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Analysis of Lanthanide-Radical Magnetic Interactions in Ce(III) 2,2'-Bipyridyl Complexes

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ABSTRACT

A series of lanthanide complexes bearing organic radical ligands, $[\text{Ln}(\text{Cp}^{\text{R}})_2(\text{bipy}^{\cdot-})]$ [$\text{Ln} = \text{La}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{tt}}$ (**1**); $\text{Ln} = \text{Ce}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{tt}}$ (**2**); $\text{Ln} = \text{Ce}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{r}}$ (**3**); $\text{Ln} = \text{Ce}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{m}}$ (**4**)] [$\text{Cp}^{\text{tt}} = \{\text{C}_5\text{H}_3^{\text{tBu}}\text{Bu}_2\text{-1,3}\}^-$; $\text{Cp}^{\text{r}} = \{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}^-$; $\text{Cp}^{\text{m}} = \{\text{C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}\}^-$; $\text{bipy} = 2,2'\text{-bipyridyl}$], were prepared by reduction of $[\text{Ln}(\text{Cp}^{\text{R}})_2(\mu\text{-I})]_2$ or $[\text{Ce}(\text{Cp}^{\text{m}})_2(\text{I})(\text{THF})]$ with KC_8 in the presence of bipy . Complexes **1-4** have been thoroughly characterized by structural, spectroscopic and computational methods, together with magnetism and cyclic voltammetry, to define an unambiguous $\text{Ln}(\text{III})/\text{bipy}^{\cdot-}$ radical formulation. These complexes can act as selective reducing agents; for example the reaction of **3** with benzophenone gives $[\{\text{Ce}(\text{Cp}^{\text{r}})_2(\text{bipy})\}_2\{\kappa^2\text{-O,O'-OPhC(C}_6\text{H}_5\text{)CPh}_2\text{O}\}]$ (**7**), a rare example of a “head-to-tail” coupling product. We estimate the intramolecular exchange coupling for **2-4** using multi-configurational and spin Hamiltonian methods, and find that the commonly used Lines-type isotropic exchange is not appropriate, even for single $4f$ e^- /organic radical pairs.

INTRODUCTION

In recent times the strong magnetic anisotropy of selected lanthanide (Ln) complexes have brought about their proposed applications in prototype magnetic devices.¹⁻³ Contrary to archetypal $3d$ -transition metal single molecule magnets (SMMs), strong intramolecular magnetic exchange interactions for polymetallic $4f$ -complexes are rare because the contracted $4f$ orbitals make superexchange pathways ineffective.⁴⁻⁷ Strong exchange interactions between Ln ions can be effected by bridging radical ligands,⁸ causing direct overlap between magnetic orbitals and resulting in a well isolated coupled ground state onto which the magnetic anisotropy of the Ln building blocks is projected. Since the first Ln -radical SMM was reported by Sessoli,⁹ seminal work by Evans and Long has showed that N_2^{3-} radicals bridging between two $\text{Ln}(\text{III})$ centers promotes strong exchange coupling.¹⁰⁻¹² In the interim, Long has extended this study to include dimeric Ln SMMs containing bridging redox non-innocent polyaromatic N -donor radical ligands,^{13,14} whilst trinuclear mixed $4f/5f$ systems were investigated by Morris and Kiplinger in prior work.^{15,16}

Despite these landmark synthetic advances, analyzing Ln-radical interactions can be computationally expensive; therefore simple models have been previously utilized.¹⁷ To obtain a rigorous theoretical analysis of the interactions in radical-bridged Ln systems, all possible electronic exchange states should be treated with a multi-configurational approach such as complete active space self-consistent field (CASSCF). Recent studies have examined the interactions in $[\{\text{Tb}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})\}_2(\mu\text{-N}_2)]^-$,^{18,19} where the Ln part of the problem was treated with CASSCF, however, the exchange states in this system were not directly probed owing to the large number of unpaired e^- and orbitals involved in the full problem. Therefore, we envisaged that the preparation of relatively simple monometallic Ce(III) complexes with a $4f^1$ center and one radical ligand would enable CASSCF calculations to be performed on the complete magnetic unit to shed light on the exchange interaction.

Irrespective of magnetic motivations, monometallic Ln complexes that contain redox non-innocent ligands^{20–22} such as bipyridines,^{23–34} phenanthrolines,^{30,32,35–37} diazenides^{38–42} and terpyridyls⁴³ have been extensively investigated. However, whilst there have been numerous studies on complexes of the general formula $[\text{Ln}(\text{L})_2(\text{bipy}^-)]$ (Ln = Eu, Sm, Yb; bipy = 2,2'-bipyridyl),^{24–30,32,33} there are relatively few reports on analogous systems for lighter Ln centers.^{44–47} Herein, we have thoroughly characterized a series of complexes of the general formula $[\text{Ln}(\text{Cp}^R)_2(\text{bipy}^-)]$ (Ln = La, Ce), examining their physical properties and reactivity, and probing the nature of 4f-electron/radical exchange interactions.

EXPERIMENTAL SECTION

General Methods

All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of dry argon. Solvents were dried by refluxing over potassium and were degassed before use. All solvents were stored over potassium mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles, and stored under argon. $[\text{Ln}(\text{Cp}^R)_2(\mu\text{-I})]_2$, $[\text{Ce}(\text{Cp}''')_2(\text{I})(\text{THF})]$ and KC_8 were prepared according to published procedures.^{48,49} Bipy was dried for 4 hours *in vacuo* before use. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded at 298 K on a spectrometer operating at 400.2, 100.6 and 79.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS. FTIR spectra were recorded as Nujol mulls in KBr discs. UV-Vis-NIR spectra were recorded in sealed 10 mm pathlength cuvettes. All the reported cyclic voltammetry experiments were carried out starting at the open circuit potential and redox potentials are referenced to the Fc/Fc^+ couple (1.8 V), which was used as an internal standard. Cyclic voltammetry was carried out using a sealed cell and a three-electrode arrangement, with a Pt wire working electrode, Pt flag secondary electrode and an AgCl/Ag wire pseudo-reference electrode.

Elemental microanalyses were carried out by Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. Magnetic measurements were obtained using a Quantum Design MPMS-XL7 SQUID magnetometer on powdered samples suspended in eicosane and sealed in a borosilicate glass NMR tube under vacuum. Q-band EPR spectra were measured with a Bruker EMX spectrometer fitted with a CF935 cryostat connected to an Oxford Intelligent Temperature Controller. The powder samples were sealed in quartz EPR tubes under vacuum and the spectra field corrected with a standard sample of DPPH. X-band EPR spectra were measured on a Bruker EMX-micro spectrometer fitted with a Super High Q X-band resonator.

[La(Cp^{tt})₂(bipy⁻)] (1). A Schlenk flask was charged with [La(Cp^{tt})₂(μ-I)]₂ (0.571 g, 0.45 mmol), KC₈ (0.131 g, 1.0 mmol) and bipy (0.144 g, 0.9 mmol). The flask was cooled to -78 °C and toluene (10 cm³) was added dropwise with stirring. The reaction mixture was allowed to slowly warm to room temperature and stirred for 16 hours, forming a dark suspension. The mixture was allowed to settle, filtered, concentrated to ca. 1 cm³ and stored at -30 °C, giving dark brown crystals of **1** (0.311 g, 52 %). Anal Calcd (%) for C₃₆H₅₀LaN₂: C, 66.55; H, 7.76; N, 4.31. Found (%): C, 66.44; H, 7.68; N, 4.41. ¹H NMR (C₆D₆, 400.2 MHz): δ = 0.98 (s, 2H, bipy-CH), 1.14-1.70 (br, v_{1/2} = 40 Hz, 38H, C(CH₃)₃ and bipy-CH), 6.27 (s, 2H, Cp^{tt}-CH), 6.39 (s, 4H, Cp^{tt}-CH), 6.67 (s, 2H, bipy-CH) 8.54 (s, 1H, bipy-CH), 8.75 (s, 1H, bipy-CH). FTIR (Nujol, cm⁻¹): ν = 2430 (w), 1593 (w), 1556 (m), 1539 (s), 1492 (s), 1366 (w), 1315 (w), 1290 (m), 1247 (m), 1209 (m), 1200 (w), 1163 (m), 1146 (m), 1111 (w), 1076 (m), 1051 (w), 1015 (w), 1005 (m), 999 (s), 937 (s), 804 (s), 745 (s), 679 (s), 665 (m).

[Ce(Cp^{tt})₂(bipy⁻)] (2). A Schlenk flask fitted was charged with [Ce(Cp^{tt})₂(μ-I)]₂ (1.275 g, 0.9 mmol), KC₈ (0.257 g, 1.9 mmol) and bipy (0.287 g, 1.8 mmol). The flask was cooled to -78 °C and toluene (20 cm³) was added dropwise with stirring. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 16 hours, forming a dark suspension. The mixture was allowed to settle, filtered, concentrated to ca. 2 cm³ and stored at -30 °C, giving dark brown crystals of **2** (0.80 g, 67 %). Anal Calcd (%) for C₃₆H₅₀CeN₂: C, 66.43; H, 7.74; N, 4.30. Found (%): C, 66.27; H, 8.09; N, 4.15. ¹H NMR (C₆D₆, 400.2 MHz): δ = -165.77 (br, v_{1/2} = 188 Hz, 1H, bipy-CH), -42.05 (br, v_{1/2} = 44 Hz, 3H, bipy-CH), -10.04 (br, v_{1/2} = 16 Hz, 3H, Cp^{tt}-CH), -1.19 (s, v_{1/2} = 16 Hz, 36H, Cp^{tt}-CH), 2.68 (br, v_{1/2} = 36 Hz, 3H, Cp^{tt}-CH), 12.49 (br, v_{1/2} = 108 Hz, 4H, bipy-CH). μ_{eff} (Evans method, 298 K, C₆D₆): 3.02 μ_B. FTIR (Nujol, cm⁻¹): ν = 1541 (m), 1492 (s), 1290(m), 1259 (m), 1211 (w), 1163 (w), 1148 (m), 1078 (br m), 1001 (m), 1014 (m), 939 (m), 806 (s), 754 (m), 746 (m), 723 (m), 678 (m).

[Ce(Cp^{''})₂(bipy⁻)] (3). A Schlenk flask was charged with [La(Cp^{''})₂(μ-I)]₂ (1.37 g, 1 mmol), KC₈ (0.30 g, 2.2 mmol) and bipy (0.31 g, 2 mmol). The flask was cooled to -78 °C and toluene (20 cm³) was added dropwise with stirring. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 16 hours, forming a dark suspension. The mixture was allowed to settle, filtered, concentrated to ca. 5 cm³ and stored at -30 °C. Colorless crystals of bipy formed

and were discarded; the mixture was filtered, concentrated to *ca.* 2 cm³ and stored at –30 °C, giving brown crystals of **3** (0.89 g, 56 %). Under a microscope light the crystals appear dark blue. Anal Calcd (%) for C₃₂H₅₀CeN₂Si₄: C, 53.74; H, 7.05; N, 3.92. Found (%): C, 53.63; H, 6.89; N, 4.02. ¹H NMR (C₆D₆, 400.2 MHz): δ = –171.08 (br, *v*_{1/2} = 256 Hz, 1H, bipy-CH), –46.68 (br, *v*_{1/2} = 84 Hz, 3H, bipy-CH), –6.02 (br, *v*_{1/2} = 56 Hz, 2H, Cp"-CH), –4.74 (s, *v*_{1/2} = 4 Hz, 1H, bipy-CH), –2.88 (br, *v*_{1/2} = 68 Hz, 2H, Cp"-CH), –2.04 (s, *v*_{1/2} = 12 Hz, 36H, Si(CH₃)₃), 12.91 (br, *v*_{1/2} = 132 Hz, 3H, bipy-CH). μ_{eff} (Evans method, 298 K, C₆D₆): 2.76 μ_{B} . FTIR (Nujol, cm^{–1}): ν = 1595 (w), 1261 (s), 1080 (br s), 1018 (br s), 949 (w), 923 (w), 905 (w), 800 (s), 754 (w).

[Ce(Cp''')₂(bipy[–])] (4). A Schlenk flask fitted was charged with [Ce(Cp''')₂(I)(THF)] (0.830 g, 1.0 mmol), KC₈ (0.149 g, 1.1 mmol) and bipy (0.156 g, 1.0 mmol). The flask was cooled to –78 °C and toluene (20 cm³) was added dropwise with stirring. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 16 hours, forming a dark suspension. The mixture was allowed to settle, filtered, concentrated to *ca.* 3 cm³ and stored at 4 °C to give a mixture of [Ce(Cp''')₂(I)(THF)] and **4**. After several recrystallizations from toluene/hexane, a small crop of dark red crystals of **4** was obtained (0.084 g, 10 %). Anal Calcd (%) for C₃₈H₆₆CeN₂Si₆: C, 53.10; H, 7.74; N, 3.26. Found (%): C, 52.92; H, 7.76; N 3.39. ¹H NMR (C₆D₆, 400.2 MHz): δ = –166.29 (br, *v*_{1/2} = 200 Hz, 1H, bipy-CH), –47.36 (br, *v*_{1/2} = 52 Hz, 3H, bipy-CH), –8.40 (s, *v*_{1/2} = 20 Hz, 3H, Cp'''-CH), –2.02 (s, *v*_{1/2} = 8 Hz, 36H, Si(CH₃)₃), 0.01 (s, *v*_{1/2} = 8 Hz, 18H, Si(CH₃)₃), 0.28 (br m, *v*_{1/2} = 12 Hz, 1H, bipy-CH), 11.97 (br, *v*_{1/2} = 36 Hz, 4H, bipy-CH). μ_{eff} (Evans method, 298 K, C₆D₆): 3.00 μ_{B} . FTIR (Nujol, cm^{–1}): ν = 1541 (w), 1246 (m), 1087 (m), 945 (m), 831 (br, m).

[{Ce(Cp''')₂(bipy)}₂{κ²-O,O'-OPhC(C₆H₅)CPh₂O}] (7). A Schlenk flask was charged with **3** (0.713 g, 1.0 mmol) and Ph₂CO (0.182 g, 1.0 mmol). The flask was cooled to –78 °C and toluene (10 cm³) was added with stirring. The reaction mixture was warmed slowly to room temperature and was stirred for 16 hours. The resultant deep purple reaction mixture was concentrated to *ca.* 1 cm³, filtered, layered with hexane and stored at –30 °C to give red crystals of **7** (0.560 g, 60 %). Anal Calcd (%) for C₉₆H₁₃₄Ce₂N₄O₂Si₈ (**7**·C₆H₁₄): 61.30; H, 7.18; N, 2.98. Found (%): C, 57.33; H, 7.25; N 3.01; low carbon values have been cited as a common occurrence for silicon-rich organolanthanides.⁵⁰ ¹H NMR (C₆D₆, 400.2 MHz): δ = –10.75 (br, *v*_{1/2} = 60 Hz, 5H, bipy-CH), –5.95 (s, *v*_{1/2} = 12 Hz, 6H, {OPhC(C₆H₅)CPh₂O}-CH), –5.28 (s, *v*_{1/2} = 12 Hz, 4H, Cp"-CH), –4.87 (s, *v*_{1/2} = 12 Hz, 8H, Cp"-CH), –1.77–1.30 (br m, *v*_{1/2} = 68 Hz, 54H, Si(CH₃)₃), 0.30 (s, *v*_{1/2} = 8 Hz, 18H, Si(CH₃)₃), 2.89 (br m, *v*_{1/2} = 48 Hz, 4H, {OPhC(C₆H₅)CPh₂O}-CH), 4.35 (br, *v*_{1/2} = 40 Hz, 2H, {OPhC(C₆H₅)CPh₂O}-CH), 6.50 (br m, *v*_{1/2} = 180 Hz, 4H, {OPhC(C₆H₅)CPh₂O}-CH), 9.80 (br m, *v*_{1/2} = 88 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 10.82 (s, *v*_{1/2} = 16 Hz, 2H, bipy-CH), 11.28 (s, *v*_{1/2} = 16 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 11.58 (br, *v*_{1/2} = 28 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 14.18 (br, *v*_{1/2} = 16 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 15.61 (br, *v*_{1/2} = 52 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 21.84 (br, *v*_{1/2} = 32 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 22.96 (br, *v*_{1/2} = 36 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 25.19 (br, *v*_{1/2} = 84 Hz, 1H, {OPhC(C₆H₅)CPh₂O}-CH), 54.42 (br, *v*_{1/2} = 88 Hz, 1H, bipy-CH), 88.27

(br, $\nu_{1/2}$ = 96 Hz, 4H, bipy-CH). μ_{eff} (Evans method, 298 K, C_6D_6): 2.61 μ_{B} . FTIR (Nujol, cm^{-1}): ν = 1658 (w), 1643 (w), 1595 (s), 1573 (w), 1541 (s), 1487 (m), 1437 (w), 1395 (w), 1312 (s), 1242 (s), 1211 (m), 1200 (w), 1173 (m), 1151 (m), 1138 (m), 1080 (m), 1006 (w), 950 (s), 937 (s), 895 (w), 827 (br s), 777 (w), 761 (w), 750 (w), 698 (m), 685 (w), 638 (m), 623 (m), 603 (w).

RESULTS

Synthesis

In order to investigate if different Cp ring substituents have a major influence on the physical properties of bipy radical La/Ce complexes, $[\text{Ln}(\text{Cp}^{\text{R}})_2(\text{bipy}^{\cdot-})]$ ($\text{Ln} = \text{La}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{tt}}$ (**1**); $\text{Ln} = \text{Ce}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{tt}}$ (**2**); $\text{Ln} = \text{Ce}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{''}}$ (**3**); $\text{Ln} = \text{Ce}$, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{'''}}$ (**4**), $\text{Cp}^{\text{tt}} = \{\text{C}_5\text{H}_3^{\text{tBu}}\text{Bu}_2\text{-1,3}\}^-$; $\text{Cp}^{\text{''}} = \{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}^-$; $\text{Cp}^{\text{'''}} = \{\text{C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}\}^-$) were prepared in fair (**1-3**) or poor (**4**) crystalline yields by reduction of $[\text{Ln}(\text{Cp}^{\text{R}})_2(\mu\text{-I})]_2$ or $[\text{Ce}(\text{Cp}^{\text{'''}})_2(\text{I})(\text{THF})]$ with KC_8 in the presence of bipy (Scheme 1). The $[\text{Ln}(\text{Cp}^{\text{R}})_2(\mu\text{-I})]_2$ precursors were prepared as previously reported,⁴⁸ apart from $[\text{La}(\text{Cp}^{\text{tt}})_2(\mu\text{-I})]_2$ (**5**), which was independently synthesized in this study by analogous methods (see ESI Section 1). Elemental analyses for **1-4** were in good agreement with expected values and their ^1H NMR spectra showed only small amounts of protic impurities (see ESI Section 2). The bipy protons in **1-4** give broad ^1H NMR signals, consistent with a radical anion formulation. For **1**, some of these signals overlapped with the $^{\text{tBu}}$ protons, making the spectrum difficult to interpret, and as such these are only tentatively assigned. In the case of **2-4**, the ^1H NMR spectra exhibit signals over a wide range of chemical shifts (δ_{H} range: -180 to $+15$ ppm), analogously to those previously reported for $[\text{Ce}(\text{Cp}^*)_2(\text{bipy}^{\cdot-})]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$; δ_{H} range: -253.11 to $+10.75$ ppm);⁴⁶ the broad range of chemical shifts is consistent with an anisotropic paramagnetic ground state arising from a Ce(III) $4f^1$ center. In all cases, $^{13}\text{C}\{^1\text{H}\}$ NMR spectra could not be assigned and no signals were observed in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **3** and **4** between -300 and $+300$ ppm.

As a benchmark of a well-defined $\text{bipy}^{\cdot-}$ radical anion, we have prepared $[\{\text{K}(\text{bipy}^{\cdot-})\}_2(\text{THF})_3]_{\infty}$ (**6**) (see ESI Section 1), which is one of many alkali metal bipy complexes previously studied.⁵¹⁻⁵³ Goicoechea reported diagnostic FTIR absorptions for the $\text{bipy}^{\cdot-}$ radical anion in $[\text{K}_4(\text{bipy}^{\cdot-})_4(\text{en})_4]$ ($\text{en} = \text{ethylenediamine}$) between ca. $900\text{-}1000$ and $1500\text{-}1600$ cm^{-1} ;⁵³ we observe these features for **1-4** and **6**, also echoed in the literature for $[\text{Ln}(\text{Cp}^*)_2(\text{bipy}^{\cdot-})]$ ($\text{Ln} = \text{Sm}$,³² Yb^{24}) and $[\text{Ln}(\text{Tp}^{\text{Me2}})_2(\text{bipy}^{\cdot-})]$ ($\text{Ln} = \text{La}$,⁴⁴ Ce^{47} ; $\text{Tp}^{\text{Me2}} = \text{HB}(\text{dmpz})_3$; $\text{dmpz} = 1,3\text{-dimethylpyrazolide}$).

Scheme 1. Synthesis of Ln complexes **1-4**.

Structural characterization

Complexes **1-6** were characterized by single crystal XRD (see ESI Section 4). Complexes **1-4** display similar geometric parameters, featuring open metallocene conformations with bidentate bipy ligands, in common with $[\text{Ln}(\text{Cp}^*)_2(\text{bipy}^{\cdot-})]$ ($\text{Ln} = \text{Sm},^{32} \text{Yb}^{24}$). Complexes **1** and **2** are structurally analogous (Figure 1 and ESI Figure S19), both crystallizing in the monoclinic space group $P2_1/c$ with near-identical cell parameters (ESI Table S1). In contrast, **3** and **4** crystallize in orthorhombic $P2_12_12_1$ and $Pbca$, respectively (Figure 1). Minor differences in the geometries of **1-4** can be ascribed to differences in the ionic radii of La(III) and Ce(III), as well as the bulk of the Cp^{R} ligands. The inter-pyridine C–C bond distances in the $\text{bipy}^{\cdot-}$ scaffolds [1.409(8), 1.423(7), 1.415(7) and 1.415(13) Å for **1-4**, respectively] are diagnostic to assess the extent of ligand reduction: these distances are statistically equivalent with those reported for other Ln complexes containing monoreduced $\text{bipy}^{\cdot-}$ radicals [1.429(4)-1.445(17) Å],^{24,32,44,47} complex **6** [1.439(14) and 1.428(14) Å] and $[\text{K}_4(\text{bipy}^{\cdot-})_4(\text{en})_4]_{\infty}$ [1.429(av) Å].⁵³ Furthermore, inter-pyridine C–C bond distances here are shorter than those found in neutral bipy [1.490(3) Å]²⁴ and longer than those reported for dianionic bipy^{2-} in $[\text{Th}(\text{C}_5\text{H}_2^t\text{Bu}_3\text{-1,2,4})_2(\text{bipy})]$ [1.382(8) Å].⁵⁴ Hence, the XRD data support an Ln(III)/ $\text{bipy}^{\cdot-}$ formulation.

Figure 1. Molecular structure of **2-4** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity.

Optical spectroscopy

The UV-vis-NIR spectra of $\text{bipy}^{\cdot-}$ radical anions, which arise from the presence of an unpaired electron in a π^* orbital, have been reported previously.^{24,32,44,47,51–53} The characteristic features consist of i) a strong absorbance in the violet region at ~ 400 nm, ii) a medium intensity band in the green region at ~ 500 nm, and iii) a weaker absorption in the NIR at ~ 900 nm.⁵¹ The UV-vis-NIR spectra of **1-4** (Figure 2 and ESI Figure S24) are nearly superimposable and display similar features to the spectrum of **6** (Figure 2, ESI Figures S25 and S26). The spectra exhibit three intense bands in the near-UV region at ~ 240 - 260 (LM), ~ 320 and ~ 390 nm, except in the case of **3**, where the band at ~ 320 nm was not observed. Two lower intensity bands are seen at ~ 490 - 520 and ~ 800 - 910 nm, which are split into a doublet and a triplet, respectively. The higher energy transitions (320 - 520 nm) are tentatively assigned as $\pi \rightarrow \pi^*$ transitions of $\text{bipy}^{\cdot-}$, whilst the lower energy ones (800 - 910 nm) as attributed to $\text{bipy}^{\cdot-}$ $\pi^* \rightarrow \pi^*$ transitions by comparison with previously reported UV-vis-NIR spectra of $\text{bipy}^{\cdot-}$ systems,^{27,32,51} and the more closely related Ln complexes $[\text{Yb}(\text{Cp}^{\text{R}})_2(\text{bipy})]$ ³² and $[\text{Ce}(\text{Tp}^{\text{Me2}})(\text{bipy}^{\cdot-})]$.⁴⁷ Thus, the UV-Vis-NIR spectra indicate that complexes **1-4** contain the $\text{bipy}^{\cdot-}$ radical.

Figure 2. UV-vis-NIR spectra of **1-4** and **6** (r.t., 0.1 mM in THF).

Magnetism and EPR spectroscopy

The magnetic moments of **2-4** at 298 K were measured by the Evans method (Table 1).^{55–57} The values obtained are higher than for other Ce(III) complexes reported in the literature (1.88 - $2.75 \mu_{\text{B}}$)^{47,58} and also higher than the predicted value for a $4f^1 \ ^2F_{5/2}$ ground state ($2.54 \mu_{\text{B}}$);⁵⁹ this is likely

due to an additional contribution arising from the bipy^{•−} radical $S = 1/2$, as previously observed for Ce(III) complexes containing radical ligands⁴⁶ and other Ln(III) ligand radicals.³² Variable temperature and field SQUID measurements were conducted to further probe the magnetic properties of solid **1-4** suspended in eicosane. The magnetic moments at 298 K for **2-4** are in excellent agreement with the Evans method values (Table 1) and are higher than that of the La(III)-bipy^{•−} analogue **1** (ESI Figure S28), indicating a magnetic contribution from the 4f electron of Ce(III). The magnetic susceptibility [$\mu_{\text{eff}} \approx \sqrt{(8 \times \chi_M T)}$] of **2-4** decreases with reducing temperature (Figure 3), which results mainly from depopulation of the Crystal Field (CF) states of Ce(III) (see below). The magnetization vs. field for **2-4** was measured at a range of temperatures (ESI Figures S29-S31); all plots are nearly linear and do not reach saturation at 7 T, indicative of highly anisotropic magnetic states – notably, such profiles cannot arise from isolated Kramers doublets, thus the magnetization data directly evidences a significant Ce(III)-radical exchange interaction.

EPR spectroscopic data was collected from 5-293 K at X-, K- and Q-band for solid samples of **1-4** and **6**. For all temperatures and microwave frequencies, no resonances were observed for **2-4**. In contrast, **1** and **6** gave strong, sharp spectra at 293 K at Q-band, indicative of organic radicals (Figure 4). The spectra can be simulated with an $S = 1/2$ model using PHI⁶⁰ with Hamiltonian Equation 1, and an isotropic Lorentzian linewidth in frequency-space. Identical simulations can also be obtained with Easy-Spin.⁶¹

$$\hat{H} = \mu_B (g_{\perp} (\hat{S}_x B_x + \hat{S}_y B_y) + g_{\parallel} \hat{S}_z B_z) \quad (1)$$

The spectra show that **1** has a significantly broader linewidth than **6** (Table 2), which is likely due to unresolved hyperfine coupling to the $I = 7/2$ ¹³⁹La nuclear spin with 99.9% abundance; this hyperfine coupling is observable in solution phase EPR spectra (see ESI section 7).

Table 1. Room temperature magnetic moments for **2-4**. Evans method measured in an NMR spectrometer operating at 298 K, SQUID values measured in a 0.5 T field at 298 K.

Method	2 (μ_B)	3 (μ_B)	4 (μ_B)
Evans	3.02	2.76	3.00
SQUID	2.76	2.89	3.02
CASSCF	2.90	2.90	2.91

Figure 3. Variable temperature magnetic susceptibility for **2-4** (solid suspended in eicosane) in a 0.5 T field. Solid lines are fits using Hamiltonian Equation 2, with parameters given in the text. Inset shows enlarged low temperature section of the main plot.

Table 2. Simulation parameters for Q-band EPR spectra of **1** and **6**.

Parameter	1	6
$g_{\perp}$	2.0005	2.0027
$g_{\parallel}$	2.0015	2.0040
Linewidth (GHz)	0.0133	0.00724

Figure 4. Solid-state Q-band EPR spectra for **1** (top) and **6** (bottom) at room temperature. Experimental data in black and simulations using Equation 2 in red. Microwave frequencies for **1** and **6** were 34.0758 and 34.0740 GHz, respectively.

Computational Characterization

To provide further evidence of the electronic configuration, *ab initio* CASSCF calculations were conducted on the solid-state structures of **1-4** using MOLCAS 8.0⁶² (see ESI Section 8 for details). The most suitable active space for **2-4** was determined using the Restricted Active Space (RAS) probing method, where electrons and orbitals around the HOMO-LUMO gap are successively added to the calculation until the static correlation in the low-lying states is captured; orbitals are included if their occupation number falls between 0.02 and 1.98.⁶³ The optimal active space for **2-4** was 6 electrons in 13 orbitals (accounting for the 4f orbital degeneracy and the Ce-ligand interaction), where 21 states were considered for the $S = 1$ and $S = 0$ configurations (ESI Table S13). This active space consists of six bipy-based orbitals and the seven 4f orbitals, and the calculations indicate well-defined Ce(III) ions and bipy^{•−} radicals for **2-4** (Table 3 and ESI Figure S34). For the 21 states, two of the six bipy orbitals are almost doubly occupied with occupation numbers > 1.88 , one is almost unoccupied (occupation < 0.05), and the other three can

accommodate the unpaired electron (*i.e.* occupation < 0.2 or > 0.92). The seven 4f orbitals accommodate a single metal-based electron, corresponding to Ce(III). The 21 states for each multiplicity are made up of three groups of seven states at 0–1700 cm⁻¹, 15000–17000 cm⁻¹ and 19000–21000 cm⁻¹, above which the next states are > 30000 cm⁻¹. The large gaps between the groups correspond to excitation of the bipy^{•-} radical electron amongst the three low-lying ligand orbitals, while the seven states within each group correspond to the low-energy 4f excitations. In the ground state the radical occupies an orbital with C-C π and π^* , and N p character (Figure 5 and ESI Figure S34c). The π -bonding character corresponds with the shorter inter-pyridine C–C bond distances observed in the solid-state structures of **2-4**. The same active space was subsequently employed for **1** however only 5 electrons were included owing to the lack of a 4f electron in the La complex. In this case, the CASSCF calculations would always rotate the 4f orbitals out of the active space, indicating there are no low-lying excitations involving the unpaired electron on the La(III) ion, thus confirming a La(III)-bipy^{•-} formulation.

Once spin-orbit (SO) coupling is included, the smallest calculated energy gaps between pairs of states (ESI Table S14) are all greater than the largest microwave quantum employed in our EPR experiments (Q-band, ~34 GHz $\approx$ 1.13 cm⁻¹) and therefore the CASSCF-SO calculations support the EPR-silent nature of **2-4**. The magnetic observables calculated on the basis of our CASSCF-SO wavefunctions compare well with those determined experimentally for **2-4** (ESI Figures S35-S37): the slow decrease in magnetic susceptibility with decreasing temperature and the near-linear magnetization isotherms are captured by the calculations. After SO coupling, the principal *g*-values extracted for **1** are in good agreement with those found by EPR spectroscopy (ESI Table S16).

Table 3. Overview of the active space for the *S* = 1 configurations for **2-4**. For *S* = 0 configurations, unpaired bipy electron is antiparallel to the 4f electron.

States	Energy (cm ⁻¹)	bipy			7×4f	
1 – 7	0 – 1700	↑↓	↑↓	↑	↑	
8 – 14	15000 17000	–	↑↓	↑↓	↑	↑
15 – 21	19000 21000	–	↑↓	↑↓	↑	↑

Figure 5. Rendering of lowest lying SOMO for **3**, showing the bipy^{•−} radical character of the MO. All MOs protrude above and below the plane of the bipy ligand and shading indicates relative phases.

Electrochemical studies

As bipy can be readily converted between neutral, monoanionic radical and dianionic forms, cyclic voltammetry experiments were carried out on **1-4** (Figure 6 and ESI Section 9). The voltammograms all exhibit similar Nernstian *quasi*-reversible events ($\Delta E = 178$ -256, 134-168, 142-173 (**3**) and 168-193 mV for **1-4**, respectively) at negative potentials vs Fc/Fc⁺ ($E_{1/2} = -2.44$, -2.47 , -2.39 and -2.43 V for **1-4**). In all cases, the voltammograms are similar to those seen for [Ce(Tp^{Me2})₂(bipy^{•−})]⁴⁷ and **6** (ESI Figure S44). For **1-3** additional and less intense events at -2.1 V were observed, which did not increase in intensity with increasing scan rates and could not be assigned. No other well-defined processes were observed at more cathodic potentials (see ESI Section 9), therefore we tentatively assign the waves observed for **1-4** at -2.39 to -2.47 V as (bipy)/(bipy^{•−}) processes (Scheme 2) due to chemically oxidation to [Ln(Cp^R)₂(bipy)]⁺ prior to the start of the electrochemical experiment. We changed the supporting electrolyte to [N^{Pr}Pr₄][B{C₆H₃(CF₃)_{2-3,5}}]₄ in an effort to prevent this pre-oxidation, but the resulting voltammogram of **4** had no clear-cut redox events that could be assigned (ESI Figure S43). It is noteworthy that the measured redox couples of **1-4** are consistent with analogous processes observed for d-transition metal complexes⁶⁴ and the first reduction of bipy ($E_{1/2} = -2.34$ V vs

Fc/Fc⁺).⁶⁵ The Ce(III)/Ce(IV) couple could not be identified for **2-4**, which is unsurprising as the Ce(IV) oxidation state is usually stabilized in the presence of electron-rich donors.^{66,67} However, it should be noted that Thiele and co-workers previously reported a potential for [Ce^{III}(Cp)₄]⁻/[Ce^{IV}(Cp)₄] in THF (-0.86 V).⁶⁸

Figure 6. Cyclic voltammogram of **4** (r.t., 0.5 mM in THF, [NⁿBu₄][BF₄] 0.1 M, referenced to Fc/Fc⁺).

Scheme 2. Proposed electrochemical reduction/oxidation of [Ln(Cp^R)₂(bipy)]⁺/[Ln(Cp^R)₂(bipy)⁻].

Reactivity studies

Intrigued by the *quasi*-reversible redox processes of the bipy⁻ radicals in **1-4**, we decided to explore the use of such complexes as selective one-electron reducing agents. Therefore, the reaction of complex **3** with benzophenone ($E_{1/2} = -2.30$ V in THF)⁶⁹ was performed to give [{Ce(Cp^R)₂(bipy)}₂{κ²-O,O'-OPhC(C₆H₅)CPh₂O}] (**7**) in fair yield (Scheme 3). In agreement with the electrochemistry experiments, the bipy⁻ radical functions as a 1e⁻ reducing agent and remains

coordinated to the metal center. We propose that **7** has formed by initial coordination of Ph_2CO , followed by electron transfer from $\text{bipy}^{\cdot-}$ to form $\text{Ph}_2\text{CO}^{\cdot-}$ radicals. Such transient species can reductively couple in a “head-to-tail” intermolecular process *via* the ketyl carbon of one radical with the *para*- carbon of a phenyl ring of the second radical. The more common pinacol “head-to-head” coupling *via* two ketyl carbon radicals is thwarted by steric crowding in the intermediate complex, which impedes the close approach of two ketyl carbons from different complexes. “Head-to-tail” coupling of ketones mediated by f-element complexes are rare,^{70–73} and the reaction of **3** with benzophenone to give **7** is, to the best of our knowledge, the first example by a Ln(III) complex with a redox-active ligand. Finally, a mixture of $[\text{Ce}(\text{Cp}''')_2(\text{I})(\text{THF})]$ and Ph_2CO was reacted with KC_8 to give a trace amount of crystals of $[\{\text{Ce}(\text{Cp}''')_2\}_2\{\kappa^2\text{-O,O'-OPhC(C}_6\text{H}_5\text{)CPh}_2\text{O}\}_2]$ (**8**), showing that the “head-to-tail” coupling of benzophenone can occur in the absence of bipy, albeit in lower yields and with ligand scrambling (See ESI Sections 1 and 10). The ^1H NMR spectrum of **7** is complex and could only be tentatively assigned, which we attribute to a monomer-dimer equilibrium in solution (Scheme 4), similar to that observed by Deacon.⁷¹ Additionally, attempts to evaluate the rate of the proposed equilibrium *via* variable temperature NMR experiments proved unsuccessful (see ESI Section 2).

Scheme 3. Reaction of **3** with Ph_2CO to give **7**.

Scheme 4. Proposed equilibrium of **7** in solution.

The structure of **7** was determined by single crystal XRD (Figure 7); Ce–N distances [2.673(11)-2.754(16) Å] are significantly longer than those in **3** [2.465(4)-2.488(4) Å] and are comparable to those reported for the neutral bipy containing complex [Ce(Cp*)₂(bipy)(I)] [2.635(5)-2.782(6) Å],⁴⁶ however the large error in the inter-pyridyl C–C distances [1.462(14) and 1.47(2) Å] for **7** precludes unequivocal assignment of the bipy oxidation state *via* XRD. The UV-vis-NIR spectrum of **7** (ESI Figure S27) does not exhibit the absorptions expected for bipy^{•−} radicals (see above); rather, we observe an absorption corresponding to the Ph₂CO^{•−} radical around 550 nm,^{74,75} further evidencing monomer-dimer equilibrium in solution.

Figure 7. Molecular structure of **7** with selective atom labelling, with displacement ellipsoids set at 50% probability level; hydrogen atoms, silyl groups and phenyl rings have been omitted for clarity.

DISCUSSION

As we have defined **2-4** as Ce(III)/bipy^{•−} formulations and successfully performed a full multi-configurational CASSCF treatment accounting for the interaction between the 4f¹ e[−] and the bipy radical, the final SO states (ESI Table S14) directly correspond to the exchange-coupled states; an approach explored previously by others.^{76–78} The electronic structure of **2-4** exhibit a hierarchy of electronic interactions where Ce(III) SO coupling > Ce(III) Crystal Field (CF) splitting > Ce(III)-radical exchange interactions (Figure 8), in stark contrast to the strong Yb(III)-bipy^{•−} exchange observed previously.^{26,79} The 4f¹ configuration defines only the ²F term (*S* = 1/2, *L* = 3) where SO coupling splits this into the lower *J* = 5/2 and upper *J* = 7/2 multiplets (Figure 8b). These are then split by the local CF into three and four Kramers doublets, respectively (Figure 8c). Owing to the two-fold multiplicity of the radical *S* = 1/2, the exchange-coupled states occur in groups of four, making two larger groups of 12 and 16, respectively, arising from the six- and eight-fold multiplicities of the SO multiplets (Figure 8d).

Figure 8. Energy splitting diagram showing the Ce(III) states for 4^+ (a-c) and the exchange coupled Ce(III)-radical states for 4 (d). Values at bottom-right show the splitting of the lowest lying exchange states for 4 (ESI Table S14).

A common approximation to model Ln-Ln or Ln-radical exchange is to assume an isotropic spin-spin Heisenberg interaction (the Lines model⁸⁰), acting in the basis of the anisotropic crystal field states of the Ln(s). After calculating the CF decomposition of the Ce(III) center (see ESI Section 8), we attempted to model the experimental magnetic data and the CASSCF-SO exchange spectrum by fitting with Hamiltonian ESI Equation S3. However, we were completely unable to find agreement to the data using a single isotropic Heisenberg interaction; this is likely due to the Lines model being inappropriate in this circumstance, adding to a growing body of work echoing this conclusion.^{79,82} Furthermore, Iwahara and Chibotaru have recently assessed Ln(III)-Ln(III) interactions in considerable theoretical detail and concluded that such a parameterization is insufficient.⁸³

Therefore, we employ the effective $S = 1/2$ dimer model to approximate the strongly anisotropic exchange interactions in **2-4**. In this approach, the ground CF Kramers doublet of Ce(III) is defined as an effective $S = 1/2$ with effective g -values, and is coupled to the true $S = 1/2$ of the bipy radical – this approach is justified when modelling the low temperature magnetic data as the first excited CF Kramers doublet of Ce(III) is ca. 260 cm^{-1} (ESI Tables S17-19). We observe for all three complexes that the ground Kramers doublets have effective g -values of $g_{xy} \sim 2.5$ and $g_z \sim 0.8$ (ESI Tables S17-19), where the g_z orientation is perpendicular to both the Ce-bipy vector and the $\text{Cp}^R\text{-Ce-Cp}^R$ vector. To estimate the exchange interactions in each case, we simultaneously fit the

magnetization, $\chi_{\text{MT}} (\leq 50 \text{ K})$, and four lowest-lying CASSCF energy levels (i.e. those resulting from the exchange interactions between the ground Kramers doublet of Ce(III) and the bipy radical) using Hamiltonian Equation 2 with PHI,⁵⁷ where $\vec{\hat{S}}_{\text{Ce}}$ are the effective spin operators for the ground Kramers doublet of Ce(III). To avoid over-parameterization, we fix $g_{\text{rad}} = 2$, $g_{xy_{\text{Ce}}} = 2.5$ and $g_{z_{\text{Ce}}} = 0.8$; as we restrict $g_{x_{\text{Ce}}} = g_{y_{\text{Ce}}}$ in this model, the J_x and J_y parameters, while distinct, have the same effect on the experimental data and thus the assignments could be switched. The global minimum for each complex is given by the effective anisotropic exchange parameters (Table 4) which provide excellent fits to the experimental magnetic data (Figure 3, ESI Figures 29-31) and reasonable agreement to the lowest-lying CASSCF energy levels (ESI Tables S21-23). As a general trend we note that the overall strength of the exchange interaction $\sqrt{J_x^2 + J_y^2 + J_z^2}$ seems to decrease across the series of compounds **2-4**, however, these parameters should be regarded as estimates as they are not defined by experimental spectroscopic data that measure the transitions between exchange multiplets directly.

$$\begin{aligned} \hat{H} = & -2 \left(J_x \hat{S}_{x_{\text{Ce}}} \hat{S}_{x_{\text{rad}}} + J_y \hat{S}_{y_{\text{Ce}}} \hat{S}_{y_{\text{rad}}} + J_z \hat{S}_{z_{\text{Ce}}} \hat{S}_{z_{\text{rad}}} \right) \\ & + \mu_B \left(g_{xy_{\text{Ce}}} \left(\hat{S}_{x_{\text{Ce}}} B_x + \hat{S}_{y_{\text{Ce}}} B_y \right) + g_{z_{\text{Ce}}} \hat{S}_{z_{\text{Ce}}} B_z + g_{\text{rad}} \vec{\hat{S}}_{\text{rad}} \cdot \vec{B} \right) \end{aligned} \quad (2)$$

Table 4. Anisotropic exchange parameters for **2-4** determined by SH modelling.

Parameter	2 (cm ⁻¹)	3 (cm ⁻¹)	4 (cm ⁻¹)
J_x	-28	-30	-19
J_y	-11	2.4	0.026
J_z	19	7.0	5.1

CONCLUSION

We have presented a series of early Ln-bipy complexes (**1-4**) and shown by physical, spectroscopic and computational techniques, that these complexes consist of a Ln(III) ion and a bipy^{•-} radical. The physical properties of complexes **2-4** that have been analyzed do not appear to be majorly affected by varying degrees of substitution of the supporting ligands. Such complexes

can also function as selective reducing agents, as shown in the reaction between **3** and Ph₂CO to form the “head-to-tail” coupling product **7**. CASSCF-SO calculations show good agreement with the physical studies and suggest a hierarchy of the electronic interactions between the Ce(III) 4f¹ and bipy^{•−} radicals in **2-4**. Attempts to model the experimental magnetic data and the CASSCF-SO energy spectrum with the simple isotropic spin-spin exchange (Lines) approach failed, showing that this model is not sufficient for even a 4f¹-organic radical pair. It is clear that further experimental studies and more theoretical work is required to provide useful tools and models to understand the nature of even relatively simple Ln-radical systems such as those presented here.

ASSOCIATED CONTENT

Supporting Information

Additional experimental details for physical and computational data associated with this manuscript. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Vincent, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Electronic read-out of a single nuclear spin using a molecular spin transistor. *Nature* **2012**, *488* (7411), 357–360.
- (2) Ganzhorn, M.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W. Strong spin–phonon coupling between a single-molecule magnet and a carbon nanotube nanoelectromechanical system. *Nat. Nanotechnol.* **2013**, *8* (3), 165–169.
- (3) Thiele, S.; Balestro, F.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W. Electrically driven nuclear spin resonance in single-molecule magnets. *Science* **2014**, *344* (6188), 1135–1138.
- (4) Layfield, R. A.; Murugesu, M. *Lanthanides and Actinides in Molecular Magnetism*; John Wiley & Sons, 2015.
- (5) Liddle, S. T.; Slagereen, J. van. Improving f-element single molecule magnets. *Chem. Soc. Rev.* **2015**, *44*, 6655–6669.
- (6) Le Roy, J. J.; Ungur, L.; Korobkov, I.; Chibotaru, L. F.; Murugesu, M. Coupling Strategies to Enhance Single-Molecule Magnet Properties of Erbium–Cyclooctatetraenyl Complexes. *J. Am. Chem. Soc.* **2014**, *136* (22), 8003–8010.
- (7) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press, 2006.
- (8) Demir, S.; Jeon, I.-R.; Long, J. R.; Harris, T. D. Radical ligand-containing single-molecule magnets. *Coord. Chem. Rev.* **2015**, *289–290*, 149–176.
- (9) Poneti, G.; Bernot, K.; Bogani, L.; Caneschi, A.; Sessoli, R.; Wernsdorfer, W.; Gatteschi, D. A rational approach to the modulation of the dynamics of the magnetisation in a dysprosium–nitronyl-nitroxide radical complex. *Chem. Commun.* **2007**, No. 18, 1807–1809.
- (10) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. Strong exchange and magnetic blocking in N_2^{3-} -radical-bridged lanthanide complexes. *Nat. Chem.* **2011**, *3* (7), 538–542.
- (11) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. A N_2^{3-} Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K. *J. Am. Chem. Soc.* **2011**, *133* (36), 14236–14239.
- (12) Meihaus, K. R.; Corbey, J. F.; Fang, M.; Ziller, J. W.; Long, J. R.; Evans, W. J. Influence of an Inner-Sphere K^+ Ion on the Magnetic Behavior of N_2^{3-} Radical-Bridged Dilanthanide Complexes Isolated Using an External Magnetic Field. *Inorg. Chem.* **2014**, *53* (6), 3099–3107.
- (13) Demir, S.; Zadrozny, J. M.; Nippe, M.; Long, J. R. Exchange Coupling and Magnetic Blocking in Bipyrimidyl Radical-Bridged Dilanthanide Complexes. *J. Am. Chem. Soc.* **2012**, *134* (45), 18546–18549.
- (14) Demir, S.; Nippe, M.; Gonzalez, M. I.; Long, J. R. Exchange coupling and magnetic blocking in dilanthanide complexes bridged by the multi-electron redox-active ligand 2,3,5,6-tetra(2-pyridyl)pyrazine. *Chem. Sci.* **2014**, *5* (12), 4701–4711.
- (15) Schelter, E. J.; Wu, R.; Veauthier, J. M.; Bauer, E. D.; Booth, C. H.; Thomson, R. K.; Graves, C. R.; John, K. D.; Scott, B. L.; Thompson, J. D.; et al. Comparative Study of f-Element Electronic Structure across a Series of Multimetallic Actinide and Lanthanoid-Actinide Complexes Possessing Redox-Active Bridging Ligands. *Inorg. Chem.* **2010**, *49* (4), 1995–2007.
- (16) Schelter, E. J.; Veauthier, J. M.; Thompson, J. D.; Scott, B. L.; John, K. D.; Morris, D. E.; Kiplinger, J. L. 4f-5f heterotrimetallic complexes exhibiting electrochemical and magnetic communication. *J. Am. Chem. Soc.* **2006**, *128* (7), 2198–2199.
- (17) Rajeshkumar, T.; Rajaraman, G. Is a radical bridge a route to strong exchange interactions in lanthanide complexes? A computational examination. *Chem. Commun.* **2012**, *48* (63), 7856–7858.
- (18) Zhang, Y.-Q.; Luo, C.-L.; Wang, B.-W.; Gao, S. Understanding the Magnetic Anisotropy in a Family of N_2^{3-} Radical-Bridged Lanthanide Complexes: Density Functional Theory and ab Initio Calculations. *J. Phys. Chem. A* **2013**, *117* (42), 10873–10880.
- (19) Zhang, Y.-Q.; Luo, C.-L.; Zhang, Q. Exchange coupling and magnetic anisotropy in a family of bipyrimidyl radical-bridged dilanthanide complexes: Density functional theory and ab initio calculations. *J. Comput. Chem.* **2014**, *35* (12), 904–909.
- (20) Berben, L. A.; Bruin, B. de; Heyduk, A. F. Non-innocent ligands. *Chem. Commun.* **2015**, *51* (9), 1553–1554.

- (21) Lyaskovskyy, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. *ACS Catal.* **2012**, 2 (2), 270–279.
- (22) Chirik, P. J. Preface: Forum on Redox-Active Ligands. *Inorg. Chem.* **2011**, 50 (20), 9737–9740.
- (23) Pappalardo, R. Absorption spectra of neutral dipyridyl complexes. *Inorganica Chim. Acta* **1968**, 2, 209–215.
- (24) Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. Coordination of 2,2'-Bipyridyl and 1,10-Phenanthroline to Substituted Ytterbocenes: An Experimental Investigation of Spin Coupling in Lanthanide Complexes. *Organometallics* **2002**, 21 (3), 460–472.
- (25) Berg, D. J.; Boncella, J. M.; Andersen, R. A. Preparation of Coordination Compounds of Cp^*_2Yb with Heterocyclic Nitrogen Bases: Examples of Antiferromagnetic Exchange Coupling across Bridging Ligands. *Organometallics* **2002**, 21 (22), 4622–4631.
- (26) Walter, M. D.; Berg, D. J.; Andersen, R. A. Coordination Complexes of Decamethylytterbocene with 4,4'-Disubstituted Bipyridines: An Experimental Study of Spin Coupling in Lanthanide Complexes. *Organometallics* **2006**, 25 (13), 3228–3237.
- (27) Nocton, G.; Booth, C. H.; Maron, L.; Andersen, R. A. Influence of the Torsion Angle in 3,3'-Dimethyl-2,2'-bipyridine on the Intermediate Valence of Yb in $(\text{C}_5\text{Me}_5)_2\text{Yb}(3,3'\text{-Me}_2\text{-bipy})$. *Organometallics* **2013**, 32 (19), 5305–5312.
- (28) Walter, M. D.; Schultz, M.; Andersen, R. A. Weak paramagnetism in compounds of the type $\text{Cp}'_2\text{Yb}(\text{bipy})$. *New J. Chem.* **2006**, 30 (2), 238–246.
- (29) Bochkarev, M. N.; Fedushkin, I. L.; Nevodchikov, V. I.; Cherkasov, V. K.; Schumann, H.; Hemling, H.; Weimann, R. Synthesis and ESR-characterization of radical anion complexes of lanthanum. X-ray crystal structure of the mixed bipy, bipy-1 complex of lanthanum(III) $[\text{La}_2(\text{bipy})(\text{bipy})(\text{DME})]$: evidence for an inter-ligand charge transfer. *J. Organomet. Chem.* **1996**, 524 (1–2), 125–131.
- (30) Nocton, G.; Booth, C. H.; Maron, L.; Ricard, L.; Andersen, R. A. Carbon–Hydrogen Bond Breaking and Making in the Open-Shell Singlet Molecule $\text{Cp}^*_2\text{Yb}(4,7\text{-Me}_2\text{ phen})$. *Organometallics* **2014**, 33 (23), 6819–6829.
- (31) Feistel, G. R.; Mathai, T. P. A new type of intramolecular antiferromagnetism. *J. Am. Chem. Soc.* **1968**, 90 (11), 2988–2989.
- (32) Evans, W. J.; Drummond, D. K. Reductive coupling of pyridazine and benzaldehyde azine and reduction of bipyridine by samarium complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$. *J. Am. Chem. Soc.* **1989**, 111 (9), 3329–3335.
- (33) Fedushkin, I. L.; Petrovskaya, T. V.; Girgsdies, F.; Köhn, R. D.; Bochkarev, M. N.; Schumann, H. Synthesis and Structure of the First Lanthanide Complex with the Bridging, Antiaromatic 2,2'-Bipyridine Dianion: $[\{\text{Yb}(\mu_2\text{-N}_2\text{C}_{10}\text{H}_8)(\text{thf})_2\}_3]$. *Angew. Chem. Int. Ed.* **1999**, 38 (15), 2262–2264.
- (34) Booth, C. H.; Kazhdan, D.; Werkema, E. L.; Walter, M. D.; Lukens, W. W.; Bauer, E. D.; Hu, Y.-J.; Maron, L.; Eisenstein, O.; Head-Gordon, M.; Andersen, R. A. Intermediate-Valence Tautomerism in Decamethylytterbocene Complexes of Methyl-Substituted Bipyridines. *J. Am. Chem. Soc.* **2010**, 132, 17537–17549.
- (35) Jacquot, L.; Xémard, M.; Clavaguéra, C.; Nocton, G. Multiple One-Electron Transfers in Bipyridine Complexes of Bis(phospholyl) Thulium. *Organometallics* **2014**, 33 (15), 4100–4106.
- (36) Nocton, G.; Lukens, W. W.; Booth, C. H.; Rozenel, S. S.; Medling, S. A.; Maron, L.; Andersen, R. A. Reversible Sigma C–C Bond Formation Between Phenanthroline Ligands Activated by $(\text{C}_5\text{Me}_5)_2\text{Yb}$. *J. Am. Chem. Soc.* **2014**, 136 (24), 8626–8641.
- (37) Nocton, G.; Ricard, L. Reversible C–C coupling in phenanthroline complexes of divalent samarium and thulium. *Chem. Commun.* **2015**, 51 (17), 3578–3581.
- (38) Bochkarev, M. N.; Trifonov, A. A.; N. Cloke, F. G.; Dalby, C. I.; Matsunaga, P. T.; Andersen, R. A.; Schumann, H.; Loebel, J.; Hemling, H. Synthesis, magnetic susceptibility and X-ray crystal structure of $(^t\text{BuNCHCHN}^t\text{Bu})_3\text{Yb}$. *J. Organomet. Chem.* **1995**, 486 (1), 177–182.
- (39) Trifonov, A. A.; Fedorova, E. A.; Ikorskii, V. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. Solvent-Mediated Redox Transformations of Ytterbium Bis(indenyl)diazabutadiene Complexes. *Eur. J. Inorg. Chem.* **2005**, 2005 (14), 2812–2818.

- (40) Trifonov, A. A. Reactions of Ytterbocenes with Diimines: Steric Manipulation of Reductive Reactivity. *Eur. J. Inorg. Chem.* **2007**, 2007 (20), 3151–3167.
- (41) Walter, M. D.; Berg, D. J.; Andersen, R. A. Coordination of 1,4-Diazabutadiene Ligands to Decamethylytterbocene: Additional Examples of Spin Coupling in Ytterbocene Complexes. *Organometallics* **2007**, 26 (9), 2296–2307.
- (42) Booth, C. H.; Walter, M. D.; Kazhdan, D.; Hu, Y.-J.; Lukens, W. W.; Bauer, E. D.; Maron, L.; Eisenstein, O.; Andersen, R. A. Decamethylytterbocene Complexes of Bipyridines and Diazabutadienes: Multiconfigurational Ground States and Open-Shell Singlet Formation. *J. Am. Chem. Soc.* **2009**, 131, 6480–6491.
- (43) Veauthier, J. M.; Schelter, E. J.; Carlson, C. N.; Scott, B. L.; Re, R. E. D.; Thompson, J. D.; Kiplinger, J. L.; Morris, D. E.; John, K. D. Direct Comparison of the Magnetic and Electronic Properties of Samarocene and Ytterbocene Terpyridine Complexes. *Inorg. Chem.* **2008**, 47 (13), 5841–5849.
- (44) Roitershtein, D.; Domingos, Â.; Pereira, L. C. J.; Ascenso, J. R.; Marques, N. Coordination of 2,2'-Bipyridyl and 1,10-Phenanthroline to Yttrium and Lanthanum Complexes Based on a Scorpionate Ligand. *Inorg. Chem.* **2003**, 42 (23), 7666–7673.
- (45) Williams, B. N.; Huang, W.; Miller, K. L.; Diaconescu, P. L. Group 3 Metal Complexes of Radical-Anionic 2,2'-Bipyridyl Ligands. *Inorg. Chem.* **2010**, 49 (24), 11493–11498.
- (46) Mehdoui, T.; Berthet, J.-C.; Thuéry, P.; Salmon, L.; Rivière, E.; Ephritikhine, M. Lanthanide(III)/Actinide(III) Differentiation in the Cerium and Uranium Complexes $[M(C_5Me_5)_2(L)]^{0,+}$ ($L=2,2'$ -Bipyridine, $2,2':6',2''$ -Terpyridine): Structural, Magnetic, and Reactivity Studies. *Chem. - Eur. J.* **2005**, 11 (23), 6994–7006.
- (47) Ortu, F.; Zhu, H.; Boulon, M.-E.; Mills, D. P. Synthesis and Reactivity of a Cerium(III) Scorpionate Complex Containing a Redox Non-Innocent 2,2'-Bipyridine Ligand. *Inorganics* **2015**, 3 (4), 534–553.
- (48) Ortu, F.; Fowler, J. M.; Burton, M.; Formanuk, A.; Mills, D. P. A structural investigation of heteroleptic lanthanide substituted cyclopentadienyl complexes. *New J. Chem.* **2015**, 39 (10), 7633–7639.
- (49) Bergbreiter, D. E.; Killough, J. M. Reactions of potassium-graphite. *J. Am. Chem. Soc.* **1978**, 100 (7), 2126–2134.
- (50) Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V. Lanthanum Does Form Stable Molecular Compounds in the +2 Oxidation State. *Angew. Chem. Int. Ed.* **2008**, 47 (8), 1488–1491.
- (51) Coombe, V. T.; Heath, G. A.; MacKenzie, A. J.; Yellowlees, L. J. Spectroelectrochemical studies on tris(bipyridyl)iridium complexes: ultraviolet, visible and near-infrared spectra of the series $[Ir(bipyridyl)_3]^{3+/2+/+0}$. *Inorg. Chem.* **1984**, 23 (21), 3423–3425.
- (52) Scarborough, C. C.; Sproules, S.; Weyhermüller, T.; DeBeer, S.; Wieghardt, K. Electronic and Molecular Structures of the Members of the Electron Transfer Series $[Cr(^t\text{bpy})_3]^n$ ($n = 3+, 2+, 1+, 0$): An X-ray Absorption Spectroscopic and Density Functional Theoretical Study. *Inorg. Chem.* **2011**, 50 (24), 12446–12462.
- (53) Gore-Randall, E.; Irwin, M.; Denning, M. S.; Goicoechea, J. M. Synthesis and Characterization of Alkali-Metal Salts of 2,2'- and 2,4'-Bipyridyl Radicals and Dianions. *Inorg. Chem.* **2009**, 48 (17), 8304–8316.
- (54) Ren, W.; Zi, G.; Walter, M. D. Synthesis, Structure, and Reactivity of a Thorium Metallocene Containing a 2,2'-Bipyridyl Ligand. *Organometallics* **2012**, 31 (2), 672–679.
- (55) Evans, D. F. 400. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc. Resumed* **1959**, 2003–2005.
- (56) Sur, S. K. Measurement of magnetic susceptibility and magnetic moment of paramagnetic molecules in solution by high-field Fourier transform NMR spectroscopy. *J. Magn. Reson.* **1969**, 82 (1), 169–173.
- (57) Grant, D. H. Paramagnetic Susceptibility by NMR: The “Solvent Correction” Reexamined. *J. Chem. Educ.* **1995**, 72 (1), 39.
- (58) Woole, A. J.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T. Lanthanide tri-benzyl complexes: structural variations and useful precursors to phosphorus-stabilised lanthanide carbenes. *Dalton Trans.* **2009**, 39 (2), 500–510.
- (59) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*, 1st ed.; Oxford University Press, 1932.

- (60) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. PHI: A powerful new program for the analysis of anisotropic monomeric and exchange-coupled polynuclear d- and f-block complexes. *J. Comput. Chem.* **2013**, *34* (13), 1164–1175.
- (61) Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* **2006**, *178* (1), 42–55.
- (62) Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.; Fdez. Galván, I.; Ferré, N.; Frutos, L. M.; Gagliardi, L.; et al. Molcas 8: New capabilities for multiconfigurational quantum chemical calculations across the periodic table. *J. Comput. Chem.* **2016**, *37* (5), 506–541.
- (63) Veryazov, V.; Malmqvist, P. Å.; Roos, B. O. How to Select Active Space for Multiconfigurational Quantum Chemistry? *Int. J. Quant. Chem.* **2011**, *111* (13), 3329–3338.
- (64) Kadirov, M. K.; Kholin, K. V.; Tselishcheva, E. Y.; Burilov, V. A.; Mustafina, A. R. Cyclic voltammetry of tris(2,2'-bipyridine)zinc(ii) diperchlorate detected by electron spin resonance. *Russ. Chem. Bull.* **2014**, *62* (6), 1327–1331.
- (65) Tabner, B. J.; Yandle, J. R. A correlation of half-wave reduction potentials with theoretical calculations for some nitrogen-containing heteromolecules in dimethylformamide. *J. Chem. Soc. Inorg. Phys. Theor.* **1968**, No. 0, 381–388.
- (66) Levin, J. R.; Dorfner, W. L.; Carroll, P. J.; Schelter, E. J. Control of cerium oxidation state through metal complex secondary structures. *Chem Sci* **2015**, *6* (12), 6925–6934.
- (67) Piro, N. A.; Robinson, J. R.; Walsh, P. J.; Schelter, E. J. The electrochemical behavior of cerium(III/IV) complexes: Thermodynamics, kinetics and applications in synthesis. *Coord. Chem. Rev.* **2014**, *260*, 21–36.
- (68) Jacob, K.; Glanz, M.; Tittes, K.; Thiele, K.-H. Beiträge zur Chemie der Alkylverbindungen von Übergangsmetallen. 52. Darstellung, Charakterisierung und Reaktionen von $(C_5H_5)_3Ce \cdot THF$ und $Na [Ce(C_5H_5)_4] \cdot THF$. *Z. Für Anorg. Allg. Chem.* **1988**, *556* (1), 170–178.
- (69) Connelly, N. G.; Geiger, W. E. Chemical redox agents for organometallic chemistry. *Chem. Rev.* **1996**, *96* (2), 877–910.
- (70) Lam, O. P.; Anthon, C.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K. Structural and Spectroscopic Characterization of a Charge-Separated Uranium Benzophenone Ketyl Radical Complex. *J. Am. Chem. Soc.* **2008**, *130* (20), 6567–6576.
- (71) Deacon, G. B.; Junk, P. C.; Wang, J.; Werner, D. Reactivity of Bulky Formamidinosamarium(II or III) Complexes with C=O and C=S Bonds. *Inorg. Chem.* **2014**, *53* (23), 12553–12563.
- (72) Maury, O.; Villiers, C.; Ephritikhine, M. Pinacol versus para coupling of aromatic ketones. *Tetrahedron Lett.* **1997**, *38* (37), 6591–6594.
- (73) Goodwin, C. A. P.; Chilton, N. F.; Vettese, G. F.; Moreno Pineda, E.; Crowe, I. F.; Ziller, J. W.; Winpenny, R. E. P.; Evans, W. J.; Mills, D. P. Physicochemical properties of near-linear Ln(II) bis-silylamide complexes (Ln = Sm, Eu, Tm, Yb). *Inorg. Chem.* **2016**, *55* (20), 10057–10067.
- (74) Matson, E. M.; Kiernicki, J. J.; Anderson, N. H.; Fanwick, P. E.; Bart, S. C. Isolation of a uranium(III) benzophenone ketyl radical that displays redox-active ligand behaviour. *Dalton Trans.* **2014**, *43* (48), 17885–17888.
- (75) Kiernicki, J. J.; Newell, B. S.; Matson, E. M.; Anderson, N. H.; Fanwick, P. E.; Shores, M. P.; Bart, S. C. Multielectron C–O Bond Activation Mediated by a Family of Reduced Uranium Complexes. *Inorg. Chem.* **2014**, *53* (7), 3730–3741.
- (76) Handrick, K.; Malrieu, J. P.; Castell, O. General strategy for the abinitio calculation of exchange coupling in polynuclear complexes. *J. Chem. Phys.* **1994**, *101* (3), 2205–2212.
- (77) Fink, K.; Fink, R.; Staemmler, V. Ab Initio Calculation of the Magnetic Exchange Coupling in Linear Oxo-Bridged Binuclear Complexes of Titanium(III), Vanadium(III), and Chromium(III). *Inorg. Chem.* **1994**, *33* (26), 6219–6229.
- (78) Wang, B.; Wei, H.; Wang, M.; Chen, Z. Ab initio multireference configuration-interaction theoretical study on the low-lying spin states in binuclear transition-metal complex: Magnetic exchange of $[(NH_3)_5Cr(\mu-OH)Cr(NH_3)_5]^{5+}$ and $[Cl_3FeOFeCl_3]^{2-}$. *J. Chem. Phys.* **2005**, *122* (20), 204310.
- (79) Lukens, W. W.; Magnani, N.; Booth, C. H. Application of the Hubbard Model to $Cp^*_2Yb(bipy)$, a Model System for Strong Exchange Coupling in Lanthanide Systems. *Inorg. Chem.* **2012**, *51* (19), 10105–10110.

- (80) Lines, M. E. Orbital Angular Momentum in the Theory of Paramagnetic Clusters. *J. Chem. Phys.* **1971**, 55 (6), 2977–2984.
- (81) Moreno Pineda, E.; Chilton, N. F.; Marx, R.; Dörfel, M.; Sells, D. O.; Neugebauer, P.; Jiang, S.-D.; Collison, D.; van Slageren, J.; McInnes, E. J. L.; et al. Direct measurement of dysprosium(III)···dysprosium(III) interactions in a single-molecule magnet. *Nat. Commun.* **2014**, 5, 5243.
- (82) Baker, M. L.; Tanaka, T.; Murakami, R.; Ohira-Kawamura, S.; Nakajima, K.; Ishida, T.; Nojiri, H. Relationship between Torsion and Anisotropic Exchange Coupling in a Tb^{III}-Radical-Based Single-Molecule Magnet. *Inorg. Chem.* **2015**, 54 (12), 5732–5738.
- (83) Iwahara, N.; Chibotaru, L. F. Exchange interaction between J multiplets. *Phys. Rev. B* **2015**, 91 (17), 174438.

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We examine a series of Ln(III)/bipy^{•-} complexes to define the radical formulation, and estimate the intramolecular exchange coupling using multi-configurational and spin Hamiltonian methods.