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First heterometallic Ga^{III}–Dy^{III} single-molecule magnets: implication of Ga^{III} in extracting Fe–Dy interaction†

Sihuai Chen,^{*a,b} Valeriu Mereacre,^{*a} Christopher E. Anson^a and Annie K. Powell^{*a,c}

The compounds of the system [M₄M'₂(μ₃-OH)₂(nbdea)₄(C₆H₅CO₂)₈]·MeCN, where M = Ga^{III}, M' = Dy^{III} (**2**), M = Fe^{III}, M' = Y^{III} (**3**) are isostructural to the known [Fe₄Dy₂] compound (**1**). Those of the system [M₄M'₄(μ₃-OH)₄(nbdea)₄(*m*-CH₃C₆H₄CO₂)₁₂]·*n*MeCN, where M = Ga^{III}, M' = Dy^{III}, *n* = 4 (**5**), M = Fe^{III}, M' = Y^{III}, *n* = 1 (**6**) are isostructural to the [Fe₄Dy₄] compound (**4**). This allows for comparisons between single ion effects of the paramagnetic ions. The structures were determined using single crystal analysis. Magnetic susceptibility measurements reveal that the Ga^{III}–Dy^{III} compounds **2** and **5** are SMMs. The energy barrier for **2** is close to that for the known isostructural Fe₄Dy₂ compound (**1**), but with a significantly increased relaxation time.

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Introduction

Single molecule magnets (SMMs) are a class of coordination clusters displaying the phenomena of slow magnetic relaxation at low temperature.^{1–3} In order to observe such behaviour, it is usually necessary to have a high spin ground state *S* and magnetic anisotropy, normally of an easy axis type as quantified by the zero-field splitting parameter, *D*. This implies using a strategy to increase the total spin quantum number *S* via the synthesis of high-nuclearity clusters,^{4–8} and/or increasing the magnetic anisotropy, with the idea of incorporating rare earth metal ions with their large single-ion magnetic anisotropies seen as an attractive proposition in the preparation of new generations of SMMs.^{9–12} This works well for many of the heterometallic 3d–4f SMMs which have been investigated and reported in recent years.^{13–16}

In terms of 3d ions in general, although the high spin Fe^{III} ion is isotropic in its ground state, the presence of nearby excited states in many Fe^{III} systems¹⁷ means that SMM properties are observed for a number of examples.^{18–23} Although in pure Fe^{III} systems, the exchange interactions are predomi-

nantly antiferromagnetic in nature, the combination of Fe^{III} ions with highly anisotropic Ln^{III} spin carriers can lead to ferromagnetically coupled Fe^{III}–4f coordination clusters exhibiting SMM behaviour.^{24–34}

Up to now, *N*-substituted diethanolamine or triethanolamine ligands have been widely used for the synthesis of the Fe^{III}–4f coordination clusters because of their chelating and bridging capabilities.^{35–39} Recently, we reported the synthesis, structures and magnetic properties of [Fe₄Dy₂(μ₃-OH)₂(nbdea)₄(C₆H₅CO₂)₈]·MeCN (**1**) and [Fe₄Dy₄(μ₃-OH)₄(nbdea)₄(*m*-CH₃C₆H₄CO₂)₁₂]·MeCN (**4**) complexes by employing *N*-butyl-diethanolamine (nbdeaH₂) as ligand.⁴⁰ Both compounds displayed ferromagnetic interactions and the [Fe₄Dy₂] compound (**1**) showed SMM behaviour. In order to study the magnetic contributions of Fe^{III} or Dy^{III} spin carriers within both compounds we have extended the work by replacing either Fe^{III} ions with diamagnetic Ga^{III} centres or the Dy^{III} ions with diamagnetic Y^{III} centres. Herein, we described the synthesis, structures and magnetic properties of two series of heterometallic complexes, namely [Ga₄Dy₂(μ₃-OH)₂(nbdea)₄(C₆H₅CO₂)₈]·MeCN (**2**) and [Fe₄Y₂(μ₃-OH)₂(nbdea)₄(C₆H₅CO₂)₈]·MeCN (**3**), which are isostructural to the [Fe₄Dy₂] compound (**1**), and [Ga₄Dy₄(μ₃-OH)₄(nbdea)₄(*m*-CH₃C₆H₄CO₂)₁₂]·4MeCN (**5**) and [Fe₄Y₄(μ₃-OH)₄(nbdea)₄(*m*-CH₃C₆H₄CO₂)₁₂]·MeCN (**6**), which are isostructural to the [Fe₄Dy₄] compound (**4**).

Experimental

General procedures

Unless otherwise stated, all chemicals and solvents were obtained from commercial sources and were used without

^aInstitute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, 76131 Karlsruhe, Germany. E-mail: valeriu.mereacre@kit.edu, annie.powell@kit.edu

^bState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. E-mail: chensihuai@fjirsm.ac.cn

^cInstitute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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further purification. All reactions were carried out under aerobic conditions. $[\text{Fe}_3\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_6(\text{H}_2\text{O})_3] \cdot (\text{O}_2\text{CC}_6\text{H}_5)$, $[\text{Ga}_3\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_6(\text{H}_2\text{O})_3] \cdot (\text{O}_2\text{CC}_6\text{H}_5) \cdot 2\text{H}_2\text{O}$ and $[\text{Fe}_3\text{O}(\text{m-CH}_3\text{C}_6\text{H}_4\text{COO})_6(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$ were prepared according to the literature procedure.^{41,42} Compound 5 was synthesised by sealing the reaction mixture in transparent 20 mL Biotage Microwave Reaction Kits (<http://www.biotage.com>) and placing the vials in an oven at 120 °C under normal solvothermal conditions, rather than under microwave conditions. Elemental analyses for C, H, N were performed using an ElementarVario EL analyzer and were carried out at the Institute of Inorganic Chemistry, Karlsruhe Institute of Technology. IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer using KBr pellets and the X-ray powder diffraction patterns were measured at room temperature using a Stoe STADI-P diffractometer with a Cu-K α radiation. The synthetic procedures for compounds 1 and 4 were previously reported.⁴⁰

Preparation of $[\text{Ga}_4\text{Dy}_2(\mu_3\text{-OH})_2(\text{nbdea})_4(\text{C}_6\text{H}_5\text{CO}_2)_8] \cdot \text{MeCN}$ (2)

A mixture of $[\text{Ga}_3\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_6(\text{H}_2\text{O})_3] \cdot (\text{O}_2\text{CC}_6\text{H}_5)$ (0.063 g, 0.06 mmol), $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.030 g, 0.07 mmol) and nbdeaH_2 (0.081 g, 0.50 mmol) in MeCN (20 ml) was stirred at room temperature for 10 minutes. This mixture was heated to 80 °C and became clear. The resulting solution was further stirred for 3 h at 80 °C and then left undisturbed in air. Colorless blocks were crystallized after one day. Yield: 15% (based on Dy). *Anal.* Calc. for $\text{C}_{90}\text{H}_{113}\text{N}_5\text{O}_{26}\text{Ga}_4\text{Dy}_2$: C, 47.31; H, 4.99; N, 3.07; found C, 47.36; H, 4.71; N, 3.37%. IR (KBr)/ cm^{-1} : 3437 (br), 2959 (s), 1962 (w), 1643 (s), 1598 (s), 1558 (s), 1493 (m), 1449 (s), 1399 (vs), 1322 (s), 1301 (s), 1174 (m), 1135 (m), 1084 (s), 1026 (s), 908 (m), 824 (m), 721 (s), 690 (m), 677 (s), 632 (w), 590 (m), 537 (mw).

Preparation of $[\text{Fe}_4\text{Y}_2(\mu_3\text{-OH})_2(\text{nbdea})_4(\text{C}_6\text{H}_5\text{CO}_2)_8] \cdot \text{MeCN}$ (3)

To a solution of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.096 g, 0.25 mmol) and nbdeaH_2 (0.322 g, 2.00 mmol) in MeCN (10 ml) was dropwise added a solution of $[\text{Fe}_3\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_6(\text{H}_2\text{O})_3] \cdot (\text{C}_6\text{H}_5\text{CO}_2)$ (0.250 g, 0.23 mmol) in MeCN (10 ml) during the stirring. The mixture was stirred at room temperature for one hour. The resulting clear solution was left undisturbed in air. Yellow blocks were crystallized after three hours. Yield: 38% (based on Y). *Anal.* Calc. for $\text{C}_{90}\text{H}_{113}\text{N}_5\text{O}_{26}\text{Fe}_4\text{Y}_2 \cdot (2\text{H}_2\text{O})$: C, 51.03; H, 5.57; N, 3.31; found C, 50.86; H, 5.18; N, 3.19%. IR (KBr)/ cm^{-1} : 3431 (br), 2960 (m), 1643 (m), 1598 (s), 1558 (s), 1493 (w), 1449 (m), 1401 (vs), 1322 (s), 1302 (m), 1174 (mw), 1135 (w), 1085 (m), 1026 (m), 905 (mw), 824 (mw), 719 (s), 690 (mw), 676 (m), 590 (m), 544 (w).

Preparation of $[\text{Ga}_4\text{Dy}_4(\mu_3\text{-OH})_4(\text{nbdea})_4(\text{m-CH}_3\text{C}_6\text{H}_4\text{O}_2)_{12}] \cdot 4\text{MeCN}$ (5)

A mixture of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.030 g, 0.12 mmol), $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.054 g, 0.12 mmol), nbdeaH_2 (0.161 g, 1.00 mmol) and $\text{m-CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{H}$ (0.067 g, 0.49 mmol) in MeCN (10 ml) was sealed in a 20 mL microwave reaction vial.

The reaction mixture was kept at 120 °C for 24 h. After cooling, the colourless crystals were collected, washed with MeCN and dried in the air. Yield: 9% (based on Dy). *Anal.* Calc. for $\text{C}_{136}\text{H}_{168}\text{N}_8\text{O}_{36}\text{Ga}_4\text{Dy}_4$: C, 47.77; H, 4.95; N, 3.28; found C, 47.36; H, 4.71; N, 3.57%. IR (KBr)/ cm^{-1} : 3546 (m), 3436 (br), 2958 (m), 1625 (s), 1612 (s), 1600 (s), 1567 (s), 1404 (vs), 1285 (m), 1225 (m), 1162 (w), 1110 (m), 1041 (w), 984 (w), 901 (m), 786 (m), 755 (s), 687 (mw), 672 (m), 585 (m), 455 (m).

Preparation of $[\text{Fe}_4\text{Y}_4(\mu_3\text{-OH})_4(\text{nbdea})_4(\text{m-CH}_3\text{C}_6\text{H}_4\text{CO}_2)_{12}] \cdot \text{MeCN}$ (6)

Compound 6 was obtained using the similar procedure as for 3, but using $[\text{Fe}_3\text{O}(\text{m-CH}_3\text{C}_6\text{H}_4\text{CO}_2)_6(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})_2] \cdot (\text{NO}_3) \cdot 2\text{H}_2\text{O}$ in place of $[\text{Fe}_3\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_6(\text{H}_2\text{O})_3] \cdot (\text{C}_6\text{H}_5\text{CO}_2)$. After one day yellow needles were crystallized. Yield: 43% (based on Y). *Anal.* Calc. for $\text{C}_{128}\text{H}_{156}\text{N}_4\text{O}_{36}\text{Fe}_4\text{Y}_4$ (loss of lattice MeCN): C, 52.91; H, 5.41; N, 1.93; found C, 52.41; H, 5.20; N, 1.90%. IR (KBr)/ cm^{-1} : 3551 (m), 3438 (br), 2958 (m), 1627 (s), 1599 (s), 1568 (s), 1405 (vs), 1286 (mw), 1226 (mw), 1163 (w), 1111 (s), 1042 (w), 986 (w), 901 (m), 786 (m), 755 (s), 686 (w), 672 (m), 584 (m), 456 (m).

Physical measurements

X-Ray crystallography. X-ray crystallographic data for 2 and 5 were collected on an Oxford Diffraction SuperNova Ediffractometer using graphite-monochromated Mo-K α radiation, and data were corrected for absorption. The structures were solved using dual-space direct methods (SHELXT), followed by full-matrix least-squares refinement against F^2 (all data) using SHELXTL-2014.⁴³ Anisotropic refinement was used for all ordered non-hydrogen atoms. Organic hydrogen atoms were placed in calculated positions, the coordinates of hydroxo hydrogen atoms were either placed in calculated positions or located from the difference Fourier map and then refined with O-H restrained to 0.88(4) Å.

Crystallographic and structure refinement data are summarised in Table 1. Crystallographic data (excluding structure factors) for the structures of 2 and 5 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1460736 and 1460737. The previously published structures of compounds 1 and 4 have deposition numbers CCDC 1000674 and 1000675.⁴⁰

Magnetic measurements. The magnetic susceptibility measurements were collected on a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were carried out on finely ground polycrystalline samples constrained with eicosane. The dc magnetic susceptibility data for compounds 2, 3, 5 and 6 were collected in the 1.8–300 K temperature range at 1000 Oe. AC susceptibility measurements were measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for diamagnetic contributions of the sample holder.



Table 1 Crystallographic and structure refinement data for compounds 2, 3, 5 and 6

	1 (ref. 40)	2	3 ^a	4 (ref. 40)	5	6 ^a
Formula	C ₉₀ H ₁₁₃ N ₅ O ₂₆ Fe ₄ Dy ₂	C ₉₀ H ₁₁₃ N ₅ O ₂₆ Ga ₄ Dy ₂	C ₉₀ H ₁₁₃ N ₅ O ₂₆ Fe ₄ Y ₂	C ₁₃₀ H ₁₅₉ N ₅ O ₃₆ Fe ₄ Dy ₄	C ₁₃₀ H ₁₆₈ N ₈ O ₃₆ Ga ₄ Dy ₄	C ₁₃₀ H ₁₅₉ N ₅ O ₃₆ Fe ₄ Y ₄
<i>M_r</i>	2229.25	2284.73	2082.10	3241.02	3419.65	2946.71
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P1</i>	<i>P1</i>	<i>P1</i>
<i>T</i> (K)	298(2)	180(2)	298(2)	180(2)	150(2)	298(2)
<i>a</i> (Å)	15.3144(16)	15.0554(5)	15.318	14.0948(11)	15.4662(4)	14.3970
<i>b</i> (Å)	29.190(4)	29.0734(11)	29.220	16.8729(5)	16.8729(5)	16.7858
<i>c</i> (Å)	22.497(2)	22.3017(8)	22.524	29.6754(19)	29.1650(8)	29.7649
<i>α</i> (°)	90	90	90	89.624(6)	87.415(2)	89.148
<i>β</i> (°)	108.001(12)	106.594(4)	107.88	87.037(6)	87.793(2)	86.314
<i>γ</i> (°)	90	90	90	73.680(6)	68.609(3)	73.756
<i>V</i> (Å ³)	9564.5(18)	9355.2(6)	9594	6755.4(9)	7077.4(4)	6883.5
<i>Z</i>	4	4	4	2	2	2
<i>D_{calc}</i> (g cm ⁻³)	1.662	1.662	1.662	1.605	1.605	1.605
<i>F</i> (000)	4608	4608	4608	3432	3432	3432
<i>μ</i> (mm ⁻¹)	2.790	2.790	2.790	2.911	2.911	2.911
Reflections collected	49 641	49 641	49 641	60 399	60 399	60 399
Unique reflections	21 420	21 420	21 420	31 158	31 158	31 158
<i>R_{int}</i>	0.0597	0.0597	0.0597	0.0454	0.0454	0.0454
Parameters	1148	1148	1148	1704	1704	1704
<i>R₁</i> (<i>I</i> > 2σ(<i>I</i>))	0.0660	0.0660	0.0660	0.0653	0.0653	0.0653
<i>wR₂</i> (all data)	0.1196	0.1196	0.1196	0.1195	0.1195	0.1195
<i>S</i> (all data)	1.103	1.103	1.103	1.122	1.122	1.122
CCDC	1000674	1460736		1000675	1460737	

^aThe structures of compounds 3 and 6 were not fully refined. The unit cells are included here for comparison: either 3 with 1 from ref. 40 and 2, or 6 with 4 from ref. 40 and 5.

Results and discussion

Synthesis and crystal structures

The reaction of Dy(NO₃)₃ with the [Ga₃O]⁷⁺ benzoate triangle and *nbdea*H₂ at 80 °C in MeCN afforded the hexanuclear Ga₄^{III}-Dy₂^{III} (2), while the octanuclear Ga₄^{III}-Dy₄^{III} (5) was synthesized at 120 °C under solvothermal conditions for 24 h using Ga(NO₃)₃/Dy(NO₃)₃/*nbdea*H₂/*m*-CH₃C₆H₄COOH in a molar ratio of 1 : 1 : 8 : 8. Compounds 3 and 6 can be obtained through the identical procedure as that reported for compound 1 or 4.⁴⁰ The reactions of [Fe^{III}O]⁷⁺/Y(NO₃)₃/*nbdea*H₂ in a molar ratio of 1 : 1 : 8 in MeCN at room temperature produced compounds 3 and 6, respectively. By comparison of their X-ray powder diffraction patterns (Fig. S1†) and unit cells, compounds 1–3 were found to crystallise isotypically. Compound 6 was shown to be crystallise isotypically with compound 4, with both having one lattice MeCN per cluster. Although compound 5 has by contrast four lattice MeCN per cluster, the unit cell is in fact rather similar to that of 4 and 6, apart from a corresponding increase in volume, and the packing is also not dissimilar.

Single-crystal X-ray diffraction studies reveal that compounds 1–3 crystallise in the monoclinic space group *P2₁/c* and compounds 4–6 in the triclinic space group *P1*.

The structure of Ga₄^{III}-Dy₂^{III} (2) is shown in Fig. 1. The hexanuclear core of 2 exhibits a curved 2Ga:2Dy:2Ga arrangement similar with the previously discussed compound 1.⁴⁰ Each Ga^{III} centre is chelated by a doubly-deprotonated (*nbdea*)²⁻ ligand, forming a cationic metalloligand, [Ga(*nbdea*)]⁺, which is bridged to another [Ga(*nbdea*)]⁺ and the central dimeric [Dy₂(μ₃-OH)₂]⁴⁺ unit. Both Dy^{III} ions are eight-coordinate with approximate square antiprismatic geometry, while all the Ga^{III} ions are six-coordinate, exhibiting a distorted octahedral coordination geometry. The central core of compound 5 is based on an approximate square of four coplanar Dy^{III} ions (Fig. 2, top). Each pair of adjacent Dy centres is bridged by a

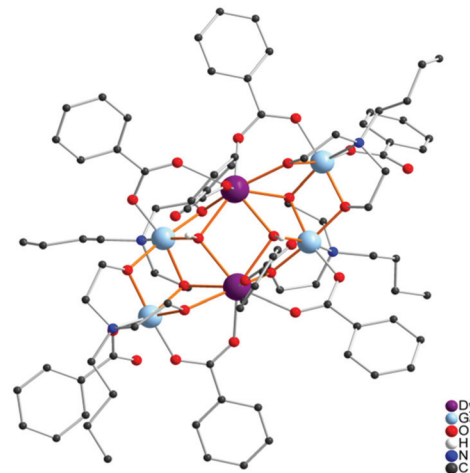


Fig. 1 Molecular structure of compound [Ga₄Dy₂(μ₃-OH)₂(*nbdea*)₄(C₆H₅CO₂)₆]-MeCN (2). Organic hydrogen atoms apart from in the core have been omitted for clarity.



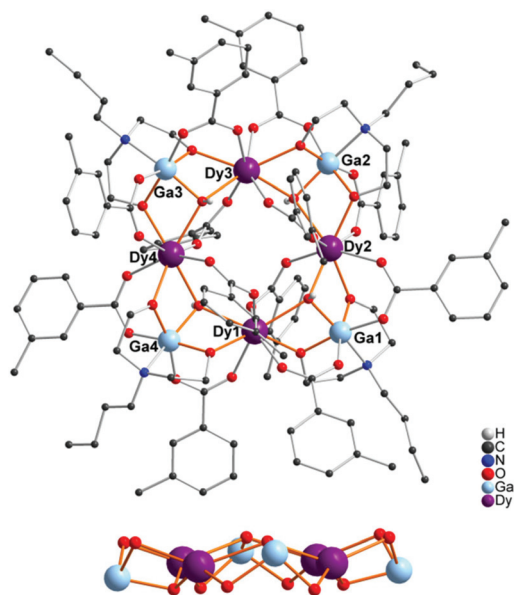


Fig. 2 Molecular structure of compound $[\text{Ga}_4\text{Dy}_4(\mu_3\text{-OH})_4(\text{nbdea})_4(m\text{-CH}_3\text{C}_6\text{H}_4\text{O}_2)_{12}] \cdot 4\text{MeCN}$ (5) (top) and a side view of the core in 5 (bottom). Organic hydrogen atoms have been omitted for clarity.

$(\mu_3\text{-OH})^-$ ligand to a Ga^{III} ion, forming an octanuclear core possessing a “ Dy_4 -square-within-a- Ga_4 -square”. All four Ga centres are nearly coplanar, displaced alternatively slightly above and below the $\{\text{Dy}_4\}$ plane; 0.346, 0.281, 0.397 and 0.450 Å for Ga1, Ga2, Ga3 and Ga4, respectively (Fig. 2, bottom).

Magnetic properties

The dc magnetic susceptibility data for compounds 2, 3, 5 and 6 were measured in the temperature range 1.8–300 K at 1000 Oe, respectively. For 2 (Fig. 3), the χT product is 27.0 $\text{cm}^3 \text{K mol}^{-1}$ at 300 K, which is in relatively good agreement with the

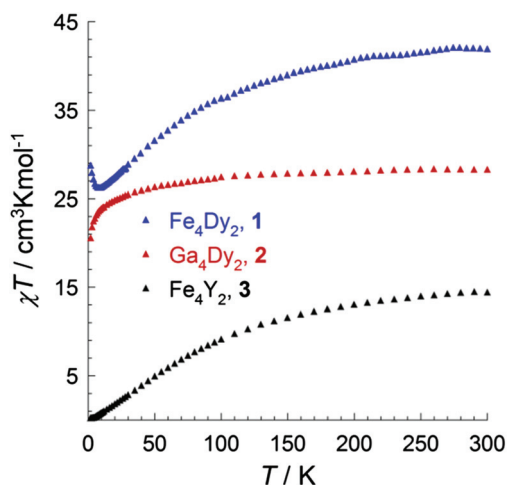


Fig. 3 Temperature dependence of the χT product at 1000 Oe for 1 (blue),⁴⁰ 2 (red) and 3 (black).

value ($28.4 \text{ cm}^3 \text{K mol}^{-1}$) corresponding to two uncoupled Dy^{III} ($S = 5/2$, $L = 5$, ${}^6\text{H}_{15/2}$, $g = 4/3$) and four Ga^{III} ($S = 0$) ions. On lowering temperature the χT product continuously decreases, reaching the minimum value of $18.8 \text{ cm}^3 \text{K mol}^{-1}$ at 1.8 K. This type of behaviour suggests that the magnetic interaction between the central Dy_2^{III} unit is weakly antiferromagnetic. The thermal depopulation of the Dy^{III} excited states could also contribute to the decrease of the χT product. In the case of compound 3 (Fig. 3), the χT product of $14.5 \text{ cm}^3 \text{K mol}^{-1}$ at 300 K is lower than the expected value of $17.5 \text{ cm}^3 \text{K mol}^{-1}$ for four Fe^{III} ($S = 5/2$, $g = 2$) and two Y^{III} ($S = 0$) non-interacting ions, which indicates the presence of antiferromagnetic interactions between spin carriers. The χT value decreases gradually with decreasing temperature, reaching the minimum value of $0.3 \text{ cm}^3 \text{K mol}^{-1}$ at 1.8 K, suggesting that the dominant antiferromagnetic interactions between Fe^{III} ions lead to a spin ground state of zero.

However, the magnetic behaviour of the reported isostructural Fe_4Dy_2 compound 1 indicates the presence of ferromagnetic interactions between spin centres at very low temperature (Fig. 3).⁴⁰ Since the Dy–Dy and the Fe–Fe exchange interactions are all antiferromagnetic, it can be concluded that ferromagnetic Fe–Dy interactions are revealed at low temperature. This could be one of the origins for the slow relaxation observed in the bulk magnetic data and the Mössbauer spectra for Fe^{III} containing compounds with antiferromagnetically coupled Fe–Fe pairs as seen in compound 1⁴⁰ and in the similar Fe_4Dy_2 compound recently reported.^{30,34} It is worth to mention that, using Co^{III} as a diamagnetic ion, recent studies have proved the strong magnetic exchange between the Cr^{III} and Dy^{III} ions.⁴⁴

The field dependences of the magnetisation at low temperatures for compounds 2 and 3 are shown in Fig. S2.† For the Ga_4Dy_2 compound 2 (Fig. S2,† left), the magnetisation increases rapidly at low fields below 10 kOe, followed by an almost linear increase till 70 kOe. The lack of saturation even up to 70 kOe suggests the thermally and/or field-induced population of low lying excited states, as well as the presence of significant magnetic anisotropy. However, the very low value of $10.1 \mu_{\text{B}}$ at 2 K and 70 kOe is in good agreement with that expected for two Dy^{III} single ions in polycrystalline samples (each $\sim 5\text{--}6 \mu_{\text{B}}$). The magnetisation measurements with varying scan rate did not show hysteresis. The field dependence of the magnetisation for the Fe_4Y_2 compound 3 shows a very slow increase with the applied fields and at 2 K only reaches $0.25 \mu_{\text{B}}$ at 70 kOe (Fig. S2,† right), which confirms the antiferromagnetic coupling between Fe^{III} ions.

To investigate the dynamics of the relaxation, ac susceptibility measurements were performed under a zero dc applied field in the 1–1500 Hz frequency range between 1.8 and 20 K. Both temperature- and frequency-dependent in-phase and out-of-phase signals were observed for the Ga_4Dy_2 compound 2 (Fig. 4 and 5), revealing slow relaxation of magnetization expected for a SMM. In the χ'' vs. T plot, no maximum is observed at lower frequencies. However, clear peaks and some shoulders are observed at higher frequencies (Fig. 4, right). In



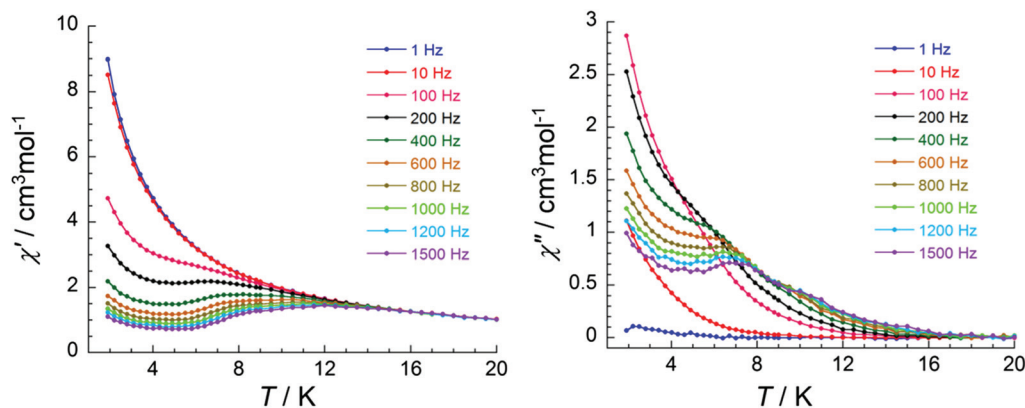


Fig. 4 Temperature dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility components at different frequencies in zero dc field for 2.

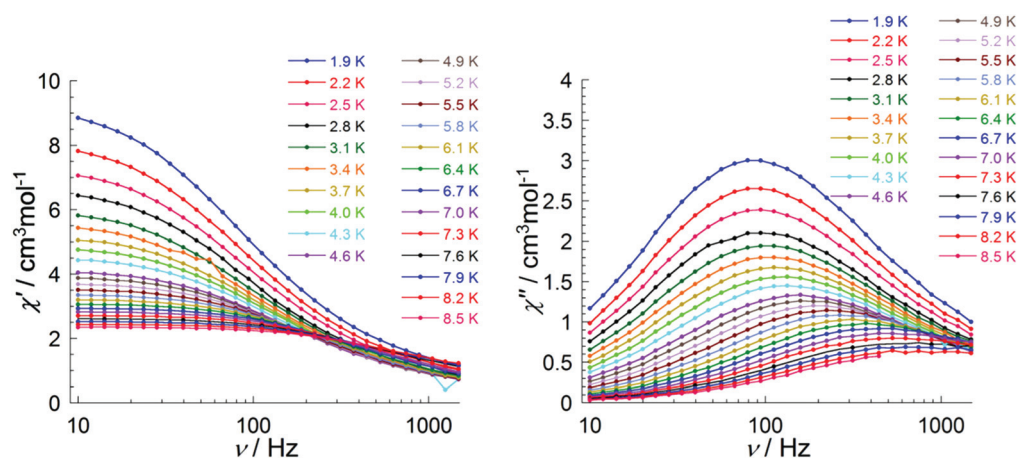


Fig. 5 Frequency dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility components at different temperatures in zero dc field for 2.

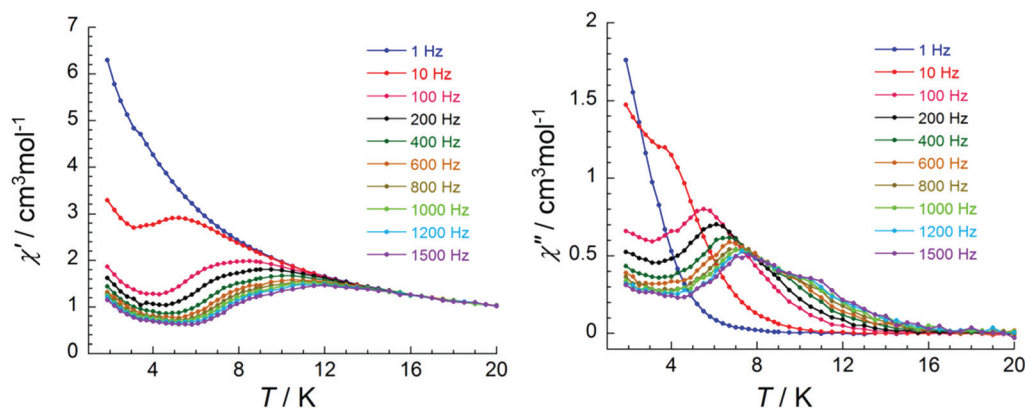


Fig. 6 Temperature dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility components at different frequencies under 1500 Oe dc field for 2.

addition, there is evidence for one peak which develops at temperatures below 1.8 K. This phenomenon suggests the presence of quantum tunnelling effects and at least two

additional relaxation processes in this system. The linear fitting of Arrhenius plots (Fig. S3†) of the data from frequency dependent measurements (Fig. 5, right) give an extracted



energy barrier U_{eff} of 20.9 K, which is very close to the value of 21.4 K for the previously reported isostructural Fe_4Dy_2 compound **1**.⁴⁰ However, the relaxation time increases significantly from $\tau_0 = 2.7 \times 10^{-8}$ s (for **1**)⁴⁰ to $\tau_0 = 1.5 \times 10^{-5}$ s (for **2**). This behaviour was also observed in the cases of the reported $\{\text{Cr}_2^{\text{III}}\text{Dy}_2^{\text{III}}\}$ and $\{\text{Co}_2^{\text{III}}\text{Dy}_2^{\text{III}}\}$ systems,^{45,46} indicating possible suppression of the quantum tunnelling. The Cole–Cole plots in Fig. S4† show nearly symmetric semicircles and were fitted to a generalised Debye function. The resulting α parameter ranges from 0.17 to 0.26 in the temperature range between 1.9 and 7.9 K, indicating a wider distribution of the relaxation time in comparison to the value ($\alpha = 0.04\text{--}0.13$ between 2.4 and 2.9 K) for **1**,⁴⁰ and the presence of multi-relaxation processes in the system.

A dc field of 1500 Oe was applied to further investigate the relaxation dynamic in compound **2** (Fig. 6 and 7). Clear shoulders are observed in the χ'' vs. T plot (Fig. 6, right). The data from frequency dependent measurements (Fig. 7) were analysed using an Arrhenius law, which gives a characteristic energy barrier U_{eff} of 41.2 K and a relaxation time τ_0 of 2.2×10^{-6} s (Fig. S5†). As shown in Fig. S6,† the Cole–Cole plots for **2** at 1500 Oe can be fitted to a generalised Debye function at high temperature, giving large α parameters in the range 0.31–0.38. At low temperature between 1.9 and 5.5 K, the Cole–Cole plots cannot be fitted well, confirming that more than one relaxation process occurs in this system.

The χT values for the Ga_4Dy_4 **5** and Fe_4Y_4 **6** with the “square-in-square” core topology are 55.7 and 18.4 $\text{cm}^3 \text{K mol}^{-1}$ at 300 K, which are close to the expected values (56.7 and 17.5 $\text{cm}^3 \text{K mol}^{-1}$) for non-interacting spin centres: four Dy^{III} ($S = 5/2, L = 5, {}^6\text{H}_{15/2}, g = 4/3$) and four Ga^{III} ($S = 0$) ions in **5** or four Fe^{III} ($S = 5/2, g = 2$) and four Y^{III} ($S = 0$) ions in **6**, respectively. On lowering the temperature from 300 to 50 K, the χT products for both compounds remain almost constant and then rapidly drop to 33.8 and 14.9 $\text{cm}^3 \text{K mol}^{-1}$ with further cooling to 1.8 K, respectively (Fig. 8, top). The overall behaviour suggests very weak antiferromagnetic interactions between Dy^{III} centres in **5** or between Fe^{III} centres in **6**. As shown in Fig. 8 (top), the increase of the χT vs. T curve on

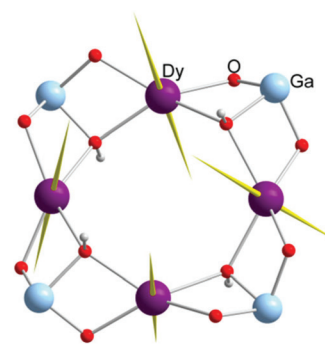
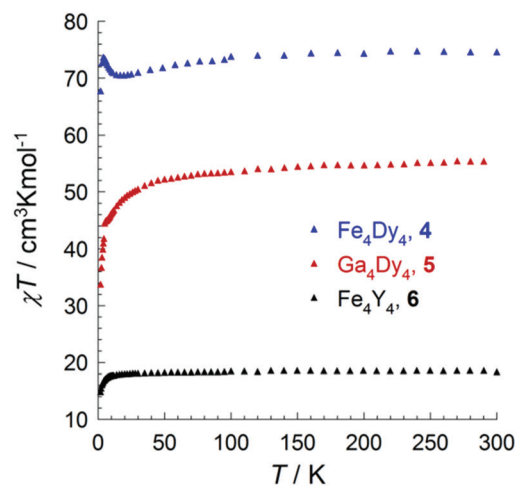


Fig. 8 (top) Temperature dependence of the χT product at 1000 Oe for **4** (blue),⁴⁰ **5** (red) and **6** (black); (bottom) the orientations of the anisotropy axes for Dy^{III} ions in compound **5**, calculated by MAGELLAN.⁴⁷

decreasing the temperature in the 4–16 K temperature range suggests the presence of weak ferromagnetic interactions as observed in the reported isostructural $\text{Fe}_4^{\text{III}}\text{Dy}_4^{\text{III}}$ compound **4**.⁴⁰ If both Fe–Fe and Dy–Dy interactions are antiferromagnetic within **4**, then the shape of χT vs. T plot for compound **4** at low temperature (Fig. 8, top) leads to the conclusion that the

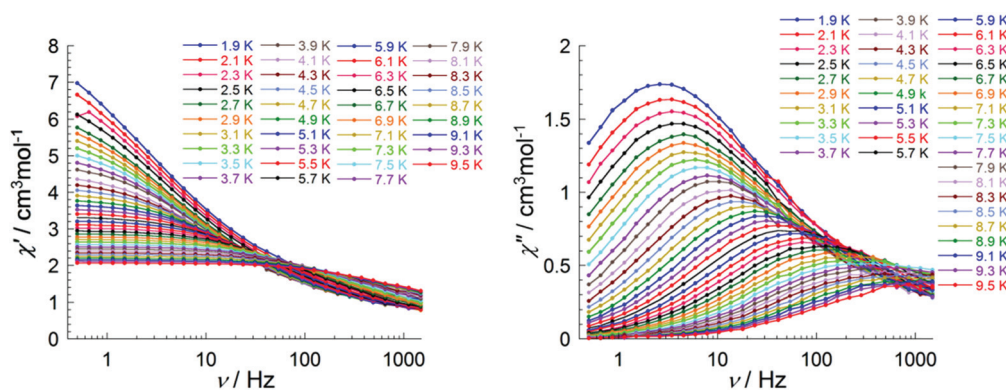


Fig. 7 Frequency dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility components at different temperatures under 1500 Oe dc field for **2**.



interactions between Fe^{III} and the adjacent Dy^{III} centres must be weakly ferromagnetic. The orientation of the anisotropy axis for each Dy^{III} ion in the Ga_4Dy_4 compound **5** was calculated using the program, MAGELLAN,⁴⁷ and shown in Fig. 8 (bottom). All four axes are nearly perpendicular to the Dy_4 plane and nearly parallel to each other, similarly to the situation reported for $[\text{Cr}_4^{\text{III}}\text{Dy}_4^{\text{III}}]$, for which the directions of main anisotropy axes were determined from *ab initio* calculations.⁴⁸

The field dependent magnetisation measurements at low temperature for **5** show that the magnetisation increases steadily with the application of the external field without saturation even at 70 kOe (Fig. S7,† left). This behaviour indicates the presence of magnetic anisotropy and/or low lying excited states in this system. However, the value of $22.6\mu_{\text{B}}$ at 2 K and 70 kOe is in good agreement with the expected saturation value for four Dy^{III} isolated ions in polycrystalline samples (each $\sim 5\text{--}6\mu_{\text{B}}$). For **6**, the magnetisation at 2 K under a field of 70 kOe is $20.7\mu_{\text{B}}$ (Fig. S7,† right), which is in very good agreement with the presence of four isolated $S = 5/2$ Fe^{III} ions aligned parallel to the dc field suggesting a possible $S =$

10 ground state for **6**. Although the ac susceptibilities for the $\text{Fe}_4^{\text{III}}\text{Dy}_4^{\text{III}}$ compound **4** did not show any sign of slow relaxation of the magnetisation,⁴⁰ the ac susceptibility measurement for **5** in zero dc field shows weak out-of-phase ac signal with no maximum is observable above 1.8 K (Fig. S8†). In order to check any quantum tunnelling effects above 1.8 K, the frequency dependence of the ac susceptibility was measured under different applied dc fields at 1.8 K (Fig. S9†). As shown in Fig. S9† (right), the maximum in the frequency dependent out-of-phase plot is only slightly moved to lower frequency, indicating the absence of quantum tunnelling effects above 1.8 K.

To study the system further, an external dc field of 1000 Oe was applied and both the in-phase and out-of-phase signals show temperature and frequency dependence (Fig. 9 and 10). Although there is no peak observed in the χ'' vs. T plot (Fig. 9, right), clear peaks are observed in the χ'' vs. ν data (Fig. 10, right). Fitting the data using an Arrhenius law leads to an estimation of the energy gap $U_{\text{eff}} = 5.4$ K and relaxation time $\tau_0 = 4.1 \times 10^{-5}$ s (Fig. S10†).

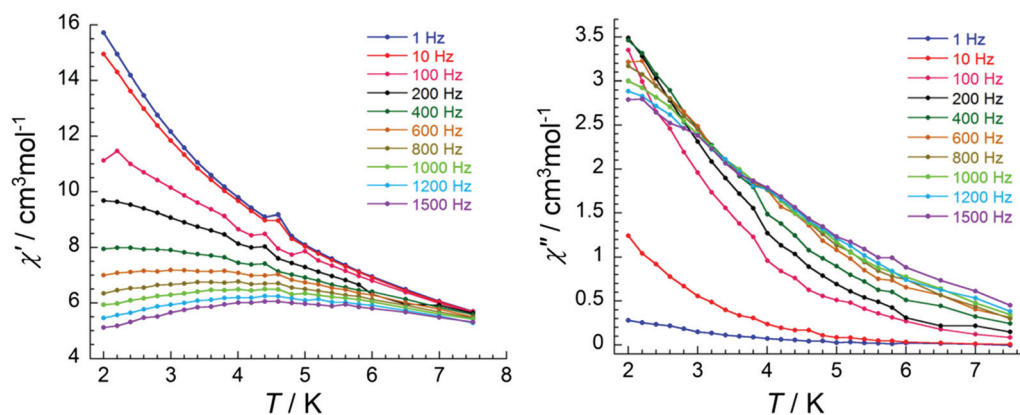


Fig. 9 Temperature dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility components at the indicated frequencies under 1000 Oe dc field for **5**.

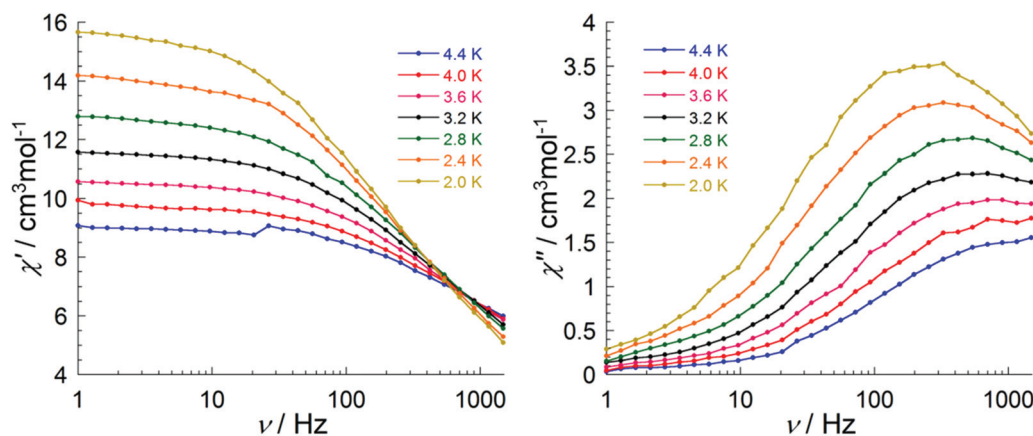


Fig. 10 Frequency dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility components at the indicated temperatures under 1000 Oe dc field for **5**.



Conclusions

Two series of $\{M_4Ln_2\}$ and $\{M_4Ln_4\}$ ($M = Fe^{III}$ or Ga^{III} ; $Ln = Dy^{III}$ and Y^{III}) complexes have been synthesised in order to study the magnetic contribution of Fe^{III} or Dy^{III} centres within 3d–4f heterometallic systems. Direct current magnetic susceptibility measurements revealed that Dy^{III} – Dy^{III} interactions within 2 or 5 and Fe^{III} – Fe^{III} interactions within 3 or 6 are all weakly antiferromagnetic. Alternating current magnetic susceptibility measurements did not show any SMM behaviour for both the $\{Fe_4Y_2\}$ compound **3** and the $\{Fe_4Y_4\}$ compound **6** containing diamagnetic Y^{III} ions, while both the $\{Ga_4Dy_2\}$ compound **2** and the $\{Ga_4Dy_4\}$ compound **5** exhibit out-of-phase ac susceptibility signals, indicating that **2** and **5** are both SMMs. The characteristic SMM energy barrier of 20.9 K for $\{Ga_4Dy_2\}$ compound **2** under zero dc field is very close to the value of 21.4 K for the reported isostructural $\{Fe_4Dy_2\}$ compound **1**. However, the relaxation time increases significantly from 2.7×10^{-8} s for $\{Fe_4Dy_2\}$ compound **1** to 1.5×10^{-5} s for $\{Ga_4Dy_2\}$ compound **2**, indicating the QTM is likely to be suppressed by replacing paramagnetic Fe^{III} ions with diamagnetic Ga^{III} centres. Furthermore, although the $\{Fe_4Dy_4\}$ compound **4** did not show any sign of magnetisation slow relaxation, the $\{Ga_4Dy_4\}$ compound **5** did show slow relaxation of magnetisation. This result suggests that the weak ferromagnetic Fe^{III} – Dy^{III} exchanges quench the magnetic anisotropy of the Dy^{III} ions and the SMM behaviour.

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