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Synthesis, structures, and magnetic properties of a family of 3d-4f[Na₂Fe₆Ln₂] complexes (Ln = Y, Gd and Dy): effect of ligands on the connection of inorganic subunits[†]

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A family of 3d–4f heterometallic compounds $[Na_2Fe^{III}_6Dy^{III}_2(N_3)_4(HL)_4(CH_3O)_4(PhCO_2)_6]$ (1, H₄L = 2-{[(2-hydroxy-3-methoxyphenyl)methylene]amino}-2-(hydroxymethyl)-1,3-propanediol), $[Na_2Fe^{III}_6-Dy^{III}_2(N_3)_4(L')_4(CH_3O)_4(PhCO_2)_6(H_2O)]$ (2, H₃L' = (*E*)-2-ethyl-2-(2-hydroxy-3-methoxybenzyl-ideneamino)propane-1,3-diol), $[Na_2Fe^{III}_6Dy^{III}_2(N_3)_4(L')_4(CH_3O)_4(Bu'CO_2)_6]$ (3) $[Na_2Fe^{III}_6Y^{III}_2(N_3)_4-(L')_4(CH_3O)_4(PhCO_2)_6(CH_3OH)_2]$ (4), and $[Na_2Fe^{III}_6Gd^{III}_2(N_3)_4(L')_4(CH_3O)_4-(PhCO_2)_6(CH_3OH)_2]$ (5) have been prepared using Schiff-base ligands, trinuclear iron precursor complexes, azides and lanthanide nitrates as reactants. In compounds 1 and 2, the structure of the $[Na_2Fe^{III}_6Dy^{III}_2]$ cluster forms a couple of *cis,trans*-isomers with substitution of methyl for a free hydroxyl group which belongs to the Schiff-base ligand. When the pivalates are employed instead of bulkier benzoates, the *trans*- $[Na_2Fe^{III}_6Dy^{III}_2]$ clusters act as network nodes in the formation of rhombic grid-like layered structures in compound 3. Compounds 2, 4 and 5 have similar metallic cores, only with different crystal solvent molecules. The magnetic measurements on all the compounds indicate dominant antiferromagnetic interactions between the metal centers.

Introduction

In recent years, the synthesis of spin coupled polynuclear paramagnetic clusters (PMCs) has attracted much attention due to their potential to act as single-molecule magnets (SMMs).^{1,2} A great number of 3d, 3d–4f and 4f polynuclear clusters have been synthesized and their magnetic properties have been widely studied, mainly because of their fascinating structures and interesting properties.³ Among those PMCs, 3d–4f clusters are more important, because they may combine the large magnetic anisotropy of lanthanide ions with the high spin-states of transition ions.⁴

To assist the formation of polynuclear clusters, chelating ligands have been widely used, which control the structures of metal cores and prevent metal ions from forming a high dimensional framework.⁵ Although chelating ligands have been

extensively employed, it is still an enormous challenge for researchers to rationally design, precisely control, and effectively re-assemble novel structures.

Among the large variety of chelating ligands, polyhydroxy Schiff-base ligands are rightly considered as one of the most important ones.^{5a,d,6} Because the soft-donor nitrogen tends to bind to transition-metal ions and the harder oxygen favors binding to oxophilic lanthanide ions, simultaneously, the deprotonated hydroxyethyl portions of these ligands are outstanding bridging groups.^{7–10} Recognizing that Schiff base ligands are a good way of connecting metal centers together for forming polynuclearities, we have obtained the octa- and hexadecanuclear manganese clusters¹¹ by using quinquedentate Schiff base H₄L 2-{[(2-hydroxy-3-methoxyphenyl)methylene]amino}-2-(H₄L. (hydroxymethyl)-1,3-propanediol), and we found an interesting phenomenon in those compounds. In comparison with tripodal alcohol ligands in which all the hydroxyl groups coordinate with metal ions,¹² the tripodal alcohol unit of H₄L has one or two hydroxyl groups which do not coordinate but form intermolecular hydrogen bonds to solvent molecules or neighboring clusters. Since the reduction of alcohol groups has been proved to show a potent effect on the structures of PMCs,^{9b,13} we employ both H₄L and a new ligand H₃L' (H₃L', (E)-2-ethyl-2-(2-hydroxy-3methoxybenzylideneamino)propane-1,3-diol, shown in Scheme 1) to investigate the effect of hydroxyl groups on the structure of polynuclear polymers.

In the present paper, we obtained a family of heterometallic Fe–Ln complexes of formulae $[Na_2Fe^{III}_{6}Dy^{III}_{2}(N_3)_4(HL)_4-$

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[†] Electronic supplementary information (ESI) available: Crystallographic details in CIF format, selected bond lengths (Tables S1–S5), $\chi_M T vs.$ T plot at 1000 Oe without the magnetic contribution of the [NaFe^{III}₃] units for 2 and 5 (Fig. S1), and XRPD patterns (Fig. S2–S6). CCDC 857518, 857519, 857520, 874772 and 874771 for compounds 1, 2, 3, 4 and 5, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31050c



Scheme 1 Schiff base ligands H_4L (left) and H_3L' (right).

(CH₃O)₄(PhCO₂)₆(CH₃OH)₂](CH₃OH)₃(CHCN)₂(H₂O)₃ (1), $[Na_2Fe^{III}_{6}Dy^{III}_{2}(N_3)_4(L')_4(CH_3O)_4(PhCO_2)_6(H_2O)](H_2O)_2$ (2) and $[Na_2Fe^{III}_{6}Dy^{III}_{2} (N_3)_4(L')_4(CH_3O)_4(Bu'CO_2)_6](CH_3CN)$ (3) using H₄L and H₃L' respectively. It should be mentioned here that although the Fe-Ln clusters have been widely reported, 5d, 6c, 7, 14 compounds 1 and 2 are the first examples to include two alternate [NaFe^{III}₃] units and one [Dy^{III}₂] unit. Furthermore, the [Na₂Fe^{III}₆Dy^{III}₂] cores of **1** and **2** form a couple of *cis,trans*isomers. In compound 3, the *trans*- $[Na_2Fe^{III}_{6}Dy^{III}_{2}]$ clusters act as network nodes in the formation of rhombic grid-like layered structures. The magnetic measurements on all the compounds indicate dominant antiferromagnetic interactions between the metal centers. In order to probe the magnetic behaviour of 3d-4f systems, $[Na_2Fe^{III}_{6}Y^{III}_{2}(N_3)_4 (L')_4(CH_3O)_4(PhCO_2)_6(H_2O)]-(H_2O)$ (4) and $[Na_2Fe^{III}_{6}Gd^{III}_2 (N_3)_4(L')_4(CH_3O)_4(PhCO_2)_6-(H_2O)]-(H_2O)_4(H_2O)_4(H_2O)_4(H_2O)_6-(H_2O)_4(H_2O)_6)-(H_2O)_6(H_2O$ $(CH_3OH)_2](H_2O)_6$ (5) were synthesized to turn off the lanthanide anisotropy and the 4f contribution.

Experimental section

All reagents and solvents were commercially available and were used without further purification. The ligands H_4L and H_3L' were synthesized by condensation of *o*-vanillin and tris(hydroxy-methyl)aminomethane (or 2-amino-2-ethyl-1,3-propanediol) (1:1) in hot methanol solution. [Fe^{III}₃O(RCO₂)₆(H₂O)₃](RCO₂) complexes were prepared using the procedures reported previously.¹⁵

$$\label{eq:2.1} \begin{split} &[Na_{2}Fe^{III}{}_{6}Dy^{III}{}_{2}(N_{3})_{4}(HL)_{4}(CH_{3}O)_{4}(PhCO_{2})_{6}(CH_{3}OH)_{2}] - \\ &(CH_{3}OH)_{3}(CH_{3}CN)_{2}(H_{2}O)_{3}\ (1) \end{split}$$

A mixture of Dy(NO₃)₃·6H₂O (1 mmol, 0.455 g), H₄L (0.6 mmol, 0.153 g) and NaN₃ (3 mmol, 0.195 g) in MeCN (10 mL) and MeOH (15 mL) was stirred for 30 min, followed by the addition of 0.3 mmol of $[Fe^{III}_{3}O(PhCO_2)_6(H_2O)_3](PhCO_2)$. The resulting dark solution was stirred for 2 h and then filtered. Subsequent slow diffusion of ether into the deep-brown filtrate yielded dark black crystals of **1** after two weeks. Yield: *ca.* 20% based on Fe. IR (KBr, cm⁻¹): 3357(w), 2925(w), 2061(s), 1619(s), 1554(m), 1398(s), 1304(w), 1216(w), 1024(m), 721(m). Elem anal. calcd (%) for C₁₀₃H₁₃₀Dy₂Fe₆N₁₈Na₂O₄₄: C, 40.82; H, 4.32; N, 8.32. Found: C, 40.86; H, 4.22; N, 8.50.

$[Na_{2}Fe^{III}{}_{6}Dy^{III}{}_{2}(N_{3})_{4}(L')_{4}(CH_{3}O)_{4}(PhCO_{2})_{6}(H_{2}O)](H_{2}O)$ (2)

A similar preparation route was conducted using H_3L' (0.6 mmol, 0.152 g) instead of H_4L in 24% yield. IR (KBr, cm⁻¹): 3453(w), 2929(w), 2059(s), 1621(s), 1554(m), 1401(s), 1311(w), 1208(w), 1041(m), 721(m). Elem anal. calcd (%) for $C_{98}H_{110}Dy_2Fe_6N_{16}Na_2O_{34}$: C, 42.61; H, 4.01; N, 8.11. Found: C, 42.21; H, 4.15; N, 8.06.

[Na₂Fe^{III}₆Dy^{III}₂(N₃)₄(L')₄(CH₃O)₄(Bu^tCO₂)₆](CH₃CN)(H₂O)₅ (3)

This was prepared in a similar way to **2**, but using $[Fe^{III}_{3}O-(Bu'CO_2)_6(H_2O)_3](Bu'CO_2)$ instead of $[Fe^{III}_{3}O(PhCO_2)_6(H_2O)_3]-(PhCO_2)$, in 21% yield. IR (KBr, cm⁻¹): 3449(w), 2967(w), 2071(s), 1623(s), 1558(s), 1425(m), 1292(w), 1220(m), 1081(m), 736(m). Elem anal. calcd (%) for $C_{88}H_{143}Dy_2Fe_6N_{17}-Na_2O_{37}$: C, 38.61; H, 5.26; N, 8.69. Found: C, 38.99; H, 5.10; N, 9.06.

$[Na_2Fe^{III}_{6}Y^{III}_{2}(N_3)_4(L')_4(CH_3O)_4(PhCO_2)_6(H_2O)](H_2O)$ (4)

This was prepared in a similar way to **2**, but using $Y(NO_3)_3$ · $GH_2O(1 \text{ mmol}, 0.383 \text{ g})$ instead of $Dy(NO_3)_3$ · GH_2O in 24% yield. IR (KBr, cm⁻¹): 3363(w), 2943(w), 2058(s), 1623(s), 1548(m), 1398(s), 1309(w), 1218(w), 1068(m), 724(m). Elem anal. Calcd (%) for $C_{98}H_{110}Fe_6N_{16}Na_2O_{34}Y_2$: C, 45.01; H, 4.24; N, 8.57. Found: C, 44.89; H, 4.35; N, 8.48.

$[Na_{2}Fe^{III}{}_{6}Gd^{III}{}_{2}(N_{3})_{4}(L')_{4}(CH_{3}O)_{4}(PhCO_{2})_{6}(CH_{3}OH)_{2}]-(H_{2}O)_{6}(5)$

This was prepared in a similar way to **2**, but using $Gd(NO_3)_3 \cdot 6H_2O(1 \text{ mmol}, 0.453 \text{ g})$ instead of $Dy(NO_3)_3 \cdot 6H_2O(1 \text{ mmol}, 0.453 \text{ g})$ instead of $Dy(NO_3)_3 \cdot 6H_2O(1 \text{ mmol}, 26\% \text{ yield})$. IR (KBr, cm⁻¹): 3363(w), 2958(w), 2059(s), 1624(s), 1549(m), 1413(s), 1309(w), 1208(w), 1083(m), 724(m). Elem anal. calcd (%) for $C_{100}H_{126}Fe_6Gd_2N_{16}Na_2O_{40}$: C, 41.59; H, 4.40; N, 7.76. Found: C, 41.63; H, 4.42; N, 7.79.

Physical measurements

Elemental analyses of C, H, and N were carried out on a Perkin-Elmer 240C elemental analyzer. IR spectra as KBr pellets were recorded using a reflectance technique over the range of 4000-400 cm⁻¹ on a Magna 750 FT-IR spectrophotometer. X-ray powder diffraction (XRPD) patterns were taken on a Rigaku D/max 2550 X-ray Powder Diffractometer. The measurements of variable-temperature magnetic susceptibility and field dependence of magnetization were obtained with a Quantum Design MPMS-XL5 SQUID magnetometer. The sample was embedded in solid eicosane to prevent torquing. Alternating current magnetic susceptibility measurements were performed in an oscillating ac field of 3.0 G and a zero dc field. The oscillation frequencies were in the 10-1000 Hz range. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities ($\chi_{\rm M}$).

X-ray crystallography

Suitable single crystals for 1–5 were glued onto a glass fiber. Single-crystal structure determination of 1 and 5 was carried out on a Rigaku RAXIS-RAPID diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. Integrated intensity was obtained with SAINT+ and was

corrected for absorption using SADABS. Diffraction intensity data for 2, 3 and 4 were collected with a Bruker Smart CCD diffractometer equipped with graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data sets were collected with the ω -scan technique and reduced by CrystalClear software. The structures of the compounds were solved by direct methods and refined with the full-matrix leastsquares technique using the program SHELXTL.¹⁶ The location of metal atoms was easily determined, and O, N, and C atoms were subsequently determined from the difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The disordered atoms were refined with constrained dimensions. The hydrogen atoms were set in calculated positions. Compounds 1 and 3 were treated with SOUEEZE which helped determine solvent molecules. The crystal data, data collection and refinement parameters for complexes 1-5 are listed in Table 1, and selected bond lengths for complexes 1-5 are listed in Tables S1-S5 in the ESI.†

Results and discussion

Syntheses

The reaction of preformed trinuclear iron complexes with rare earth ions represents a commonly employed and successful route to a wide range of Fe-4f clusters, including Fe₂Ln₂,¹⁷ Fe₄Ln₂,^{6c} $Fe_5Ln_8^{14c}$ and $Fe_{12}Ln_4^{14g}$. In the present work, the reaction of trinuclear iron complexes with Ln(NO3)3.6H2O and the Schiff base ligands in the presence of NaN_3 in a 1:3:2:10 ratio in an acetonitrile-methanol (2:3) solvent followed by slow diffusion of ether into the mixture led to the dark black crystals. The same product can also be obtained from reactions with different reagent ratios, but in lower yields. Trinuclear complexes of other transition metal ions were also employed in place of [Fe₃O- $(RCO_2)_6(H_2O)_3$ (RCO₂). We obtained a known octanuclear manganese cluster¹¹ when $[Mn_3O(O_2CR)_6(H_2O)_3]$ complexes were used as the starting materials; and no crystals could be formed by using Cr₃ or Co₃. In order to discuss the magnetic behaviour of 3d-4f systems, we tried to use Gd^{III} or Y^{III} instead of Dy^{III}. Compounds 4 and 5 were obtained, all of which were in the chair conformation. But all attempts to substitute for Dy ions were unsuccessful in the reactions of compounds 1 and 3. In order to investigate the effect of ligands on the structure, a ligand H_3L'' (H_3L'' , (E)-2-(2-hydroxy-3-methoxybenzylideneamino)-2-methylpropane-1,3-diol (shown in Scheme S1⁺) was also employed, but unfortunately our efforts resulted in failure. This may be due to an absence of the methyl or the hydroxyl, and the compound is more difficult to crystallize under these conditions.

Crystal structure

Compound 1 crystallizes in the monoclinic space group $P2_1/c$ and the structure is shown in Fig. 1a. The $[Na_2Fe^{III}_{6}Dy^{III}_{2}]$ cluster of 1 contains two outer $[NaFe^{III}_{3}]$ units and one central $[Dy^{III}_{2}]$ unit (Fig. 1b). In the first $[NaFe^{III}_{3}]$ unit, three Fe ions and one Na ion form a defect double-cubane. μ_3 -O33 bridges three Fe ions (Fe1, Fe2, Fe3) forming an isosceles triangle with the Fe–Fe distances of 3.166(7) Å, 3.160(2) Å, 3.250(2) Å. Fe1

Compound	1	2	3	4	S
Formula	$C_{103}H_{130}Dy_2Fe_6N_{18}Na_2O_{44}$	$C_{98}H_{110}Dy_2Fe_6N_{16}Na_2O_{34}$	$C_{88}H_{143}Dy_2Fe_6N_{17}Na_2O_{37}$	$C_{98}H_{110}Fe_{6}N_{16}Na_{2}O_{34}Y_{2}$	$C_{100}H_{126}Fe_{6}Gd_{2}N_{16}Na_{2}O_{40}$
$f_{\rm w}$ (g mol ⁻¹)	3030.28	2762.13	2737.27	2614.94	2887.75
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_{1/C}$	$P2_1/c$	$P2_{1/C}$
$a^{i}(A) \tilde{A}$	23.567(5)	12.781(5)	12.408(3)	12.647(9)	12.659(3)
$b(\hat{A})$	23.458(5)	35.763(7)	41.897(8)	35.280(6)	35.205(7)
$c(\mathbf{\hat{A}})$	29.624(6)	17.068(5)	13.420(3)	16.918(8)	17.180(3)
$\beta (\circ)$	121.65(3)	126.19(8)	114.04(3)	126.42(5)	124.37(3)
$V(Å^3)$	13.941(5)	6296(5)	6371(2)	6075.1(5)	6320(2)
Z	4	2	2	2	2
F(000)	6024	2824	2692	2696	2928
D_{calcd} (g cm ⁻³)	1.418	1.476	1.427	1.439	1.518
$M(\text{mm}^{-1})$	1.748	1.927	1.903	1.726	1.792
$T(\mathbf{K})$	293	293	293	293	293
R_1^{a}	0.0790	0.0796	0.0579	0.0789	0.0700
wR_2^b	0.2117	0.1593	0.1448	0.1577	0.1827
$^{a}R_{1}=\Sigma F_{\mathrm{o}} - F_{\mathrm{c}} /$	$\Sigma F_0 \cdot {}^b WR_2 = \{\Sigma [W(F_0^2 - F_c^2)^2] / \Sigma [W(.)]$	F_0^2)] ² $^{1/2}$; w = 1/ $[\sigma^2 F_0 ^2 + (0.0511P)$	$^{2} + 19.56P$], where $P = [F_{o} ^{2} + 2 F_{c}]$	²]/3.	

Fig. 1 (a) Molecular structure of compound **1**. (b) The structure of the $[NaFe^{III}_3]$ unit and the $[Dy^{III}_2]$ unit in compound **1**. (c) The metallic core of compound **1**. The C–H hydrogen atoms and minor disordered components have been omitted for clarity.

and Fe2 adopt distorted octahedral geometries with the coordination spheres completed by two HL³⁻ ligands and two terminal azido ligands. Fe3 also adopts distorted octahedral geometries with the coordination spheres completed by four ethanolic O from the two Schiff base ligands and one bridging benzoate. The Na1 is linked to the Fe1 and Fe2 via µ₃-O35 which bridges the atoms forming another isosceles triangle with the Fe-Na distances of 3.527(6) Å, 3.490(5) Å. Na1 is considered six-coordinate with the coordination spheres completed by two phenol O and two methoxy O from the two Schiff base ligands and one methanol molecule. The dihedral angle between the two triangles is 147.98°. The μ_3 -O33 and μ_3 -O35 atoms from two deprotonated methanol molecules sit 1.04 Å and 1.07 Å above the triangular planes, respectively. The Dy1 is linked to the Fe3 via two ethanolic O (O3, O8) from the two Schiff base ligands and one bridging benzoate to construct the unit, and the Dy1 and Fe3 ions are separated by a distance of 3.337(2) Å. The structures of the two units are very similar, with some slight differences in triangles and distances. In the other [NaFe^{III}₃] unit, the Fe-Fe distances in the triangle are 3.171(8) Å, 3.167(4) Å, 3.222(1) Å, and the Fe-Na distances in another triangle are 3.483(3) Å, 3.417(1) Å. The dihedral angle between the two triangles is 150.92°. The dysprosium and iron ions are separated by a distance of 3.290(5) Å. In the [Dy^{III}₂] unit, the distance between Dy1 and Dy2 is 3.914(7) Å. As the two Dy ions are bridged by one benzoate in a μ_2 - η^1 : η^2 -fashion and three in a μ_2 - η^1 : η^1 fashion, Dy1 is considered eight-coordinate, Dy2 is considered seven-coordinate. Interestingly, the two [NaFe^{III}₃] units are



Fig. 2 (a) Molecular structure of compound 2. (b) The structure of the $[NaFe^{III}_3]$ unit and the $[Dy^{III}_2]$ unit in compound 2. (c) The metallic core of compound 2.

linked through $[Dy^{III}_2]$ units to form a novel *cis*- $[Na_2Fe^{III}_6Dy^{III}_2]$ cluster, and the metal atoms are organized in the boat conformation along the backbone of the cluster (Fig. 1c). This structure of boat conformation is not common, with only a few similar small clusters such as the complexes $[Fe_2Ln_2]$,¹⁷ $[Mn_4]^{18}$ and $[Mn_2Ln_3]$.¹⁹

Compounds 2, 4 and 5 have similar metallic cores, only with different crystal solvent molecules. As an example, the structure of compound **2** will be described (Fig. 2a). The $[Na_2Fe^{III}_{6}Dy^{III}_{2}]$ cluster of 2 also contains two outer [NaFe^{III}₃] units and one central [Dy^{III}₂] unit (Fig. 2b). It is very similar to the unit of compound 1. The differences are that the L^{3-} ligands take the place of the HL³⁻ ligands, and the coordination sphere of the Na⁺ ion is completed by one H₂O molecule replacement of the methanol molecule. In the unit, the Fe-Fe distances in the first triangle are 3.176(2) Å, 3.167(9) Å, 3.246(0) Å, and the Fe-Na distances in the second triangle are 3.439(7) Å, 3.501(8) Å. The dihedral angle between the two triangles is 152.88°. The dysprosium and iron ions are separated by a distance of 3.380(4) Å. As the $[Dy_{2}^{III}]$ unit is bridged by four benzoates in a $\mu_{2}-\eta^{1}:\eta^{1}-\eta^{1}$ fashion, all the dysprosium ions of compound 2 are considered seven-coordinate, and the distance between the two Dy ions is 4.046(2) Å. Interestingly, complex 2 is centrosymmetric. The two outer $[NaFe^{III}_{3}]$ units and the central $[Dy^{III}_{2}]$ unit form a *trans*- $[Na_2Fe^{III}_{6}Dy^{III}_{2}]$ cluster, and the metal atoms are organized in the chair conformation along the backbone of the cluster (Fig. 2c). There are only a few similar clusters which have been obtained, for example the complexes $[Mn_4Dy_6]^{20}$ and [Fe₄Ln₂].^{6c} Furthermore, to the best of our knowledge, the boat conformations of those metallic cores have never been reported.



Fig. 3 (a) Molecular structure of the $[Na_2Fe^{III}_6Dy^{III}_2]$ SBU in compound **3**. (b) The structure of the $[NaFe^{III}_3]$ unit and the $[Dy^{III}_2]$ unit in compound **3**. (c) Polyhedral 2D structure (left) and view of the (4,4) grid (right).

Compound 3 crystallizes in the monoclinic space group $P2_1/c$ and the structure is shown in Fig. 3a. The [Na₂Fe^{III}₆Dy^{III}₂] cluster of 3 also contains two outer [NaFe^{III}₃] units and one central [Dy^{III}₂] unit (Fig. 3b). Complex 3 is also centrosymmetric and the *trans*-[Na₂Fe^{III}₆Dy^{III}₂] clusters of complexes 3 and 2 are almost the same. The differences lie in that the bridging pivalates take the place of bridging benzoates, and the coordination sphere of the Na⁺ ion is completed by one $\mu_{1,3}$ azide of a neighboring cluster replacement of the H₂O molecule. Each cluster is then connected to four others via azide ligands resulting in a 2D (4,4) grid framework. Up to now, azide ions have been employed frequently to assemble 3d polynuclear paramagnetic clusters as the available building blocks into multidimensional network systems.²¹ However, to the best of our knowledge, it is the only example known where an azido has been used to bridge discrete Fe-Ln clusters in a stepwise manner to form a polymer. Thus, compound 3 exhibits a perfect rhombic-grid with rhombus dimensions of 22.00 × 22.00 Å represented by a rhombic grid model (Fig. 3b).

We have obtained three complexes with $[Na_2Fe^{III}_{6}Dy^{III}_{2}]$ clusters *via* different ligands. The $[Na_2Fe^{III}_{6}Dy^{III}_{2}]$ clusters of compounds **1** and **2** form a couple of *cis,trans*-isomers with similar synthetic methods. There are two possible reasons for the difference: (1) Each HL³⁻ ligand in **1** possesses a free alcohol group that is involved in the formation of hydrogen bonds to solvent molecules. As a methyl group takes the place of a hydroxyl, there is no free alcohol group that can form hydrogen bonds to

solvent molecules in compound **2**. (2) Since a methyl group is considered to be bulkier than a hydroxyl group, the steric hindrance of methyls may lead two $[NaFe^{III}_3]$ units to form a *trans*- $[Na_2Fe^{III}_6Dy^{III}_2]$ cluster. When $[Fe^{III}_3O(Bu'CO_2)_6(H_2O)_3]$ - $(Bu'CO_2)$ is used instead of $[Fe^{III}_3O(PhCO_2)_6(H_2O)_3](PhCO_2)$ in the reaction of compound **2**, compound **3** is obtained. The minor steric hindrance of pivalates may be responsible for the formation of rhombic grid-like layered structures in compound **3**.

Magnetic properties

Solid-state, variable-temperature dc magnetic susceptibility measurements for the compounds have been carried out in an applied magnetic field of 1000 Oe in the temperature range 2–300 K. The plots $\chi_{M}T$ vs. T are shown in Fig. 4, where χ_{M} is the molar magnetic susceptibility. For compound 1, the room temperature $\chi_{\rm M}T$ value is 47.7 cm³ K mol⁻¹, and decreases steadily to $33.2 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K and then to $22.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. Complexes 2 and 3 behave in a similar fashion to 1. For compound 2, the $\chi_{\rm M}T$ value of 42.4 cm³ K mol⁻¹ at 300 K decreases with decreasing temperature to $32.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K, and then to 22.4 cm³ K mol⁻¹ at 2 K. For compound **3**, the $\chi_{\rm M}T$ value of 46.1 cm³ K mol⁻¹ at 300 K decreases with decreasing temperature to 34.1 cm³ K mol⁻¹ at 50 K, and then to 23.1 cm³ K mol⁻¹ at 2 K. The overall behavior of $\chi_{\rm M}T$ is consistent with antiferromagnetic exchange interactions between the constituent metal atoms, and the thermal depopulation of the Stark sublevels of the anisotropic Dy^{III} ion may also participate in it. The experimental data of all compounds can be fitted satisfactorily to the Curie–Weiss law down to 100 K (Fig. S1–S3[†]), leading to the following Curie and Weiss constants: C =53.96 cm³ K mol⁻¹ and $\theta = -41.31$ K for 1; C = 46.73 cm³ K mol^{-1} and $\theta = -30.11$ K for 2; C = 51.47 cm³ K mol⁻¹ and $\theta =$ -34.36 K for 3, respectively. The Curie constants are in relatively good agreement with the value of 54.59 cm³ K mol⁻¹ expected for six Fe^{III} (S = 5/2, g = 2, and C = 4.375 cm³ K mol^{-1}) and two Dy^{III} (S = 5/2, L = 5, ${}^{6}H_{15/2}$, g = 4/3 and $C = 14.17 \text{ cm}^3 \text{ K mol}^{-1}$) noninteracting ions. The negative θ



Fig. 4 Temperature dependence of the $\chi_M T$ product for compounds 1–5 at 1000 Oe. The red line is a simulation of the experimental data for 4.

indicates antiferromagnetic interactions between the spins within the cluster.

It is generally known that the 4f contribution can be removed by using Y ions, and the lanthanide anisotropy can be removed by using Gd ions.²² Hence, compounds **4** and **5** which contain Y ions and Gd ions have been prepared. For compound 4, the $\chi_{\rm M}T$ value of 19.9 cm³ K mol⁻¹ at 300 K decreases with decreasing temperature to 2.4 cm³ K mol⁻¹ at 2 K. The experimental data can be fitted satisfactorily to the Curie-Weiss law down to 100 K (Fig. S4[†]) with a Weiss constant (θ) of -153.5 K and a Curie constant (C) of 30.4 cm³ K mol⁻¹. The Curie constant is in relatively good agreement with the value of 26.3 cm³ K mol⁻¹ expected for six Fe^{III}. The negative θ indicates antiferromagnetic interactions between the spins within the cluster. While the 4f contributions are removed by using Y ions in compound 4, the magnetic behaviours are dominated by the [NaFe^{III}₃] unit. The temperature dependence of the magnetic susceptibility can be analyzed by assuming isotropic exchange with the spin-only Hamiltonian for trinuclear iron complexes $H = -2J_1(S_1 \cdot S_2 +$ $S_1 \cdot S_3$ - $2J_2(S_2 \cdot S_3)$. The energies of the spin states as functions of the exchange integrals J_1 and J_2 were derived by using the Kambe²³ vector coupling approach model. A fit to the experimental data gives $J_1 = -5.01 \text{ cm}^{-1}$, $J_2 = -8.74 \text{ cm}^{-1}$, and g =2.08 with $R = 1.48 \times 10^{-3} (R = \sum (\chi_{obs}T - \chi_{calc}T)^2 / \sum (\chi_{obs}T)^2)$. The absolute value of J is significantly less than the magnitude of the antiferromagnetic coupling constants $(-45.4 \text{ cm}^{-1} \text{ to} -80.1 \text{ cm}^{-1})$ found for the $[\text{Fe}_3\text{O}]^{7+}$ cores,²⁴ but similar to the values (-4.2 cm^{-1}) observed for the $[\text{Fe}_4\text{O}_2]^{8+}$ cores^{14e} which are in the 3d-4f system. Since the exchange integrals are closely related to the distances between μ_3 -O and Fe,²⁵ this difference may be due to the fact that the distances between μ_3 -O and Fe in compound 4 are about 2.10 Å, which are obviously longer than those in the $[Fe_3O]^{7+}$ compounds, but close to those in the $[Fe_4O_2]^{8+}$ compounds.

For compound **5**, the $\chi_{\rm M}T$ value of 34.1 cm³ K mol⁻¹ at 300 K decreases with decreasing temperature, reaching a minimum of 19.8 cm³ K mol⁻¹ at 5 K, and then increases to 20.8 cm³ K mol⁻¹ at 2 K. The experimental data can be fitted satisfactorily to a Curie–Weiss law down to 100 K (Fig. S5†) with a Weiss constant (θ) of –44.9 K and a Curie constant (C) of 39.1 cm³ K mol⁻¹. The Curie constant is in relatively good agreement with the value of 42.0 cm³ K mol⁻¹ expected for six Fe^{III} and two Gd^{III}. The negative θ indicates that antiferromagnetic interactions between the spins within the cluster are dominant. Nevertheless, the increase of the low temperature $\chi_{\rm M}T$ value suggests the presence of ferromagnetic interactions in compound **5**. Although both 3d–4f and 4f–4f interactions are weak, ^{5d,14/26} this is probably ascribed to the Fe–Gd and Gd–Gd interactions.

For compound **5**, the lanthanide anisotropy has been removed by using Gd^{III} ions. We can subtract the magnetic contribution of [NaFe^{III}₃] units found in compound **4** to investigate the interactions of Fe–Gd and Gd–Gd. The profile of the subtracted $\chi_M T$ *vs. T* curve (Fig. 5a) suggests an obviously ferromagnetic behaviour. For compound **2**, the $\chi_M T$ *vs. T* curve with the contribution of [NaFe^{III}₃] units subtracted from the data (Fig. 5b) is plotted. The decrease in $\chi_M T$ is probably ascribed to the interactions of Fe–Dy and Dy–Dy, but the progressive depopulation of excited Stark sublevels and magnetic anisotropy may be more important in the complexes which contain Dy^{III} ions.²⁷





Fig. 5 $\chi_{M}T$ vs. *T* plot at 1000 Oe without the magnetic contribution of the [NaFe^{III}₃] units for **5** (a) and **2** (b).

Field-dependence measurements of the magnetization up to 5 T were performed at 2 K for compounds 1–5, and are shown in Fig. S6.[†] For compounds 1, 2 and 3, the values of the magnetization at 5 T are 23.8, 21.2 and 22.6 $\mu_{\rm B}$, respectively. All of them are far lower than the value expected if all the spins are ferromagnetically aligned. The lack of saturation on the M vs. Hdata also supports the presence of antiferromagnetic interactions and the intrinsic magnetic anisotropy of the Dy^{III} ions. For compound 4, the magnetization at 2 K shows a gradual increase without clear saturation up to 5 T, where it reaches 4.3 $\mu_{\rm B}$. For compound 5, the value of the magnetization at 5 T is 17.6 $\mu_{\rm B}$. It is in relatively good agreement with the value expected for the two [NaFe^{III}₃] units and two Gd^{III}. The ac susceptibility measurements were carried out in a zero dc field with a 3.0 G ac field oscillating at frequencies 10, 50, 100, 1000 Hz. The out-ofphase signals of the complexes show no peaks down to 2.0 K, and no frequency-dependence of out-of-phase signals was observed. The results indicate that all the complexes are not SMMs in the temperature range studied.

Although the structures of compounds 1, 2 and 3 are different, their magnetic behaviors are similar. It may be the result of the weak magnetic interactions between the two central Ln^{III} ions and the Ln^{III} –Fe^{III} interactions, and the magnetic behaviors are mainly due to $[NaFe^{III}_{3}]$ units.

Conclusions

We have shown that the Schiff-base ligands with different numbers of hydroxyl groups can provide access to two unusual polynuclear 3d-4f compounds **1** and **2**, in which the $[Na_2Fe^{III}_6-Dy^{III}_2]$ cores form a couple of *cis,trans*-isomers. Furthermore, the *trans*- $[Na_2Fe^{III}_6Dy^{III}_2]$ clusters in compound **3** act as network nodes in the formation of a 2D rhombic grid-like layered structure, when the pivalates take the place of bulkier benzoates. In order to investigate the magnetic behaviour of 3d-4f systems, compounds **4** and **5** which differ in the lanthanide have also been prepared. The magnetic properties of these compounds are dominated by antiferromagnetic interactions between

 $[NaFe^{III}_{3}]$ units, and the interactions between Ln^{III}–Fe^{III} and Ln^{III}–Ln^{III} also make some contribution. To some extent, this research opens up a promising pathway to investigate the effect of organic ligands on the structure of polynuclear polymers. Though all the compounds are not SMMs themselves, the successful synthesis of the compounds may suggest new methods to construct novel 3d–4f magnetic materials.

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