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A cyclic tetranuclear Ni_2Gd_2 complex bridged by amino acidato ligands, with an $S = 9$ ground state, derived from ferromagnetic spin-coupling between nickel(II) and gadolinium(III) ions†

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Synthesis and structure of a cyclic tetranuclear Ni_2Gd_2 complex bridged by amino acidato ligands, with an $S = 9$ spin ground state, derived from ferromagnetic spin-coupling between $S_{\text{Gd}} = 7/2$ and $S_{\text{Ni}} = 1$ are reported.

The metal complexes of amino acids interest biochemists as models for the metal-binding sites on proteins. From the point of view of coordination chemistry, an amino acid, which is safe and easily obtained, can be regarded as a typical multidentate ligand. Taking advantage of the properties of the amino acid ligand, we have been carrying out the syntheses of heteronuclear complexes bridged by amino acidato ligands.^{1,2} Recently, such research has achieved remarkable development with contributions by many groups.³ Heteronuclear complexes have attracted special attention because of their versatile magnetic behaviour derived from large ground spin state and large magnetic anisotropy. The forthcoming target in this field is the magnetic chemistry of d–f and f–f transition metal complexes. In order to obtain information on the magnetic properties of d–f interactions, d–f heteronuclear complexes have been synthesized.^{4,5} In these complexes there are some single molecule magnets. The first mixed-metal 3d–4f SMM to exhibit hysteresis loops and quantum tunnelling of the magnetization, $[\text{Mn}_{11}\text{Dy}_4\text{O}_8(\text{OH})_6(\text{OMe})_2(\text{O}_2\text{CPh})_6(\text{NO}_3)_5(\text{H}_2\text{O})_3] \cdot 15\text{MeCN}$ was reported by Christou and co-workers.^{4b} Matsumoto and co-workers have reported synthesis, structures, and magnetic properties of d–f extended cyclic tetranuclear compounds by using a ligand complex having a copper(II) ion.⁵ Some of these compounds exhibited the behaviour of a single molecule magnet.^{5c} Although the ligand complex applied by Matsumoto *et al.* is useful to synthesize different combinations of d–f metal cyclic tetranuclear compounds, the coordination sphere of the transition metal site is square planar. Therefore, the nickel ions in the Ni_2Gd_2 cyclic compound are diamagnetic. Here we demonstrate a new cyclic tetranuclear Ni_2Gd_2 complex, $[\text{Gd}_2\text{Ni}_2(\text{pro})_4(\text{NO}_3)_6(\text{CH}_3\text{CN})_4]$ (**1**) ($\text{Hpro} = \text{L-proline}$), in which the nickel ions have an octahedral

coordination geometry, by using amino acidato bridging ligands (Scheme 1).

Scheme 1

$[\text{Gd}_2\text{Ni}_2(\text{pro})_4(\text{NO}_3)_6(\text{CH}_3\text{CN})_4]$ **1** is formed from the reaction of hexahydrated gadolinium(III) nitrate (1 mmol) with $[\text{Ni}(\text{pro})_2(\text{H}_2\text{O})_2]$ (1 mmol) in acetonitrile (20 ml). The reaction mixture was layered with diethyl ether and kept at room temperature for several days. Although dark blue blocks were crystallized at a bottom or on the walls of a glass vessel, such crystals immediately decayed after filtration. Upon crystallization, the addition of 1,2-dihydroxybenzene resulted in large and stable crystals. It is not certain what the role of 1,2-dihydroxybenzene is during crystallization. 1,2-Dihydroxybenzene might arrange suitable conditions for crystal growth, although 1,2-dihydroxybenzene did not react.

The structure was determined by single-crystal X-ray diffraction analysis.† Fig. 1 shows an ORTEP drawing of **1**.

The Ni^{II} ion has a distorted octahedral coordination geometry with two acetonitrile nitrogen atoms and two amino nitrogen and two carboxylato oxygen atoms of pro ligands: $\text{N}(1)\text{--Ni}(1)\text{--N}(2) = 168.2(3)^\circ$, $\text{O}(1)\text{--Ni}(1)\text{--N}(11) = 172.7(3)^\circ$, $\text{O}(3)\text{--Ni}(1)\text{--N}(12) = 172.0(3)^\circ$, Ni--O (2.070(5)–2.045(5) Å) and Ni--N (2.065(7)–2.099(7) Å). The carboxylato oxygen atom O(1) bridges Gd^{III} and Ni^{II} ions: $\text{Gd}(1)\text{--O}(1) = 2.495(5)$ Å, $\text{O}(1)\text{--Ni}(1) = 2.070(5)$ Å, $\text{Gd}(1)\text{--O}(1)\text{--Ni}(1) = 152.4(2)^\circ$, $\text{Gd}(1) \cdots \text{Ni}(1) = 4.434(1)$ Å. One carboxylato oxygen atom is coordinated to both Ni^{II} and Gd^{III} ions and the other is coordinated to the Gd^{III} ion, thus forming five- and four-membered chelate rings, as shown in Scheme 1. The Gd^{III} ion has a ten-coordination geometry including the coordination of three bidentate nitrato ions ($\text{Gd--O} = 2.424(8)\text{--}2.552(6)$ Å) and two four-membered chelate rings formed by a carboxylato group of a pro ligand ($\text{Gd--O} = 2.433(6)\text{--}2.547(5)$ Å). The separations between metal ions in neighbouring molecules are larger than

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Fig. 1 ORTEP drawing of the cyclic Ni_2Gd_2 tetranuclear complex with selected atom labelling scheme. Thermal ellipsoids are drawn at 30% probability level.

9.58 Å, suggesting the absence of any significant intermolecular interactions.

Solid-state direct current (dc) magnetic susceptibility (χ_M) data for **1** were collected in the 2–300 K range, with applied magnetic fields of 0.1, 0.5 and 1 T.⁶ The $\chi_M T$ value (Fig. 2) is 18.56 cm³ K mol⁻¹ at 300 K, which compares with the expected value of 18.17 cm³ K mol⁻¹ for two Ni^{II} and two Gd^{III} non-interacting metal ions ($S_{\text{Gd}} = 7/2$, $S_{\text{Ni}} = 1$, $g_{\text{Gd}} = 2$, $g_{\text{Ni}} = 2.2$). This value remains almost constant down to ca. 80 K, at which the value starts to increase rapidly to reach 29.02 cm³ K mol⁻¹ at 2 K (for 0.1 T magnetic field). This is consistent with the presence of weak ferromagnetic super-exchange between Ni^{II} and Gd^{III} ions, leading to an $S = 9$ ground state. This affirmation is also supported by the variable-field magnetization data depicted in the insert in Fig. 2. The $\chi_M T$ curves recorded at 0.5 and 1 T (not presented here) show a maximum at 3.2 (23.4 cm³ K mol⁻¹) and 5.5 K (21.4 cm³ K mol⁻¹), respectively, and a sharp decrease in $\chi_M T$ below these temperatures, due to zero-field splitting. We used MAGPACK⁷ to simultaneously simulate the susceptibility data at 0.1 T magnetic field and also the magnetization data at 2 and 4 K (inserted in Fig. 2) of **1**.

Fig. 2 Plots of $\chi_M T$ vs. T at 0.1 T and $M/N\beta$ vs. H (inset) of **1**. The solid curves represent the theoretical curves with the parameters of $J_{\text{Gd-Ni}} = +0.15$ cm⁻¹ and $D_{\text{Ni}} = 3.0$ cm⁻¹, with $g_{\text{Ni}} = 2.33$ and $g_{\text{Gd}} = 2.0$.

The best simulation was reached by full-matrix diagonalization of the following spin Hamiltonian: $H = -2J_{\text{Gd-Ni}}(S_1 S_2 + S_2 S_3 + S_3 S_4 + S_1 S_4) + 2D_{\text{Ni}}[S_{\text{Ni},z}^2 - (1/3)S_{\text{Ni}}(S_{\text{Ni}} + 1)]$, where $J_{\text{Gd-Ni}}$ and D_{Ni} represent the isotropic exchange and single-ion ZFS parameters, respectively. The best set of parameters that match the experimental data was found to be $J_{\text{Gd-Ni}} = +0.15$ cm⁻¹ and $D_{\text{Ni}} = 3.0$ cm⁻¹, with $g_{\text{Ni}} = 2.33$ and $g_{\text{Gd}} = 2.0$. The solid lines in Fig. 2 correspond to the calculated curves. The J value obtained here is somewhat smaller than that reported by Costes *et al.* for a ferromagnetic Gd...Ni dimer with two phenoxo bridges of +3.6 cm⁻¹,⁸ but comparable to those obtained by Yamaguchi *et al.* for metal complexes with Ni...Gd and Ni...Gd...Ni cores supported by tripodal ligands, of +0.34 cm⁻¹ and +0.19 cm⁻¹, respectively.⁹ Another phenoxo-bridged trinuclear Ni...Gd...Ni complex was also reported to be ferromagnetic ($J = +0.54$ cm⁻¹).¹⁰

The present study demonstrates that using amino acids as ligands it is possible to assemble cyclic 3d–4f tetranuclear compounds with a large spin ground state. Compound **1** has a remarkable $S = 9$ ground state that results from ferromagnetic coupling between Gd^{III} and Ni^{II} ions. We are presently attempting to synthesize analogs containing anisotropic 4f metals such as Tb or Dy to create systems with large spin ground states and large anisotropy that might lead to potential single molecule magnets.

Notes and references

† Crystal data for **1**: $\text{C}_{28}\text{H}_{52}\text{Gd}_2\text{N}_{14}\text{Ni}_2\text{O}_{30}$, $M = 1496.69$, blue prism, monoclinic, $P2_1$, $a = 10.1979(3)$, $b = 18.8871(5)$, $c = 15.4161(5)$ Å, $\beta = 99.493(1)^\circ$, $V = 2928.6(2)$ Å³, $Z = 2$, $T = 298(1)$ K, 27 717 reflections of which 15 892 were unique ($R_{\text{int}} = 0.045$), 672 variable parameters, $R = 0.083$ [based on all F^2], $R_w = 0.142$. Four oxygen atoms of H₂O were found in an asymmetric unit: two of them have occupancy 1 and the others are located on different four sites with occupancy 0.5. Hydrogen atoms of H₂O could not be found. The Flack parameter supported the chirality of the structure. Data were collected over the $2\theta < 60.1^\circ$ on a Rigaku RAXIS-IV Imaging Plate diffractometer with graphite monochromated MoK α radiation.

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