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ARTICLE TYPE

# Squashed $\{\text{Fe}^{\text{III}}_2\text{M}^{\text{III}}_4\}$ octahedra (M = Y, Gd, Dy) from the first use of the cyanoacetate ligand in 3d/4f coordination chemistry†

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The first use of the cyanoacetate ligand in 3d/4f- metal chemistry leads to  $\{\text{Fe}^{\text{III}}_2\text{M}^{\text{III}}_4\}$  (M = Dy, Gd, Y) coordination clusters with a squashed octahedral core structure unprecedented in Fe/4f compounds; the Dy<sup>III</sup> compound exhibits slow relaxation of the magnetisation.

The area of mixed-metal materials continues to attract the intense interest of many groups around the world working in condensed-matter physics and solid-state chemistry.<sup>1</sup> Molecular inorganic chemists are also interested in mixed-metal compounds. The main reason for this is the search for coordination complexes with interesting magnetic properties, such as 3D molecule-based magnets,<sup>2</sup> single-chain magnets<sup>3</sup>, single-molecule magnets (SMMs)<sup>4</sup> and molecular magnetic refrigerants.<sup>5</sup> Another reason is the continuing effort in synthesising molecular compounds that simultaneously exhibit two different physical properties, e.g. SMM behaviour and electric conductivity.<sup>6</sup> Polynuclear 3d/4f-metal complexes (coordination clusters) are central ‘players’ in the area of mixed-metal molecular materials<sup>7</sup> because they provide alternatives<sup>4b,8</sup> to homometallic 3d-metal-based SMMs and magnetic refrigerants. In the former area, the high spin and/or the often significant magnetic anisotropy of some trivalent lanthanides (Ln<sup>III</sup>) can lead to 3d/4f-metal SMMs with properties different from those of homometallic 3d-metal ones. In the search for 3d/4f-metal SMMs, attention has turned in the last 5 years to Fe<sup>III</sup>/4f heterometallic clusters because these combine the readily and cheaply available, highly paramagnetic high-spin Fe<sup>III</sup> ion with highly anisotropic 4f ions,<sup>9,10</sup> and some of the complexes have been shown to exhibit exciting magnetic behaviours.<sup>11</sup>

From a synthetic inorganic chemistry viewpoint, methods must be developed to combine Fe<sup>III</sup> and Ln<sup>III</sup> ions within a cluster. This is not an easy goal because both metal ions are oxophilic. A useful route to Fe<sup>III</sup><sub>x</sub>Ln<sup>III</sup><sub>y</sub> clusters is the reaction of salts containing the oxo-centred triangular cation  $[\text{Fe}^{\text{III}}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^+$  (R = Me, Et, Ph, etc.) with potentially chelating ligands in the presence of Ln starting materials.<sup>9a,10a,b</sup> The identity and nuclearity of the obtained products depend on several parameters such as the nature of the carboxylate, the Ln<sup>III</sup> source, reagent ratio, ‘pH’ and the nature and complexity of the chelating ligand, among others. However, the use of the cyanoacetate group (NC-CH<sub>2</sub>COO<sup>-</sup>) in 3d/4f cluster chemistry has never been reported. We have therefore investigated the use of this ligand in Fe/Ln chemistry, and here report the synthesis of a family of squashed

octahedral  $\{\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_4\}$  complexes with interesting structural features and magnetic properties, including SMM behaviour for the  $\{\text{Fe}_2\text{Dy}_4\}$  member.

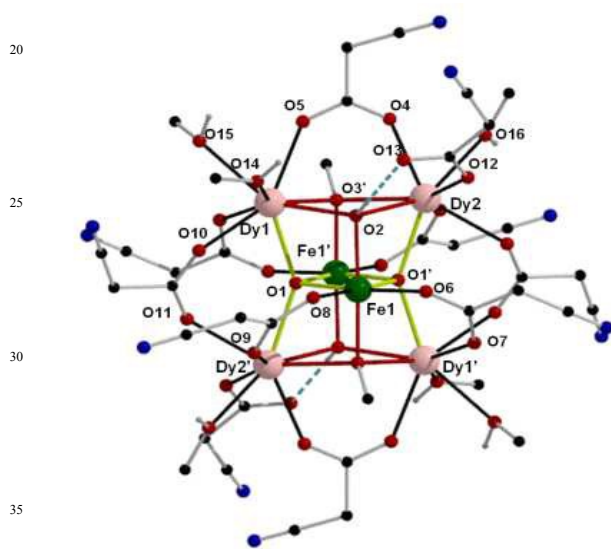
The reaction of  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_2\text{CN})_6(\text{H}_2\text{O})_3](\text{NO}_3)_5\text{H}_2\text{O}$ ,<sup>12</sup> Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in the presence of (±)-3-diisopropylamino-1,2-propanediol, added as a potential ligand able to introduce chirality into the products,<sup>10d</sup> in a 1:1.5:5.5 molar ratio in MeOH gave an amorphous yellow powder which was removed by filtration. The filtrate was allowed to stand at room temperature and orange crystals of  $[\text{Fe}_2\text{Dy}_4(\mu_4\text{-O})_2(\mu_3\text{-OH})_{2.36}(\mu_3\text{-OMe})_{1.64}(\text{O}_2\text{CCH}_2\text{CN})_{10}(\text{MeOH})_5(\text{H}_2\text{O})] \cdot 0.36\text{H}_2\text{O} \cdot 3\text{MeOH}$  (**1**·0.36H<sub>2</sub>O·3MeOH) slowly grew from this in a yield of ~10%. The related  $\{\text{Fe}_2\text{Y}_4\}$  (**2**·0.36H<sub>2</sub>O·3MeOH) and  $\{\text{Fe}_2\text{Gd}_4\}$  (**3**·0.36H<sub>2</sub>O·3MeOH) complexes can be prepared analogously or else using a modified procedure, which for the Gd analogue (**3**) gave an improved yield (ca. 30 %) with very little formation of the yellow powder being observed. Clearly these compounds do not contain the (±)-3-diisopropylamino-1,2-propanediol ligand. In order to probe the reaction further, direct reactions between the iron(III) cyanoacetate triangle and Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O in MeOH, i.e. without (±)-3-diisopropylamino-1,2-propanediol present, and in the absence or presence of common bases were performed. In all cases these led to the formation of the above mentioned insoluble, intractable yellow powder which appears to be a mixture of iron/carboxylato species. Furthermore, we assume that since the presence of (±)-3-diisopropylamino-1,2-propanediol in the reaction mixture is required to isolate the  $\{\text{Fe}_2\text{Ln}_4\}$  species, this molecule plays some important role which so far cannot be fulfilled by any other additives we have tried such as common bases.

The structure of **1**·0.36H<sub>2</sub>O·3MeOH was solved by single-crystal X-ray crystallography; the Y(III) and Gd(III) complexes are isomorphous with **1**·0.36H<sub>2</sub>O·3MeOH as revealed by unit cell determination.<sup>‡</sup>

Complex **1**·0.36H<sub>2</sub>O·3MeOH crystallises in the triclinic space group *P*-1 with *Z* = 1; the molecule (Fig. 1) therefore has a crystallographic inversion symmetry. The molecule can be regarded as being based on a heterodicycubane, in which two  $\{\text{Fe}_2\text{Dy}_2\text{O}_2(\text{OH}/\text{OMe})_2\}$  cubanes share an  $\{\text{Fe}_2\text{O}_2\}$  face to give the  $\{\text{Fe}_2\text{Dy}_4(\mu_4\text{-O})_2(\mu_3\text{-OH})_{2.36}(\mu_3\text{-OMe})_{1.64}\}^{10+}$  core (Fig. S1). The four Dy<sup>III</sup> centres form a truly planar (by symmetry) rectangle with sides of 4.398 by 3.998 Å and Dy2-1-2’ angles of 90.6°, to which the Fe<sup>III</sup>-Fe1’ vector is almost exactly

perpendicular (deviating only 0.3° from the normal). The metallic skeleton can thus be described as squashed octahedral with two Fe<sup>III</sup> ions at the axial positions 3.008 Å apart.

The  $\mu_4\text{-O}^{2-}$  ligand (O1) has a geometry much distorted from regular tetrahedral, with Fe1-O1-Fe1' only 97.7(1)°, while Dy1-O-Dy2' is 145.4(1)°. Of the triply-bridging atoms O2 and O3, the former is a  $\mu_3\text{-OH}^-$  group, while the latter is a disordered superposition of methoxy (~88%) and hydroxo (~12%) ligands. Eight of the ten  $\text{NCCH}_2\text{CO}_2^-$  ligands form syn,syn- $\eta^1\text{-}\eta^1\text{:}\mu$  bridges between Dy<sup>III</sup> ions or Fe<sup>III</sup> and Dy<sup>III</sup> ions, while the remaining two coordinate to Dy2 and Dy2' in a monodentate manner with their non-coordinated oxygen atoms (O13, O13') accepting H bonds from the  $\mu_3$ -hydroxo oxygens (O2, O2'). Additional peripheral ligation to the Dy<sup>III</sup> centres is provided by one aqua and five MeOH ligands. Of these, the MeOH O(15) makes an intermolecular H bond to the cyano N4 on the molecule at -x, -y, 1-z; the cluster molecules are thus linked into supramolecular 1D chains (Figure S4).



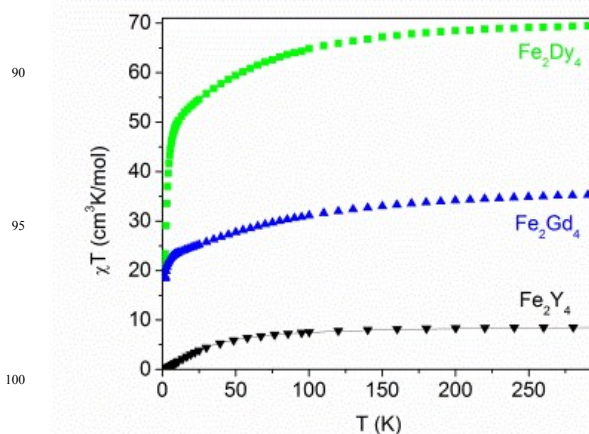
**Fig. 1** The molecular structure of **1**·0.36H<sub>2</sub>O·3MeOH; organic H atoms and minor disorder components have been omitted for clarity. Primed atoms are related by the symmetry operation 1-x, 1-y, 1-z. Intramolecular H bonds are shown as light blue dashed lines. Selected interatomic distances (Å) and angles (°): Fe<sup>III</sup>-Fe1' 3.008(8), Dy1<sup>III</sup>-Dy2 3.998(1), Dy1<sup>III</sup>-Dy2' 4.398(1), Fe1<sup>III</sup>-Dy1 3.321(1), Fe1<sup>III</sup>-Dy1' 3.311(1), Fe1<sup>III</sup>-Dy2 3.352(7), Fe1<sup>III</sup>-Dy2' 3.338(1), Fe1-O 1.990(2)-2.051(2), Dy1-O 2.299(2)-2.434(3), Dy2-O 2.307(2)-2.474(2); Fe1-O1-Fe1' 97.7(1), Dy1-O-Dy2 112.3(1), Dy1-O3-Dy2 109.1(1), Dy1-O1-Dy2' 145.4(1), Fe1-O1-Dy1 101.2(1), Fe1-O2-Dy1 98.7(1), Fe1-O1'-Dy1' 100.5(1), Fe1'-O3-Dy1 96.0(1), Fe1-O2-Dy2 97.9(1), Fe1-O1'-Dy2 101.9(1), Fe1-O1-Dy2' 101.6(1), Fe1'-O3-Dy2 95.7(1), O-Fe1-O 82.3(1)-176.5(1), O-Dy1-O 68.1(1)-147.5(1), O-Dy2-O 67.6(1)-145.8(1).

Both Dy1 and Dy2 have 8-coordinate oxygen environments that approximate very closely to square antiprismatic geometries (Fig. S2). Furthermore, the principal axes of these square antiprisms are aligned very close to co-parallel in the molecule (Fig. S3). If each axis is defined here as the vector joining the

centroids of the two square faces, then the angle between the axes for Dy1 and Dy2 is only 4.2°; they subtend angles of 34.0 and 34.9°, respectively, to the Fe<sup>III</sup>-Fe1' vector. The Fe<sup>III</sup> centres have a slightly distorted octahedral geometry.

Compounds **1-3** are the first 3d/4f-metal complexes with cyanoacetate ligation and new members of a very small family<sup>9,10a,d,13</sup> of hexanuclear Fe<sup>III</sup><sub>x</sub>Ln<sup>III</sup><sub>y</sub> (x+y=6) clusters and the first members with the x=2, y=4 combination. A similar {M<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>4</sub>(μ<sub>4</sub>-O)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>4</sub>}<sup>10+</sup> core has been observed only once, for the hydrothermally-synthesised SMM (pipzH<sub>2</sub>)[Cr<sub>2</sub>Dy<sub>4</sub>(μ<sub>4</sub>-O)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(μ<sub>3</sub>-SO<sub>4</sub>)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O.<sup>14</sup> We note that this Cr-containing system is a coordination cluster anion rather than the neutral coordination clusters we report here and that the ligand shell is rather different, being formed from sulfate groups. Furthermore, the coordination geometries around the Dy centres are not regularly square antiprismatic, as we see in our compounds, but can be described as having distorted dodecahedral geometry.

The temperature dependence of the magnetic susceptibilities of **1-3** was measured over the range 1.8-300 K under an applied field of 0.1 T (Fig. 2). The  $\chi_M T$  products tend to saturate at high temperatures, although only for **1** and **2** the room temperature values are close to those expected for six noninteracting ions (65.50 and 8.75 cm<sup>3</sup> K mol<sup>-1</sup>, respectively). Upon lowering the temperature, the  $\chi_M T$  product continuously decreases for the three complexes, attributable in part to the thermal depopulation of the Stark sublevels of the anisotropic Dy<sup>III</sup> ions in **1**, but certainly pointing towards the presence of antiferromagnetic interactions in **2** and **3**.



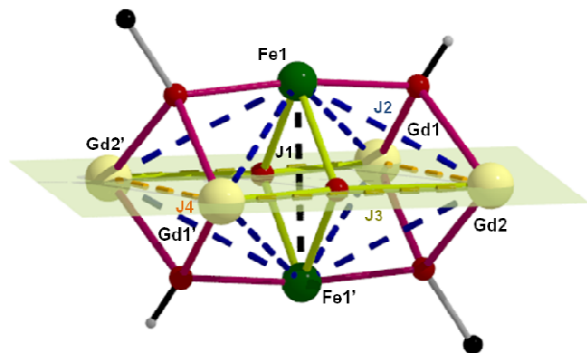
**Fig. 2** Plots of  $\chi_M T$  as a function of  $T$  for complexes **1** (Fe<sub>2</sub>Dy<sub>4</sub>), **2** (Fe<sub>2</sub>Y<sub>4</sub>) and **3** (Fe<sub>2</sub>Gd<sub>4</sub>). The solid line for **2** is the best fit to the experimental data.

To verify this, the experimental data for the Fe<sub>2</sub>Y<sub>4</sub> complex **2** were fitted to the expression for the molar susceptibility derived from the Hamiltonian  $H = -2JS_1S_2$ ; the best fit to the  $\chi_M T$  versus  $T$  curve gave  $g = 2.03$  and  $J_{\text{Fe-Fe}} = -3.0$  K (-2.1 cm<sup>-1</sup>), the small Fe-O1-Fe1' angle (97.7°) certainly contributing to the weak antiferromagnetic exchange interaction.<sup>15</sup>

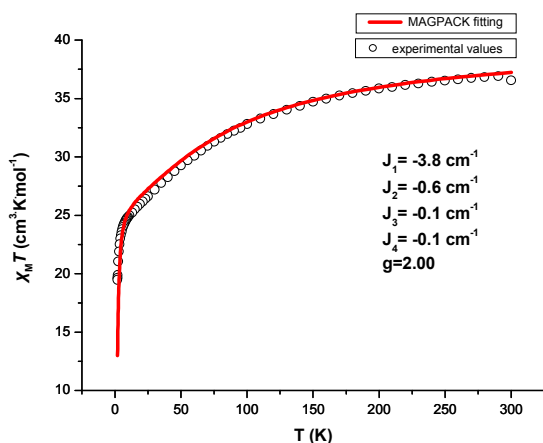
The data for the Fe<sub>2</sub>Gd<sub>4</sub> complex **3** were simulated using the program MAGPACK<sup>16</sup> using the coupling scheme shown in Figure 3 and the Hamiltonian:

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2) - 2J_2(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_5 + \hat{S}_1\hat{S}_6 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_2\hat{S}_5 + \hat{S}_2\hat{S}_6) - 2J_3(\hat{S}_3\hat{S}_4 + \hat{S}_5\hat{S}_6) - 2J_4(\hat{S}_3\hat{S}_6 + \hat{S}_4\hat{S}_5)$$

where  $S_1 = S_2 = 5/2$ ,  $S_3 = S_4 = S_5 = S_6 = 7/2$ , and with  $J_3$  and  $J_4$  constrained to be equal. All attempts to constrain  $J_1$  to the value from the  $\text{Fe}_2\text{Y}_4$  complex gave unsatisfactory simulations. The data could be simulated (Figure 4) using the parameters  $J_1 = -3.8 \text{ cm}^{-1}$ ,  $J_2 = -0.6 \text{ cm}^{-1}$  and  $J_3 = J_4 = -0.1 \text{ cm}^{-1}$  with  $g = 2.00$ . This  $J_{\text{Fe-Fe}}$  value is clearly larger than for the  $\text{Fe}_2\text{Y}_4$  analogue. The ground state of the cluster was found to be  $S = 0$ , with the first excited state of  $S = 1$  located only at  $\sim 0.2 \text{ cm}^{-1}$  above. The magnitudes of the coupling constants are consistent with what is expected from the squashed core topology where, in spite of their *trans* disposition, the two Fe(III) centres are only separated by about 3 Å.



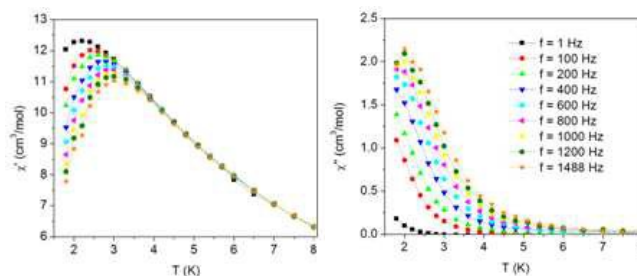
**Fig. 3**  $J$ -interaction scheme employed for the analysis of cluster **3** ( $\text{Fe}_2\text{Gd}_4$ ).



**Fig. 4** Plot of  $\chi_M T$  versus  $T$  for complex **3** ( $\text{Fe}_2\text{Gd}_4$ ). The solid line represents a simulation of the data (see text for details).

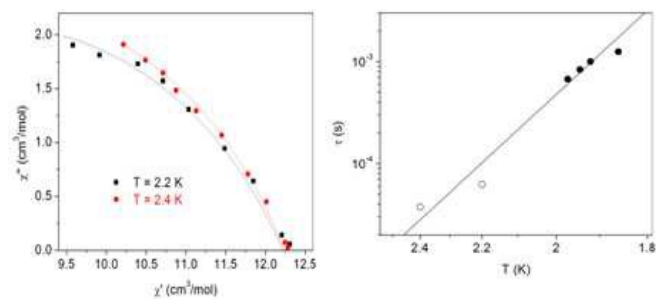
The field dependence of the magnetization was also studied at low temperatures (Fig. S5). The curves for **2** at 2, 3 and 5 K are far from saturation even under an applied field of 7 T. The data are in satisfactory agreement with those calculated by using the above mentioned values of  $J_{\text{Fe-Fe}}$  and  $g_{\text{Fe}}$ . The data for **1** reveal a relatively rapid increase in the magnetization at low fields ( $\sim 20 \mu_B$  around 1.5 T at 2 K) and then a linear increase without clear saturation. The high field linear variation of  $M$  suggests the presence of a significant anisotropy or low lying excited states in this compound.

The paramagnetism at 1.8 K and the considerable single-ion anisotropy of  $\text{Dy}^{\text{III}}$  suggested that **1** might be a SMM. The relaxation of its magnetisation was studied using *ac* susceptibility measurements as a function of temperature at different frequencies at zero dc field with a 3.0 G ac oscillating field (Fig. 5). Slow relaxation of the magnetization is observed for **1** with a strong frequency dependence for both the in-phase,  $\chi'$ , and out-of-phase,  $\chi''$ , susceptibilities, indicating that this compound behaves as a SMM with a blocking temperature around 2 K.



**Fig. 5** Temperature dependence of the in-phase (left) and out-of-phase (right) components of the ac magnetic susceptibility for **1** under zero dc field.

In order to obtain the characteristic parameters for the relaxation pathway, the temperature dependence of the relaxation time,  $\tau$ , was extracted from the maxima of the out-of-phase magnetic susceptibility curves. The position of the maxima in the present data sets allows one only to obtain information within a limited temperature range (roughly between 1.8 and 2 K); therefore we fitted the Cole-Cole plots (Fig. 6, left) at two additional temperatures with a modified Debye model, and added the corresponding relaxation times to the Arrhenius plot (Fig. 6, right). The best fit of the available data to an Arrhenius law allows us to estimate the characteristic energy barrier for reversal of the magnetisation,  $U_{\text{eff}}$ , as 34.0 K with a pre-exponential factor,  $\tau_0$ , of  $2.0 \times 10^{-11} \text{ s}$ . For comparison, the highest value for the anisotropy energy barrier reported so far for  $\text{Fe}^{\text{III}}/\text{Ln}^{\text{III}}$  SMMs is  $\sim 65 \text{ K}$ .<sup>10b</sup> Both the small  $\tau_0$  value and the high values obtained for the exponent  $\alpha$  (between 0.3 and 0.5) indicate that the relaxation time distribution may be dominated by more than one relaxation process in this temperature region, which might result from the presence of two  $\text{Dy}^{\text{III}}$  ions with different coordination spheres in **1**,<sup>14</sup> but clearly requires further investigation.



**Fig. 6** Cole-Cole plots at 2.2 and 2.4 K (left) and Arrhenius plot fits (right) for cluster **1** (filled circles: data from  $\chi''$  -v-  $T$ ; open circles: data from Cole-Cole plots)

The  $U_{\text{eff}}$  value of 34.0 K found for compound **1** can be compared with the value of 39.7 K found for the {Cr<sub>2</sub>Dy<sub>4</sub>} compound,<sup>14</sup> but the  $\chi T$  vs  $T$  plots for the two compounds show different behaviour. Since the Y and Gd analogues of the {Cr<sub>2</sub>Dy<sub>4</sub>} are not available, it is difficult to draw any more detailed conclusions concerning the coupling amongst the metal centres.

In conclusion, the initial use of the CNCH<sub>2</sub>CO<sub>2</sub><sup>-</sup> ligand in 3d/4f-metal cluster chemistry has led to compounds with a novel {Fe<sup>III</sup><sub>2</sub>M<sup>III</sup><sub>4</sub>} squashed octahedral core (M=Y, Gd, Dy). This result shows that this group can indeed lead to polynuclear transition metal/lanthanide products with unusual core structures and interesting magnetic properties. The squashed octahedral topology of the core means that the capping Fe(III) centres are only 3 Å apart, allowing for the antiferromagnetic coupling of this unit to dominate the behaviour. Although no ancillary organic ligand is incorporated into the final structure, the presence of the co-ligand (±)-3-diisopropylamino-1,2-propanediol is required to access these compounds for reasons which are yet not understood. Work is in progress to investigate properties (including the <sup>57</sup>Fe – Mössbauer spectra) of other congeners of this {Fe<sub>2</sub>Ln<sub>4</sub>} system (our ongoing investigations reveal that the Fe<sub>2</sub>Eu<sub>4</sub> and Fe<sub>2</sub>Tb<sub>4</sub> clusters are isostructural with **1-3**) and to discover how to incorporate the chiral co-ligand (±)-3-diisopropylamino-1,2-propanediol into new coordination clusters.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details for the synthesis and characterization of 3-diisopropylamino-1,2-propanediol, and the metal complexes, experimental for single-crystal X-ray crystallography, structural plots (Figs. S1-S4) and magnetization data for the three complexes (Fig. S5). See DOI: 10.1039/b000000x/

‡ Crystal data for 10.36H<sub>2</sub>O·3MeOH: C<sub>39.64</sub>H<sub>62</sub>N<sub>10</sub>O<sub>35.36</sub>Fe<sub>2</sub>Dy<sub>4</sub>,  $M_r=2006.13$ , triclinic,  $P-1$ ,  $a = 10.226(2)$ ,  $b = 12.250(3)$ ,  $c = 13.744(3)$  Å,  $\alpha = 102.500(3)$ ,  $\beta = 97.563(3)$ ,  $\gamma = 104.646(3)^\circ$ ,  $V = 1594.3(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 150(2)$  K,  $\rho_c = 2.090$  g cm<sup>-3</sup>,  $F(000) = 969$ ,  $\lambda = 0.80000$  Å,  $\mu = 7.134$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 65.3^\circ$ , 20261 data, 7495 unique ( $R_{\text{int}} = 0.0437$ ), 481 parameters, final  $wR_2 = 0.0657$ ,  $R_1$  (7000 data with  $I > 2\sigma(I)$ ) = 0.0257.  
 60 CCDC 1021088. Unit cell determination for 20.36H<sub>2</sub>O·3MeOH: triclinic,  $P-1$ ,  $a = 10.228(2)$ ,  $b = 12.090(3)$ ,  $c = 13.719(3)$  Å,  $\alpha = 102.693(2)$ ,  $\beta =$

97.670(2),  $\gamma = 104.771(2)^\circ$ ,  $V = 1567.0(6)$  Å<sup>3</sup>. Unit cell determination for 30.36H<sub>2</sub>O·3MeOH: triclinic,  $P-1$ ,  $a = 10.252(3)$ ,  $b = 12.138(3)$ ,  $c = 13.737(3)$  Å,  $\alpha = 102.82(1)$ ,  $\beta = 97.47(1)$ ,  $\gamma = 104.45(1)^\circ$ ,  $V = 1582.6(6)$  Å<sup>3</sup>.

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