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Four tri-spin lanthanide–nitronyl nitroxide (Ln^{III}=Gd^{III}, Dy^{III}, Er^{III}, and Ho^{III}) complexes: syntheses, structures, and magnetic properties

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Four tri-spin lanthanide–nitronyl nitroxide (Ln^{III} = Gd^{III}, Dy^{III}, Er^{III}, and Ho^{III}) complexes: syntheses, structures, and magnetic properties

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Four radical–Ln(III)–radical complexes, [Ln(hfac)$_3$(NITPhSCH$_3$)$_2$] (Ln = Gd (**1**), Dy (**2**), Er (**3**), Ho (**4**); hfac = hexafluoroacetylacetonate; NITPhSCH$_3$ = 4′-thiomethylphenyl-4,4,5,5tetramethyl-imidazoline-1-oxyl-3-oxide), have been synthesized, and structurally and magnetically characterized. The X-ray crystal structures show that the structures of the four complexes are similar, consisting of isolated molecules in which Ln(III) ions are coordinated by six oxygen atoms from three hfac and two oxygen atoms from nitronyl radicals. The temperature dependences of magnetic susceptibilities for the four complexes show that in the Gd(III) complex, ferromagnetic interactions between Gd(III)–radical and antiferromagnetic interactions between the radicals coexist with $J_{\text{Rad–Gd}} = 1.09 \, \text{cm}^{-1}$, $J_{\text{Rad–Rad}} = -1.85 \, \text{cm}^{-1}$.

1. Introduction

The design of new molecular-based magnetic materials, combining lanthanide ions with organic radicals as magnetic ligand center, has attracted considerable interest [1–9]. Nitronyl nitroxide radicals are especially attractive due to their exceptional stability and easy chemical modification [10]. Lanthanide ions, except for gadolinium(III), and especially heavy lanthanide ions such as terbium(III) and dysprosium(III), have large anisotropies, which arise from strong spin–orbit coupling, and are good candidates for construction of single-molecule magnets (SMMs) and single-chain magnets (SCMs) [11–14]. Therefore, chemists pay attention to different radical–lanthanide complex architectures with appropriate organic nitronyl nitroxide radicals [15–21]. Compared to other radical–lanthanide complexes, more Gd(III)–radical complexes have been obtained and their magnetic properties are studied in detail [1, 22–28], because gadolinium(III) has a half-filled *f*-shell electron configuration and quenched orbital angular momentum in the $^8S_{7/2}$ ground state makes it easier to study. In order to develop rare-earth complexes containing organic radical ligands, very recently, we used Tb(hfac)$_3 \cdot$ 2H$_2$O and NITPhSCH$_3$ radical ligand (hfac = hexafluoroacetylacetonate;

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NITPhSCH$_3$ = 4′-thiomethylphenyl-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide) to obtain tri-spin mononuclear [Tb(hfac)$_3$(NITPhSCH$_3$)$_2$] (5) and 1-D chain [Tb(hfac)$_3$ (NITPhSCH$_3$)]$_n$ (6) [29]. The complexes exhibit slow magnetic relaxation resembling SMM and SCM behavior, respectively.

In this article, we synthesized four rare-earth-radical complexes by using the same nitronyl nitroxide, [Ln(hfac)$_3$(NITPhSCH$_3$)$_2$] (Ln = Gd (1), Dy (2), Er (3), Ho (4)) and describe their crystal structures and magnetic properties. These complexes are isostructural to reported tri-spin mononuclear [Tb(hfac)$_3$(NITPhSCH$_3$)$_2$] (5).

2. Experimental

2.1. *Materials and instrumentation*

All reagents used in the syntheses were of analytical grade; hexafluoroacetylacetone and 4-thiomethylbenzaldehyde were purchased from Aldrich Chemical Company, and the NITPhSCH$_3$ radical [30, 31] and [Ln(hfac)$_3$] · 2H$_2$O [32] were synthesized according to literature methods. Elemental analyses (C, H, and N) were carried out with a Perkin-Elmer 240 elemental analyzer. Infrared spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} with a Bruker Tensor 27 IR spectrometer. Magnetic measurements were performed with an MPMS XL-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. *Preparation of [Ln(hfac)$_3$(NITPhSCH$_3$)$_2$] (1–4)*

All four complexes were synthesized by the same method. Therefore, the synthesis of 1 is detailed here. A solution of Gd(hfac)$_3$ · 2H$_2$O (0.05 mmol) in 20 mL of dry *n*-heptane was heated under reflux for 2 h. After that, the solution was cooled to about 60°C, and a solution of NITPhSCH$_3$ (0.1 mmol) in 3.0 mL of CH$_2$Cl$_2$ was added. The resulting mixture was stirred for 15 min and then cooled to room temperature. The filtrate was allowed to stand at room temperature for 3 days to give blue elongated crystals suitable for X-ray analysis. Complexes 2–4 were obtained in the similar manner using Ln(hfac)$_3$ · 2H$_2$O (Ln = Dy, Er, Ho) instead of Gd(hfac)$_3$ · 2H$_2$O.

For 1, yield [Gd(hfac)$_3$(NITPhSCH$_3$)$_2$] (0.043 g, 65%) Analysis: C$_{43}$H$_{41}$F$_{18}$N$_4$ O$_{10}$S$_2$Gd: Calcd: C 38.59, H 3.09, N 4.19. Found (%): C 38.52, H 3.10, N 4.16. IR data (KBr, cm^{-1}): 1654 (vs), 1557 (w), 1532 (w), 1501 (s), 1396 (m), 1256 (s), 1207 (s), 1147 (s), 790 (m), 666 (m).

For 2, yield [Dy(hfac)$_3$(NITPhSCH$_3$)$_2$] (0.046 g, 68%) Analysis: C$_{43}$H$_{41}$F$_{18}$N$_4$ O$_{10}$S$_2$Dy: Calcd: C 38.47, H 3.08, N 4.17. Found (%): C 38.44, H 3.10, N 4.16. IR data (KBr, cm^{-1}): 1655 (s), 1556 (w), 1531 (w), 1502 (s), 1376 (m), 1256 (s), 1208 (s), 1146 (s), 781 (m), 663 (m).

For 3, yield [Er(hfac)$_3$(NITPhSCH$_3$)$_2$] (0.044 g, 66%) Analysis: C$_{43}$H$_{41}$F$_{18}$N$_4$ O$_{10}$S$_2$Er: Calcd: C 38.30, H 3.07, N 4.16. Found (%): C 38.31, H 3.09, N 4.18. IR data (KBr, cm^{-1}): 1655 (s), 1556 (w), 1532 (w), 1501 (s), 1370 (m), 1256 (s), 1203 (s), 1147 (s), 780 (m), 662 (m).

For 4, yield [Ho(hfac)$_3$(NITPhSCH$_3$)$_2$] (0.048 g, 71%) Analysis: C$_{43}$H$_{41}$F$_{18}$N$_4$ O$_{10}$S$_2$Ho: Calcd: C 38.37, H 3.07, N 4.16. Found (%): C 38.39, H 3.09, N 4.17.

IR data (KBr, cm^{-1}): 1658 (s), 1557 (w), 1532 (w), 1501 (s), 1369 (m), 1256 (s), 1208 (s), 1145 (s), 783 (m), 662 (m).

2.3. *X-ray crystallographic study*

Diffraction intensity data were collected on a Rigaku Saturn CCD diffractometer at room temperature employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXS-97 [33] and SHELXL-97 [34] programs, respectively. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Disordered fluorines were observed in hfac for **1**–**4**. The crystallographic data for **1**–**4** and the reported isomorphous complexes are listed in table 1, and the important interatomic distances and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis and crystal structure*

As the chemical reactivity of the lanthanides used is basically the same, the syntheses of the four radical–lanthanide complexes were performed in heptane/dichloromethane according to previously reported procedures [29]. We used 1 mol of [Ln(hfac)$_3$] and 2 mol of NITPhSCH$_3$ to obtain blue species with isostructural systems which are all mononuclear Ln^{III} complexes with two radical ligands.

X-ray crystallography shows that the four complexes are isomorphous, each consisting of isolated molecules where nitronyl nitroxide radicals are monodentate ligands toward Ln^{III} through oxygen of N–O to form the tri-spin complexes [Ln(hfac)$_3$(NITPhSCH$_3$)$_2$] (Ln = Gd (**1**), Dy (**2**), Er (**3**), Ho (**4**)). The structure of **1**, shown in figure 1, is detailed herein. It is an asymmetric isolated molecule [Gd(hfac)$_3$(NITPhSCH$_3$)$_2$], in which the central Gd^{III} is eight-coordinate by six oxygen atoms from three bidentate hfac and two oxygen atoms from two NITPhSCH$_3$ radicals. The coordination polyhedron of Gd^{III} can be best described as a distorted dodecahedron with triangular faces [22, 35, 36]. The bond distances between Gd^{III} and oxygen atom of hfac are in the range 2.317(5)–2.410(5) Å, while the Gd–O bond lengths from the two nitroxide groups are 2.329(5) and 2.322(5) Å, comparable to those of the reported Ln(hfac)$_3$ with nitronyl nitroxides [1]. The distances of uncoordinated N–O (1.284(8), 1.244(8) Å) are shorter than the coordinated ones (1.304(7), 1.301(7) Å), indicating that coordination of N–O weakens the bond energy of N–O. The dihedral angles formed by the phenyl ring and nitroxide groups of the radical ligand are 33.5° and 38.3° for the two NITPhSCH$_3$ ligands, respectively. While for **2**–**4**, [Ln(hfac)$_3$(NITPhSCH$_3$)$_2$] has similar structure to **1** except for the substitution of Gd^{III} with Dy^{III}, Er^{III}, Ho^{III} ions.

Figure 2 shows the packing diagram of **1**. The shortest distance between Gd and Gd is 10.696 Å. The nearest distance of the uncoordinated NO groups is 2.862 Å, which indicates that weak magnetic coupling may exist between NITPhSCH$_3$ radicals.

Table 1. Crystallographic data for **1**–**5**.

Complex	1	2	3	4	5
Empirical formula	$C_{43}H_{41}F_{18}N_4O_{10}S_2Gd$	$C_{43}H_{41}F_{18}N_4O_{10}S_2Dy$	$C_{43}H_{41}F_{18}N_4O_{10}S_2Er$	$C_{43}H_{41}F_{18}N_4O_{10}S_2Ho$	$C_{43}H_{41}F_{18}N_4O_{10}S_2Tb$
Molecular weight	1337.17	1342.42	1347.18	1344.85	1338.84
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å, °)					
a	12.782(3)	12.781(3)	12.733(3)	12.721(3)	12.821(3)
b	16.989(3)	17.097(3)	17.045(3)	17.025(3)	16.783(3)
c	25.125(5)	25.211(5)	25.183(5)	27.226(5)	24.736(5)
β	94.56(3)	94.70(3)	94.80(3)	112.90(3)	94.58(3)
Volume (Å³), Z	5438.8(19), 4	5490.3(19), 4	5446.4(19), 4	5431.8(18), 4	5305.5(18), 4
Calculated density (g cm⁻³)	1.633	1.624	1.643	1.645	1.676
Absorption coefficient (mm⁻¹)	1.413	1.553	1.734	1.651	1.532
$F(000)$	2660	2668	2676	2672	2664
θ range for data collection (°)	3.02–25.02	3.02–25.02	3.03–25.02	2.66–25.02	1.65–25.02
I_{hkl} collected/unique	29,431/9365	26,928/9137	31,795/9594	30,605/9307	35,227/9321
R_{int}	0.0684	0.0768	0.0735	0.0481	0.0280
Max. and min. transmission	0.8487 and 0.7653	0.7465 and 0.6883	0.8189 and 0.7230	0.8265 and 0.7337	0.7493 and 0.6915
Data/restraints/parameters	9365/542/845	9137/542/845	9594/536/845	9307/542/845	9321/72/740
Goodness-of-fit on F^2	1.117	1.130	1.121	1.113	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0692$, $wR_2 = 0.1210$	$R_1 = 0.0808$, $wR_2 = 0.1236$	$R_1 = 0.0666$, $wR_2 = 0.1205$	$R_1 = 0.0649$, $wR_2 = 0.1579$	$R_1 = 0.0270$, $wR_2 = 0.0675$
R indices (all data)	$R_1 = 0.1126$, $wR_2 = 0.1350$	$R_1 = 0.1312$, $wR_2 = 0.1393$	$R_1 = 0.0974$, $wR_2 = 0.1314$	$R_1 = 0.0845$, $wR_2 = 0.1705$	$R_1 = 0.0303$, $wR_2 = 0.0697$

Table 2. The important interatomic distances (Å) and angles (°) for **1**–**5**.

Complex	**1**(Ln = Gd)	**2**(Ln = Dy)	**3**(Ln = Er)	**4**(Ln = Ho)	**5**(Ln = Tb)
Ln–O_{Rad} length (Å)	2.322(5), 2.329(5)	2.321(6), 2.323(6)	2.284(5), 2.296(5)	2.287(5), 2.288(5)	2.3340(18), 2.3245(19)
Ln–O_{hfac} length (Å)	2.317(5), −2.410(5)	2.299(6), −2.394(6)	2.285(5), −2.374(5)	2.284(6), −2.389(6)	2.3173(19), −2.4003(19)
Coordinated N–O_{Rad} length (Å)	1.304(7), 1.301(7)	1.296(8), 1.300(8)	1.297(7), 1.310(7)	1.295(8), 1.307(9)	1.303(3), 1.308(3)
Uncoordinated N–O_{Rad} length (Å)	1.244(8), 1.284(8)	1.259(10), 1.271(9)	1.271(8), 1.275(8)	1.275(10), 1.270(10)	1.275(3), 1.280(3)
Angle of O_{Rad}–Ln–O_{Rad} (°)	138.04(18)	137.7(2)	137.71(17)	134.4(2)	137.50(6)

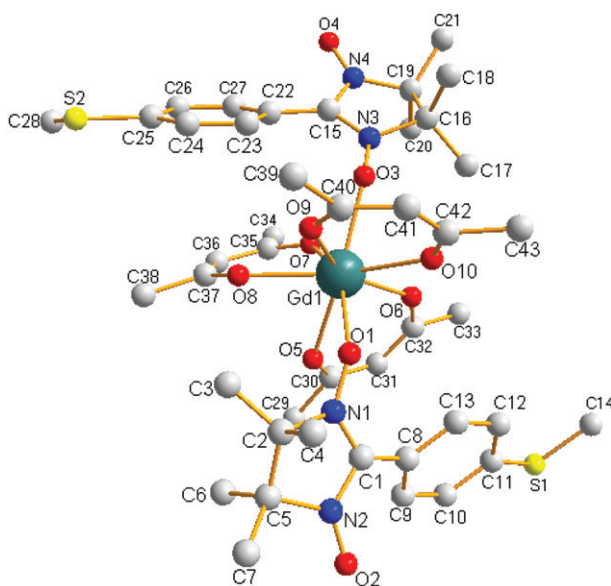O_{Rad}: oxygen atoms of nitronyl nitroxide radicals; O_{hfac}: oxygen atoms from hfac.

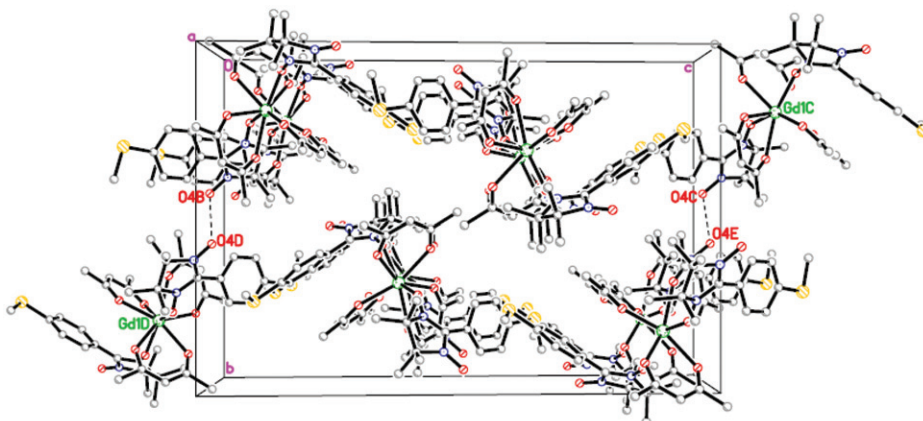Figure 1.   The molecular structure of **1**. Fluorine and hydrogen atoms are not shown for the sake of clarity.

Figure 2.   Packing diagram of **1**.

3.2. *Magnetic properties for 1*

The magnetic properties of **1** were measured from 2 to 300 K under applied magnetic field of 2000 G and the magnetic behaviors are shown in figure 3. At room temperature, the value of $\chi_M T$ for **1** is 8.42 cm^3 K mol^{-1}, corresponding to the value (8.62 cm^3 K mol^{-1}) expected for an uncoupled system for one Gd(III) ($^8S_{7/2}$, $g = 2$) and two organic radicals ($S = 1/2$) [22, 37]. Upon cooling, the $\chi_M T$ value gradually increases to a maximum of 9.74 cm^3 K mol^{-1} at 6 K, afterward decreasing to 9.56 cm^3 K mol^{-1} at 2 K. The increasing trends of $\chi_M T$ value upon cooling suggest the presence of ferromagnetic interactions in the molecule, while the decrease in the $\chi_M T$ below 6 K may be due to the intermolecular antiferromagnetic interactions and the
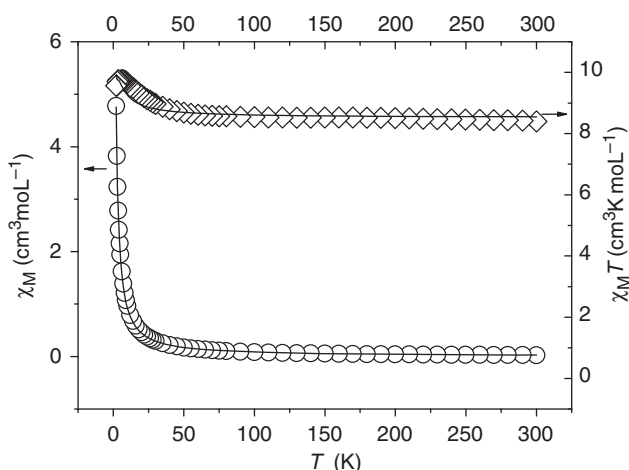
Figure 3. Plots of χ_M (O) *vs.* *T* and $\chi_M T$ ($\Diamond$) *vs.* *T* for **1**; the solid lines represent the theoretical curve with the best-fit parameters.

proximity of the uncoordinated N–O groups may be the origin of the intermolecular antiferromagnetic interactions [38, 39].

The gadolinium(III) is in an $^8S_{7/2}$ ground state without the orbital angular momentum contribution, and any exchange interaction should be essentially isotropic. Therefore, its magnetic interactions with the radicals can be described by isotropic exchange interaction. The magnetic behavior of **1** can be analyzed with the susceptibility equation (1) based on the Hamiltonian $H = -J(\hat{S}_{Rad1} \cdot \hat{S}_{Gd} + \hat{S}_{Rad2} \cdot \hat{S}_{Gd}) - J'\hat{S}_{Rad1}\ \hat{S}_{Rad2}$ for R–Gd(III)–R system with $S_R = 1/2$, $S_{Gd} = 7/2$, where J is the exchange coupling between Gd(III) and the radical, and J' refers to the exchange integral between radical and radical

$$\chi_m = \left[\frac{479\exp(16J/KT) + 252\exp(7J/KT) + 105 + 252\exp(9J/KT - 2J'/KT)}{10\exp(16J/KT) + 8\exp(7J/KT) + 6 + 8\exp(9J/KT - 2J'/KT)} \right]. \quad (1)$$

The least-squares fitting of the experimental data leads to $g = 1.99$, $J = 1.09\,\text{cm}^{-1}$, $J' = -1.85\,\text{cm}^{-1}$, $R = 1.87 \times 10^{-4}$ ($R = \sum(\chi_M^{calcd} - \chi_M^{obsd})^2/(\chi_M^{obsd})^2$).

The very small positive J indicates the very weak intramolecular ferromagnetic coupling between Gd(III) and NITPhSCH$_3$ radical. This may be attributed to the fact that the unpaired electron of the organic ligands transfers into the empty 5d and 6s orbitals of the metal, resulting in parallel alignment of the 4f and 5d, 6s electrons according to Hund's rule [40]. Thus in this mechanism the extent of the ferromagnetic interaction may depend on the overlap between the SOMO π^* orbital of the nitroxide and the 5d and/or 6s orbitals of the metal as proposed for Gd(III)–Cu(II) [41]. On the basis of the fact that the Gd–radical complex is ferromagnetic, the electron transfer integral $\beta_{5d–SOMO\ \pi^*}$ or the overlap of the 5d, 6s orbital with the NITPhSCH$_3$ SOMO π^* orbital is considered to be appreciable. In order to reproduce the experimental data, an antiferromagnetic coupling (J') between the NITPhSCH$_3$ radicals has to be involved in equation (1). The fitting found that a long-range weak antiferromagnetic coupling ($J' = -1.85\,\text{cm}^{-1}$) exists between the radicals.
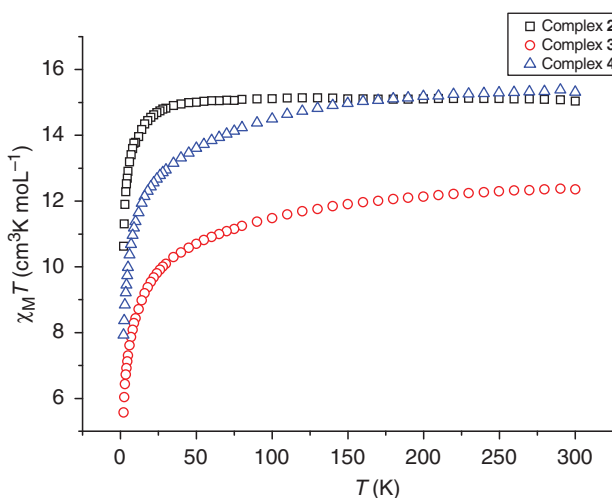
Figure 4. Plots of $\chi_M T$ (O) *vs.* T and χ^{-1} ($\square$) *vs.* T for **2–4.**

3.3. *Magnetic properties for 2–4*

The temperature dependences of magnetic susceptibility of **2–4** were measured in the 2–300 K range under applied magnetic field of 2000 G. Figure 4 shows the temperature dependences of $\chi_M T$ for **2–4**. At room temperature, the values of $\chi_M T$ are 15.04 cm^3 K mol^{-1} for **2**, 12.36 cm^3 K mol^{-1} for **3** and 15.31 cm^3 K mol^{-1} for **4**, in agreement with the expected values (14.92, 12.23, and 14.82 cm^3 K mol^{-1}) for one uncoupled Ln(III) ($^6H_{15/2}$ and $g = 4/3$ for the Dy(III) ion, $^4I_{15/2}$ and $g = 6/5$ for the Er(III) ion, $^5I_8$ and $g = 5/4$ for the Ho(III) ion) and two organic radicals ($S = 1/2$) [42]. Upon cooling, for **2**, the $\chi_M T$ stays almost constant until 45 K, and then decreases rapidly to reach a minimum of 10.63 cm^3 K mol^{-1} at $T = 2$ K, while for **3** and **4**, the $\chi_M T$ decreases slowly until 45 K, then decreases rapidly to reach a minimum of 5.57 and 7.93 cm^3 K mol^{-1} at $T = 2$ K, respectively. This probably arises from depopulation of the Ln Stark levels due to the spin–orbit coupling and crystal field perturbation. For such an Ln(III), the 4f^n configuration is split into $^{2S+1}L_J$ spectroscopic levels by interelectronic repulsion and spin–orbit coupling. Each of these states is further split into Stark sublevels by the crystal field perturbation. For most of the Ln(III) ions, the energy separation between the $^{2S+1}L_J$ ground state and the first excited state is so large that only the ground state is thermally populated at room and low temperatures.

4. Conclusion

We report four new mononuclear tri-spin lanthanide–nitronyl nitroxide complexes. The results show that these complexes have similar structures and all consist of isolated molecules. They are isostructural to our previously reported tri-spin mononuclear [Tb(hfac)$_3$(NITPhSCH$_3$)$_2$] (**5**) complex, which is an SMM containing one Tb(III) ion and two NITPhSCH$_3$ radicals. The magnetic studies show that in the Gd(III) complex,

there are ferromagnetic Gd(III)–Rad interactions and antiferromagnetic Rad–Rad interactions. The weak magnetic interactions show that though the f orbitals of Gd(III) are relatively shielded, they can nevertheless interact with the orbitals of the radical, thus giving appreciable coupling [1, 9], but the magnitude of the $J_{Rad–Gd}$ trend is not clear at all and further study is needed.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 786032, 832552, 832553, and 832554. The data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44 1223336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

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