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ARTICLE

Comparison of Two Field-Induced Er^{III} Single Ion Magnets

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We present the synthesis, magnetic and photophysical properties of four mononuclear Ln^{III} complexes in two isostructural lattices containing Gd^{III} and Er^{III}. A heptadentate Schiff base ligand and acetate versus trifluoroacetate were used to synthesise complexes **1**–**4**, where both Er^{III} complexes **2** and **4** exhibit field-induced SIM behaviour with similar U_{eff} values (31.6 K for **2** and 32.7 K for **4**). *Ab initio* calculations show the structure of the low-lying energy states and highlight that there is significant tunnelling already in the ground doublet state, but the application of a weak magnetic field of 0.05 T is sufficient for the ac magnetic measurements to suppress the tunnelling in the ground state. The calculated main magnetic axes (g_z) in the ground Kramers doublets show small differences between the two Er^{III} compounds **2** and **4**, due to their different ligand field.

Introduction

Since the discovery of slow magnetic relaxation at low temperature in a Mn₁₂ complex,¹ the pursuit of single molecule magnets (SMMs) has generated intense interest. The majority of reports of monometallic lanthanide SMMs, termed single ion magnets (SIMs), focus overwhelmingly on Tb^{III} and Dy^{III},^{2–5} ions which have an oblate distribution of their electron density. This has culminated in the recent report of a record magnetic blocking temperature (80 K) in a Dy^{III} metallocene compound.⁶ The design features of Tb^{III} and Dy^{III} SIMs often feature strongly axial ligands which maximize the magnetic anisotropy along one axis.⁷ This design paradigm should be reversed for 4f-ions with prolate electron density such as Er^{III} and Tm^{III}, *i.e.* ligands with many equatorial donors should promote slow magnetic relaxation in these ions. The shape of the free Er^{III} ion is rather prolate, although not as prolate as in case of Tm^{III} or Yb^{III}.⁷ In case of Er^{III} based SMMs it is often seen that the shape cannot strictly defined as oblate or prolate.^{8,18} And although this is a popular approach, Sessoli *et al.* have highlighted recently that the general assumption that the slow dynamics of magnetization is associated with the magnetic

anisotropy in lanthanide complexes is invalid.⁸ The design principles for successful SIM preparation have matured over the last five years and reports of both field-induced and natural SIMs using Er^{III} ions have appeared steadily since then. These include sandwich complexes with pairs of COT or COT'' derivative ligands,^{9–12} pairs of cp* or mixed COT/cp ligands^{13,14} or pairs of phthalocyanine donors.^{15,16} Tang *et al.* reported the magnetic properties of [Er^{III}{N(SiMe₃)₂}₃], the first example of an equatorially coordinated Er-SIM.¹⁷ Notably, the isostructural Dy analogue does not show any SIM behaviour. To some extent, this discrepancy is expected due to the equatorially coordinating crystal field, which is more favourable towards the prolate Er^{III} ion, than to the oblate Dy^{III} ion.⁷ More recently, Dunbar *et al.* reported the first trigonal-pyramidal Er^{III} SIM, which shows slow relaxation of the magnetization under zero applied dc field with an effective barrier of U_{eff} = 63.3 K.¹⁸ Many of these highlighted compounds are, however, air-sensitive which complicates their integration into devices for practical applications.

Here we report two new Er^{III} SIMs using a heptadentate Schiff base chelating ligand and different anionic exogenous donors. The aim was to use our previous experience with designing targeted binding pockets utilising Schiff base reactions¹⁹ to synthesise this heptadentate ligand, H₂L₁ (Scheme 1), for its ability to form a large pocket suitable for capturing a single Ln^{III} ion. In a second step we tried to fine tune the crystal field around the Ln^{III} by using different types of capping ligand. The analogous Gd^{III} complexes were prepared to assess the degree of intermolecular magnetic interaction in order to show that the magnetic centres were well separated.

This approach resulted in a monomeric coordination complex, similar to the previously published Lu^{III} containing complex.²⁰

The reaction using Ln(OAc)₃ led to the formation of the monomeric structures [LnL₁(OAc)]·H₂O·EtOH with Ln = Gd (**1**) and Er (**2**). Since the ligand field around the metal centre has

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an influence on the magnetic properties,²¹ the electron withdrawing trifluoro group was introduced under the same reaction conditions, we observe the formation of the monomeric structures $[\text{GdL}_1(\text{CF}_3\text{CO}_2)]$ **3**, and $[\text{ErL}_1(\text{CF}_3\text{CO}_2)]$ **4**.

Scheme 1. General synthetic approach leading to the formation of the monomeric compounds $[\text{LnL}_1(\text{OAc})]\cdot\text{H}_2\text{O}\cdot\text{EtOH}$ with $\text{Ln} = \text{Gd}$ (**1**) and Er (**2**) and $[\text{GdL}_1(\text{CF}_3\text{CO}_2)]$ with $\text{Ln} = \text{Gd}$ (**3**) and Er (**4**).

Results and discussion

In order to stabilise the formation of a monomeric species, we decided to introduce the bulky anionic ligands, acetate and trifluoroacetate, respectively, since the heptadentate ligand only provides two negative charges, it is necessary to have a third negative charge to support a Ln^{3+} centre. This approach was taken as the design of the molecular symmetry is only one method for controlling the magnetic behaviour of mononuclear lanthanide compounds, while ligand modification provides a second route towards improving/changing the magnetic properties. This is confirmed by recent experimental and theoretical studies of low coordinate Ln complexes which suggest that it is not only the coordinating donor atoms and their ligand field that determine the anisotropy of Ln SIMs but also the electrostatic potential of the entire ligand.²²

Single crystal structural analysis reveals that complexes **1** and **2** are isostructural and crystallise in the orthorhombic space group $P2_12_12_1$ with $Z = 4$, while complexes **3** and **4** crystallise in the monoclinic space group $P2_1/c$, also with $Z = 4$. The coordination sphere in all compounds is composed by the $\text{N}_5\text{O}_2^{2-}$ donor set from the chelating ligand and the additional carboxylate oxygen (Figure 1).

Figure 1. Molecular structure of **2** (left) and **4** (right) (organic H atoms and solvent molecules omitted for clarity; carbon - black, nitrogen - blue, oxygen - red, fluorine - yellow, erbium - pink). The red dashed lines represent the calculated main magnetic axes (g_z) in the ground Kramers doublets with respect to the molecular frames. For **2** (left), the g_z axis makes an angle of 70.5° with Er-O5, 23.8° with Er-N2 and 28.9° with Er-N5. For **4**, the g_z axis makes an angle of 69.5° with the Er-O5, 61° with Er-O1, and 34.6° with Er-N1.

The central lanthanide ion is chelated by the dianionic heptadentate Schiff base ligand, L_1^{2-} , and the deprotonated

oxygen atom, O5, of the carboxylate co-ligand, resulting in an eight-coordinated environment, (Figure 1).

All bond lengths are summarized in Table S1, ESI. There are three Ln-O bonds in the acetate containing complexes **1** and **2**, where the bond to the acetate oxygen O5 is 2.31 Å, slightly longer than the Ln-O bonds to the phenol oxygen atoms, O1 and O4, which are 2.22 and 2.26 Å, respectively. Complexes **2** and **4** show similar bond lengths towards O1 and O4, but the bond lengths to the deprotonated oxygen O5, are about 0.1 Å longer than in case of complex **1** and **2**, this is expected due to the electron withdrawing nature of the trifluoroacetate. The Ln-N bond lengths range from 2.51-2.62 Å for **1** to **2**, which is similar for **3** and **4**. The Schiff base ligand contains two types of nitrogen donors, two imines, N1 and N5, and three amines, N2, N3 and N4. The bond lengths to the imine nitrogen atoms are, as expected, slightly shorter than those to the amines. In the case of complexes **3** and **4**, the tetraethylenepentamine backbone shows a disorder around the N2 atoms.

It is well known, that the coordination geometry of lanthanide ions has an important influence on the magnetic behaviour.^{3,7,23} The pentaamine backbone (N1 - N5) together with one phenyl ring of the ligand, O4, form an almost perfect plane around the central Ln^{III} (see Figure 2) with only N1 and N2 being slightly above and below the plane, (N4 and N5 for compounds **3** and **4**, respectively). A second plane, almost perpendicular to the first one (82° for complex **2** and 87° for complex **4**), is spanned by the second phenol ring, and the carboxylic oxygens, O5 and O6 (see Figure 2).

Figure 2. Molecular structure of **2** (left) and **4** (right) forming two almost perpendicular planes around the central Ln^{III} centre, with an angle between the planes of 82° for complex **1** and 87° for complex **3**.

Since Rinehart and Long have published their article about the relation between anisotropy and structure in 2011⁷ it is known that the coordination geometry around the lanthanide ion influences the magnetic behavior. The shape of the free Er^{III} ion is rather prolate, although not as prolate as in case of Tm^{III} or Yb^{III} .⁷ In case of Er^{III} based SMMs it is often seen that the shape cannot strictly be defined as oblate or prolate.^{8,18} In order to describe the geometries of the lanthanide ions within the structures, they were analysed using the software SHAPE.²⁴ The continuous shape measure accompanying each geometry is a measure of how much it deviates from an idealized polyhedron, zero being ideal. While compounds **1** and **2** are closer to a biaugmented trigonal prismatic geometry, as shown in Figure 3, complexes **3** and **4** show less deviation from an

idealized triangular dodecahedron (see Table S2). Due to the flexibility of the Schiff base ligand, the coordination geometry around complexes **2** and **4** are rather spherical, with compounds **1** and **2** close to a C_{2v} symmetry and **3** and **4** closer to D_{2d} .

Figure 3. SHAPE analysis showing the biaugmented trigonal prismatic environment of complex **2** (left) and the triangular dodecahedron of complex **4** (right).

The molecular structures of **1** and **2** contain a water molecule and an ethanol molecule, leading to an overall formula of $[LnL_1(OAc)] \cdot H_2O \cdot EtOH$, which is due to the formation of hydrogen bonds (see Figure 4) between the hydrogen atoms of the water molecule, O8, and the neighbouring carboxylate oxygen, O6, and the oxygens of the Schiff base ligand, O3 and O4. In addition, the hydrogen atom of one of the amine groups of the ligand's backbone, N2, exhibits a hydrogen bond to the oxygen atom of the water molecule, as highlighted in Figure 4. On the other hand, complexes **3** and **4** crystallize without any solvent in the crystal lattice but form strong H-bonds though the electronegative trifluoro group (see Figure 4, right), leading to the formation of two closely neighboured monomeric units along the c-axis.

Figure 4. Molecular structure of $[ErL_1(OAc)] \cdot H_2O \cdot EtOH$ **2** (left) and $[ErL_1(CF_3CO_2)]$ **4** (right) highlighting the formation of hydrogen bonds as turquoise dashed lines.

The dc susceptibility measurements were performed on all four compounds and were studied between 1.8–300 K under an applied field of 1000 Oe (Figure 5). The room temperature $\chi_M T$ values for all complexes are in good agreement with the expected values for non-interacting Ln^{III} ions (Gd^{III} , $^8S_{7/2}$, $g = 2$, $C = 7.88 \text{ cm}^3\text{K/mol}$ and Er^{III} , $^4I_{15/2}$, $g = 6/5$, $C = 11.48 \text{ cm}^3\text{K/mol}$)²⁵ with values of $7.85 \text{ cm}^3\text{Kmol}^{-1}$ for **1** ($7.89 \text{ cm}^3\text{K/mol}$ for **3**) and $11.28 \text{ cm}^3\text{K/mol}$ for complexes **2** ($11.48 \text{ cm}^3\text{K/mol}$ for **4**). On lowering the temperature, the $\chi_M T$ product of the Gd^{III} containing complexes **1** and **3** stays almost constant, while that for the Er^{III} containing complexes **2** and **4**

starts to decrease on cooling to reach the final minimum at 1.8 K.

Figure 5. Temperature dependence of the $\chi_M T$ product at 1000 Oe for complexes **1** and **2** with the acetate co-ligand (left) and for complexes **3** and **4** containing the trifluoroacetate co-ligand (right).

Field dependence of magnetization was measured at different temperatures and the data are shown in Figure 6 for the Gd^{III} containing complexes **1** and **3**. For both compounds, the magnetization curves measured at low temperatures show a clear saturation above 3 T and the reduced magnetization shows the superposition of all isotherms on one master curve, as expected for an isotropic system. The saturation value of $7.05 \mu_B$ at 7 T and 2 K for **1** and $6.95 \mu_B$ for **3**, respectively, is in good agreement with the expected $7.0 \mu_B$ for one completely uncoupled Gd^{III} ($S = 7/2$) ion. This demonstrates that there are no long-range interactions which is important when investigating the magnetic response of the anisotropic Er^{III} compound.

The field dependence of magnetization for both Er^{III} containing compounds, **2** and **4**, are were measured at 2, 3 and 5 K and are shown in Figure S1 and S2. In both cases, the magnetization curves do not saturate at high fields which indicates the presence of significant magnetic anisotropy and/or low-lying excited states. The values of the isotherms rapidly increase at low field before following a more gradual linear increase after 1.5 T, without saturation, reaching at 7.0 T a value of $5.2 \mu_B$ in both complexes. The anisotropy present in both compounds can be seen from the reduced magnetization plots shown as M vs. H/T (see Figure S1 and S2) which clearly do not superimpose on to a single master curve.

Figure 6. Field dependence of the magnetization and reduced magnetization (inset) for $[GdL_1(OAc)]EtOH \cdot H_2O$ **1** (left) and $[GdL_1(CF_3CO_2)]$ **3** (right) measured between 0 and 7 T at different temperatures.

In order to investigate the potential presence of slow relaxation of the magnetization caused from SMM behaviour, ac magnetic susceptibility measurements were performed on both Er^{III} containing complexes **2** and **4**. In attempts to suppress any quantum tunnelling of the magnetization (QTM),

the frequency-dependent ac susceptibility was measured at dc fields ranging from 0 to 3000 Oe (Figure S3 and S4), which in both cases show field-dependent signals in the in-phase and out-of-phase ac susceptibility, and the optimum field was found to be 500 Oe. For both Er^{III} complexes, **2** and **4**, the ac measurements were carried out under this external dc field of 500 Oe and the in-phase and out-of-phase susceptibility signals are shown in Figure 7.

In both cases, the ac measurements reveal temperature dependent in- and out-of-phase signals over the whole applied temperature range with clear maxima up to 3.5 K. The maxima of the frequency dependent out-of-phase susceptibility curves were used to extract the relaxation time as a function of temperature and were plotted as $\ln(\tau)$ versus $1/T$ (see Figure S5). In case of $[\text{ErL}_1\text{OAc}]\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ **2**, the in-phase and out-of-phase susceptibility was also measured as temperature-dependency under a variety of frequencies (see Figure S6), in order to check for secondary relaxation processes at higher temperatures, which were found to be absent.

Figure 7. Frequency-dependence of the in-phase (left) and out-of-phase susceptibility (right) at 500 Oe of $[\text{ErL}_1\text{OAc}]\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ **2** (top) and $[\text{ErL}_1\text{F}_3\text{CO}_2]$ **4** (bottom) in a temperature range between 1.8–4.0 K. (solid line represents the best fit obtained using CC-Fit which uses a generalized Debye model).

Cole-Cole plots of χ_M' versus χ_M'' between 1.8 to 4.0 K (Figure S7) have semi-circular profiles, indicative of a single relaxation process and were fitted with CC-Fit,²⁶ which uses a generalized Debye model.²⁷ The obtained α -values which are in a range between 0.1 (2.2 K) to 0.02 (4.0 K) for complex **2** and between 0.08 (1.8 K) to 0.04 (3.5 K) for complex **4**, indicating a narrow relaxation time distribution. The extracted parameters (see Tables S3 and S4 ESI) were plotted as $\ln(\tau)$ versus $1/T$ (see Figure S5, ESI), leading to a linear fit curve, resembling the Arrhenius equation giving $U_{\text{eff}} = 31.6$ K and $\tau_0 = 2.6 \cdot 10^{-8}$ s ($R = 0.99$) for complex **2**. The Arrhenius fit for complex **4** shows a slight increase in the energy barrier, $U_{\text{eff}} = 32.7$ K and deceleration of the relaxation time to $\tau_0 = 7.7 \cdot 10^{-9}$ s ($R = 0.99$) in comparison to complex **2**. In case of complex **4**, the Cole-Cole plots reveal the start of a second process at small

frequencies and at temperatures above 2.8 K. Therefore, the ac measurements were carried out under an external dc field of 1500 Oe for complex **4** to investigate the dynamic magnetic processes and the in-phase and out-of-phase susceptibility signals (Figure S8, ESI). The Cole-Cole plots at 1500 Oe of χ_M' versus χ_M'' between 1.8 to 3.0 K (Figure S9, ESI) clearly show the beginning of the second process over the full temperature range and the plots were fitted to the sum of two modified Debye functions, but the resulting parameters did not lead to satisfying results which indicates that there is probably more than one relaxation process taking place.

The Er^{III} ion in the first Er^{III} SIM, the $[\text{ErDOTA}]$ complex, from Sessoli *et al.*²⁸ exhibits a quite regular square antiprismatic geometry and shows the anticipated frequency-dependence in the out-of-phase susceptibility, leading to U_{eff} of 39 K.²⁸ Due to the flexibility of the heptadentate ligand, the symmetry around the Ln^{III} centres within compounds **1** – **4** is quite low. While complex **2** which exhibits a biaugmented trigonal prismatic geometry, complex **4** is closer to have a triangular dodecahedral environment. Both have shown to exhibit similar energy barriers.

Ab initio calculations using CASSCF/RASSI and CASPT2/RASSI were performed in order to get additional insight into the low-lying energy structure and magnetic properties of the investigated compounds. Such calculations have been previously shown to be efficient for Er^{III} compounds.^{29,30,31} The calculated energy spectra for complexes **2** and **4** is shown in Figure 8, where the states are plotted in function of the intrinsic magnetic moment. Each doublet state $\pm M_J$ arising from a given atomic multiplet is placed according to its magnetic moment (horizontal axis). The intensity of the red lines indicates the amplitude of the average transition magnetic dipole moment in Bohr magnetons between the connected states (see the legend on the left of each plot), the square of which roughly scales with the rate of spin-phonon transition between them.^{32,33} The red lines connecting the states are average values of the transition magnetic moment connecting the states, while the intensity of the colour is dependent on the absolute magnitude of the respective matrix element and the most intense lines outline the magnetization blocking barrier (shown red lines). Table 1 gives the numerical values of the calculated energy spectra in several computational approximations alongside with the g -tensors of the low-lying Kramers doublets. The orientation of the ground state g_z main magnetic axes of **2** and **4** with respect to their molecular frames are depicted in Figure 1, using the calculated results. We notice that $g_{x,y}$ are, on average, larger for **4** compared to **2**, for all computational models employed. This is in line with the fact that the peaks in χ_M'' appear at larger frequencies for **4** (see Figure 7), which is a direct sign of the higher speed of magnetic relaxation of **4** compared to **2**.

The data in Figure 8 and Table 1 show that there is significant tunnelling already in the ground doublet state (reflected in large values of the g_x and g_y). The temperature assisted tunnelling in the first and higher excited doublet states for **2** and **4** are also significant (Figure 8). This means that, even if the weak applied magnetic field for the ac magnetic

measurements (Figure 7) may suppress the tunnelling in the ground state, it is not sufficient to prevent relaxation via the excited states and other mechanisms.

Figure 8. Energy diagram for the blocking barrier for complex **2** (top) and **4** (bottom) using the VDZP basis set. Energy spectrum and the blocking barrier of **2** (top) and **4** (bottom). Each doublet state $\pm M_J$ arising from a given atomic multiplet is placed according to its magnetic moment (horizontal axis). The intensity of the red lines indicates the amplitude of the average transition magnetic dipole moment in Bohr magnetons between the connected states (see the legend on the left of each plot), the square of which roughly scales with the rate of spin-phonon transition between them.^{32,33} The most intense lines outline the magnetization blocking barrier (shown red lines).

Table 1. Energy spectra (cm⁻¹) of the investigated compounds and main values of the *g* tensors in the ground Kramers Doublet in various computational approximations.

[ErL ₁ (OAc)]·H ₂ O·EtOH (2)			[ErL ₁ (CF ₃ CO ₂)] (4)		
VDZP, CASSCF	VTZP, CASSCF	VDZP, CASPT2	VDZP, CASSCF	VTZP, CASSCF	VDZP, CASPT2
0	0	0	0	0	0
42	41	63	39	39	58
89	91	135	66	71	102
118	122	180	107	110	161
173	175	266	163	163	251
236	239	361	219	227	337
273	277	416	248	259	383
353	367	533	296	301	454
Main values of the <i>g</i> tensor in the ground Kramers Doublet					
0.212	0.231	0.180	0.183	0.161	0.306
0.830	0.883	0.720	1.158	1.326	1.599
15.413	15.317	15.301	14.867	15.000	14.664

Diffuse spectral reflectance measurements of the ground crystalline powders of the two Gd^{III} containing complexes **1** and **3** show the characteristic triple peaks associated with *o*-vanillin based complexes (see Figure S10). However, they have been shifted to a lower energy with the peaks here reported at 363 nm, 280 nm, and 232 nm compared with 348 nm, 266 nm, and 220 nm respectively. When examining the Er^{III} containing complexes **2** and **4**, shown in Figure 9, the sharp peaks characteristic of the erbium transitions are observed. These are assigned to $^4I_{15/2}$ to $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{9/2}$, based upon previously reported solid state samples.^{34,35}

Figure 9. Electronic absorption spectra of powdered samples of the Er^{III} containing complexes **2** and **4** in the visible range (200–800 nm) at 293 K. Spectra were recorded in diffuse reflectance mode.

Conclusions

We have presented the synthesis, structural and magnetic properties of a family of two almost isostructural Er^{III} compounds. The heptadentate ligand and the acetate derivative lead to the formation of mononuclear species which show field-induced SIM behaviour with similar U_{eff} values (31.6 K for **2** and 32.7 K for **4**). The rather flexible heptadentate Schiff base ligand is responsible for the low symmetry around the Ln^{III} centres and while complexes **1** and **2** exhibit a biaugmented trigonal prismatic geometry, compounds **3** and **4** are closer to have a triangular dodecahedral environment. *Ab initio* calculations highlight the low-lying energy spectra. The values of the calculated *g*-tensors of the low-lying Kramers doublets which show one preferred direction, g_z , as the easy axis of the molecule. While $g_{x,y}$ are, on average, larger for **4** in comparison to complex **2**, this is in agreement with the higher speed of magnetic relaxation of **4** compared to **2**. The magnetic data and the calculations are in good agreement and show that there is significant tunnelling already in the ground doublet state which is reflected in large values of the g_x and g_y . Both compounds, **2** and **4**, exhibit significant temperature assisted tunnelling in the first and higher excited doublet states, but the application of a weak magnetic field of 0.05 T for the ac magnetic measurements can suppress the tunnelling in the ground state. At the same time, though, this field is not sufficient to prevent relaxation via the excited states and other mechanisms.

Although the Schiff base ligand has not promoted the desired high symmetry around the Ln^{III} centre, it still leads to field-induced slow relaxation of magnetization and the calculated main magnetic axes (g_z) in the ground Kramers doublets with respect to the molecular frames shows the desired outcome. This work presents a new route towards air-stable Er^{III} SIMs which have the possibility of fine-tuning, especially of the ligand, towards future applications.

Experimental

A General Experimental

Physical Measurements. All measurements were carried out on powdered samples of the respective polycrystalline compound. Elemental analysis (C, H, and N) were performed using a Perkin Elmer Vario EL. A Bruker Alpha PlatinumATIR spectrometer was used to record the Infrared Spectra, and an Mass spectra were recorded on a Waters 2695 Separations Module Electrospray Spectrometer. Solid state Raman spectra were recorded using 532 nm excitation using a specifically tailored low-frequency configuration setup.³⁶ In this configuration, an ASE filter to filter spontaneous emission and an ONDAX XLF to eliminate Rayleigh scattering was used with a holospec f/1.8 monochromator imaging the spectra onto a cooled Andor Newton EMCCD.³⁷

Magnetic Measurements. The magnetic susceptibility measurements were recorded on a Quantum Design SQUID magnetometer MPMS-XL operating between 1.8 and 300 K. DC measurements were performed on a polycrystalline sample of 14.5 mg of $[\text{Gd}(\text{L}_1)\text{OAc}]$ **1**, 26.0 mg $[\text{Er}(\text{L}_1)\text{OAc}]$ **2**, 9.8 mg $[\text{Gd}(\text{L}_1)(\text{CF}_3\text{CO}_2)]$ **3** and 12.8 mg $[\text{Er}(\text{L}_1)(\text{CF}_3\text{CO}_2)]$ **4**. Each sample was wrapped in a polyethylene membrane and subjected to fields in the range from 0 to 7 T. The magnetization data was collected at 100 K in order to check for ferromagnetic impurities, which were found to be absent in the samples. Diamagnetic corrections were applied to correct for contribution from the sample holder, and the inherent diamagnetism of the sample was estimated with the use of Pascal's constants. AC measurements were carried out in with frequencies between 1 to 1500 Hz.

UV-Vis Collection Details. Solid state diffuse spectral reflectance measurements were carried out on lightly ground crystalline samples of complexes **1** – **4** pressed onto a flat barium oxide surface against a barium oxide standard. The spectra were collected using a Shimadzu UV-2700 Spectrophotometer equipped with an ISR-2600 Integrating sphere attachment.

B Materials and synthetic procedures

Starting Materials. All chemicals and solvents if not otherwise mentioned were purchased from chemical companies and were reagent grade. They were used without further purification or drying. All reactions were carried out under ambient conditions. All measurements were carried out on powdered samples of the respective polycrystalline compound. The $\text{Ln}(\text{OAc})_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{CF}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$ salts were prepared from Ln_2O_3 with the respective acid, according to the literature.

Synthesis and characterization of complexes 1-4.

1: $[\text{Gd}(\text{L}_1)(\text{OAc})] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$: Tetraethylenepentamine (0.25 mmol, 47 mg) was dissolved in a 1:1 mixture of EtOH/MeCN (20 ml). 3-Ethoxysalicylaldehyde (0.5 mmol, 83 mg) was added to the solution, yielding an immediate colour change to bright yellow. The ligand solution was stirred for one hour under ambient conditions to complete the Schiff base reaction and was then used directly without further purification.

Solid $\text{Gd}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ (0.25 mmol, 96 mg) was then added to the ligand solution and the pale-yellow solution was stirred for

one hour at room temperature, before being left to stand for crystallization without filtration. After one week complex **1** crystallized as pale-yellow blocks suitable for single crystal X-ray analysis.

Elemental analysis for $[\text{Gd}(\text{L}_1)(\text{OAc})] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ ($\text{C}_{30}\text{H}_{48}\text{GdN}_5\text{O}_8$) (%): calculated: C: 47.16, H: 6.33; N: 9.17; found: C: 47.02; H: 6.10; N: 8.94.

IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 3540 (w) O-H; 1570 (s), 1417 (s) C-O from the acetate; 3253 (w), 1466 (s) amine N-H; 1626 (s) imine C=N; 1389 phenol. (see Figure S11).

2-4: The complexes were synthesized following the procedure for complex **1**, with use of the required lanthanide acetate, or lanthanide trifluoroacetate, respectively.

2: Elemental analysis for $[\text{Er}(\text{L}_1)(\text{CH}_3\text{CO}_2)] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ ($\text{C}_{30}\text{H}_{48}\text{ErN}_5\text{O}_8$) (%): calculated: C: 46.55, H: 6.25; N: 9.05; found: C: 46.42; H: 5.99; N: 8.97.

IR spectrum is shown in Figures S12 and S13.

3: Elemental analysis for $\text{C}_{28}\text{H}_{37}\text{N}_5\text{O}_6\text{GdF}_3$ (%): calculated: C: 44.61, H: 4.95; N: 9.29; found: C: 44.49; H: 4.73; N: 9.16.

IR spectrum is shown in Figures S14 and S15.

4: Elemental analysis for $\text{C}_{28}\text{H}_{37}\text{N}_5\text{O}_6\text{ErF}_3$ (%): calculated: C: 44.03; H: 4.88; N: 9.17; F: 7.46; found: C: 43.83; H: 4.78; N: 8.95; F: 7.76.

IR spectrum is shown in Figures S16 and S17.

The solid-state Raman spectra of complexes **2** and **4** are shown in Figure S18.

C Crystallography

Crystal Data Collection and Refinement. Suitable single crystals of complexes **1** to **4** were mounted on Oxford Diffraction Supernova E diffractometer fitted with an Atlas detector; datasets were measured using monochromatic Cu- $K\alpha$ radiation (complex **3** (Gd-F₃) or Mo- $K\alpha$ radiation (complex **1** (Gd-OAc), **2** (Er-OAc) and **4** (Er-F₃)) and corrected for absorption.³⁸ The temperature (100 K) was controlled with an Oxford Cryosystem instrument. Structures were solved by dual-space direct methods (SHELXT)³⁹ and refined with full-matrix least-squared procedures based on F^2 , using SHELXL-2016. Non-hydrogen atoms were refined with independent anisotropic displacement parameters, organic H-atoms (i.e. bonded to C) were placed in idealized positions, while the coordinates of H-atoms bonded to O were generally refined with their O-H distance restrained to 0.88(4) Å. Selected crystallographic data and structure refinements are summarized in Table S6 and crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-1916223: **1**, CCDC-1916225: **2**, CCDC-1916224: **3** and CCDC-1916226: **4**.

D Computational details

The XRay molecular structure corresponding to the CCDC number for compounds **2** and **4** were employed for the theoretical calculations. The *ab initio* calculations of RASSCF/RASPT2/ RASSI/ SINGLE_ANISO level were carried out within the MOLCAS package.^{40,41} In this computational approach,

relativistic corrections are included via the Douglas-Kroll-Hess formalism, in two steps.^{42–47} In the first step, scalar corrections are included in the basis sets used for the expansion of the molecular orbitals of the corresponding eigenstates at the multiconfigurational self-consistent field level of theory (RASSCF). To this end, we have employed the atomic natural orbital with relativistic core corrections (ANO-RCC) basis sets for this study.^{48,49} Spin-orbit coupling is included in the second step (RASSI), using the obtained RASSCF states as input.^{45,50} In this approach, spin-orbit interaction is described by an effective mean-field operator (AMFI). Dynamical electron correlation was considered within multiconfiguration at second-order perturbation theory (RASPT2).^{40,47,51–54} All anisotropic magnetic properties (EPR g-tensors, magnetic susceptibility, molar magnetization, parameters of the effective crystal field for the ground *J*-multiplet), were computed by the SINGLE_ANISO module.^{55,56}

Conflicts of interest

There are no conflicts to declare.

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