will be nil. When the field is removed, as shown in Figure 6, right, one of the two magnetised states required for SMMs has been reached ($-M$); if a magnetic field had been applied in the opposite direction then an exclusive population of the $m_s = +10$ state would have been obtained ($+M$) and the same arguments apply.

Clearly, upon moving from the case shown in Figure 6, centre, to that in Figure 6, right, states will have moved and become degenerate on the way to their final energies. This is important as it represents a way in which magnetisation will be lost; if states with $\Delta m_s = \pm 1$ “cross” in this way then magnetisation (spin population) can be transferred, and the magnetisation will be lost. This scenario is not possible in the negative zero-field splitting case as the $m_s = -10$ state is always lowest in energy, but, conversely, a positive zero-field-splitting, $+D$, would order the $m_s$ states to
give $m_s = 0$ as lowest in energy in the absence of a magnetic field. Upon removal of the field we would then have a non-magnetised ground state, which is unsuitable for conventional SMMs. Note that the $m_s = -10$ state would always be lowest in energy in the high-field limit, but removal of the field depopulates the $m_s \neq 0$ levels, by the crossing mechanism mentioned above. Separately, with no (or very small) zero-field splitting, all $m_s$ states are degenerate at zero field and a magnetised state cannot be maintained.

1.11 Origin of $D$

In $\{\text{Mn}_{12}\}$ a Jahn-Teller (JT) elongated co-ordination environment for each Mn$^{\text{III}}$ ion contributes to a large zero field splitting. These JT axes are aligned approximately co-parallel and so their individual ion zero field splittings, $d$, combine to a larger total zero field splitting, $D$. Experiments demonstrated that $D = -0.70$ K, giving an energy gap, $U$, between ground and highest excited states ($m_s = \pm 10$ and $m_s = 0$) of 70 K, by Equation 14. For $\{\text{Mn}_{12}\}$ the next challenge is in maintaining these magnetised states in zero field.

$$U = |D|S^2 \text { Equation 14}$$

1.12 Anisotropy barriers to relaxation of magnetisation

Two relaxation processes hinder the retention of magnetisation in zero-field by reversion to an equal population of states. Simplifying this example to an $S = 3$ system, with states ordered by increasing energy as $\pm 3$, $\pm 2$, $\pm 1$ and 0, depicted in Figure 7, we assume that only the $m_s = -3$ state is populated. Thermal relaxation of magnetisation, or the “over the barrier” process, requires enough thermal energy for the spin population of the $m_s = -3$ state to be promoted to the highest energy state, here the $m_s = 0$, via a series of $\Delta m_s = +1$ steps. From here, via emission of thermal energy, the spin can populate other states by $\Delta m_s = -1$ steps to the $m_s = +3$ state (Figure 7, black dotted arrows). This equalises the populations of the $m_s = \pm 3$ states, removing any retained magnetisation.
Fig. 7. Energy level diagram for the $S = 3$ spin state in zero field with $-D$. Two relaxation processes are shown: i) thermal relaxation as dotted arrows and ii) quantum-tunnelling of magnetisation (QTM) as the solid black arrow. $U$, given by the green arrow is the gap between the ground and $m_s = 0$ state. Key: $m_s = \pm 3$, red; $\pm 2$, blue; $\pm 1$, green and 0, black.

The gap between ground and highest $m_s$ states, $U$, as given by Equation 14 for integer spin systems, is the energy required for this process.

In practice the barrier to relaxation of magnetisation is smaller than expected as another process reduces the amount of energy required, called the zero-field quantum-tunnelling mechanism\(^2\) (Figure 7, solid black arrow). This is a “through-the-barrier” process where the “spin” can shortcut the thermal barrier by moving from the $m_s = -3$ state to the $m_s = +3$ state directly, eventually equalising the populations of these states. This is temperature independent and so dominates at lower temperatures, where the thermal process cannot operate.

Combinations of these mechanisms are also possible, called thermally assisted quantum tunnelling, and are easily envisaged between, say, the $m_s = \pm 2$ states above. Overall, these relaxation processes combine to give an anisotropy barrier $U_{\text{eff}}$, which represents one of the ways in which the performance of SMMs is quantified.

1.13 Hysteresis and blocking temperatures to relaxation of magnetisation

In addition to $U_{\text{eff}}$, a second parameter can be used to quantify and to compare the performance of different SMMs; this is the “blocking temperature”, $T_B$, and is the highest temperature at which “hysteresis” loops are seen when the compound is magnetised. Hysteresis here means the maintaining of one of two distinct magnetised states depending on the history of the material. In an SMM these are only maintained below a certain temperature, $T_B$. Using Figure 8 it is possible to follow the results when $\{\text{Mn}_{12}\}^{20}$ is magnetised. This shows two loops, representing two different temperatures at which the experiment was performed, the outer loop at 2.2 K and the inner at 2.8 K. What these do not show is that at zero field the sample will initially be unmagnetised and $M$ (“Magnetization”) would be zero. However, once a field has been applied and removed, then there
will always be some remnant magnetisation, a finite value at zero field, as seen here for either temperature.

In either direction applying a field of ca. 1.75 T saturates the magnetisation. Crucially upon removing this field the remnant magnetisation is noticeably smaller for the 2.8 K loop, as the $U_{\text{eff}}$ barrier can be overcome by the thermal energy available to a greater extent in the timescale of the experiment. Lower temperatures “open” or widen these loops as the thermal energy barrier is harder to overcome. and a point will be found where $M = 0$ at zero field.

![Hysteresis loops for $\{\text{Mn}_{12}\}$ in a 0-2 T magnetic field for 2.2 K (●) and 2.8 K (○). Taken directly.](image)

Quantum-tunnelling in zero-field can prevent hysteresis loops from being seen at significant temperatures (> 1 K), despite the presence of large energy barriers. The hysteresis experiment shows this phenomenon as a series of steps at regular intervals of applied field. In Figure 8, seen best for the outer, 2.2 K loop there are rapid steps in the magnetisation periodically. This occurs when pairs of $m_s$ states on either side of the thermal barrier become degenerate and the spin population is equalised between them at a very low cost in energy, resulting in a sharp decrease in the magnetisation. These are dependent on how quickly the magnetic field is changed, the sweep rate of the field, as sweeping quickly can prevent the avoided-crossings of states that cause this phenomenon.

Of the two parameters $U_{\text{eff}}$ and $T_B$, Rinehart and Long identified that the former is the most suitable measure if only very brief periods of magnetisation are required but the second is more appropriate when timescales of about a second are needed. This is straightforward, because only in the absence of quantum-tunnelling will there be a remnant magnetisation for any appreciable length of time.
1.14 Quantifying the performance of SMMs

$U_{\text{eff}}$ and $T_B$ can be obtained by applying an a.c. field to an SMM, i.e. a field which continuously changes its direction at a given frequency (Hertz, Hz). For a compound which is not an SMM, in an a.c. field, the magnetisation would be continuously flipped between $-M$ and $+M$ states without a barrier. The susceptibility (which is all in the same phase as the field, hence $\chi'$) would be identical to that seen in a static d.c. field. A signal for the out-of-phase part of the susceptibility, $\chi''$, would necessarily be zero. If we now consider a SMM, an obvious change will be apparent: the $\chi''$ signal will be non-zero. This arises from the rapid attempt to flip the magnetisation to the same phase as the field; in the presence of an energy barrier to doing so there will come a point, upon lowering the temperature, for example, when this is not possible and the $\chi''$ signal is seen: some magnetisation still lies in the opposite phase. If the frequency of the field is increased, this flipping becomes harder still and the $\chi''$ maxima shifts to higher temperatures, this allowing easier thermal relaxation. The temperature at which the onset of these frequency-dependent processes is seen defines a different indicator of an SMMs performance, confusingly also called the “blocking temperature”. The positions of the $\chi''$ maximum, at a frequency $\nu$, give the relaxation time, $\tau$, by Equation 15.

$$\tau = \frac{1}{2\pi\nu} \text{ Equation 15}$$

By obtaining a number of these values at different frequencies it is possible with the appropriate data to extract both the energy barrier, $U_{\text{eff}}$, and information on the relaxation processes of the compound. Equation 16 relates $\tau$ with the time constant $\tau_0$, $U_{\text{eff}}$ and the temperature $T$.

$$\tau = \tau_0 e^{\frac{U_{\text{eff}}}{k_B T}} \text{ Equation 16}$$

By taking the natural logs of this Arrhenius equation and plotting $\ln \tau$ versus $1/T$, as shown in Figure 9 for [[Dy$^{III}$Cp’$_2$(μ-SSiPh$_3$)$_2$], we see two distinct regions. At high temperatures, where the points can be fitted by a straight line, shown in black, is a temperature dependent “regime,” where the gradient of this slope gives $U_{\text{eff}}$. The intercept of this line with the y-axis gives $\tau_0$. This thermal relaxation process becomes less important and less viable at lower temperatures, as indicated by the second region of Figure 9, where the points begin to level off (i.e. the gradient decreases) at lower temperatures. This indicates the so-called “quantum-regime”, where temperature independent quantum-tunnelling is the dominant relaxation process.
Fig. 9. Arrhenius plot of $\ln \tau$ versus $1/T$ for $[[\text{Dy}^{\text{III}}\text{Cp’}_2(\mu-\text{SSiPh}_3)]_2]$, showing the thermal energy barrier by the gradient of the linear data points (solid black line) and the quantum-tunnelling regime where data begin to approach temperature independence. Points are collected via two different sources: (○) from $\nu$ dependent $\chi''$ data and (●) from $T$ dependent $\chi''$ data.24

For $\{\text{Mn}_{12}\}$ an energy gap between ground and highest excited states ($m_s = \pm 10$ and $m_s = 0$) of 70 K was found with a $U_{\text{eff}}$ of around 60 K, due to quantum-tunnelling. For the related $[\text{Mn}^{\text{III}}_{8}\text{Mn}^{\text{IV}}_{4}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{H}_2\text{O})_{4}]^{2+}$ a.c. susceptibility measurements, shown in Figure 10, found two peaks in $\chi''$ at ca. 6.5 K and 2.5 K, for a 997 Hz field, indicating SMM behaviour. The first maximum signifies the compound as described, but the second is due to an isomeric form, where one JT axis is not aligned axially with those of the other Mn$^{\text{III}}$ ions, but equatorially. This results in a lower $U_{\text{eff}}$ species, possibly as a result of increased symmetry-induced quantum-tunnelling and the lower overall $D$ that such a misaligned $d$ (the single-ion zero-field splitting parameter) would give. This demonstrates the problems with aligning the anisotropy axis of multiple spin centres in designing SMMs. In fact, this may have influenced the search for smaller, monometallic compounds, which has proved highly successful, as will be seen in Section 2.
Fig. 10. $\chi'$ (upper) and $\chi''$ (lower) versus $T$ plots for $[\text{Mn}_{8}^{\text{III}}\text{Mn}_{4}^{\text{IV}}\text{O}_{12}(\text{O}_{2}\text{CCH}_{2}\text{Br})_{16}(\text{H}_{2}\text{O})_{4}]$, in a 0-$\pm3.5$ G a.c. field at 50, 250 and 997 Hz.\textsuperscript{21}

{Mn\textsubscript{12}} remained one of the best performing SMMs for around ten years until the incorporation of lanthanide(III) ions into cages and single-ion species began to develop in the early 2000s, looking ahead to Section 2. Clearly, the application of this technology to the “real-world” requires practical hysteresis temperatures and large energy barriers, and efforts to this end have been ongoing for more than twenty years.
2 An overview of 3d, 3d-4f and 4f SMMs

Having explained how 3d SMMs operate, this section examines some of the most important work reported, and how lanthanide(III) ions can help to improve upon this.

2.01 Progressing from \{\text{Mn}_{12}\} to larger energy barriers

Many high spin 3d compounds have been investigated since \{\text{Mn}_{12}\} and its derivatives were synthesised, but the largest $U_{\text{eff}}$ value has increased by only sixty percent in the more than twenty years hence. Most research groups utilised Equation 14 as their guiding principle, which says that to increase $U_{\text{eff}}$ one must synthesise compounds with a larger ground state spin and/or anisotropy, so increasing $U$, which is related to $U_{\text{eff}}$. Chasing high-spin clusters is conceptually simpler, and many high nuclearity manganese clusters were indeed synthesised, the apotheosis of this approach being the torus-wheel \([\text{Mn}^{\text{III}}_{84}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}(\text{OH})_{6}]\cdot x\text{H}_2\text{O} \cdot y\text{CHCl}_3\), \{\text{Mn}^{\text{III}}_{84}\}, shown in Figure 11.

![Figure 11](image)

*Fig. 11. The torus-wheel \([\text{Mn}^{\text{III}}_{84}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}(\text{OH})_{6}]\cdot x\text{H}_2\text{O} \cdot y\text{CHCl}_3\). Key: Mn^{\text{III}}, purple; O, red; C, grey; no H atoms or solvent molecules shown for clarity.*

Unfortunately, this has an $S = 6$ ground state due to dominant antiferromagnetic coupling between ions with a $U_{\text{eff}}$ of only 18 K and hysteresis below 1.5 K, ascribed to a ground-state tunnelling relaxation process. \{\text{Mn}^{\text{III}}_{84}\} therefore performs less well as an SMM than \{\text{Mn}_{12}\}. This illustrates one of several problems with designing SMMs, namely that controlling the interaction between ions is difficult, if not impossible, so lower spin ground states than could be expected are often found.
Fig. 12. The vertex-sharing supertetrahedron \([\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7\text{O}_8(\text{N}_3)_8(\text{L}_3)_{12}(\text{MeCN})_6]\)\(\cdot\)10\text{MeOH}\cdot\text{MeCN}. Key: Mn^{\text{III}}, purple; Mn^{\text{II}}, pink; O, red; C, grey; N, light blue; no solvent or H atoms are shown for clarity. \(\text{H}_3\text{L}_3\) is 2,6-bis(hydroxy-methyl)-4-methylphenol.26

The largest spin ground state so far, \(S = \frac{83}{2}\), was found in the vertex-linked super-tetrahedron structure \([\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7\text{O}_8(\text{N}_3)_8(\text{L}_3)_{12}(\text{MeCN})_6]\)\(\cdot\)10\text{MeOH}\cdot\text{MeCN} or \{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7\}\), where \(\text{H}_3\text{L}_3\) is 2,6-bis(hydroxy-methyl)-4-methylphenol. This is shown in Figure 12, and unfortunately, is also disappointing in terms of SMM performance, because of the very small anisotropy. A second problem is well demonstrated by this, which is the deliberate alignment of the JT axes of the Mn\(^{\text{III}}\) ions. If these cancel out, then the resultant anisotropies will be small, or zero. As this concerns the geometry of the compounds, then it too can be impossible to manipulate.

Generalising the work done with transition metals, the conclusion is that “the challenge now is to find a means of introducing not only maximum spin but also greater anisotropy”.

This challenge, as Neese and Pantazis27 and others, have addressed, may prove more complicated than Equation 15 would indicate, i.e. no relation between \(D\) and \(S\) is implied. In fact \(D\) is inversely proportional to \(S^2\), as given by Equation 17, such that it is difficult to obtain compounds with both high \(S\) and \(D\) values.

\[D \propto -\frac{1}{S^2} \text{ Equation 17}\]

**2.02 If there’s a new way... lanthanide(III) ions**

One alternative strategy is the incorporation of a highly anisotropic lanthanide(III) ion or ions, such as terbium(III) or dysprosium(III), into manganese(III), or transition metal, clusters. As described above, lanthanides have large, unquenched orbital angular momentum and hence large anisotropy.
This approach gave the first $3d$-$4f$ cluster with $U_{\text{eff}} > 100$ K, namely $[\text{Mn}^{\text{III}}_{6}\text{Th}^{\text{III}}_{2}\text{O}_{3}(\text{saO})_{6}(\text{CH}_{2}\text{OH})_{6}\text{(H}_{2}\text{O})_{2}]^{28}$. $\{\text{Mn}^{\text{III}}_{6}\text{Th}^{\text{III}}_{2}\}^{28}$, where saOH$_2$ is 2-hydroxybenzaldehyde oxime.

2.03 A milestone in $3d$-$4f$ SMMs: $[\text{Mn}^{\text{III}}_{6}\text{Th}^{\text{III}}_{2}\text{O}_{3}(\text{saO})_{6}(\text{CH}_{2}\text{OH})_{6}\text{(H}_{2}\text{O})_{2}]^{28}$ and waypoints

A number of examples of $3d$-$4f$ SMMs were investigated in the hope that the large anisotropy of the lanthanide ions would lead to larger energy barriers and hysteresis temperatures. The first of these to compete with $\{\text{Mn}^{12}\}$, was as recent as 2010. This cluster, fully $[\text{Mn}^{\text{IV}}_{3}\text{Mn}^{\text{III}}_{18}\text{Dy}^{\text{III}}_{0}\text{O}_{2}\text{(OH)}_{2}\text{(O}_{2}\text{C}^{\text{Bu}}\text{)}_{20}\text{(O}_{2}\text{CH})_{4}\text{(NO}^{\text{3}}\text{)}_{3}\text{(H}_{2}\text{O})_{2}\text{]}^{28}\cdot\text{MeNO}_{2}\cdot\text{H}_{2}\text{O}$, $\{\text{Mn}^{21}\text{Dy}^{\text{III}}\}$, had a $U_{\text{eff}}$ of 74 K, which was still below the best performing transition metal clusters $\{\text{Mn}^{6}\}^{30}$ (86 K), fully $[\text{Mn}^{\text{III}}_{6}\text{O}_{2}(\text{saO})_{6}(\text{O}_{2}\text{CPh})_{2}(\text{EtOH})_{4}]_{2}$, and $\{\text{Co}^{\text{II}}(\text{hfpip})_{2}\}^{31}$ (96 K), $\{\text{Co}^{\text{II}}(\text{hfpip})_{2}[\text{D}^{2}\text{py}^{2}\text{(TBA)}]\}^{28}$. Indeed, for $\{\text{Mn}^{21}\text{Dy}^{\text{III}}\}$, $T_{\text{B}}$ was 3 K compared to a record at that time of 5 K for $\{\text{Co}^{\text{II}}(\text{hfpip})_{2}\}$. A breakthrough arrived with $[\text{Mn}^{\text{III}}_{6}\text{Th}^{\text{III}}_{2}]^{28}$, in which six Mn$^{\text{III}}$ ions in a chair-conformation are capped by a lanthanide ion above and below the plane, and has an energy barrier of 103 K.$^{28}$ Comparison with $[\text{Mn}^{\text{III}}_{6}\text{La}^{\text{III}}_{2}]^{28}$ shows the terbium(III) ion contributes to a higher energy barrier. Lanthanum(III) has a [Xe]-type valence electronic structure and so is diamagnetic, leaving only the manganese(III) ions as paramagnetic in this compound. The energy barrier is now much smaller with $U_{\text{eff}} = 33$ K. The higher energy barrier of the former is rationalised by the high anisotropy of the terbium(III) ion.

2.04 Lanthanide(III) ions and 4f orbitals

The lanthanides, shown in Figure 13, make up a series of fourteen elements of decreasing size in which valence electrons sequentially fill the seven 4f orbitals. Lanthanum (La) and yttrium (Y) are included in this series despite their respective [Xe] 5$d^1$ 6$s^2$ and [Kr] 4$d^1$ 5$s^2$ configurations on account of their similar ionic radii and chemistry.

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Fig. 13. The lanthanide elements from Ce ($4f^1$) to Lu ($4f^{14}$) and including La and Y along with their atomic numbers.
The 4f orbitals can be described by a “general set”. Electrons in these orbitals each have distinct orbital angular momentum values, $m_l$, which are important when looking at how lanthanide ions operate in SMMs (see Section 2.04). As shown in Figure 14, these values and orbitals are, from top to bottom and left to right, $m_l = 0$ for $4f_\alpha$; $±1$ for $4f_{\alpha\beta}$ and $4f_{\alpha\gamma}$; $±2$ for $4f_{(x^2-y^2)}$ and $4f_{(3x^2-y^2)}$; and $±3$ for $4f_{xyz}$ and $4f_{(x^2-y^2)}$. This representation is not unique and several others, such as the “cubic set”, for cubic arrangements of electron density around the ion, may be more appropriate.

![Diagram of 4f orbitals](image)

**Fig. 14.** Representation of the 4f orbitals by a general set, from top to bottom, left to right: $4f_\alpha$; $4f_{\alpha\beta}$; $4f_{\alpha\gamma}$; $4f_{(x^2-y^2)}$; $4f_{(3x^2-y^2)}$; $4f_{xyz}$ and $4f_{(x^2-y^2)}$.  

The most common oxidation state by far is the +3 state, leaving valence electrons in only the core-like 4f orbitals, which are poorly shielded with respect to the nucleus and low in energy. This has a strong influence on the bonding, exchange interactions and magnetism of the lanthanides. Firstly, the tightly held valence electrons lead to more ionic bonding with predominantly hard donor atoms, such as fluorine, oxygen and nitrogen. Secondly, weak exchange coupling, *via* super-exchange with
other metal ions is generally observed, of the order of $10^{-1}\,\text{cm}^{-1}$ \cite{33}. This compares with values of the order of tens of $\text{cm}^{-1}$ for $3d$ compounds, \cite{34} with their more expanded valence orbitals. Thirdly, only weak crystal fields are generated around the lanthanides, hence orbital angular momentum contributions to magnetic moments are unquenched, in contrast to most complexes of $3d$ metals.

2.05 Orbital angular momentum and spin-orbit coupling

In the above discussion $L$ has been neglected, although it too can contribute to the magnetic moment of compounds.\cite{16} A total $L$, found by summing the individual $m_l$ contributions of each electron in its orbital, itself has $2L+1$ $m_l$ microstates. A combination of $S$ and $L$, spin-orbit coupling (SOC), occurs such that overall angular momentum, $J$, can be defined by Equation 18.

\[
J = L + S, L + S - 1, \ldots, L - S \quad \text{Equation 18}
\]

This separates the magnetic properties of $3d$ and $4f$ metal ions as, although the orbital angular momentum contribution can often be quenched by ligand fields in $3d$ metals, this is not the case for lanthanides, because their interaction with ligands is weak. Therefore the nature of the $4f$ orbitals leads directly to considerably different magnetic properties between $3d$ and $4f$ compounds.

2.06 Electronic properties of the lanthanide(III) ions and their role in SMMs

To understand why lanthanides can be useful in SMM research their electronic structure must be examined. As mentioned above, the nature of the $4f$ orbitals, in which the valence electrons reside, are crucial and, as a consequence, $S$ is not the best quantum number to describe the overall angular momentum of these ions, but $J$.

For example, considering the ground states of samarium(III) and terbium(III), which have $4f^6$ and $4f^8$ electronic configurations, see Figure 15, we find $S = \frac{5}{2}$ and $L = 5$ and $S = \frac{6}{2}$ and $L = 3$ respectively, as electrons fill orbitals to give the maximum $L$ in the ground state.
Combining $S$ and $L$, via spin-orbit coupling (SOC), and using Hund’s rules, gives $J$ values of $\frac{5}{2}$ and 6, for Sm$^{III}$ and Tb$^{III}$ respectively. These parameters can be collected to give the term symbol for each ion, generically $^nX_z$, where $n$ signifies the spin multiplicity ($2S+1$), X a letter designating the value of $L$ (where $S = 0$, $P = 1$, $D = 2$, $F = 3$, $G = 4$, $H = 5$, etc.) and $z$ denotes the total angular momentum $J$. Thus, we have the term symbols $^6H_{9/2}$ for samarium(III) and $^7F_6$ for terbium(III).

Isotropic ions such as gadolinium(III) are not suitable for use in SMMs, on account of their small $D$ values. Also, the larger lanthanide(III) ions may not be so useful, as they have small magnetic moments as their $J$ values in the ground state are small, for example, compare samarium(III) and terbium(III), above. Those lanthanides smaller than gadolinium(III), such as terbium(III) ($J = \frac{6}{2}$) and dysprosium(III) ($J = \frac{15}{2}$) will be the most useful as they can combine large moments and high anisotropies.

For all the lanthanide(III) ions, except gadolinium, $J$ is more useful in describing the overall angular momentum than $S$. Indeed these spin-orbit coupled states, as described by term symbols, are the key to understanding how lanthanide compounds operate as SMMs. Considering *Figure 16*, for a dysprosium(III) ion, $4f^9$, it is seen that different states are generated by filling the $4f$ orbitals in different ways. Firstly, states are split by electronic repulsion, *i.e.* $S$ and $L$ are maximised for the ground state, then with decreasing $L$ for excited states, and so forth. Spin-orbit coupling then splits each of these states according to the possible combinations of $S$ and $L$ to give the state with $J_{\text{max}}$ as the ground state. Thirdly, the crystal field splits these states further into their paired $\pm m_J$ multiplets (assuming $m_s \neq 0$. Also, note that these paired states can be split further in non-Kramers systems, *vide infra*).
Fig. 16. From left to right, the energy level diagram of the electronic states in dysprosium(III) when electronic repulsion, spin-orbit coupling, and the crystal field are taken into account, respectively. Taken directly.\textsuperscript{23}

The crucial factor is the last step shown, where each spin-orbit-coupled $J$ multiplet is split into its $(2J+1) m_J$ components by the crystal field, ordering these according to their $m_J$ values. For dysprosium(III) and all other lanthanide ions with an odd number of 4$f$ electrons (Kramers ions),\textsuperscript{17} this will produce pairs of $\pm m_J$ states. However, for those with an even number (non-Kramers ions), such as terbium(III), this only occurs in axially symmetric environments. This so-called “bi-stability” of the ground state is conceptually similar to that seen in $3d$ SMMs. Figure 17 shows the energies of these $\pm m_J$ levels for dysprosium(III) and terbium(III) in such an environment, namely the first lanthanide(III) SMMs, and the first with only a single-ion: TBA$^+[\text{Ln}^{\text{III}}\text{Pc}_2]^{-}$, where Ln$^{\text{III}}$ is Tb$^{\text{III}}$ or Dy$^{\text{III}}$. TBA$^+$ is tetra-butyl-ammonium and H$_2$Pc is phthalocyanine, from Ishikawa et al.\textsuperscript{35,36} These will be returned to later, when they can be understood in relation to the crystal field around the ions. For now we can note the significance of the energy gap between the two states of lowest energy.
2.07 Relating crystal fields to SMM performance

It has been shown that the crystal field environment around an ion can change the ordering of the \( m_J \) states of the \( J \) ground state. To understand why and how requires a more detailed examination of the electron distribution in each ion and then in each \( m_J \) state, a task which was performed by Rinehart and Long.\(^{23}\)

Using \( J \), the overall angular momentum for each ion, the second order Steven’s coefficient \( \alpha \), and the square of the 4\( f \) shell radius, \( r^2 \), can give a quadrupolar approximation of the ground state electron distribution in the 4\( f \) orbitals, shown in Figure 18.

For example, the spherical gadolinium(III) \( f \)-electron distribution arises from an equal population of each of the individual 4\( f \) orbitals, which were shown in Figure 14, whilst the strongly and
oppositely directed shapes of cerium(III) or ytterbium(III) are due to the unpaired electron which lies in an oblate $m_l = +3$ orbital for the former, whilst the similar $m_l = -3$ is vacant for the latter, resulting in a prolate shape.

From Figure 18, it can be seen that for dysprosium(III) the ground term ($J = \frac{15}{2}$) electron density has an oblate distribution. When dysprosium(III) is in an axial ligand geometry this will tend to increase the energy of low $m_J$ states, whilst at the same time lowering that of those states of highest $m_J$, a situation very promising for the performance of this ion in SMMs, as it will give a large magnetic moment in the ground state, related to Equation 2.

There is, in fact, an even finer level of tuning in the ordering of $m_J$ pairs from the crystal field: Considering the angular-dependence of the $4f$ electron distribution for each $m_J$ state of a given ion gives information on the anisotropy of that state and how it will react to a certain crystal field. These dependencies are shown in Figure 19 for the lanthanide(III) ions from cerium(III) to ytterbium(III), excepting europium(III) and gadolinium(III). For example, cerium(III) illustrates that the $m_J = \pm \frac{5}{2}$ state is oblate, whereas the $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$ states are increasingly prolate. Stabilisation of the $m_J = \pm \frac{5}{2}$ could be achieved by considering an electron-electron repulsion model, where one state can be lowered in energy relative to the $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$ pairs; minimisation of this repulsion for the $m_J = \frac{5}{2}$ state is achieved by adopting an axial ligand set, whereby electron density of the ligands is in the equatorial region, away from the electron density in the $m_J = \frac{5}{2}$ state, which is concentrated in the axial regions (Figure 19).

Fig. 19. The angular dependence of the $4f$ electron density for the lanthanide(III) series, from cerium(III) to ytterbium(III), omitting europium(III) and gadolinium(III), where blue shapes represent non-Kramers ions, and green Kramers ions. Taken directly.
Similar chemical environments can stabilise the highest $m_J$ states on those ions with oblate electron distributions such as terbium(III) and dysprosium(III).

2.08 The mechanism of lanthanide(III) SMMs

SMM behaviour is achieved in lanthanide SMMs via a similar mechanism, conceptually, to that seen in 3$d$ SMM chemistry (1.11), but which varies in several important aspects. Just as the $m_s$ states of a transition metal SMM are ordered according to the zero-field-splitting in an applied magnetic field, so too are the $m_J$ states of lanthanide SMMs. Therefore the challenge is to find geometries which stabilise high $m_J$ pairs and allow two distinct magnetic states to be maintained. Just as a $-D$ was important for transition metals, the equivalent essential in 4$f$ chemistry is the axial (or bistable) ground state, which is also described as being of the Ising type.\(^{35}\) The discrepancy arises as $D$ is not a good description of the ground state for lanthanides, there being many more terms to consider in the operation of the crystal field on the electronic structure of the 4$f$ ions. In fact up to twenty seven such Stevens' Operators could be taken into account.\(^{17,19}\) A further difference to 3$d$-metals is that in zero field the $m_J$ states of a lanthanide SMM may not necessarily be arranged in order of either increasing or decreasing $m_j$ and the lowest energy pair of a single-ion may not be that of largest $m_j$, the crystal field making changes to the energy levels of the SOC states. Stablising a pair of $\pm m_J$ states relative to the next highest is analogous to creating a large energy gap, $U$, between states of varying $m_s$ values. Creating at least one large energy gap between adjacent $m_J$ states is thus the key to large energy barriers, as a more detailed comparison between the first terbium(III) and dysprosium(III) SMMs demonstrates.

2.09 The first lanthanide SMMs: TBA$^+$[Tb$^{III}$Pc$_2$]$^-$ and TBA$^+$[Dy$^{III}$Pc$_2$]$^-$

Despite the advances which 3$d$-4$f$ compounds brought to SMM research they had already been surpassed by the SMMs TBA$^+$[Ln$^{III}$Pc$_2$]$^-$, where Ln$^{III}$ is Tb$^{III}$ or Dy$^{III}$, which were discovered almost ten years ago (2003).\(^{35,36}\) Just as $\{\text{Mn}_{12}\}$ remained a high performing transition-metal SMM for many years, so TBA$^+$[Tb$^{III}$Pc$_2$]$^-$ and its derivatives still have the largest $U_{eff}$ values amongst single-ion species, suggesting a series of breakthroughs, rather than any gradual progression has occurred. These double-decker structures have the four N donors of the phthalocyaninate ligand bonded to the central metal which are non-eclipsing above and below (Figure 20).
Fig. 20. Structure of TBA\(^+[\text{Ln}^\text{III}\text{Pc}_2]^−\), where Ln\(^{\text{III}}\) is Tb\(^{\text{III}}\) or Dy\(^{\text{III}}\), TBA\(^+\) is tetra-butyl ammonium and Pc is phthalocyaninate.\(^{35}\)

Diluted samples of TBA\(^+[\text{Y}^\text{III}\text{Pc}_2]^−\):TBA\(^+[\text{Tb}^\text{III}\text{Pc}_2]^−\) show frequency dependence of \(\chi''\) at around 40 K (1 KHz), higher than any previously seen, and \(U_{\text{eff}} = 331\) K under no d.c. field; TBA\(^+[\text{Y}^\text{III}\text{Pc}_2]^−\):TBA\(^+[\text{Dy}^\text{III}\text{Pc}_2]^−\) gives \(U_{\text{eff}} = 40\) K. Samples diluted in the equivalent yttrium analogues, such as these, are useful because they can remove the effects of inter-molecular interactions. What is then examined is known to be a uniquely single-molecule property. The former compound showed the highest anisotropy barrier at the time and is far in excess of any transition or mixed 3\(d\)-4\(f\) compound, up to the present time (2013). To rationalise these unprecedentedly large numbers, NMR spectroscopic and magnetic susceptibility data were used to derive the energy levels of the \(m_J\) multiplets for each compound, by analysis of the whole series of isostructural lanthanide derivatives. For TBA\(^+[\text{Tb}^\text{III}\text{Pc}_2]^−\) (with its \(7\text{F}_6\) ground term), this revealed a large separation between the ground state \(m_j = \pm 6\) and the first excited state \(m_j = \pm 5\) of 576 K (recalling Figure 17), of comparable magnitude to the energy barrier to relaxation found experimentally by magnetometry, above. The dysprosium(III) \((6\text{H}_{15/2})\) compound showed no large separations between states of this magnitude, supporting the above ideas that the energy gap between \(m_j\) states is the crucial factor in lanthanide SMMs, a property which can in theory be tuned and controlled by a choice of ligand and resulting ligand geometry, because the relaxation pathway must go by a series of \(\Delta m_j = \pm 1\) steps for the thermal process. Quantum-tunnelling, which can lead to very small blocking temperatures, is very much a feature of lanthanide SMMs, as well as 3\(d\) compounds.

Of course, this does not mean all terbium(III) compounds are superior to all dysprosium(III) compounds as SMMs (i.e. have a larger \(U_{\text{eff}}\)). Only in this geometry and environment is this necessarily true. By contrast, in the intriguing class of materials known as polyoxometalates
(POMs) different behaviour has been seen, such as erbium compounds showing slow relaxation but not the dysprosium analogue.\textsuperscript{37} vide infra.

2.10 Strong-exchange in the hetero-spin radical-bridged lanthanide(III) SMMs: \([\text{K}(18\text{-crown-6})]\textsuperscript{+} [\text{Dy}^{III} \text{2}(\text{Me}_3\text{Si})_{2}\text{N}_4(\text{THF})_{2}(\mu-\eta^2:\eta^2-\text{N}_2)]\textsuperscript{−}\) and \([\text{K}(18\text{-crown-6})(\text{THF})_{2}]\textsuperscript{+} [\text{TB}^{III} \text{2}(\text{Me}_3\text{Si})_{2}\text{N}_4(\text{THF})_{2}(\mu-\eta^2:\eta^2-\text{N}_2)]\textsuperscript{−}\)

Although large energy barriers were generated by the previously discussed double-decker compounds, the blocking temperatures were still relatively small. A new strategy that has dramatically improved the situation was demonstrated by Long and Rinehart, by strongly coupling lanthanide(III) ions through a radical (\(\text{N}_2\))\textsuperscript{3−}· bridge.\textsuperscript{38,39} \([\text{K}(18\text{-crown-6})(\text{THF})_{n}]\textsuperscript{+} [\text{Ln}^{III} \text{2}(\text{Me}_3\text{Si})_{2}\text{N}_4(\text{THF})_{2}(\mu-\eta^2:\eta^2-\text{N}_2)]\textsuperscript{−}\), henceforth \{\text{Ln}^{III} \text{2}(\text{N}_2)\}\textsuperscript{−}, is shown in Figure 21, left, where when \(\text{Ln} = \text{gadolinium(III)}\) or dysprosium(III), \(n = 0\) whereas with terbium(III), holmium(III) or erbium(III), \(n = 2\). The radical (\(\text{N}_2\))\textsuperscript{3−} ligand bridges between lanthanides with both N atoms, whilst the remaining ligands all bond in a mono-dentate fashion via O (THF) and N ((Me\textsubscript{3}Si)\textsubscript{2}N) atoms.

![Fig. 21. Left: \{\text{Ln}^{III} \text{2}(\text{Me}_3\text{Si})_{2}\text{N}_4(\text{THF})_{2}(\mu-\eta^2:\eta^2-\text{N}_2)\}\textsuperscript{−}\}. Key: \text{Ln}^{III}, deep purple; \text{N}, light blue; O, red; C, grey; Si, pale yellow; H atoms are not shown. Centre: \(\chi_M T\) versus \(T\) for \{\text{Gd}^{III} \text{2}(\text{N}_2)\} (blue) and \{\text{Gd}^{III} \text{2}(\text{N}_2)\}\textsuperscript{−} (red), the latter showing much stronger coupling. Right: \(\chi_M T\) versus \(T\) for \{\text{Dy}^{III} \text{2}(\text{N}_2)\} (blue) and \{\text{Dy}^{III} \text{2}(\text{N}_2)\}\textsuperscript{−} (red), showing similar qualitatively behaviour to the gadolinium(III) analogue. \(\chi T(T)\) figures taken directly.\textsuperscript{38}

Evidence for this unusually strong coupling comes from a comparison of the isotropic-spin analogue \{\text{Gd}^{III} \text{2}(\text{N}_2)\}\textsuperscript{−} and its non-radical bridged counterpart \{\text{Gd}^{III} \text{2}(\text{N}_2)\}. The (\(\text{N}_2\))\textsuperscript{3−} radical-bridged form is generated by potassium graphite reduction of this non-radical (\(\text{N}_2\))\textsuperscript{2−} form, with the addition of the [\text{K}(18\text{-crown-6})(\text{THF})_{n}]\textsuperscript{+} counter-ion.

From a fitting and modelling of susceptibility data, using the spin-only Hamiltonian given in Equation 19, the strength of coupling was found to be fifty times larger in the reduced compound \{\text{Gd}^{III} \text{2}(\text{N}_2)\}\textsuperscript{−}: \(J\) being −38.9 K (−27 cm\textsuperscript{−1}) compared to −0.71 K (−0.49 cm\textsuperscript{−1}) in \{\text{Gd}^{III} \text{2}(\text{N}_2)\}. By
this model, in which $J$ and $J'$ are intra- and inter-molecular coupling constants, $\hat{S}$ appropriate spin operators, $z$ the number of nearest neighbour interactions, $S_z$ the $z$-component of the spin operator and $\langle S_z \rangle$ its mean value, these values represent antiferromagnetic interactions.

\[
\hat{H} = -2J \hat{S}_{\text{radical}} \cdot (\hat{S}_{\text{Gd1}} + \hat{S}_{\text{Gd2}}) - zJ'\langle S_z \rangle S_z \tag{Equation 19}
\]

The fits are shown in Figure 21, centre, as black lines to the experimental data plotted as red and blue circles for $\{\text{Gd}^{\text{III}}_2(\text{N}_2)\}$ and $\{\text{Gd}^{\text{III}}_2(\text{N}_2)\}$, respectively. Quantitatively similar behaviour was seen for the pair of anisotropic dysprosium(III) compounds, as shown on the right of Figure 21, although the magnetic data were not fitted. In both cases, strong coupling is believed to be due to the increased overlap of the valence ligand orbitals with the metal orbitals compared to the reduced overlap in the non-radical compound and is clearly very different from all lanthanide SMM compounds studied in the field up to that point.

2.11 Consequences of stronger coupling on $U_{\text{eff}}$ and an interpretation

$\{\text{Tb}^{\text{III}}_2(\text{N}_2)\}\}$\textsuperscript{39} has an energy barrier of 327 K whilst for $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}$\textsuperscript{\textsuperscript{-}} $U_{\text{eff}} = 184$ K, which, whilst not the largest reported, are still significant. Interestingly, the increased strength of exchange in these anisotropic radical compounds corresponds with significantly larger $U_{\text{eff}}$ values, compared to the non-radical version. This assumes that the behaviour of the exchange parameters modelled in the pair of isotropic gadolinium analogues above is transferable, qualitatively, to the other members of this series.

For $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}$ $U_{\text{eff}}$ is only 26 K, around seven times smaller than the strongly exchange-coupled counter-part, as depicted in the Arrhenius plot in Figure 22, where the red line is data for $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}$\textsuperscript{\textsuperscript{-}} and the blue for $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}$. The presence of a measurable quantum-tunnelling process for the non-radical compound is also clearly visible as a temperature-independent, i.e. horizontal, plot. Given that strong-exchange has been found to remove quantum-tunnelling in 3d-metal SMMs\textsuperscript{40} it is promising that this has now been shown to operate in lanthanide SMMs too.
Why $U_{eff}$ should be so much larger for $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}^-$ than $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}$, though, is a source of speculation, but a plausible suggestion is that the radical and non-radical compounds have different relaxation mechanisms.

### 2.12 Distinct mechanisms of relaxation

The non-radical compounds $\{\text{Ln}^{\text{III}}_2(\text{N}_2)\}$ essentially behave as if the ions are distinct, so weak is the coupling, and the SMM properties occur as a result of individual anisotropies. The slow relaxation is then a “single-ion” effect. This can be seen especially well in several lanthanide compounds where there are weakly coupled ions with distinct coordination geometries and hence anisotropies. There, separate relaxation processes would be in operation for each ion, which are often visible as individual peaks in $\chi''$ versus $T$ plots.

An alternative to this is a “Giant-Spin” mechanism, which operates where the individual spins (or angular momenta) are combined into a larger spin through exchange-coupling. This is extremely common, in fact the norm, in 3$d$ SMMs, where the resultant $m_s$ (max) states are of larger magnitude than any possible due to a single ion; e.g. in $\{\text{Mn}_{12}\}$ the lowest $m_s$ pairs are $\pm 10$, whereas for a single ion this would be $\pm 2$ ($\text{Mn}^{\text{III}}$) or $\pm 3/2$ ($\text{Mn}^{\text{IV}}$). This creates a larger barrier between the lowest and highest $m_s$ states, so increasing the size of the thermal energy barrier.

A similar effect, though with $m_J$ states, may operate in the radical compounds $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\}^-$ and $\{\text{Tb}^{\text{III}}_2(\text{N}_2)\}^-$ above, as speculated upon by the authors, which would be the first examples of any lanthanide SMMs. Currently this proposition is unconfirmed, though fascinating.
2.13 The effect of strong exchange-coupling on hysteresis temperatures

Although a direct comparison of radical and non-radical compounds is not available for the terbium(III) compounds, $T_B$ for $\text{Tb}^{\text{III}}_2(\text{N}_2)\text{\textsuperscript{-}}$ is the highest of any SMM measured, opening below 15 K, the hysteresis loops for which are given below (Figure 23).

![Hysteresis loops](image)

Fig. 23. Hysteresis loops between 11 and 15 K for $\text{Tb}^{\text{III}}_2(\text{N}_2)\text{\textsuperscript{-}}$; remnant magnetisation is seen below 15 K, in a 0-±7 T field. Taken directly.$^{39}$

Similarly, $\{\text{Dy}^{\text{III}}_2(\text{N}_2)\text{\textsuperscript{-}}\}$ shows a $T_B$ of around 8.3 K, which is dependent on sweep-rate. Therefore both radical compounds show larger $T_B$ values than for any 3$d$ or 3$d$-4$f$ SMM. It seems likely, too, that here the strong-exchange coupling negates quantum-tunnelling, allowing large $T_B$ values to be recorded. If confirmed, this suggests a promising new direction for further improvements in SMM performance.

There are two more categories of lanthanide SMMs which are among the more remarkable, namely the lanthanide alkoxide compounds, $\{\text{Ln}^{\text{III}}_5\}_{41,42}$ and $\{\text{Ln}^{\text{III}}_4 \text{K}_2\}_{42}$ and the $\{\text{Dy}^{\text{III}}_3\}$ triangles.$^{44,45}$ The dysprosium(III) pyramid held the largest $U_{\text{eff}}$ of any polymetallic compound and the triangles show SMM behaviour despite their diamagnetic ground state.

2.14 “Single-pyramid magnets”: $[\text{Dy}^{\text{III}}_3\text{O}(\text{O}^\prime\text{Pr})_{13}]$ and $[\text{Ho}^{\text{III}}_3\text{O}(\text{O}^\prime\text{Pr})_{13}]$

The square-based pyramids $[\text{Ln}^{\text{III}}_5\text{O}(\text{O}^\prime\text{Pr})_{13}]^{41,42}$ (where Ln = dysprosium(III) or holmium(III)), $\{\text{Ln}^{\text{III}}_5\}$, are composed of five lanthanide ions, all bonding to a $\mu_5$ oxide; $\mu_2$ iso-propoxides bridge the basal metal ions, $\mu_3$ iso-propoxides cap the four faces and $\mu_1$ terminal groups cap all metals, each metal having a distorted octahedral geometry (Figure 24).
Fig. 24. The square-based pyramid \([\text{Dy}^{\text{III}}_5\text{O(OPr)}_{13}]\). Key: Dy\(^{\text{III}}\), deep purple; O, red; C, grey; H atoms are not shown. The uppermost O bonding to the apical Dy\(^{\text{III}}\) is part of an OPr group pruned for clarity.\(^{41}\)

For \(\{\text{Dy}^{\text{III}}_5\}\) \(U_{\text{eff}}\) is 528 K, the largest of any poly-metallic compound. This is ascribed to the almost four-fold symmetry (\(C_{4v}\)) at each site, which is similar to \([\text{Ln}^{\text{III}}\text{Pc}_2]^-\), described above, and others, such as \([\text{Er}^{\text{III}}(\text{W}_3)_2]^{-}\);\(^{36}\) presumably these geometries stabilise high-value \(m_t\), giving a high energy thermal process. Doping the pyramid compound with diamagnetic yttrium increases \(U_{\text{eff}}\) as the effect of local fields are removed.

Despite this barrier, hysteresis of magnetisation is seen only below 1.9 K, because of a quantum-tunnelling mechanism identified at low temperatures in the \(\chi''\) versus \(T\) data. This is in addition to the relaxation process seen at around 40 K (for the highest frequency field), representing the large thermal barrier (Figure 25). Despite the high symmetry of individual ions, all five metals are crystallographically unique, and thus there is no “crystallographic symmetry” which could remove the quantum-tunnelling mechanism. Chemical control of the space group, though, has not yet been achieved in this case. Intriguingly, a second thermal process is identified, where \(U_{\text{eff}}\) is 47 K, at around 12 K. The discovery of two “thermal” relaxation processes has also been reported for species which only have a single-ion elsewhere\(^{46}\) and is likely due to one of these being via a thermally assisted quantum-tunnelling mechanism. Interestingly, \textit{vide infra} to 2.17, this may be due to both the first and second excited states being involved in the relaxation mechanisms.
Fig. 25. $\chi''$ versus $T$ for $[\text{Dy}^{\text{III}}\text{O(O}'\text{Pr})_{13}]$, showing relaxation processes at 40 and 2 K for $\nu = 1400$ Hz, in a 0-±1.5 G a.c. field.\textsuperscript{42}

The analogue $\{\text{Ho}^{\text{III}}\}$ shows slow relaxation only under applied d.c. fields of 800 G or more and optimised at around 5000 G, where $U_{\text{eff}}$ was found to be 400 K. The lack of holmium(III) SMMs (only two others had been reported at the time) was reason enough to examine this compound, as well as an unusual relaxation mechanism. As for the $\{\text{Dy}^{\text{III}}\}$ compound, no hysteresis was observed due to a quantum-tunnelling process. Here, this is due to the hyperfine interaction of the nuclear and electronic systems of the holmium(III) ion, and could be suppressed under applied fields above 2000 G.

2.15 A digression upon quantum-tunnelling: transverse fields

The occurrence of QT is intimately linked to the crystal field about the lanthanide ion. For those symmetries which are termed “axial”, this mechanism is forbidden between states at the same level (i.e. $\pm m_J$), which is desirable for increased performance.\textsuperscript{17}

In reality, although QT is forbidden in Kramers ions it is frequently seen and can be caused by transverse magnetic fields.\textsuperscript{22} These may be caused by neighbouring molecules with their own magnetic fields, which if they interact with other molecules, cause previously resonant energy levels to have their degeneracy removed, allowing a tunnelling to occur. These transverse magnetic fields can also arise from non-axial components of the magnetisation, where certain states ($\pm m_J$ levels) have values of $g_x$ or $g_y$ which are non-zero.\textsuperscript{17}

This is related to the way in which QT can be prevented in a.c. susceptibility experiments; the application of a magnetic field changing the relative energies of previously resonant states by the Zeeman effect.\textsuperscript{17}
2.16 Hyperfine relaxation

A further hyperfine mechanism can also enable QT to occur. This is due to a coupling of the nuclear spin, $I$, with the overall angular momentum to generate $m_F$ states. To illustrate, a nuclear spin of $I = 3/2$ will split each $m_J$ state into $2I + 1 = 4$ levels. Through this, states can mix and exchange spin population at a lower energy cost than through the thermal relaxation process.

2.17 [Dy$^{III}$]$_4$K$_2$O(O'Bu)$_{12}$: pushing $U_{eff}$

Very recently, Blagg et al. have found even larger energy barriers of up to 842 K, from a compound based on the octahedral [Dy$^{III}$]$_4$K$_2$O(O'Bu)$_{12}$, shown in Figure 26, when doped by site and matrix, i.e. for [Dy$^{III}$]$_3$Y$^{III}$K$_2$O(O'Bu)$_{12}$ in a [Y$^{III}$]$_3$K$_2$O(O'Bu)$_{12}$ matrix. The undoped compound showed $U_{eff}$ barriers at 692 K and 312 K, which differ substantially from the doped material. In this, the lowest energy doublets are $\pm \frac{15}{2}$ and $\pm \frac{13}{2}$, both of which are of the Ising-type (i.e. $g_z$ is substantial, while $g_x$ and $g_y$ are negligible. This is dependent on geometry). The energy gap to these two excited states corresponds to the two thermal barriers in the pure compound, accounting for thermally-assisted QT (TA-QT).

![Fig. 26. The octahedral [Dy$^{III}$]$_4$K$_2$O(O'Bu)$_{12}$. Key: Dy$^{III}$, purple; K, green; O, red; C, black; H atoms are not shown. Taken directly.](image)

The site and matrix doping method with [Dy$^{III}$]$_4$K$_2$O(O'Bu)$_{12}$] removes the lower thermal process and leaves only a single high energy barrier, the mechanism of which is in itself interesting as it proceeds via a second excited state. Similarly, doping of the {Dy$^{III}$}$_5$ pyramid in the same way gives a single relaxation pathway, via the second excited state.
2.18 Unusual SMM behaviour in toroidal spin systems

The planar {Dy\textsuperscript{III}} triangles, [Dy\textsuperscript{III}\textsubscript{3}(\mu\textsubscript{3}-OH)\textsubscript{2}(L)\textsubscript{3}Cl(H\textsubscript{2}O)\textsubscript{5}]\textsubscript{2}Cl\textsubscript{5}·19H\textsubscript{2}O and [Dy\textsuperscript{III}\textsubscript{3}(\mu\textsubscript{3}-OH)\textsubscript{2}(L)\textsubscript{3}Cl(H\textsubscript{2}O)\textsubscript{5}]Cl\textsubscript{3}·4H\textsubscript{2}O·2MeOH·0.7MeCN, (HL=\textit{o}-vanillin) (Figure 27, left) are composed of three Dy\textsuperscript{III} ions bridged by two \mu\textsubscript{3}-OH groups.\textsuperscript{44,45} The deprotonated \textit{o}-vanillin bridges two metals and caps them with its three O donors, with Cl or H\textsubscript{2}O groups also connecting to the Dy\textsuperscript{III}, giving a coordination number of eight.

![Diagram of Dysprosium(III) magnetisation vectors in a toroidal arrangement.](image)

\textit{Fig. 27.} Left: [Dy\textsuperscript{III}\textsubscript{3}(\mu\textsubscript{3}-OH)\textsubscript{2}(L)\textsubscript{3}Cl(H\textsubscript{2}O)\textsubscript{5}]. Key: Dy\textsuperscript{III}, blue; O, red; C, grey; Cl, green; no H atoms are shown. HL=\textit{o}-vanillin. Right: A representation of the orientation of the three dysprosium(III) magnetisation vectors in a toroidal arrangement. Taken directly.\textsuperscript{45}

These triangles behave in a different way to almost all other SMMs on account of the non-alignment of the dysprosium(III) magnetisation vectors; these point away at 120° from each other in a toroidal arrangement (\textit{Figure 27}, right) in the plane of the triangle. This gives an almost diamagnetic ground state, confirmed by the levelling off of magnetisation at low field (\textit{Figure 28}, main), from cancelling of the magnetic vectors.

Substantial energy barriers of 36 K (in zero-applied field) and 120 K (3000 G) correspond to the reorientation of spins pointing in opposite directions in the plane. These compounds realised the long-held idea that information on the magnetisation can be maintained in a non-magnetic ground state. Only a very small hysteresis was seen (\textit{Figure 28}, inset) on account of the presence of quantum tunnelling, indicated by the small opening of the loop at zero field.
Fig. 28. Main, magnetisation versus field for both isomers of \(\text{Dy}^{\text{III}}\), water solvate in a 0-7 T field: □ and acetonitrile / methanol solvate: ●. Inset, Hysteresis of magnetisation loops for the latter version in a 0-±1 T a.c. field. Taken directly.  

2.19 Larger barriers

Improving the performance of existing lanthanide(III) SMMs is rarely done by merely altering ligand groups, as suggested by the 4f orbitals contracted nature, giving more ionic bonding. Nevertheless there is at least one impressive example based on Ishikawa’s first 4f SMMs. Using a substituted phthalocyanine ligand, \([\text{Pc(OEt)}_8\text{Tb}^{\text{III}}]^{-}\), it was possible to find an 8 % increase in \(U_{\text{eff}}\) upon a two-electron oxidation to the \([\text{Pc(OEt)}_8\text{Tb}^{\text{III}}]^{+}\) species, to over 790 K. This result was rationalised by the change in the ligand-metal distance that resulted, the donor atoms moving closer to the Tb\(^{\text{III}}\) ion and so increasing the strength of the axial ligand field at that site.

2.20 Welcome to the “real world”

If SMMs are to be useful in applications, then they will need to be attached to a surface, for easy fabrication and incorporation into devices. Investigations with another derivative of the first 4f SMM showed that this can be achieved without loss of the slow relaxation.

Incorporating an isopropylidene dioxy group onto the Pc ligand previously used, enabled \([\text{TbPc}_2]^{-}\) to be made. Evaporation of a solution of this onto a highly orientated pyrolytic graphite (HOPG) surface gave an ordered arrangement of the complex. \(U_{\text{eff}}\) was found to be 800 K, the largest of any compound measured so far, and a hysteresis loop is seen at 7 K (cf. 1.7 K for \([\text{TbPc}_2]^{-}\)).

2.21 Work in Progress: actinide SMMs

Even more recently, research into the 5f metals, or actinides, has produced several fascinating results, which are being investigated further. Uranium(III) in particular is promising as it possesses a very large spin-orbit-coupling and potentially larger crystal field effects than 4f ions,
which may also be exploited with stronger exchange coupling, the 5f orbitals being less contracted than in 4f ions.

One of the most intriguing examples, considering the effect of the crystal field in lanthanides is the discovery of SMM behaviour in three distinct U single-ion species, whose coordination geometries were also quite different. \([\text{U}^{III}_3(\text{THF})_4], [\text{U}^{III}(\text{N(SiMe}_3)_2)_3]_2\) and \([\text{U}^{III}\{\text{CH(PPh}_2\text{NSiMe}_3)_2\}2\text{I}_2(\text{THF})]\), which are depicted in Figure 29.\(^5\) Energy barriers for powdered samples of these are rather similar at 19, 31 and 23 K despite the three point groups of \(C_{2v}\), \(C_{3v}\) and \(C_1\), respectively. An open question is the cause of the QT, which persists even in frozen solutions, \textit{i.e.} highly diluted.

![Figure 29. Left to Right, \([\text{U}^{III}_3(\text{THF})_4], [\text{U}^{III}(\text{N(SiMe}_3)_2)_3]_2\) and \([\text{U}^{III}\{\text{CH(PPh}_2\text{NSiMe}_3)_2\}2\text{I}_2(\text{THF})]\). Adapted.^5](image)

\[2.22\text{ Conclusions}\]

There has been a trend in SMM research towards utilising lanthanide compounds in search of higher energy barriers and blocking temperatures. It appears that \(d\)-transition metals are hindered by the balance between \(S\) and \(D\), and their inverse mutuality, and that lanthanides can be markedly superior to \(3d\) metal clusters in this field, on account of their very high single-ion anisotropy and spin. The progression from the first lanthanide SMMs into polymetallic clusters and, lately, using radical bridges, to link these metals represents some of the best performing and most stimulating work in this class of molecules, not to mention the novel realisation of diamagnetic SMMs, \{\text{Dy}^{III}\}. Clearly, lanthanide(III) SMMs represent fascinating and challenging platforms for synthetic chemists and physicists to work with in understanding the synthetic routes to these compounds and their magnetic behaviour. Chapters 4, 5, 6 and 8 demonstrate some examples of efforts to investigate these facets of SMM research and those towards improved MCE materials, which will be examined next in Chapter 3 as a review of the past twenty years of work into this. Chapter 7 will review the synthesis and magnetic properties of \(3d\)-4f and 4f coordination compounds using teaH\(_3\) (triethanolamine) and RdeaH\(_2\) (functionalised diethanolamines), focusing on their SMM and MCE properties.
References


Chapter 3: Areas to Explore
Chapter Three: Areas to Explore

As outlined in Chapter 2, lanthanide(III)-based molecules are highly promising candidates for superior SMMs to conventional 3d-transition metal compounds. Furthermore, as outlined in Chapter 4, vide infra, they can act as some of the best magnetocaloric materials. Therefore the principal aims of this project are the synthesis, characterisation and evaluation of new (and old) lanthanide(III) materials to these ends. The primary synthetic method will be solvothermal synthesis, in which reagents are reacted together under high pressure and carefully controlled conditions of heating and cooling. Characterisation will utilise conventional methods including powder X-ray diffraction and single-crystal X-ray diffraction where appropriate. Evaluation of a materials’ performance as an SMM or magnetic cooler can be undertaken by SQUID analysis at The University of Manchester, with several groups, such as that of Marco Evangelisti at The University of Zaragoza, capable of extending these measurements with heat capacity and micro-SQUID analysis. Further investigations into their properties will involve luminescence measurements, electron paramagnetic resonance (EPR) spectroscopy, and computational analysis. The above goal deliberately includes old materials, i.e. those which have already been reported. It is worth remembering that the first SMM was a variation of a compound synthesised long before\textsuperscript{1}, and recent spectacular lanthanide(III) examples utilised syntheses established in the literature\textsuperscript{2} long prior to their investigations in these “new” fields. Deliberately used is the word “material”, rather than “molecule”, as polymeric compounds will be a focus, particularly for refrigerants.

The ligands used to connect these metals are four classes well established in 3d and 3d-4f chemistry; in principle they seem ideal for application to lanthanide(III) ions on account of their flexibility in bonding and oxygen-rich nature, ideal for the oxophilic lanthanide(III) ions. Namely, these are i) thme\textsubscript{3}, tris(hydroxymethyl)ethane, a tripodal alcohol ligand; ii) tea\textsubscript{3}, triethanolamine, a ligand similar in concept, but with the added functionality and basicity of an N-donor atom; iii) \textsuperscript{1}BuPO\textsubscript{3}H\textsubscript{2}, tert-butyl phosphonic acid, which can later be extended with a range of R groups for tuning purposes; and finally iv) RCO\textsubscript{2}H, the carboxylic acids, which span an enormous range of solubilities, bulk and further functionality with their choice of R group. There is a natural gravitation towards the extremes of size in this regard, and the ligands HCO\textsubscript{2}H, formic acid, and Ph\textsubscript{3}CCO\textsubscript{2}H, triphenylacetic acid, will be used in conjunction with others or alone.

Thus, using lanthanide(III) ions and flexible ligands, improved magnetocaloric and slowly-relaxing materials are the goal.

References
Chapter 4: Paper 1

Coordination compounds and the magnetocaloric effect

Coordination compounds and the magnetocaloric effect

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Abstract

This review article examines the impact of zero-dimensional compounds in the field of magnetic refrigeration, 20 years after the modern age of molecular magnetism began. The remarkable advances in this area are brought out here by an examination of 3d, 3d–4f and 4f molecular compounds and more recent polymeric materials; we then assess which of these shows most promise for this application.

1. Introduction

When the first single-molecule magnet (SMM) was discovered in 1993 [1] it ushered in a change in the old discipline of magnetometry and the beginning of a new one, molecular magnetism. A "side-product", distinct from the anisotropic high spin clusters, were magnetocaloric molecules, based on electronically isotropic metal clusters, using metals with high spin values, such as gadolinium(III), manganese(II) and iron(III). We should really say that this field was rediscovered by inorganic chemists. Since Giauque used \[\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}\] to achieve low temperatures in the early 1930s [2a], much research, particularly with alloys and metallic materials has followed, the major successes of which are refrigeration proto-types of gadolinium metal at room temperature [2b–d] and the gadolinium gallium garnet (GGG) [2e] for low temperature work. Molecular magnetism has greatly benefited from an unprecedented collaboration between physicists and chemists in recent years and we have a much improved understanding of what is required to improve the performance of magnetic refrigerants. This understanding suggests improvements can be made, regarding the effect of factors such as anisotropy, spin and molecular interactions [2g]. Therefore, this review article will survey the literature since the beginning of this new age, by examining 3d, 3d–4f and 4f magnetic refrigerants, noting their suitability in various areas of their structure, synthesis, composition and their magnetic properties. Its organisation is as follows: we will begin with a brief look at the first 3d SMMs investigated for their magnetocaloric effect (MCE), followed by the more suitable isotropic iron(III) and manganese(II) clusters and isolated examples of other transition metal compounds. Then we will introduce 3d–4f compounds, examining the influence of lanthanide ions, including an extensive series of phosphonate grids and cages. Next will be homo-metallic gadolinium compounds segueing into polymeric species, which appear to offer significant advantages over zero-dimensional molecules. First of all, though, we will examine the origin of the magnetocaloric effect and its quantification from a chemist’s point of view.

2. Refrigeration and the beginnings of magnetic cooling

Currently, cooling things down is most commonly achieved by the vapour–compression cycle for everyday applications such as refrigerators or air-conditioning units [3a]. For more specialist applications, such as low temperature magnetism or work in extreme environments such as outer space [3b,c], the use of dilution refrigeration can achieve temperatures down to around 2 mK, using the isotopes ⁴He and ³He. Paramagnetic materials can replace and outperform these methods through a physical process called the magnetocaloric effect and specifically through an adiabatic demagnetisation mechanism. An understanding of the physics of this process allows chemists to design and to synthesise compounds which may be useful in this context [3d]. Then, using the two parameters – \(\Delta S_B\) and \(\Delta T_{AD}\), the magnetic entropy change and adiabatic temperature change respectively, the performance of these materials can be quantified.

If we apply a magnetic field to a paramagnet, it will increase in temperature, hence the term magnetocaloric, under adiabatic conditions (constant entropy). This occurs through a redistribution of entropy in the system [3e], the total entropy being given by

\[
S_{\text{total}} = S_{\text{m}} + S_{\text{molec}} + S_{\text{electronic}}.
\]  

As the spin angular momenta, \(S\), of each paramagnetic component, previously randomly arranged, align in the field, the
magnetic entropy will decrease, as the spins become ordered (Fig. 1). As entropy is constant $S_m$ increases to compensate; this can be imagined as the ions in the lattice moving around more and becoming more disordered, hence the material is hotter. An alternative view is that, upon applying a field, phonons are exchanged between the magnetic spin system and the lattice and the latter is raised to a higher vibrational state. Taking the hot paramagnet as a magnetically ordered system we can see how a refrigerant can be obtained thus: if a fluid at ambient temperature is passed over this material then we can obtain an ordered system at the same temperature as its surroundings, whilst remaining in a magnetic field. Switching this field off, an adiabatic demagnetisation, then cools the material below its starting temperature by $\Delta T_{AD}$ as $S_m$ is converted back to $S_g$. Alternatively phonons are passed back from the lattice to the magnetic system and a lower vibrational state is obtained. Either way, we end with a paramagnet cooler than its surroundings: a refrigerator.

All paramagnets exhibit this effect, but in order to classify a material as “good” or “bad” many chemists simply take the magnitude of $-\Delta S_m$ as a guide. In fact the $\Delta T_{AD}$ is a more direct measure of the performance. A majority of papers only report the $-\Delta S_m$ measurements as this can be derived using the familiar Maxwell equations [3e] from magnetisation data, and so is more readily available than heat capacity analysis, which can give both parameters. A third parameter, the product of density and $-\Delta S_m$ ($-p - \Delta S_m$), with units of mJ cm$^{-3}$ K$^{-1}$, can also be straightforwardly obtained and accounts for the composition of the material in bulk.

Out of necessity this review looks primarily at $-\Delta S_m$ changes, unless a fuller characterisation is available, where $\Delta T_{AD}$ will be described.

The magnetic entropy change is given by,

$$S_m = nR\ln(2S + 1) \tag{2}$$

where $R$ is the gas-constant, In the natural logarithm and $S$ the ground spin state of the components and $n$ is the number of spins of the given $S$ [3d]. As a large enough field will saturate the spins and give a zero magnetic entropy state, this is equivalent to the largest possible magnetic entropy change $-\Delta S_m$. In a homo-metallic coordination compound this is simply the number of metals with the given spin, whereas the calculation is a sum for hetero-metallic systems with different spins. Note that antiferromagnetic coupling can give ground state spins less than the possible maximum spin. For non-zero dimensional paramagnets $n$ is the number of spins in the repeat unit. The magnetic entropy of the system is related to the magnetic degrees of freedom or spin multiplicity ($\langle S \rangle$ term), such that increasing the maximum entropy change depends on increasing $S$, and, as the units of $-\Delta S_m$ are J kg$^{-1}$ K$^{-1}$, minimising the diamagnetic mass of the compound, this not contributing to magnetic entropy. Furthermore, anisotropy and consequent zero field splitting (ZFS) should be minimised as this decreases the maximum magnetic entropy change by ordering and splitting the ground spin state in zero field, reducing the entropy of this otherwise degenerate arrangement. Anisotropy barriers arising from ZFS, such as in SMMs, will hinder any repetition of magnetisation and demagnetisation below the blocking temperature, $T_B$, as the magnetisation is not easily saturated over several cycles.

The magnetic entropy change, $-\Delta S_m$, is maximised at the ordering-temperature of the material, i.e. the paramagnetic to (anti)ferromagnetic transition point, $(T_F/T_C)$, greatly influencing the range in which a given material is useful. Indeed, below these ordering-temperatures $-\Delta S_m$ decreases quickly [3e]. In principle the same metal ion can be used in a range of materials, each tuned by their ordering-temperatures for a particular temperature regime by a ligand set which governs its interactions with neighbouring ions. For example, to replace the dilution refrigeration method a material with almost non-interacting spins is required to maintain a high $-\Delta S_m$ at low temperatures (mining the moon for the required, expensive and rare $^3$He is currently only a science-fiction alternative, source is there a valid need for a replacement). One challenge here is to keep metals well separated in the crystal lattice, perhaps using sterically bulky ligands, whilst maintaining a low molecular weight for useful performance (vide infra) [3c]. Room temperature application of this to currently centre on various alloys and metals, such as gadolinium, which has a $T_F$ of 293 K. The main focus of this article lies between these extremes, and is the small but rapidly increasing collection of metal coordination compounds, often termed clusters, which have been shown to outperform rivals in the low-temperature 0.5–20 K range.

The first significant $-\Delta S_m$ for a cluster of the 21st century was found in [FeIII(bta)$_6$O$_6$(OMe)$_{18}$Cl$_6$] where Hbta is benzotriazole [4a] (vide infra). High-spin clusters such as this can give larger $-\Delta S_m$ values than for single ion species and this requires either ferromagnetic interactions between metals or non-complete cancelation of spins where antiferromagnetic coupling is present to give a high spin ground state; weakly coupled systems which can easily be saturated under applied field can also provide a further increase to $-\Delta S_m$ due to the extra low lying magnetic states that are generated. These are populated under zero-field, providing extra degrees of freedom, but depopulated under applied field, giving a larger $-\Delta S_m$. Finally, clusters can also provide a benefit based on the geometrical arrangement of their spins in a spin frustrated system [5], a system where “all spin requirements cannot be satisfied simultaneously”, e.g. in an antiferromagnetically coupled, half-integer spin, equilateral triangle arrangement of metals. This generates easily accessible states in zero-field which contribute to a larger $-\Delta S_m$ under applied field in a similar fashion to weak coupling. It is only with molecular materials that we can tune these properties of spin, anisotropy, geometry, and intra- and inter-molecular interactions, offering significant potential advantages over other materials in this field such as glasses and alloys.

3. Transition metal compounds

3.1. From chaos, order

$\left\{\text{Fe}^{3+}\text{O}_2\text{(OH)}\_{12}\text{[tacn]}\_{6}[\text{Br}_2\text{H}_2\text{O}]8\text{H}_2\text{O}\right\}$ (1), where tacn is 1,4,7-triazacyclononane, $\left\{\text{Mn}^{4+}\text{Mn}^{4+}\text{[CH}_3\text{CO}_2\text{]}_{\text{6}}\text{[H}_2\text{O}]_{\text{12}}\right\}$ 2CH$_3$ COOH 4H$_2$O (2) and $\left\{\text{Mn}^{8+}\text{Mn}^{8+}(2\text{-ClPhCOO})_{\text{16}}\text{H}_2\text{O}_{\text{12}}\right\}$ 2CH$_3$ Cl$_4$ S$_2$H$_8$O (3) [4b–d] are three of the first and most well known SMMs, compounds with large and well defined, isolated $S = 10$ ground states and high axial anisotropy. Investigations into their NCE found significant magnetic entropy changes that rivalled super-paramagnets and the inter-metallic compounds previously investigated. A major problem with these is the dependence of the magnetic entropy changes on the rate at which the field is
swept, due to the anisotropy barriers present. Thus, although these studies and forthcoming theoretical calculations and experiments (vide infra) would show anisotropy to be detrimental to a high MCE in clusters, these were the forerunners towards subsequent improvements.

Anisotropy removes the spin degeneracy of a spin state S in zero-field, giving ordered m, states. To saturate the spin system, populating only the ground state, requires a larger field than for a less anisotropic system and gives, equivalently, a lower magnetic entropy change in the same strength field. This was demonstrated neatly by Evangelisti and Brechin for a hypothetical system [34]. This showed that, for three cases of increasing axial anisotropy (D = 0.5, 1.5 and 3.0 K) the maximum magnetic entropy change – ΔS_M at a field change of 1–7 T, decreases in magnitude by around 50% and also increases to a higher temperature. This second effect occurs because, below a certain temperature, some of the spins will lie in the opposite sense to the field, being held by the anisotropy barrier, so more thermal energy is needed to reach a saturated state.

3.2. The iron age

Following these studies the first cage to confirm how promising isotropy could be in molecular refrigerators was \(\text{Fe}_{14}\) [42], or \(\text{Fe}^{\text{III}}\text{O}_{2}\text{(bta)}_{3}\text{O}_{2}\text{(OMe)}_{3}\text{Cl}_{6}\) [4] (Fig. 2), where Hbta is benzo triazole. In contrast to the above early work with \(\text{Mn}_{12}\) and \(\text{Fe}_{8}\) this has a very low cluster anisotropy, ΔD_{ax} ≈ 0, derived from a symmetrically hexacapped hexagonal bipyramid core, removing the disadvantages discussed above. The high ground state spin, where S = 25, from an alignment of all but the two apex iron(III) spins, is ill-defined according to susceptibility and magnetisation data, which suggest additional populated low lying states and hence extra magnetic entropy in zero field. Magnetisation and heat capacity measurements found – ΔS_M to be 15.9 J·K\(^{-1}\)·kg\(^{-1}\) at 6 K for a 0–7 T field change, larger than anything previously measured at these low temperatures. Although these two techniques are complementary, a more complete characterisation is offered by the latter giving ΔD_{ax} as ca. 6 K and information on the inter-cluster interactions. These interactions are evident at T_N = ca. 1.9 K, and may tune the range of the magnetocaloric response. – ΔS_M and ΔD_{ax} decreasing rapidly below this temperature. Interestingly, for \(\text{Fe}_{14}\) – ΔS_M is shown to be larger than that calculated for an S = 25 paramagnet, showing how an isotropic ground state can favour a large MCE. This “enhancement” of magnetic entropy over an equivalent spin paramagnet (and super-paramagnets) is due to the spin degeneracy of the ground spin state.

A more recent iron cluster, \(\text{Fe}_{13}\), \(\text{Fe}^{\text{III}}\text{O}_{2}\text{(OH)}_{2}\text{(py)}_{2}\text{Br}_{4}\text{Br}_{5}\) (S = 4\(\text{e}\)), where py is pyridine, is similar in concept with a large spin and low D anisotropy. Thus, with its truncated tetrahedral core, has an approximate S = 35 ground state, from antiferromagnetic coupling between the two Fe\(^{\text{III}}\) geometries present, five ions having a tetrahedral geometry and the remainder octahedral, (S = 12\(\text{e}\) + 5\(\text{e}\)). By fitting of magnetisation, D is very small at 0.023 K as required. Of additional interest here is the compound with cubic symmetry, Pa-3, and not the otherwise identical trigonal analogue, R-3. The former offers a minimising of the dipolar interactions between clusters by chemical control of the crystallisation process, resulting in a lower ordering temperature, seen as a shift in T_N. This lowering, combined with the spatially isolated clusters in the crystal structure, shifts the useful range of operation to very low temperatures. Indeed, although – ΔS_M is relatively low, 8.9 J·K\(^{-1}\)·kg\(^{-1}\) (2.7 K, ΔM ≈ 0–7 T), on account of the large ligand mass, this may still be useful compared to materials with large – ΔS_M values at higher temperatures, whereas here down to at least 0.3 K no phase change is seen.

3.3. Manganese(II/III) clusters

The use of polyligand ligands in synthesising 3D transition metal clusters has been very productive [6], particularly with manganese(II/III). This is a well-trodden route to SMMs as these ligands combined the flexibility useful with a “serendipitous” approach with the multi-dentate abilities that enable high nuclearity clusters to be formed. In turn this could give high-spin molecules, depending on the coupling between the ions. In pursuing increasingly large energy barriers, many groups held the equation U_M = D|S|^2 (for integer spins) the key. Although only later was it appreciated that high spin and a large D are not independent [7], these molecules could be useful as magnetic refrigerants, if D was small. Using the ligand H_4amp, 2-amino-2-methyl-1,3-propanediol, a diol with an NH\(_2\) arm, so potentially adding extra bonding modes, two clusters were synthesised: namely \([\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{O}_6\text{Br}_4\text{amp}]_2\) and \([\text{ampH}_2\text{H}_{\text{amph}}\text{H}_2\text{Br}_6\text{Hexane}]_2\) (amp, which has a super-tetrahedral structure distinct from its close relation \([\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{O}_6\text{Br}_4\text{amp}]_2\text{ampH}_2\text{H}_{\text{amph}}\text{H}_2\text{H}_{\text{amph}}\text{H}_2\text{OH}]_2\text{EtOH}]_2\text{EtOH}\) (7), which is a planar disc [41] (Fig. 3). An important difference between them is that the oxido of the former are now hydrides in the latter, dictating the...
structure and also generating weaker coupling through the super-exchange mechanism between metals. Each has an $S = 22$ ground state from ferromagnetic coupling between all spins, although only the magnetisation data of the first (6) were fitted, with $g = 2.00$ and a desirable $D = 0$, arising from the almost $T_2$ cluster symmetry. A tetrahedral $0$ anions are spheres, outer $O$ atoms are red wireframe. Right, the planar disc of (8), directed by pseudo-planar $OH$ groups; colours are $Mn$ dark pink, and $O$, red spheres. (Colour online).

3.4. Super-tetrahedral world

A second series of $[M_{10}]$ (9), $[M_{11}]$ (10) and $[M_{13}]$ (11) [46] compounds, more fully $[M_{11}Mn^{II}O_2(LH_3)Br_3(N_3)_2Cl_2]$, $[Mn^{II}ClO_2(MeOH)]_2$, $[MeCN]_2$, and $[Mn_{11}^{II}O_2(L_3)H_2(MeCN)]_2K_2$, MeCN and $[Mn_{11}^{II}O_2(L_3)H_2(MeCN)]_2$, MeCN and $[Mn_{11}^{II}O_2(L_3)H_2(MeCN)]_2K_2$, MeCN, were found to have enormous ground spin states of $S = 22$, $23 \pm 1$ and $81/2$. These are based on the $[M_{10}]$ super-tetrahedral core, the larger clusters linking this unit by an edge (with three common metals) or vertex (one common metal), respectively. Compound (9) was synthesised using the pro-ligand 3-methyl pentane-1,3,5-triol ($H_4$peol) and has similar magnetic behaviour and magnetic structure to (6), giving $\Delta S_{M}\Delta T$ of 10.3 J kg$^{-1}$ K$^{-1}$ (2.6 K, $\Delta H = 0\rightarrow 9$ T). Using the diol, 2,2-dimethyl-1,3-propanodiol ($H_4$peol) gave the vertex-joined super-tetrahedron ($M_{10}$) with a larger $\Delta S_{M}\Delta T$ of 13.3 J kg$^{-1}$ K$^{-1}$ (5.2 K, $\Delta H = 0\rightarrow 7$ T), larger than those above, despite the lower ground state, due to an even larger enhancement from low-lying states. Magnetic data of the first ($M_{10}$) was found to be 13.1 K. Although it is difficult to reach the $S = 32$ ground state and two $\Delta S_{M}\Delta T$ maxima of 9.5 J kg$^{-1}$ K$^{-1}$ (6 and 10 K, $\Delta H = 0\rightarrow 7$ T) for the tetra-deca-hexadecahedral $H_4$peol pro-ligand, pentaerythritol, gave a tetra-deca-hexadecahedral spin state $S = 32$, so enhancing the possible entropy change, in a similar way to $(Fe_3)$. Clearly, the weaker the interactions, the smaller the energy gap between states of different spin in zero-field. This has strong and promising implications for lanthanide compounds, more fully $[Mn^{III}O_2Cl_2(2,6-(hydroxymethyl)-phenol)]_2$ with two apex manganese(II) ions replaced by sodium(II) ions [48]. Fitted magnetisation data gave an $S = 32$ ground state and two $\Delta S_{M}\Delta T$ maxima of 9.5 J kg$^{-1}$ K$^{-1}$ (6 and 10 K, $\Delta H = 0\rightarrow 7$ T). Lastly, using another triol ($H_4$peol) 2,6-bis-hydroxy-methyl-4-methylphenol, produced the vertex-linked cage ($M_{10}$). Ferromagnetic coupling of spins gives the largest $S$ possible, and the largest of any polymeric cluster, though the very small anisotropy means no SMM behaviour was seen and $\Delta S_{M}\Delta T$ of 8.9 J kg$^{-1}$ K$^{-1}$ (4.2 K, $\Delta H = 0\rightarrow 7$ T) is rather modest, too. The almost identical compound $[Mn_{11}^{II}O_2(H_4peol)_2(N_3)_2]$ ($M_{10}$), has a similar $\Delta S_{M}\Delta T$, at a slightly higher temperature, due to a larger anisotropy, matching previous theoretical ideas [48]. This arises from an overall Jahn–Teller axis of the cage which is less symmetrical than in the related compound.

3.5. Cold stars

The more recent $[M_{11}]$ cluster $[Mn_{10}^{III}bipy]_{12}[Mn_{10}^{III}thme]_{12}(bipy)_{12}(OAc)_{12}(ClO_4)_{2}$ (15) [48], where $H_4$thme is tris(hydroxymethyl)ethane, has several interesting features. Firstly, it has an unusual “truncated-cube structure” which is made up of $[Mn_{10}^{III}Mn_{10}^{III}]$ metal–metal bonds. Isolated metal stars [8] are desirable, as they have non-zero and high $S$ states: if the points of the star couple antiferromagnetically to the central metal, this gives an overall spin equal to the sum of these outer contributions minus the centre spin. Susceptibility data suggested an ill-defined ground state, a common theme throughout manganese chemistry on account of weak manganese(II) coupling and also the high nuclearity of this compound. The magnetisation was found to increase even at 0.35 K and 7 T, approaching the maximum possible by alignment of the eight resultant $S = 6$ spins of the metal stars. Heat capacity data found $\Delta S_{M}\Delta T$ of $8.2 J kg^{-1} K^{-1}$ (1.6 K, $\Delta H = 0\rightarrow 7 T$) and $\Delta T_{Max}$ of 6.7 K, combined with a high efficiency, which relates how large the field must be to reach the $\Delta T_{Max}$ (2 K T$^{-1}$). For a spin $S = 48$, $\Delta S_{M}\Delta T$ can only reach $3.6 J kg^{-1} K^{-1}$, a massive difference compared to that seen, showing just how important the spin degeneracy of a system is for MCE. Most of the zero-dimensional compounds described here have densities of around 2 g cm$^{-3}$ (see S.I. for more precise values), so there are no remarkable changes in their apparent usefulness when this is taken into account. Compound (12), though, is unusual among cluster compounds as it has a density of around 3 g cm$^{-3}$ – (see S.I. for more precise values). This means that, despite its $\Delta S_{M}\Delta T$ value being half that of (15), its maximum $\rho\Delta S_{M}\Delta T$ is superior. This important consideration will be re-examined later, when we consider polymeric compounds and their superiority in this regard over their zero-dimensional counterparts.

3.6. Frustration

Before we conclude this look at transition metal compounds a brief diversion from manganese(II/III) clusters will be instructive by looking at an isolated example of a nickel(II) cluster, $[Ni^{II}(OH)_{12}(chp)_{12}(MeOH)]_{10}[OAc]_{12}$ (16) [48]. This has an unusual geometry, where two triangular-based pyramids share a common apex leading to a high degree of magnetic frustration, arising from the antiferromagnetic exchange between basal and apical spins. Frustrated topologies are seen later for, in particular, two homo-metallic gadolinium cages, vide infra. First, though, we will look at how 3d–4f compounds can give improvements in $\Delta S_{M}\Delta T$ over the transition metal cages above.
4. 3d–4f Compounds

Lanthanide ions can have a larger ground state spin than transition metals and a small anisotropy, particularly gadolinium(III) with its ground term 5S_{5/2}, which can provide large δAS values even for single ions. In fact for an isolated ion, δAS is theoretically 110 J kg⁻¹ K⁻¹. Weak coupling is almost guaranteed, given the ionic nature of the bond in lanthanides, using the core-like valence 4f orbitals, and this can result in spin degeneracy, which was shown to be important in 3d magnetocaloric materials. Incorporating gadolinium(III) (and less often, other lanthanides) into 3d metals has resulted in a larger MCE than with 3d metals alone, as has also occurred in the search for larger Uα anisotropy barriers. This shows how important it is to explore all areas of the Periodic Table.

4.1. Adding lanthanides to manganese clusters

4.1.1. The calix-4-arene cooler

Although Glauser’s [Gd6(SO4)3][H3O] was the first molecular refrigerant using gadolinium, the [Gd4Mn6] calix-4-arene complex [10a] from Katsoris et al. is the first with organic ligands and is a neat example of how lanthanides and transition metals can give significant MCE properties. [Gd4Mn6(OH)4(tetrahydrocalix[4]arene)4]Cl0.5(2H2O)6(ΟΗ2)16, where dmf is dimethylformamide and the calix-4-arene pro-ligand is a tetraloan, is made up of a gadolinium square in a manganese square, which could be called an empty 3 × 3 grid. Magnetisation and susceptibility data indicate that there is weak coupling between spins and several states other than the ground state populated down to low temperatures. The potential anisotropy due to the manganese(III) ions is removed by the perpendicular alignment, and hence cancelation, of their Jahn–Teller (anisotropy) axes. The resulting δAS of 19 J kg⁻¹ K⁻¹ (4 K, ΔH = 0–7 T), twice that expected from the S = 22 state given by ferromagnetic exchange confirmed that these extra states have a significant effect on the performance.

4.1.2. A coaxial double screw

The similarity of lanthanides across the series in their size and chemistry can allow for iso-structural analogues of compounds, particularly those with lanthanides. This three oxygen donors bond to the phosphonate oxygen atoms and Y1, Y2 and Y3 the number bonded to each oxygen. This ligand’s bonding aldoxime. Here, when Ln is dysprosium(III) the compound shows as was the case for [Ln3MnIII4O3(OH)(O2C(η3-Bu))6(Et-sao)3](17) where Et-saoH2 is ethyl-salicylaldoxime; Ln, purple; MnII, pink; O, red; N, pale blue. (Colour online).  

4.2. Phosphonic acids

4.2.1. 3d–4f Phosphonate clusters

The phosphonic ligand has been extremely useful in the preparation of a large number of coordination compounds, particularly those with lanthanides. Its three oxygen donors bond to up to nine metals in a variety of modes. This is easily described by Harris notation [11a] such that XY1Y2Y3 where X is the total number of metals bonded to the phosphonate oxygen atoms and Y1, Y2 and Y3 the number bonded to each oxygen. This ligand’s bonding flexibility is enhanced by the large choice of R groups (RPO3H2) available, assisting solubility or bonding by incorporating functionalities other than and including oxygen atoms. Although many 3d-phosphonate molecules have been synthesised for transition metals, only molecular 3d–4f phosphonates have been studied for their magnetic properties. These works followed from two CeIV–MnIV compounds [11b], [Ce4Mn6] the zero dimensional cluster [Ce4Mn6O3(OH)(O2C(η3-Bu))6(Oh)3]2H2O and [CeIV n+2MnIV]3. The one dimensional polymer [CeIV n+2MnIV]3(O2PMe)2(C2Me3)(OMe)4(NO3)(H2O)4], which were studied for their SMM behaviour, Baskar et al. also prepared a series of compounds using the bulky ttrityl-phosphonic acid ligand [11c]; two [Ln(CuIIEtO)3(EtOH)3(Et-sao)]4(NO3)2(dmf)6(H2O)6(OH)2 are a magnetisation derived from a significant MCE properties. [Gd4MnIII4(OH)(O2C(η3-Bu))6(Et-sao)3](17), where Et-saoH2 is ethyl-salicylaldoxime; Ln, purple; MnII, pink; O, red; N, pale blue. (Colour online).
which has a spherical-type core, despite the similarity of the two lanthanide(III) ions in terms of size and reactivity. Thus, three rather different topologies were obtained from only marginal variations in starting material.

In choosing the appropriate lanthanide Yan-Zhen et al. have shown that dysprosium(III), which has a large single-ion anisotropy can dramatically hinder a large \( -\Delta S_{\text{M}} \). In (20), the maximum theoretical value is around 43 J kg\(^{-1}\) K\(^{-1}\), which is much larger than that found by magnetisation of 13 J kg\(^{-1}\) K\(^{-1}\) (3 K, \( \Delta H = 0-7 \) T), an effect seen in several other dysprosium-transition metal phosphonate clusters, vide infra. In fact, the largest magnetic entropy change for any molecule with dysprosium(III) is only 13.8 J kg\(^{-1}\) K\(^{-1}\), for the large \([\text{Dy}_{24}]^{-} \) cluster. Despite its large spin of \( ^{7/2} \), the same as for manganese(II) and iron(III) (high spin), its large anisotropy will generally lead to a much lower MCE than gadolinium analogues of these compounds, indeed \([\text{Gd}_{24}]^{2+} \) (60) is much more promising, vide infra.

From susceptibility data, dominant antiferromagnetic interactions could be inferred for the gadolinium(III) compounds, although these were significantly weaker for (19) than (18). This manifests itself as a much larger \( -\Delta S_{\text{M}} \) of 34 J kg\(^{-1}\) K\(^{-1}\) (3 K, \( \Delta H = 0-7 \) T) for the former, which was the highest reported at the time and in excess of that seen for all transition metal compounds. When compared to the \( -\Delta S_{\text{M}} = 28 \) J kg\(^{-1}\) K\(^{-1}\) found under the same conditions for the latter, well below the theoretical maximum values of ca. 57 J kg\(^{-1}\) K\(^{-1}\), we can see how detrimental antiferromagnetic coupling can be. This feature is clearly seen later in the homo-metallic compounds \([\text{Gd}_{x}]^{2+} \) (55) and \([\text{Gd}_{2}]^{2+} \) (56), where the slow magnetisations rates associated with this type of coupling are easily visible.

4.2.3. Cobalt(II)–lanthanide phosphonate compounds

The general synthetic route to 3d–4f phosphonates can be modified to give structures with many of the 3d transition metals so the choice of cobalt(II) here may seem surprising, given that the free ion has a large orbital contribution to its magnetic moment, which can give significant zero field splitting. This, though, is frequently quenched in an appropriate crystal field, such as the tetrahedral arrangement encountered in a number of the following compounds. Excellent reviews by Yan-Zhen (10d,e) describe all the cobalt(II)–lanthanide(III) compounds mentioned here with much more detail and illustration, so the following is a brief summary.

Six distinct clusters were synthesised based on grids: \([\text{Gd}_{6}\text{Co}_{2}^{3+}(O\text{PCH}_{2}\text{Ph})_{3}(O\text{CBu})_{4}(\text{MeCN})_{6}]^{2+} \) (21), \([\text{Gd}_{6}\text{Co}_{2}^{3+}(O\text{PPh})_{3}(O\text{C Bu})_{4}(\text{MeCN})_{6}]^{2+} \) (22), \([\text{Gd}_{6}\text{Co}_{2}^{3+}(O\text{PPh})_{3}(O\text{C Bu})_{4}(\text{MeCN})_{6}]^{2+} \) (23) (Fig. 5) and \([\text{Gd}_{6}\text{Co}_{2}^{3+}(O\text{PBu})_{3}(O\text{C Bu})_{4}(\text{MeCN})_{6}]^{2+} \) 2MeCN (24), respectively a \([3 \times 3]\) square with double central node, a \([4 \times 4]\) square with rotated inner square and a bi-capped \([2 \times 2]\) square. Two further clusters can best be described as cages, namely \([\text{Gd}_{6}\text{Co}_{2}^{3+}(O\text{PCH}_{2}\text{Ph})_{3}(O\text{C Bu})_{4}(\text{HO}_{2}\text{CMe})_{6}]^{6+} \) 2MeCN (25) and \([\text{Gd}_{6}\text{Co}_{2}^{3+}(O\text{PPh})_{3}(O\text{C Bu})_{4}(\text{HO}_{2}\text{CMe})_{6}]^{6+} \) 2MeCN (26).

There is a direct correlation between the percentage of gadolinium in each compound and its maximum magnetic entropy change, as expected given the favourable properties of that ion compared to cobalt(II) \((x = \frac{7}{2})\). The largest found in this series is for (26), and from magnetisation data this is 28.6 J kg\(^{-1}\) K\(^{-1}\) (3 K, \( \Delta H = 0-7 \) T, and for all phosphonate compounds unless stated), one of the highest for a 3d–4f cluster compound. Extending this analysis using heat capacity data and high field magnetisation found this rises to 33 J kg\(^{-1}\) K\(^{-1}\) at 4 K and a huge 14 T field change, the maximum possible being ca. 48 J kg\(^{-1}\) K\(^{-1}\), still some way off, and probably attributable to the lack of saturation of the cobalt(II) spin, as evidenced by the magnetisation data of the \([\text{Y}_{2}\text{Co}_{2}^{3+}]^{2+} \) analogue, which itself has a rather small MCE of \( -\Delta S_{\text{M}} = 4.5 \) J kg\(^{-1}\) K\(^{-1}\). The dysprosium compound \([\text{Dy}_{2}\text{Co}_{2}^{3+}]^{2+} \) (28) shows expectedly lower values \((11.6) \) J kg\(^{-1}\) K\(^{-1}\).
4.2.5. Further prospects for 3d–4f phosphate compounds

There are still several areas to explore for this methodology, not least in the discovery of aesthetically pleasing new topologies. Chiefly is whether copper(II)–gadolinium clusters benefit from the favoured ferromagnetic interactions between these two ions and to what this will lead, vide infra. Several examples above, particularly with manganese(II)–gadolinium, were hampered by an antiferromagnetic interaction. Given this, zinc(II)–gadolinium(III) compounds may be interesting, with no interactions between the diamagnetic ion and lanthanide, although this also adds to the redundant mass in the cluster (the authors of this review are currently investigating a close analogue of (24), namely [Gd2Zn9O2(C2O4)2(Bu4N)2] (32) [10g], which has −ΔSM = 15.1 J kg⁻¹ K⁻¹ (3 K, ΔH = 0–7 T), suggesting the cobalt(II) ions are useful despite their anisotropy). Previous results above with iron(III) clusters suggest iron(III)–gadolinium(III) might have an appreciable MCE. One broader point may be that, when the diamagnetic yttrium(III) analogues have been made, the magnetic entropy changes are rather small. This strong dependence of the MCE in 3d–4f compounds on the lanthanide suggests homo-metallic 4f compounds using gadolinium could be superior to 3d–4f compounds, vide infra.

4.3. An earnest study of substituting metals: [Gd4MII(II)(O3PMe2)3(OH)(L)2]2+(ClO4)3

Comparing the MCE of 3d–4f clusters with different transition metal ions can be difficult owing to the lack of iso-structural analogues so far studied. However, the following is such a series [10h]: The 3d–4f clusters [Gd4MII(II)(O3PMe2)3(OH)(L)2]2+(ClO4)3, where MII is zinc(II) (33), nickel(II) (34) or copper(II) (35). HL is 2-(hydroxymethyl)pyridine and R are small carboxylates. These are made up of a square of lanthanides with each edge having one transition metal above and below the plane. Comparing the effect of changing the transition-metal(II) ion, confirmed that antiferromagnetic interactions can be extremely detrimental to the cooling performance of a material. This trio of compounds exhibit significantly different magnetic interactions resulting, unexpectedly, in a lower −ΔSM for [Gd4CuII8] than [Gd4Zn8], despite the higher ground state spin of the former. The diamagnetic zinc(II) ion in [Gd4Zn8] allows a fitting of susceptibility data to reveal very weak antiferromagnetic coupling between gadolinium(III) ions. Saturation magnetisation indicates S = 14, as expected for all four gadolinium(III) spins aligning in field, with the resulting −ΔSM, from only the lanthanide ion contribution, ca. 18 J kg⁻¹ K⁻¹ (2 K, ΔH = 0–7 T), thus approaching the theoretical maximum of ca. 21 J kg⁻¹ K⁻¹. This occurs at rather low temperatures, which is ascribed to weak exchange coupling between metals from heat capacity measurements. This is different to [Gd4CuII8], where Cu³⁻–Cu²⁺ exchange is much stronger than Gd³⁺–Cu²⁺ (by 10 times) increasing the position of the −ΔSM maximum to 5.6 K. Surprisingly, this maximum −ΔSM is only 14.6 J kg⁻¹ K⁻¹, and, despite the presence of a paramagnetic 3d metal, lower than in [Gd4Zn8]. The exchange between copper and gadolinium spins results in a ferromagnetic molecule, which, although a S = 18 ground state is reached at 7 T, means the field must align spins. In fact −ΔSM is −0.7 J kg⁻¹ K⁻¹ at 0.9 K (ΔH = 0–1 T), the material warming rather than cooling in an applied field and thus giving a rather low value at higher fields, compared to that expected theoretically. This striking negative −ΔSM value demonstrates well the malign effect of antiferromagnetic exchange. The largest entropy change is found in [Gd4MII8], which has dominant ferromagnetic coupling between nickel(II) ions. Compound (34) has the largest ground state of the three, with S = 22, although this is more promising as there are no antiferromagnetic interactions to overcome. This, combined with a fast magnetisation rate, means that the −ΔSM maximum of 22 J kg⁻¹ K⁻¹ (3.6 K, ΔH = 0–7 T) occurs at higher temperatures than for the weakly coupled (33). From heat capacity data, which confirm the entropy changes derived from magnetisation data, the magnetic contribution to the entropy change can be seen as a peak in C|H at low temperatures for (33), but moves to higher temperatures for the other compounds, so shifting the maximum −ΔSM to higher temperatures. This system will doubtless reveal more in the future about the effects of ligand, counter-ion and metal influence on the MCE as these parts are substituted.

4.4. CuIcooling with gadolinium clusters

Despite (35), a ferromagnetic interaction between gadolinium(III) and copper(II) is generally favoured, although only a small number of clusters have taken advantage of this for their magnetocaloric properties. One of these is [Gd6Cu3(O2C2Me2)3(teaH3)6Cl2]6[J2H6O]5, which has an octahedron of gadolinium ions inside a larger copper(II) octahedron. A fit of susceptibility data gave the hoped for interaction, helping to give a magnetic entropy change of 23.5 J kg⁻¹ K⁻¹ (2.3 K and ΔH = 0–7 T), which is the expected maximum value and second to only (37) amongst copper(II)–gadolinium clusters.

In their attempts to synthesise 3d–4f compounds, Murray et al. used the pro-ligand teaH3, or triethanolamine, which can be useful on account of its flexibility in bonding. The benefits of the resulting [Gd4Cu3(O2C2Me2)3(teaH3)6Cl2]6[J2H6O]5 [37] (Fig. 6) are clear: the metal ions have high spin values, the lanthanides being isotropic and generally weakly coupled and these make up around forty percent of the total molecular weight; this is a conceptually ideal 3d–4f cluster for a large MCE. The topology is a planar ‘X’-shape of five copper(II) ions, or vertex sharing triangles, with one gadolinium ion above and below the centre of each copper(II) triangle. Susceptibility data indicate dominant ferromagnetic interactions between the more strongly coupled copper(II) ions, with magnetisation data suggesting one of these is aligned opposite to the outer four. Therefore, the expected 3d–4f interaction makes up an S = 3/2 state, enhanced by necessarily weak lanthanide exchange so giving numerous low-lying excited states that increase the magnetic entropy. This is realised by the maximum −ΔSM of 31.1 J kg⁻¹ K⁻¹ (3 K, ΔH = 0–9 T) which approaches the theoretical limit for fully decoupled spins and was the largest at the time. From both heat capacity and magnetisation data, the former also found an impressive maximum ΔSM of more than 10 K at 2 K (ΔH = 0–9 T), showing how the copper(II)–gadolinium interaction, when harnessed appropriately,
and combined with other advantages, can confer high performance on these compounds.

4.5. A valiant effort

\[ \text{[Gd}_2\text{Ni}^2\text{Cl}_8\] is made up of two \((\text{GdN}_3)\) tetratomic units linked by water. Each unit is itself held together with the amino acid valine, the \(\text{NH}_2\) group of which favours bonding to the 3d metal. A fit of magnetisation data was complicated by the anisotropy of the nickel(ii) ions, though this suggested an \(S = 7\) ground state with \(S = 8\) and \(S = 6\) states very close in energy. Density functional theory (DFT) calculations gave a different conclusion of an \(S = 13\) ground state, this using a more realistic model of the system. The \(\Delta S_{\text{M}}\) is 17.6 J kg\(^{-1}\) K\(^{-1}\) (3 K, \(\Delta H = 0\)–5 T) is that expected from uncoupled ions, remembering the presence of a gadolinium containing counter-ion.

4.6. Chromium(III)–gadolinium fluoride cages: something completely different

The use and study of chromium(III) in 3d–4f molecular magnetism has been limited. As most work has concentrated on SMFs this is perhaps due to the near-isotropy of the d\(^3\) ion in the commonly adopted octahedral crystal field environment. In the field of magnetic cooling, though, it could be more useful. Also rather rare in molecular magnetism is the use of ligands where the donor atoms are not all nitrogen and oxygen. Particularly for "hard", largely ionic, lanthanides these are of course a good match. With 3d–4f compounds this presents a problem if an ion such as fluoride is used. Its preference for the lanthanide, and the stable Ln–F bonds in LnF\(_3\), which result, have prevented mixed 3d–4f cluster compounds being isolated in all but a handful of cases. Birk et al.’s series of chromium(III)–gadolinium–fluoride compounds \[10\] is therefore extremely interesting. \[\text{[Gd}_2\text{Cr}^3\text{I}^3\text{Cl}_8\text{MeCN}]\] is a \((\text{Gd}[\text{I}^3\text{MeCN}]\) planar triangle capped by two \((\text{Cr}^3\text{I}^3\text{MeCN})\) groups, where \(\text{MeCN}\) is 1,1,1-tris-((methylamino)methyl)ethane and HfIac is hexafluoroacetylacetonate. Mild conditions appear to prevent the thermodynamically very stable GdF\(_3\) forming and removing these components from the reaction. The second cluster of interest is \([\text{Gd}_2\text{Cr}^3\text{I}^3\text{C}^2\text{F}_2\text{py}](\text{I}^3\text{MeCN})\] \[10\] with a rather splendid planar almost-square arrangement of alternating metals. For \((39)\) magnetisation data were fitted and showed weak exchange between all metals though this was antiferromagnetic. This fit also suggested ZFS was negligible, as desired. These properties suggest that chromium(III)–gadolinium compounds could be among the best 3d–4f coolers. \(\Delta S_{\text{M}}\) from both magnetisation and heat capacity data, reached 28.7 J kg\(^{-1}\) K\(^{-1}\) (2.2 K, \(\Delta H = 0\)–9 T), equivalent to that found for uncoupled ions and above that expected for an \(S = \frac{7}{2}\) paramagnet, as discussed elsewhere. Compound \((40)\) shows a smaller MCE of 11.4 J kg\(^{-1}\) K\(^{-1}\) (4.1 K, \(\Delta H = 0\)–9 T). A similar treatment as above found significantly stronger chromium(III)–gadolinium antiferromagnetic coupling, owing to the changing Cm\(^{\text{III}}\)–F–Gd bridging angle; this leads to a much smaller MCE of 11.4 J kg\(^{-1}\) K\(^{-1}\). The relationship between these angles and exchange coupling is well established for several systems. Understanding this could lead to more desirable ferromagnetic exchange if this parameter can be manipulated by other factors.

4.7. Giant metal cages: forty metal ions or more

The majority of investigations into molecular magnetism tend to look at clusters up to around ten metals. This can limit their magnetic entropy changes, as the spin ground state is limited; in other cases the metal to ligand ratio can be low. One way around these problems is to use small ligands to increase the percentage of "active" metal which can be achieved by packing a large number of metals, so increasing \(S\), into a compact core using a template approach. This technique was used to synthesise giant metal cages of forty metals or more, leading to the largest MCE seen for 3d–4f cages.

4.8. Many metals in a compact cage

\[ \text{[Gd}_2\text{Co}_3\text{Ni}^2\text{Cu}^2\text{Al}^2\text{Cl}_8\text{OH}_2\text{H}_2\text{O}] \text{[CO}_3\text{]}_2\text{OH}_2\text{H}_2\text{O} (41) \] and \[\text{[Gd}_2\text{Ni}^2\text{Al}^2\text{Cl}_8\text{OH}_2\text{H}_2\text{O} (41) \] and \[\text{[Gd}_2\text{Co}_3\text{Ni}^2\text{Cu}^2\text{Cl}_8\text{OH}_2\text{H}_2\text{O} (42) (13a)\] have unusual and complicated bowl-like cores made up of \((\text{Gd})\), \((\text{GdNi})\) and \((\text{Ni})\) units templated by \((\text{ClO}_4)^-\) anions with the lightweight \(\text{CO}_3\) and \(\text{OH}\) ligands. Carboxylate groups coat the exterior. For \((41)\) the susceptibility data were not unambiguous in suggesting dominant antiferromagnetic coupling, there also being the possibility of an orbital contribution from the cobalt(ii) ion, these are suggested by the difference between the experimental value of \(\Delta S_{\text{M}}\) and the theoretical maximum of ca. 52 J kg\(^{-1}\) K\(^{-1}\), which accounts for the diamagnetic cobalt(III), assigned by charge balancing. Dominant antiferromagnetic coupling was also deduced, though the value of \(\Delta S_{\text{M}}\) reached 41.3 J kg\(^{-1}\) K\(^{-1}\) (2 K, \(\Delta H = 0\)–7 T), owing to the large number of isosotropic spins and large metal to ligand ratio. Heat capacity measurements confirmed this, though no \(\Delta T_{\text{M}}\) maximum was seen down to the lowest temperatures utilised (2 K). For \((42)\) \(\Delta S_{\text{M}} = 38.2 J kg^{-1} K^{-1} (2 K, \Delta H = 0-7 T)\), which for similar reasons to \((41)\) is smaller than the theoretical maximum value. This group also synthesised the conceptually similar \[\text{[Gd}_2\text{Ni}_2\text{Cu}_2\text{Cl}_8\text{OH}_2\text{H}_2\text{O} (43) \] also have large densities of around 2.8 g cm\(^{-3}\), translating to some of the largest \(\Delta S_{\text{M}}\) values and superior to all but a handful of polymeric compounds, vide infra.

Extending this to copper(II)–gadolinium compounds led to the wheel structure \([\text{Gd}_2\text{Co}_3\text{Al}^2\text{Cu}^2\text{Ni}^2\text{Cl}_8\text{OH}_2\text{H}_2\text{O} (41) \] and \([\text{Gd}_2\text{Ni}^2\text{Al}^2\text{Cl}_8\text{OH}_2\text{H}_2\text{O} (42) (13a)\] (Fig. 7), which is almost 5 nm in width. This is made up of alternating hexagonal \((\text{Cu}^3)\) units in boat-configurations and \((\text{Gd})\) cubanes. Although the larger ligand mass, consequent reduced metal percentage, and antiferromagnetic interactions deduced from magnetisation data mean that the maximum magnetic entropy change is less than in \((41–43)\), this still reaches 21 J kg\(^{-1}\) K\(^{-1}\) (2.1 K, \(\Delta H = 0–7 T)\), lower than the maximum possible for uncoupled spins of around 36 J kg\(^{-1}\) K\(^{-1}\). Despite the disadvantages of antiferromagnetic coupling and some ZFS, the approach taken here, using lightweight ligands, with metals tightly arranged, was successful, producing a very large MCE in all cases. Compounds \((41)\) and \((42)\) also have large densities of around 2.8 g cm\(^{-3}\), translating to some of the largest \(\Delta S_{\text{M}}\) values and superior to all but a handful of polymeric compounds, vide infra.

In a category of its own is the 4d–4f compound \([\text{Gd}_2\text{MoO}_4\text{NiL}_2\text{MeCN}]_2 \text{[ClO}_4\text{]}_2\text{MeOH} \text{[ClO}_4\text{]}_2\text{MeCN} (44) [13c] \) (Fig. 7). In a category of its own is the 4d–4f compound.
4.10. Cobalt(II)–lanthanide cubanes

\[ \text{[LnCo}_3\text{hmpa(OAc)H}_2\text{O]} \], where Ln is dysprosium, holmium, erbium, thulium, ytterbium or yttrium (46–51) [10m] and hmpa is \( 2\)-hydroxymethylpyridine, make up a set of cubane compounds, where the lanthanide can be selected by the choice of starting material. Here only the later, and anisotropic, lanthanides could be selected in this way. Also the cobalt(II) ions, which here have an octahedral geometry, preclude any rigorous magnetic analysis by their significant orbital contribution. Comparison with the yttrium analogue (51) suggested overall ferromagnetic coupling for the dysprosium, erbium, thulium and ytterbium compounds. Despite this the maximum \(-\Delta S_m\) values are not predicted to be large, and reach a maximum of \(12.6 \text{ J kg}^{-1} \text{ K}^{-1} \) (5.5 K, \( \Delta H = 0–7 \text{ T} \)) for (46).

4.11. Chromium wheels

There have been two studies on the MCE of chromium wheels relating to the linked \( [\text{Cr}^6\text{N}^6]\) units. \([\text{NH}_3\text{Pr}_2]\text{[Cr}^6\text{NO}_5\text{Fe}_2\text{O}_C\text{Bu}_3\text{O}(\text{OCC}_5\text{H}_4\text{N})\text{[Cr}_3\text{CC}_6\text{H}_4\text{N]}\text{[Cr}^6\text{NO}_5\text{H}_2\text{O}])\] (32) [13a], and the single ring \([\text{MeNH}_2]\text{[Cr}^{27}\text{Fe}_2\text{O}_C\text{Bu}_3\text{]}\) (53) [15b]. These are beyond the scope of this review, being focussed on detailed modelling of the electronic structure of the former while the latter builds on theories of the early SMMs investigated, in showing how their lattice contributions to entropy disfavour their use as low temperature refrigerants.

5. Homo-metallic gadolinium compounds

We have shown several examples of how the lanthanide ion is the most significant contributor to a large MCE in 3d–4f compounds. Also the cobalt(II) ions, which here have an octahedral geometry, preclude any rigorous magnetic analysis by their significant orbital contribution. Comparison with the yttrium analogue (51) suggested overall ferromagnetic coupling for the dysprosium, erbium, thulium and ytterbium compounds. Despite this the maximum \(-\Delta S_m\) values are not predicted to be large, and reach a maximum of \(12.6 \text{ J kg}^{-1} \text{ K}^{-1} \) (5.5 K, \( \Delta H = 0–7 \text{ T} \)) for (46). The overall antiferromagnetic interaction and slight ZFS. The prototype \([\text{Gd}_4\text{]}\text{[Gd}_5\text{O}_5\text{H}_2\text{O}])\) \( 4\text{H}_2\text{O} \) (54), was therefore rather different, having only two metals and acetate ligands bridging the two metals. 4.11. Chromium wheels

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5.1. Lightening up

A feature of most of the molecular clusters analysed is that their metallic cores are surrounded by a large ligand set. This brings the disadvantage of a small metal to molecular weight ratio, as explained above. The 3d–4f compounds with the largest \(-\Delta S_m\) values were those which incorporated light-weight ligands, though even these giant clusters were hampered by the antiferromagnetic interaction and slight ZFS. The prototype \([\text{Gd}_4\text{]}\text{[Gd}_5\text{O}_5\text{H}_2\text{O}])\) \( 4\text{H}_2\text{O} \) (54), was therefore rather different, having only two metals and acetate ligands bridging the two metals. 4.11. Chromium wheels

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5. Homo-metallic gadolinium compounds

We have shown several examples of how the lanthanide ion is the most significant contributor to a large MCE in 3d–4f compounds. It follows that homo-metallic 4f compounds could be superior, although it took several years before this was exploited. One possible reason is that the familiarity with transition metals put people off the synthetic challenge, there being higher coordination numbers to control as well as the initial lack of connection to the main research on SMMs that was in motion. The discovery of the first lanthanide SMMs in 2003 by Ishikawa brought these metals into the forefront of molecular magnetism. There are several examples of homo-metallic gadolinium compounds investigated for their MCE properties, ranging from single ions for ultra-low temperatures to hepta-metallic discs and twenty-four membered cages. Firstly, though, is a "proto-type" \([\text{Gd}_5\text{]}\) [12d] which was an exemplar of some important principles of MCE, namely a low molecular weight and a ferromagnetic interaction.

5.2. A great pyramid refrigerant

\([\text{Gd}_6\text{O}(\text{OH})_3\text{]}\) [55] [12h], a square-based pyramid and the isotropic member of a single-molecule magnet family appears an ideal material for an enormous magnetic entropy change: A low molecular weight relative to the metal content, with \( 50\% \) of isotropic, weak coupling metal, and a topology based around triangular faces, with potential for spin degeneracy via frustration. This first of these properties is made possible because this is an air-sensitive compound, so coordination numbers smaller than usual for lanthanides can be maintained without ligand bulk, hence the lower ligand mass. In fact, \(-\Delta S_m\) is "only" ca. \( 34 \text{ J kg}^{-1} \text{ K}^{-1} \) (3 K, \( \Delta H = 0–7 \text{ T} \)), one of the highest, but still much lower than the theoretical maximum of \( 55 \text{ J kg}^{-1} \text{ K}^{-1} \). The overall antiferromagnetic coupling seems to be the reason for this, despite its weak nature. Therefore, this is a frustrated system where a simple spin up-spin down picture cannot be used. The benefits of this, explained elsewhere, are hidden by the extremely slow magnetisation, seen by comparison against the Brillouin function (which represents the magnetisation of uncoupled ions). This compound, though, still outperforms all transition metal compounds at these low temperatures. From the \( S = 7/2 \) ground state from magnetisation the maximum \(-\Delta S_m\) is around \( 19 \text{ J kg}^{-1} \text{ K}^{-1} \), so the effects of spin degeneracy are apparent.

Fig. 7. \( \text{Gd}_6\text{O}(\text{OH})_3\text{]} \) core of \([\text{Gd}_6\text{Cu}_3\text{hmpa(OAc)H}_2\text{O}])\) \([\text{NO}_3\text{]}_3\text{H}_2\text{O} \) (8MeOH 18MCN (44): \( \text{Gd}, \text{purple; Cu}^\text{II}, \text{green; O, \text{red lines; N, pale blue lines.} \) (Colour online).
5.3. Gadolinium discs chill well

The \{(Gd\textsubscript{4})\} \{(Gd\textsubscript{4}OH\textsubscript{12}H\textsubscript{12}(tmeH\textsubscript{5})(tmeH)(tpa)(MeCN\textsubscript{3}))\}NO\textsubscript{3}\textsubscript{2}\textsubscript{2} \textsubscript{61} \textsubscript{12c} disc (Fig. 8), where tpaH is triphenylacetic acid and MeCN is acetonitrile, is the first 4f cluster to incorporate the triol ligand tmeH, and is made up of six vertex-sharing triangles.

Interestingly the triods bridge around the edges of the disc rather than directing the formation of triangles as in various transition metal structures. Antiferromagnetic coupling was deduced from the susceptibility data and slow magnetisation found, which, as for \{(Gd\textsubscript{4})\}, is not desirable. The resulting magnetic entropy change is 23 J kg\textsuperscript{-1} K\textsuperscript{-1} (3 K, \Delta H = 0–7 T), less than the maximum for uncoupled spins, but more than for an S = 7/2 paramagnet, the field induced ground state, by almost three times, due to the frustrated topology and consequent low-lying excited states. These last two effects suggest that, to improve upon (54), despite increasing the ground spin state, this is not always enough. The maximum entropy changes could be reached with large and impractical field strengths, though this is not desirable for any applications. Compound (56) Also uses ligands which are bulky and reduce the gadolinium content to less than 30%.

The use of another triol ligand N\textsubscript{3}(CH\textsubscript{2}CH\textsubscript{2}OH), triethanolamine, is limited to one example (in preparation), namely \{(Gd\textsubscript{2}taeH\textsubscript{2})(tpa\textsubscript{2})(NO\textsubscript{3}\textsubscript{2})\textsubscript{2}\} \textsubscript{57} \textsubscript{12f}, a dimer where metals are bridged by one of the alcohol groups. This shows a moderate MCE of 5.5 J kg\textsuperscript{-1} K\textsuperscript{-1} (3 K, \Delta H = 0–7 T), which is expected considering its antiferromagnetic coupling and low gadolinium content. The bulky carboxylate ligands in (56) and (57) may be necessary given the harsh nature of the solvothermal conditions used to prepare these. Not all gadolinium compounds are suitable for this type of application!

5.4. Splendid isolation

The millikelvin range of operation for magnetocaloric materials is important in space, where satellite sensors must be protected from the extreme environment. For instance, the Herschel satellite requires a 260 mK refrigeration with superconducting sensors needing 50 mK temperatures to operate. Magnetic refrigeration devices could be useful to replace the He dilution technique under zero gravity. One potential coolant is chromium–potassium alum, where the magnetic interactions are kept to a minimum by water molecules separating them; this principle, which also follows from the previous \{(Gd\textsubscript{2}Zn\textsubscript{2})\} cluster, is encapsulated by \{(Gd\textsubscript{2}W\textsubscript{10})\} \{Gd\textsubscript{2}W\textsubscript{30}\}, more fully Na\textsubscript{9}\{Gd(W\textsubscript{5}O\textsubscript{18})\} \{Gd\textsubscript{2}W\textsubscript{30}\}, to capture and transfer the magnetic entropy. For (60), this gives a \(\Delta S\textsubscript{M} \approx 46.1\text{ J} \text{kg}^{-1} \text{K}^{-1}\) (2.5 K, \(\Delta H = 0–7\) T), the largest for a lanthanide cluster, with (61), as mentioned above, the largest for a dysprosium cluster. These results confirm how important the percentage of gadolinium is in 4f cluster synthesis for use as refrigerants in sensible fields, as long as antiferromagnetic coupling is not so strong.

5.6. Ex uno plures

The strategy which gave the proto-type \{(Gd\textsubscript{4})\} (54) was extended by the synthesis of four related compounds \textsubscript{12g}, two of which have led the way to more recent advances in thinking in this field, vide infra. The other two discrete compounds were prepared by modifying that proto-type. The first, \{(Gd\textsubscript{2}O\textsubscript{4}acac\textsubscript{2})(Ph\textsubscript{2}acac\textsubscript{4})(MeOH\textsubscript{2})\} \textsubscript{62}, by adding a methanolic solution of dibenzoylmethane (Ph\textsubscript{2}acacH) and acetic acid to the precursor, and \{(Gd\textsubscript{4}O\textsubscript{4}acac\textsubscript{4})(acac\textsubscript{4})\}H\textsubscript{2}O\textsubscript{4}\textsubscript{1}\textsubscript{63}, by addition of a methanolic solution of triethylenediamine and acetylacetonate, crystals formed from standing and slow evaporation, respectively.

The former has a structure related to the precursor, whilst the latter is a linear tetrametallic chain. \(\Delta S\textsubscript{M} \approx 23.7\text{ J} \text{kg}^{-1} \text{K}^{-1}\) (2.4 K, \(\Delta H = 0–7\) T), which almost reach the maximum predicted, are smaller than the precursor owing to the larger molecular weight. The larger value of \(\Delta S\textsubscript{M}\) in the tetrametallic compound is again due to the increased percentage of gadolinium with ferromagnetic exchange being seen for each.

5.7. Porphyrins

The porphyrin complexes [GdTPP(Oac)] \textsubscript{64} and [GdTPP(C1)] \textsubscript{65}, where TPP is 5,10,15,20-tetraphenylporphyrinato, had...
heat capacity measurements performed on aqueous solutions above 278 K for 0–1 T field changes, so are outside the scope of this review, the maximum $\Delta T_{\text{MCE}}$ values being found as ca. 0.2 K.

6. Life in another dimension: polymeric compounds

Although polymeric compounds, such as Prussian Blue analogues, have been known for many years in magnetic refrigeration research, only recently have investigations of gadolinium one-, two- and three-dimensional compounds been undertaken and it is these compounds which show the largest $\Delta S_{\text{M}}$ values found so far, excepting a manganese(II)–gadolinium three-dimensional compound [71] [16], the only published magnetic entropy change over 50 J kg$^{-1}$ K$^{-1}$. Amongst others, the authors of this review have found an improvement upon this with a high-density gadolinium network (in preparation). The main advantage of polymeric compounds over their zero-dimensional rivals can be their increased metal percentage found, there being no need to prevent aggregation of the compounds over their zero-dimensional rivals. Thus, these are closer to isolated metals which necessarily have the highest $\Delta S_{\text{M}}$ values for a given metal. Indeed, it could be argued that the only challenges are to increase the metal to ligand ratio, given a large S and small D, and find higher density materials.

6.1. Transition metal polymeric compounds

The Prussian Blue analogues Ni$^{3+}[\text{Cr}^{3+} \text{(CN)}_6]_2 \text{O}_6$ (66) and Cs$^+\text{Ni}^3[\text{Cr}^{3+} \text{(CN)}_6]_2$ (67) [17] undergo a magneto caloric effect due to a ferromagnetic ordering process, the maximum of which can be shifted by the chemical composition of the material and number of vacant sites. Magnetisation studies found very similar $\Delta S_{\text{M}}$ values for each of ca. 7.7 Kg$^{-1}$ K$^{-1}$ under a 0–7 T field change, but at temperatures of ca. 70 and 100 K respectively.

$[\text{Co}^{2+}\text{O}_6][\text{Cu}_{2}\text{H}_{3}\text{O}_{6}](\text{OH})_2]$ (68) [18] is made up of chains of cobalt(II) ions linked by long acid groups. Although this work did not target refrigerants directly, the heat capacity data allowed MCE parameters to be calculated, finding $\Delta S_{\text{M}} = 2.4$ J kg$^{-1}$ K$^{-1}$ (11 K, $\Delta H = 0–5$ T) and $\Delta T_{\text{MCE}} = 1.5$ K under the same field change. These were ascribed to a long range ordering effect leading to, revealingly, an inverse MCE at temperatures above the ordering region, as antiferromagnetic interactions dominate. This is similar to the heating measured in [35].

6.2. 3d–4f polymeric compounds

The only 3d–4f compounds measured for their MCE are the related [Mn$^2+$[pyrazole]$]_2[Ni$^{3+}$[CN]$]_2$4H$_2$O, (69) and [(Ni$^{3+}$[pyrazole]$]_2][Ni$^{3+}$[CN]$]_2$4H$_2$O, (70) [19]. The $\Delta S_{\text{M}}$ values were found by magnetisation and heat capacity data to be at the Curie temperature and are associated with the ferrimagnetic (69) and ferromagnetic (70) ordering that occurs. Although these are unremarkable, ca. 6 J kg$^{-1}$ K$^{-1}$ ($\Delta H = 0–5$ T) and with $\Delta T_{\text{MCE}}$ around 2 K (3 K for $\Delta H = 0–9$ T) the MCE was here used to investigate the ordering of the materials, rather than a test for their refrigeration power. The MCE of these network compounds above is associated with a phase transition. In the gadolinium networks below, the MCE is ascribed to the spin of the individual metal ions.

6.3. 3d–4f polymeric compounds

6.3.1. A manganese(II)–gadolinium network

The largest – $\Delta S_{\text{M}}$ found to date in the literature is for [Mn$^2+$[H$_2$O],][Gd$^{3+}$O$_6$(OAc)$_4$][Gd$^{3+}$O$_6$(OAc)$_4$] (71) [16], a three-dimensional network which incorporates the two metals with the highest individual spin values, manganese(II) ($s = \frac{7}{2}$) and gadolinium ($s = \frac{7}{2}$), into a framework with little additional ligand mass (Hoda is oxalic acid). Ferromagnetic interactions were reported between these ions contributing to the huge value of 50.1 J kg$^{-1}$ K$^{-1}$ (1.8 K, $\Delta H = 0–7$ T). This is useful down to 1.4 K, heat capacity data showing the absence of ordering at these temperatures and doubtless will be investigated further. The $\Delta T_{\text{MCE}}$ is around 10.1 K for a field change of only 0–3 T showing the benefit of ferromagnetic coupling and the advantage offered at relatively mild conditions of temperature and field. The entropy change at only a 1 T field change was found to be in excess of even the industry standard material GGG, or [Gd$^{3+}$Ga$_5$O$_{12}$] (72) [26], a gadolinium gallium garnet, which reaches around 20 J kg$^{-1}$ K$^{-1}$ for a 2 T field change, confirming how promising a refrigerant (71) is. The slight downside of this compound is its relatively low density compared to GGG, 2.2 versus 7.1 g cm$^{-3}$ respectively. This large density is the key to GGGs deceptive importance, which may not be apparent from $\Delta S_{\text{M}}$ considerations alone.

6.3.2. Zinc(II)–Ln$_5$ nodes

[Ln$_2$(Zn$^{2+}$[BF$_4$])$_2$(H$_2$O)$_4$][OAc]$^+$[CO$_3$]$^-$[NO$_3$]$^-$[eH$_2$O], where Ln can be gadolinium (73) or dysprosium (74) [20] and H$_2$BF$_4$ is 4,4-dicarboxyloxy-2,2-dipyridine, is made up of a trigonal bipyramidal unit (Ln$^+$), interspersed with a Zn$^{2+}$[BF$_4$]$^-$ unit, into a three dimensional network. The maximum $\Delta S_{\text{M}}$ of 30.7 J kg$^{-1}$ K$^{-1}$ (3 K, $\Delta H = 0–7$ T), which is only approaching the maximum possible due to antiferromagnetic coupling. The dysprosium compound reconfirms previous ideas concerning anisotropy, the maximum calculated change being around three times larger than that found experimentally.

6.3.3. Et cetera: gadolinium goes on and on and on

The polymers [Gd(OAc)$_3$(MeOH)$_2$]$_2$ (75) and [Gd(OAc)$_3$(H$_2$O)$_{13}$]$_2$ (76) [12g], were prepared from [Gd$^3+$[OAc]$^-$][H$_2$O], 4H$_2$O [54] and both show an improvement in $\Delta S_{\text{M}}$ over the precursor on account of their larger gadolinium content. These are one-dimensional chain compounds where an extension of the acetate bonding mode allow formation of a chain, so decreasing the number of capping groups required. Comparing these to (54) one sees an increase of more than 10% in gadolinium content resulting in a $\Delta S_{\text{M}}$, of 45 and 47.7 J kg$^{-1}$ K$^{-1}$ (1.8 K, $\Delta H = 0–7$ T) respectively, showing how chemical control of ligand arrangements could influence the MCE positively. Although there is similar magnetism in the first compared to (54), the second shows antiferromagnetic coupling probably due to slight geometrical changes. Therefore, although the one has a larger “headline” figure, the ferromagnetically coupled chain could be more useful for applications, as it offers improved performance under milder conditions.
6.3.4. Networking and the formation of lightweight carboxylate polymers

The formate ligand, (O₂CH)⁻, derived from formic acid, is an attractive choice for gadolinium network formation in magnetic refrigeration. It is small and can give polymeric materials with large gadolinium contents. Because of the small size the materials formed can have high densities, which may have practical implications. The following are three gadolinium networks which incorporate this ligand, all amongst the very best performing refrigerants by their –ΔSM values. The magnitude of this is proportional to the percentage of metal, as it is for all the gadolinium networks here.

\[[\text{Gd(O}_2\text{CH})_3\text{OAc}_2\text{H}_2\text{O}]\] (77) [12], a two dimensional network, where each metal is eight coordinate and linked to one adjacent metal through each formate group, forming a chain-like arrangement. The antiferromagnetic coupling, which is very weak, is almost unimportant here because the maximum entropy change of 45.9 J kg⁻¹ K⁻¹ (1.8 K, ΔH = 0–7 T) is very nearly the maximum value allowed. The three dimensional MOF \[[\text{Gd(O}_2\text{CH})_3\text{Cl}_2\text{H}_2\text{O}]]\] (78) [12], is composed of dimer units of eight coordinate metals, which follow layers and these are linked by benzene–dicarboxylic acid groups. –ΔSM is larger than (76) [12g] only at a larger field change of 0–9 T and 2.3 K, reaching 47.0 J kg⁻¹ K⁻¹. This compound is paramagnetic down to 1.8 K, with Curie-like behaviour, with extremely small interactions between metals in each unit. The \[[\text{Gd(O}_2\text{CH})_3\text{Cl}]]\] (79) [12e] compound (Fig. 11), currently being investigated by ourselves and others (in preparation) has an even higher maximum than 0–55 J kg⁻¹ K⁻¹ , with an enormous ΔTAD of around 25 K (around 2 K and ΔH = 0–7 T), superior to the GGG standard compound (72) [2e]. The density of (79), around 3.9 g cm⁻³, leads to a much larger maximum –ρΔSM compared to GGG of ≈210 mJ cm⁻³ K⁻¹ (GGG reaches 191 mJ cm⁻³ K⁻¹, vide supra), though one must be careful in comparing directly. Indeed, another feature of GGG is its high performance under very mild conditions of field and here the two (79) and (72) are more comparable [12e].

Two further three-dimensional compounds, namely \[[\text{Gd}_2(\text{fum})_3(\text{H}_2\text{O})_4\text{H}_2\text{O}]]\] (80) [12k], where fum is fumarate, and \[[\text{Gd}_2(\text{N-BDC})_3(\text{dmf})_4\text{H}_2\text{O}]]\] (81) [12i], where N-HBDC is 2-amino-1,4-

Fig. 10. Gd–Mn–O–C core of \[[\text{Mn}_3(\text{H}_2\text{O})_6]\] \[[\text{GdMn}_3(\text{odma})_3\text{H}_2\text{O}]]\] (71), where Hoda is oxydiacetic acid: Gd, purple; Mn⁴⁺, pink; O, red lines; C, blue lines. (Colour online).

Fig. 11. Part of the three-dimensional structure \[[\text{Ln(O}_2\text{CH})_3\text{O}]]\] (79): Ln, purple; O, red lines; C, blue lines; no H shown. (Colour online).

benzenedicarboxylic acid, show –ΔSM values of 20.7 and 29.0 J kg⁻¹ K⁻¹ (at 1.3 K, ΔH = 0–5 T and 1.8 K, ΔH = 0–7 T, respectively), the first an early example of how these materials could compete with the gadolinium molecular clusters that were attracting much attention at the time. Interestingly, (80) shows a ΔTAD of more than 10 K (at ca. 12 K, ΔH = 0–5 T), giving a large efficiency comparable to proposed alloys for low temperature refrigeration, making this material more useful than it might appear from considerations of only the magnetic entropy change.

The fact that of the nine or so compounds which show –ΔSM values over 40 J kg⁻¹ K⁻¹, six are non-zero dimensional suggests that these are the most promising. When one takes –ρΔSM as a guide the distinction becomes almost abrupt, with the best performing polymeric compounds vastly superior to all but (41) and (42), which come quite close (see S.I. Table for more of these parameters and the dimensionalities of these compounds). Zero-dimensional compounds, though, should not be discounted as they offer ways to control various parameters of spin and anisotropy in order to investigate new ideas and theories that could not otherwise be seen.

7. Onwards

Despite the advantages of gadolinium(III) compounds, (71) [16] shows that transition metal–gadolinium compounds are strong candidates in this field, along with formate networks. Whilst we cannot tell the future, we can forecast some likely developments in this field. Many metal clusters containing lanthanides will probably be assessed for their MCE properties, but show no improvement on those already published; the development of network materials will probably grow rapidly, these offering many advantages over 0-D compounds, as shown; the use of radical ligands [21] so minimising the redundancy of ligand mass would be an interesting test, particularly with a ferromagnetic interaction with gadolinium; we can also speculate as to whether the recently found strongly coupled lanthanide systems would actually hinder the MCE, by increasing the energy of the previously low-lying excited states. At some point in the future doubtless there will be a large expansion in the practical application of this technology, so perhaps this requires more collaboration with materials chemists and engineers. We are sure, though, that there are more advances to come.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.02.034.

References


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<td>23.6</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Co$<em>2^{II}$,(OH)$</em>{10}$,(NO)$</em>{14}$,(O,P$<em>{Bu}$)$<em>6$,(O,C$</em>{Bu}$)$</em>{14}$]</td>
<td>23</td>
<td>21.4</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Co$<em>2^{II}$,(O,P$</em>{Bu}$)$<em>6$,(O,C$</em>{Bu}$)$</em>{14}$,(MeCN)$_{12}$]·2MeCN</td>
<td>24</td>
<td>21.1</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Co$<em>2^{II}$,(OH)$</em>{10}$,(O,P$</em>{CH$<em>2$Ph}$)$<em>6$,(O,C$</em>{Bu}$)$</em>{14}$,(H$<em>2$O)$</em>{30}$]·6MeCN</td>
<td>25</td>
<td>11.8</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Ni$<em>2^{II}$,(OH)$</em>{10}$,(CO)$</em>{12}$,(CH$<em>2$COO)$</em>{14}$,(H$<em>2$O)$</em>{30}$]·(ClO$<em>4$)$</em>{25}$·80H$_2$O</td>
<td>42</td>
<td>38.2</td>
<td>7</td>
<td>2.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Ni$<em>2^{II}$,(CH$<em>2$COO)$</em>{10}$,(OH)$</em>{14}$,(O,C$</em>{Bu}$)$<em>{14}$,(H$<em>2$O)$</em>{30}$]·(NO)$</em>{14}$,(Cl)$_{25}$·30H$_2$O</td>
<td>43</td>
<td>36.3</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Ni$<em>2^{II}$,(OH)$</em>{10}$,(O,P$</em>{CH$<em>2$Ph}$)$<em>6$,(O,C$</em>{Bu}$)$</em>{14}$,(MeCO,H$<em>2$)$</em>{12}$]·4MeCN</td>
<td>29</td>
<td>26.5</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Ni$<em>2^{II}$,(OH)$</em>{10}$,(O,C$</em>{CH$_2$Me$_2$})$_6$]·(ClO$<em>4$)$</em>{14}$</td>
<td>34</td>
<td>22.0</td>
<td>7</td>
<td>5.6</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$_2$Ni$<em>2^{II}$,(val)$</em>{12}$,(MeCN)$_6$,(H$<em>2$O)$</em>{30}$]·(N$^+$Et$_4$)·[Gd(NO$_3$)$_3$]·(ClO$<em>4$)$</em>{15}$</td>
<td>38</td>
<td>17.6</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$_2$Cu$_2^{II}$,(O$_2$)$_2$,(OMe)$<em>4$,(O,C$</em>{CH$<em>2$Me$<em>2$})$</em>{12}$,(NO)$</em>{14}$]·2MeOH·2Et$_2$O</td>
<td>37</td>
<td>31.0</td>
<td>9</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$_2$Cu$_2^{II}$,(HL)$_4$,(dmf)$_2$,(H$<em>2$O)$</em>{30}$]·6dmf</td>
<td>36</td>
<td>23.5</td>
<td>7</td>
<td>2.3</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Cu$<em>2^{II}$,(OH)$</em>{10}$,(O,C$</em>{Ph$<em>3$})$<em>6$,(MeCN)$</em>{12}$,(H$<em>2$O)$</em>{30}$]·(NO)$</em>{14}$·39H$_2$O·8MeOH·18MeCN</td>
<td>44</td>
<td>21.0</td>
<td>7</td>
<td>2.1</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Cu$<em>2^{II}$,(OH)$</em>{10}$,(O,C$</em>{CH$_2$Me$_2$})$_6$]·(ClO$<em>4$)$</em>{14}$</td>
<td>35</td>
<td>14.6</td>
<td>7</td>
<td>3.6</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Mn$^{III}$,(H$<em>2$O)$</em>{12}$]·[GdMn$^{III}$,(oda)$_{30}$]·6H$_2$O</td>
<td>71</td>
<td>50.1</td>
<td>7</td>
<td>1.8</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Mn$<em>2^{III}$,(O,P$</em>{CH$<em>2$Ph}$)$<em>6$,(O,C$</em>{Bu}$)$</em>{14}$,(H$<em>2$O)$</em>{14}$,(MeCN)$</em>{12}$]·3MeCN</td>
<td>19</td>
<td>33.7</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td><a href="O,C$_%7BBu%7D$">Gd$<em>2$Mn$<em>2^{III}$,(O,P$</em>{Me$<em>2$})$<em>6$,(O,C$</em>{Bu}$)$</em>{12}$,(OH)$</em>{14}$</a>$_{14}$]</td>
<td>18</td>
<td>28.0</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$<em>2$Mn$<em>2^{III}$,(OH)$</em>{22}$,(tetrahydrocalix[4]arene)$</em>{(NO)_2}$,(dmf)$_6$,(H$<em>2$O)$</em>{14}$]·(OH)$_2$</td>
<td>16</td>
<td>19.0</td>
<td>7</td>
<td>4.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Gd$_2$Mn$<em>2^{III}$,(Mn$^{IV}$),(OH)$</em>{(piv)$_6$}(EtO)$_6$(EtOH)$_6$(Et-sao)$_6$]</td>
<td>17</td>
<td>7.4</td>
<td>5</td>
<td>6.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>Formula</td>
<td>No.</td>
<td>$-\Delta S_{\text{M}}$ / J kg$^{-1}$ K$^{-1}$</td>
<td>$\Delta H / T$</td>
<td>$T / K$</td>
<td>n-D</td>
<td>$\Delta T_{\text{AD}} / K$</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>-----</td>
<td>---------------------------------------------</td>
<td>----------------</td>
<td>--------</td>
<td>------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>$\left[\text{Gd}_2\text{Zn}^{\text{II}}(\text{BPDC})_3(\text{H}_2\text{O})_6(\text{OH})_6(\text{CO}<em>3)</em>{0.5}(\text{NO}_3)_4\cdot 12\text{H}_2\text{O}\right]_n$</td>
<td>73</td>
<td>30.7</td>
<td>7</td>
<td>3.0</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>$\text{Gd}_2\text{Zn}^{\text{II}}(\text{OH})_6(\text{O}_2\text{CCHMe}_2)_3(\text{ClO}_4)_3\cdot 4\text{H}_2\text{O}$</td>
<td>33</td>
<td>18.0</td>
<td>7</td>
<td>2.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\text{Gd}_2\text{Zn}^{\text{II}}(\text{BuCOO})_7(\text{BuPO}_3)_2(\text{NET}_3)_2$</td>
<td>32</td>
<td>15.1</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Gd}_{\text{III}}\text{Fe}_2(\text{Me},\text{tame})_3(\text{hfac})_6\right]\cdot 7\text{MeCN}$</td>
<td>39</td>
<td>28.7</td>
<td>9</td>
<td>2.2</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Gd}_{\text{III}}\text{Fe}_2(\text{py})_6(\text{hfac})_6\right]$</td>
<td>40</td>
<td>11.4</td>
<td>9</td>
<td>4.1</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Gd}_2\text{Mo}_2\text{O}_6(\text{HL})_6(\text{OH})_4(\text{OOCCH}_3)_2\right]\cdot 12\text{MeOH}\cdot 8\text{H}_2\text{O}$</td>
<td>45</td>
<td>35.3</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Gd}_2\text{O}<em>3\text{O}</em>{12}\right]_n$</td>
<td>72</td>
<td>27.00</td>
<td>5.00</td>
<td>5.00</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Dy}<em>{2}\text{(DMC)}</em>{16}(\text{CO}<em>3)</em>{14}(\text{H}_2\text{O})_2\right]\cdot 2\text{H}_2\text{O}$</td>
<td>61</td>
<td>13.8</td>
<td>7</td>
<td>7.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{DyCo}^{\text{II}}_3(\text{hmp})_4(\text{OAc})_5\text{H}_2\text{O}\right]$</td>
<td>46</td>
<td>12.6</td>
<td>7</td>
<td>5.5</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{DyCo}^{\text{II}}_3(\text{OH})_4(\text{NO}_3)_4(\text{O}<em>2\text{C'}\text{Bu})</em>{16}\right]$</td>
<td>28</td>
<td>11.6</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Dy}_2\text{Ni}_2\text{O}_6(\text{O}_2\text{PCH}_3\text{Ph})_6(\text{O}<em>2\text{C'}\text{Bu})</em>{16}(\text{MeCO}_2\text{H})_2\cdot 4\text{MeCN}\right]$</td>
<td>30</td>
<td>12.2</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Dy}_2\text{Mn}_2\text{O}_6(\text{O}_2\text{PCH}_3\text{Ph})_6(\text{O}<em>2\text{C'}\text{Bu})</em>{16}\right]\cdot 5\text{MeCN}$</td>
<td>20</td>
<td>13.00</td>
<td>7</td>
<td>3.00</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{Dy}_2\text{Zn}^{\text{II}}(\text{BPDC})_3(\text{H}_2\text{O})_6(\text{OH})_6(\text{CO}<em>3)</em>{0.5}(\text{NO}_3)_4\cdot 10\text{H}_2\text{O}\right]_n$</td>
<td>74</td>
<td>10.82</td>
<td>7</td>
<td>4.0</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{YCo}^{\text{II}}_3(\text{hmp})_4(\text{OAc})_5\text{H}_2\text{O}\right]$</td>
<td>51</td>
<td>6</td>
<td>7</td>
<td>5.5</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{YCo}^{\text{II}}_3(\text{OH})_4(\text{NO}_3)_4(\text{O}<em>2\text{C'}\text{Bu})</em>{16}\right]$</td>
<td>27</td>
<td>4.5</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{YNi}^{\text{II}}_4(\text{OH})_2(\text{O}_2\text{PCH}_3\text{Ph})_6(\text{O}<em>2\text{C'}\text{Bu})</em>{16}(\text{MeCO}_2\text{H})_2\cdot 4\text{MeCN}\right]$</td>
<td>31</td>
<td>5.6</td>
<td>7</td>
<td>3.0</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{ErCo}^{\text{II}}_3(\text{hmp})_4(\text{OAc})_5\text{H}_2\text{O}\right]$</td>
<td>48</td>
<td>11.5</td>
<td>7</td>
<td>5.5</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{TmCo}^{\text{II}}_3(\text{hmp})_4(\text{OAc})_5\text{H}_2\text{O}\right]$</td>
<td>49</td>
<td>10.3</td>
<td>7</td>
<td>5.5</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>$\left[\text{YbCo}^{\text{II}}_3(\text{hmp})_4(\text{OAc})_5\text{H}_2\text{O}\right]$</td>
<td>50</td>
<td>9.9</td>
<td>7</td>
<td>5.5</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>Formula</td>
<td>No.</td>
<td>−ΔS / J kg⁻¹ K⁻¹</td>
<td>ΔH / T</td>
<td>T / K</td>
<td>n-D</td>
<td>ΔTAD / K</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>-----</td>
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<td>--------</td>
<td>-------</td>
<td>-----</td>
<td>----------</td>
</tr>
<tr>
<td>[HoCo⁺(hmp)₄(OAc)₂,H₂O]</td>
<td>47</td>
<td>8.9</td>
<td>7</td>
<td>5.5</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>Ni⁺₄(Cr³⁺(CN)₆)₂₆₆</td>
<td>66</td>
<td>6.9</td>
<td>7</td>
<td>68</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>Cs⁺₂Ni⁺₄(Cr₆(CN)₆)₄</td>
<td>67</td>
<td>6.6</td>
<td>7</td>
<td>95</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>[Mn⁺(pyrazole)₄₂][Nb⁺(CN)₆·4H₂O]ₙ</td>
<td>69</td>
<td>6.5</td>
<td>5</td>
<td>25</td>
<td>Three</td>
<td>NA</td>
</tr>
<tr>
<td>{[Ni⁺(pyrazole)₄₂[Nb⁺(CN)₆·4H₂O]ₙ</td>
<td>70</td>
<td>5.9</td>
<td>5</td>
<td>14</td>
<td>Three</td>
<td>2.9 (9 T) 2 (5 T)</td>
</tr>
<tr>
<td>[Cu⁺(OH)₃(C₁₀H₁₆O₄)₃]</td>
<td>68</td>
<td>2.4</td>
<td>5</td>
<td>11.0</td>
<td>One</td>
<td>NA</td>
</tr>
<tr>
<td>[Ni⁺⁺(OH)₂(chp)]₂(MeOH)₆</td>
<td>14</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[Me₂NH₂][Cr⁺⁺⁺⁺⁺(O₂C₅Bu)₁₆]</td>
<td>53</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Zero</td>
<td>NA</td>
</tr>
<tr>
<td>[[NH₃Pr₂][Cr⁺⁺⁺⁺⁺(O₂C₅Bu)₁₆(O₂CC₃H₇N)]₂[Cu⁺⁺(NO₃)₂(H₂O)]]</td>
<td>52</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Zero</td>
<td>Yes</td>
</tr>
<tr>
<td>Formula</td>
<td>( \rho / \text{g cm}^{-3} )</td>
<td>Maximum (-\rho \Delta S_{M} / \text{mJ cm}^{-3} \text{ K}^{-1} )</td>
<td>Reference</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>-----------------------------</td>
<td>-------------------------------------------------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Gd(HCOO)(<em>{3})](</em>{8})</td>
<td>3.9</td>
<td>212</td>
<td>12e</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="H(_%7B2%7D)O">Gd(OAc)(_{3})</a>(_{3})</td>
<td>2.2</td>
<td>106</td>
<td>12g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Gd(HCOO)(C(<em>{2})H(</em>{4})O(_{2}))]</td>
<td>2.7</td>
<td>125</td>
<td>12j</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Gd(<em>{2})(DMC)(</em>{3})(CO(<em>{3}))(</em>{12})(H(<em>{2})O)(</em>{6})]·6H(_{2})O</td>
<td>2.0</td>
<td>90</td>
<td>12a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="H(_%7B2%7D)O">Gd(HCOO)(OAc)(_{2})</a>(_{2})</td>
<td>2.4</td>
<td>110</td>
<td>12i</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="MeOH">Gd(OAc)(_{3})</a>(_{8})</td>
<td>2.2</td>
<td>97</td>
<td>12g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="H(_%7B2%7D)O">Gd(<em>{2})(OAc)(</em>{3})</a>(<em>{4})·4H(</em>{2})O</td>
<td>2.0</td>
<td>85</td>
<td>12d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="acac">Gd(<em>{2})(OAc)(</em>{3})</a>(<em>{3})(H(</em>{2})O)(_{4})</td>
<td>1.9</td>
<td>70</td>
<td>12g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Gd(<em>{3})(O(</em>{2}))(<em>{3})](</em>{13})</td>
<td>1.9</td>
<td>65</td>
<td>12b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="N-BDC">Gd(_{3})</a>(<em>{3})(dmf)(</em>{4})</td>
<td>1.4</td>
<td>41</td>
<td>12i</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="Ph(_%7B3%7D)">Gd(<em>{2})(OAc)(</em>{3})</a>acac(<em>{3})(MeOH)(</em>{2})</td>
<td>1.5</td>
<td>36</td>
<td>12g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="OH">Gd(_{2})</a>(<em>{3})(</em>{4})(tpt)(<em>{3})(MeCN)(</em>{2})](<em>{2})NO(</em>{3})(_{2})</td>
<td>1.8</td>
<td>41</td>
<td>12c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="fum">Gd(_{2})</a>(<em>{2})(H(</em>{2})O)(<em>{4})·3H(</em>{2})O</td>
<td>2.5</td>
<td>52</td>
<td>12k</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="tta">Gd(_{2})</a>(<em>{3})(tpt)(</em>{3})NO(<em>{3})(</em>{2})</td>
<td>1.7</td>
<td>35</td>
<td>12f</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[GdTPP(OAc)]</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>[GdTPP(Cl)]</td>
<td>NA</td>
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<td>NA</td>
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<tr>
<td>Na(<em>{2})[Gd(</em>{3})(H(<em>{2})O)(</em>{6})]·35H(_{2})O</td>
<td>3.4</td>
<td>16</td>
<td>3c</td>
<td></td>
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<tr>
<td>K(<em>{2})[Gd(</em>{3})(H(<em>{2})O)(</em>{6})]·54H(_{2})O</td>
<td>3.4</td>
<td>6</td>
<td>3c</td>
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<tr>
<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(OH(</em>{2}))(<em>{4})Hpeol(</em>{4})(<em>{4})EtOH(</em>{4})IL(_{2})</td>
<td>1.7</td>
<td>43</td>
<td>4f</td>
<td></td>
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<tr>
<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(OH(</em>{2}))(<em>{4})(bipy)(</em>{4})(<em>{4})N(</em>{2})(OAc)(<em>{2})(</em>{4})Cl(_{2})</td>
<td>1.4</td>
<td>25</td>
<td>4i</td>
<td></td>
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<tr>
<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(OH(</em>{2}))(<em>{4})ampH(</em>{4})(<em>{4})EtOH(</em>{4})IL(_{2})</td>
<td>1.5</td>
<td>26</td>
<td>4f</td>
<td></td>
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<tr>
<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(O(</em>{2}))Cl(<em>{2})O(</em>{2})CMe(<em>{2})(</em>{2})L(<em>{10})Cl(</em>{2})(O(<em>{2})CMe(</em>{2})O(<em>{2})l6py(</em>{3})(MeCN)(<em>{2})](</em>{7})MeCN</td>
<td>1.6</td>
<td>22</td>
<td>4g</td>
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<tr>
<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})O(</em>{2})Br(<em>{3})ampH(</em>{4})HampH(<em>{2})Br(</em>{3})8Hex</td>
<td>1.6</td>
<td>21</td>
<td>4f</td>
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<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(OH(</em>{2}))(HL)(<em>{3})N(</em>{1})Br(<em>{4})N(</em>{1})Br(_{4})3MeCN·2MeOH</td>
<td>1.8</td>
<td>18</td>
<td>4g</td>
<td></td>
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<tr>
<td>[Na(<em>{2})]Mn(</em>{3})](<em>{3})Mn(</em>{3})(OH(<em>{2}))(</em>{4})(OAc)(<em>{2})(MeOH)(</em>{2})(MeO)(<em>{1})(N(</em>{2}))(<em>{3})OAc·10H(</em>{2})O·2MeOH</td>
<td>3.0</td>
<td>28</td>
<td>4h</td>
<td></td>
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<tr>
<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(OH(</em>{2}))(<em>{4})(N(</em>{1}))(<em>{3})(MeO)(</em>{4})3(MeOH)(<em>{3})2(H(</em>{2})O)(<em>{1})(OH)(</em>{1})3(OAc)·10H(_{2})O</td>
<td>1.5</td>
<td>13</td>
<td>4h</td>
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<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})O(</em>{2})N(<em>{2})(L(</em>{2}))(<em>{4})(MeCN)(</em>{3})Cl(_{2})·10MeOH·MeCN</td>
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<td>4g</td>
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<td>[Mn(<em>{3})](</em>{3})Mn(<em>{3})(CH(</em>{2}))COO(<em>{2})(</em>{4})(H(<em>{2})O)(</em>{2})O(<em>{2})(</em>{2})2CH(<em>{2})COOH·4H(</em>{2})O</td>
<td>NA</td>
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<td>NA</td>
<td>NA</td>
<td>4d</td>
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<tr>
<td>Formula</td>
<td>$\rho$ / g cm$^{-3}$</td>
<td>Maximum $-\rho\Delta S_M$ / mJ cm$^{-3}$ K$^{-1}$</td>
<td>Reference</td>
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<tr>
<td>$[\text{Fe}^{\text{III}}<em>{16}(\text{bta})</em>{6}\text{O}<em>{6}(\text{OMe})</em>{3}\text{Cl}_{6}]$</td>
<td>2.1</td>
<td>33</td>
<td>4a</td>
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<td>$[\text{Fe}^{\text{III}}<em>{15}\text{O}</em>{16}(\text{OH})<em>{2}\text{py}</em>{1}\text{Br}<em>{4}]\text{Br}</em>{3}$</td>
<td>1.9</td>
<td>17</td>
<td>4e</td>
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<td>$[[\text{Fe}^{\text{III}}<em>{6}\text{O}</em>{2}(\text{OH})<em>{12}(\text{tacn})</em>{6}]\text{Br}<em>{2}\text{H}</em>{2}\text{O}]\text{Br}<em>{8}\text{H}</em>{2}\text{O}$</td>
<td>NA</td>
<td>NA</td>
<td>4b</td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{2}\text{Co}^{\text{III}}<em>{6}(\text{OH})</em>{6}(\text{CO}<em>{3})</em>{6}(\text{CH}<em>{2}\text{COO})</em>{6}(\text{H}<em>{2}\text{O})</em>{3}]\cdot(\text{ClO}<em>{4})</em>{2}5\cdot(\text{CH}<em>{2}\text{CH}</em>{2}\text{OH})\cdot\text{n}70\text{H}_{2}\text{O}$</td>
<td>2.7</td>
<td>113</td>
<td>13a</td>
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<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{P}^{\text{III}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{H}</em>{2}\text{O})_{2}]\cdot2\text{MeCN}$</td>
<td>1.7</td>
<td>48</td>
<td>10e</td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{P}^{\text{III}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})_{16}]$</td>
<td>1.7</td>
<td>41</td>
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<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{P}^{\text{III}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})_{16}]$</td>
<td>1.8</td>
<td>37</td>
<td>10d</td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{P}^{\text{III}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})_{16}]$</td>
<td>1.5</td>
<td>31</td>
<td>10d</td>
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</tr>
<tr>
<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{P}^{\text{III}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})_{16}]$</td>
<td>1.4</td>
<td>29</td>
<td>10e</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$[\text{Gd}<em>{2}\text{Co}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{P}^{\text{III}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})_{16}]$</td>
<td>1.6</td>
<td>18</td>
<td>10e</td>
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<td></td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Ni}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{CO}</em>{3})<em>{6}(\text{CH}</em>{2}\text{COO})<em>{6}(\text{H}</em>{2}\text{O})<em>{3}]\cdot(\text{ClO}</em>{4})<em>{2}2\cdot80\text{H}</em>{2}\text{O}$</td>
<td>2.8</td>
<td>105</td>
<td>13a</td>
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<td>2.3</td>
<td>83</td>
<td>13b</td>
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<td>$[\text{Gd}<em>{2}\text{Ni}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{S}^{\text{II}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{MeCO}</em>{2}\text{H})_{2}]\cdot4\text{MeCN}$</td>
<td>1.7</td>
<td>44</td>
<td>10f</td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Ni}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{L})</em>{6}(\text{O})<em>{2}\text{C}^{\text{II}}\text{C}^{\text{II}}\text{Me}</em>{6}]\cdot(\text{ClO}<em>{4})</em>{4}$</td>
<td>1.8</td>
<td>40</td>
<td>10h</td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Ni}^{\text{III}}</em>{6}(\text{OH})<em>{6}(\text{L})</em>{6}(\text{O})<em>{2}\text{C}^{\text{II}}\text{C}^{\text{II}}\text{Me}</em>{6}]\cdot(\text{ClO}<em>{4})</em>{4}$</td>
<td>1.6</td>
<td>28</td>
<td>10k</td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Cu}^{\text{II}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{S}^{\text{II}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{MeCO}</em>{2}\text{H})<em>{2}]\cdot2\text{MeOH}2\cdot2\text{Et}</em>{2}O$</td>
<td>2.0</td>
<td>62</td>
<td>10j</td>
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<td>$[\text{Gd}<em>{2}\text{Cu}^{\text{II}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{S}^{\text{II}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{MeCO}</em>{2}\text{H})<em>{2}]\cdot2\text{MeOH}2\cdot2\text{Et}</em>{2}O$</td>
<td>1.7</td>
<td>40</td>
<td>10i</td>
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<td>$[\text{Gd}<em>{2}\text{Cu}^{\text{II}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{S}^{\text{II}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{MeCO}</em>{2}\text{H})<em>{2}]\cdot2\text{MeOH}2\cdot2\text{Et}</em>{2}O$</td>
<td>2.0</td>
<td>15</td>
<td>32</td>
<td>13c</td>
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<td>$[\text{Gd}<em>{2}\text{Cu}^{\text{II}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{S}^{\text{II}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{MeCO}</em>{2}\text{H})<em>{2}]\cdot2\text{MeOH}2\cdot2\text{Et}</em>{2}O$</td>
<td>1.5</td>
<td>32</td>
<td>13c</td>
<td></td>
<td></td>
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<tr>
<td>$[\text{Gd}<em>{2}\text{Cu}^{\text{II}}</em>{6}(\text{OH})<em>{6}(\text{O}</em>{2}\text{S}^{\text{II}}\text{Bu}<em>{6})(\text{O}</em>{2}\text{C}^{\text{II}}\text{Bu})<em>{16}(\text{MeCO}</em>{2}\text{H})<em>{2}]\cdot2\text{MeOH}2\cdot2\text{Et}</em>{2}O$</td>
<td>2.0</td>
<td>29</td>
<td>10h</td>
<td></td>
<td></td>
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<tr>
<td>$[\text{Mn}^{\text{III}}<em>{6}(\text{H}</em>{2}\text{O})<em>{6}][\text{GdMn}^{\text{III}}(\text{oda})</em>{3}]<em>{3}\cdot6\text{H}</em>{2}\text{O}$</td>
<td>2.2</td>
<td>112</td>
<td>16</td>
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<td>$[\text{Gd}<em>{2}\text{Mn}^{\text{III}}</em>{6}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu}</em>{6})(\text{O}<em>{2}\text{C}^{\text{II}}\text{Bu})</em>{16}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu})</em>{16}(\text{MeCN})_{12}]\cdot3\text{MeCN}$</td>
<td>1.6</td>
<td>54</td>
<td>10c</td>
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<td>$[\text{Gd}<em>{2}\text{Mn}^{\text{III}}</em>{6}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu}</em>{6})(\text{O}<em>{2}\text{C}^{\text{II}}\text{Bu})</em>{16}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu})</em>{16}(\text{MeCN})_{12}]\cdot3\text{MeCN}$</td>
<td>1.7</td>
<td>47</td>
<td>10c</td>
<td></td>
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<td>$[\text{Gd}<em>{2}\text{Mn}^{\text{III}}</em>{6}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu}</em>{6})(\text{O}<em>{2}\text{C}^{\text{II}}\text{Bu})</em>{16}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu})</em>{16}(\text{MeCN})_{12}]\cdot3\text{MeCN}$</td>
<td>1.6</td>
<td>30</td>
<td>10a</td>
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<td>$[\text{Gd}<em>{2}\text{Mn}^{\text{III}}</em>{6}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu}</em>{6})(\text{O}<em>{2}\text{C}^{\text{II}}\text{Bu})</em>{16}(\text{O}<em>{2}\text{S}^{\text{II}}\text{Bu})</em>{16}(\text{MeCN})_{12}]\cdot3\text{MeCN}$</td>
<td>1.6</td>
<td>12</td>
<td>10b</td>
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</tr>
<tr>
<td>Formula</td>
<td>$\rho$ / g cm$^{-3}$</td>
<td>Maximum $-\rho\Delta S_M$ / mJ cm$^{-3}$ K$^{-1}$</td>
<td>Reference</td>
<td></td>
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<td>------------------------------------------------------------------------</td>
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<tr>
<td>${[\text{Gd}_5\text{Zn}^{II}\text{BPDC}]{(\text{H}_2\text{O})}{(\text{OH})}{(\text{CO}_3)}{\text{(NO}<em>3)</em>{12}}\cdot12\text{H}_2\text{O}}^n$</td>
<td>1.9</td>
<td>58</td>
<td>20</td>
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<tr>
<td>${[\text{Gd}_5\text{Zn}^{II}\text{Zn}^{II}\text{BPDC}]{(\text{H}_2\text{O})}{(\text{OH})}{(\text{CO}_3)}{\text{(NO}<em>3)</em>{12}}\cdot4\text{H}_2\text{O}}^n$</td>
<td>1.9</td>
<td>34</td>
<td>10h</td>
<td></td>
<td></td>
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<tr>
<td>${[\text{Gd}_5\text{Zn}^{II}\text{Zn}^{II}\text{BuCOO}]{(\text{BuPO}<em>3)</em>{2}}{(\text{NEt}<em>3)</em>{2}}}^n$</td>
<td>1.3</td>
<td>20</td>
<td>10g</td>
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<tr>
<td>${[\text{Gd}_5\text{Zn}^{II}\text{Zn}^{II}\text{Me}<em>3\text{tame}]{(\text{tBuCOO})</em>{2}}{(\text{tBuPO}<em>3)</em>{2}}{(\text{NEt}<em>3)</em>{2}}}^n$</td>
<td>1.3</td>
<td>20</td>
<td>10g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.8</td>
<td>52</td>
<td>10l</td>
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<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
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<tr>
<td>${[\text{Gd}_5\text{Zn}^{III}\text{F}<em>9\text{Me}<em>3\text{tame}]{(\text{hfac})</em>{2}}{(\text{MeCN})</em>{2}}\cdot7\text{MeCN}}^n$</td>
<td>1.9</td>
<td>22</td>
<td>10m</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Formula</td>
<td>( \rho / \text{g cm}^{-3} )</td>
<td>Maximum (-\rho \Delta S_{M} / \text{mJ cm}^{-3} \text{K}^{-1} )</td>
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Chapter 5: Paper 2

Lanthanide discs chill well and relax slowly

Lanthanide discs chill well and relax slowly†

Joseph W. Sharples, Yan-Zhen Zheng, Floriana Tuna, Eric J. L. McInnes and David Collison*

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The synthesis, structure and magnetic properties of two isostructural heptametallic lanthanide discs are reported, showing single molecule magnet (SMM) behaviour with a large energy barrier for the dysprosium analogue and a large magnetocaloric effect (MCE) for the gadolinium analogue.

Transition metal clusters are being intensively studied because of their fascinating magnetic properties, including as molecular magnetic coolers1–2 or SMMs.3 There has been a recent increase in interest in lanthanides in these areas, in particular with dysprosium-based SMMs4 and gadolinium-containing mixed d–f species as magnetic coolers.5 This exploits the large spins seen for 3d metals including Ni, Fe, Cu, Co and Mn,6 but not for Ln (although ‘‘empty’’ Ln6 rings are known).7 T h e mol e c u l e lies on a crystallographic inversion centre; the central Ln3+ ion lies just out of the Ln6 plane (and hence is disordered over two sites). The peripheral and central Ln ions are bound by six μ3-OH groups, alternating above and below the Ln4 plane. Each edge of the Ln6 hexagon is bridged by a triphenylacetate and a (thmeH)2 ligand. The latter are singly deprotonated, the alkoxide arm 2-bridging while the protonated arm μ2-bridging with the protonated arms each bind terminally to one of the Ln ions. Charge balance requires that only one ligand must lose an additional proton, but this must be disordered. Although thmeH3 has been used extensively in 3d metal cluster chemistry,10 to the best of our knowledge this is the first example of a homometallic 4f cluster incorporating this ligand. The central Ln ion has two terminal MeCN groups, making all metal ions eight co-ordinate. The coordination geometry at the central ion approximates closely to 3-fold symmetric (Fig. S3†). The cluster is a dication, with nitrates providing the charge balance.

We start with the magnetic properties of 2 containing the spin-only Gd3+ ion. At room temperature ΔMT (ΔM is the molar magnetic susceptibility) is 54.3 cm3 K mol−1 (Fig. 2), in agreement with the value for seven uncoupled s = 7/2 ions with g = 2.0. On cooling, ΔMT decreases slowly until ca. 30 K where it decreases more rapidly. We have not attempted to model the data given the 8-dimensional spin system, but it is only consistent with weak antiferromagnetic coupling between the Gd3+ ions. The low temperature molar magnetisation (M) saturates at 49 μB above ca. 6 T (Fig. S4†). Note that this does not indicate an S = 49/2 ground state, simply that this state becomes the ground state in these applied fields. The centred-hexagonal topology, consisting of six edge-sharing triangles is highly frustrated and this, combined with the weak antiferromagnetic nature of the coupling, will give...
rise to many low-lying states that are populated even at base temperature. The maximum spin state \( S = 49/2 \) will then become the ground state in relatively small applied magnetic fields. This situation is promising for a large low-temperature MCE because the possible magnetic entropy change on magnetisation is enhanced by the multiple low-lying states that are thermally accessible in zero-field (large entropy) while the magnetisation can still be saturated (nil entropy) in applied field.\(^1\),\(^5\)

We have calculated the magnetic entropy change \(-\Delta S_m\) for various field changes and temperatures from the \( M(H,T) \) data (Fig. 3). The maximum change, at 3 K and for a field change of 0–7 T, is 23 J kg\(^{-1}\) K\(^{-1}\). This compares against 26 and 31 J kg\(^{-1}\) K\(^{-1}\), the largest values reported to date, for \( \text{NiGd}_6 \) \((\Delta H = 7 \text{ T at } 3 \text{ K})\) and \( \text{CuGd}_4 \) \((\Delta H = 9 \text{ T at } 3 \text{ K})\).\(^2\) This \(-\Delta S_m\) value, equivalent to 10.6 R where R is the gas constant, is much larger than that expected for an \( S = 49/2 \) paramagnet (3.9 R), showing the massive enhancement due to the high density of low-lying states in low fields, a result of the weak coupling and spin frustration. The maximum possible value for seven \( \text{Gd}^{3+} \) ions is 14.6 R.

However, a disadvantage of the antiferromagnetic nature of the coupling is shown by comparison of the experimental low temperature \( M(H) \) curves against the calculated Brillouin curves for seven uncoupled \( s = 7/2 \) ions (Fig. S4t). The antiferromagnetic coupling leads to slower magnetisation as a function of applied field of uncoupled ions. This would translate as a slower cooling rate. The conclusion is that a weakly ferromagnetically coupled system would be ideal for magnetic cooling, coupling the advantages of low-lying excited states with ease of magnetisation. A recent example is Murray’s \( \text{Cu}_5\text{Gd}_4 \) cluster.\(^2\)

For the isostructural \( \text{Dy}_7 \) analogue \( \text{I} \), \( \Delta M(T) \) is 98.0 cm\(^3\) K mol\(^{-1}\) at room temperature (Fig. 4), in good agreement with the calculated value of 99.2 cm\(^3\) K mol\(^{-1}\) for seven uncoupled \( \text{Dy}^{3+} \) ions \(({}^{7}H_{1/2} \text{ ground term, } g = 4/3)\). \( \Delta M(T) \) decreases gradually on cooling, then more rapidly below 30 K. This indicates either weak antiferromagnetic interactions and/or depopulation of the \( \text{Dy}^{3+} \) excited Stark sub-levels.\(^1\) \( \Delta M(T) \) displays a maximum at 2.9 K (Fig. 4, inset) which shifts to lower temperatures for applied fields > 3 kG. \( M(H) \) approaches saturation at ca. 36 \( \mu_B \) at low temperature (Fig. S5t). Reduced magnetisation curves do not superimpose, suggesting the presence of significant magnetic anisotropy and/or low-lying excited states.

The magnetisation dynamics were investigated by alternating current (ac) susceptibility measurements as a function of temperature (2–25 K) and frequency (\( \nu = 0.1–1400 \text{ Hz} \)), in zero dc field (Fig. 5 and S6t). Both the in-phase \( (\chi_M) \) and out-of-phase \( (\chi''_M) \) components of the susceptibility show frequency dependence below ca. 28 K; maxima are observed in \( \chi''_M(T) \). These observations are characteristic of SMM behaviour.

Although at lower frequencies only a single peak is observed in \( \chi''_M(T) \) (e.g. at 3 K for 1 Hz; Fig. 5), multiple peaks are observed at higher frequencies (at 2.9 and 14.1 K, with a shoulder at 24 K, for \( \nu = 1.2 \text{ kHz} \)) indicating multiple relaxation processes. This is likely due to the presence of two types of \( \text{Dy}^{3+} \) ion, the central ion and peripheral sites, because their anisotropy axes are not expected to be collinear.\(^12\),\(^13\) Relaxation time constant \( (\tau) \) data, evaluated from \( \chi''_M(T,\nu) \), are linear with \( 1/\nu \) above 10.5 K (Fig. 5); fitting to an Arrhenius law gives a thermal energy barrier to magnetisation relaxation \( U_{\text{eff}} = 140 \text{ K} \) with \( \tau_0 = 7.2 \times 10^{-8} \text{ s} \). This is among the highest observed for a cluster SMM, exceeded only by two \( \text{Dy}_3 \) (at 170 K),\(^11\) a \( \text{Dy}_8 \) (200 K),\(^13\) and the recent observation of 530 K in a Dy\(_5\) cluster.\(^14\) Higher barriers have been reported for high symmetry monometallic Tb\(_3^{3+}\) complexes.\(^15\)

Below 10 K, \( \tau \) tends to saturate, suggesting a quantum tunneling relaxation pathway. This is supported by field-dependence studies at 1.8 K, which show a minimum in \( \tau \) in zero applied field, and is also consistent with the lack of hysteresis in \( M(H) \) at 1.8 K (Fig. S7t). The latter has an inflection point at 4.3 kG, presumably indicating a level crossing. The onset of quantum behaviour is also reflected in Cole-Cole
under zero dc field, based on data collected in frequency (1 MHz - 1400 Hz).

Data are corrected for the diamagnetism of the compounds (Pascal constants) and sample holder and eicosane by measurement. Ac susceptibility measurements were performed with an ac magnetic field of 1.55 G oscillating at frequencies ranging from 1 to 1400 Hz.

Crystal data. For 1, C_{14}H_{10}Dy_7N_4O_{42}, M_r = 3880.39, monoclinic, space group P1_2_1/c, a = 16.263(4), b = 16.500(4), c = 17.299(4) Å, β = 97.217(10)°, V = 115.0080(10) Å³, Z = 1, µ = 1.795 g cm⁻³, total data 2916, unique data 1227 (R_c = 0.1473), μ = 3.680 mm⁻¹, 937 parameters, R = 0.0725 for I ≥ 2σ(I) and wR = 0.2585 for all data. For 2, C_{14}H_{10}Gd_7N_4O_{42}, M_r = 3843.64, triclinic, space group P1_1_1, a = 16.1991(8), b = 16.3943(8), c = 17.2829(9) Å, β = 113.8990(10), γ = 114.9720(10), R = 0.1013 for I ≥ 2σ(I) and wR = 0.2293 for all data. The data of 1 and 2 were recorded on a Bruker SMART CCD diffractometer with Mo-Kα radiation (λ = 0.7073 Å). The structures were solved by direct methods and refined on F² using SHELXTL. CCDC 829587 and 829588 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk).

In summary, two isostructural heptametallic lanthanide discs were prepared, and the diamagnetic properties of polycrystalline samples were discussed. Further analysis of the thermally activated region (solid line). The magnetic properties of polycrystalline samples were investigated in the temperature range 1.8-300 K using a Quantum Design MPMS-XL SQUID magnetometer; loose samples tended to orient in the magnetic field and hence were fixed in eicosane. Data are corrected for

In conclusion, two isostructural heptametallic lanthanide discs were prepared, and the diamagnetic properties of polycrystalline samples were discussed. Further analysis of the thermally activated region (solid line). The magnetic properties of polycrystalline samples were investigated in the temperature range 1.8-300 K using a Quantum Design MPMS-XL SQUID magnetometer; loose samples tended to orient in the magnetic field and hence were fixed in eicosane. Data are corrected for

Fig. 5: Temperature dependence of: (top) Χ(θ) and (bottom) Χ'(θ) for 1, measured in 1.55 G ac field and zero dc field. Inset: τ(T)⁻¹ for 1, under zero dc field, based on data collected in frequency (1 MHz - 1400 Hz). The plots are asymmetric and increase with decreasing temperature; between 18 and 10 K θ is almost constant at 0.22. We can speculate that at the higher temperatures the slow relaxation is dominated by the single ion behaviour of the central (highly symmetric) Dy³⁺ ion, while at low temperatures the weak coupling with the peripheral ions is important.

In summary, two isostructural heptametallic lanthanide discs have been made. Magnetic investigations show a significant MCE for the Gd³⁺ disc and slow relaxation behaviour with a high thermal energy barrier for the Dy³⁺ analogue. Further analysis of the complicated Dy³⁺ dynamic behaviour will require single crystal magnetic studies, including doped diamagnetic and isostructural analogues: efforts towards this are underway.

We are grateful to the EPSRC (UK) and the EC (Marie Curie International Incoming Fellowship to YZZ) for funding, and to the referees for helpful comments.

Notes and references

1. Elemental analyses (calc: found): (1) Dy 29.29: 28.78, C 47.63: 47.18, H 4.33: 3.77, N 1.44: 1.29; (2) Gd 28.61: 27.25, C 48.08: 46.08, H 4.38: 4.26, N 1.46: 1.55. The magnetic properties of polycrystalline samples were investigated in the temperature range 1.8-300 K using a Quantum Design MPMS-XL SQUID magnetometer; loose samples tended to orient in the magnetic field and hence were fixed in eicosane. Data are corrected for
Supplementary Information for

Lanthanide Discs Chill Well and Relax Slowly

Joseph W. Sharples, Yan-Zhen Zheng, Floriana Tuna, Eric J. L. McInnes and David Collison

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Fig S1. Schematic of organic ligands thmeH₃ (left) and tpaH (right).

Fig. S2. Left: core of Ln₇ [Ln (purple), O (yellow), C (grey), H omitted]. Right: Space-filling diagram, viewed in the Ln₇ plane.
**Fig S3.** Views of the \{\text{LnN}_2\text{O}_6\} (left) and \{\text{LnO}_8\} (right) coordination polyhedra; the two disordered metal ion sites are shown in the former. The geometry at the central ion can be described as bi-capped compressed octahedral, with the caps on the trigonal compression axis (N-Dy-N). [An alternative description is as distorted cubic, with elongation along the N-Dy-N body diagonal.] The peripheral ions are lower symmetry, best described as bicapped trigonal prismatic.

**Fig. S4.** Experimental $M(H)$ for 2 at 2, 3 and 4 K, with calculated Brillouin curves for seven uncoupled $s = 7/2$ ions ($g = 2.0$).
**Fig. S5** Left: $M(H)$ for 1 at 2-15 K. Right: $M(H/T)$ for 1 at 2, 4, 6, 10 and 15 K.

**Fig S6.** Frequency dependence (in zero-dc field) of the (left) in-phase ($\chi_M'$) and (right) out-of-phase ($\chi_M''$) ac susceptibility of 1 at several temperatures between 4 and 21 K.
**Fig S7.** $M(H)$ for 1 at 1.8 K between -60 and 60 kG.

**Fig S8.** Left: Cole-Cole diagrams for 1 at different temperatures between 4 and 14 K. Right: temperature dependence of $\alpha$ parameter from fits to Cole-Cole plots (shown as solid lines in inset).
Chapter 6: Paper 3

Using heat capacity measurements to probe magnetocaloric materials

Joseph W. Sharples, Floriana Tuna, Marco Evangelisti, Jürgen Schnack and David Collison, *manuscript in preparation*. 

66
Introduction

Carboxylic acid ligands do not come simpler or smaller than formic acid, HCOOH, but they can give structurally fascinating and complex lanthanide(III) compounds such as the homoleptic formates [Ln(HCOO)]₃, Though studied for many years, new and fascinating properties continue to be discovered, e.g. their ferroelectric and luminescent behaviour [1a,b]. We wished to investigate these compounds for their slow relaxation and magnetocaloric effect (MCE) [1c,d]. Applying a magnetic field to a paramagnet minimises one component of its total entropy, namely –ΔSₘ, so that under adiabatic conditions, the material warms. Decoupling from the surroundings followed by demagnetisation results in the paramagnet being cooled relative to its environment, thus acting as a refrigerant. The key to maximising this performance is to use high spin ions or ligands (usually ions), as suggested by Equation 1, where n is the number of spins of a given S, and R is the gas constant.

\[-\Delta S_m = nR\ln(2S+1)\] Equation 1

Compounds with the highest gadolinium percentage give the largest –ΔSₘ values [1e] (as adjusted for by their molecular weight), which is one powerful indicator of the material’s usefulness. The caveat to this is that at some point we reach Gd³⁺ metal, where the maximum response is found at its near room temperature ordering point [1f]. Since our interest lies in low temperature cooling we require ligands to separate the spins, so that maximum –ΔSₘ changes are seen only well into the low temperature region. Further qualities are the use of isotropic spins and weak interactions between metals. Gd³⁺ compounds are acknowledged as most promising in this regard [1e].

Our previously reported [Gd(HCOO)]₃ [1g], by contrast, employed the large triphenyl acetic acid group. This compound showed a large low temperature MCE and we report more detailed investigations into its exchange and ordering processes via heat capacity experiments, which can give useful information on the magnetic structure and magnetothermal behaviour of materials and computational results. Separately slow relaxation in zero-dimensional cages, or molecules (SMMs) [1h] are often demonstrated when Dy³⁺ or other anisotropic ions [1i,j,k] are used. Here we investigate the homoleptic formates above for these properties, though Uₘₘₜ was found only for (1).

Highlights of Ln³⁺ Formate Compounds

Surprisingly, we could no magnetic studies on the Gd³⁺, Tb³⁺ or Dy³⁺ homoleptic compounds constituting our main interest. However, there are several rare-earth compounds containing the formate ligand HCOO⁻. We summarise some of the most recent and interesting here, which demonstrate the diverse applications in which compounds with the formate ligand have been utilised. Rossini et al. [2a] found that, from the solvothermal reaction (130 °C, 24 h) of [Ln(NO₃)₃·nH₂O], cyclobutane-1,1'-dicarboxylic acid in formamide (HCO(NH₂)), [Ln(HCOO)₄(FMD)]₃, was synthesised where Ln³⁺ = Eu³⁺, Gd³⁺, Tb³⁺ and Dy³⁺ and FMD is NH₂-CH=NH₂, from formamide hydrolysis. X-ray diffraction (XRD) found formate ligands bridge (anti-anti) between metal ions and the FMD H-bonds (N–H·O) to an oxygen atom of this ligand. Thermal analysis found these break down into [Ln(HCOO)₃]₃ and LnIII·O₃ successively at around 300 and 650 °C respectively. In addition to the familiar Tb³⁺ and Eu³⁺ emission, with long lifetimes of ca. 2.0 x 10⁵ µs, Dy³⁺ emission was also observed displaying the F₇/₂ → ℋ₁₅/₂ and ℋ₁₃/₂ bands and was maintained on surfaces of ITO (Indium-Tin-Oxide). For [Gd(HCOO)]₃, the simple magnetic behaviour was fitted to a Curie-Weiss law, with 0 = –0.54 K, confirming antiferromagnetic exchange. The anisotropy expected in [Th(HCOO)]₃ and [Dy(HCOO)]₃ prevents a similar analysis, though θT decreased with decreasing temperature in each case. Interestingly, in an applied static field,
a.c. measurements showed only \([\text{Gd}^{III}\]) has an appreciable \(g\)-component, from which a \(\Delta\) of ca. 25 K was extracted, though, assigned to a phonon-bottle-neck effect rather than anisotropy-derived slow relaxation. A promising MCE can be expected from this compound, too.

The \([\text{AH}]\) of \([\text{Er}^{III}(HCOO)_{2}\]) frameworks, where \(\text{AH}\) is a monoamine, of Bin Liu et al. \([2b]\) were investigated for their magnetic properties for a range of ligands, which were found to have a significant influence. For example, when ethanolaminium or ammonium are used ferromagnetic exchange is seen, whereas using methylammonium, formamidinium, guanidinium, imidazolium or ethylammonium result in antiferromagnetic exchange or simple decreasing \(x(T)\) with decreasing temperature due to Stark level depopulation.

Jiao-Min et al.
investigated both a range of \([\text{Ln}^{III}\text{(BTA)(HCOO)}(\text{H}_{2}\text{O})_{3}]\) compounds \([2c]\), where \(\text{Ln}^{III}\) = Pr\(^{III}\), Eu\(^{III}\), Gd\(^{III}\), Tb\(^{III}\), Dy\(^{III}\), Er\(^{III}\) or Yb\(^{III}\) and \(\text{H}_{2}\text{BTA}\) is bis[triazolyl]amine and two of the homoleptic compounds \([\text{Ln}^{III}(\text{HCOO})_{3}]\), where \(\text{Ln}^{III}=\text{Pr}^{III}\) or \(\text{Nd}^{III}\). The former contains Ln\(^{III}\) ions with an unusual distorted pentagonal bipyramidal, seven-coordinate, geometry, arranged into a 1-D chain structure, further linked by \(\text{H}_{2}\text{O} \cdot \text{HO-N}(\text{BTA})\) H-bonds into a three dimensional supramolecular “grid”. Luminescence experiments found lanthanide emission for the Eu\(^{III}\), Tb\(^{III}\) and Dy\(^{III}\) versions, with only BTA based emission seen for the Gd\(^{III}\) analogue, as the ligand could not excite the \(S_{0}\rightarrow S_{1}\) transition. For this latter magnetic data could be fitted with \(\theta=0.49\) K, hence another example of weak antiferromagnetic coupling through the formate ligand. Interestingly, the difference in these structures resulted from only the small change of the N-ligand in the solvothermal reaction (150 °C, 72 h) of \([\text{Ln}^{III}(\text{Cl}_{2},\text{n-H}_{2}\text{O})] \) and \(\text{HCOOH}\) in water, with either \(\text{BTAH}_{2}\) or \(\text{NEt}_{3}\).

A more rigorous magnetic analysis was performed on the \([\text{Ln}^{III}(\text{phen})](\text{HCOO})_{2}(\text{HCOO})_{2}(\text{NO})_{2}]\) compounds of Liu et al. \([2d]\), which were synthesised by stirring \([\text{Ln}^{III}(\text{NO})_{2},\text{n-H}_{2}\text{O}]\) in methanol with \(\text{MeOH/DMF}\) solutions of formic acid and phen, where phen = \(\alpha\)-phenanthroline and \(\text{Ln}^{III}=\text{Gd}^{III}\) or \(\text{Eu}^{III}\). There is some ambiguity about the nature of these ligands in the crystal structure and whether nitrate or formate is involved, but the coordination is the same with nine-coordinate metal ions. The 3d structure is made up of these units with \(\pi\)-stacking of the phen groups. Decreasing \(x(T)\) products with decreasing temperature are ascribed to a mixture of Stark sublevel depopulation and/or antiferromagnetic coupling, where \(\text{Ln}^{III}=\text{Er}^{III}\). This decrease only occurs below 50 K for \(\text{Gd}^{III}\) and, by comparison with the Brillouin function, is basically paramagnetic behaviour. Only in a static field is slow relaxation seen in both compounds, with frequency dependent maxima observed, resolved as two relaxation processes: a slow, low temperature, spin-lattice effect and faster, higher temperature spin-spin effect. These are similar in this regard to a further pair of \(\text{Er}^{III}\) formate-based structures, by Mengyuan et al. which also show a spin-lattice relaxation \([2e]\).

Xun et al. investigated \(\text{[Ln}^{III}(\text{Hpipma})_{2})(\text{HCOO})\text{5H}_{2}\text{O}]\), where \(\text{Ln}^{III}=\text{Sm}^{III}, \text{Eu}^{III}, \text{Gd}^{III}, \text{Dy}^{III}\) or \(\text{Ho}^{III}\) and \(\text{Hpipma}=1H-2-propyl-4,5-imidazoledicarboxylic acid \([2f]\), from another solvothermal route (135 °C, 72 h), combining \(\text{Hpipma}\) with \(\text{NaHCOO} \cdot \text{H}_{2}\text{O}\) and \([\text{Ln}^{III}(\text{NO})_{2},\text{n-H}_{2}\text{O}]\) in \(\text{H}_{2}\text{O} / \text{EtOH}\) with nitric acid. The repeat unit has three metals linked, with two distinct square antiprismatic geometries. Luminescence experiments found ligand to metal energy transfer in the \(\text{Ce}^{III}\) and \(\text{Eu}^{III}\) analogues, being more efficient in the latter. Magnetic data indicate a size dependent exchange coupling between metals, with antiferromagnetic to paramagnetic to ferromagnetic transitions as the lanthanides become smaller.

A lanthanide MOF incorporating formate ligands, namely \([\text{Ln}^{III}[(\text{Me})_{2}\text{P}^{2+}(\text{HCOO})_{3}])\text{(Me}_{2}\text{NH})_{2}\text{DMF})_{2}\text{(H}_{2}\text{O})_{n}\), where \(\text{Ln}^{III}=\text{Y}^{III}\) and \(\text{Sm}^{III-\text{Lu}^{III}}\), and \(\text{H}_{2}\text{P}^{2+}\) is tris-(4-carboxyphenyl)phosphineoxide \([2h]\), were shown to store \(\text{CO}_{2}\), being synthesised by a little-used microwave-based process. This has the potential, like solvothermal synthesis, to produce products relatively quickly, often different to conventional bench chemistry.

Something rather different is the \(\text{Sm}^{III}\) “nanotube” arrangement in \([\text{Sm}^{III}(\text{HCOO})_{3}(\text{tmtnz})]\), where \(\text{tmtnz} = 2,6\text{-tris-(2-pyridyl)-s-triazine} \([2i]\). This has its origin in a happy “accidental” synthesis. Here the nanotubes arrange to form a material with two sets of channels, one hydrophobic and the other hydrophilic. \(\text{H}_{2}\text{O}^{+}\) uptake was recorded making this a promising flexible gas storage MOF. This also adds to the field of lanthanide MOFs in general which include, for example, Vaidyanathan et al.’s, \([\text{NH}_{3}\text{C}_{2}\text{H}_{4}\text{C}_{2}\text{H}_{4}\text{CH}_{3}][\text{Nd}^{III}(\text{C}_{2}\text{O}_{4})(\text{HCOO})\text{H}_{2}\text{O}]\).

Separately, Zhong-Hua et al.’s series of \([\text{Ln}^{III}(\text{L})\text{(HL)}_{3}\text{(HCOO)})\text{3CH}_{3}\text{OH} \([2k]\), where \(\text{Ln}^{III}=\text{Eu}^{III}, \text{Gd}^{III}, \text{Th}^{IV}, \text{Dy}^{III}, \text{Er}^{III}\) or \(\text{Yb}^{III}\) and \(\text{L}=1,3,5\text{-tris(imidazole-1-ylmethyl)}\text{-}2,4,6\text{-trimethylbenzene},\) was shown to display sensitised \(\text{Eu}^{III}\) and \(\text{Th}^{IV}\) emission. These have three dimensional structures which incorporate channels. Only \(\text{Dy}^{III}, \text{Th}^{IV}\) and \(\text{Er}^{III}\) compounds show increasing \(\chi{T}\) at lower temperatures, the rest decreasing, again implying the exchange mechanism has a size dependence, though dipolar interactions may be important.

Atrasheuski and Tsvirko \([1b]\) found enormous quantum yields for \(\text{Eu}^{III}\) along with \(\text{Th}^{IV}\) and \(\text{Gd}^{III}\) (unlike in \([2c]\) this was a direct f-f transition \(\text{2g}\) homoleptic formates and their transition probabilities. Extensive measurements also found beautifully resolved emission spectra with extensive multiplet splitting.

The two 3-D compounds explored for their MCE which incorporate the formate ligand are amongst the best of all measured for low temperature work so far. Namely these are \([\text{Gd}^{III}(\text{HCOO})\text{C}_{2}\text{H}_{4}\text{O}_{3}])\) and \([\text{Gd}^{III}(\text{HCOO})(\text{OAc})_{2}\text{H}_{2}\text{O}])\).

Conceptually these are similar to \([\text{Gd}^{III}(\text{HCOO})]_{n}\) as discussed in this work. Both show tiny antiferromagnetic coupling, almost indistinguishable from paramagnetic behaviour until the very lowest temperatures recorded. Similar \(\Delta S_{m}\) values of 47 (\(\Delta H = 9\) T, 2.3 K) and 46 J kg\(^{-1}\)K\(^{-1}\) (\(\Delta H = 7\) T, 1.8 K) are exceeded only by a handful of compounds reported so far. \([2l,m]\) Work with another homoleptic compound, \([\text{Sm}^{III}(\text{HCOO})]_{n}\), found it to show antiferromagnetic interactions, as previously seen with this ligand and a ferroelectric response whereby a polarisation hysteresis loop is seen on application of an electric field \([1a]\).

Interestingly the homoleptic \([\text{Lu}^{III}(\text{HCOO})]_{n}\) materials have also been synthesised for use as precursors to \(\text{Gd}^{III}\) dopant-\(\text{Ce}^{III}\) solid-oxide fuel cells \([2n]\).

Experimental Procedure and Characterisation

Metal and ligand reagents were purchased from Sigma-Aldrich and used without further purification.
Though there are many ways to prepare these compounds in the literature, including from Ln(NO$_3$)$_3$ [1b, 3a], Ln(HCOO)$_3$ [1a, 2c] and Ln(NO$_3$)$_3$·H$_2$O [2k], we found the following, rather simple, method gave crystalline material quickly and in good yield within a few days in most cases, summarised in Figure 1.

\[
\text{Ln(NO$_3$)$_3$} \cdot n\text{H$_2$O} + \text{HCO$_2$H} \rightarrow \text{Ln(HCOO)$_3$} \cdot n\text{H$_2$O}
\]

Fig.1. Scheme showing the reaction of [Ln(NO$_3$)$_3$·nH$_2$O] and HCOOH in H$_2$O to give [Ln(HCOO)$_3$] $n$.

$\text{[Gd(HCOO)$_3$]}_n$ (1)

$\text{[Gd(NO$_3$)$_3$} \cdot n\text{H$_2$O}$ (1 g, 2.2 mmol, assuming a typical value of $n = 5$), excess formic acid (10 mL, ca. 200 mmol) and H$_2$O (2.5 mL) were stirred together at room temperature for five minutes then left to stand overnight open to the atmosphere. Crystalline material was found after 12-24 h and collected by filtration, retaining crystallinity upon air-drying as expected. When more water was used in further reactions the crystallisation time was extended, though these often led to none of the desired product being produced. Analyses as GdC$_3$H$_6$O$_n$ gave (experimental/calculated): Gd 53.77:53.80; C 12.32:12.33; H 5.99:6.03; N 0.0:0.0. Note that the $n$ at the end of the formula signifies a polymeric compound, where $n$ is infinity. Yields are variable at around 20-30% based on the lanthanide(III) salt.

$\text{[ Tb(HCOO)$_3$]}_n$ (2)

The synthesis was analogous to (1), using [Tb(NO$_3$)$_3$·nH$_2$O] (1 g, 2.2 mmol), and analysed as TbC$_3$H$_6$O$_n$ giving: Tb 53.90:54.06; C 12.21:12.26; H 0.99:1.03; N 0.0:0.0.

$\text{[ Dy(HCOO)$_3$]}_n$ (3)

The synthesis was analogous to (1), using [Dy(NO$_3$)$_3$·nH$_2$O] (1 g, 2.2 mmol), and analysed as DyC$_3$H$_6$O$_n$ giving: Dy 54.80:54.61; C 12.14:12.11; H 0.99:1.02; N 0.0:0.0.

PXRD

Powdered crystalline solids of (1)-(3) were analysed by PXRD in order to assess the phase-purity of the bulk materials. Each of these showed a good agreement with the published data calculated from XRD of [Sm(HCOO)$_3$] $n$ [3a] (see S. I. 1) and checked with that of [Gd(HCOO)$_3$] $n$ [3b] previously reported. Additionally, thermogravimetric analysis of (2) is included as S. I. 2, showing the stability up to around 250 °C.

XRD and Structure

Small hexagonal blocks of (1) and (3) were examined by XRD, which found the expected structure. These crystallises in the R3m spacegroup with a hexagonal crystal system (unit cell shown in S. I. 3). Briefly, this is as follows: the whole is a three-dimensional network based around linked chains of lanthanide(III) ions. Each individual metal ion is nine-coordinate with a tri-capped square antiprismonic geometry giving each ion three-fold $D_3d$ symmetry (detail shown in S. I. 4). Each formate ion bonds with the bridging mode 3.2.1, as Harris notation [3c], i.e. between two ions with one O atom and bonding terminally with other metals.

One way to describe the extended structure, depicted in Figure 2, is to view the arrangement down the $c$-axis. “Chains” of lanthanide ions extend along this axis, connected by the bridging formate O, which bonds in anti-anti fashion. Six of the nine formate groups are bonded to the 4th metal coordinate in this way with the other three oxygen atoms bonding terminally. We find $Z = 3$, giving a density of 3.9 g cm$^{-3}$, which is promising for a large adjusted MCE ($-\mu\Delta\mu_a$, vide infra).

Magnetic Properties of (1)-(3)

We begin our investigations with the magnetic properties of the isotropic $\text{[Gd(HCOO)$_3$]}_n$ before continuing with the more anisotropic (2) and (3). This work builds on that reported previously on $\text{[Gd(HCOO)$_3$]}_n$ by some of the authors [3d].

$\text{[Gd(HCOO)$_3$]}_n$ (4)

For (1) static (d.c.) field measurements (Figure 3) were carried out between 1.8-300 K under an applied 0.1 K field. $\chi(T)$ was found to be 7.9 cm$^{-1}$ mol$^{-1}$ K at room temperature, matching that expected [4a] for a single Gd$^{3+}$ ion ($\mu = S=\gamma g = 2$) of 7.875 cm$^{-1}$ mol$^{-1}$ K. With decreasing temperature this is almost constant down to around 50 K before undergoing a more rapid decrease around 25 K (ca. 7.75 cm$^{-1}$ mol$^{-1}$ K), reaching almost 6.9 cm$^{-1}$ mol$^{-1}$ K at 1.8 K. This behaviour is redolent of a weakly coupled system with $\chi(T)$ indicating antiferromagnetic exchange between spin centres, $\chi(T)$ data (Figure 3 inset) showed a typical low temperature increase for a paramagnetic system though no maximum was seen, which would have indicated an ordering temperature. These data were modelled with the Curie-Weiss Law in Equation 2, where $g$ is the Landé $g$-factor, $\mu$ the electronic Bohr magneton, $\beta$ the spin $\gamma S$, $k_B$ the Boltzmann constant, $T$ the temperature, and $\theta$ the Weiss constant:

$$\chi = g^2\mu_B^2 S(S+1)/(3k_BT-\theta)$$

Equation 2

This gave a good agreement with experiment, as shown in Figure 3 by the red line, confirming the initial suggestion on the nature of the network based around linked chains of lanthanide(III) ions. Each individual metal ion is nine-coordinate with a tri-capped square antiprismonic geometry giving each ion three-fold $D_3d$ symmetry (detail shown in S. I. 4). Each formate ion bonds with the bridging mode 3.2.1, as Harris notation [3c], i.e. between two ions with one O atom and bonding terminally with other metals.

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The Weiss constant, \(\theta\), is required to flip adjacent spins rather than simply aligning them as in the paramagnetic case. The field of the exchange \([4a]\). Equivalently, from the \(\chi_T\) versus \(T\) (Figure 3 inset) data the Weiss constant, \(\theta\), is \(-0.3\) K.

\(\Delta S_M\) data (Figure 4) were collected at a range of temperatures between 2 and 10 K and 0-7 T. These showed saturation at only 5 T and 2 K, reaching 7 \(N\alpha_b\) (as expected by \(M_{ca}/N\alpha_b = gS\)), which bodes well for a large magnetic entropy change under relatively mild conditions.

**Magnetocaloric Effect**

Using the following Maxwell relation \([1c]\) (Equation 3) one can obtain the magnetic entropy change from magnetisation data. This gives the first real indicator of how useful a material will be as a magnetic refrigerant.

\[
\Delta S_M(T, \Delta H) = \mu \left[ \frac{\partial \chi}{\partial T} \right]_{H} dH \quad \text{Equation 3}
\]

Even before measuring this compound, though, we can calculate an extremely large value of \(-\Delta S_M = 59.16 \text{ J kg}^{-1} \text{K}^{-1}\) from

\[
\mu \left[ \frac{\partial \chi}{\partial T} \right]_{H} dH
\]

For \((1)\), a huge \(-\Delta S_M = 55.1 \text{ J kg}^{-1} \text{K}^{-1}\) at 3 K and for a 0-7 T field change was found (shown in Figure 5 for a range of fields and temperatures). This is the highest found so far at low temperatures for any magnetocaloric material. Furthermore, when one examines these values at less extreme conditions, large entropy changes are still observed. For example the industry standard material GGG (\(\text{Ga}_{20}\text{Gd}_{30}\text{O}_{32}\)) \([4b]\) shows a maximum value of \(-\Delta S_M = 27.1 \text{ J kg}^{-1} \text{K}^{-1}\) for \(\Delta H = 0-5\) T and 5 K; for \((1)\) this is \(43.3 \text{ J kg}^{-1} \text{K}^{-1}\). Thus, even at such mild conditions, \((1)\) still outperforms all known molecular examples reported so far \([4c]\).

To help us evaluate the effect of the exchange on the MCE we used the program PHI, developed by Chilton et al. \([4d]\) to simulate \(-\Delta S_M\) for a paramagnetic system, i.e. one where there are no interactions. Shown in S. I. 5, these found that for both \(\Delta H = 5\) T and 7 T, \(-\Delta S_M\) reaches almost \(59.3 \text{ J kg}^{-1} \text{K}^{-1}\), showing the slight negative influence of the weak exchange here; the field is first required to flip adjacent spins rather than simply aligning them as in the paramagnetic case.

The parameter \(-\Delta S_M\) whilst ubiquitous in the literature (it being the easiest of several indicators to obtain), does not completely describe how useful magnetocaloric materials would be in practice, a fact noted by several groups \([4e]\). A second, more useful, marker is to take the density of a compound into account to give \(-\rho\Delta S_M\), thus incorporating a real world dimension to the quantification; i.e. how much material is needed to be useful, which can be important in proposed space agency (NASA or ESA) applications, where (storage) space can be valuable. For \((1)\), from a density of 3.9 \text{ g cm}^{-3} this gives \(-\rho\Delta S_M = 216 \text{ mJ cm}^{-3}\). Compared to GGG this is larger, though only under our most extreme conditions, as the latter has a rather large density of 7.1 \text{ g cm}^{-3}. Thus GGG may remain more useful if space (volume) is an issue. In the vast majority of reported molecular examples of MCE compounds the density is less than 2 \text{ g cm}^{-3} and the highest 3.4 \text{ g cm}^{-3} in the gadolinium tungsten compounds \(\text{Gd}^{12}\text{W}_{12}\)) and \(\text{Gd}^{12}\text{W}_{12}\) \([4f]\), which have large masses and low \(-\Delta S_M\) values (though this highlights another danger of using only \(-\Delta S_M\) as a guide; these compounds promise much for extremely low temperature cooling).

**Equation 1** \((n = 1)\) and \(S = \text{Tr}\)\(^{-1}\) is the maximum possible for a system of this spin and molecular weight.

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Clearly, the low molecular weight of the ligands contributes to the large $-\Delta S_M$ of (1), with ca. 54% (by weight) gadolinium(III) in this compound. In this respect there is a large advantage of polymeric species over molecular compounds as the former are not “required” to have a shell of organic ligands encapsulating a metal core, so the ligands can in general be smaller. For example, see the Gd(III) acetate polymers [1e] with large $-\Delta S_M$ values; the best of these offer improvements over the Gd(III) acetate dimer, [Gd(III)$_2$(OAc)$_6$](H$_2$O)$_3$·4H$_2$O, [4g] by almost 15% in this regard.

Interestingly, whilst a completely non-interacting system will offer the largest MCE, a slight ferromagnetic interaction will give better performance at lower temperatures and fields and thus be more practical. Formate ligands, though, rarely give ferromagnetic exchange in gadolinium(III) compounds, as far as we can tell, so this would be hard to engineer deliberately [2e,j].

Although [Dy(III)(HCOO)$_3$]$_n$ is similarly light and dense we did not record the $-\Delta S_M$ due to the strong anisotropy in this ion which has been shown [4h] to greatly reduce the maximum values compared to the isotropic gadolinium(III) analogue, which also has the largest spin of any ion.

**Ordering temperature from heat capacity data**

Heat capacity data, in addition to giving extra magnetocaloric data, see below, can give information on the magnetic ordering of the material. From this it can be seen that (1) undergoes two phase transitions marked by abrupt changes in the heat capacity profile, assigned as $T_{C1}$ and $T_{C2}$, see Figure 6. At 0.8 K a maximum in C/R confirms the postulated antiferromagnetic (AF) magnetic transition, not detected in the $\chi(T)$ data, above 2 K. At lower temperatures of 0.4 K one can also see a second ordering temperature which relates to a ferromagnetic process. Fits of the lines are calculated Schottky terms [4i].

![Fig. 6. C/R versus T for (1) at 0, 1, 3 and 7 T shown as open shapes, with lattice contribution as orange dotted line. Solid lines are calculated Schottky terms. Key: As shown.](image)

**Heat Capacity Measurements**

A complete characterisation of the MCE of a compound requires heat capacity measurements [4i] to be undertaken and so give the adiabatic temperature change $\Delta T_{AD}$, which gives directly the amount by which the material can cool its surroundings.

![Fig. 7. Upper: Overlay of $-\Delta S_M(T)$ derived from $M(H)$ data, shown as stars (1), and from heat capacity data, shown as open spheres. Key: Given for 1 T Red, 3 T Blue and 7 T Black. Lower: $\Delta T_{AD}(T)$ shown as spheres derived from heat capacity data for 1, 3 and 7 T. Inset: Enlarged view of $\Delta T_{AD}(T)$ showing direct MCE.](image)

For this the appropriate Maxwell relations are given in Equations 4 and 5, where $C$ is the heat capacity, $C_{mag}$ heat capacity of magnetisation, $H_f$ final applied field and $H_i$ initial applied field [1c]:

$$\Delta T_{AD} = \left[ \frac{\mu}{\frac{C_{mag}}{C}} \right] \left[ \frac{\partial H(T,H)}{\partial H} \right]_{T,H} dH \quad \text{Equation 4}$$

$$S_M(T) = \int_0^T \frac{C_{mag}(T)}{T} dT \quad \text{Equation 5}$$

Experiments found that $\Delta T_{AD}$ was ca. 25 K at 2 K ($\Delta H = 0.7$ T), the largest recorded as far as we can tell, depicted in Figure 7, lower section. Even at only a $\Delta H = 3$ T, the change $\Delta T_{AD}$ is larger than any previous molecular example, the largest of which is for the aforementioned Gd(III) acetate dimer at ca. 13 K ($\Delta H = 0.7$ T, 1.8 K) [4g].

As stated, heat capacity data can also give $-\Delta S_M$ and thus corroborate those values obtained via magnetisation. Indeed, a good overlap between these two independent techniques was found, as shown in Figure 7, upper section, which also indicates the alternative form of units which incorporate density, vide supra.
Fig. 8. Experimental $\chi''(T)$ and $\chi'(T)$ for (1) below 1 K ($H_{d.c.} = 0$ mOe, $H_{a.c.} = 10$ mOe) shown as solid circles, where $\nu = 1.7$ Hz–6.8 kHz. Measured by micro-SQUID on a single-crystal orientated down the c-axis. Key for frequencies: As shown.

**Single crystal a.c. susceptibility results for [Gd$^{III}$HCOO$_3$]$_n$**

We examined (1) for any evidence of slow relaxation characteristics, taking advantage of the extremely low temperatures and sensitivity of the micro-SQUID apparatus. These measurements were performed in the absence of a static field, where $H_{d.c.} = 0$ and $H_{a.c.} = 10$ mOe, between frequencies of 1.7 Hz to 6.8 kHz. Single crystals of (1) were utilised with the orientation of the applied field being parallel to the long length of the crystal, which is the (3-fold) c-axis. Below 1 K substantial increases in $\chi'$ are seen from ca. 10 cm$^3$ mol$^{-1}$ to a maximum value of 45 cm$^3$ mol$^{-1}$ for the lowest frequencies (from Figure 8). These maxima all pre-empt precipitous decreases where $\chi$ falls to almost zero. The position of these maxima changes with frequency, shifting to higher temperatures as expected as the frequency increases, for a slow relaxation mechanism. Similarly for $\chi''(T)$ frequency dependent maxima were observed, with the highest temperature maxima being found at ca. 0.4 K, which is extremely low compared to the highest in SMMs, such as (Dy$^{III}$)$X_3$ [4] and (Th$^{III}$Pc$_2$) [4k]. From these data the Arrhenius equation was used to determine $U_{e ff}$, the anisotropy barrier, which was found to be 0.9 K and $\tau$, the time constant equal to $10^5$ s, of the order seen in other gadolinium(III) networks, above. Clearly this energy barrier is nothing like as substantial as in SMMs, which are several orders of magnitude greater.

The coincidence of the $\chi''$ maximum with that seen in the heat capacity data ($T_C$) is not an accident, we believe, and may indicate that the origin of slow relaxation is due to the very small anisotropy generated by the ligand geometry. Although in SMMs usually the more anisotropic variants in a series (i.e. where Ln$^{III}$ = Dy$^{III}$ or Tb$^{III}$) would be best considered for slow relaxation of magnetisation, in three-dimensional materials, compounds with “isotropic” ions, such as gadolinium(III), are known to show this, vide supra, via the phonon-bottle neck effect, for example in [2a]. Computational results may yet assist in determining the ordering processes and mechanism of slow relaxation.

**Anisotropic variants**

Static and variable field magnetic measurements were performed on the more anisotropic variants (2) and (3) between 1.8-300 K for an applied 0.1 kG field, and found the following.

For (3), $\chi''(T)$ values (Figure 9) for a single Dy$^{III}$ ion ($^{5}H_{15/2}$, $g = 4/3$), at around 8.5 cm$^3$ mol$^{-1}$ K, much lower than the maximum possible for a single uncoupled ion at room temperature. Upon lowering the temperature there is a shallow decrease down to around 60 K, whereupon a slight step leads to a more rapid
with no frequency dependence found. This suggests that the slow relaxation, thus requiring lower temperatures, i.e. micro-SQUID analysis.

\[\text{[Tb}^{III}(\text{HCOO})_3]_n(2)\]

For (2), from \(\chi(T)\) (Figure 11), a room temperature value of around 12.7 cm\(^3\) mol\(^{-1}\) K was recorded, higher than that expected for a single Tb(III) ion \((\chi_{\text{spin}} f_s^3 g^2 = \gamma T)\) of 11.81 cm\(^3\) mol\(^{-1}\) K, which suggests a slight ferromagnetic interaction between spins. Indeed, upon decreasing the temperature \(\chi(T)\) increases smoothly, reaching a maximum of 26.0 cm\(^3\) mol\(^{-1}\) K at 5 K, i.e. \(T_C = 5\) K. Below this there is a rapid decrease to 20.0 cm\(^3\) mol\(^{-1}\) K at 1.8 K. Assigning a ferromagnetic transition from \(\chi(T)\) is more difficult than for an antiferromagnetic system, but these data are consistent with the presence of a \(T_C\), \(\chi\) increasing much more significantly and rapidly than in (3). From 1/kG versus \(T\) data (S. I. 8), also, we see a distinction with (1) and (3), \(\theta\) being +8.4 K. From earlier reports (e.g. [21]), we noted that the exchange between lanthanide(III) ions could change across the 4f series, likely due to the small changes in bridging angle between ligands and metal ions of varying size. If, as has been shown, the exchange is very weak between lanthanide(III) ions when the formate ligand is employed, then even small changes in geometries could lead to large differences in observed exchange, as demonstrated here. We believe, though, these effects cannot be disentangled from dipolar interactions without further investigations. \(M(H)\) for (2) shown in Figure 12, at 2 and 3 K between 0–7 T, indicate no saturation of magnetisation, as previously seen for anisotropic Tb(III) materials [40], in a similar fashion to (3).

The qualitatively rapid magnetisation compared to (2) suggests another difference in the exchange between spins here, also. As for (3), in both zero and applied static fields \((H_{\text{ac}} = 0, \nu = 1, 700\) and 1100 Hz, and 1 KG, where \(v = 1, 100, 700\) and 1100 Hz respectively) a.c. susceptibility measurements \(H_{\text{ac}} = 1.55\) G, found no evidence of slow relaxation above 2 K (see S. I. 9). Given the strongly axial crystal field, the ground state can be tentatively expected to be a doublet, despite the non-Kramers ion designation of Tb\(^{III}\), which would reinforce our earlier ideas, vide supra, about the nature of this process.

\[\text{[Gd}^{III}(\text{HCOO})_3]_n(3)\]

Further Investigations

Our previous work showed how the disc-like \{Gd\} (4) [1g] showed a now only moderate MCE of \(-\Delta\delta m = ca. 23\) J kg\(^{-1}\) K\(^{-1}\) (AH = 0–7 T, 3 K), which demonstrates how much the field has progressed in such a short time for molecular examples [14]. This analysis was achieved using magnetisation data, which we here expand upon using heat capacity results to give more information on the magnetothermal behaviour and ordering processes. The following data are included here to demonstrate the heat capacity technique in a different way.

\[\text{Susceptibility}\]

Measuring below our previous limit of 1.8 K we see a marked decrease in \(\chi(T)\) at ca. 1.1 K, in Figure 13, indicating the Néel temperature of the compound (i.e. the antiferromagnetic to paramagnetic transition temperature). From this maximum the decrease continues to a minimum at ca. 0.6 K. Upon cooling even...
further, achieved with a set-up described elsewhere [4m], we see how \( \chi(T) \) increases again to a second maximum at 0.2 K before decreasing again. This implies two ordering processes, which we assign as follows. The higher temperature effect is caused by the exchange between spins, confirmed as antiferromagnetic from the profiles of \( \chi(T) \) and \( T \chi(T) \). The second weaker process, at lower temperatures is likely the effect of dipole-dipole interactions, i.e. intermolecular exchange, owing to the large separation of the molecules in the crystal structure. As gadolinium(III) compounds only rarely show \( \chi(T) \) data, from which ordering temperatures can be extracted, these measurements should become more routine for analysis of such systems, perhaps when magnetocaloric cooling removes the need for expensive \(^{3}\)He systems.

Heat Capacity

A slightly different approach was adopted to that shown above for (1) taking advantage of the availability of the isostructural relative of \( \{\text{Gd}^3\}_2 \) (4), namely \( \{\text{Y}_3 \} \) (5) (the structure of the former is included as S. I. 14 for reference [1g]). This was assigned as being analogous by a combination of elemental analysis and powder X-ray diffraction (S. I. 10 and S. I. 11, respectively). We also obtained a unit cell from the slightly poorer crystals of the latter which matches that of (4). The synthesis was also identical so will not be described again, but (obviously) used \([\text{Y}^3\text{(NO}_3)_3\cdot n\text{H}_2\text{O}]\) instead of \([\text{Gd}^3\text{(NO}_3)_3\cdot 3\text{H}_2\text{O}]\) in the same ratio with respect to the other required starting materials.

As the heat capacity is composed of several parts \( C_{\text{Total}} \), including lattice \( C_{\text{latt}} \) and magnetic \( C_{\text{mag}} \) components, one can use the diamagnetic \( 5 \) to screen out the magnetic contribution by considering the sum in Equation 6: The remaining parts should be identical as the structure is analogous.

\[
C_{\text{Total}} = C_{\text{mag}} + C_{\text{latt}}, \text{ Equation 6}
\]

From this sum, the 0-7 T magnetic heat capacity (Figure 14) was calculated which, via the Maxwell equations given above, gave the magnetic entropy changes at these fields which are shown in S. I. 12. This shows the overlap of \( -\Delta S_M \) derived from heat capacity data at \( T \) with that from magnetisation, the pleasing match showing that the approach shown here is as valid as that from using SQUID data.

From the resulting magnetic entropy curves it is shown (S. I. 13) how the theoretical value of \( -\Delta S_M \) is reached, being equal to \( nR\ln(2S+1) \), where \( n \) is here seven, to give 14.56 K. Clearly, when a magnetic field is applied, this will decrease as the spins order. Given by the black line for \( 7 \) T, the difference gives the maximum \( -\Delta S_M \) values, i.e. the change between \( H = 0 \) and \( H = 7 \) T. We obtained the exchange interactions between the spins by a computational model described elsewhere [4m] which sampled the best fit of the magnetic entropy by comparing different \( J \) interactions. This found \( J_1 \) and \( J_2 \), i.e. the exchange between the inner and outer metals and that for the outer-outer pairs, was antiferromagnetic in both cases, in agreement with our interpretation of the magnetic data (\( \chi(T) \) and low temperature \( T \chi(T) \)) and low temperature \( \chi(T) \). \( J_1 \) was \(-0.09 \) K and \( J_2 \) = \(-0.08 \) K with an essentially isotropic \( g = 2.02 \). Such exchange parameters are well within the previously established lanthanide(III)-lanthanide(III) interactions as is the isotropic \( g \). This provided the fits to experimental data shown in the heat capacity profiles.

Future Work

Further work involving computer simulations will be conducted to elucidate the ordering mechanisms in (1). In addition INS (Inelastic Neutron Scattering) will probe the deuterated analogue \( [\text{Ln}^{3\text{d}}(\text{HCOO})_3]_n \) to assist in this. We and others have shown how lightweight polymeric materials can exhibit large magnetic entropy changes. This is relatively easy to consider: choose the material with the largest gadolinium(II) to ligand ratio (this works up to a point). The next challenge we see is to increase the densities of these materials, which does not have an obvious solution. One material we have identified that may be extremely promising is \( \text{Gd}^{3\text{d}}\text{F}_2 \), which has a large density (\( \rho = \text{ca.} \ 7.1 \text{ g cm}^{-3} \)) and low ligand percentage (\( \text{Gd}^{3\text{d}} \) \( \left\{ \right\} \text{ to ca.} \ 75 \%), which we hope to investigate in due course using heat capacity data as an extension of this work.

Conclusions

The known rare-earth formates \( [\text{Ln}^{3\text{d}}(\text{HCOO})_3]_n \) were...
synthesised, characterised and reinvestigated for their magnetocaloric and slow relaxation properties. [Gd(dhacO)]$_3$ shows the largest low temperature magnetocaloric effect discovered so far, at 25 J kg$^{-1}$ K$^{-1}$ ($\Delta H$ = 0–7 T, 3 K) due to a light ligand set and polymeric structure. a.c. susceptibility studies also showed $U_{	ext{eff}}$ was 0.9 K. (2) and (3) showed no definitive slow relaxation at the higher temperatures at which they were investigated, disappointingly. We also showed how the diamagnetic $\{\text{Y}_{1.6}\}$ analogue of (Gd$_{1.6}$) can assist in giving useful information on the magnetothermal behaviour and hence magnetic entropy of the paramagnetic sibling, which matches with magnetisation and theoretical data. This procedure could be extended to many other compounds profitably, we believe. Finally, we note the use of very low temperature susceptibility measurements to reveal previously unseen information on the exchange processes between spins.

Acknowledgements

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Notes and references


Using Heat Capacity Measurements to Probe Magnetocaloric Materials

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Further Characterisation of [Ln\textsuperscript{III}(HCOO)\textsubscript{3}]\textsubscript{n} (1)-(3)

S. I. 1. Experimental PXRD data for [Gd\textsuperscript{III}(HCOO)\textsubscript{3}]\textsubscript{n}, black line, [Tb\textsuperscript{III}(HCOO)\textsubscript{3}]\textsubscript{n}, magneta line, and [Dy\textsuperscript{III}(HCOO)\textsubscript{3}]\textsubscript{n}, blue line, compared to simulated data for [Sm\textsuperscript{III}(HCOO)\textsubscript{3}]\textsubscript{n}, red line, recorded at room temperature on static powdered samples between 0 and 45 ° and shown between 10-45 °. Intensities have been normalised for comparison.
S. I. 2. Thermo-gravimetric analysis for (2), recorded between 30-1000 °C under N₂ at 10 K min⁻¹.
Structural Details of $[\text{Ln}^{III}(\text{HCOO})_3]_n$

S. I. 3a: Unit-Cell of $[\text{Ln}^{III}(\text{HCOO})_3]_n$ as viewed down the $a$-axis. Key: Ln$^{III}$ purple spheres; C grey wire; O red wire, H white wire.

S. I. 3b: Unit-Cell of $[\text{Ln}^{III}(\text{HCOO})_3]_n$ as viewed down the $b$-axis.
S. I. 3c: Unit-Cell of \([\text{Ln}^{\text{III}}(\text{HCOO})_3]_n\) as viewed down the \(c\)-axis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(\alpha) (°)</th>
<th>(\beta) (°)</th>
<th>(\gamma) (°)</th>
<th>Volume (Å(^3))</th>
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<tr>
<td>([\text{Sm}^{\text{III}}(\text{HCOO})_3]_n)</td>
<td>10.503(3)</td>
<td>10.503(3)</td>
<td>4.006(3)</td>
<td>90.0</td>
<td>90.0</td>
<td>120.0</td>
<td>382.709</td>
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<td>(3)</td>
<td>10.4711(10)</td>
<td>10.4711(10)</td>
<td>3.9828(4)</td>
<td>90.0</td>
<td>90.0</td>
<td>120.0</td>
<td>378.185</td>
</tr>
</tbody>
</table>

S. I. 3d: Comparison of reported \([\text{Sm}^{\text{III}}(\text{HCOO})_3]_n\) with that of (2).

S. I. 4. Left, coordination geometry about the lanthanide(III) ions in \([\text{Ln}^{\text{III}}(\text{HCOO})_3]_n\). Right, as viewed down the \(c\)-axis.

Key: Ln\(^{\text{III}}\) purple spheres; O red spheres.
Simulations of the Magnetocaloric Effect

S. I. 5. PHI\(^5\) simulation of \(-\Delta S_M\) at 5 T (red filled squares) and 7 T (black filled squares) with zero exchange between metals, showing the slight increase this would give if replicated in (I). Lines connect the points only.
Further Magnetic Data for (2) and (3)

S. I. 6. Experimental $1/\chi$ for (3), shown as hollow squares (□) and with linear fit through these data shown as red line.
S. I. 7. Upper: Experimental $\chi''$ and $\chi'$ versus T plot for (3): $H_{ac} = 0$, $\nu = 1, 100$ and 957 Hz and $H_{dc} = 1.55$ G, between 2 and 12 K. Lower: Experimental $\chi''$ and $\chi'$ versus T plot for $H_{dc} = 1$ kG, $\nu = 1, 100$ and 957 Hz and $H_{ac} = 1.55$ G, between 4 and 20 K. Key: 957 Hz black squares; 100 Hz red circles; 1 Hz green triangles.

S. I. 8. Experimental $1/\chi$ for (2), shown as hollow squares (□) and with linear fit through these data shown as red line.
S. I. 9. Upper: Experimental $\chi''$ and $\chi'$ versus $T$ plot for (2): $H_{dc} = 0$, $\nu = 1$, 700 and 1100 Hz and $H_{ac} = 1.55$ G, between 1.8 and 12 K. Lower: Experimental $\chi''$ and $\chi'$ versus $T$ plot for $H_{dc} = 1$ kG, $\nu = 1$, 100, 700 and 1100 Hz and $H_{ac} = 1.55$ G, between 1.8 and 12 K. Key: 1100 Hz black squares; 700 Hz red circles; 100 Hz upward green triangles; 1 Hz blue downward blue triangles.
Further Characterisation of \{Y_7\} (5)

<table>
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<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Cell Volume (Å³)</th>
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<tr>
<td>(4)</td>
<td>16.991(8)</td>
<td>16.3943(8)</td>
<td>17.2829(9)</td>
<td>97.2230(10)</td>
<td>113.8890(10)</td>
<td>114.9720(10)</td>
<td>3551.81</td>
</tr>
<tr>
<td>(5)</td>
<td>16.2134(6)</td>
<td>16.4619(6)</td>
<td>17.2292(6)</td>
<td>97.183(3)</td>
<td>113.929(3)</td>
<td>115.067(3)</td>
<td>3554.2</td>
</tr>
</tbody>
</table>

S. I. 10. Unit cell comparison of (4) and (5).

Elemental analysis for (5) (Y\textsuperscript{III}\textsubscript{7}C\textsubscript{154}H\textsubscript{164}N\textsubscript{4}O\textsubscript{42}) (found : calculated): C 53.26 : 54.96; H 4.45 : 4.91; N 1.74 : 1.66.

S. I. 12. Overlap of $-\Delta S_M$ for (5) as derived by magnetisation data, shown as open cyan circles, with that from heat capacity data, as shown by black circles ($\bullet$).

S. I. 13. Experimental magnetic entropy $/ R$ from heat capacity measurements at the limiting fields of 0 and 7 T, shown as solid circles. Key: In zero field: black circles; In 7 T field: red circles.
Structure of $\{\text{Gd}^{III}\}_7$ for reference

S.I. 14. Upper (view in the plane) and Lower: the cation of $\{\text{Gd}^{III}\}_7^+$, isostructural to $\{\text{Y}^{III}\}_7$. Key: Gd$^{III}$ purple, O yellow, C grey, N blue. H atoms and nitrate groups are omitted for clarity.
References:


Chapter 7: Paper 4

Investigations into the magnetocaloric and single-molecule magnet behaviour of [Ln$^{III}$-Zn$^{II}$] bicapped butterflies

Joseph W. Sharples, Nicholas F. Chilton, Adam N. Swinburne, Louise S. Natrajan, Stephen Sproules, Floriana Tuna and David Collison, *manuscript in preparation.*
Investigations into the magnetocaloric and single-molecule magnet behaviour of \([\text{Ln}^{\text{III}}\text{Zn}^{\text{II}}\text{]}_{4}\) bicapped butterflies

Joseph W. Sharples \(^{a,*}\), Nicholas F. Chilton \(^{a}\), Adam N. Swinburne \(^{a}\), Louise S. Natrajan \(^{a}\), Stephen Sproules \(^{b}\), Floriana Tuna \(^{a}\) and David Collison \(^{a}\)

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3d-4f Phosphonate compounds can act as promising magnetic refrigerants and single-molecule magnets and up until now these have utilised a paramagnetic 3d metal. Here we show how using the diamagnetic ion Zn\(^{II}\) can give the novel phosphonate compounds \([\text{Lu}^{III}\text{Zn}^{II}\text{]}_{4}\text{BuPO}_{3}\text{]}_{2}\text{BuCO}_{2}\text{]}_{2}\text{NEt}_{3}\text{2}])\), where Lu\(^{III}\) = Pr\(^{III}\) (1), Nd\(^{III}\) (2), Sm\(^{III}\) (3), Eu\(^{III}\) (4), Gd\(^{III}\) (5), Tb\(^{III}\) (6), Dy\(^{III}\) (7), Ho\(^{III}\) (8) and Y\(^{III}\) (9), by solvothermal methods. For (5) a moderate magnetic entropy change of around 13 J kg\(^{-1}\) K\(^{-1}\) (\(\Delta H = 0.7\) T, 3 K) was seen and ascribed to a small metal content. For (7), slow relaxation in zero-field was found, with \(U_{\text{ad}} = 38\) K, one of only a handful of 3d-4f phosphonate SMMs, though such behaviour was absent in (6). Characteristic fluorescence was observed by direct \(\epsilon\)-\(f\) excitation for (3), (4), (6) and (7), showing decay lifetimes of more than 3 ms in the solid-state and well resolved multiplet detail. These data were used with \(ab\) \(initio\) calculations to further understand the single-molecule magnet (SMM) behaviour or otherwise of (6) and (7) finding a significant difference in the ground multiplet structures. Finally, an unusual Gd\(^{III}\) signal was discovered in the electron paramagnetic resonance (EPR) spectrum of (9), the features of which were dominated by the tiny \(D\) anisotropy of the paramagnetic metal ions.

Introduction

Molecular magnetism relies on the synthesis of new metal cages \([\text{a}]\) or single-ion species \([\text{b}]\) to investigate. Myriad compounds \([\text{b}]\) incorporating up to more than one hundred and fifty metals have been discovered \([\text{c}]\). A common approach is to react metal salts with flexible, multidentate ligands, which dovetails elegantly with solvothermal synthesis \([\text{d}]\). Here ovens are used to heat reagents in sealed autoclaves to temperatures in excess of \(150^\circ\)C. This technology which may be used in high-density memory devices \([\text{e}]\). This relies on the population of one state of a bi-stable ground-state spin in an applied field, and its retention in the absence of said field. How difficult the equalising of each of these states will be is given by the anisotropy barrier \(U_{\text{ad}}\), equal in transition metal compounds to \(\Delta S^c\), where \(D\) is the anisotropy and \(S\) the ground state spin. Following the first cages to demonstrate this effect, such as \([\text{Mn}_{12}\text{O}_{12}\text{]}\) \([\text{f}]\), larger \(\text{Mn}^{III}\) structures \([\text{g}]\) were synthesised, in an attempt to increase \(U_{\text{ad}}\). That they met with little success is partly due to the mutual dependence of \(S\) and \(D\) \([\text{h}]\). 3d-4f and 4f compounds show larger \(U_{\text{ad}}\) barriers and \(T_{\text{h}}\) (hysteresis temperatures) as a result of large single-ion anisotropy, with \(U_{\text{ad}}\) values reaching up to 842 K for \([\text{Dy}^{III}\text{K}_{2}\text{]}\) \([\text{i}]\) and 15 K for \([\text{Tb}^{III}\text{]}\) \([\text{j}]\), respectively. 3d-4f phosphonate chemistry has had only one reported success in the synthesising of SMMs, namely the Cu\(^{II}\) Dy\(^{III}\) of Baskar et al. \([\text{k}]\), which encouraged us to attack the problem, though in a slightly different way: previous efforts used paramagnetic 3d metals to increase the spin of the compound and contribute to \(U_{\text{ad}}\). Another path may be fruitful in this regard, though.

Zn\(^{II}\)-Ln\(^{III}\) SMMs

Several groups have reported \([\text{Zn}^{II}\text{La}^{III}\text{]}\) SMMs where the La\(^{III}\) of the spatial separation of the ions and low ordering temperatures \([\text{a}]\).

Notably [\(\text{Gd}^{III}\text{2N}_{2}\text{2(OH)2}(O\text{O}^{3-}\text{Bu})\text{]2MeCN}\) \([\text{k}]\) and \([\text{Gd}^{III}\text{2N}_{2}\text{2(OH)2}(O\text{O}^{3-}\text{Pr})\text{]2MeCN}\) \([\text{l}]\) showed some of the largest magnetic entropy changes, which quantify the MCE, at the time (> 25 J kg\(^{-1}\) K\(^{-1}\), at \(\Delta H = 0.7\) T, 3 K). Incorporation of lanthanide ions into phosphonate compounds has also led to improvements in SMM research, a technology which may be used in high-density memory devices \([\text{m}]\). This relies on the population of one state of a bi-stable ground-state spin in an applied field, and its retention in the absence of said field. How difficult the equalising of each of these states will be is given by the anisotropy barrier \(U_{\text{ad}}\), equal in transition metal compounds to \(\Delta S^c\), where \(D\) is the anisotropy and \(S\) the ground state spin. Following the first cages to demonstrate this effect, such as \([\text{Mn}_{12}\text{O}_{12}\text{]}\) \([\text{f}]\), larger \(\text{Mn}^{III}\) structures \([\text{g}]\) were synthesised, in an attempt to increase \(U_{\text{ad}}\). That they met with little success is partly due to the mutual dependence of \(S\) and \(D\) \([\text{h}]\). 3d-4f and 4f compounds show larger \(U_{\text{ad}}\) barriers and \(T_{\text{h}}\) (hysteresis temperatures) as a result of large single-ion anisotropy, with \(U_{\text{ad}}\) values reaching up to 842 K for \([\text{Dy}^{III}\text{K}_{2}\text{]}\) \([\text{i}]\) and 15 K for \([\text{Tb}^{III}\text{]}\) \([\text{j}]\), respectively. 3d-4f phosphonate chemistry has had only one reported success in the synthesising of SMMs, namely the Cu\(^{II}\) Dy\(^{III}\) of Baskar et al. \([\text{k}]\), which encouraged us to attack the problem, though in a slightly different way: previous efforts used paramagnetic 3d metals to increase the spin of the compound and contribute to \(U_{\text{ad}}\). Another path may be fruitful in this regard, though.

Zn\(^{II}\)-Ln\(^{III}\) SMMs

Several groups have reported \([\text{Zn}^{II}\text{La}^{III}\text{]}\) SMMs where the La\(^{III}\)
ions are isolated spatially by the spacer Zn
II
 ions, so removing the intra- and inter- molecular interactions to rely on the single-ion anisotropy of the individual Ln
III
 ions. Understanding such isolated environments could in future be extrapolated to exchange coupled systems. One highlight, from Yamashita et al. [2a], is the "star" compound, \( [\text{Zn}^\text{II}(\text{L}1)(\text{O}_2\text{CCH}_3)(\text{NO})_2]_2\text{H}_2\text{O}_{0.5}\text{MeOH}_{3.5}] \), where L1 is a macrocyclic Schiff base ligand (given in S. I. 1) in conjunction with Table 1 in S. I.), providing pockets for metal ions, which in turn are capped by small co-ligands. Transition metal ions bond to N-donor sites preferentially, with strong axial coordination of the lanthanide by oxygen atoms. Applied fields of 1000 Oe gave \( \gamma^\ast \) maxima and two \( U_{\text{eff}} \) values of ca. 4 and 25 K, which may be assigned to two thermal relaxation processes.

Feltham et al. [2b,e] made a similar family of compounds, namely \( [\text{Zn}^\text{II}(\text{L}2)(\text{NO})_3]_2\text{H}_2\text{O provisional spectrum fits using information from the ground multiplet emission}

\[
[\text{Ln}^\text{III}(\text{O}_2\text{C}^3\text{Bu})_6(\text{HO}_2\text{C}^3\text{Bu})_6] + [\text{Zn}^\text{II}(\text{O}_2\text{C}^3\text{Bu})_2]
\]

100 °C 12 h NEt_3 MeCN

\[
[\text{Ln}^\text{III}_2\text{Zn}^\text{II}(\text{O}_2\text{C}^3\text{Bu})_4(\text{O}_3\text{P}^\text{Bu})_2(\text{NEt}_3)_2]
\]

75 spectrum allowed the \( B^\text{eff} \), \( B^\text{a} \) and \( B^\text{b} \) parameters to be deduced, according to the axial approximation used. These strategies led us to the synthesis of a family of new \( [\text{Ln}^\text{III}_2\text{Zn}^\text{II}(\text{O}_2\text{C}^3\text{Bu})_6(\text{O}_3\text{P}^\text{Bu})_4(\text{NEt}_3)_2] \) compounds, where \( \text{Ln}^\text{III} = \text{Pr}^\text{III} (1); \text{Nd}^\text{III} (2); \text{Sm}^\text{III} (3); \text{Eu}^\text{III} (4); \text{Gd}^\text{III} (5); \text{Tb}^\text{III} (6); \text{Dy}^\text{III} (7); \text{Ho}^\text{III} (8); \) and \( \text{Y}^\text{III} (9) \). We probed these with several techniques, finding SMM behaviour in (7), though not in (6). We attempted to find out why this was by utilising \( ab\) initio calculations, finding the ground \( m_\text{S} \) states are distinct in this regard, being a doublet in (7), and a singlet in (6), showing the differing subtleties of the effects of ligand geometry on these ions. Luminescence measurements revealed multiplet structure of these compounds to assist in this characterisation, and were also performed on (3) and (4). For the isotropic compound (5) we find a moderate magnetic entropy change which we discuss with the aid of simulations. A gadolinium(III) signal in (9) was also detected by EPR, showing the small \( D \) in this ion.

Experimental Details

All reagents were obtained from Sigma-Aldrich and used without further purification. Overall the reaction scheme for (1)-(9) is summarised as shown in Figure 1.

\[
[\text{Ln}^\text{III}_2\text{Zn}^\text{II}(\text{O}_2\text{C}^3\text{Bu})_6(\text{O}_3\text{P}^\text{Bu})_4(\text{NEt}_3)_2] \quad (\text{Ln}^\text{III} = \text{Pr}^\text{III} (1); \text{Nd}^\text{III} (2); \text{Sm}^\text{III} (3); \text{Eu}^\text{III} (4); \text{Gd}^\text{III} (5); \text{Tb}^\text{III} (6); \text{Dy}^\text{III} (7); \text{Ho}^\text{III} (8) \) and \( \text{Y}^\text{III} (9) \))
\]

Summarised in Figure 1 and being representative of (1)-(9) \( [\text{Ln}^\text{III}_2\text{Zn}^\text{II}(\text{O}_2\text{C}^3\text{Bu})_6(\text{HO}_2\text{C}^3\text{Bu})_6] \) (0.15 g, 0.6 mmol) (see S. I Experimental Details) were stirred together for 5 minutes in acetone (2 mL), then a solution of tert-butyl phosphonic acid (0.014 g, 0.1 mmol) and triethylamine (0.045 mL, 0.33 mmol) in acetone (6 mL) added dropwise. The resulting solution was transferred to an autoclave and heated for 12 h at 100 °C, before cooling slowly at 0.05 °C min \(^{-1}\) to room temperature. Small block crystals were found in most cases (typical yield ca. 60 %), though these were of poorer quality for the lighter lanthanides in general, and analysed as \( \text{Ln}_2\text{Zn}_2\text{C}_3\text{H}_8\text{O}_8\text{P}_2 \); (4) Pr (calculated found): 13.89:13.69 C 41.43:41.20 H 6.85:6.97 N 1.38:1.35 P 3.05:3.07 Zn 12.89:12.60
from the highly coordinating species that are likely present. On a
broader note, reported compounds synthesised using phosphonic
acids in 3d-4f chemistry have been susceptible to a change in
structures to the later lanthanides. Work is ongoing in these areas to perturb this reaction
purposes here these are redundant, and so are not further
suggested these were isostructural and led us to perform single-
crystal XRD on (5) of this first series (the Gd\(^{3+}\) derivative). For the second group single-crystal XRD was performed for the Dy\(^{3+}\)
(7) compound, with unit-cell data being collected for (2), (8) and
(9). Although we initially thought that this distinction was due to a
different structure forming, as has occurred with different lanthanides along a series in phosphonate chemistry, they were found to be chemically identical, though the molecules pack differently, *vide infra*.

The similarity of the patterns within a given set, in conjunction with the similarity of the synthesis and elemental analysis
suggested these were isostructural and led us to perform single-
crystal XRD on (5) of this first series (the Gd\(^{3+}\) derivative). For the second group single-crystal XRD was performed for the Dy\(^{3+}\)
(7) compound, with unit-cell data being collected for (2), (8) and
(9). Although we initially thought that this distinction was due to a
different structure forming, as has occurred with different lanthanides along a series in phosphonate chemistry, they were found to be chemically identical, though the molecules pack differently, *vide infra*.

Single-crystal XRD upon Gd (5) and Dy (7) compounds found these to be hexa-metallic phosphonate compounds, with four Zn\(^{2+}\) ions, two La\(^{3+}\) ions and two such ligands. Common to (1)-(9) is the general butterfly topology, capped at either end by a Zn\(^{2+}\) ion as shown in Figure 2.

The butterfly, or incomplete double cubane, core of this is widely known in coordination chemistry, including examples for 3d-4f compounds, where the 3d metal is Mn, Fe, Co and Ni [3a-d], though not to our knowledge with Zn\(^{2+}\). The outer metals (left and right), with the core viewed as in Figure 2, are here La\(^{3+}\) ions, though there are situations known where these are the inner metals (above and below) of the four and, indeed, recent examples have demonstrated that this can be controlled by synthetic routes [3e]. Here, though, the 4f metals are quite separated. The planar (Zn\(^{2+}\), La\(^{3+}\)) core is framed by four pivalate groups, again with the 2.1.1 mode. The phosphonate group bonds with the nitrogen of the pivalate, which implies the source of the pivalate ligand can be solely from the highly coordinating species that are likely present. On a broader note, reported compounds synthesised using phosphonic acids in 3d-4f chemistry have been susceptible to a change in structures to the later lanthanides. Work is ongoing in these areas to perturb this reaction purposes here these are redundant, and so are not further described.

Structure of (1)-(9) by Single Crystal X-ray Diffraction and Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) was performed on ground samples of (1)-(9) and found two distinct sets of patterns. The first encompasses the earlier lanthanide containing structures (1)-(5) *i.e.* Dy\(^{III}\), Gd\(^{III}\), and separately, those with the heavier elements (6)-(9), Tb\(^{III}\), Ho\(^{III}\), and Y\(^{III}\), with a similar ionic radius to Dy\(^{III}\). These are given in S. I. 3a-d, clearly showing the distinction between these two series.

Fig. 2. The dimeric molecule [Gd\(^{III}\)Zn\(^{II}\)(O\(_2\)C(CH\(_3\))\(_3\))\(_2\)(O\(_2\)PC(CH\(_3\))\(_3\))(NEt\(_2\))\(_2\)] (5). Key: Ln\(^{III}\) purple spheres; Zn\(^{II}\) pink spheres; P yellow spheres; C grey wireframe; N blue spheres; No H atoms are shown for clarity.

Fig. 3. Highlighted bonding mode of the phosphonate O\(_2\)PC(CH\(_3\))\(_3\) in (7); 4.2.2.1. Key: As for Fig. 4 with O red spheres. No H’s are shown for clarity.
is 1.932(4)-1.987(4) Å. At each 4f metal the geometry is eight coordinate [DyIII\(\text{O}_4\)] with a square antiprismatic geometry, as shown in Figure 4, this being the best description as given by SHAPE analysis [3g] (see Table 2 in S. I. for more details). There is a narrow distribution of bond lengths to the pivalate O atoms of 2.293(4)-2.357(6) Å; to the phosphorus oxygens these range from 2.26(1) Å for the non-bridging, to 2.537(4) Å for the longest DyIII-O interaction which bridges ZnII and DyIII. Both Zn-O-Dy bond angles are ca. 111° between the inner metals. The intra-molecular separation of the DyIII ions is 5.701 Å, suggesting any exchange coupling will be extremely weak between them, with inter-molecular distances well over 10 Å. This degree of separation is not unprecedented, but combined with the diamagnetic nature of the ZnII ions, will likely leave the single-ion properties dominant, and magnetic properties easier to interpret than in 3d-4f systems.

In general terms this lanthanide geometry may be promising for SMM behaviour as Long and Rinehart [3h] have explained, though slow relaxation is highly sensitive to crystal field geometry and even small differences are known to have a great influence.

The asymmetric unit contains half of the molecule, crystallising in the \(P2_1/n\) space group for GdI\(\text{II}\) (representative for the first series, vide supra) in the monoclinic crystal system. Indeed, for DyIII (representative for the second series) this is the same (\(P2_1/n\), but the unit cell lengths are different and a different packing arrangement is found (as shown in S. I. 4a-c for (7) along \(a, b\) and \(c\)-axes and S. I. 5a-c for (5)).

A very similar compound was prepared by Zheng et al. [3i] as part of his series of cobalt-lanthanide compounds, namely \(\text{[La}^{III}\text{Co}^{II}\text{O}_8\text{(O,PBu)}_{12}\text{MeCN}]_{2}\cdot2\text{MeCN}\), where \(\text{La}^{III}\) was only either \(\text{Nd}^{III}\) or \(\text{Gd}^{III}\). These are identical to (1)-(9) except for the changed groups at the end, where MeCN, through the \(N\)-atom, bonds instead of \(\text{NEt}_3\). No SMM behaviour was reported for either, with a maximum \(\Delta S_m\) for the gadolinium(III) compound of 20 J kg\(^{-1}\) K\(^{-1}\) (\(\Delta H = 0.7\) T, 3 K).

**Luminescence Properties**

Powdered samples of (4) and (6) had their luminescent properties measured after initial checks under a U.V. lamp found the solids appeared red and green respectively. The position of the emission bands is largely environment invariant in general and so easily be assigned via standard methods of comparison [4a,b]. This characterisation can also suggest the presence of a single

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nm, albeit weak in intensity, whilst the n = 4 transition is found at around 690 nm and that for n = 5, on 700 nm. From the relative intensities of the n = 2 to n = 1 bands, at around 0.5, we note that this implies a relatively high symmetry lanthanide(III) environment [44].

For (6) we can assign the emission bands as follows, with approximate positions, as shown in Figure 5, lower. For 5D2→F3 we here see a broad band around 480-510 nm which is obviously made up of several other transitions due to the effect of the crystal field splitting. From fitting with IGOR this is centred on 499.9 nm, shown in green. These data were recorded at both room and low (liquid N

2) temperatures and, as shown in the normalised spectrum, overlap well with the same relative intensities of bands, though the higher temperature data is the smoother of the two, being collected at a lower resolution. The 5D2→F1 band spreads over the ca. 530–570 nm range, again with significant structure, though we can only assign a broad band as the bands are not sufficiently resolved (shown in green). 5D2→F4 centres on ca. 580 nm and 5D2→F5 upon ca. 620 nm. The 5D2→F2 transitions and beyond are extremely weak in comparison and assigned to the features at ca. 640–660 nm.

For (3) emission bands were also recorded as follows. From the excited state 5G5/2, transitions to the 5H9/2 were seen. Where n = 5 this was at 560 nm; for n = 7, at 600 nm; for n = 9, at > 650 nm and a broad band for n = 11 at ca. 700 nm. Excitation into the SmIII absorbance bands is shown in S. 1. 6.

Lifetimes of (4) and (6) were obtained by mono-exponential fitting of the decay data and were, in the solid-state, 3.3 and 3.5 ms respectively, which are relatively long, albeit in the absence of H2O (solvent) quenching.

Dysprosium(III) emission for (7), shown in Figure 6 is rarely reported in the literature, though we obtained the following for an excitation of 350 nm between 450 nm and 610 nm. This shows two prominent transitions. These are assigned as the 5F9/2 to 7H5/2 transition, centred on 480 nm, and 5F9/2 to 7H11/2 transition, centred on 580 nm. In each of these, significant splitting of the spin orbit coupled (SOC) states can be observed. No visible emission was found. In principle for Dy(III), a Kramers ion, there are up to nine states in the ground multiplet, representing the mJ = 0 state and the ±1/2, ±3/2, ±5/2, ±7/2, ±9/2, ±11/2, ±13/2 and ±15/2 doublets. Although not as well defined as, for example, Sessoli’s DOTA complex [46] we can observe an envelope of slightly overlapping features at lower energies, with a large gap to a rather more sharply defined higher energy transition, fitted by IGOR at 490 nm, or 20,400 cm–1 by the red open squares.

At a first approximation we can relate the size of the ΔM, energy barrier to the gap between the ground and first excited state, i.e. between the first emission line in the ground multiplet and the second. In (7), we note that these have an appreciable separation, whereas for (6), these merge into one broad band which is ill resolved. Qualitatively, from these data we could expect a larger barrier for (7) than (6), in the absence of other factors such as QTM.

**Magnetic Properties of (1)-(8)**

Magnetic measurements were recorded on poly-crystalline ground solids fixed in eicosane on a Quantum-Design MPMS XL7 SQUID magnetometer, and corrected for sample holders and diamagnetism as appropriate.

**Magnetic Properties of (GdIII,ZnII) (5)**

Considering d.c. magnetic measurements (Figure 7) of (5) first, \( \chi(T) \) measurements at 1 K between 1.8-300 K found a general decrease at low temperatures, shown in Figure 7, upper. Beginning at ca. 300 K \( \chi(T) \) was 15.75 cm3 mol–1 K, matching that expected for two GdIII \( (\text{S}=\text{F}) \) uncoupled ions \([\text{e.g. 4f_g}]\), where \( g_{\text{so}} = 2.01 \). Decreasing in temperature \( \chi(T) \) is constant until low temperatures, implying any interactions between the paramagnetic ions are very weak, as expected for lanthanides, these also being well separated here. The final change implies the nature of this exchange is antiferromagnetic, though \( \chi(T) \) data were inconclusive with no maximum seen at the lowest temperatures.

Magnetisation data (Figure 7, lower), recorded between 0-7 T at 2-9 K found a saturation of spins only with the lowest temperatures and highest applied fields, reaching MNmag = 8S, \( i.e.\) 14, The rate of magnetisation at lower fields is obviously significantly slower than in DyIII, which may be attributed to a difference in the nature of the exchange, vide infra.

Using these \( M(H) \) data the maximum magnetic entropy changes could be calculated and used to evaluate the MCE of (5), using the Maxwell Equations and ENTROPY software [4h], developed by Evangelisti, as shown in Figure 8.

The calculated maximum is given by \(-S_m = nR\ln(2S+1)\), where \( n \) is the number of ions of spin, S, and R is the gas constant, or around 17 J kg–1 K–1. Experimentally this reaches ca. 15.5 J kg–1 K–1 with the largest \(-\Delta S_m \) values being found at the lowest temperatures calculated, of 3 K and highest fields (\( \Delta H = 0-7 \) T, 3 K); despite these conditions no maximum was seen.

Amongst GdIII based compounds this is rather low, especially when compared to the largest found for any three-dimensional compound, ca. 55 J kg–1 K–1 (\( \Delta H = 7 \) T, 3 K) for [Gd(HCOO)]3, \( [1q] \).
are redundant in this reckoning. The low density, 15%, due to the presence of Zn II, leads to a very low – $\Delta S_p$ (ca. 1.3 g cm$^{-3}$), which seems to be evident here. Although we only measure down to 3 K for $\Delta S_{M}$, no maximum is evident. More useful, perhaps, than the maximum values for this parameter, is the temperature at which it occurs.

**Simulations of the MCE**

Simulations with PHI were used to calculate $\Delta S_M$ for a range of hypothetical compounds with the same molecular weight as (5), for two Gd III spins, but with varying exchange parameters (using the same Hamiltonian as above for equivalence) and under two different fields. These were: weakly ferromagnetic coupling at 5 and 7 $T$ (+0.1 K), weakly antiferromagnetic coupling (−0.1 K) and paramagnetic (0 K). The results are shown in S. I. 7 and found that with $J_{12} = 0$ K, $\Delta S_M$ is 15.2 J kg$^{-1}$ K$^{-1}$ at 3 K and $\Delta H = 0-7$ $T$ in good agreement with that found. Knowing this we can assess the effects of a stronger ferromagnetic and antiferromagnetic exchange and also see the position of the maximum response of the MCE in terms of temperature. These results show that temperatures of ca. 1-2 K give the best MCE response for the paramagnetic system. For a ferromagnetic interaction, whilst the MCE is higher at milder conditions, the absolute value shifts to higher temperatures and is actually smaller. From this and the antiferromagnetic case, essentially uncoupled systems should give the highest MCE at the lowest temperatures, which presents an interesting challenge: non-interaction of spins implies separation, but density falls, a practical consideration, and/or increases the mass of the system, decreasing the “headline” MCE, which it occurs.

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The main reason for this is the low percentage of gadolinium (ca. 15%), due to the presence of Zn II ions and many ligands, which are redundant in this reckoning. The low density, ca. 1.3 g cm$^{-3}$, leads to a very low $\Delta S_M$ of 20 mJ cm$^{-3}$ K, compared to the largest observed in [Gd(HCOO)$_2$]$_n$ [1q] of over 200 mJ cm$^{-3}$ K. This reflects the usefulness of the material when the amount of compound needed is taken into account; polymeric species have a large advantage of increased density over most 0-D materials and, thus, (5) is not very useful for magnetic refrigeration purposes.

Rationalising this lower than expected MCE and the magnetic exchange, we obtained the interaction between the Gd III ions by a fit of the magnetisation data (shown in Figure 7 as the solid lines through the points), using the software program PHI, developed by Chilton et al. [4i]. This found $g_{\text{iso}} = 2.02$ and $J = -0.01$ cm$^{-1}$, from the Heisenberg-Dirac-van Vleck (HDVV) isotropic Hamiltonian given below (Equation 1), where $J_{12}$ is the isotropic exchange constant, $S_1$ and $S_2$ the spin operators for each Gd III; $\mu_B$ the electronic Bohr magneton and $H$ applied field, and including the spin and Zeeman terms. This confirms the postulated magnitude and sign of the exchange from above, and matches in magnitude with previously analysed Gd III compounds.

$$\hat{H} = -2J_{12}(S_1S_2) + \mu_B g_{\text{iso}}(S_1 + S_2)$$  **Equation 1**

As demonstrated more dramatically by Evangelisti et al. [1s] the lack of exchange interactions can shift the maximum magnetocaloric response down to much lower temperatures, which reflects the usefulness of the material when the amount of compound needed is taken into account; polymeric species have a large advantage of increased density over most 0-D materials and, thus, (5) is not very useful for magnetic refrigeration purposes.

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Magnetic Properties of \{\text{Dy}^{III}_{2}\text{Zn}^{II}_{4}\} (7)

For (7), d.c. magnetic measurements found $\chi(T)$ (between 1.8-300 K (H$_{dc}$ = 1 kG)), shown in black squares (■), black lines connect points only. Lower: experimental $M(H)$ for (7) at 1.8, 3, 5 and 8 K (H$_{dc}$ = 0.7 T) as solid shapes. Lines connect points only. Key: As shown.

Even then, intra-molecular coupling must also be weak, necessarily because f-orbital to ligand orbital overlap is small, and the Dy$^{III}$ ions are spatially separated, vide supra. $M / N_{\mu}$ versus H measurements for a range of temperatures (0-7 T, 1.8-8 K) found the curves at lowest and highest temperatures only overlap at the higher field strengths. No saturation was recorded with the values still increasing above 13 N$_{\mu}$, seen in Figure 9, lower, though the magnetisation rate was rapid at 1.8 K, quantitatively supporting the idea of ferromagnetic exchange. Other dysprosium compounds which show quantitatively similar behaviour exhibit significant anisotropy or low lying states which are populated even at larger applied fields and so these results motivated a.c. measurements on (7), in order to look for any SMM behaviour.

The a.c. magnetic susceptibility of (7) was measured under zero applied field and a 1.55 G oscillating field ($H_d = 0$ G and $H_a = 1.55$ G), respectively to probe the relaxation dynamics. This found that $\chi''(T)$ signals (i.e. the out-of-phase susceptibility) diverged for different applied frequencies, $\nu$, measured for 1-1200 Hz, beginning most obviously below 12 K, for a 400 Hz oscillating field and above, as indicated in Figure 10, lower.
Figure 11. Upper: Arrhenius Plot of ln(τ) for (7) (H₀ = 0 G), where fitting the higher temperature data gives $U_{\text{eff}} = 38.1 \text{ K}$ and $\tau_0 = 8.7 \times 10^{-7}$.
Key: Squares are experimental data and the fit to higher temperature data shown as the red line. Lower: Cole-Cole Plot of $\chi''(T)$ maxima. From this two distinct “regimes” can be seen (Figure 11, upper).

Towards lower temperatures the existence of a temperature-independent regime is seen as the points level off, or saturate, implying a quantum-tunnelling relaxation process around 2 K, indicating the presence of additional relaxation processes, ascribed as the increasing influence of QTM.

The largest anisotropy barriers found previously are for [DyIII$_2$(O(OEt)$_2$)$_2$]$_2$]$_2$] doped in yttrium [4n], for monometallic compounds (ca. 842 K and 790 K, respectively), so (7) is far off this (see also Woodruff et al.’s comprehensive review [4p]). Anisotropy barriers seem sensitive to ligand geometry, and although we have here a square-antiprism it is not as perfect as that seen in the best monometallic compounds. Nevertheless the energy barrier is not insignificant compared to all but one previous La$_n$Zn$_n$ compound, vindicating this approach. In fact it is the largest we could find for any La$_n$-3d phosphonate compound [1k]. Further experiments could dope this compound in yttrium to further remove the possible effects of transverse fields which can allow for QTM even in Kramer ion systems, such as with DyIII.

Magnetic Properties of [TbIII$_2$Zn$_3$] (6)

For (6), we began with the static field measurements (Figure 12, upper): $\chi(T)$ (1.8-300 K, $H_0 = 1 \text{ kG}$); at room temperature the calculated value of 23.63 cm$^3$ mol$^{-1}$ K matches with the experimental value of 23.71 cm$^3$ mol$^{-1}$ K [1k]. $\Gamma_{\text{exp}}$, $S = 3$, $L = 3$, $J = 6$, $g = 4/3$. $M(0)$ values do not reach saturation, attaining ca. 7.5 Nm at 7 T for 2 and 3 K (Figure 12, lower). Although DyIII compounds, amongst La$_n$ SMMs, are the most common, there
are several Tb^III SMMS of note, in addition to that mentioned. This "difficulty" has been mentioned by Long and Rinehart, amongst others, as being due to the non-Kramers ground state, i.e. Tb(III) has an even number of electrons, which necessitates an axial ligand geometry to maintain a bi-stable ground state, the essence of SMM behaviour. With this in mind we investigated the relaxation behaviour of (6).

From the $\chi''(T)$ data, recorded between 2-20 K and for $\nu = 1, 100$, in 700 and 1100 Hz applied fields of 1 kG, a significant increase in each signal regardless of frequency can be seen at low temperatures (shown in S. I. 9). This, with the fact that there is a significant difference in the amount by which each increases suggests a thermal energy barrier mechanism, although we do not see "frequency dependent maxima". The largest increase for this is then expectedly found when $\nu = 1100$ Hz, reaching ca. 0.2 cm$^{-1}$ mol$^{-1}$ K compared to around half this for the remaining signals. To the same end, $\chi'$ showed a small decrease with increasing frequency. Together these results suggest (6) may be an SMM, albeit at temperatures lower than we can obtain with our set-up. This is not too surprising in the light of (7)'s performance, as discussed in the ab initio studies below.

For (8), we observed no frequency dependence in the a.c. experiment so this, too, is not an SMM.

**Magnetic Properties of {Pr^III}_2Zn^II_4** (1), **{Nd^III}_2Zn^II_4** (2), **{Sm^III}_2Zn^II_4** (3) and **{Eu^III}_2Zn^II_4** (4)

From the above we observe that the exchange between metals is weakly antiferromagnetic for (5) but weakly ferromagnetic for (6) and (7). Thus we decided to investigate the magnetic properties of the earlier lanthanide compounds to assess whether we could see a trend across the series. We found that $\chi T$ decreases for (1)- (4) with decreasing temperature and so were unable to distinguish between this being a result of the depopulation of sublevels with decreasing thermal energy, or antiferromagnetic exchange. Given the relative weakness of the exchange in (5), the former is more likely, though assigning this behaviour to exchange would fit in with a size dependent coupling mechanism. For (4), only susceptibility data were recorded (collated with the $\chi T$ data for (1), (2), (3) and (4); Figure 13, upper), Eu(III) being diamagnetic at low temperatures and therefore making our standard
magnetisation experiments (at 2-4 K) redundant for comparison. 

$\chi(T)$ at room temperature is ca. 2.6 cm$^{-1}$ K, in line with expected values and by comparison with other Eu$^{3+}$ compounds (note that this must account for the population of terms other than the ground state: $^5$D$_{0}$, $S = 3$, $L = 3$, $J = 0$, $g = 0$). There is a steady decrease in this product with decreasing temperature, indeed, this almost reaches zero at 1.8 K which is as expected for the Eu$^{3+}$ ion, as only the diamagnetic $^5$D$_{0}$ ground term becomes populated. No maximum in $\chi(T)$ was seen to assist in assigning this behaviour, which is true for all the compounds measured.

Expected room temperature $\chi$ values for two Nd$^{3+}$ ions ($^4$I$_{13/2}$, $S = 7/2$, $L = 6$, $J = 7/2$, $g = 4/3$) are 3.27 cm$^{-1}$ K, which (2) exceeds, reaching 4.3 cm$^{-1}$ K, likely as a result of the strong orbital contribution to the moment. A smooth decrease with decreasing temperature is seen, with $\chi$ reaching ca. 1.5 cm$^{-1}$ K at 2 K.

For (4), Sm$^{3+}$, the results are much lower than the expected 3.2 cm$^{-1}$ mol$^{-1}$ K, respectively. For the former this is in excess of that expected for two Sm$^{3+}$ ions ($^4$I$_{15/2}$, $S = 15/2$, $L = 7$, $J = 15/2$, $g = 1.975$) at 0.18 cm$^{-1}$ mol$^{-1}$ K, for similar reasons as (2). Conversely for (1), experimental $\chi$ values are much lower than the expected 3.2 cm$^{-1}$ mol$^{-1}$ K ($^4$I$_{15/2}$, $S = 1$, $L = 5$, $J = 4$, $g = 4/3$). The linear nature of this and the magnetisation plot suggest that we are actually detecting a ferromagnetic impurity, probably connected to problems with centring such weakly magnetic samples.

$M(H)$ (collated for (1)-(9) in Figure 13, lower) was found to reach 2.75 N$\mu$B for (2) without saturation at 7 T and 3 K (2.5 N$\mu$B, 4 K, 7 T), in line with previously reported anisotropic dimetallic neodymium compounds. $M(H)$ for (3) was small, reaching 0.22 (0.16) N$\mu$B at 2 K (3) at 7 T, confirming the anisotropy present.

Experimental and Simulated EPR spectra of

[$\text{Y}^{3+}$$\_2$($\text{Gd}^{3+}$)$\text{Zn}^{2+}$(O$_3$C$\text{Bu}$)$_{10}$(O$_4$P$\text{Bu}$)$_2$(NE$_3$)$_2$] (9)

Electron Paramagnetic Resonance (EPR, a.k.a. electron spin resonance ESR) is a hugely sensitive technique for probing paramagnetic nuclei in order to obtain magnetic and structural information.[5a,b] In these nuclei, where the spin, $S \geq 1/2$, the resulting $m_s$ states can be split by the application of a magnetic field, $H$, through a process called the Zeeman effect and according to the Equation 4.

$$E(m_s) = m_s g_s \mu_B H \text{ Equation 4}$$

When $S \geq 1/2$, axial zero field splitting, $D$, must be accounted for. This splits the $m_s$ states according to their $m_l$ magnitude, according to Equation 5.

$$E(m_l) = m_l^2 S(S+1) \text{ Equation 5}$$

In addition to the paramagnetic analogues above, we prepared [$\text{Y}^{3+}$$\_2$($\text{Zn}^{2+}$)(O$_3$C$\text{Bu}$)$_{10}$(O$_4$P$\text{Bu}$)$_2$(NE$_3$)$_2$] (9), the “completely” diamagnetic equivalent. Intriguingly, we found we were able to detect a signal in the EPR experiment (Q-band, room temperature), indicating the presence of a paramagnetic impurity.

![Figure 14. Q-band Electron Paramagnetic Resonance spectrum (intensity versus field) of (9)](image)

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In order to help unravel the detail of the overlapping states, which were hard to resolve by fitting with Gaussian functions, we performed *ab initio* calculations to give the energies of each multiplet state and assess these in the light of the experimentally determined SMM behaviour, the most intriguing difference being the magnetically slowly relaxing determined SMM behaviour, the most intriguing difference being the magnetically slowly relaxing (7), and (6), which only showed divergent \( \chi^{\prime\prime} \) “tails”. As described below, the principal difference is the nature of the ground-state doublets. Importantly, for Dy\( ^{\text{III}} \) a Kramers ion, the ground state is always a doublet, *i.e.* \( \pm m_J \), regardless of the ligand geometry about it, though the labelling of these states is not always well-defined and may be better described by a linear combination of states. For Tb\( ^{\text{III}} \), a non-Kramers ion, doublets only occur exclusively when there is strict axial symmetry (though there is also always a singlet \( m_J = 0 \) state), which is here absent, so doublet states cannot be guaranteed, unlike, for example, in Ishikawa’s \([\text{Tb}\,(\text{PC})_3]^{4-}\) complex [6a].

Taking the simplified model shown in S. I. 10, incorporating one Lu\( ^{\text{III}} \) and one Dy\( ^{\text{III}} \) (or Tb\( ^{\text{III}} \)), the former chosen on account of its being electronically diamagnetic and of similar ionic radius to the paramagnetic ions, *ab initio* optimisation calculations were performed in MOLCAS 7.8 (6b) to determine the ground multiplet structure of these ions along with the \( g \)-matrices for each of these states. For these purposes, the terminal amine groups were cut to ammonia molecules, and the pivalate groups were reduced to acetate ligands. For Dy\( ^{\text{III}} \) the states used were the \( ^{2}H \) and \( ^{4}E \), and for Tb\( ^{\text{III}} \), only the \( ^{2}F \) and \( ^{3}D \), for reasons of computational limitation.

The most interesting results found an obvious difference which seems to account for the behaviour qualitatively with the relative energies of the \( m_J \) states in each of (7) and (6) being shown in Figure 15 (numbers given in S. I. 11). The relative energies of the doublet \( m_J \) states for (7) show a significant step between the ground and excited state which was used to rationalise the slow relaxation of the first lanthanide SMM, \([\text{Tb}\,(\text{PC})_3]^{4-}\), and is equivalent conceptually to the \( SD^2 \) barrier in transition metal SMMs. The gap of 71.9 cm\(^{-1} \) between these is of the same order as the energy gap found experimentally (ca. 24 K), though this cannot account for other factors such as quantum tunnelling, *vide infra*, and so represents an upper limit on the \( U_{\text{sd}} \).

There follows a succession of well separated states at 104.8 cm\(^{-1} \), 158.2 cm\(^{-1} \), 243.5 cm\(^{-1} \), 346.6 cm\(^{-1} \) before a small gap to 366 cm\(^{-1} \). A large jump to the final state is then observed to 580.5 cm\(^{-1} \), matching that expected from the optical emission data. In Figure 16, upper, the quantitative agreement is seen between the *ab initio* energies, shown as red lines, and the emission bands in black for the \( ^{4}F_{9/2} \) to \( ^{6}H_{15/2} \) multiplet only (noting the change in units to cm\(^{-1} \) from those seen above). Note that for (7) and (6) we fitted the highest and most well separated emission band with a Gaussian function, using IGOR, and then used this as the assignment for the highest energy state, so all states are relative to this (the calculated energies are relative and not absolute).

(6), by contrast, from this method, shows a singlet ground-state with a low lying \( ^{3}H_{15/2} \) excited state at only 5.3 cm\(^{-1} \) above. By the mechanism proposed by Ishikawa *et al.*, this could rationalise the non-SMM behaviour as a doublet ground-state is required. The non-zero \( \chi^{\prime\prime} \) signal, though, may suggest that these states are in fact acting as pseudo-doublets, and are one each of a \( \pm m_J \) state. Following this we see a succession of singlet states, at 37.2 cm\(^{-1} \),...
The electrostatic model of Chilton et al. [6c] is a much more accessible approach, relying on a minimisation of the electrostatic interaction between the ligands and metal, i.e. a purely classical approach. For DyIII compounds this can be employed to obtain information about the ground-state anisotropy axis at a metal site and its orientation. The results for (7) are given in Figure 17 and show how this is aligned (also see S. I. 12) roughly along what could be called the principal axis for the square-antiprismatic geometry, which is here non-idealised. As a result of crystal symmetry the anisotropy axes of each crystallographically equivalent ion are necessarily parallel, or collinear, so maximise the anisotropy, though a cancellation is only possible where there are more than two metals.

Comparison with the above ab initio calculations shows a rather poor agreement with a deviation angle of 25.3° between the two approaches, i.e. the axes lie at this angle to one another. The main difference is most likely in the assumptions made by the electrostatic model, i.e. that the ground state must be $m_g = 0$, which was shown to be almost always the case even in other low symmetry environments in SMMS. It is probable that, in light of the large difference here, much larger than in those cases documented [6a], along with the rather low $g_z$ values, the ground state is something else, though we were unable to determine the $m_1$ "label" by our calculations. Most likely there is actually a significant mixing of states on account of transverse influences, and so these labels are not as useful as they would be in a well-defined Ising-like system.

Conclusions

A series of hexametallic [LaIII2ZnII4] compounds were synthesised using solvothermal synthesis and phosphonic acid pro-ligands. These were found to have bi-capped butterfly cores and showed SMM behaviour when the LnIII was DyIII, with $U_{iso} = ca. \ 38 \ \text{K}$. For TbIII no energy barrier could be obtained. Correlations between luminescence data and ab initio calculations justify the difference in terms of the ground state multiplet structure and highlight the difference between Kramers and non-Kramers ions explicitly. With GdIII (5) a small but noticeable MCE was found and a small antiferromagnetic exchange coupling fitted to susceptibility and magnetisation data. Though so far resilient, we intend to explore further the reaction parameters of different solvents, heating and pro-ligand regimes and stoichiometries for ZnII-LnIII-phosphonate systems to obtain new topologies and variations upon that here shown, a strategy which, given the diversity seen in Mn, and Co-LnIII-phosphonate chemistry, is likely to be fruitful here, also. Although refrigerant compounds do not seem to benefit from additional diamagnetic bulk, ZnII could potentially be used to isolate the metal centres for extremely low temperature work, as seen in lanthanide-tungstate cages elsewhere [6d]. The strategy shown here towards SMMS adds to the current body of results confirming this as a valid proposition, and also gives the largest energy barrier for a 3d-4f phosphonate compound.

Acknowledgements

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Thanks to Eufemio Moreno, James Walsh and George Whitehead for helpful input.

Notes and references

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4 Electronic Supplementary Information (ESI) available: [details are given in text of all S. I. Figures and discussion points. Also cif files are provided for (5) and with CHECKCIF analysis of (5) is S. 1]. Further XRD details are provided in the S.I. See DOI: 10.1039/b000000x/

References


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were recorded on a QD-MPMS-XL magnetometer between 1.8–300 K, with data corrected for eicosane fixant, holder and diamagnetism as appropriate. EPR results were collected on a Bruker EMX spectrometer at room temperature with Q-band resonator. Powder X-ray diffraction was performed at room temperature using a Bruker D8 and Phillips PANalytical X’Pert. Single-crystal XRD were measured with a Bruker Apex II Prospector (CuKα source) and Agilent SuperNova (MoKα source). Data were solved with Direct Methods and refined using SHELXTL with F2. Steady state emission spectra were recorded using an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 W microsecond pulsed xenon flashlamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in a Peltier housing (air cooled, Hamamatsu R928P). Where indicated delay time and gate time were applied during emission measurements. Lifetime data were recorded following excitation with a microsecond xenon flashlamp, using the multi-channel scaling method. Lifetimes were obtained by tail fit on the data, and the quality of fit judged by minimization of reduced $\chi^2$ and residuals squared. Where the decay profiles are reported as mono-exponential, fitting to a double exponential yielded no improvement in fit.
Investigations into the magnetocaloric and single-molecule magnet behaviour of \([\text{Ln}^{\text{III}}_2\text{Zn}^{\text{II}}_4]\) bicapped butterflies

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Zn\textsuperscript{II}-Ln\textsuperscript{III} SMMs

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<td><img src="Image4" alt="Microcyclic Compounds" /></td>
<td>L.3</td>
<td>2d, 2h, 2i</td>
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S. I. 1. Top left: [Zn$_2$Er$_3$(L1)(O$_2$CCH$_3$)$_2$(NO$_3$)$_2$(H$_2$O)$_{1.5}$(MeOH)$_{0.5}$] from Yamashita et al. R = [2a]. Ligands are those used in those compounds reviewed.
Table 1. List of compounds described in the main text and their energy barriers at the specified fields, with references.

<table>
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<td>$[\text{Zn}^{II}\text{Er}^{II}(\text{L1})(\text{O}_2\text{CCH}_3)(\text{NO}_3)<em>2\text{(H}<em>2\text{O})</em>{1.5}(\text{MeOH})</em>{0.5}]$</td>
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<td>NA</td>
<td>2e</td>
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<tr>
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Experimental Details and Characterisation

\([\text{Ln}^{III}_2(\text{O}_2\text{C}^\text{Bu})_6(\text{HO}_2\text{C}^\text{Bu})_6] \quad (\text{Ln}^{III} = \text{Pr}^{III}, \text{Nd}^{III}, \text{Sm}^{III}, \text{Eu}^{III}, \text{Gd}^{III}, \text{Tb}^{III}, \text{Dy}^{III}, \text{Ho}^{III} \text{and} \text{Y}^{III})^{1}\)

From an established synthesis, for each of Pr\(^{III}\)-Ho\(^{III}\) (Pm\(^{III}\) excluded) and Y\(^{III}\), \([\text{Ln}^{III}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}] \quad (5 \text{ g, 15 mmol})\) and pivalic acid (30 g, ca. 300 mmol) were stirred together in toluene (50 mL) and heated to 140 °C in an open flask. Upon evaporation of the solvent, fresh batches of toluene were added (3 x 50 mL) before leaving the remaining solution to stir overnight (14 h) at 105 °C. At room temperature, acetonitrile (100 mL) was added and stirred for 3 h, giving a solid (coloured depending on the choice of lanthanide) the product being filtered and washed with more acetonitrile (3 x 30 mL), then dried under vacuum. These products were used as obtained without further purification or extensive analysis. Further product could be extracted by leaving the filtrate to cool overnight in the freezer. Typical analysis characteristic of each: Eu\(^{III}\)C\(_{60}\)H\(_{114}\)O\(_{24}\) (calculated:found): Eu\(^{III}\) 19.95:19.93; C 47.30:47.43; H 7.54:7.72.

\([\text{Zn}^{II}(\text{O}_2\text{C}^\text{Bu})_2]^2\)

Zn\(^{II}\)(OAc)\(_2\)·2H\(_2\)O (5 g, 23 mmol) was dissolved in pivalic acid (30 g, ca. 300 mmol) and the solution stirred at 140 °C in toluene for 1 h in an open flask. After this time, toluene having been replenished as appropriate (2 x 50 mL) a white precipitate formed. This was filtered, washed with toluene (3 x 50 mL) and dried overnight under vacuum and used without further purification. Analysed as: ZnC\(_{10}\)H\(_{18}\)O\(_4\) (calculated:found): Zn 24.43:24.46; C 44.88:44.53; H 6.78:7.04.
Powder X-ray Diffraction Results: S. I. 3a, b, c and d.

S. I. 3a. PXRD spectra of (6), (7) and simulated data of (7) from single-crystal XRD. Key: (6) blue; (7) red; and simulated (7) green.

S. I. 3b. PXRD spectra of (1), (4), (5) and simulated data of (2) from single-crystal XRD. Key (1) red; (4) green; (5) blue; and simulated (7) green.
Fig. 3c. PXRD spectra of (2), (3) and simulated data of (2) from single-crystal XRD. Key (2) red; (3) blue; and simulated (2) black.
Fig. 3d. PXRD spectra of (8), (9) and simulated data of (7) from single-crystal XRD. Key (8) red; (9) blue; and simulated (7) black.

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Table 2. Results of SHAPE$^3$ analysis upon the Dy$^{III}$ ion in (7) showing the match between the known geometries listed, their symmetries and the match with the geometry about said ion.
Packing down a, b and c-axes (7)
S. I. 4. Packing of (5) along the (upper) $a$-axis; (middle) $b$-axis; and (lower) $c$-axis. Key: Ln$^{III}$ Purple Spheres; Zn$^{II}$ Pink Spheres; C Grey Wire; O Grey Wire; P Orange Wire; N Blue Wire. H atoms are omitted for clarity.
Packing down a, b and c-axes (5)
S. I. 5. Packing of (5) along the (upper) $a$-axis; (middle) $b$-axis; and (lower) $c$-axis. Key: As for Fig. S. I. 4.
Excitation Spectra (Grouped for (3), (4), (6) and (7))

S. I. 6. Collated Solid State Excitation Spectra for (3), (4), (6) and (7). Key: (3) magenta; (4) red; (6) green; (7) blue. Recorded at room temperature at 600 nm (3), 617 nm (4), 545 nm (495 nm filter) (6) and 575 nm (7)

PHI Simulations for (5)

S. I. 7. Simulated $-\Delta S_m(T)$ for (5) by considering three pairs of cases: i) Ferromagnetic interaction of $+0.1$ K (all with the same Hamiltonian as in the main text) at 5 T (Black) and 7 T (Red); ii) Antiferromagnetic interaction of $-0.1$ K at 5 T (Green) and 7 T (Blue); iii) Paramagnetic (no exchange), i.e. ±0 K at 5 T (Cyan) and 7 T (Magenta). Lines connect the points only.
Additional a.c. magnetic susceptibility data for (7) and (6)

S. I. 8. Upper: experimental \( \chi' (v) \) (Upper) and \( \chi'' (v) \) (Lower) for (7) between 0.1-1200 Hz (\( H_{dc} = 0 \) T, \( H_{ac} = 1.55 \) G), where \( T = 2-9 \) K, shown as solid shapes. Lines connect points only. Key: As shown.
Experimental $\chi''$ and $\chi'$ versus T plot for (6): $H_d = 1$ kG, $\nu = 100, 700$ and $1100$ Hz and $H_{ac} = 1.55$ G, between 1.8 and 20 K. Key: 1100 Hz Red Squares (closed $\chi'$; open $\chi''$); 700 Hz Black Circles; 100 Hz Green Triangles.
Ab Initio calculations for (6) and (7)

S. I. 10. Fragment used for ab initio calculation. Key: As for S. I. 2 and Lu$^{III}$ shown in light green where Ln$^{III}$ = Dy$^{III}$ or Tb$^{III}$.

Calculation Details
Calculations were performed using a pruned structure taken from the X-Ray crystal geometry with no optimization. The pivalate molecules were substituted with acetate molecules and the terminal amine groups were substituted with ammonia molecules. The lanthanide ion that was not the focus of the calculation was substituted for diamagnetic Lu. The ab-initio calculations were performed using the CASSCF /CASSI approach in MOLCAS 7.8$^{4-6}$. The Complete Active Space methodology was used to accurately model the orbital degeneracy of the 4f orbitals of terbium(III) and dysprosium(III), where the active spaces were 8 and 9 electrons in 7 orbitals, respectively. The ANO-RCC basis sets were used exclusively, where the paramagnetic lanthanide was treated with VTZP quality, the eight coordinating oxygen atoms were treated with VDZP quality and all other non-hydrogen atoms were treated with VDZ quality, while the hydrogen atoms were treated with a minimal basis (MB). The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions are taken into account in the basis set and the spin-orbit coupling is handled separately in the RASSI module.

In the CASSCF procedure for terbium(III), the septets were given 7 roots and the quintets were given 140 roots. In the CASSI procedure, 7 septets and 105 quintets were mixed by spin-orbit coupling. Due to computational limitations, the triplets and singlets were not included in the calculation.

In the CASSCF procedure for dysprosium(III), the sextets were given 21 roots and the quartets were given 224 roots. In the CASSI procedure, 21 sextets and 128 quartets were mixed by spin-orbit coupling. Due to computational limitations, the doublets were not included in the calculation.
### (7): results (dysprosium)

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### (6): results (terbium)

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S. I. 11. Relative energies of states (cm⁻¹) for (7), upper, and (6), lower, by *ab initio* calculations, with their $gₓ$, $gᵧ$, and $gₙ$ values and angle (orientation / degrees) relative to the ground state.
S. I. 12. **Electrostatic Model** (for details see main text) to (7), showing the orientation of the anisotropy axes (green rods) of each Dy$^{III}$ ion. Key: As for S. I. 2. No H’s are shown for clarity: 'Bu groups have been removed.

**Thermogravimetric Analysis**

TGA analysis was also performed between 30-1000 °C in N$_2$ (0.5 °C min$^{-1}$) upon (6). This demonstrates the thermal stability of these compounds to only a moderate value of 137 °C, the point at which there is a loss in weight of ca. 12 %, to 193 °C, which could relate to the loss of the terminal amine groups. Further steps between ca. 195-233 °C account for around 5 %, before a very broad step between ca. 240-570 °C which removes around 66 %.
S. I. 13. Thermo-gravimetric analysis data for (6), recorded between 30-1000 °C under N₂ at 10 K min⁻¹.
S. I. 14. Numbering scheme for ASU of (5). Key: Gd$^{III}$ green, Zn$^{II}$ purple, N blue, O red, C grey. No H atoms are shown for clarity.

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<thead>
<tr>
<th>Atoms</th>
<th>Distance / Å</th>
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<tbody>
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<td>Gd1</td>
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<td>Gd1</td>
<td>O4</td>
</tr>
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<td>O11</td>
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<tr>
<td>Zn1</td>
<td>O2</td>
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Table 3a. Bond lengths for specified pairs of atoms for (5).

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<tbody>
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<td>Zn2</td>
<td>O8</td>
</tr>
<tr>
<td>Zn2</td>
<td>N1</td>
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<td>P1</td>
<td>O3</td>
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<td>P1</td>
<td>O10</td>
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<td>P1</td>
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Table 3b. Selected bond angles between the given atoms for (5). (a) denotes symmetry equivalent atoms.

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<td>Gd1</td>
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S. I. 15. Numbering scheme for ASU of (7). Key: Dy$^{III}$ green, Zn$^{II}$ purple, N blue, O red, C grey. No H atoms are shown for clarity.
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Table 4a. Bond lengths for specified pairs of atoms for (7).

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<td>Dy1 O11 Zn2(a)</td>
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<td>Dy1 O12 P1</td>
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Table 4b. Selected bond angles between the given atoms for (7).
Table 4c. Summarised crystallographic information for (7) and (5).

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<th>(5)</th>
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<td>wR2</td>
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References

Chapter 8: Paper 5

The coordination chemistry and magnetism of some 3d–4f and 4f amino poly-alcohol compounds

Review

The coordination chemistry and magnetism of some 3d–4f and 4f amino-polyalcohol compounds

Joseph W. Sharple \*, David Collison

School of Chemistry, The University of Manchester, Oxford Road, Manchester, Lancashire M13 9PL, United Kingdom

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Abbreviations: tacn, 1,4,7-triazacyclononane; bmmH\textsubscript{2}, 1,2-bis(2-hydroxy-3-methoxybenzylidene)hydrazine; mchbH, 3-methoxybenzylidenehydrazine; 4-Me-py, 4-methyl-pyridine; chph, 6-chloro-2-hydroxy-pyridine; acacH, acetylacetone; \textit{ΔT}_{\text{ad}}, adiabatic temperature change; \textit{J}_{\text{ac}}, alternating current; \textit{I}_{0}, anisotropy barrier; \textit{H}_{0}, applied magnetic field; \textit{D}, axial anisotropy; \textit{H}_{0}/\textit{C}, benzonic acid; H\textsubscript{a}, benzotriazole; \textit{k}_{\text{B}}, Boltzmann constant; \textit{R}, bond valence sum; ^\textit{A}BuMe\textsubscript{2}A\textsubscript{3+}, n-butyldiethanolamine; C\textit{ASSP}, complete active space perturbation theory 2; C\textit{ASSCF}, complete active space self consistent field; \textit{J}_{\text{AC}}, coupling constant; \textit{g}, direct current; \textit{μ}_{\text{B}}, electronic Bohr magneton; \textit{E}_{\text{FD}}H\textsubscript{2}, ferrocene dicarboxylic acid; \textit{K}_{\text{D}}/\text{H}\textsubscript{2}, functionalised diethanolamines; HDV, Heidenberg Dirac van Vleck; ib, isobutryrate; n, O, isopropoxide; \textit{JT}, Jahn–Teller; \textit{g}, Landé g-value; \textit{ΔS}_{\text{m}}, magnetic entropy change; MCE, magnetocaloric effect; mdeA\textsuperscript{3+}, methyldehlanolamine; Micro-SQUID, micro-superconducting quantum interference device; ms, microsolvate; \textit{B}_{\text{value}}, n-butyldehlanolamine; edeh, N,N,N-triethyl2-hydroxyethyl(ethylenediamine; sappeH\textsubscript{2}, N-salicylidene-2-bis(2-hydroxyethyl)amine)ethylamine; NMR, nuclear magnetic resonance; \textit{χ'}, out-of-phase susceptibility; \textit{H}_{0}/\text{P}, phthalocyanine; HO\textsubscript{2}/\text{C}, pivalic acid; py, pyridine; QT, quantum tunneling; RSSI, restricted active space state interaction; E, rhombus ZFS; SMM, single-molecule magnet; \textit{χ}, susceptibility; \textit{ΔT}, susceptibility temperature product; \textit{S}_{\text{c}}, spin operator; \textit{r}, ta, teH\textsubscript{3}, trithanolamine; THF, tetrahydrofuran; tpaH, triphenyl acetylene acid; ZFS, zero-field splitting.

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1. Introduction

1.1. Molecular magnetism and poly-alcohol ligands

Molecular magnetism is a wide ranging area of research that began around 20 years ago, primarily involving the synthesis and study of metal coordination compounds. Twin pillars of this effort, amongst others, are the discovery of single-molecule magnets (SMMs) [1], in which data can in principle be stored at a molecular level, and magnetic refrigerants [2], compounds with a large magnetocaloric effect (MCE) that can be used to cool to and below liquid $^4$He temperatures. Much early research in the former area involved transition metal compounds, such as [Mn$^3+$(Me$_3$)$_2$O$_2$(CO)OH]$_6$(H$_2$O)$_4$·2CH$_3$COOH·4H$_2$O [2] and [Fe$^{II}$(CO)$(OH)_2(tacn)Br$_2$·H$_2$O·Br$_2$·BH$_3$O], where tacn is 1,4,7-triazaacyclonane [4], whilst the latter topic involved cages such as [Fe$^{II}$(CO)$_2$(tca)$(OMe)_2$(Cl)$_2$], where tca is benzotriazole [5]. Many subsequent efforts [e.g. 6] used polyalcohol pro-ligands, amongst others, to connect the metals into larger assemblies, so increasing the ground state spin, $S$, as this was initially believed to be the key to increasing the temperatures at which SMMs could maintain magnetised states to a practical level. The challenge of achieving this is still on-going. Selected examples were well reviewed by Brechin in 2005 [7], who showcased the SMM behaviour of mostly Mo$^{III}$ and Fe$^{III}$ cages. The first of these ions was particularly prevalent in early research, having a sizable single-ion anisotropy when in the octahedral configuration, which can define an Ising-type ground state. Introducing lanthanides into molecular magnetism, a more recent development, led to large improvements in the energy barriers of SMMs, on account of the anisotropy of Ln$^{III}$ ions such as Dy$^{III}$, Tb$^{III}$ and Ho$^{III}$, particularly by Ishikawa, with a [Tb$^{III}$(PC$_3$)$_2$]$^-$ compound [8]. The high spin and isotropy of Gd$^{III}$ has achieved similarly impressive results in increasing the $-\Delta S_M$ (MCE) of molecule-based refrigerants, for example [Gd$^{III}$(O$_2$CCH$_3$)$_2$(H$_2$O)$_4$]$^-$·4H$_2$O [9].

Therefore, combined with the established benefits of appropriate d-transition metals, or as homometallic species, lanthanide-based compounds impart significant structural and magnetic properties, distinct from their 3d cousins, giving some of the best performing SMMs and magnetic refrigerants.

1.2. Amino-polyalcohol ligands

An extension of this work uses amino-polyalcohol pro-ligands. These would seem an ideal continuation of previous efforts as they possess an affinity to lanthanides due to their O donors, but also incorporate a new N functionality which can take part in bonding, though to date there are significantly fewer 3d–4f and 4f compounds of this type than with 3d metals alone, so this is an ongoing area of research. The focus here will be on those compounds prepared with the pro-ligands tetra, triethanolamine, and DedaH$_2$, functionalised diethanolamines, where R is H or C$_2$H$_5$; these being shown in Fig. 1. These are flexible pro-ligands that can bond to metals in many ways, or with many “moders”. Their polyfugacy also stems from the way they exist in a variety of forms, depending on the basicity of the conditions, as singly, doubly or triply protonated species as appropriate, in addition to their completely...
deprotonated forms. Indeed, the \(\text{teal}^+\) pro-ligand bonds to metals in each of the \(\text{teal}^+\), \(\text{teal}^2^+\), \(\text{teal}^3^+\) and \(\text{teal}^4^+\) forms in 3d metal chemistry in a wide variety of ways, also featuring as a \(\text{teal}^-\) cation [10]. Co-ordination occurs through O or OH arms and the N-donor, in addition to any other functionalities, with the flexible OH arms accommodating a large range of ionic radii of metals. These properties assist in a common technique in co-ordination chemistry, so-called “serendipitous” assembly [11], which involves combining reagents to form unpredictable products; beginning with flexible starting materials can improve one’s chance of forming a product. Modifications of “successful” syntheses can then be used to explore further.

This review article examines the synthesis, structure and magnetic properties of 3d-4f and 4f coordination compounds with aminopolyalcohol ligands and their magnetic properties. In addition to reviewing these we assess the suitability of these ligands to this research and why they are such a double-edged sword in the fight for improved SMM and MCE molecular materials.

2. Incomplete double cubanes

2.1. Beginnings: \(\{\text{Fe}^\text{III}_{2}\text{Ln}^\text{III}\}\)

Christou’s group were the first to synthesise 3d-4f triethanolamine cages [12] in 2006, namely \(\text{Fe}^\text{III}_{2}\text{Ho}^\text{III}\text{(OH)}_{2}(\text{teal}^3)^{2+}\text{(O}_2\text{CPh})_{4}\text{(NO}_3)_{2}\) 5MeCN (1) and \(\text{Fe}^\text{III}_{2}\text{Ln}^\text{III}\text{(OH)}_{2}(\text{teal}^3)^{2+}\text{(O}_2\text{CPh})_{4}\) 4MeCN 3H\(_2\)O (2) \((\text{Ln}^\text{III} = \text{ Tb}^\text{III} \text{ or } \text{ Dy}^\text{III}) \text{ and } \text{ HO}_2\text{CPh is benzoic acid}) giving the first Fe\(^{III}\)-4f SMMs (see Fig. 2). All were prepared from a reaction of the iron tri-angle \(\text{Fe}^\text{III}_{2}\text{(O}_2\text{CPh})_{4}\text{(H}_2\text{O})_{2}\text{(O}_2\text{CPh})\). \(\text{Ln}^\text{III}\text{(NO}_3)_{2}\text{nH}_2\text{O}\). teal\(^+\) and acetonitrile stirring at room temperature giving what is a common structural motif in 3d-4f teal\(^+\) chemistry, and already known beyond this niche [13,14]: the incomplete double-cubane. This is made up of two “M\(_4\)O\(_4\)” cubanes fused on one face and each missing a metal vertex, making a planar tetrametallic core.

Alternative descriptions include a rhombus or butterfly. This structure, with several variations, is common to (1) and (2) and in more detail, for (1), is thus: The planar core is composed of two “inner” octahedrally co-ordinated Fe\(^{III}\) ions which are formed into triangles by an OH group, bonding to two outer Ln\(^{III}\) ions with four carboxylate groups bonding between hetero-metals. These ligands “frame” the rhombus and lead to inter-molecular interactions as a result of the π-π stacking between aromatic groups.

The singly protonated teal\(^{2+}\) exhibits the bonding mode 3.2.2.1.1, described using Harris notation [15], used here throughout. This lists the total number of metals bonded, the number attached to each arm, then the number bonded to the N atom and is followed even when an arm is non-bonding, represented by a zero, and extended to other ligand types such as carboxylates and nitrates. Thus the aforementioned carboxylates show the 2.1.1 mode. Note that all modes of amine-polyol bonding in this review are collated in Scheme 1 for easy reference.

The teal\(^{2+}\) ligand is centred on the outer lanthanide ions by the N-donor atom with two unprotonated arms linking this to each of the inner 3d metals. The third protonated arm bonds terminally to the same Ln\(^{III}\) ion. This is the most common bonding mode found where triethanolamine features in polymetallic compounds, often as part of many different topologies, vide infra. The H on the teal\(^{2+}\) has here is assigned by assuming that unprotonated arms bond to more metal ions, though only after metal oxidation states have been assigned by geometries (3d metals) or experience (Ln\(^{III}\)). Filling the coordination sphere of the 4f ions is a nitrate (2.1.1.0), whereas in (2) these are replaced by capping 2.1.1’ \(\text{O}_2\text{CPh}\) ligands, the geometry around these ions being a capped square antiprism.

Magnetic measurements show similar decreases in \(\chi T\) with decreasing temperature for (1) and (Tb-2 and Dy-2), consistent with overall antiferromagnetic interactions between spins. \(\chi T\) falls gradually with decreasing temperature and then rapidly at low temperature, though this behaviour may also be assigned completely or in part to the anisotropy of the Ln\(^{III}\) ions and the depopulation of Stark levels, which precluded a fit of these data, a.c. susceptibility data hinted at SMM behaviour for (1) and (Dy-2), with plots of \(\chi T\) versus temperature for different frequencies of applied field divergent at low temperatures, though no maxima were observed above 1.8 K. Further micro-SQUID measurements on (1) and (Dy-2), though, revealed these compounds are SMM by the discovery of hysteresis loops at lower temperatures. For the former, loops opening below 0.3 K were smooth (upper panel, Fig. 3) and assigned to the inter-molecular stacking interaction. Step-structured loops indicating a quantum tunnelling process (QTM) were found for the latter, opening below 1.1 K (lower panel, Fig. 3). The presence of this relaxation at zero-field gives a rapid decrease of the magnetisation and no \(U_{\text{eff}}\) values could be extracted.

Although the isotropic Gd\(^{III}\) analogues were not prepared, which could be used to assess the extent of magnetic anisotropy involving the Ln\(^{III}\) ion, the likely origin is the 4f metal, notwithstanding the presence of anisotropy in some Fe\(^{III}\) cages, which is dependent on geometry and factors of molecular symmetry. The rapid quantum tunnelling, though, is a feature noted elsewhere in Ln\(^{III}\) SMMs [e.g. 16].

2.2. Variations on a theme: \(\{\text{Mn}^\text{III}_{2}\text{Gd}^\text{III}\}\)

Near-identical analogues of (1) and (2) were found with different d transition metals, such as \([\text{Mn}^\text{III}^2\text{Gd}^\text{III}_{2}\text{(OH)}_{2}(\text{teal}^3)^{2+}\text{(O}_2\text{CPh})_{4}\text{(NO}_3)_{2}\) (3) [17], also from Christou’s group, and part of a series. Only the one lanthanide compound was reported, prepared from a modification of the above reaction by using \([\text{Mn}^\text{III}\text{Mn}^\text{III}\text{(O}_2\text{CPh})_{6}\text{(py)}_{2}\text{(H}_2\text{O})]\), where py is pyridine. The structure is the same as (1) with the presence of H on the
Scheme 1. Bonding modes of the teaH$_x$($^{1−4}$) and $\text{RdeaH}_x$($^{2−4}$) ligands in this review (numbered), and where M is a transition metal ion and Ln is a lanthanide; Harris notation describes the bonding of the ligands to these metals.
teal$_2$– ligand assigned after confirmation of the Mn$^{III}$ oxidation state by Bond Valence Sum (BVS) analysis and geometries. These ions also show characteristic Jahn–Teller distortion down the O$_2$(CPh)–Mn$^{III}$–OH axis. H-bonds between the OH of the teal$^-$ arm and the oxygen atom (HO·H) of a nitrate group form a supra-molecular chain structure.

Qualitatively similar behaviour in $\gamma(T)$ to (1) and (2) was assigned to the intra-molecular H-bonding interaction, though fits of these data could not be obtained using a HDVV spin Hamiltonian, which was reported to be due to the presence of weak interactions between spins, which would help to quantify exchange interactions and any anisotropy present. a.c. susceptibility data suggested an ill-defined $S = 4$ ground state from the frustrated triangular Mn$^{III}$-Gd$^{III}$ topology, though no SMM behaviour was discovered. The lack of SMM behaviour here suggests the importance of the anisotropic Ln$^{III}$ ions and so most likely the slow relaxation in (1) and (2) is due to the 4f ions.

2.3. Mössbauer and EPR analysis of $[\text{Fe}^{III}\text{Ln}^{III}]_2$

Powell’s group investigated the effects of the pora-R substituent in $[\text{Fe}^{III}\text{Dy}^{III}(\text{OH})_2(\text{teaH})_2(\text{O}_2\text{CPh})_2]$ (4) [18] (R = H, Me, Bu, NO$_2$ or CN) on the coupling between the 3d and 4f ions. This variation in R does nothing to change the overall molecular structure, which is identical to those seen in (2), and prepared in a similar way, with slight variations in solvent. Using $^{57}$Fe Mössbauer spectroscopy a significant change in the internal field at the $^{57}$Fe ion was detected, and ascribed to the differing environment of the Dy$^{III}$ ions, the $^{57}$Fe “electron cloud” being polarised by their influence.

The Fe$^{III}$ spins cancel in an Y$^{III}$ analogue (Y-4), giving an $S = 0$ ground state, so allowing the results of the changing orientation of the Dy$^{III}$’s principal magnetic anisotropy axes to be probed (shown in Fig. 4 for each substituent). Thus the influence of a ligand substituent on the Dy$^{III}$ ion can have a significant effect on the magnetic properties overall. The ultimate application of this Mössbauer technique is the determination of the orientation of the magnetisation axes on anisotropic ions.

The syntheses of (1)–(4) have relied on beginning with a 3d-metal triangle, which appears to act as a scaffold for incorporating lanthanides around a part of it, after breaking up in solution, at room temperature, then capping the high coordination number 4f metal with the bulky co-ligands added. This is different from the following (5), where the components are added separately to achieve a different result.

Briefly, recent work, explained in much greater detail in [19] on the compounds $[\text{Fe}^{III}\text{Ln}^{III}(\text{OH})_2(\text{teaH})_2(\text{O}_2\text{CPh})_2]$, where Ln$^{III}$ is Ce$^{III}$–Yb$^{III}$ (excluding Pr$^{III}$) or Y$^{III}$, is also particularly interesting. This utilised EPR (Electron Paramagnetic Resonance spectroscopy) on the latter (Y-4), amongst other investigations with variable temperature X-band data used to determine D, E and g values for the Fe$^{III}$ ions. With Nd$^{III}$ and Dy$^{III}$, this revealed the importance of Ln$^{III}$–Ln$^{III}$ dipole–dipole interactions at less than 20 K.

2.4. Inside-out: $[\text{Co}^{III}\text{Ln}^{III}]_2$

Further variations with 3d-transition metals are possible: from the Murray group, stirring Co$(\text{NO}_3)_2$ . 6H$_2$O, Ln$^{III}$(NO$_3$)$_3$ nH$_2$O, teal$_2$, benzoic acid and the base triethylamine in acetonitrile at room temperature gave the double cluster compound $[\text{Co}^{III}\text{Ln}^{III}$(OMe)$_2$(teaH)$_2$(O$_2$CPh)$_2$(MeOH)$_2$(NO$_3$)$_3$] MeOH . H$_2$O: $[\text{Co}^{III}\text{Ln}^{III}$(OMe)$_2$(teaH)$_2$(O$_2$CPh)$_2$(MeOH)$_2$(NO$_3$)$_3$] MeOH . H$_2$O (5) [20] (Ln$^{III}$ is Gd$^{III}$, Tb$^{III}$ or Dy$^{III}$) where Co$^{III}$ is oxidised in air to Co$^{III}$ during the reaction. Significant differences were found compared with (1–4), though (5) too has an incomplete double cubane core. Notably, two forms exist in the crystal structure in a 1:1 ratio: a further difference is that here we find the Ln$^{III}$ ions...
as the central pair and the CoIII ions as the outer metals, OMe groups bridging a LnIII-CoIII triangular arrangement. The teaH−ligand here has the bonding mode 3.2.2.0.1 and is centred by the N-donor atom on CoIII so it links the outer and inner metals as before, but the protonated arm is unbound. Most likely this arm is unable to add to the already complete co-ordination sphere of a 3d metal, unlike when centred on LnIII, with its larger ionic radius and co-ordination number. In one of the structural pairs, two methanol groups bond to each LnIII, but in the second compound one is replaced by a nitrate, with resulting nitrate-methanol H-bonding. Though these lanthanide(III) ions have qualitatively the same square-antiprismatic geometry, these are distorted away from regularity by differing amounts.

The reasoning behind the inversion in position of CoIII and LnIII cf. FeIII and LnIII (e.g. (1)) is still unknown and not speculated upon by the authors, though there is an obvious dependence on synthetic route, judging by this and also the latest results from Powell [14]. This latter example is the only one so far of a controllable synthesis where the position of the 4f and 3d ions in incomplete double cubanes can be altered in their positions, though does not involve teaH3 or RedeH2.

As this CoIII is diamagnetic the interpretation of the magnetic data is simplified to that of the central LnIII dimer. For (Gd-5) the exchange constant was fitted using the isotropic Hamiltonian below (Eq. (1)), incorporating a Zeeman term, where \( J_{12} \) is the exchange between the inner 4f ions, \( S_1 \) and \( S_2 \), the spin operators for these ions, \( g \) the Landé g-value, \( \mu_B \) the electronic Bohr magneton and \( H \) the applied magnetic field,

\[
\hat{H} = -J_{12}S_1S_2 + g\mu_B(HS_1 + S_2)
\]  

(1)

This yielded \( J_{12} = 0 \), i.e. the metals were non-interacting; hence the measured decrease in \( \chi_T \) at low temperatures was assigned to depopulation of the \( m_I \) levels, rather than to antiferromagnetic coupling, though more significant exchange was found by fitting the results of ab initio calculations to magnetic data. For (Th-5) and (Dy-5) similar depopulation, this time of the \( m_J \) states, was initially postulated; a c.s. susceptibility data for the latter, (Dy-5), showed clear frequency and temperature dependent \( \chi' \) maxima (upper panel, Fig. 5), from which a significant energy barrier of 88 K was extracted. The range of \( v \) values from the Cole-Cole (Argand) plot (Fig. 5, lower panel, inset) suggested discrimination between the differing DyIII environments in the crystal structure, though only one maximum in \( \chi' \) was seen. From the Arrenhius plot (Fig. 5, lower panel, main), \( T \) was temperature-dependent down to 2.5 K, suggesting quantum tunnelling of magnetisation below this temperature; curiously this was very inefficient, as evidenced by the lack of increase in \( \chi' \) in field, when compared to other lanthanide compounds [21]. (Th-5) displayed the opposite behaviour, with a significant QTM and consequent lack of \( \chi' \) maxima in zero-field. This unusually inefficient, but desirable, QTM of (Dy-5) was then explored in some detail using CASCF/RASSI/SINGLE_ANISO calculations by Ungur and Chibotaru on \( \text{(CoIII}_{2}\text{DyIII}_{2}\text{LnIII}) \) models [20].

QTM is effectively suppressed in the following manner: the ground doublet has a small splitting (10−6 cm−1), due to the non-Kramer’s state resulting from two coupled DyIII ions, which reduces QT. A second reason is the non-magnetic ground state, from strong dipolar coupling, which reduces the transverse influence from neighbouring molecules.

In modelling the magnetic data, the exchange postulated in (Gd-5), i.e. zero, was also indistinguishable from models where it was finite, taking into account the effects of zero field splitting (ZFS), meaning that this technique could not confirm the presence or otherwise of an interaction.

Further magnetic measurements with the doped DyIII:LnIII compounds (Dy3Y5), where the percentage ratios were altered, indicated that the SMM behaviour of (Dy-5) was a single-ion effect and that the exchange between ions is indeed the source of the reduced QTM, being less prominent as the DyIII−LnIII contribution is removed.

Rinehart et al. [22] have also seen much reduced QTM in a \( \text{LnIII}_{2}\text{N}_{2}\text{Me}_{2}\text{NSMe}_{2}\text{TeaH}_{3}\text{[THF]}_{2}^{-} \) compounds, where LnIII is TbIII or DyIII, bridged by a radical N2−ligand. The unusually strong coupling between lanthanide ions, several orders of magnitude larger than is normally found, appeared to be the key to obtaining the large hysteresis temperatures, without zero-field relaxation, though (Dy-5) would suggest qualitatively similar results can be obtained without resorting to such a “radical” approach. This reduction of QT by exchange-biasing has been well explored for 3d-transition metals, but is poorly understood in 4f compounds at present.

2.5. Developments

More recently, several variations on the \( \text{(CoIII}_{2}\text{DyIII}_{2}) \) arrangement were discovered with teaH3 also by utilising acacH (acetylactone). These [23,24] are quite similar and formulated as \( \text{(CoIII}_{2}\text{DyIII}_{2}\text{OMe}_{2}\text{[teaH][acac]}_{4}\text{(NO3)}_{2}] \) (6), \( \text{(CoIII}_{2}\text{DyIII}_{2}\text{OH}_{2}\text{[teaH][acac]}_{4}\text{(NO3)}_{2}] 4\text{H}_{2}\text{O} \) (7) and \( \text{(CoIII}_{2}\text{DyIII}_{2}\text{OMe}_{2}\text{(mdea)}_{2}[acac]}_{4}\text{(NO3)}_{2}] \) (8), with the now familiar butterfly arrangement of metals. The teaH ligands bond...
with the 3.2.2.0.1 mode, centred on an outer CoIII and the mdeaz2– showing the 3.2.2.1 mode in the same way. Energy barriers, UTij, for each are single-ion in origin, and around 30 K, with more than one thermal process detected at higher applied frequencies of a.c. field.

More variations show the large effects of subtle changes in geometry and lanthanide: a.c. susceptibility measurements on $[\text{Co}^\text{II}]_2\text{Ln}^\text{III}_2(\text{OH})_2(\text{bdea})_2(\text{acac})_2(\text{NO}_3)_4$, where LnIII is TbIII or DyIII (9), showed only the latter is an SMM, with a large UTij of ca. 169 K and no pure QTM above 7 K. The bdea2– bonds with the previously known 3.2.2.1 mode, being centred on Co2II. Compared to (6) this energy barrier is increased by almost six times; that the enhancement arises from only a change in ligand is noted as a potentially useful way to tune the relaxation properties of existing compounds.

2.6. Strong lanthanide(III) dependence: ($\text{Mn}^\text{II}L\text{Ln}^\text{III}$) and ($\text{Mn}^\text{III}L\text{Ln}^\text{III}$)

Using $\text{BudaH}_2$, the strong influence that the choice of lanthanide can have on the structure of coordination compounds was revealed. [$\text{Mn}^\text{II}L\text{Ln}^\text{III}$]($\text{BudaH}_2)_2(\text{L})$,$\text{O}_2\text{C}^\text{Bu}_3$]$\text{MeCN}$ (10) [25] and [$\text{Mn}^\text{II}L\text{Ln}^\text{III}$]($\text{BudaH}_2)_2(\text{Ln}^\text{III})_2\text{MeCN}$ (11) [26] (shown in Fig. 6, where for clarity MnIII is shown in pale pink to distinguish it from a LaIII), was reported to be of the same reaction; $\text{Mn}^\text{II}(\text{O}_2\text{C})_2\text{C}^\text{H}_2\text{OH},\text{pivalic acid, }\text{BudaH}_2$, and $\text{Ln}^\text{III}(\text{NO}_3)_3\text{H}_2\text{O}$ being stirred in acetonitrile.

Depending on the size of the lanthanide used, one of the two products forms: (10) from LaIII, CeIII, PrIII or NdIII or (7) from TbIII, DyIII, HoIII, ErIII or YIII. The former has an incomplete double cubane structure, with slight changes to those previously seen. The outer metals are lanthanides, (cf (5)) linked to one of the inner MnIII ions by a pivate group and all metals have one amine-diol ligand centred on them by N-bonding; for LnIII this is “BudaH2–”, with the mode 2.2.1.1, the alloy arms linking LnIII and MnIII and capping the former. For each MnIII the diol is “Budea2–”, bonding with the 4.3.2.2.1 mode. One arm links three metals in a MnIII triangle and the other links a MnIII and LnIII. The remaining pivate groups bond with 1.1.1.0 modes to each lanthanide. BVS and geometric analysis assigned the MnIII oxidation states in this pair of compounds.

Given that the coordination number increases upon moving from the heavier, smaller lanthanides to the lighter, larger, metals, from eight to nine, this may explain the resulting change in topology, ligands moving to accommodate these preferences. However, given that the compounds above, e.g. (2) feature nine-coordinate DyIII, this cannot be the only factor. The relatively bulky butyl “tail” of the diethanolamine ligand in (11), relative to tetaH2– in (2) may block the extra site from becoming involved.

(11) has a “horse-shoe” topology made up of alternating 3d and 4f metals. Rooted with an N-donor to the central LnIII are two 3.2.2.1 “Buda–” ligands, both linking this metal to adjacent MnIII ions. Pivolate groups bridge the four pairs of adjacent metals in 2.1.1 fashion and cap the terminal lanthanides in both a 1.1.0 and 1.1.1 manner. This leaves the “Buda–” ligands that link the outer-most metals on each end and cap the lanthanide with a protonated arm, overall being 2.2.1.1. The third “Buda” links across the end of the “horse-shoe” with the 4.2.2.0 mode, a rare example where the N-atom is unbound. The sharp break with lanthanide size again suggests this is an important factor, the “break” usually occurring around GdIII, though this metal ion was not reported for either (10) or (11) here. Each lanthanide(III) in (11) has a distorted eight coordinate $[\text{N}_2\text{O}_6]$ square-antiprismatic geometry, where the LnIII–N bonds are significantly longer than those to oxygen atoms, ca. 2.7 versus 2.3 Å.

Qualitatively similar magnetic behaviour in $\chi'(T)$ was found for both of (10) and (11), showing a decrease at lower temperatures, after expected values were found at room temperature for uncoupled ions. Furthermore the non-saturation and overlapping of magnetisation curves suggested anisotropy in each case, presumably at least partly due to the MnIII, because of its presence in the LaIII and YIII compounds, the (approximately) aligned Jahn-Teller axes in (6) likely contributing. These latter two were available to give information on the magnetic interactions between the MnIII ions. For the former this was (La-10) and, using Eq. (11), $J = 5.0 K$ when $g = 2.12$.

For (Y-11), using Eq. (2) gave $D/k_B = 4.2 K$, $g = 2.074$ and with $D/k_B = 0.055 K$, the latter value from the mean-field approximation, indicating a large anisotropy and weak coupling. The anisotropy here must be due to the aligned JT axes of the MnIII ions.

$$\hat{H} = D[(S_x^2 - 1/3S_z^2 + 1)] + g_u \mu_B H$$

(2)

$\chi'$ frequency dependence was found in (Ce-30), (Nd-10), (Tb-11) and (Dy-11), though only for (Nd-10) could $U_{\perp}$ be determined above 1.8 K and with $v = 1500 \text{Hz}$, as 10 K.

Overall, the lanthanide ions must play a role, as not all compounds exhibit this dependence, though most likely this will be in concert with the MnIII ions, given the $D/k_B = 4.2 K$ observed in (Y-11). Elsewhere the DyIII compound in isostructural series gives the largest barrier, though here this does not show maxima in $\chi'$, which should motivate further investigations.

2.7. Lanthanides only: ($\text{Ln}^\text{III}$)

The first and so far only reported BdeH2 4f butterfly was $[\text{La}^\text{III}(\text{OH})_2\text{(mdeH}_2)_2\text{(O}_2\text{C}^\text{Bu}_3)_2]$. [27] ($\text{La}^\text{III} = \text{TbIII, DyIII, HoIII, ErIII or TmIII and mdeH}_2$ is methyl diethanolamine) (shown in Fig. 7,
rather distorted from square-antiprismatic in (12). In fact there are two types, both eight coordinate, and described as distorted dodecahedral, and shown in Fig. 7, right.

A more axial geometry appears, in general, in those compounds with the highest \( U_H \) values, namely Blagg et al.'s [La(\(\text{H}^+\))] series [28] and Ishikawa's [Ln(\(\text{H}^+\))] series, where H\(_2\)Pc is phthalocyanine [8], which seems to favour the stabilisation of the highest magnitude \( m \) states relative to others, so creating a large thermal barrier to relaxation, as demonstrated by Rinehart and Long [29].

2.8. Thoughts on incomplete double cubanes

The formation of tea3\(^+\) and Rdea3\(^+\) butterflies has been reported for combinations of heavier lanthanides and Fe\(^{III}\), Mn\(^{II}\), and Co\(^{III}\) using the tea3 \(^+\) pro-ligand. This has involved room temperature reactions where components of acid, amino alcohol and lanthanide nitrate are reacted at room temperature, or with gentle heat. In (5) the acid was supplied as a pro-ligand instead of as the carbonate via a 3d metal triangle with the effect that Co\(^{III}\) was on the outer position of the compound. Perhaps there is a greater competition for the inner site, and the lanthanide is better protected there, so wins out, requiring this due to its higher coordination number. Only in (5) was base added, being required to deprotonate the acid, with the effect that we do not see a fully deprotonated tea3 ligand in any of compounds examined so far. This leads to somewhat reduced coordination modes compared to those seen for tea3\(^-\), e.g. 7.3.3.3.1 in (19) and 4.2.2.2.1 for (25)–(26), vide infra. For the Rdea3\(^+\) compounds (12) a similar synthesis was used, with the available ligands seemingly accommodating the reduced bonding of this ligand cf. teaH\(^-\). The most unusual set of compounds here are (10) and (11) with such a large structural change, depending on the lanthanide used. Unfortunately this exploration across the 4f series has not been tested for the others in this set of butterflies (1)–(10), only the "magnetically interesting" compounds being reported, so conclusions cannot be extrapolated.

Already we can see how these flexible ligands have stabilised structures with different, albeit similar sized, transition metals, including by modifying their own state of protonation. Furthermore different structures across the lanthanide series were stabilised, accounting for the change in size from La\(^{III}\) to Er\(^{III}\).

We now turn to larger ring structures and the even richer variety of bonding modes that they display.

3. Metallo-rings

3.1. Go large: [Fe\(^{III}\)\(_4\)Ln\(^{III}\)\(_4\)]

The largest 3d–4f cage yet discovered is the metallo-ring [Fe\(^{III}\)\(_4\)Ln\(^{III}\)\(_4\)\(\text{teaH}^\circ\)\(_2\)\(\text{O}_2\text{CCH}_3\)\(_8\)\(\text{H}_2\text{O}\)]\(_6\)NO\(_3\)\(_4\)16H\(_2\)O and MeCN (13) [30] (Ln\(^{III}\) = Sm\(^{III}\), Eu\(^{III}\) or Gd\(^{III}\), \( y = 11 \), and when Dy\(^{III}\), Tb\(^{III}\) or Ho\(^{III}\), \( y = 10 \) shown in Fig. 9. The synthesis is very similar to that of the incomplete double cubanes above, despite obvious topological differences, though there appears a direct correlation between the smaller carboxylate ligand with a larger resultant structure.

The [Fe\(^{III}\)\(_4\)] horse-shoes at either end of the structure, the whole of which could be thought of as two [Fe\(^{III}\)\(_4\)La\(^{III}\)\(_2\)] rings linked by two [Fe\(^{III}\)\(_4\)] chains, is held together by four 3.2.2.1.1 tea\(^-\) ligands, which are centred on each of the four inner metals and connect them to their two neighbours; this is a ubiquitous mode, though the only one found so far for tea\(^-\), rather than teaH\(^-\). In 3d–4f chemistry and is unusual because an O-donor is only bonding terminally, though there is some partial H-bonding to other OH functionalities. The occurrence of this mode across numerous topologies indicates co-ligands play a significant role in deciding the shapes of the metal cores, expectedly, since the amino-alcohols are flexible.
The two FeIII ions on the end of this ring are linked to one LnIII by a 3.2.2.0.1 teaH2 ligand, the protonated arm being unbound. The terminal FeIII and LnIII are also bridged by an acetate group 2.1.1, linking to a different FeIII, one of a bridging dimer on either side of the structure by a 3.2.2.1.1 teaH2, centred on the 4f metal. These 4f ions are also linked by an acetate group to the equivalent ion on the opposite side, forming two sets of cross-links (not shown) and so have a dodecahedral eight coordinate geometry, though this has not precluded SMM behaviour in the past. The key may be in the alignment and cancelling of the DyIII anisotropy axes, which are not co-parallel.

The two FeIII ions of each bridging dimer are linked by an acetate ligand and to adjacent lanthanides on either side by two 3.2.2.0.1 teaH2 ligands, so linking the two halves. (13) demonstrates the versatility of the triol ligand, which shows three distinct bonding modes depending on its form and to which metals it bonds.

In the six cases investigated, antiferromagnetic interactions were dominant, again signified by decreasing $\chi T$ products with temperature. The use of (Eu-13) and (Sm-13) enabled an S=0 ground state to be deduced as EuII, becomes diamagnetic at the lowest temperatures investigated and the even number of FeIII spins cancel out, hence antiferromagnetic FeIII exchange was postulated.

Based on Mössbauer investigations of (Dy-13) the DyIII–FeIII interaction was very small and the FeIII exchange dominates the magnetic behaviour.

3.2. Octa-ring: (CrIII-DyIII)

The use of CrIII is rather rare in 3d–4f molecular magnetism though recently has become a focus for isotropic magnetic refrigerants [31]. A beautiful example in amine-diol chemistry is the “square-in-butterfly” [CrIII4DyIII4(OH)4(mdea)4(N3)4(O2CCH2CH2OH)4]3CH2Cl2 (14) [32], from the reaction of DyIII(NO3)3 nH2O, pivalic acid, methylthioaniline (mdeaH2), NaN3 and CrIIICl3 in dichloromethane under an inert atmosphere, the oxidation of the transition metal taking place upon exposure to air. (14), shown in Fig. 11 as its otherwise identical MnIII cousin, vide infra, where Jahn–Teller effects will be discussed, is composed of four linked (CrIII-DyIII)2 units. These are themselves linked by a 3.2.2.1 mdeaH2 ligand, this being centred on the CrIII ion, and two pivalates that bridge between a lanthanide and two 3d metal neighbours as 2.1.1, N3 groups and O2CCH2CH2OH groups link adjacent lanthanides into an inner square, these lying in one plane, with a (CrIII2) butterfly lying above (two ions) and below (two more).

Extensive modelling and magnetic measurements were performed, the latter indicating anisotropy from non-superimposable magnetisation versus reduced field curves. From the Arrhenius plot, a $\mu_B$ value of 15 K was observed with hysteresis loops obtained below 1.1 K confirming this is unambiguously an SMM.

From these data we infer the presence of quantum-tunnelling by their stepped nature, features absent in measurements above 1.8 K. CASSCF/CASPT2 calculations were performed to obtain fits of the magnetisation data; for DyIII a satisfactory fit used the parameters $g_x = 1.7$, $g_y = 5.8$ and $g_z = 14.4$, and a negative $J$ value, indicating antiferromagnetic exchange between CrIII and other metal ions.

These significant transverse $g_x$ and $g_y$ values also contribute to significant QT. The avoided crossings observed in the energy spectrum for (10), are in agreement with the observed quantum tunneling steps in the single-crystal hysteresis data, shown in the upper panel of Fig. 10, for the variable temperature experiment, with the sweep dependent curves shown in the lower panel.

Both coordination and site symmetries play an important role in the SMM: CrIII is basically isotropic, owing to the octahedral geometry at each site but the DyIII ions, with $D_{5h}$ site symmetry, have significant anisotropies which have a none-zero sum.

3.3. Ringing the changes: (MnIII-LnIII)2

Using modifications of the above procedure, several close MnIII analogues of (14) were synthesised, though requiring ‘BudeH2, tert-butyli diethanolamine, and a selection of co-ligands and solvents. Formulated as MnIII4LnIII4(OH)4(Budea)4(X)2(O2CCH2Bu)4 solvent (15) [33] (LnIII is YIII, EuIII, GdIII, TbIII, DyIII or HoIII, $X = N_3^-$; with DyIII, $X$ may
also be $\cdot$OCN; and, where $X = \text{NO}_3^-$, GdIII, TbIII, DyIII, HoIII and ErIII analogues can be made with solvent being toluene or acetonitrile. The changing of the $N_1$ bridges from those seen in (10) does not change the overall structure, given in Fig. 11, though a change in prodgand from mdeaH$_2$ to BudeaH$_2$ is required.

All DyIII and TbIII compounds showed out of phase $\chi'$ frequency dependence, though energy barriers could not be obtained in the absence of maxima, invariance to applied d.c. fields, though, suggested QTM is absent. The lanthanide(III) ions are the source of this, as the anisotropy axes, arising from a Jahn–Teller elongation about MnIII will approximately cancel. The change in the amine-
diol ligands between (14) and (15) for the DyIII compounds should not significantly alter the magnetic properties in general, though the SMM behaviour are different. Further results may be needed to elucidate the reasons why.

### 3.4. Saddle-up: \(\text{Fe}^{III}_4\text{Dy}^{III}_4\)

The pair of structurally related \(\text{Fe}^{III}_4\text{Dy}^{III}_4\) and \(\text{Mn}^{III}_4\text{Ln}^{III}_4\) saddle-compounds were prepared using distinct amine-triol and diols, respectively, indicating a robust topology, which though superficially similar to (13) and (14), are quite distinct.

An octametallic “saddle”, incorporating the $N_2$ co-ligand, was made by allowing a refluxed solution of DyCl$_6$·6H$_2$O, FeCl$_3$, Na$_2$ and teaH$_3$ in methanol:acetoneitrile (1:2) to stand for 3 days, giving crystals of \(\text{Fe}^{III}_4\text{Dy}^{III}_4\text{(teaH$_3$)}_2\text{(N$_2$)}_2\text{(H$_2$O)}\) 4MCH$_2$H$_2$O (16) [34]. This is made up of alternating 3d and 4f ions, with one of the DyIII sites distinct by the bonding of a water molecule. The 4f ions are linked to their adjacent 3d neighbours by two teaH$_3^-$ ligands, on the inside and outside of the saddle (3.2.2.1.1 mode). H-bonding is extensive and is seen between each of the two $N_1$ ligands bound to each FeIII and the OH arm of teaH$_2^-$ and between the solvent water molecule protons and the O of teaH$_2^-$.

This structure is remarkable for its lack of large co-ligands, though its similarity to those seen above suggests these are not a significant factor, as long as coordination numbers can be filled.

---

[Fig. 11. \([\text{Mn}^{III}_4\text{La}^{III}_4\text{(OH)}_4\text{(Budea)}_4\text{(NH}_3)_4\text{(C}_2\text{H}_4\text{Bu})_4\text{(O}_2\text{C})_4\text{]}\text{(15)}\) Key: LaIII, purple spheres; MnIV, pink; O, red wireframe; N, blue spheres; C, carbonates grey wireframe, spheres for Budea C atoms; no H atoms or carboxylate `H groups are shown for clarity. See Ref. [33] for structural information.]

[Fig. 12. \([\text{Mn}^{III}_4\text{La}^{III}_4\text{(Budea)}_4\text{(O}_2\text{CH})_4\text{(OMe)}_4\text{(O}_2\text{C})_2\text{(C}_2\text{H}_4\text{Bu})_4\text{(Me}OH)_4\text{]}\text{(13)}\) Key: LaIII, purple spheres; MnIV, pale pink; O, red spheres ("Budea") and wireframe (OH and carboxylate—note only the inner ligands are therefore really formates); N, blue spheres ("Budea")-C, grey wireframe and spheres for carboxylate bridges and Budea; no H atoms or Et groups are shown for clarity. See Refs. [35,36] for structural information.]

The closed structures (rings and cubanes and partial chains) seen so far may be expected, as an organic coating encloses a metal core.

The isotropy of the octahedral FeIII simplifies the analysis of magnetic data: ferromagnetic interactions are implied by $\chi(\mathcal{T})$ measurements which, with magnetisation measurements, imply anisotropy, likely due to DyIII, as supported by Mössbauer studies. The capped square-antiprismatic geometry is theoretically not ideal for SMM behaviour, though, this compound is in fact an SMM, as shown by both a frequency dependence of $\chi'$ below 2.8 K and a temperature dependent regime in the Arrhenius plot, corresponding to an energy barrier of 30.5 K. SMM behaviour is confirmed by the presence of smooth hysteresis loops below 1.4 K, and so also show the lack of a QTM.

#### 3.5. Keep on riding: \(\text{Mn}^{III}_4\text{La}^{III}_4\)

\([\text{Mn}^{III}_4\text{La}^{III}_4\text{(Budea)}_4\text{(O}_2\text{CH})_4\text{(OMe)}_4\text{(O}_2\text{C})_2\text{(C}_2\text{H}_4\text{Bu})_4\text{(Me}OH)_4\text{]}\text{(17)}\) or \([\text{Ln}^{III}_4\text{Gd}^{III}_4\text{(Budea)}_4\text{(O}_2\text{CH})_4\text{(OMe)}_4\text{(O}_2\text{C})_2\text{(Me}OH)_4\text{]}\text{(18)}\) or \([\text{La}^{III}_4\text{Gd}^{III}_4\text{(Budea)}_4\text{(O}_2\text{CH})_4\text{(OMe)}_4\text{(O}_2\text{C})_2\text{(Me}OH)_4\text{]}\text{(19)}\) were synthesised using the lightest carboxylate, $\text{O}_2\text{CH}$, by combining MnIII(O$_2$(OEt)$_3$), sodium formate, LaIII(NO$_3$)$_3$·nH$_2$O and BudeaH$_2$ in methanol. An alternative preparation [36] gave the analogues with SmIII, TbIII, HoIII, ErIII and YIII. Similar in its saddle structure to (16), and shown in Fig. 12, this has alternating 3d and 4f ions where the diol bridges across an N-bonded MnIII and adjacent LnIII ions with a 3.2.2.1.1 mode.

One methanol bonds to each of the latter, and a methoxy group bridges between distinct hetero-metal pairs. The presence of two different carboxylates here and three distinct bonding modes is uncommon; an ethanoate bonds 1.1.0 to each 4f metal and bridges distinct hetero-metal pairs. Formate bonds with the 3.2.1 mode between two lanthanides and one MnIII. All of the 3d ions can be viewed in a plane, a difference to (11) that has a more marked distortion. Both compounds show decreasing $\chi$ T products with decreasing temperature, which could be assigned to anti-ferromagnetic coupling for (Gd-17) and possibly a combination of this and anisotropy effects for (Dy-17). Only the latter of
these two compounds is an SMM, though, suggesting the importance of the LnIII ion, with $T_{\text{onset}} = 12$ K. The stepped micro-SQUID hysteresis loops below 0.5 K indicate QTM is important at these low temperatures also confirming this as a true SMM. Later, SMM behaviour was observed in SmIII, TbIII and YIII analogues, the last rather interestingly as this must arise from the MnIII ions only, despite the alignment of their JT axes, as above, meaning that their anisotropies must almost cancel. Furthermore, SMM behaviour was curiously absent in the [MnIII4GdIII3] compound, which implies the anisotropy of the lanthanide(III) ions is playing a major role, despite the lack of a fine-tuning for each 4f metal, these being in a common environment.

3.6. The free-wheeling: [LnIII6]

The intriguing [LnIII6(teaH)6(NO3)6]·8MeOH [37,38] (LaIII = GdIII or DyIII) wheel, shown in Fig. 13, is formed by layering ether upon a solution of LnIII(NO3)3·H2O, triethylamine and teaH in MeOH. Remarkably, these small ligands are able to stabilise a hexametallacore by coating inside and outside the metal. teaH2− bonds across three lanthanides by linking adjacent metals to a central ion, then capping this with an OH arm and N, as is now familiar (3.2.2.1.1 mode), alternately above and below the plane. An H-bonded network is formed through the OH proton of teaH2− to the solvent MeOH O-atom through further solvents to a different teaH2− H-atom, so arranging three wheels. The wheel topology is rare in lanthanide chemistry, though examples of [LnIII6] have been previously reported [39]. This is also one of only two polymetallic 4f teaH2− compounds currently published, though the unusual SMM properties surely motivate further interest. However, the probable antiferromagnetic coupling in (Gd-18), which showed decreasing $xT$ at low temperatures and slow magnetisation rates, would likely be a hindrance to a large magnetoacoric effect at low applied fields. This behaviour was projected to (Dy-18), which showed intriguing SMM behaviour; the $x'$ plots being divergent at low temperatures, though no maxima were seen down to 2 K. The understanding of the magnetism of this compound was later expanded upon in an ab initio theoretical study that revealed, amongst other details, a non-magnetic, toroidal, ground state; i.e. the anisotropy axes of DyIII ions lie in the plane of the wheel, as was also seen in the celebrated [DyIII4] triangles of Powell [40]. This arrangement is more perfectly realised here and so the ground state spin is zero, i.e. S = 0 under zero-field, due to the $S_g$ symmetry of the molecule. An appreciable quantum tunnelling for each DyIII was ascribed to the significant transverse g-components supporting the experimental discovery of SMM behaviour only at low temperatures. In practice, such an arrangement is described as ideal for a robust qubit, though requires NMR investigations to elucidate to energy barrier of the degenerate toroidal ground states.

3.7. Thoughts on metallo-rings

In these later structures we find rather complex SMM behaviour. For instance, in (14) and (15) changing the 3d metal to MnIII apparently turns off the SMM behaviour compared to the GdIII analogue. (17) shows a remarkable intransigence to the lanthanide(III) ion, which appears the source of SMM behaviour considering its absence in the isotropic gadolinium(III) compound. Finally, (18) is one of a handful of toroidal spin examples with potentially fruitful technological applications.

4. Hepta-metallic discs

4.1. Cooler than thou?: [MnIII4LnIII2]

Hepta-metallic compounds are relatively common in 3d chemistry with examples known for Mn, Fe, Co, Ni and Cu [41–45]. In 3d–4f and teaH3 chemistry, though, they are rare, there being only a recent single example, namely [MnIII2LnIII4(tea)2(O2CtBu)12(H2O)2][H2O] [46] (LaIII = LnIII, NiIII or GdIII) as shown in Fig. 14. Amongst teaH2 and teaH3 compounds there are also very few prepared by solvothermal synthesis, as (19) is, though a common technique in molecular magnetism as a whole. Here, [MnIII2(O2CtBu)12(4-Me-py)2]2+ [H2O]2[ HO2CtBu]3, where 4-Me-py is 4-methyl-pyridine, is
combined with LnIII(NO3)3.nH2O, teah2, triethylamine at 120 °C in acetonitrile, where MnII is reduced in situ.

The planar disc is made up of alternating outer 3d MnII (confirmed by BVS) and 4f metals, around a central LnIII hub. A tea+ ligand is centred above and below on this hub, bridging with all three arms in an extensive 7.3.3.3.1 mode, each arm bonding between {LnII3MnII} triangles, giving the most coordinating tri-alcohol so far.

Six small groups bridge adjacent metals in 2.1.1 fashion around the edge of the disc, the remaining six with a 2.2.1 mode with one water molecule bound to each of the outer LnII s. All MnII ions are octahedrally coordinated, so S = 5/2, which, along with the high spin, S = 7/2, and isotropy of GdIII, should make this compound a useful magnetic refrigerant, not involving the general low densities of coordination compounds, a hindrance in that application.

Fitting the magnetic data of (Gd-19) with the anisotropic Hamiltonian (Eq. (3)), where D ≠ 0, gave g = 2.06, D = -0.011 cm⁻¹, expectedly small, and a large ground state spin of S = 17/2, where D is axial zero-field splitting (ZFS) and E is rhombic ZFS, with no J value reported.

\[ H = D \hat{S}_3^2 + E \hat{S}_x^2 + E \hat{S}_y^2 + g \mu_B S \cdot H \]  
(3)

Separately, using (La-19), and Eq. (4), below, the MnII exchange was reported as -0.2013 cm⁻¹, i.e. ferromagnetic, where g = 1.99, fitted above 50 K, to prevent ZFS from interfering with the fitting to susceptibility data. These results may prove rewarding in the quest for SMMs if the planned oxidation of the MnII ions to MnIII is successful.

\[ H = -2J \hat{S}_2 \hat{S}_5 + \hat{S}_1 \hat{S}_5 + \hat{S}_2 \hat{S}_5 \]  
(4)

What is most fascinating here is that the solvothermal technique results in the largest coordination mode yet found for a tea+ ligand, 7.3.3.3.1. This behaviour was previously seen with other triodal alcohol ligands to give more extensive bonding modes and may represent a future route to high performance MCE materials. The best materials require a low ligand to metal ratio so increasing the number of bonds that each ligand could improve matters in this regard. Other examples, though show that this synthetic strategy is not generally applicable, though, vide infra.

5. Two to Tango: dimeric 4f compounds

5.1. mdeaH2 and (LnIII3)

Dimeric structures represent simple compounds with which to investigate exchange interactions and there are three examples with amine-polyol ligands. The first is [LnIII(mdea)2(O3C)2Bu4] (20) [47] (LnIII = LaIII, CeII, PrII, NdIII, SmIII, EuIII or GdIII), shown in Fig. 15 in cutaway form, synthesised from refluxing of the appropriate LnIII(NO3)3.nH2O, mdeaH2 and pivalic acid in acetonitrile. This is made up of two pivalate bridged LnIII ions, two ligands bonding with the mode 2.2.1, two with a 2.1.1 mode and one capping each of the ions as 1.1.0. The mdeaH2 ligand caps on each ion with the 1.1.1 mode where the protonated arm H-bonds to the terminal carboxylate O-atom. Therefore, this is more of a capping than bridging ligand, likely due to the lack of base added and the ligand remaining doubly protonated, which reduces the extent of the bonding. The magnetic data of (Gd-20) were fitted using the Hamiltonian given in Eq. (1) above, finding a best fit of g = 2.03 and J = 0.605 K, an extremely small ferromagnetic interaction, in line with an increase in χT at very low temperatures.

For the other analogues the decreasing χT with decreasing temperature was not fitted, but could be ascribed to either antiferromagnetic interactions, depopulation of Stark levels, or both.

5.2. H3sabhe and (LnIII2)

[GdIII2(sabheH)2(NO3)2]2MEOH (21) [48] was synthesised from methanolic solutions of Gd(NO3)3.nH2O, sabheH2, and NaOH where here the addition of base appears to assist in increasing the coordination mode. (21), sabheH2, N-salicylidene-2-(2-hydroxyethyl)amino ethylamine, is shown in Scheme 1, and comprises a functionalised RdeAH2, where the R group is C6H4NCH2p-OH. One amine-diol arm bridges the two metals with one arm bonding terminally and H-bonding to solvent methanol. The phenol-OH simply bonds terminally to one LnIII, its bulk seemingly assisting in enclosing the dimer from further aggregation, so overall the mode is 2.2.1.1.1. The coordination sphere of the metals is fitted by a 1.1.1.0 nitrate. A decreasing χT product with decreasing temperature was assigned qualitatively to antiferromagnetic coupling and quantitatively to an exchange of J12 = -0.198 cm⁻¹, g = 1.975, from the single J Hamiltonian, different to those seen previously, and given in Eq. (5).

\[ H = -J_{12} \hat{S}_1 \cdot \hat{S}_2 \]  
(5)

5.3. teaH2 and (LnIII3)

[LnIII3(2teaH2)(tpaH)2(NO3)2] (22) [49] (LnIII = SmIII, GdIII, TbIII, DyIII or HoIII) and tpaH is triphenyl acetic acid, shown in Fig. 16, is formed from the solvothermal reaction at 100 °C of Ln(NO3)3.nH2O, teaH2, NEt3 and tpaH in acetonitrile. This type of synthesis is rare in teaH2 and RdeAH2 chemistry, despite the advantages of solubility and crystallinity that it can bring. The preparation is related to that previously reported for the (LnIII2) disc-like structures using the thmeH3 tri-alcohol ligand [50].

The metals are bridged by the deprotonated arm of teaH2 and the protons assigned by charge balancing considerations. The remaining donor atoms bond solely to each metal, giving the 2.2.1.1.1 mode of bonding. Each ion is therefore nine-coordinate in a rather low symmetry environment, which accounts for the lack of SMM behaviour. The steric bulk of the triphenyl acetate, conceptually similar to the sabheH2 employed in (21) may contribute to the relatively unusual bonding mode, both being rather restricted compared to other polymeric compounds. The nitrate and tpaH ligands cap both metals with two O atoms each.

Magnetic data were fitted using the Hamiltonian given in Eq. (3), finding a weak antiferromagnetic interaction of -0.114 cm⁻¹, hindering the magnetocaloric response, which shows a maximum -ΔS value of ca. 20 JK⁻¹mol⁻¹ at (AH = 0–7.7, 3 K).

Exchange between metals is dependent on the bridging angle between metals, though for (20) there are also alternative exchange pathways other than through the amino-polyalcohol ligands, so this may not be a straightforward analysis.
5.4. Thoughts: base versus bulk?

The above highlights an important synthetic challenge when using lanthanides. From our own failures and other reports, it is rather easy when using hydrated starting materials such as LnIII(NO3)3·nH2O to form insoluble precipitates when adding base, likely as the water is deprotonated and the resultant OH group bonds to more metals uncontrollably. So, whilst, the synthesis of high nuclearity clusters from teaH3 (or RdeH2) implies deprotonation of the ligand to give bridging O− groups, this must be done carefully. A different means of preventing the formation of the insoluble precipitates is the addition of bulky co-ligands, though this strategy can cap the formation of extended structures. This balancing act is clearly achievable, though may explain the lack of solvothermal success with these ligands, more energetic conditions being harder to tame.

6. Metallo-stars

6.1. Old: \(\{\text{Nb}^V\text{La}^III\}\) and new: \(\{\text{Mn}^III\text{Ln}^III\}\) and \(\{\text{Fe}^III\text{Ln}^III\}\)

An older and elegant gem is the first 4d–4f teaH3 compound, the metallo-star \(\{\text{Nb}^V\text{La}^III\text{(tea)}_2\text{(PrO)}_3\}\) (23) [51], although no magnetic properties were reported, as the metals are diamagnetic. The synthesis involves stirring \(\{\text{Nb}^V\text{(PrO)}_3\}\) and \(\{\text{H}_3\text{La}^III\text{tea}_2\}\) in toluene. The H3 atoms of the latter are reported as the hydroxo-functional of the tea2− ligand, presumably three H atoms distributed between the six arms of two ligands for charge balancing. The final product has three outer Nb^V diamagnetic ions as the points of the star, each capped by four terminal (PrO) groups. The two tea2− ligands have the 4.2.2.2.1.1 mode, centred on La^III, with one above and one below the plane. Whilst no analogous structures to (23) with paramagnetic 4f ions were reported, the first 3d–4f metallo-stars [52] are similar: \(\{\text{Mn}^III\text{Ln}^III\text{(tea)}_2\text{(acac)}_3\}\) and \(\{\text{Fe}^III\text{Ln}^III\text{(tea)}_2\text{(acac)}_3\}\) (24), shown in Fig. 17, left, and \(\{\text{Fe}^III\text{Ln}^III\text{(tea)}_2\text{(acac)}_3\}\) (25) (Ln^III = Gd^III or Dy^III in both cases). Synthesis was by refluxing [MIII(acac)]3, where MIII is Ln^III or Fe^III, Ln(NO3)_3·nH2O, teaH3 and triethylamine in methanol, with crystals grown from a dichloromethane: hexane solution. These structures are identical save for the additional [Mn^III(acac)]3.

unit in the former, and have the same tea3− arrangement and mode as in (23), visible as the polar ligands around the central ion, shown in Fig. 17, right; completing the octahedral environment of the 3d metals are two (acac)− ligands, bonding terminally (1.1.1.) to the outer metals, here, a balance of deprotonating the teaH3 and stoichiometric bulk has given a compact arrangement of metals with a large number of metals bonded to the amino-alcoholate. Despite the similar structures their magnetic properties are pleasingly distinct. For \(\{\text{Gd}^III-\text{24}\}\), using the isotropic Heisenberg–Hamiltonian in Eq. (6), \(J_{xy}\), the interaction between Mn^III and Gd^III, was weakly antiferromagnetic at \(-0.23\text{ cm}^{-1}\) and \(J_{xx}\), between Mn^III ions, a slightly stronger 0.56 cm\(^{-1}\), as fitted to \(\chi T\) data, which qualitatively agree with that for \(\{\text{Dy}^III-\text{24}\}\), though other effects of Stark level depopulation with decreasing temperature may account for this behaviour in the latter.

\[
\hat{H} = -2 \sum \langle \hat{S}_i \hat{S}_j \rangle 
\]

(6)

This means the Gd^III spins align opposite to that of the central ion, though this does not give an isolated ground state. The Fe^III compounds \(\{\text{Gd}^III-\text{25}\}\) and \(\{\text{Dy}^III-\text{25}\}\) show contrasting magnetic exchange; the former has \(J_{xy} = 0.73\text{ cm}^{-1}\) (between heterometals) and \(J_{xx} = -0.30\text{ cm}^{-1}\) (between like metals) giving an 5 = 11 ground state, i.e. where all spins are aligned. \(\{\text{Dy}^III-\text{25}\}\) was qualitatively similar. So far a.c. susceptibility studies are yet to be reported on these compounds, there being no other 3d–4f metallostars with which one could speculate upon the likely results, particularly the effect of the equatorial bonding on the SMM behaviour of the dysprosium[III] compounds.

7. Double cubanes

7.1. Christou’s \(\{\text{Mn}^III\text{Mn}^III\text{Ln}^III\}\)

Billed as the first 3d–4f double-cubane, \(\{\text{Mn}^III\text{Mn}^III\text{Ln}^III\text{(edteH)}_2\text{O}_2\text{CIBu}_2\text{H}_2\text{(NO}_3\text{)}_2\}\) (26) [53] (Ln=3Dy, Tb, Dy, Ho or Er and edteH = N,N,N’-tetraakis(2-hydroxyethyl)ethylenediamine) is shown in skeletal view in Fig. 18, left, and incorporates a functionalised amine-diol giving four possible OH groups to bond and two N-donors. The structure is related to the incomplete double cubanes seen above, but maintains the missing metal vertices, so giving a hexa-metallic compound, the core of which is shown in Fig. 13, right and lower. We find the edteH2 groups link the Mn^III corner metals, BVS calculations being used to assign the oxidation states, to both inner Mn^III ions and one Ln^III, with the mode 3.3.1 for each “half”, the first arm linking the hetero-metals, the second to only a Mn^III, to which the N also bonds. For the complete ligand this mode is 4.3.3.1.1.1.1. Oxygen atoms connect one Ln^III, Mn^III and both Mn^III

![Fig. 16. \(\{\text{La}^III\text{(tea)}_2\text{(tpa)}_2\text{(NO}_3\text{)}_2\}\) (22), where tpaH is tris(phenylacetylene) ethylene. Key: Ln^III, purple spheres; O, red spheres (teaH); N, blue spheres; C, grey wireframe; no H atoms or CP2H3 groups are shown for clarity. See future work [49] for structural information.](image1)

![Fig. 17. Left, a fragment of \(\{\text{Mn}^III\text{La}^III\text{(tea)}_2\text{(acac)}_3\}\) (24) showing \(\{\text{Mn}^III\text{La}^III\text{tea}\}\) only. Right, the ligand geometry around the central Ln^III ion. Key: Ln^III, purple spheres; Mn^III pink; O, red; N, blue; C, grey; no H atoms are shown for clarity. See Ref. [52] for structural information.](image2)
ions with a tetrahedral arrangement. Carboxylate groups join each lanthanide to two MnIII ions, each of these ligands bonding in 2.1.1 fashion between heterometals. A further carboxylate bond terminates to each lanthanide in 1.1.1 fashion, with a terminal NO3, 1.1.1, completing the nine-coordinate geometry, given in Fig. 18, right and upper. The double-N bonding of edteH2 may encourage a preference of this ligand for MnIII(III) rather than LnIII bonding.

Beautifully defined magnetic data were obtained from single-crystal studies of (Tb-26), the only SMM of this series, reproduced in Fig. 19, upper panel, shows hysteresis loops opening below 0.9 K (0.035 T s−1) with a multi-step structure. This shows a significant zero-field QT relaxation. At 0.04 K the loop was sweep rate dependent, indicating QTM, as shown in the lower panel of Fig. 19. The Arrhenius plot shows the distinct thermal and quantum relaxation processes at 0.3 K, the former giving an energy barrier of 20 K, modest but significant. The choice of lanthanide(III) ion is important here, suggesting a tuning of the coordination environment. The MnIII ions are believed to be unimportant in this regard, as they couple antiferromagnetically to give an S=0 state.

7.2. Powell’s FeIII-LnIII:

From the same ligand as above [FeIII4LnIII2O2(edteH)2(O2CCH2Cl2)·C6H5OH] ([26], [27]) has a similar formulation and structure to (26) though has a slightly more distorted metal core. Here, though, the edteH ligand bonds with a 4.2.2.2.0.1.1 mode where the OH ascribed is unbound to a metal, and directs an H-bonded 1D network. Each FeIII atom, which is bound to both the N-donor atoms in the poly-al ligand, making up the outer metals of the [FeIII4L] rhombus, is bonded to both the inner 3d metals and a lanthanide ion. Oxo ligands bridge between three metals of the rhombus directing triangular arrangements.

These compounds enabled a good understanding of the exchange interactions to be determined, by fitting to magnetic data. For (Y-27) using the Hamiltonian below (Eq. (7)) gave Fe–Fe interactions of JFeFe = −4.17 cm−1 (antiferromagnetic) and JFeLn = 1.1 cm−1 for g = 2.01. For (Gd-27) this was extended to the following Hamiltonian (Eq. (8)), giving JFeFe = −4.4 cm−1, JFeLn = 1.6 cm−1 and JFeFe-out-Ca = −0.12 cm−1, JFeLn-out-Ca = 0.24 cm−1.

\[
\hat{H} = -2J_{FeFe}(S_1 \cdot S_2 + S_3 \cdot S_4 + S_5 \cdot S_6) - 2J_{FeLn}S_1 \cdot S_5
\]

\[
\hat{H} = -2J_{FeFe}(S_1 \cdot S_2 + S_3 \cdot S_4 + S_5 \cdot S_6) - 2J_{FeFe-out-Ca}(S_1 \cdot S_3 + S_2 \cdot S_4)
\]

These competing FeIII–FeIII interactions were related to the bond length and bridging angle and matched with parameters from previous work. For (Dy-27) an energy barrier, Ueff, was 30.85 K in a d.c. field of 1200 Oe, though SMM behaviour was not seen for the other derivatives and so was assigned to the lanthanide ion. Mössbauer studies of these compounds revealed a trend of increasingly slow spin fluctuation from (Y-27) through (Gd-27) to (Dy-27).

7.3. Thoughts on double cubanes

From these two similar compounds the extra donor atoms of the edteH4 ligand appear not to give extensive increases in the coordination, compared to tridentateRe(aq) pro-ligands, or tetH4, despite its hexadentate nature. The propensity for the N atoms to anchor, here on the same atom, likely due to their proximity, may hinder the coordination and force the ligand to act as a capping group. Interesting is the change in protonation of this ligand to accommodate the charge balance, well demonstrating its flexibility, and also the change in bonding mode; although in the iron compound this is less protonated and the bonding is less extensive.
8. Double cubane variations

8.1. A former champion: \([\text{Mn}^{II}\text{Mn}^{IV}\text{Ln}^{III}]_2\)

\[
[\text{Mn}^{II}\text{Mn}^{IV}\text{Ln}^{III}\text{O}_2]\text{mdea}^2_4[\text{mdea}^2\text{H}_2\text{O}_2\text{Cu}^{II}\text{C}_8\text{Bu}_2\text{(NO)}_2]\text{L}_2[\text{H}_2\text{O}_2]\text{M}2\text{MeCN} (28) \quad [55]
\]

(\text{Lu}^{III} = \text{Th}^{IV}, \text{Dy}^{III}, \text{Ho}^{III} \text{or} \text{Y}^{III}) has an intriguing core comprised of vertex-joined \text{Lu}^{III}\text{Mn}^{III}\text{O}_4 \text{cubanes similar to (26), with a common Mn}^{II}, \text{and two additional Mn}^{IV} \text{ions bonded to two of the corner oxygen atoms.}

A common \text{Mn}^{IV} \text{links two} \text{[Lu}^{III}\text{Mn}^{IV}\text{Mn}^{III}\text{O}_4\text{]} \text{cubanes with two axes defined by} \text{[Mn}^{II}\text{Mn}^{IV}\text{]} \text{and [Lu}^{III}\text{Mn}^{III}\text{]} \text{planes. Outside of this are the} \text{extra two Mn}^{II} \text{ions, with aligned Jahn–Teller axes. O atoms linking these to the} \text{[La}^{III}\text{Mn}^{IV}\text{]} \text{ions and bonding to the cubane metals} \text{[La}^{III}\text{Mn}^{III}\text{]} \text{. These} \text{mdea}^2^+ \text{ligand bonds with the 4.3.2.1 mode joining a} \text{[Lu}^{III}\text{Mn}^{III}\text{]} \text{unit in the cubane with one arm and connecting the N-bonded} \text{Lu}^{III} \text{with the non-cubane Mn}^{III}. \text{For mdea}^2^+ \text{the unprotonated arm centres on the extra Mn}^{III}, \text{bending this with a cubane Mn}^{III}, \text{while the OH arm bridges with a Lu}^{III} \text{ion, NO}_2 \text{and H}_2\text{O groups bond to the lanthanide ions with pivalate groups bonding in 2.1.1 fashion between the cubane Lu}^{III} \text{ions and non-cubane Mn}^{III}, \text{and hetero-metals in the cubane, i.e. Mn}^{IV} \text{and Lu}^{III}. \text{These were the first 3d–4f compounds using mdea}^2_4\text{, with} \text{(Dy}^{III} \text{as the largest} \text{U}_{\text{eff}} \text{at the time for any 3d–4f compound, this being ca. 40K and significantly less for the other variants, particularly} (Y-28) \text{ (ca. 20K). Micro-sqaud single crystal measurements revealed QTMs, characterised by stepped hysteresis loops at 1.9K (0.002 T s}^{-1} \text{sweep rate). Though there are two distinct lanthanide(III) geometries, one a tricapped triangular prism, the other a distorted square antiprism, there appears only one} \chi' \text{ maximum. This may suggest only one ion is playing a role in the slow relaxation, though this must be in concert with the Mn}^{III} \text{ions.}

8.2. Thoughts on double cubane variations

This familiar pattern of the dysprosium compound showing the largest \(U_{\text{eff}}\) in a series is likely due to \(Dy^{III}\)’s status as a Kramers ion (with an odd number of electrons), whereby the ground state is always bi-stable in any crystal field environment, though not necessary optimised to separate the high magnitude \(m_l\) states from others. This is not true for \(Th^{IV}\) and \(Ho^{III}\), where symmetrical ligand environments are required, deviations impinging on the relaxation mechanism. In that sense it is “easier” to make a \(Dy^{III}\)-based SMM especially when the ligand geometry cannot be controlled as is the case with such flexible ligands. There is also a broader point about all of the compounds measured and analysed in this review. It is debatable, indeed unlikely, that any researchers have achieved the necessary degree of “control” over the ligand geometry that is the key for SMM optimisation; these ligands are amongst the most flexible families in the literature, along with phosphonic acids, perhaps, so this control is extremely difficult and probably impossible, in this context. The search for high performance SMMs, then, with these ligands, involves a good degree of luck. Lifting this somewhat gloomy outlook, as we move to the second section of this review, is the fact that there are very few ligands that can achieve reliable metal-topology control in molecular magnetism as a whole; there is still a certain alchemy in the synthesis of most SMMs and a hit-and-hope approach, we believe.

9. Lanthanides and copper

9.1. Le Corbusier’s choice?: \([\text{Cu}^{II}\text{Lu}^{III}\text{O}_2\text{TeaH}^2_4\text{OMe}^2\text{C}_8\text{Bu}_2\text{(NO)}_2]\text{L}_2\text{M}2\text{MeOH} 2\text{Et}_2\text{O}\)

The search for compounds with high-spin and low anisotropy as magnetic refrigerants led to several investigations with \(Cu^{III}\)

\[\Delta S_{\text{up}} = 31 \text{ J kg}^{-1} \text{K}^{-1} \quad \Delta H_{\text{A}} = 9, 3 \text{ K for (Gd–29) going alongside a large } \Delta T_{\text{A}} \text{, one of the largest for any molecule.}

The SM behaviour of the anisotropic variants revealed small energy barriers using a non-conventional (non-Arrhenius) method, giving \(U_{\text{eff}}\) at 12.7 and 10 K for (Th–29), (Dy–29) and (Ho–29) compounds, respectively.

Amusingly, for (Gd–29) a fitting of magnetic data using the Hamiltonian in Eq. \((9)\) revealed that the \((\text{Cu}^{III}–\text{Gd}^{III})\) was actually antiferromagnetic, though competing \(\text{Cu}^{II}–\text{Cu}^{II}\) interactions and ferromagnetic \(\text{Gd}^{III}–\text{Gd}^{III}\) coupling were also observed, so the explanation is not straightforward.

\[
\hat{H} = - \sum (\hat{s}_i \cdot \hat{s}_j)
\]  

Further study with (Dy–29) revealed dominant weak ferromagnetic coupling though this is composed of several different interactions, namely a rather complicated coupling scheme with the Hamiltonian given below (Eq. \((10)\)) with each spin operator
given using the numbering system shown in Fig. 20.

\[
H = -J_1(S_1S_2 + S_1S_3 + S_1S_5 + S_2S_5 + S_2S_6 + S_3S_5 + S_3S_6 + S_5S_6) \\
+ S_2S_4 + S_3S_4 + S_4S_5 + S_4S_6 - J_2(S_3S_4 + S_4S_5 + S_4S_6 + S_5S_6) \\
- J_3(S_1S_2 + S_3S_5)
\]

(10)

In contrast to this, the expected ferromagnetic CuII–DyIII interaction was present, \(J = +1.0 \text{ cm}^{-1}\), with competing interactions between inequivalent pairs of CuII ions of +1.3 and −4.6 cm\(^{-1}\), though the DyIII–DyIII interaction was negligible. Despite the differences these compounds vindicate LnIII–CuII teah\(_3\) compounds both as an approach to molecular refrigerants, using GdIII, and as SMMs, where anisotropic lanthanides are included.

10. Why so Serious?

10.1. \(\text{BudaH}_2\) and \(\text{CeIIIVIII}_\text{MnIII}\)

\[
\text{[Ce}^{\text{IV}}\text{VIII}_{\text{CeIIIVIII}}\text{MnIII}_2\text{O}_9\text{(Buda)\_2}\text{(O}_2\text{CBu})_2\text{(NO}_2)_3\text{]}\text{]}_2\text{[O}_2\text{CCCH}_3\text{]}_2\text{]}
\]

\[
4\text{CH}_2\text{Cl}_2
\]

\[\text{Ce}^{\text{IV}}\text{VIII}_{\text{CeIIIVIII}}\text{MnIII}_2\text{O}_9\text{(OH)}\text{(Buda)\_2}\text{(O}_2\text{CBu})_2\text{]}_2\text{(NO}_2)_3\text{]}_2\text{[O}_2\text{CCCH}_3\text{]}_2\text{]}

[1.5MeCN (31) and \(\text{Ce}^{\text{IV}}\text{VIII}_{\text{MnIII}}\text{O}_4\text{(Buda)\_2}\text{(O}_2\text{CBu})_2\text{(NO}_2)_3\text{]}\text{]}_2\text{[MeCN]}_2\text{]}

These are amine-diol compounds amongst several \(\text{Ce}^{\text{IV}}\text{VIII}_{\text{MnIII}}\) structures prepared \([58]\), these being subject to single crystal XRD and other characterisation techniques. Similar preparations were used for each of these, namely stirring \(\text{Mn}^{\text{III}}\text{(O}_2\text{CCCH}_3\text{)}_2\text{H}_2\text{O}\) \(\text{Ce}^{\text{IV}}\text{VIII}_{\text{NO}_2}\text{]}_3\text{]}\text{]}_2\text{[H}_2\text{O}\) pivalic acid and the appropriate \(\text{Mn}^{\text{III}}\text{H}_2\text{O}\), in varying ratios. \(\text{[32]}\) also requires the addition of \(\text{[NO}_2\text{]}_3\text{]}\text{]}_2\text{[Ce}^{\text{IV}}\text{VIII}_{\text{NO}_2}\text{]}_3\text{]}\text{]}_2\text{[H}_2\text{O}\). As these have no magnetic studies attached they will only be described briefly:

The first of these, \([30]\), is based around a \(\text{Ce}^{\text{IV}}\text{VIII}\) octahedron, where N-bonded MnIII ions are linked to an equatorial CeVII by a \(\text{Buda}^{\text{II}}\) ligand, which bonds this same 3d metal to an equatorial CeVII, hence the 3.2.2.1.2 mode. The MnIII–N bond defines the Jahn–Teller axis. The second compound \([31]\) also displays the 3.2.2.1.2 mode, the amino-alcoholate centred on both a MnIII, bridging to two lanthanides and the remaining four ligands centred on a lanthanide, bridging to two further lanthanides. The last, \([32]\), also shows the 3.2.2.1.2 mode, centred on a MnIV, through which a N\(=\text{Mn}^{\text{IV}}\text{N}\)–O\(=\text{Jahn–Teller}\) axis is defined.

10.2. \(\text{mdexH}_2\) and \(\text{CeIII}\)

\[
\text{NaCeIII}_{\text{mdexH}_2}\text{O(NH)}_2\text{(OH)}\text{[b}(\text{O}_4\text{CH}_2\text{OH})]\text{[mdexH}_2\text{CH}_2\text{OH}]}_2\text{[H}_2\text{O}\text{]}
\]

\[\text{[NaCeIII}_{\text{mdexH}_2}\text{O(NH)}_2\text{(OH)}\text{[b}(\text{O}_4\text{CH}_2\text{OH})]\text{[mdexH}_2\text{CH}_2\text{OH}]}_2\text{[H}_2\text{O}\text{]}\quad \text{(33)}
\]

\([\text{b} = \text{iso-suberate}]\) was characterised structurally only, having been synthesised from the starting material \(\text{Ce}^{\text{IV}}\text{VIII}_{\text{mdexH}_2}\text{CH}_2\text{OH}, \text{mdexH}_2\text{, sodium iso-suberate and acetonitrile using the uncommon reaction method of ultra-sonication. This can be thought of as having a cerium(III) hexanuclear core capped by a (CeIII)Na} \text{tetrahedron. Briefly, these are three bonding modes of mdex}\text{\textsuperscript{a}}, \text{three of the five ligands displaying the 3.2.2.1.2 mode to a trio of cerium ions, and two with the 4.3.2.1 mode, though one of these bonds a sodium ion onto the hight denticity arm. An exciting prospect for all these compounds from the 4f perspective, would be the inclusion of more magnetically "interesting" ions, such as Dy\text{\textsuperscript{III}} or Gd\text{\textsuperscript{III}}, though these would require changes in ligands to balance charges where CeIV is involved.}

11. Tea for one

11.1. Monomeric \(\text{teah}_3\) compounds

A number of monomeric lanthanide(III) compounds with various forms of \(\text{teah}_3\) ligand have been recorded over the past 25 years or so. Several of these contain fully protonated \(\text{teah}_3\) bonding to a single metal, the charge being balanced by various anions, for example \(\text{[La}^{\text{III}}(\text{teah})_3\text{(Cl}_2\text{SO}_4)_3\text{]}\text{]}_3\text{THF} \quad \text{(34)} \\text{[La}^{\text{III}}\text{Pr}^{\text{III}}, \text{Yb}^{\text{III}} \text{or Lu}^{\text{III}}, \text{and THF is tetrahydroduran]}\text{]}_\text{was synthesised by Hahn and Mohr by partial replacement of a labile triflate with \(\text{teah}_3\) in THF. These have a nine co-ordinate capped square-antiprismic geometry, due to the two amino-alcohol ligands bonding with the 1.1.1.1.1 mode and a single THF. This is related to \(\text{[La}^{\text{III}}(\text{teah})_3\text{(NO}_3)_2\text{]}\text{]}_2\text{N}_{\text{O}}\text{]}_\text{3} \quad \text{(35)} \\text{[La}^{\text{III}}\text{Hf}^{\text{III}} \text{and Lu}^{\text{III}} \text{were synthesised by high pressure synthesis.}}\]
adjacent lanthanides; and a second 3.2.2.0.1 mode where the iron is bridged to heterometals. \((O_2CBu)\) groups show diversity in their bonding, too, with two bridging pairs of lanthanides, three bridging pairs of iron, and capping groups with the modes 1.1.1 and 1.1.0 to lanthanide ions. Nitrites cap 1.1.0 iron ions and there is also one water on each of one iron(III) and one dysprosium(III). Magnetic data were ambiguous regarding the interactions within this compound, with an explanation for the increase in \(\chi/T\) at low temperatures being sought with \(^{57}\)Fe Mössbauer spectroscopy, which showed an antiferromagnetic exchange between these 3d ions and a ferromagnetic exchange between the Dy\(^{III}\) ions.

13.2. \([\text{Fe}^{III}_{7}\text{Dy}^{III}_{3}]\)

\([\text{Fe}^{III}_{7}\text{Dy}^{III}_{3}(\text{OH})_{2}(\text{mdea})_{2}(\text{tea})_{2}(\text{teaH})_{3}(\text{O}_{2}\text{CCH}_{3})_{4}(\text{N}_{3})_{6}]\) \(2\text{H}_{2}\text{O} 7\text{CH}_{3}\text{OH}\) (42), a decametallic cage, was formed from melt-solutional syntheses of \(\text{Fe}^{III}\text{Cl}_3\), \(\text{Dy}^{III}\text{Cl}_3\) \(6\text{H}_{2}\text{O}\), \(\text{Na}_3\text{benzoic acid and mdea}_2\), growing crystals from the reflexed mixture. Each ion is unique in the crystal structure, which is based around a \([\text{Fe}^{III}_{7}\text{Dy}^{III}_{3}]\) core, where \(O\) bridges \([\text{Dy}^{III}_{2}\text{Fe}^{III}_{2}]\) units. OH groups link the outer \([\text{Dy}^{III}_{2}]\) part of this core to an outer \(\text{Fe}^{III}\) which is linked in turn by a \(\text{mdea}_2\) ligand to a different \(\text{Fe}^{III}\) and one of the core \(\text{Dy}^{III}\) ions. All \(\text{Fe}^{III}\) ions have an \(\text{mdea}_2\)-ligand centred on them, all with the 3.2.2.1.1 mode. Three \text{mdea}_2- groups link \([\text{Fe}^{III}_{7}\text{Dy}^{III}_{3}]\) units, and four link together \([\text{Dy}^{III}_{2}\text{Fe}^{III}_{4}]\) parts of the structure, which also incorporates benzolate groups bridging hetero-metals. Six \(\text{N}_3\) ligands bond terminally to all 3d metals with the exception of one "core" iron. The energy barrier, \(U_{\text{eff}}\), for this SMM was ca. 33 K, with no quantum tunnelling observed from the single crystal experiment in an applied field, though this effect was present when \(H_{\text{app}}\) = 0, and there was hysteresis below 2.0 K (0.035 T \(^{-1}\)). Mössbauer studies were also able to establish a barrier to relaxation below 35 K. Rationalising the rather low barrier value one may point to the slightly distorted square-antiprismic geometry around the lanthanide(III) ion, with a range of bond lengths.

13.3. \([\text{Mn}^{III}_{5}\text{Dy}^{III}_{4}]\)

The hepta-decametallic cage \([\text{Mn}^{III}_{5}\text{Dy}^{III}_{4}\text{OH}]_2(\text{tea})_2(\text{teaH})_2(\text{O}_{2}\text{CCH}_{3})_6(\text{N}_{3})_6(\text{H}_{2}\text{O})_4\cdot 3\text{MeCN}\) (43), which shows signs of SMM behaviour at low temperatures is synthesised from \(\text{Mn}^{III}(\text{NO}_3)_2\cdot 4\text{H}_{2}\text{O}\) \(\text{Dy}^{III}(\text{NO}_3)_3\cdot n\text{H}_{2}\text{O}, \text{sodium acetate, triethylamine and teaH}_2\), which were stirred in methanol:acetone with crystals obtained from the ether layer. Solution. That slight variations in synthesis can lead to large differences in topology should now be apparent, which we could rationalise here by the sterically small ligands unable to stabilise a relatively low nuclearity structure by encapsulation.

One way to represent the structure is to see it as based around an almost planar \([\text{Mn}^{III}_5\text{Lan}^{III}_4]\) disc. Linked to this and offset above and below is a \([\text{Lan}^{III}_5\text{Mn}^{III}_5]\) triangular based pyramid with outlying \(\text{Lan}^{III}\) atoms almost in the disc plane on either side giving the seventeen metal core, held together by \(O\) and \(OH\) ligands, pivots and \(\text{tea}\) and \(\text{derivatives. N}_3\) and \(\text{H}_2\text{O}\) groups are only terminal here. Depending on how deprotonated the \(\text{tea}\) ligand is, there are three different bonding modes are seen, namely the highly coordinating 3.2.3.2.1.1 for \(\text{tea}^-\), which joins a basal "pyramidal" \(\text{Dy}^{III}\) with a planar and basal \(\text{Mn}^{III}\) to a planar \(\text{Dy}^{III}\), and to an apical \(\text{Dy}^{III}\). 3.2.2.1.1 for \(\text{teaH}^{2-}\), these joining a "disc" \(\text{Dy}^{III}\) to adjacent "disc" \(\text{Mn}^{III}\) ions; and 2.2.1.1.1.1 for \(\text{teaH}_2\), these linking an outlying \(\text{Dy}^{III}\) to a disc \(\text{Mn}^{III}\), repeated for the apical \(\text{Dy}^{III}\) of the pyramid unit, all having \(\text{N}_3\)-\(\text{Dy}^{III}\) bonding. \(\chi(T)\) is constant down to 25 K before increasing significantly from a room temperature value of \(132\) cm\(^{-1}\) mol\(^{-1}\) K (in line with that expected for uncoupled ions) to a \(3\) K value of \(211\) cm\(^{-1}\) mol\(^{-1}\) K. This would imply ferromagnetic interactions.
between ions, though the decrease in $\chi_T(T)$ below this temperature also suggests some antiferromagnetic interactions (or a depopulation of Stark sublevels) are present. Quantifying the SMM behaviour of (43) was hindered by the lack of maxima in $\chi'$, even at low temperatures in the a.c. susceptibility experiment.

13.4. Organometallics: [$\text{Mn}^{III}_5\text{Nd}^{III}_4$]

Taking a larger 3d starting material, here [$\text{Mn}^{III}_2\text{Mn}^{III}_2\text{O}_2$ ($\text{O}_2\text{C} \text{Bu})_1$]4-(4-Me-py)$_3$((HO$_2$C)Bu)$_1$] (44) [69] and reacting this with $^8$$\text{BudeaH}_3$, $^8\text{Nd}^{III}$(NO$_3$)$_3$·nH$_2$O and ferrocene (Fe$^{III}$) dicarboxylic acid (fcdcH$_2$) in acetonitrile gave the [$\text{Mn}^{III}_2\text{Nd}^{III}_4$(OH)$_4$($^8\text{Budea}$_4)(\text{fcdc})$_2$($\text{O}_2\text{C} \text{Bu})_8$]·H$_2$O square-wheel, which is an almost planar arrangement of a 4f square inside a 3d one. Pivalate groups frame the whole by bridging adjacent pairs of metals in 2.1.1 fashion and $^8$Budea$^{2-}$ centres on the corner Mn$^{III}$ ions and bridges between this and the neighbouring lanthanides in a 3.2.2.1 manner. OH groups centre between two inner Nd$^{III}$ ions and a corner Mn$^{III}$. One fcdc$^{2-}$ sits above and another below the metal core, only bonding to Nd$^{III}$ ions via the carboxylate groups. Interestingly this gives three different coordination numbers of 8, 9 and 10 for each Nd$^{III}$. The $\chi_T$ (behaviour) at low temperature, signifies a rapid low temperature decrease that suggested overall antiferromagnetic interactions, though cautioned by the anisotropy of the Nd$^{III}$ ion. Further investigations will seek SMM behaviour, perhaps with Dy$^{III}$ and Tb$^{III}$ ions as the Mn$^{III}$ anisotropy is expected to be very small as their Jahn–Teller anisotropy axes will cancel out, from geometrical considerations. Nevertheless, the combination of conventional molecular magnetism synthesis with an organo-metallic staple (fcdcH$_2$), thus this basically acts as a “conventional” dicarboxylic, shows promise. Whether the Fe$^{III}$ ion can be replaced by a more anisotropic ion is a further question to ponder. Furthermore, the large differences in geometry at the metals would make a very interesting test for resolution of any differences in relaxation at each individual site, already seen for at least two different coordination environments in Dy$^{III}$ compounds.

13.5. Similar but different: [Fe$^{III}$(L$_{n}$)$_{8}$] and [Mn$^{III}$(L$_{n}$)$_{8}$]

A series of analogous complexes, using Fe$^{III}$ and Mn$^{III}$ is the tridecametallic [$\text{Mn}^{III}_5\text{Ln}^{III}$(OH)$_2$(Rdea)$_4$ ($\text{O}_2\text{C} \text{Bu})_1$]$_2$$(\text{NO}_3)$(O$_2$CCH$_3$)$_4$]$_2$·nH$_2$O, where Mn$^{III}$ is Mn$^{III}_5$ [70] (Lu$^{III}$ is Pr$^{III}$, Nd$^{III}$, Sm$^{III}$, Gd$^{III}$ or Tb$^{III}$, R is ‘Bu’ or Fe$^{III}$ [46] [71] (Lu$^{III}$ is Pr$^{III}$, Nd$^{III}$ or Gd$^{III}$, R is ‘Bu’ (Fig. 22). Despite the similarities in the structure, the syntheses are different, though they could be viewed as having the same parts in a different order. (45) requires addition of the ‘BudeaH$_3$’ ligand in acetonitrile to Mn$^{III}$(OAc)$_2$. 4H$_2$O, Ln$^{III}$(NO$_3$)$_3$·nH$_2$O and pivalic acid in acetonitrile and stirring at room temperature. Crystals were grown from the filtered mixture. For (46), the source of Fe$^{III}$ and pivalate was ($\text{Fe}^{III}$(O$_2$C$_2$Bu)$_2$(H$_2$O)$_2$)(O$_2$C$_2$Bu)$_2$, which was stirred with NaOAc:3H$_2$O, $^8$BudeaH$_3$ and Ln$^{III}$(NO$_3$)$_3$·nH$_2$O in acetonitrile, giving crystals directly.

The tri-decametallic topology common to both is based around a core of vertex sharing triangular-based pyramids, where only their common vertex is a Mn$^{III}$, other ions being lanthanides. This is bonded to by two of the “basal” lanthanides making up triangles of (Lu$^{III}$,Mn$^{III}$). These are themselves linked by a common lanthanide vertex. The four triangular faces of the pyramid are capped by OH groups, which also centre the aggregated triangles. Pivalate groups “frame” the structure, all bonding 2.1.1. (46) was in fact the first 3d–4f compound incorporating $^8$Budea$^{2-}$ in 2007. Viewing this compound such that it appears as a “rectangle”, four Rdea$^{2-}$ ligands centre on each of the corner 3d transition metals, bonding with the mode 3.2.2.1, as previously seen (see Scheme 1) to two lanthanides. Nitrates adopt a familiar role in capping 1.1.1.0 onto the innermost pyramid-type lanthanides.

Comparing the magnetic properties of these two series we find the following: The Mn$^{III}$ compounds were synthesised in the hope of finding SMM behaviour lacking in any Fe$^{III}$ derivative. Unfortunately this was unsuccessful and ascribed to the amusingly named “magnetic death zone”, a region whereby the Mn$^{III}$(O$_2$C$_2$Bu)$_4$ and Lu$^{III}$(O$_2$C$_2$Bu)$_4$ bond angles and lengths lead to extremely weak interactions between spins, behaviour which was extrapolated from the Gd derivative of the Fe$^{III}$ and Mn$^{III}$ compounds, where $\chi'$ increases only at low temperatures, signifying overall weak ferromagnetic coupling. In neither case, though, were any fits of the magnetic data to a spin coupling model obtained. Also, this does not explain why single-ion effects were not apparent, as individual lanthanide(III) ions can produce enormous energy barriers, though the dysprosium(III) compound was not prepared which is the most likely candidate.

13.6. Mixing it up

Recently demonstrating that combinations of conceptually similar ligands can be profitable is (47) [72], [$\text{Mn}^{III}_2\text{Nd}^{III}$(O$_2$C$_2$Bu)$_2$(thme)$_2$(teal)$_2$], where thmeH$_3$ is tris(hydroxymethyl)ethane and Lu$^{III}$ is Pr$^{III}$–Dy$^{III}$ and Eu$^{III}$. There are two separate tripod alcohol ligands employed here to give a structure made up of a bipacap Mn$^{III}_2$Lu$^{III}_2$ defect cubane. Although neither of (Tb$^{III}$–Gd$^{III}$) or Dy$^{III}$ show confirmed SMM behaviour, the presence of frequency-dependent signals in the a.c. susceptibility suggest these may behave as such, at lower temperatures. The bonding mode of Teal$^{2-}$ is seen elsewhere, being 2.2.1.1.1 and centred on a Lu$^{III}$ ion.

13.7. Thoughts on cages

The myriad cages here demonstrate how many different topologies and shapes of cages could be waiting to be discovered. Particularly interesting is the use of organometallic ligands, which could open up interesting new avenues to explore.
14. Conclusions

We hope to have shown that the ligands 1H2 and 1Hd2 are extremely versatile, flexible and so are useful tools in the synthetic chemistry of hard metal ions, leading to a wide variety of structurally diverse and topologically interesting molecules. These have shown how a single ligand can bond up to seven ions and down to a single one. This could lead to promising magnetocaloric materials, where the ligand to metal ratio is crucial in determining the usefulness of such compounds. One problem here may be a lack of control of the magnetic exchange, which is not just a limitation of polyaminoalcolholates, though. When one considers SMMs, further downsides of these ligands become apparent, for instance, manipulating the exchange between spins, or the alignment of MnH aniostropy axes, as factors such as the length of the pendant arms, variable donor–atom–metal interactions and variations in denticity make targeted syntheses conceptually difficult.

We have described some indications as to why certain compounds show such slow relaxation though more work is clearly required on several more compounds to understand this, through factors of exchange interactions, molecular symmetry and coordination geometry. We remain far from truly being able to tailor reliably in most areas of molecular magnetism, and especially when there is also the complication of such flexible ligands.

These topological problems are challenges that we feel will not be met by these ligands. Nevertheless several important results have been made incorporating them, such as high performance refrigerants and energy barriers, LFER in SMMs, up to ca. 170K (Dy9). There are also problems of assessing why 3d–4f or 4f SMMs behave in the way they do whilst square anti-prismatic geometries are generally favoured in Dy9 and Th9 SMMs, the discovery of one does not lead to the other. This is because there are far too many parameters hidden behind such a facile description, which describe the crystal field and simplistic descriptions often hide quite substantial distortions from the “real” geometry. These ligands also have none of the redox chemistry that promises so much in the improvement of hysteresis temperatures in lanthanide(I1) SMMs [29]. Whilst we could go on, we should perhaps merely say that these ligands are fun for chemists, who probably just want to make something with a new structure, but less so for physicists who may know what they want.

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References

Chapter 9: Paper 6

Lanthanide(III) triethanolamine dimetallic compounds with bulky carboxylate ligands and the magnetocaloric effect

Joseph W. Sharples, Lois R. Lindley, Nicholas F. Chilton, Floriana Tuna, Adam N. Swinburne, Louise S. Natraj and David Collison, manuscript in preparation.
Lanthanide(III) triethanolamine dimetallic compounds with bulky carboxylate ligands and the magnetocaloric effect

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A series of lanthanide(III) dimetallic compounds, [LnIII(teaH3)(tpa)(NO3)2], where LnIII = SmIII, EuIII, GdIII, TbIII, DyIII or HoIII, teaH is triethanolamine and tpaH is triphenyl acetic acid, were synthesised from solvothermal reactions and their physical properties investigated. The bulky carboxylate appears to stabilise and encapsulate the small core. The GdIII is triethanolamine and tpaH is triphenyl acetic acid, were synthesised from solvothermal reactions and their physical properties

Murray

magnetic entropy change, −ΔS, being that much smaller than for polymeric materials, along with

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Highlights include the {Cu2 or tris(hydroxymethyl)ethane, being similarly useful [5].

particularly well explored [4], with the related proligand thmeH

proposed as excellent candidates for this application, owing to

aggregation of reactants, they may still provide useful instruction on the effects of magnetic coupling and anisotropy on −ΔS. Importantly, there is a possibility of tuning the metal interactions for specific applications, by ligands, which may be harder in alloys and intermetallic compounds.

Distinct from these, basically isotropic, refrigerants are anisotropic single-molecule magnets (SMMs) [13]. Much work on LnIII compounds has found that these can outperform 3d transition metal compounds in terms of their anisotropy barriers, Ueff, and hysteretic temperatures.

We sought to synthesise homometallic 4f-teaH3 compounds to investigate these properties, continuing our work which gave the first 4f-tripodal alcohol (thmeH3) compounds, {LnIII} disc-like structures [14], using solvothermal synthesis. Here we report the synthesis, structure and physical properties of a family of [LnIII(teaH3)(tpa)(NO3)2] compounds, where LnIII = SmIII (1), EuIII (2), GdIII (3), TbIII (4), DyIII (5) or HoIII (6). These were studied for their MCE response (3), luminescent properties (1), (2), (4) and (5) and, as was discovered, non-existent, SMM behaviour (4)-(6). An electrostatic model was used to interpret this in (5) with a discussion of the emission data from which we could extract information on the energies of states in the 4f15/2 and 5f14/2 (ground) multiplets of (5) and (6), respectively.

2. Experimental Section

The synthesis is related to that of the heptametallic lanthanide discs [14] and is given in Figure 1. The appropriate lanthanide nitrate hydrate is reacted with teaH3, NEt3 (triethylamine) and tpaH in acetonitrile at 100 °C for 12 hours, i.e. thmeH3 is simply replaced by teaH3, cooling giving crystalline material (for more details see Supplementary Information and S. I. 1).
Fig. 1. Reaction scheme showing [Ln(III)(NO₃)₃]·nH₂O; teaH₂, tpaH and NEt₄ in MeCN reacting solvothermally at 100 °C to give [Ln(III)(teaH₂)(tpaH)₂(NO₃)₃].

Fig. 2. The dimetallic [Ln(III)(teaH₂)(tpaH)₂(NO₃)₃]. Key: LnIII purple spheres; O red wireframe; C grey wireframe; N (teaH₂) blue spheres; N (NO₃) blue wireframe; No H atoms are shown for clarity.

Whilst that reaction was rather robust to changes in amounts of thmeH₃, added, this seems to be rather sensitive to the concentration of teaH₂, with larger amounts giving amorphous insoluble material, perhaps because of the basic nature of the ligand N-donor. In line with this is the sensitivity of this reaction to the rate of addition of base and amino-alcohol. If these are added slowly then the reaction fails, giving unidentified triethanolamine ligands are assigned by charge balancing to the rate of addition of base and amino-alcohol. If these are added, this seems to be rather sensitive to the concentration of teaH₂, larger amounts giving amorphous insoluble material, perhaps because of the basic nature of the ligand N-donor. In line with this is the sensitivity of this reaction to the rate of addition of base and amino-alcohol. If these are added slowly then the reaction fails, giving unidentified triethanolamine ligands are assigned by charge balancing.

3. Characterisation and structure

3.1 X-ray Diffraction of (3) and (5) and Powder X-ray Diffraction of (1)-(6)

Both (3) and (5) crystallise in the triclinic crystal system, with the structure solved in the P-1 space group for each. Hence half of the molecule forms the asymmetric unit (shown in S. I. 2) with each lanthanide ion being crystallographically equivalent.

The basic structure of (3) and (5), common to each of (1)-(6), vide infra, is a [LnIII] dimer, and given in Figure 2. The triethanolamine ligands are assigned by charge balancing considerations to be doubly protonated and, although not found by XRD directly, it is likely that the deprotonated arm bonds to more metals, as established by previous literature reports of 3d and 3d-4f compounds [4]. Here the bonding mode of teaH₂ in Harris notation [15], is 2.2.1.1.1, highlighted in Figure 3 (left), the O’ arm linking the two metals, with the three remaining donor atoms (NO₃) bonding to the same ion. The O’CCPh₃ ligands bond in 1.1.1 fashion, both donor atoms bonding to a single metal, as do the bidentate NO₃ groups (1.1.0), meaning the only bridging ligands between the metals are the O atoms of each teaH₂.

Dimetallic (LnI) triethanolamine compounds are unknown in the literature to our knowledge, although there are a series of [Ln(III)(mdeaH)₂(O₃C₃Bu)₃] compounds from Abbas et al. [16], where the mdeaH ligand, i.e. methylidethanolamine, is purely terminal, and does not bridge. This bonding mode in (1)-(6) of teaH₂ is novel in 4f-teaH₃ chemistry, although has a precedent in [M(H₂DyIII)(O₂C₃)₄(teaH₂)(teaH₂)(O₃C₃)(NO₃)₃] (H₂O) d(NO₃)·8H₂O [17] when teaH₂ bridges between a 3d and 4f ion and also in ‘Pass and Fries’ [GaIII(Hsabhea)(NO₃)₂·2MeOH compound from 1997 [18], where Hsabhea is the amino-alcohol N-salicylidene-2-(bis-(2-hydroxyethyl)amino)ethylamine.

The coordination geometries around each metal ion are composed of a (NO₃) nine-coordinate geometry, which is best described as a slightly distorted spherical capped square-antiprism by SHAPE analysis of (5) (see Table 1 in S. I. for more information); the range of bond lengths is between 2.318(5) Å of the oxygen of the non-capping (bridging) teaH₂ ligand and 2.6596(6) Å to the N atom. Such Ln-O bond distances are typical of lanthanide compounds previously seen, along with the relatively elongated Ln-N bond. See supporting information for more details and images on these geometries and parameters. The full structure was collected only for (5) and (3) (see parameters in S.I. 3.).

Obtaining crystals was difficult and, despite repeated efforts, only these two compounds could be crystallised satisfactorily for any single-crystal XRD analysis of the six compounds synthesised. As good quality crystals were rather difficult to obtain, PXRD was performed on (1)-(6) to confirm their structures were analogous. This found matching diffraction patterns for each, and are shown in S. I. 4, where data are offset for comparison purposes. These data are in agreement with those generated from the single-crystal XRD data of (5), confirming that all six compounds are isostuctural, in conjunction with the matching and satisfactory elemental analyses (see S.I.; TGA analysis of (4) is also described to assess the thermal stability, as discussed with S.I.).

The packing of unit cells in (5) is summarised in S. I. 5 and shows how individual molecules arrange down the b-axis to form a zig-zag chain-like alignment, though no H-bonds connect the adjacent units and inter-metallic distances are around 7.52 Å. In
Fig. 4. Space-filling representation of (5) viewed along the (left) $a$-axis; (centre) $b$-axis; and (right) $c$-axis. Key: Colours as for Fig. 2.

the plane these “chains” are separated by 13.85 Å, and by 9.70 Å to chains above and below. Qualitatively we can expect intramolecular exchange to dominate, these distances being significantly larger than the intra-Dy$^{III}$ ion separation (3.78 Å), with no obvious exchange pathways.

3.2 Steric Bulk

Space filling models (shown in Figure 4, as viewed down $a$, $b$ and $c$-axes from left to right, respectively) show that the steric bulk of the triphenylacetate group protects a central metal core, dominating the space. This may hint at the mechanism of formation, whereby the inner metal ions are protected from bridging species such as OH$^-$ groups that are likely present, arising from deprotonation of water molecules. This picture supports our synthetic observations in that there is a point when too much base is added, perhaps where the concentration of these bridging groups becomes too great and unknown insoluble material forms. Furthermore, reducing the amount of tpaH in this reaction has a similar effect, giving intractable products.

Replacement of the starting lanthanide(III) salt with lanthanide(III) chloride has been similarly unsuccessful so far.

The combination of bulk and increased denticity of the nitrate ligand over chloride may be the reason, though this is again speculation. We note that there are very few compounds incorporating tpaH prepared via solvothermal means, namely only the disc-like [Mn$^{III}$,La$^{III}$]$_2$ [20]. This may suggest that the less coordinating 3d metals do not require such measures as the extreme bulk of a ligand, as they have less sites to fill, though a larger sample size is required for a more general explanation.

4. Magnetic Properties of (3)-(6)

We investigated the magnetic properties of (3)-(6) as these are directly in our areas of interest, i.e. (3) for its magnetocaloric effect, and also for the direct ability to model the interactions between isotropic spins. For the later lanthanide(III) compounds we were primarily interested in whether they showed slow relaxation and could be considered SMMs, vide infra.

4.1.1 [Gd$^{III}$](teaH$_2$)$_2$(tpa)$_2$(NO$_3$)$_2$ (3)

Direct current magnetic studies ($H = 1$ kG, 1.8-300 K) on (3), found a near room temperature $\chi T$ product of 15.94 cm$^3$ mol$^{-1}$ K, as seen in Figure 5, upper, as hollow squares, in line with that expected for two, isotropic, uncoupled ions (f$^7$, $S_{tot} = 7/2$, $L = 0$) of 15.75 cm$^3$ mol$^{-1}$ K. Upon decreasing the temperature this remains almost constant, with only a slight decrease to 15.19 cm$^3$ mol$^{-1}$ K at 50 K, before beginning a rapid decrease below this point.

Susceptibility ($\chi$($T$)) data (S.I. 7) show a smooth exponential type increase from room temperature to 1.8 K, without any maximum being seen, which would have indicated an ordering temperature. However, the $\chi$(T) data can only mean the presence of an antiferromagnetic interaction between spins, which is rather weak, as evidenced by the low temperature decrease and lack of ordering point. From the $\chi$($T$) versus $T$ plot, the Weiss constant $\theta = -2.73$ K (see S. I. 6) is in line with that seen in other lanthanide$^{III}$ compounds with antiferromagnetic exchange between spins. We sought other lanthanide compounds where these ions were bridged solely by triethanolamine oxygen atoms in order to find a correlation between bridging angles and exchange-coupling strengths but were thwarted by the lack of evidence to build up this picture, though weak exchange is typical of gadolinium(III) compounds bridged by all but the radical ligands used by Long et al. [21].
suggesting the antiferromagnetic coupling is a great hindrance to reaching higher values. Indeed, simulations in PHI, in which \( J_{12} \) is arbitrarily set to zero (shown in S. I. 7), i.e. no exchange between isolated metal ions, found that maximum values of \(-\Delta S_M\) of ca. 24 J kg\(^{-1}\) K\(^{-1}\) could be reached under our best obtainable conditions, a twenty percent increase. In any case, to approach truly useful numbers for the purposes of refrigeration, one must consider the ligand and metal ratios and here the presence of bulky triphenylacetate ligands do not favour a large MCE, the percentage mass of gadolinium(III) being only ca. 25%: much lower than in the three-dimensional compounds that exemplify this effect, e.g. Sharples and Collison [24]. Further simulations where \( J_{12} \) was arbitrarily set to +0.15 cm\(^{-1}\) at 5 and 7 T show the advantage of a ferromagnetic exchange under conditions of higher temperatures for a given field, with larger values attained for \(-\Delta S_M\), with the disadvantage of lowering the overall \(-\Delta S_M\). Conversely an antiferromagnetic exchange of \(-0.15\) cm\(^{-1}\) will shift the \(-\Delta S_M\) to a lower temperature whilst reducing its magnitude, which raises a possibility of tuning magnetocaloric molecules for specific applications in future.

4.1.2 Categorising the magnetocaloric effect further

When the density of (3) is taken into account we see another disadvantage of zero-dimensional compounds: for [Gd(HCOO)\(_3\)]\(_{24}\) the term \( -\rho\Delta S_M \) is around 200 mJ cm\(^{-3}\) K\(^{-1}\), whereas for (3) this is only around 35 mJ cm\(^{-3}\) K\(^{-1}\). Typically, molecular compounds have densities of around 2 g cm\(^{-3}\) and for (5) this is ca. 1.7 g cm\(^{-3}\). The best performing materials, though, have values around 4 g cm\(^{-3}\) ([Gd\(_{12}\)(HCOO)\(_5\)\(_3\)]\(_n\)) and, indeed, up to 7 g cm\(^{-3}\) for [Gd\(_{12}\)Ga\(_3\)I\(_5\)(O\(_2\)C\(_2\))\(_{25}\)]. Clearly for practical purposes this must be taken into account for space limited applications, for example in satellite sensors.

Even \( -\rho\Delta S_M \) is a somewhat limiting descriptor: heat capacity measurements can give \( T_{AD} \) more useful as it directly measures the temperature changes which can be attained. Still further, it could be argued, the ordering temperature of a proposed coolant material is more important. Below such a point, the parameter \(-\Delta S_M\) approaches zero, limiting how the material could be used. In this light there have been three main categories identified [25c] within “low temperature” applications, which polymetallic molecules are targeting: these compete with three alternative means of cooling. We assign these here as Type α, \(^{1}\)He rivaling−down to 1.2 K; Type β, \(^{4}\)He−down to 400 mK; and Type γ, \(^{3}\)He dilution refrigerators−below 400 mK. In addition to the ordering temperature, the refrigerant capacity, using the full-width-half-maximum term (FWHM), reports on how large the \(-\Delta S_M\) quantifies performance over a larger range, a practical guide; this may be unimportant for very specific applications but it shows the versatility of a material.

The refrigerant capacity (RC) of (3) is lacking, \textit{vide infra}, compared to the best found so far and is defined by Equation 3, where \( T_1 \) and \( T_2 \) are the positions of the full width-half-maximum (FWHM) of the largest \(-\Delta S_M\) found [25d].

\[
RC = \Delta S_M (T_1−T_2) \quad \text{Equation 3}
\]

For (3) we are unable to measure this directly as there is no maximum recorded at our lowest available temperature; indeed, it
has been seen that obtaining the ordering temperature and RC present a problem as, especially for lanthanide(III) compounds, the former is often below that experimentally obtainable in conventional SQUID analysis (ca. 1.8 K), on account of the poor overlap of ligand orbitals with the contracted 4f orbitals of the metal ion. Related to this an actual maximum in $-\Delta S_M$ is often not seen. Thus, we used simulations based on the programme PHI, to obtain these data for (3) and categorise other homometallic gadolinium(III) compounds. Table 2 (S. I. and best referred to in parallel with this discussion) lists those examined, with their molecular weight, exchange interactions and their classification by the above scheme. Even within these weakly interacting compounds we find a range of potential applications based on the above criteria. Finally we highlight something which is apparent quickly from the below (4.1.3) simulations. This is the fact that the maximum in $-\Delta S_M$ shifts to larger temperatures with larger applied fields. Thus, if a material requires a larger field to operate at a useful value of $-\Delta S_M$ then it will be less useful at lower temperatures; a double-downside.

### 4.1.3 Results and discussion of PHI simulations

From simulations in PHI, using the appropriate Hamiltonians reported, we can obtain the maximum $-\Delta S_M$ values for a given field, which we tabulate in Table 2 (S. I.) for 1, 5 and 7 T, where we see the expected relationship with percentage of gadolinium, with a slight discrepancy between (3) and (Gd$^{III}\cdot$Ph) [25e], which we account for by their similarity in weight and difference in the nature of their exchange. Experimentally reported values are in reasonably good agreement with those calculated by this method as tabulated. Significant errors were found for (Gd$^{III}$) [13], perhaps because the magnetisation data could be fitted by more than the one exchange value used. Noticeably the maximum $-\Delta S_M$ is found at lower temperatures for a given compound with increasing applied field, thus we classify each material separately for 7 and 5 T. The exchange strength is clearly related here to the Type α, β or γ assignment. Only at the lower fields for the paramagnetic materials do we see materials capable of competing in the $^4$He-$^4$He dilution refrigerators range, for example the tungstanate [25t] and formate [25a] compounds. Interestingly, when we compare the two gadolinium dimers (3) and [Gd($\infty$)$_2$] [25g], the latter of which has extremely small antiferromagnetic exchange ($-0.0092$ cm$^{-1}$ versus $-0.13$ cm$^{-1}$ for (3)), we see how, although this makes a large difference in the temperatures at which the largest $-\Delta S_M$ values are found, the categorisations based on real-world use remain the same. Indeed, the most striking feature is that all of the so-called “low-temperature” coolers are Type α when under an applied field of 7 T, where the majority approach their maximum values of $-\Delta S_M$ (as calculated by Equation 2). In turn, this shows how useful having a large gadolinium content is, so as to maximise this at lower temperatures, for example.

Comparison of the calculated and maximum experimental $-\Delta S_M$ values at the same temperature show a good agreement which confirms the accuracy of these methods. For (3) we calculated the RC at 7 and 5 T as ca. 210 and 140 J kg$^{-1}$, respectively which compares moderately with the polymeric material Gd$^{III}$ formate [25a], which gives larger values even at only $\Delta H = 2$ T, which accounting for densities, is ca. 520 mJ cm$^{-3}$ compared to only 340 mJ cm$^{-3}$ ($\Delta H = 7$ T) for (3). Obtaining these data would not be possible using only experimental results. The only significant change we see when the refrigerant capacity is taken into account in assessing how useful these ten materials are, is the reversal (at $\Delta H = 5$ T) of (3) and [Gd$^{III}\cdot$Zn$_2$] [25h], though only a very small adjustment. In fact, for these compounds the RC is almost identical in terms of parameterising these compounds as the simple $-\Delta S_M$, which is accounted for by the nature of the MCE, i.e. dominated by spin, and the lack of significant other factors, such as $D$, anisotropy, or intermolecular exchange in these simulations. Among the molecular examples, [Gd$^{III}$] [25j] is superior to all others by any measure, and in the same temperature range to any competitor. This method of simulation may prove useful in assessing new materials, especially when fuller descriptions of parameters can be utilised, without the need for heat capacity measurements or extremely low temperature measurements. Investigations into (3) by Electron Paramagnetic Resonance are currently in progress, which may give information upon the $g$-value (so fixing this for simulations) and $D$, anisotropy, parameter.
25.5

20.5

15.5

10.5

5.5

10

15

20

25

30

35

40

45

50

55

60

65

70

75

80

85

90

95

100

Fig. 8. Upper: experimental $\chi'(T)$ and $\chi''(T)$ for (4) between 1.8 and 300 K ($H_{dc} = 0$), shown in solid squares. Lower: experimental $M(H)$ for (4) at 1.8, 3 and 5 K ($H_{dc} = 0$) as solid squares (extrapolation as dotted lines). Key: As shown.

4.2 $[\text{Dy}^{III}_3(\text{teaH}_2)(\text{tpa})_2(\text{NO}_3)_2]$ (5)

For (5) (Figure 7, upper), the room temperature value of $\chi'$ is around 30 cm$^{-1}$ mol$^{-1}$ K, in line with that expected for two Dy$^{III}$ ions ($F$, $^9\text{H}_{15/2}$, $S = 6$, $L = 5$, $J = 15/2$, $g = 1$) of 28.34 cm$^{-1}$ mol$^{-1}$ K, if perhaps slightly high. Below a 40 K value of ca. 27 cm$^{-1}$ mol$^{-1}$ K, there is a rapid decrease to the lowest temperatures investigated of ca. 14 cm$^{-1}$ mol$^{-1}$ K at 2 K. $\chi''(T)$ behaves qualitatively similarly to (2), no ordering temperature being seen, and showing a smooth increase with decreasing temperature.

Such behaviour is tentatively assigned to antiferromagnetic coupling in line with that seen for (2), though it is difficult to distinguish from the depopulation of Stark sublevels with decreasing temperature via a Boltzmann distribution. A more complete explanation could be ascertained from modelling the magnetisation data and ab initio calculations.

Magnetisation versus field plots (Figure 7, lower) at 1.8, 3 and 5 K show saturation is not reached, consecutively larger values of 14.09, 14.15 and 14.19 Nμ being found at 7 T. This matches previous reports of anisotropic compounds [13].

Zero-field a.c. susceptibility measurements ($H_{dc} = 0$) were performed on (5) between 2 and 12 K, for 1, 100 and 957 Hz, finding no SMM behaviour, as evidenced by the lack of $\chi''$ signal and the smooth increase in $\chi'$ shown in S. I. 9. When repeated under $H_{dc} = 1$ kG between 4-20 K at 1, 100 and 957 Hz, there was no discernible difference qualitatively. The slight uniform increase in the $\chi''$ signal, though, may suggest quantum-tunnelling, suppressed in applied fields, is in operation here, which is accompanied by a decrease in magnitude in field of $\chi'$ by almost half (ca. 9.8 cm$^{-1}$ mol$^{-1}$ to 4.4 cm$^{-1}$ mol$^{-1}$) compared to the zero-field case.

We can attribute the lack of SMM behaviour in (5) to several factors. One possibility is the non-symmetrical coordination geometry at each ion described above, as this controls the ordering and splittings of $\pm m$ states. Although dysprosium(III) is a Kramers ion, and so maintains degenerate $\pm m$ pairs, the ordering of these may not be favourable to produce a large $U_{dc}$ in such a crystal field. The largest such barriers have arisen in regular axial geometries, although there are several examples of nine-coordinate SMMs, with capped geometries (see Woodruff et al.’s extensive review of these and other lanthanide SMMs for more detail [26]).

Secondly, a possible cause of the QT mechanism may be the orientation of the anisotropy axes of the states; if these have significant transverse terms in their $g$-matrices, then QT may be allowed even in Kramers systems.

4.3 $[\text{Th}^{III}_3(\text{teaH}_2)(\text{tpa})_2(\text{NO}_3)_2]$ (4) and $[\text{Ho}^{III}_3(\text{teaH}_2)(\text{tpa})_2(\text{NO}_3)_2]$ (6)

For (4) (Figure 8, upper), $\chi'(T)$ at room temperature was 23.47 cm$^{-1}$ mol$^{-1}$ K, in line with both previously seen similar terbium(III) dimetallic compounds and the expected values for Tb(III) ($t^6$, $^7F_{6}$, $S = 3$, $L = 3$, $g = 7/2$) of 23.63 cm$^{-1}$ mol$^{-1}$ K. This shows a sloping descent with decreasing temperature, reaching 18.3 cm$^{-1}$ mol$^{-1}$ K at 10 K, before a rapid decrease to reach 9.8 cm$^{-1}$ mol$^{-1}$ K at 2 K. Such behaviour, as for (4) is suggestive of a combination of antiferromagnetic interactions and/or sublevel depopulation. $M(H)$ values (Figure 8, lower) reach 10.95 and 11.09 Nμ at 4 and 2 K respectively, the non-saturated a feature of terbium(III) compounds [13].

From a.c. susceptibility measurements of (4) and (6) no indication of any out-of-phase component ($\chi''$) was found, in zero $H_{dc} = 0$ kG, $v = 1$, 100, 700 and 1100 Hz, 2-12 K) or applied fields ($H_{dc} = 1$ kG, $v = 1$, 100, 700 and 1100 Hz, 2-20 K) (collected in S. I. 10 for (4)). Computational [27] or even luminescence studies [28a] can assist in finding anisotropic $g$ matrices and the alignment of the anisotropy axes, which may provide more understanding of the correlation between the crystal field and the non-SMM behaviour of these compounds. In fact, there are relatively few Tb(III) homometallic SMMs reported in the literature, less than forty or so, with a handful of Ho(III) SMMs [26], and these require strictly axial symmetry to maintain the zero-field case.

Furthermore, many of these only show $\chi''$ maxima under applied static fields, on account of their quantum tunnelling [13, 26].

What is interesting is the lack of decrease in $\chi''$ with the increase in field as seen for (5), which may suggest that quantum tunnelling is either not operating in this compound or that it requires larger fields to suppress. The former situation is extremely unlikely, given the non-Kramers ion status of Th$^{III}$ and its coordination geometry.
led us to investigate them, along with other reasons given below, which, along with the f–f bands, hence the tpa group appears not to act as a chromophore. For (1) (615 nm excitation, 450 nm filter), we were surprised to (repeatedly) find overlap of the emission and excitation spectrum with the EuIII compound, showing that we are in fact detecting the latter, presumably by some small impurity in the sample, despite careful washing of the whole experimental set-up.

5. Luminescence data of (1), (2), (4) and (5)

A particular advantage of TbIII and EuIII is the strongly luminescent behaviour even in the absence of a sensitising ligand [28b]. When subjected to UV light, (4) and (2) glowed green and red respectively, which, along with other reasons given below, led us to investigate them, along with (1) and (5) for their UV-Vis luminescent properties. No emission was recorded for (3) or (6). For solid state samples, measured at room temperature and 1 nm resolution (except where noted), then, the following emission properties were found (note that all emission spectra are collated in Figure 9, upper, excepting for (4), shown in the lower panel, with all excitation spectra collated in S. I. 11).

5.1. [EuIII2(teaH)2(tpa)2(NO3)2] (2)

For (2) with a 395 nm excitation (455 nm filter) the emission bands were assigned as the following characteristic EuIII transitions, being centred on the following positions: 3D<n→2F> : n = 0: ca. 580 nm, 1: 590 nm, 2: 620 nm, 3: 650 nm, 4: 680 nm, 5: and a broad feature at 680–700 nm. A degree of splitting is seen in those bands to give m states where n > 1, i.e. non-singlet in character. From the ratio of the n = 2: n = 1 bands, which is ca. 5, we can describe the EuIII site as being of low symmetry, far from the expected values of less than 1 if this was a centrosymmetric environment. This is in general agreement with the low symmetry environment about the metal ions seen in the crystal structure of (5).

The excitation spectrum of (2) (615 nm, 550 nm filter) shows a strong feature at around 400 nm and confirms that the emission is EuIII and not ligand-based and so we excite directly into the f–f bands, hence the tpa group appears not to act as a chromophore. For (1) (615 nm excitation, 450 nm filter), we were surprised to (repeatedly) find overlap of the emission and excitation spectrum with the EuIII compound, showing that we are in fact detecting the latter, presumably by some small impurity in the sample, despite careful washing of the whole experimental set-up.

5.2. [TbIII2(teaH)2(tpa)2(NO3)2] (4)

For (4) (Figure 9, lower), the emission spectrum was recorded for a 365 nm excitation (355 nm filter). The bands are assigned generally as follows: 3D<n→2F> : n = 6: ca. 480–510 nm, 5: ca. 530–570 nm, 4: ca. 580–600 nm, 3: ca. 610–635 nm and 2: ca. 640–660 nm. Further detail at lower energies for n = 1 or 0 are hard to resolve from noise, being quite weak.

In (4), from the highest energy multiplets, then, we were able to observe emission bands corresponding to the two lowest energy transitions, 3D<n→2F> and 3D<n→3F> where n = 1–6. These positions give information upon the energies of the spin-orbit-coupled (SOC) states. In reality these are further split by the effect of the crystal field into their composite m states. The ordering and separation of these states is known to be directly related to the SMM behaviour (or otherwise). We performed a fit of the ground multiplet using IGOR 6 Pro [29] software, as shown in S. I. 12, fitting three bands in the envelope of states at higher energies, though there are likely to be several more, and a single peak, better separated at lower energies; quantum tunnelling is likely to play a large role in the relaxation behaviour of non-Kramers ions, particularly those in low symmetry environments, so luminescence is not a reliable guide to predicting whether a compound will show SMM behaviour, yet. Here, though, these results support the observed a.c. susceptibility results, showing the absence of a well separated ground state.

The excitation spectrum shows direct energy transfer to the TbIII f–f bands at around 370 nm and 490 nm, in line with that seen for (2). Exponential fitting of the emission decay for these gave moderate lifetimes of τ = 2.1 ms for (2) and 1.7 ms for (4), each assigned to a single species (i.e. mono-exponential; decay profiles are given in S. I. 13 and 14 for (2) and (4) respectively). This was reassuring in light of the imperfect match between calculated and experimental elemental analysis values and suggests the impurity which must cause this discrepancy to be ligand based; a second metal species would show a different decay profile. This argument is supported by the fairly sharply resolved emission lines of (2) and (4). The lack of quenching means we could also expect reasonable solution-state life-times, though problems with solution stability precluded these measurements.

5.3. [DyIII2(teaH)2(tpa)2(NO3)2] (5)
We were able to observe emission in (5), which, from Boulon et al. and others, can be profitable in understanding the relaxation properties of SMMs [30]. The two bands can be assigned as the $^{5}F_{2}\rightarrow{}^{5}I_{5/2}$ transition and to the next spin-orbit coupled state $^{5}H_{10/2}$. Unfortunately, here, the multiplet structure is poorly resolved so the energies of crystal field states cannot be determined and, indeed, (5) does not act as an SMM. The excitation spectrum is given in S.I. 11 confirming the direct excitation. When we performed decay measurements on the lifetime of (5) we found that this was so short as to be impossible to determine with the apparatus used.

Work is in progress targeting the earlier lanthanides in this series (Ca$^{lll}$–Nd$^{lll}$) to probe their emissive properties, though so far has been hindered by what we believe is the strong dependence of the reaction upon the size of the lanthanide(III) chosen, where only the Sm$^{lll}$–Ho$^{lll}$ grouping are attained with acceptable purity.

6. Theoretical Studies

6.1 Electrostatic Model of Ligand-dysprosium(III) Interactions

A relatively simple means of obtaining information on the ground state of low symmetry dysprosium(III) compounds was recently developed by Chilton et al. [31]. This electrostatic model regards the problem as minimising the energy of metal-ligand interactions and assumes an $n_{l}=13/2$ ground state. From the XRD data this gives the orientation of the ground state anisotropy axis, as shown in Figure 10. This axis is aligned at 67° to what could be considered the principle axis down the long N–Dy$^{lll}$ bond. ab initio calculations could help to expand on this picture.

Fig. 10. Anisotropy axis of the ground-state for (5), calculated by the electrostatic model, shown as a green bar. Key as for Fig. 2.

7. Conclusions

We have synthesised, characterised and investigated the magnetic properties of a family of [Ln$^{lll}$$(\text{teaH}_{3})_{2}(\text{tpa})_{2}(\text{NO}_{3})_{2}$] compounds, using solvothermal synthesis with the teah$_{3}$ ligand; a unique bond. Opening up this combination of methodologies should prove fruitful in the hunt for further such compounds, in light of the variety seen elsewhere in 3d chemistry. No SMM behaviour was found in any of (1)–(6), likely due to the mono-capped distorted square antiprisymatic geometry around the ions. The MCE of the Gd$^{lll}$ derivative was moderate, hindered by large carboxylate ligands and subsequent relatively low Gd$^{lll}$% compared to the best performing molecules, and antiferromagnetic exchange between spins. Nevertheless this motivates the study for more homometallic teah$_{3}$ compounds, using different combinations of co-ligands and bases, which are underway. Luminescence studies found characteristic emission by direct excitation of the La$^{lll}$ ions which may also assist in understanding the none-SMM behaviour seen in (4) and (5). We are also exploring ways to tune the nuclearity of 4f cages by switching the carboxylate ligand to one with less steric bulk.

Acknowledgements

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References

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1 Electronic Supplementary Information (ESI) available: [experimental details, characterisation, magnetic properties and analysis, and luminescence details as mentioned in the text are provided in the supplementary information. cif files and CHECKCIF files are also included for (3) and (5)]. See DOI: 10.1039/b000000x/ Further XRD data are provided in the S.I.

19. M. Lunelli, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, SHAPE User’s Manual, Universitat de Barcelona. SHAPE is a programme which can be used to analyse the ligand orientation around a metal ion and gives a figure relating how close this geometry is to idealised reference geometries.
23. M. Evangelisti, *Unpublished Results* (ENTROPY is a programme used to convert magnetisation data at variable temperature into magnetic entropy changes.
   c. N. Abbondante, M. Grabowski, M. Hirsch, *Unpublished Results*.
31. N. F. Chilton *et al.* Submitted. 2013 (Named MAGELLAN this software calculates the anisotropy axis of anisotropic magnetic molecules).
32. Magnetic measurements were recorded on a QD-MPMS-XL magnetometer between 1.8-300 K, with data corrected for eicosane fixant, holder and diamagnetism as appropriate. Powder X-ray diffraction was performed at room temperature using a Bruker D8 and Philips PANalytical X’Pert. Single-crystal XRD was measured at the Diamond Light Source Synchrotron. We thank Diamond Light Source for access that contributed to the results presented here. Data were solved with Direct Methods and refined using SHELXTL with F2. Steady state emission spectra were recorded using an Edinburgh Instrument F920 Phosphorescence Lifetime Spectrometer equipped with a 5 W microsecond pulsed xenon flashlamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in a Pellet housing (air cooled, Hamamatsu R928P). Where indicated delay time and gate time were applied during emission measurements. Lifetime data were recorded following excitation with a microsecond xenon flashlamp, using the multi-channel scaling method. Lifetimes were obtained by tail fit on the data, and the quality of fit judged by minimization of reduced χ and residuals squared. Where the decay profiles are reported as mono-exponential, fitting to a double exponential yielded no improvement in fit.
Lanthanide(III) triethanolamine dimetallic compounds with bulky carboxylate ligands and their physical properties

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Experimental details and elemental analyses

All chemicals were purchased from Sigma-Aldrich and used without further purification.

Synthesis of (1)-(6)

In a typical synthesis, Ln11(NO3)3·6H2O (0.1 g, ca. 0.22 mmol, given for Ln11 = Dy11) and triphenylacetic acid (0.033 g, 0.11 mmol) were stirred in acetonitrile (6 mL) for 5 minutes. To this, a solution of teaH3 (0.018 g, 0.12 mmol) and triethylamine (0.045 mL, 0.33 mmol) in acetonitrile (2 mL), which had also been stirred for 5 minutes, was added as quickly as possible. The resultant solution was stirred for 5 minutes, remaining clear, and then heated for 12 hours at 100 °C in a PTFE-lined steel autoclave. After slow cooling at 0.05 °C min−1, poorly crystalline material was obtained in good yield (ca. 40 %). Careful sifting found very small colourless plate-like crystals suitable for X-ray diffraction of (3) and (5), whereas for the remaining compounds the material was microcrystalline and no crystals large enough for XRD could be found, despite repeated efforts.

Characterisation Data (1)-(6)

Acceptable elemental analysis, for Ln2C52H54N4O16 gave the following (calculated : experimentally found):
(1) Sm 23.28:25.23; C 48.35:45.79; H 4.21:4.30; N 4.34:4.20; (2) Eu 23.47:22.20; C 48.23:47.41; H 4.20:4.37; N 4.33:4.64; (3) Gd 24.09:23.83; C 47.84:46.54; H 4.17:4.23; N 4.29:4.71; (4) Tb 24.28:24.19; C 47.72:45.60; H 4.16:4.23; N 4.28:4.40; (5) Dy 24.70:24.75; C 47.46:46.58; H 4.14:4.25; N 4.26:4.96; (6) Ho 24.97:24.79; C 47.28:46.91; H 4.12:4.38; N 4.24:4.36.
S. I. 2. ASU of (5). Key: Ln$^{III}$ purple spheres; O red; C grey; N blue; No H’s are shown for clarity.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Symmetry</th>
<th>Factor (lower is closer to shape listed)</th>
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</thead>
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<td>Enneagon</td>
<td>$D_{9h}$</td>
<td>35.155</td>
</tr>
<tr>
<td>Octagonal Pyramid</td>
<td>$C_{8v}$</td>
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<td>Heptagonal Bipyramid</td>
<td>$D_{7h}$</td>
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<td>Capped Cube (J8)</td>
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<td>Spherical-relaxed Capped Cube</td>
<td>$C_{4v}$</td>
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<tr>
<td>Capped Square Antiprism (J10)</td>
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<td>Spherical Capped Square Antiprism</td>
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<td>Tricapped Trigonal Prism (J51)</td>
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<tr>
<td>Spherical Tricapped Trigonal Prism</td>
<td>$D_{3h}$</td>
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<tr>
<td>Tridiminished Icosahedron (J63)</td>
<td>$C_{3v}$</td>
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<tr>
<td>Hula-hoop</td>
<td>$C_{2v}$</td>
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<td>Muffin</td>
<td>$C_{1}$</td>
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Table 1. Results of SHAPE analysis upon the Dy$^{III}$ ion in (5).

<table>
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<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3) Gd$^{III}$</td>
<td>9.6987(9)</td>
<td>10.9701(8)</td>
<td>13.8535(8)</td>
<td>106.302(6)</td>
<td>90.176(6)</td>
<td>112.552(8)</td>
<td>1296.28</td>
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<tr>
<td>(5) Dy$^{III}$</td>
<td>9.5848(6)</td>
<td>10.8159(6)</td>
<td>13.7116(8)</td>
<td>105.961(5)</td>
<td>90.324(5)</td>
<td>112.492(6)</td>
<td>1252.83</td>
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</tbody>
</table>

S. I. 3. Unit Cells of (3) and (5).
Powder X-ray Diffraction Results: S. I. 4a, b and c.

S. I. 4a. Powder X-Ray diffraction pattern recorded between θ = 5 and 40 for (2) and as calculated from the X-ray diffraction data for (5). Key: Eu black line; Dy XRD red line.

S. I. 4b. Powder X-Ray diffraction pattern recorded between θ = 5 and 40 for (1) and (3) and as calculated from the X-ray diffraction data for (5). Key: Sm black line; Gd green line; Dy XRD red line.
S. I. 4c. Powder X-Ray diffraction pattern recorded between $\theta = 5$ and 40 for (4), (5) and (6) and as calculated from the X-ray diffraction data for (5). Key: Tb blue line; Ho black line; Dy cyan line; Dy XRD red line.

Packing of (5)
S. I. 5. Packing of (5) along the (upper) a-axis; (middle) b-axis; and (lower) c-axis. Key: As for S. I. 2. Also, phenyl groups are removed for clarity.
Magnetic Properties of (3)

S. I. 6. $\chi(T)$ and $1/\chi(T)$ for (3) as points between 1.8-300 K, where $H = 1$ kG. Fitting by solid line through these points. Key: Experiment: open squares (□). Fit: Solid lines.

S. I. 7. Simulated $-\Delta S_M(T)$ for (3) by considering three pairs of cases: i) Ferromagnetic interaction of +0.15 cm$^{-1}$ (all with the same Hamiltonian as in the main text) at 5 T (black) and 7 T (red); ii) Antiferromagnetic interaction of −0.15 cm$^{-1}$ at 5 T (green) and 7 T (blue); iii) Paramagnetic (no exchange), i.e. ±0 cm$^{-1}$ at 5 T (cyan) and 7 T (magenta). Lines only connect the points.
<table>
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<th>Compound (ref)</th>
<th>Calc. $-\Delta S_M$ (Max) 7T (T / K)</th>
<th>Exp. 7 T Values (T / K)</th>
<th>Further Calc. 7 T Values (T / K)</th>
<th>Calc. $-\Delta S_M$ (Max) 5T (T / K)</th>
<th>Calc. $-\Delta S_M$ (Max) 1T (T / K)</th>
<th>Type (7 T)</th>
<th>Type (5 T)</th>
<th>Type (1 T)</th>
<th>RC (7 T)</th>
<th>RC (5 T)</th>
<th>$M_w$</th>
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<tr>
<td>[Gd(HCOO)$_3$]$_n$ (1)</td>
<td>58.7 (1.3)</td>
<td>56 (1.8)</td>
<td>58.1 (1.8)</td>
<td>58.7 (0.8)</td>
<td>58.7 (0.2)</td>
<td>α</td>
<td>β</td>
<td>γ</td>
<td>552</td>
<td>355</td>
<td>292.25</td>
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<td>Na$_8$[Gd(W$_2$O$_9$)$_2$]-35H$_2$O (2)</td>
<td>5.0 (1.2)</td>
<td>4.7 (1.8)</td>
<td>4.98 (1.8)</td>
<td>5.0 (0.8)</td>
<td>5.0 (0.2)</td>
<td>α</td>
<td>β</td>
<td>γ</td>
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<td>34</td>
<td>3409.17</td>
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<tr>
<td>K$<em>{12}$[GdP$<em>2$W$</em>{10}$O$</em>{110}$]-54H$_2$O (2)</td>
<td>1.9 (1.2)</td>
<td>1.9 (1.3)</td>
<td>1.9 (1.3)</td>
<td>1.9 (0.8)</td>
<td>1.9 (0.2)</td>
<td>α</td>
<td>β</td>
<td>γ</td>
<td>18</td>
<td>13</td>
<td>9029.56</td>
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<tr>
<td>[Gd$_2$(teaH)$_2$]$_2$(tpa)$_2$(NO$_3$)$_2$ (this work)</td>
<td>20.5 (2.4)</td>
<td>20.3 (3)</td>
<td>20.2 (3)</td>
<td>18.0 (1.8)</td>
<td>1.1 (0.5)</td>
<td>α</td>
<td>α</td>
<td>β</td>
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<td>141</td>
<td>1305.52</td>
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<tr>
<td>[Gd$_2$(OAc)$_2$(Ph$_3$acac)$_4$(MeOH)$_2$] (3)</td>
<td>25.8 (1.5)</td>
<td>23.7 (2.4)</td>
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<td>21.6 (0.4)</td>
<td>α</td>
<td>α</td>
<td>β</td>
<td>249</td>
<td>180</td>
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<tr>
<td><a href="ClO$_4$">Gd$_2$Zn$_8$(OH)$_6$(hmp)$_8$ (O$_2$CCHMe$_2$)$_2$</a>$_8$·4H$_2$O (4)</td>
<td>20.0 (1.3)</td>
<td>18 (2)</td>
<td>19.98 (2)</td>
<td>19.7 (0.9)</td>
<td>15.0 (0.3)</td>
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<tr>
<td>[Gd$_2$Zn$<em>4$(tBuCOO)$</em>{10}$(tBuPO$_3$)$_2$ (NEt$_3$)$_2$] (5)</td>
<td>16.6 (1.7)</td>
<td>15.1 (3)</td>
<td>15.26 (3)</td>
<td>16.5 (1.3)</td>
<td>31.9 (0.5)</td>
<td>α</td>
<td>α</td>
<td>β</td>
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<tr>
<td>[Gd$_2$(OAc)$_4$(H$_2$O)$_4$]·4H$_2$O (6)</td>
<td>40.9 (1.7)</td>
<td>41.6 (1.8)</td>
<td>40.9 (1.8)</td>
<td>40.1 (1.4)</td>
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<td>α</td>
<td>α</td>
<td>β</td>
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<td>812.89</td>
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<tr>
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<td>39.4 (1.4)</td>
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<td>38 (2.4)</td>
<td>38.9 (0.9)</td>
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<td>β</td>
<td>β</td>
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<tr>
<td>[Gd$<em>5$(O)O(Pr)$</em>{13}$] (7)</td>
<td>44.7 (1.2)</td>
<td>34 (3)</td>
<td>38.4 (3)</td>
<td>40.0 (0.6)</td>
<td>1.70</td>
<td>α</td>
<td>β</td>
<td>NA</td>
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<td>199</td>
<td>1582.40</td>
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Table 2. Selected experimental and simulated parameters (using PHI) for the given magnetocaloric materials and a classification based on their potential use.
S. I. 8. Thermo-gravimetric analysis for (4), recorded between 30-1000 °C under N₂ at 10 K min⁻¹.
TGA of (4) was recorded between 30-1000 °C under N₂, for a sweep rate of 10 °C min⁻¹. From this we can see that (4) is stable up to 255 °C before losing 53 % of its weight up to 343 °C, perhaps indicating that the molecule has split in half. Thus, these compounds have a degree of thermal stability comparable with 3D-MOFs, which is often held up as a reason for their superiority in future practical applications. This may be due to the lack of solvent in the structure. A second loss between 348 and 504 °C accounts for a further 10 % of the weight, more of which is gradually lost up to 1000 °C, to around 30 %. As expected from the structure there is no solvent or water loss so we can ascribe this loss to a breakdown of the ligands.

A.C. susceptibility results for (5)
S. I. 9. Upper: Experimental $\chi''$ and $\chi'$ versus T plot for (5): $H_{\text{d.c.}} = 0$, $\nu = 1, 100$ and 957 Hz and $H_{\text{a.c.}} = 1.55$ G, between 2 and 12 K. Lower: Experimental $\chi''$ and $\chi'$ versus T plot for $H_{\text{d.c.}} = 1$ kG, $\nu = 1, 100$ and 957 Hz ($\chi'$ only) and $H_{\text{a.c.}} = 1.55$ G, between 4 and 20 K. Key: 957 Hz black squares (solid for $\chi'$ and hollow for $\chi''$); 100 Hz red circles; 1 Hz green triangles.

A.C. susceptibility results for (4)
S. I. 10. Upper: Experimental $\chi''$ and $\chi'$ versus $T$ plot for (4): $H_{dc} = 0$, $\nu = 1, 100, 957$ and 1100 Hz and $H_{ac} = 1.55$ G, between 1.8 and 12 K. Lower: Experimental $\chi''$ and $\chi'$ versus $T$ plot for $H_{dc} = 1$ kG, $\nu = 1, 100, 957$ and 1100 Hz and $H_{ac} = 1.55$ G, between 1.8 and 20 K. Key: 1100 Hz black squares (solid for $\chi'$ and hollow for $\chi''$); 700 Hz red circles; 100 Hz green upward triangles; 1 Hz blue downward triangles.
Luminescence Results for (1), (2), (4) and (5)

S. I. 11. Collated excitation spectra for (1) (excitation wavelength: 400 nm, 550 nm filter), (2) (615 nm, 550 nm filter), (4) (545 nm, 395 nm filter) and (5) (575 nm). Key: Sm black line; Dy blue line; Tb green line; Eu red line.

S. I. 12. Fitting by Gaussian Deconvolution using IGOR software of the ground multiplet $^5D_4 \rightarrow ^7F_n$ for (4). Key: peaks are centred on the following: 483.4 nm magenta line; 487.0 nm green line; 491.7 nm red line; 500.5 nm cyan line; Experimental black line. Data are normalised for ease of comparison.
Gaussian Deconvolution fits peaks using S.I. Equation 1 below, where $a$ is the amplitude of the peak, $b$ is the wavelength upon which the peak is centred, $c$ is the width of the peak, and $x$ is the wavelength variable, $f(x)$ being the intensity:

$$f(x) = ae^{\frac{-(x-b)^2}{2c^2}}$$

S. I. Equation 1

In order to more accurately determine the positions of the peaks making up the multiplet, the software package IGOR was used. Manually fitting the multiplet by adding four peaks using S. I. Equation 1 and then refining this to give more accurate positions gave the width and positions of the four peaks shown. Intensities were adjusted later to normalise these by comparison with the experimental data to give S. I. 12. Although many more peaks are likely contained within the multiplet, there are only four features visible with this data.

Lifetime Measurements

S. I. 14. Decay profile for (4) (365 nm, 495 nm filter). Key: Experimental data in open squares (□) fitted with blue line and residual given in green.
XRD Data for (5) and (3) (Electronic versions of .cif files and CHECKCIF / PLATON Report included)

S. I. 15. Numbering scheme for the ASU of (5). Key: Dy$^{III}$ green, O red, N blue, C grey. No H atoms are shown for clarity.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy1</td>
<td>O1</td>
</tr>
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<td>Dy1</td>
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<td>C21</td>
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<td>O4</td>
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Table 3. Bond distances in the ASU of (5).

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<td>1.29(1)</td>
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<td>1.48(2)</td>
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<tr>
<td>N1</td>
<td>C25</td>
<td>1.48(1)</td>
</tr>
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</table>

S. I. 16. Numbering scheme for the ASU of (3). Key: Gd$^{III}$ green, O red, N blue, C grey. No H atoms are shown for clarity.
Table 4a. Bond distances in the ASU of (3).

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd1</td>
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<td>O1</td>
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Table 4b. Bridging angles between metal ions in (5) and (3). Ln1(a) refers to the symmetry equivalent metal ion.

<table>
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<tr>
<th>Atoms</th>
<th>Angles / °</th>
<th>Compound</th>
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Table 4b. Bridging angles between metal ions in (5) and (3). Ln1(a) refers to the symmetry equivalent metal ion.
Table 4c. Crystallographic information for (5) and (3).

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References for compounds used in PHI simulations


Chapter 10: Future Work and Conclusions
Chapter 10: Future Work

For improving the magnetocaloric effect

i) Radical ligands

There were several areas to explore for improving the magnetocaloric effect of lanthanide-based materials that we were unable to realise. The first concerns the development and investigation of what would be a new class of magnetocaloric-material; namely those where there is an exchange interaction between a ligand-based radical spin and that on the metal. This could assist in removing one of the principal disadvantages of molecular-magnetocaloric materials: the passivity of the ligand framework, though this is less of a problem for 3D-compounds; as can be demonstrated with [Gd\textsuperscript{III}(HCOO)\textsubscript{3}]\textsubscript{n} (Chapter 6-refers back to the given chapter) the ligand percentage is relatively small. The main challenges associated with radical-Ln\textsuperscript{III} materials would include the generation of a sufficiently weak exchange between these spins so the maximum magnetocaloric response is at low temperature, though control over exchange is by no means a unique problem in magnetochemistry, and also their real-world, long-term stability at useful temperatures. Nevertheless there are reported examples from more than twenty five years ago with which to test the concept,\textsuperscript{1} indeed the idea of radical-Ln\textsuperscript{III} compounds has been applied successfully to SMMs,\textsuperscript{2, 3} as discussed elsewhere.

This could lead to an improvement in various magnetocaloric materials, whether with transition metals, particularly Mn\textsuperscript{II}, which is isotropic and has a spin of \(\frac{5}{2}\), or Gd\textsuperscript{III}. The exchange between transition metals is known to vary through “simple” bridging angle relationships,\textsuperscript{4,5} potentially allowing tuning using different ligand substituents. For low temperature work, the weaker exchange coupling between the 4f ions would be more favourable, though. Interestingly, despite the attractions of Gd\textsuperscript{III}, Mn\textsuperscript{II} actually has a larger “spin per unit of atomic weight” than Gd\textsuperscript{III}: \(\frac{5}{2}\) and 54.94 versus \(\frac{7}{2}\) and 157.25, respectively, so could be regarded as more efficient in this way. Also, Mn\textsuperscript{II} requires fewer ligands to fill its smaller coordination sphere and so may lead to compounds with larger metal percentages. There have been few Mn\textsuperscript{II} compounds with diamagnetic ligands reported for their MCE (Chapter 3 and therein), though, which may indicate problems with controlling the exchange and oxidation state.

ii) Increasing density

The second performance enhancement would come from a large increase in the density of such materials, good candidates being Gd\textsuperscript{III}F\textsubscript{3} and [Gd\textsuperscript{III}(CO\textsubscript{3})OH]\textsubscript{n}. Specifically then, we would aim to measure the MCE via heat capacity data for Gd\textsuperscript{III}F\textsubscript{3} and [Gd\textsuperscript{III}(CO\textsubscript{3})OH]\textsubscript{n}, for which we anticipate
the extremely large $-\Delta S_M$ values of ca. 81 J kg$^{-1}$ K$^{-1}$ and 74 J kg$^{-1}$ K$^{-1}$, respectively (adjusted for density as ca. 560 mJ cm$^{-3}$ K and 240 mJ cm$^{-3}$ K). The first is commercially available and the second readily synthesised from the hydrothermal reaction of $[\text{Gd}^{III}\text{(NO}_3\text{)}_3\cdot n\text{H}_2\text{O}]$ and urea. We attempted to measure the magnetic properties of these using our SQUID set-up, but were hampered by what appeared to be movement of the samples in the holder, notably even with the capsule fully packed with well powdered samples for $\text{Gd}^{III}\text{F}_3$. This resulted in poor quality data unsuitable for analysis. Possibly this arises from movement of the samples due to their contraction and expansion under measurement with varying temperatures, so fixing the sample in gel or eicosane may prevent this. A better and fuller solution would be to use heat capacity measurements, so obtaining $\Delta T_{AD}$ and $-\Delta S_M$ directly, though these facilities are not widely available. This does present some problems for the $\text{Gd}^{III}\text{F}_3$ sample: $\text{Gd}^{III}\text{F}_3$ is extremely hygroscopic and will readily absorb water from the atmosphere, so reducing the measured $-\Delta S_M$ by virtue of the increased diamagnetic contribution of water to the molecular weight and would also change the structure by coordination of $\text{H}_2\text{O}$ groups to the metals; fixing a sample for heat capacity measurements exposes the sample wrapped in gel for around five minutes and accurately determining the water absorbed may be difficult.

This echoes in some way a problem we had when attempting to synthesise $[\text{Gd}^{III}\text{(BH}_4\text{)}_3\cdot n\text{(THF)}]$, where $n < 3$. We attempted to synthesise the solvated version, rather than the “dry”, though even this was unsuccessful, likely because the THF was not dry enough. The more interesting compound is actually the desolvated version, which itself has problems of purification, being made by a mechanical milling technique, grinding together $\text{Ln}^{III}\text{Cl}_3$ and $\text{NaBH}_4$. This compound could have a $-\Delta S_M$ of up to 86 J kg$^{-1}$ K$^{-1}$, so all three of these targets could potentially outperform all existing published magnetocaloric materials at low temperatures.

### For 4f phosphonates as better SMMs and MCE materials

An area that we explored was the synthesis of 3d-4f phosphonate compounds via solvothermal synthesis, giving $[\text{Ln}^{III}\text{Zn}^{II}_3\text{(BuCO}_2\text{)}_{10}\text{(BuPO}_3\text{)}_2\text{(NEt}_3\text{)}_2]$, henceforth $[\text{Ln}^{III}\text{Zn}^{II}_3]$ (Chapter 7), which follows a well-established research effort towards 3d-4f phosphonate cages. The phosphonate ligands were known to be flexible and oxygen-rich, favouring bonding to the oxophilic lanthanides, making them useful for bonding to lanthanide ions in “serendipitous” syntheses. These studies have resulted in only a handful of SMMs, perhaps because of the adverse effects of the 3d ions, and MCE materials, hampered by, for example, anisotropic $\text{Co}^{II}$ and diamagnetic $\text{Zn}^{II}$. Removing the 3d metal may be a better proposal, which is effectively what we achieved with our work by inclusion of diamagnetic $\text{Zn}^{II}$ for SMMs. Optimising 3d-4f compounds also requires changing both the 3d and 4f metals for different applications.
0-D 4f phosphonates from solvothermal synthesis, both simplify the situation and are rare, making them an appealing target in themselves and could act as improvements over the 3d–4f phosphonate compounds as SMMs, by leaving only single-ion effects dominant, and as refrigerants, all the metals contributing positively to the MCE. Our only success in this area, and an area to return to in future, was in synthesising a bicapped trigonal prism, formulated to the best of our knowledge as [Gd₈(OH)₈(NO₃)₃(EtOH)₆(H₂O)₃PCPh₃]₆, following Chandrasekhar and Sasikumar’s methodology with trityl phosphonic acid (H₂O₃PCPh₃) and [Ce(NO₃)₃•nH₂O] in a water:ethanol mixture. Though we grew crystals from the solution, these were hard to characterise, with the inclusion of vast amounts of solvent, and were also found to be unsatisfactory by elemental analysis. Nonetheless, this and other novel phosphonate complexes remain appealing targets.

Although the bulky trityl phosphonic acid ligand necessarily reduces metal content, it may help to stabilise these compounds in the harsh conditions of solvothermal reactions, which we have shown with our work using the triphenyl acetic acid group.

For deeper understanding

Computer calculations and modelling of the [Gd³⁺(HCOO)₃]ₙ (Chapter 6) and [Gd³⁺₇(OH)₆(thmeH)₈(thmeH₂)(MeCN)₂](NO₃)₂, hereafter {Ln³⁺₇} (Chapter 4, 5 and 6), compounds are underway and will investigate the ordering mechanisms in these compounds by comparison of experimental with calculated heat capacities and the exchange interactions in more detail. This will involve collaboration with Marco Evangelisti and Jürgen Schnack (Universität Bielefeld). Furthermore, [Gd³⁺(HCOO)₃]ₙ is being investigated for deposition on surfaces for applications in spintronic devices.⁹

Conclusions and Perspective

Cool Runnings

What, then, has been achieved? We aimed to synthesise zero-dimensional compounds using the tripodal alcohol ligands thmeH₃ and teaH₃ and assess them for their magnetocaloric and slow-relaxation behaviour, believing that they could be superior to 3d and 3d–4f compounds. The former, {Gd³⁺₇} (Chapter 4, 5 and 6), showed a large (at the time) MCE of 23 J kg⁻¹ K⁻¹ (ΔH = 0-7 T, 3 K), which still compares to all current 3d compounds favourably when analysed in this way, the highest recorded value being from [Mn³⁺₆Mn²⁺₈(OH)₂(Hpeol)₄(H₂peol)₄EtOH]₄₄ at 25 J kg⁻¹ K⁻¹. [Gd³⁺₂(teaH)₂(Ph)₃CCO₂][NO₃]₂] (Chapter 9) is similarly competitive (20 J kg⁻¹ K⁻¹, ΔH = 0-7 T, 3 K). The point here is that the last few years have seen a huge increase in magnitude of the
–ΔSM achieved by compounds where metals are linked by diamagnetic ligands (not alloys), now reaching over 50 J kg⁻¹ K⁻¹. Whilst, as explained elsewhere (Chapter 4), this is not the only parameter for assessment, it is a useful guide. We had noted how compounds with small ligand sets were found to have the largest –ΔSM values and found what was then a record value in [GdIII(OAc)₃MeOH]ₙ, which we accidentally synthesised while searching for lanthanide phosphonate compounds solvothermally. This and others were published shortly after by Guo et al.,¹¹ being synthesised in a more systematic way, and confirmed the hypotheses: i) the percentage of lanthanide(III) in the compound is important, and ii) that the dimensionality is not. Bizarrely, in retrospect, almost the whole focus of this field was upon zero-dimensional clusters, aping SMM research, though these have large associated ligand masses. We have assisted we think in reorienting the field towards a different type of solution in these high-dimensionality, high metal content materials. [GdIII(HCOO)₃]ₙ (Chapter 6) is currently the primary exemplar of this approach and compares well with all other materials for its ΔTAD and −ΔSM values, indeed it outperforms the industry standard GdIII₃GaIII₅O₁₂ (GGG)¹² in some scenarios and may be deposited on surfaces for testing in spintronic devices, a distinct advantage over metal alloy materials. Therefore, whilst meeting our initial aims of synthesising 0-D compounds, we found a rather different approach would eventually be needed.

**An Elephantine Problem**

We have added to the now rapidly growing collection of LnIII SMMs with {DyIII₇} (Chapter 5), and to the 3d-4f catalogue with {DyIII₇ZnII₄} (Chapter 5), Ueff barriers for these being ca. 135 K and 38 K, respectively. Although at the time the former was competitive with the best LnIII multi-metallic compounds, recent developments have moved the field on somewhat. This area of research still seems to possess an element of chance, we feel, as it remains conceptually difficult to deliberately synthesise new SMMs. Important discoveries such as the relaxation mechanism of [DyIII₄K₂O(OtBu)₁₂],¹³ are rationalised after the event rather than used to tailor the design of new molecules. Even this “post-rationalisation”, though, is an improvement on no understanding, and we, too, have used computer modelling on {LnIII₃ZnII₄} (Chapter 7) to rationalise their SMM behaviour, or lack of it. The latest models may help to screen new compounds before they are even measured with SQUID techniques, purely based on the ligand type and geometry at the metal sites.

**United Utilities**

The utility of all the SMMs and magnetocaloric materials made is, of course, an intriguing point. Magnetocaloric materials have long been mooted for use in space technologies,¹⁴ because they offer a reliable and repetitive cooling system, without a gas storage requirement conventionally
used in terrestrial applications, which could be a problem for unmanned long-term missions. Low temperature work required for detectors on satellites is an interesting area. Several devices have been constructed, including examples designed to operate below 1 K,\textsuperscript{15} foregoing the need for \(^4\text{He}\), \(^3\text{He}\) and \(^3\text{He}/^4\text{He}\) cooling procedures, the last of which requires gravity to operate. \([\text{Gd}^{\text{III}}(\text{HCOO})_3]_n\) may be unsuitable for this, despite the large \(-\Delta S_M\) value, because the maximum response is at 2 K. There is a large range of applications for the catch-all term “low-temperature” cooling, where \(^4\text{He}\) is useful down to 1.2 K there may be one category, and below this to 0.04 K another, competing with \(^3\text{He}\), and another down to the lowest temperatures achievable, competing with \(^3\text{He}/^4\text{He}\) devices.\textsuperscript{16}

There are several candidates amongst molecules other than SMMs for storing data. In fact, one of these has been more successful, namely DNA (deoxyribonucleic acid). This was recently used\textsuperscript{17} to store words, images and a JavaScript program at a tiny-scale: the point of making SMMs for this application has now been achieved by something else. In principle, up to 455 exabytes of information can be stored on only 1 g of DNA. Furthermore, DNA has long since been incorporated onto chips for easy storage and manipulation. The main problems with SMMs as a rival to these and other devices are much the same as they have been for the last twenty years and more, despite the huge advantages in percentage terms of the parameters used to quantify their performance: i) low energy barriers are still the main problem, being nowhere near that required for substantial lifetimes of magnetisation at room temperature. ii) Hysteresis temperatures have also been improved, though most of this increase has come recently with the introduction of 4f lanthanide ions into this field. Whether we can expect a similar improvement by examining 5f actinides remains to be seen, with relatively early work seeming promising.\textsuperscript{18} iii) Surface fabrication\textsuperscript{19} has shown that some SMMs retain their properties on surfaces, though not all SMMs can be manipulated in this way. It may be a harsh reality but, as a practical memory device, all SMMs require significant improvements.

On a more positive note, we observe that the field of spintronics may eventually profitably employ SMMs in small scale transistors and spin valves. This field attempts to mimic macroscale components at the nanoscale. One of several pioneers here is Wolfgang Wernsdorfer, who, amongst other things, has demonstrated the possibility of reading nuclear spins\textsuperscript{20} from individual SMMs with potential applications in quantum information storage, and spin valves,\textsuperscript{21} nanoscale devices with magnetisation dependent variable resistances.

Of course, one may also feel that the synthesis and investigation of new (and old) compounds is an end in itself, for curiosity’s sake.
References

Appendix

A Dense Metal-Organic Framework For Enhanced Magnetic Refrigeration

Recent years have witnessed a terrific increase in the number of molecule-based materials proposed as magnetic refrigerants for liquid-helium temperatures. Refrigeration proceeds adiabatically via the magnetocaloric effect (MCE), which describes the changes of magnetic entropy ($\Delta S_m$) and adiabatic temperature ($\Delta T_A$), following a change in the applied magnetic field ($\Delta B$). As in the first paramagnetic salt that permitted sub-Kelvin temperatures to be reached in 1933, gadolinium is often present because its orbital angular momentum is zero and it has the largest entropy per single ion. The controlled spatial assembly of the Gd$^{3+}$ spin centers is vital for designing the ideal magnetic refrigerant. On the one hand, the magnetic density should be maximized by, for example, limiting the amount of non-magnetic elements which act passively in the physical process. On the other hand, magnetic ordering for $B = 0$ should be avoided, since this results in the decrease of MCE above the target working temperature of the refrigerant. Therefore a compromise becomes necessary, especially for reaching low temperatures.

Metal–organic framework (MOF) materials have recently attracted interest for their cooling properties, combined with their synthetic variety and intrinsic robustness. Indeed, the dimensionality of Gd-MOFs has no effect in itself on the MCE, but its intrinsic density. Light and short bridging ligands, such as the formate ion, are clearly advantageous in this regard.

The molar magnetization ($M$) was collected for temperatures between 2 and 10 K (Figure S1, Supporting Information). The magnetization saturates to the expected value of 7 $\mu_B$ for a Gd$^{3+}$ spin moment, according to which $s = 7/2$ and $g = 2$. The M(B) curves can be described well by a Brillouin function – see the dashed line in Figure S1 for an ideal paramagnet at $T = 2$ K. Deviations of the experimental data from the paramagnetic
behavior are barely noticeable, and only for the lowest temperatures, and can be ascribed to the presence of a weak antiferromagnetic interaction. This is corroborated by the temperature dependence of the magnetic susceptibility \( \chi \). As shown by the solid line in the inset of Figure S1, the susceptibility data can be fitted above 2 K to a Curie–Weiss law \( \chi = \frac{g^2 \mu_B^2 (s + 1)}{3k_B (T - \theta)} \), obtaining a negative, although small, \( \theta = -0.3 \) K, which suggests that the Gd\(^{3+} \) moments are weakly antiferromagnetically correlated in the paramagnetic phase.

The top panel of Figure 2 shows the measured low-temperature heat capacity \( C \) as a function of temperature for several applied fields. A sharp lambda-like peak can be observed in the zero-field data for \( T_{C1} = 0.8 \) K, denoting the presence of a phase transition, which is accompanied by a smooth, tiny feature at \( T_{C2} = 0.4 \) K. The magnetic origin of both anomalies is proved by the fact that external applied fields fully suppress them.\(^{[29]} \)

In agreement with \( M(T,B) \), the analysis of the field-dependent \( C \) reveals that magnetic interactions between the Gd\(^{3+} \) spin centers are relatively weak, since an applied field \( B = 1 \) T is sufficient for fully decoupling all spins. As shown in Figure 2, the calculated Schottky contributions (solid lines) for the field-split levels of the non-interacting \( s = 7/2 \) multiplet nicely account for the magnetic contribution to the experimental heat capacity \( C_m \). For \( T \geq 7 \) K, the large field-independent contribution can be attributed to the lattice phonon modes of the crystal. The dashed line in the top panel of Figure 2 represents a fit to this contribution, with the well-known Debye function yielding a value of \( \Theta_D = 168 \) K for the Debye temperature, which is remarkably large for molecular\(^{[21]} \) and MOF\(^{[15]} \) materials, denoting a relatively rigid lattice. A larger \( \Theta_D \) implies a correspondingly lower lattice entropy in the low-temperature region, ultimately favoring the MCE. From the experimental heat capacity the temperature dependence of the magnetic entropy \( S_m(T) \) is derived by integration, i.e.,

\[
S_m(T) = \int_0^T C_m(T) \frac{dT}{T}
\]

where \( C_m \) is obtained by subtracting the lattice contribution to the total \( C \) measured. The so-obtained \( S_m(T) \) is shown in the bottom panel of Figure 2 for the corresponding applied fields. For \( B = 0 \), the lack of experimental \( C_m \) for \( T \leq 0.3 \) K has been taken into account by matching the limiting \( S_m \) at high temperature with the value obtained from the in-field data. One can notice that there is a full entropy content of \( \ln(8) = 17.3 \) J mol\(^{-1} \) K\(^{-1} \) = 59.0 J kg\(^{-1} \) K\(^{-1} \) per mole Gd\(^{3+} \) involved, as expected from \( \ln(2s + 1) \) and \( s = 7/2 \), where \( R \) is the gas constant and the molecular mass is \( m = 292.30 \) g mol\(^{-1} \).

Next, we indirectly evaluate the MCE of Gd(HCOO)\(_3\) from the experimental data presented so far. From the bottom panel of Figure 2, we obtain the magnetic entropy changes \( \Delta S_m(T,\Delta B) \) for different applied field changes \( \Delta B = B_f - B_i \). The so-obtained results are depicted in Figure 3. A similar set of data can also be derived from an isothermal process of magnetization by employing the Maxwell relation, i.e., \( \Delta S_m(T,\Delta B) = \int_{B_i}^{B_f} \frac{\partial M(T,B) }{ \partial T}dB \). From the experimental \( M(T,B) \) data in Figure S1, we then obtain curves that rather beautifully agree with the corresponding results previously derived from the heat capacity – see the top panel of Figure 3. Furthermore, to a cooling process under adiabatic conditions, one naturally associates a
Figure 2. A far more elegant and reliable method for determining temperature change whose estimate is made feasible by knowing C and thus \( S_m \). The bottom panel of Figure 2 shows \( \Delta T_{ad} (\Delta B) \), where \( T \) denotes the final temperature of the adiabatic cooling, e.g., going from \( C(T = 3.4 \text{ K}, B = 1 \text{ T}) \) to \( A(T = 0.95 \text{ K}, B = 0) \) in Figure 2. A far more elegant and reliable method for determining the MCE is by directly measuring \( \Delta T_{ad} (\Delta B) \) under quasi-adiabatic conditions. Following the procedure described in the Supporting Information, we have performed measurements for the experimental conditions corresponding to the magnetization (\( A \rightarrow C \)) and demagnetization (\( D \rightarrow B \)) processes highlighted in Figure 2. Starting from \( T_i = 0.98 \text{ K} \), the result, depicted in Figure S2, Supporting Information, yields \( T_i \rightarrow T \rightarrow 3.45 \text{ K} \) for \( 0 \rightarrow B \rightarrow 1 \text{ T} \) and \( T_i \rightarrow T \rightarrow 0.47 \text{ K} \) for \( 1 \text{ T} \rightarrow B \rightarrow 0 \), thus corresponding to \( \Delta T_{ad} = 2.47 \) and 0.51 K for magnetization and demagnetization, respectively, in good agreement with what is obtained from the entropy data (see Figure 2).

The MCE of Gd(HCOO)\(_3\) is exceptionally large, especially in comparison with other molecule-based magnetic refrigerants, as summarized in Table 1 for three representative examples from the recent literature. All of them are characterized by a pronounced maximum of the MCE at \( T_{max} = 1 \text{ K} \) for \( \Delta B = 2 \text{ T} \), as for Gd(HCOO)\(_3\). The choice of \( \Delta B = 2 \text{ T} \) is dictated by the fact that, for widespread applications, the interest is chiefly restricted to applied fields which can be produced with permanent magnets. In Table 1, the maximum entropy changes \( -\Delta S_m^{max} \) are reported per unit volume. Although these units are not often used, they are better suited for assessing the implementation of the refrigerant material in a designed apparatus. On this point, one could correctly argue that the MCE of molecule-based refrigerant materials is disfavored by their typically low mass density, \( \rho \). However, Gd\(^{4+}\) centers in Gd(HCOO)\(_3\) are interconnected only by short and extremely lightweight HCOO\(^-\) ligands, resulting in a relatively large \( \rho \) of 3.86 g cm\(^{-3}\). Ultimately, this enhances the MCE, favored by a larger weight of magnetic elements with respect to non-magnetic ones, which act passively. To the best of our knowledge, no other molecule-based refrigerant material has a MCE as large as in Gd(HCOO)\(_3\); \( -\Delta S_m^{max} \approx 168.5 \text{ and } 215.7 \text{ mJ cm}^{-3} \text{ K}^{-1} \) for \( \Delta B = (2-0) \text{ T} \) and \( (7-0) \text{ T} \), respectively, as shown in Figure 3. This comparison would not be complete without assessing the efficiency of refrigeration for every selected material. This is accomplished by estimating the relative cooling power (RCP), defined as the product of \( -\Delta S_m^{max} \) and the full width at half maximum (FWHM) of the corresponding \( -\Delta S_m (T) \) curve, i.e., \( \delta T_{FWHM} \). Among the other molecule-based refrigerants in Table 1, Gd(HCOO)\(_3\) shows the largest relative cooling power with an RCP of 522.4 mJ cm\(^{-3}\). Lastly, we extend this comparison to also include gadolinium gallium garnet (GGG), which is the reference magnetic refrigerant material for the 1 K < T < 5 K range. Indeed, its functionality is commercially exploited, also owing to its large \( \rho \) of 7.08 g cm\(^{-3}\), which contributes to provide record values for \( -\Delta S_m^{max} \approx 145 \text{ mJ cm}^{-3} \text{ K}^{-1} \) and an RCP of 478.5 mJ cm\(^{-3}\) for the same applied field change of 2 T. As can be seen in Table 1, these values are close to, but still lower than, the reported ones for Gd(HCOO)\(_3\).

In conclusion, we experimentally determined the MCE of the Gd(HCOO)\(_3\) MOF material. Under quasi-adiabatic conditions, sub-Kelvin direct measurements of the temperature change corroborate the results inferred from indirect methods. The comparison of gadolinium formate with other excellent magnetic refrigerants for liquid-helium temperatures, such as the benchmark GGG, reveals that Gd(HCOO)\(_3\) has an unprecedentedly large MCE. Our observations are interpreted as the result of a light and compact

Table 1. Parameters of selected refrigerant materials with a high magnetocaloric effect at liquid-helium temperatures and for the applied field change \( \Delta B = (2-0) \text{ T} \). From left to right: \( \rho \), mass density; \( -\Delta S_m^{max} \), maximum magnetic entropy change; \( T_{max} \), temperature of the corresponding \( -\Delta S_m^{max} \); \( \delta T_{FWHM} \), full width at half maximum of the corresponding \( -\Delta S_m (T) \); RCP, relative cooling power; ref., corresponding reference.

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<td>[Gd(HCOO)(OAc)(_2)(H(_2)O)(_4)]</td>
<td>2.397</td>
<td>88.9</td>
<td>0.9</td>
<td>3.2</td>
<td>284.5</td>
<td>[13]</td>
</tr>
<tr>
<td>Gd(_2)(fum)(_3)(H(_2)O)(_4)·3H(_2)O</td>
<td>2.515</td>
<td>45.3</td>
<td>1.0</td>
<td>2.4</td>
<td>108.7</td>
<td>[12]</td>
</tr>
<tr>
<td>Gd(_2)Ca(_2)O(_6) ( \alpha ) (CCG)</td>
<td>7.080</td>
<td>145.0</td>
<td>1.2</td>
<td>3.3</td>
<td>478.5</td>
<td>[23]</td>
</tr>
</tbody>
</table>
structural framework promoting very weak magnetic correlations between the Gd\(^{3+}\) spin centers.

Finally, we foresee that synthetic and technological strategies, already developed for the surface deposition of MOF materials, could ultimately facilitate the integration and exploitation of Gd(HCOO), within molecule-based microdevices for on-chip local refrigeration.\(^{26}\)

Experimental Section

**Single-Crystal Structure Determination:** Data were obtained from a colorless block on an Agilent Technologies SuperNova diffractometer with a Mo microsource (\(\lambda = 0.71073 \text{ Å}\)). Cell refinement, data reduction, and absorption corrections were performed with Crystals Pro.\(^{37}\) Coordinates from the ytrrium structure (code LOSKUA)\(^{25}\) were used as an initial solution, and refinement on \(F^2\) was done with SHELXTL.\(^{39}\) Crystallographic and refinement parameters are summarized in Table S1. Supporting Information, while full data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-914467.

**Magneto-Thermal Characterization:** Magnetization measurements down to 2 K and heat capacity measurements using the relaxation method down to \(0.35\) K were carried out on powder samples by means of commercial setups (QDMPPS-XL and QD-PPMS, respectively) for \(0 < \theta < 5 \text{ T}\) and \(0 = \theta < 7 \text{ T}\), respectively. Direct measurements of the MCE were performed on a powder sample using a sapphire plate to which a Cernox (CX-1010) resistance thermometer was attached, installed in the same setup employed for heat capacity.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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\(^{[1]}\) For a recent review see, e.g., M. Evangelisti, E. K. Brechin, Dalton Trans. 2010, 39, 4672 and references therein.


\(^{[18]}\) Gd(HCOO)₃ crystallizes in space group \(R3\bar{m}\) with \(a = b = 10.4583(4) \text{ Å}, c = 3.8669(3) \text{ Å}, \alpha = \beta = 90°, \gamma = 120°\) and \(Z = 3\). The distance between nearest and next-nearest Gd neighbors is 3.98 Å and 6.19 Å, respectively. CCDC-914467 contains the supplementary crystallographic data, which can be obtained free of charge from the Cambridge Crystallographic Data Centre.


\(^{[20]}\) We refrain from discussing the magnetic ordering mechanism any further since this topic exceeds the scope of this article and its full comprehension requires additional measurements, whose results will be exhaustively presented elsewhere.


A Dense Metal–Organic Framework for Enhanced Magnetic Refrigeration

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**Figure S1.** Field-dependence of the experimental molar magnetization $M$ for temperatures ranging from 2 to 10 K, with a 1 K step between adjacent isothermal curves. Dashed line is the calculated $M$ of a paramagnet for $s = 7/2$, $g = 2$ and $T = 2$ K. Inset: temperature-dependence of the inverse of the experimental molar susceptibility collected for $B = 0.1$ T and Curie-Weiss fit (solid line).
Direct measurement of MCE

The procedure for the direct determination of \( \Delta T_{ad} \) comprises a full magnetization-demagnetization cycle, during which the experimental \( T \) and \( B \) are continuously recorded. In a half cycle, starting with the sample at an initial \( T_i \), we magnetize (demagnetize) by gradually increasing (decreasing) the applied field from \( B_i \) to \( B_f \) and let the sample relax to the final \( T_f \). In order to compute the temperature evolution for an ideal adiabatic process, one requires a precise knowledge of the heat that unavoidably is absorbed from (released to) the thermal bath during the direct measurement. For this purpose, the thermal conductance \( k \) of the wires holding our sensor was previously determined as a function of \( T \), using a standard copper piece as the sample. The non-adiabaticity induces a variation of the entropy \( \Delta S = S(t) - S(t_0) \) in a time interval \( t - t_0 \), which can be expressed as \( \Delta S = \int_{t_0}^{t} k(T - T_0) / T dt \) at every time instant.

From Eq. 1 we also have \( \Delta S = \int_{B_i}^{B_f} C(T, B) / T dT \), where the adiabatic temperature \( T_{ad} \), viz., the temperature if the sample would have been kept thermally isolated, is the only unknown and can therefore be deduced numerically. In our treatment, we safely disregard the entropy contribution due to the heat transferred from the sample holder to the refrigerant material, i.e., \( \Delta S = \int_{T_i}^{T_f} C_{sh} / T dT \), since the heat capacity of the sample holder \( C_{sh} \) is negligible with respect to that of \( \text{Gd(HCOO)}_3 \) below liquid-helium temperature. An overall error of less than 1 % is estimated for the whole procedure.

Figure S2 shows the time evolution of \( B \), \( T \) and \( T_{ad} \) for a full magnetization-demagnetization cycle, starting at \( T_i = 0.98 \) K and for a field change \( \Delta B = B_f - B_i = (1 - 0) \) T or \( (0 - 1) \) T, depending on whether we deal with the magnetization or demagnetization process, respectively. We note that the exact same conditions are highlighted in Figure 2: process A \( \rightarrow \) C for the magnetization and process D \( \rightarrow \) B for the demagnetization. In the top panel of Fig. S2, we observe \( T \) to increase while we magnetize to 1 T. Here \( T_{ad} \) increases more
than $T$ because the thermal losses to the bath are compensated to obtain $T_{ad}$. Upon reaching $B_f$, $T$ decays back towards $T_i = 0.98$ K but $T_{ad} = 3.45$ K is constant, since it corresponds to an adiabatic process at constant $B$. In the bottom panel, $T$ decreases below $T_i$, while we demagnetize to zero field, whereupon $T$ gradually relaxes back to equilibrium, while constant $T_{ad} = 0.47$ K. Remarkably, the final adiabatic temperatures of 3.45 K and 0.47 K obtained after sweeping the field up and down, respectively, corroborate the results independently inferred by an indirect method – see C and B, respectively, in Figure 2.

**Figure S2.** Time evolution of the applied field $B$, experimental temperature $T$ and deduced adiabatic temperature $T_{ad}$, as labeled, during a magnetization (top) and a demagnetization (bottom) process, both starting from $B_i$ and $T_i = 0.95$ K.
Table S1. Crystal data and structure refinement for Gd(HCOO)$_3$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$_3$H$_3$GdO$_6$</td>
</tr>
<tr>
<td>$F_w$ (g mol$^{-1}$)</td>
<td>292.30</td>
</tr>
<tr>
<td>CCDC number</td>
<td>914467</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>$R3m$</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.20x0.16x0.12</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>10.4583(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>3.9869(3)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>120</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>377.65(3)</td>
</tr>
<tr>
<td>$Z$</td>
<td>3</td>
</tr>
<tr>
<td>$\rho_{calc}$</td>
<td>3.856</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>13.132</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>399</td>
</tr>
<tr>
<td>$\theta$ for data collection (°)</td>
<td>3.90-29.18</td>
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<td>Reflections collected / unique</td>
<td>1174 / 240</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>240 / 26 / 1</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.139</td>
</tr>
<tr>
<td>Final R indices [$I&gt;2\sigma(I)$]</td>
<td>0.0131 / 0.0303</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>0.0131 / 0.0303</td>
</tr>
<tr>
<td>largest diff. peak and hole (e Å$^3$)</td>
<td>1.266 / −0.656</td>
</tr>
</tbody>
</table>
Figure S3. Experimental powder X-Ray Diffraction (XRD) pattern (top – black line), together with the calculated XRD for a Gd(HCOO)₃ single-crystal (red line), and XRD peak positions from JCPDS 42-0676 (bottom – black lines).