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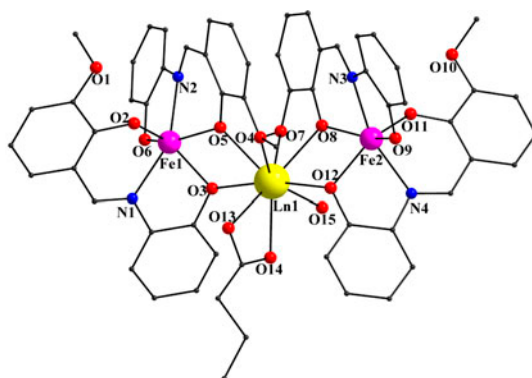
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## Syntheses, crystal structures, and magnetic properties of a series of $\text{Fe}_2\text{Ln}$ complexes

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The syntheses, crystal structures, and magnetic properties of four heterometallic Schiff base trinuclear  $[\text{Fe}_2\text{Ln}]$  complexes are reported. Single-X-ray diffraction analysis reveals that the four complexes contain a blade, propeller-like configuration. Magnetic analysis of  $\text{Gd}^{\text{III}}$  complex shows that the magnetic interaction between  $\text{Gd}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  ions is weak ferromagnetic.

A family of phenoxo-bridged heterometallic Schiff base trinuclear complexes,  $[\text{Fe}_2\text{LnL}_2(\text{C}_3\text{H}_7\text{COO})(\text{H}_2\text{O})]\cdot\text{CH}_3\text{OH}\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$  ( $\text{Ln} = \text{Sm}$ , **1**;  $\text{Gd}$ , **2**;  $\text{Tb}$ , **3**;  $\text{Dy}$ , **4**) is reported. Those complexes were afforded by “one-pot” reaction of a polydentate Schiff base ligand 2-hydroxy-3-methoxy-phenylsalicylaldehyde ( $\text{H}_2\text{L}$ ) with  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  and sodium butyrate ( $\text{C}_3\text{H}_7\text{COONa}$ ) in a mixture of methanol and acetonitrile in the presence of triethylamine as a base. Single-crystal X-ray diffraction analysis reveals that the structures of the four complexes are isomorphous. In each complex, two anionic  $[\text{FeL}_2]^-$  units coordinate to the central lanthanide ion as a tetradentate ligand using its four phenoxo oxygens, forming a two-blade propeller-like molecular shape. Magnetic properties of **1–4** were investigated using variable temperature magnetic susceptibility, and weak ferromagnetic exchange between the  $\text{Fe}^{\text{III}}$  and  $\text{Ln}^{\text{III}}$  ions has been established for the  $\text{Gd}$  derivative. The  $\text{Tb}$  and  $\text{Dy}$  complexes show no evidence of slow relaxation behavior above 2.0 K.

**Keywords:** Polydentate Schiff base ligand; Trinuclear  $\text{Fe}_2\text{Ln}$  complex; Magnetic properties

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## 1. Introduction

Since the discovery of single-molecule magnets (SMMs) in a dodecanuclear manganese complex [1], much interest has focused on new SMMs because of their promising applications, including high-density information storage, quantum computing, and molecular spintronics [2–5]. SMMs can act as nanomagnets at a certain blocking temperature in the absence of an external magnetic field, retaining its magnetization once magnetized [6]. Efforts devoted to the quest for SMMs have mainly concentrated on transition metal clusters [7]; however, the blocking temperature of these reported SMMs remained low. Recently, lanthanide ions have proved to be good candidates for the preparation of large barrier SMMs due to their significant magnetic anisotropy arising from large orbital angular momentum [8]. Since the first discovery of SMM behavior in a 3d–4f complex (a Cu<sub>2</sub>Tb<sub>2</sub> complex) [9], research into heterometallic complexes has developed as a significant branch in the field of SMMs.

There are two advantages in using 3d and 4f metal ions to build a single molecular magnet: (i) ferromagnetic coupling between 3d and 4f ions are likely to lead to greater spin state; (ii) 4f ions can provide large magnetic anisotropy. Thus, the 3d–4f system is likely to construct better SMMs [10]. However, it is not easy to achieve the goal because simply mixing the starting materials does not lead to self-assembly of the desired mixed-metal complexes, but often to pure 3d-metal clusters. A common synthetic approach is based on “one-pot” procedure, involving a mixture of 3d and 4f metal salts, and an elaborately chosen ligand. Indeed, this approach has led to a number of 3d–4f compounds exhibiting SMM behavior, displaying a variety of regular and irregular structure topologies. Such systems have involved Ln–Mn [11–14], Ln–Fe [15–17], Ln–Co [18], Ln–Ni [19], and Ln–Cu [20], with the majority of them being Ln–Mn species containing Mn<sup>III</sup>. Although some Fe–Ln clusters exhibiting SMM behavior have been observed in trinuclear [Fe<sub>2</sub>Ln] [21], tetranuclear [Fe<sub>2</sub>Ln<sub>2</sub>] [22], [FeDy<sub>3</sub>] [23], high nuclear [Fe<sub>5</sub>Ln<sub>8</sub>] [24], [Fe<sub>12</sub>Sm<sub>4</sub>] [25], and [Fe<sub>18</sub>Ln] [26] compounds, Fe–Ln Schiff base complexes have been seldom studied. Polydentate hydroxy-rich Schiff bases, derived from condensation of o-vanillin with all kinds of amino alcohols, are appealing for construction of polynuclear metal clusters, especially when an alkoxide can serve as a bridge between metal centers. For example, polydentate hydroxy-rich 2-hydroxy-3-methoxy-phenylsalicylaldimine (H<sub>2</sub>L) (scheme 1), derived from condensation of o-vanillin with o-aminophenol, has been used previously in homometallic systems [27] and 3d–4f heterometallic clusters [21, 28, 29].

In this article, we choose H<sub>2</sub>L reacting with iron nitrate, lanthanide nitrate, and sodium butyrate in methanol/acetonitrile solution by “one-pot” self-assembly approach and obtained a series of trinuclear heterometallic [Fe<sup>III</sup><sub>2</sub>Ln<sup>III</sup>] complexes, [Fe<sub>2</sub>LnL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)]·CH<sub>3</sub>OH·CH<sub>3</sub>CN·H<sub>2</sub>O (Ln = Sm, **1**; Gd, **2**; Tb, **3**; Dy, **4**). Single-crystal X-ray diffraction analysis reveals that the [Fe<sub>2</sub>LnO<sub>4</sub>] core in **1–4** arranges a two-blade, propeller-like molecular shape. Although a similar [Fe<sub>2</sub>LnO<sub>4</sub>] core constructed by H<sub>2</sub>L has been reported [21], complexes **3** and **4** show no evidence of slow relaxation behavior above 2.0 K, which is different from the behavior of [Fe<sub>2</sub>TbL<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)] (**5**) and [Fe<sub>2</sub>DyL<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)] (**6**). Such a difference may be attributed to weak intermolecular interactions between trinuclear complexes.

## 2. Experimental

### 2.1. Starting materials and general synthesis

All chemical reagents used in this experiment were of analytical grade and used as received. H<sub>2</sub>L was prepared according to the literature [30]. All experiments were performed under aerobic conditions.

IR spectra were recorded as KBr pellets on a Bruker Vector 22 FTIR spectrophotometer from 400 to 4000 cm<sup>-1</sup> in transmittance mode and elemental analyses on C, H, and N were performed using an Elementar Vario EL analyzer. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL7. Alternating current (ac) susceptibility measurements have been measured with an oscillating ac field of 3.5 Oe and ac frequencies from 10 to 1300 Hz. Samples were restrained in eicosane to prevent torquing. The experimental magnetic susceptibility data are corrected for diamagnetism estimated from Pascal tables [31] and sample holder calibration.

### 2.2. Synthesis of [Fe<sub>2</sub>LnL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)]·CH<sub>3</sub>OH·CH<sub>3</sub>CN·H<sub>2</sub>O. General method

Triethylamine (0.2 mM) was added to a stirring solution of Ln(NO<sub>3</sub>)<sub>3</sub> (0.1 mM), Fe(NO<sub>3</sub>)<sub>3</sub> (0.1 mM, 0.0404 g) and sodium butyrate (0.2 mM, 0.0220 g) in CH<sub>3</sub>OH (10 mL) and MeCN (10 mL). The solution immediately became claret and was stirred for further 4 h at room temperature. The red-brown solution was filtered and left undisturbed during which brown-black crystals suitable for X-ray analysis were obtained after four days. The fully grown crystals were collected by filtration, washed with methanol, and dried in air.

**2.2.1. [Fe<sub>2</sub>SmL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)]·CH<sub>3</sub>OH·CH<sub>3</sub>CN·H<sub>2</sub>O (1).** Yield: 0.0471 g, 66% (based on Fe). IR (KBr) cm<sup>-1</sup>: 2945 (m), 2834 (m), 1610 (s), 1584 (s), 1540 (s), 1474 (s), 1458 (s), 1432 (s), 1377 (m), 1285 (m), 1260 (s), 1185 (s), 1106 (s), 1041 (s), 975 (m), 873 (m), 820 (m), 742 (m), 567 (m), 525 (m). Anal. Calcd for C<sub>63</sub>H<sub>62</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>17</sub>Sm (Mr = 1423.23): C, 53.17; H, 4.39; N, 4.92. Found: C, 53.20; H, 4.36; N, 4.93.

**2.2.2. [Fe<sub>2</sub>GdL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)]·CH<sub>3</sub>OH·CH<sub>3</sub>CN·H<sub>2</sub>O (2).** Yield: 0.0450 g, 63% (based on Fe). IR (KBr) cm<sup>-1</sup>: 2938 (m), 2834 (m), 1607 (s), 1585 (s), 1546 (s), 1479 (s), 1458 (s), 1437 (s), 1379 (m), 1288 (m), 1254 (s), 1183 (s), 1105 (s), 1044 (s), 974 (m), 876 (m), 826 (m), 743 (m), 569 (m), 529 (m). Anal. Calcd for C<sub>63</sub>H<sub>62</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>17</sub>Gd (Mr = 1430.13): C, 52.91; H, 4.37; N, 4.90. Found: C, 52.91; H, 4.33; N, 4.94.

**2.2.3. [Fe<sub>2</sub>TbL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)]·CH<sub>3</sub>OH·CH<sub>3</sub>CN·H<sub>2</sub>O (3).** Yield: 0.0493 g, 69% (based on Fe). IR (KBr) cm<sup>-1</sup>: 2949 (m), 2830 (m), 1605 (s), 1588 (s), 1538 (s), 1470 (s), 1453 (s), 1435 (s), 1370 (m), 1286 (m), 1262 (s), 1185 (s), 1107 (s), 1042 (s), 974 (m), 877 (m), 818 (m), 746 (m), 562 (m), 521 (m). Anal. Calcd for C<sub>63</sub>H<sub>62</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>17</sub>Tb (Mr = 1431.80): C, 52.85; H, 4.36; N, 4.89. Found: C, 52.89; H, 4.34; N, 4.87.

**2.2.4. [Fe<sub>2</sub>DyL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)]·CH<sub>3</sub>OH·CH<sub>3</sub>CN·H<sub>2</sub>O (4).** Yield: 0.0447 g, 62% (based on Fe). IR (KBr) cm<sup>-1</sup>: 2942 (m), 2833 (m), 1606 (s), 1588 (s), 1542 (s), 1476 (s),

1458 (s), 1436 (s), 1378 (m), 1289 (m), 1256 (s), 1185 (s), 1108 (s), 1044 (s), 976 (m), 875 (m), 822 (m), 742 (m), 568 (m), 528 (m). Anal. Calcd for C<sub>63</sub>H<sub>62</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>17</sub>Dy (Mr = 1435.38): C, 52.72; H, 4.35; N, 4.88. Found: C, 52.70; H, 4.31; N, 4.85.

### 2.3. Single-crystal X-ray structure determinations

Crystal data for the four complexes were collected by a Rigaku Saturn X-ray diffractometer using monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 113 K. Data collection ( $\omega$  scans) and processing (cell refinement, data reduction, and empirical absorption correction) were performed using the crystal clear program package. The structures were solved by direct methods (SHELXS-97) [32] and refined by full-matrix least squares (SHELXL-97) [33] on  $F^2$ . The locations of Fe and rare earth were easily determined and other nonhydrogen atoms were located in difference Fourier maps. All of them were refined anisotropically. Subsequently, hydrogens were introduced in calculated positions and refined isotropically as riding with a common fixed isotropic thermal parameter. Information on the crystallographic data collection and structure refinements of the four complexes are summarized in table 1.

## 3. Results and discussion

### 3.1. Synthesis of heterometallic trinuclear complexes

The Schiff base 2-hydroxy-3-methoxy-phenylsalicylaldehyde (H<sub>2</sub>L) was prepared by condensation between o-vanillin and o-aminophenol. With good selectivity of this type of Schiff base ligand, the 3d ions enter into the NO<sub>2</sub> cavity of H<sub>2</sub>L, providing an intermediate [ML]<sup>o/-</sup> and then the open O<sub>4</sub> cavity is able to accommodate the Ln<sup>III</sup>. Ancillary carboxylate ligands can be used as bridging ligands or to meet the coordination spheres of metal ions. Thus, we used H<sub>2</sub>L reacting with iron nitrate, lanthanide nitrate, and sodium butyrate in methanol/acetonitrile solution by a “one-pot” self-assembly approach and obtained four propeller heterometallic trinuclear complexes with the Fe–Ln–Fe motif. Here, the carboxylate ligand is bis-chelating to one Ln<sup>III</sup>.

### 3.2. Crystal structures of 1–4

The molecular structures of 1–4 are shown in figures 1 and S1–S3 (see online supplemental material at <http://dx.doi.org/10.1080/00958972.2015.1013947>) and selected distances for 1–4 are summarized in table 2. Single-crystal X-ray diffraction revealed that the structures of 1–4 are isomorphous and all of them crystallize in monoclinic P2<sub>1</sub>/c space group. Here, we describe the structure of 3 in detail as a representative.

As shown in figure 1, the structure of 3 contains a neutral trinuclear [Fe<sub>2</sub>TbL<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>COO)(H<sub>2</sub>O)], which possesses a [Fe<sub>2</sub>TbO<sub>2</sub>] core in a two-blade propeller-like shape. Each Fe<sup>III</sup> is six coordinate by two L<sup>2-</sup> ligands through two imine nitrogens, two phenolate oxygens, and two methoxy oxygens, in a N<sub>2</sub>O<sub>4</sub> coordination environment. The bond lengths of Fe–O and Fe–N are 1.913(4)–2.055(4) Å and 2.145(5)–2.190(4) Å, respectively, which are close to those in other iron(III) ( $S = 5/2$ ) Schiff base [21, 34] complexes, showing typical values for a high-spin Fe<sup>III</sup> ion.

The Tb<sup>III</sup> is nine coordinate with O<sub>9</sub> coordination environment, six oxygens from two [FeL<sub>2</sub>]<sup>-</sup> units, one from a water, and two from the bidentate chelating butyrate. The Tb–O

Table 1. Crystallographic data and structure refinement for 1–4.

	1	2	3	4
Formula	$C_{63}H_{62}Fe_2SmN_5O_{17}$	$C_{63}H_{62}Fe_2GdN_5O_{17}$	$C_{63}H_{62}Fe_2TbN_5O_{17}$	$C_{63}H_{62}Fe_2Dy_2N_5O_{17}$
$M_r$ ( $g \cdot mol^{-1}$ )	1423.23	1430.13	1431.80	1435.38
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
$a$ ( $\text{\AA}$ )	10.927(2)	10.882(2)	10.962(2)	10.927(2)
$b$ ( $\text{\AA}$ )	26.132(5)	26.186(5)	26.124(5)	26.105(5)
$c$ ( $\text{\AA}$ )	22.949(5)	22.761(5)	22.845(5)	22.828(5)
$\beta$ ( $^\circ$ )	93.90(3)	93.45(3)	93.49(3)	93.57(3)
$V$ ( $\text{\AA}^3$ )	6537(2)	6474(2)	6530(2)	6499(2)
$Z$	4	4	4	4
$\mu$ ( $mm^{-1}$ )	1.395	1.526	1.580	1.649
$F(000)$	2900	2908	2912	2916
Crystal size ( $mm^3$ )	$0.24 \times 0.20 \times 0.18$	$0.20 \times 0.16 \times 0.12$	$0.22 \times 0.20 \times 0.16$	$0.22 \times 0.20 \times 0.16$
Limiting indices	$-13 \leq h \leq 13$ , $-31 \leq k \leq 30$ , $-26 \leq l \leq 27$	$-12 \leq h \leq 12$ , $-31 \leq k \leq 26$ , $-25 \leq l \leq 27$	$-13 \leq h \leq 13$ , $-27 \leq k \leq 31$ , $-27 \leq l \leq 27$	$-12 \leq h \leq 13$ , $-31 \leq k \leq 31$ , $-24 \leq l \leq 27$
Reflections collected	52,499	51,411	53,016	52,194
Theta range for data collection ( $^\circ$ )	1.18–25.02	1.56–25.02	1.56–25.02	1.19–25.02
GOF on $F^2$	1.060	1.113	1.005	1.053
Completeness to theta = 25.02	99.7%	99.9%	99.9%	99.8%
Data/restraints/parameters	11,474/80/852	11,400/78/853	11,510/78/853	11,430/78/853
$R_i$ [ $I > 2\sigma(I)$ ]	0.0581	0.0601	0.0540	0.0515
w $R_2$ (all data)	0.1725	0.1821	0.1731	0.1531
Largest diff. peak/hole ( $e \text{\AA}^{-3}$ )	2.274/–1.557	2.300/–2.212	2.135/–1.078	2.174/–1.028

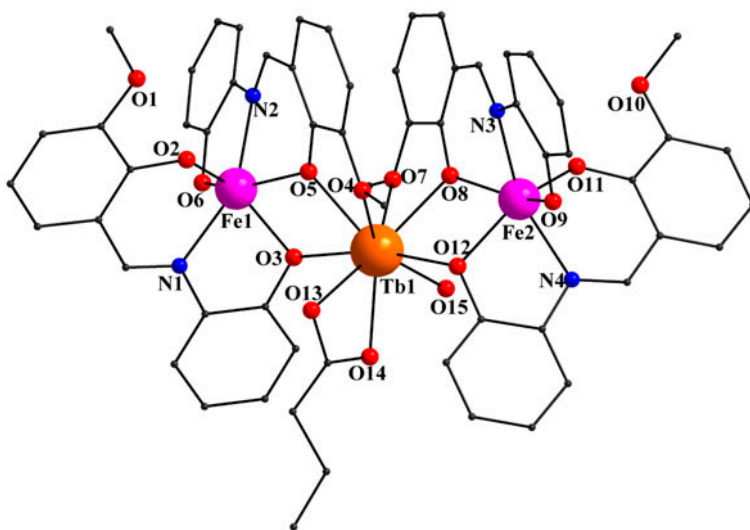


Figure 1. Molecular structure of  $[\text{Fe}_2\text{TbL}_2(\text{C}_3\text{H}_7\text{COO})(\text{H}_2\text{O})]$  in **3** (hydrogens and solvent molecules have been omitted for clarity).

Table 2. Selected bond lengths (Å) and angles (°) for 1–4.

	Ln = Sm	Ln = Gd	Ln = Tb	Ln = Dy
Fe(1)–O(2)	1.913(4)	1.917(4)	1.913(4)	1.919(4)
Fe(1)–O(3)	2.039(4)	2.042(4)	2.048(4)	2.043(3)
Fe(1)–O(5)	2.031(4)	2.023(4)	2.031(4)	2.029(3)
Fe(1)–O(6)	1.963(4)	1.962(4)	1.966(4)	1.957(4)
Fe(1)–N(1)	2.145(5)	2.142(5)	2.145(5)	2.137(4)
Fe(1)–N(2)	2.180(5)	2.177(5)	2.188(5)	2.181(4)
Fe(2)–O(8)	2.043(4)	2.045(4)	2.047(4)	2.042(3)
Fe(2)–O(9)	1.965(4)	1.960(4)	1.968(4)	1.965(4)
Fe(2)–O(11)	1.925(4)	1.924(4)	1.929(4)	1.930(4)
Fe(2)–O(12)	2.049(4)	2.060(4)	2.055(4)	2.054(4)
Fe(2)–N(3)	2.187(5)	2.155(5)	2.190(4)	2.191(4)
Fe(2)–N(4)	2.164(5)	2.194(5)	2.163(5)	2.158(4)
Ln(1)–O(3)	2.409(4)	2.384(4)	2.371(4)	2.360(4)
Ln(1)–O(5)	2.376(4)	2.343(4)	2.341(4)	2.326(3)
Ln(1)–O(8)	2.382(4)	2.346(4)	2.342(4)	2.329(3)
Ln(1)–O(12)	2.412(4)	2.385(4)	2.374(4)	2.360(3)
Ln(1)–O(13)	2.417(6)	2.399(5)	2.383(6)	2.381(5)
Ln(1)–O(14)	2.413(5)	2.401(5)	2.391(4)	2.375(4)
Ln(1)–O(15)	2.433(5)	2.343(4)	2.395(5)	2.375(4)
Fe(1)–O(3)–Ln(1)	108.88(16)	108.39(17)	108.36(16)	108.28(15)
Fe(1)–O(5)–Ln(1)	110.44(16)	110.62(17)	110.09(16)	110.04(14)
Fe(2)–O(8)–Ln(1)	111.24(16)	110.80(16)	110.66(16)	110.57(14)
Fe(2)–O(12)–Ln(1)	109.86(16)	108.76(16)	109.12(16)	108.98(14)

bond lengths are similar, 2.341(4)–2.395(4) Å. The distances of Fe1–Tb1 and Fe2–Tb1 are 3.534(8) and 3.513(8) Å, respectively. The metal ions are in a bent arrangement with a Fe1–Tb1–Fe2 angle of 138.49°, smaller than that of  $[\text{Fe}_2\text{TbL}_2(\text{NO}_3)(\text{H}_2\text{O})]$  (**5**). Further,

unlike **5**, intermolecular interactions found in **3** are much simpler, weak hydrogen bond interactions of O...H-C and  $\pi$ ... $\pi$  interactions mediate **3** to a (2-D) network (figure S3).

The isostructurality of the [Fe<sub>2</sub>Ln] family gives an opportunity to track the impact of variation of ionic radius of lanthanides on structural parameters of clusters. As may be expected, the Fe...Fe and Fe...Ln distances are 6.794, 3.641 Å for **1**, 6.735, 3.608 Å for **2**, 6.732, 3.600 Å for **3**, and 6.705, 3.585 Å for **4**, increasing with the ionic radii of lanthanides. In contrast, the angles of Fe–Ln–Fe are 137.78°, 138.01°, 138.42°, and 138.49°, respectively, decreasing with the ionic radii of lanthanides.

### 3.3. Magnetic properties

The variable temperature magnetic susceptibilities of **1–4** have been measured under an applied magnetic field of 1000 Oe from 2 to 300 K using a SQUID magnetometer. Plots of  $\chi_M T$  versus  $T$  are shown in figure 2 where  $\chi_M$  is the molar magnetic susceptibility.

For **1**, the  $\chi_M T$  value at room temperature is 8.89 cm<sup>3</sup> K M<sup>-1</sup>, close to the expected value of 8.85 cm<sup>3</sup> K M<sup>-1</sup> for two uncoupled Fe<sup>III</sup> ions ( $C = 4.38$  cm<sup>3</sup> K M<sup>-1</sup>,  $S = 3/2$ ,  $g = 2$ ) and one Sm<sup>III</sup> ion. On lowering the temperature, the values remain almost constant between 300 and 12 K and on further cooling the  $\chi_M T$  values rapidly decrease to the minimum of 4.36 cm<sup>3</sup> K M<sup>-1</sup> at 2 K. The decrease below 12 K is probably due to intermolecule antiferromagnetic interactions and magnetic anisotropy. The curve of  $\chi_M^{-1}$  versus  $T$  above 12 K obeys the Curie–Weiss law [35] (shown in figure S5).

Complexes **2–4** give similar magnetic susceptibility as a function of temperature. At room temperature, the  $\chi_M T$  product of **2–4** is in relatively good agreement with the expected value for two noninteracting Fe<sup>III</sup> ions and one Ln<sup>III</sup> ion (shown in table 3). Upon cooling, the  $\chi_M T$  products of **2–4** increase slowly to about 40 K and then rapidly increase to the maximum of 30.07 cm<sup>3</sup> K M<sup>-1</sup> at 5 K for **2**, 36.19 cm<sup>3</sup> K M<sup>-1</sup> at 5 K for **3**, and 36.98 cm<sup>3</sup> K M<sup>-1</sup> at 4 K for **4**, respectively. This behavior demonstrates a ferromagnetic Fe–Ln interaction within the trimer, as confirmed by the positive Weiss constant [35] in the range of

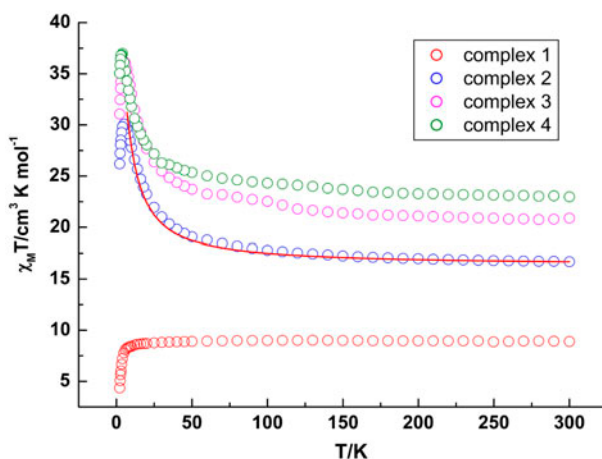


Figure 2. Temperature dependence of the  $\chi_M T$  product at 1 kOe for **1–4**. Solid line is the best fit obtained with the model as described in the text.



Table 3. Magnetic parameters extracted from the data for **1–4**.

Complex	1, [Fe <sub>2</sub> Sm]	2, [Fe <sub>2</sub> Gd]	3, [Fe <sub>2</sub> Tb]	4, [Fe <sub>2</sub> Dy]
Ground state term of Ln <sup>III</sup> ion	<sup>6</sup> H <sub>5/2</sub>	<sup>8</sup> S <sub>7/2</sub>	<sup>7</sup> F <sub>6</sub>	<sup>6</sup> H <sub>15/2</sub>
Curie constant expected for each Ln in cm <sup>3</sup> K M <sup>-1</sup>	0.09	7.875	11.81	14.17
Curie constant expected for each [Fe <sub>2</sub> Ln] in cm <sup>3</sup> K M <sup>-1</sup>	8.85	16.64	20.58	22.93
<i>T</i> measured at 300 K in cm <sup>3</sup> K M <sup>-1</sup>	8.89	16.68	20.88	22.97
Experimental Curie constant in cm <sup>3</sup> K M <sup>-1</sup>	8.94	16.31	20.24	22.58
<i>θ</i> (K)	0	8.05	8.36	6.45

40–300 K (shown in table 3 and figures S6–S8). On further cooling, the  $\chi_M T$  values sharply decrease to 26.18, 31.06, and 35.04 cm<sup>3</sup> K M<sup>-1</sup> for **2**, **3** and **4**, respectively, at 2.0 K, which can be attributed to intermolecule antiferromagnetic interactions and the magnetic anisotropy of Fe and Ln atoms.

To reveal the basic characteristics of the magnetic interactions between the 3d and 4f centers, a detailed magnetic data analysis of **2** is carried out because of the isotropy of Gd<sup>III</sup>. Based on the crystal structure of **2**, we use 1-*J* model to simulate the data and the spin Hamiltonian formalism is applicable in equation (1), which can be converted to the equivalent one in equation (2) using Kambe vector-coupling method [36]. The Kambe equivalent operator method gives the eigenvalue expression in equation (3).

$$\hat{H} = -2J\hat{S}_2(\hat{S}_1 + \hat{S}_3) \quad (1)$$

$$\hat{H} = -2J\hat{S}_2\hat{S}' \quad (2)$$

$$E = -J[S(S+1) - S'(S'+1)] \quad (3)$$

where

$$\hat{S}' = \hat{S}_1 + \hat{S}_3 \text{ and } \hat{S} = \hat{S}_2 + \hat{S}' \quad (4)$$

This eigenvalue expression and the Van Vleck equation were used to derive a theoretical  $\chi_M T$  versus *T* expression for **2** and this was used to least squares fit the experimental data. The results of fitting the experimental data below 5 K are shown as solid lines in figure 2, with final parameters being  $J_1 = 0.46$  cm<sup>-1</sup>,  $g = 2.00$ , and  $R = 8.90 \times 10^{-4}$ . The fitting results indicate the presence of ferromagnetic exchange interactions within **2**. The Fe<sup>3+</sup>...Gd<sup>3+</sup> interaction is weaker than the reported [Fe<sub>2</sub>Gd] complex [21], which may be attributed to the smaller Fe–O–Gd angle and the longer Fe<sup>3+</sup>–Gd<sup>3+</sup> distance.

Ac magnetic susceptibility data of powder crystalline samples of **3** and **4** in zero dc field with an ac field of 3.5G oscillating at frequencies in the 100–900 Hz range were studied. The results are given in figures 3 and 4 as plots of  $\chi'$  versus *T* and  $\chi''$  versus *T*. For **3** and **4**, the ac susceptibilities show absence of out-of-phase component confirming that those two complexes do not behave as SMMs above 2.0 K. However, [Fe<sub>2</sub>TbL<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)] (**5**) and [Fe<sub>2</sub>DyL<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)] (**6**) have a nonzero imaginary ac susceptibility signal. The different behavior may be caused by weak intermolecular interactions between trinuclear complexes mediated by the hydrogen bond and  $\pi \dots \pi$  interactions. This would be in accord with the prerequisites for SMM behavior, where, besides the large spin and anisotropy of the ground state, the absence of intermolecular interactions is also needed [21].

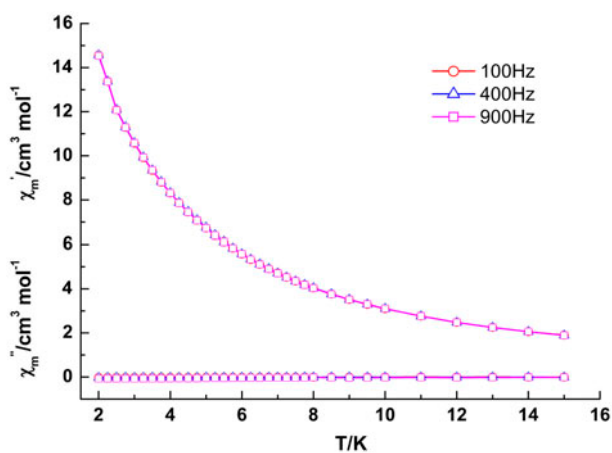


Figure 3. Temperature dependence of ac susceptibilities of **3** under a zero dc field with an oscillating field of 3.5 Oe in frequencies of 100–900 Hz.

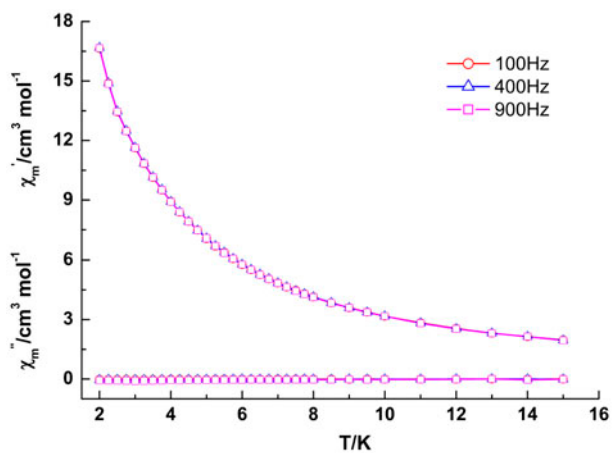
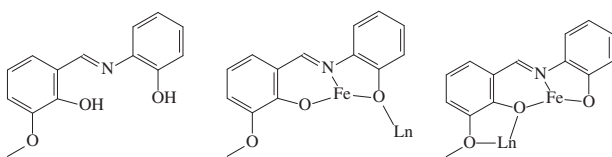


Figure 4. Temperature dependence of ac susceptibilities of **4** under a zero dc field with an oscillating field of 3.5 Oe in frequencies of 100–900 Hz.



Scheme 1.  $H_2L$  and the coordination modes in **1–4**.

## 4. Conclusion

A series of phenoxo-bridged trinuclear [Fe<sub>2</sub>Ln] complexes have been assembled on the basis of a Schiff base ligand by a convenient “one-pot” self-assembly approach. X-ray diffraction analysis reveals that the complexes are comprised of a blade propeller-like configuration. The magnetic analysis of the Gd<sup>III</sup> complex shows that the magnetic interaction between Gd<sup>III</sup> and Fe<sup>III</sup> ions is weakly ferromagnetic. Furthermore, the Tb<sup>III</sup> and Dy<sup>III</sup> complexes show no evidence of slow relaxation behavior above 2.0 K.

## Supplementary material

Crystallographic data (excluding structure factors) for the structures of **1–4** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 1030405–1030408. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223336033; or E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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