216 *Inorg. Chem.* **2010**, *49*, 216–221
DOI: 10.1021/ic901781a

Inorganic Chemistry
Article

An S-Shaped $[Fe_4Dy_2]$ Complex Exhibiting Slow Relaxation of Magnetization: Synthesis, Magnetism, and Crystal Structures of a Family of $[Fe_4Ln_2][Ln]$ Coordination Compounds (Ln = Nd, Gd, Tb, Dy, and Ho)[†]

Sanjit Nayak,[‡] Olivier Roubeau,[§] Simon J. Teat,[⊥] Christine M. Beavers,[⊥] Patrick Gamez,[‡] and Jan Reedijk*[,‡]

[‡]*Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands,* [§]*Instituto de Ciencia de Materiales de Aragón, CSIC and Universidad de Zaragoza, Plaza San Francisco, s/n 50009 Zaragoza, Spain, and* [⊥]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

Received September 6, 2009

A series of heterobimetallic 3d−4f cluster coordination compounds has been synthesized using a Schiff-base ligand (H_3L), a trinuclear iron(III) precursor complex and lanthanide nitrates as reactants. Five new isostructural complexes were prepared with the ligand in 4 different forms, i.e., neutral and 3 different levels of deprotonation, and with the general formula $[Fe^{III}_4Ln^{III}_2(H_2L)_2(HL)_2L_2(CH_3OH)_2((CH_3)_3CCOO)_2(NO_3)_2][Ln^{III}(NO_3)_4(H_3L)(CH_3OH)]\cdot NO_3\cdot H_2O$, where Ln is Nd, Gd, Tb, Dy, and Ho for compounds **1**, **2**, **3**, **4**, and **5**, respectively. The single-crystal structures of two complexes were determined by X-ray diffraction, consisting of an original $[Fe^{III}_4Ln^{III}_2]^{2+}$ moiety with a linear S-shaped [Ln-Fe_4-Ln] core and an isolated Ln^{III} ion coordinated by nitrate anions and the neutral Schiff-base ligand. The isostructural nature of all five coordination compounds is further illustrated both by XRPD and IR analysis. Magnetic properties of all five compounds have been studied and are discussed in light of magnetostructural considerations. Among these five compounds, the Dy (**4**) cluster shows frequency-dependent ac-susceptibility indicative of probable single-molecule magnet behavior.

Introduction

The design, preparation, and investigation of polynuclear transition-metal and lanthanide complexes is presently a hot area of research stimulated by their potential applications in quantum computing and magnetic data storage devices.[1−3] Most of the early studies in the field, in the late 20th century, were focused on the investigation of transition-metal clusters.[4,5] Single-molecule magnets (SMMs) are a special class of compounds characterized by the slow relaxation of the magnetization originating from a high-spin ground state and the magnetic anisotropy of single molecules.[6,7] Recent reports have shown that the combination of transition metals and lanthanides in polynuclear cluster complexes may generate both a high-spin state and magnetic anisotropy.[8−10] However, as this concept is relatively new, there are only a few mixed metal 3d−4f complexes reported, which show single-molecule magnet behavior. For instance, the first 3d−4f SMM with a Cu_2Tb_2 core was reported in 2004 by Mrozinski et al., followed by a few other compounds namely, Dy_6Mn_6, Mn_2Dy_2, $Mn_{11}Gd_2$, Mn_5Dy_4, $Mn_{18}Dy$, and $Mn_{12}Gd$ complexes.[11−17] A literature survey reveals that most of the so far studied 3d−4f

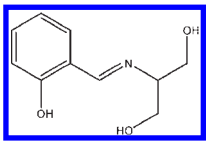
---

[†] Paper dedicated to Prof. Annie Powell, on the occasion of her 50th birthday.

*To whom correspondence should be addressed. E-mail: reedijk@chem.leidenuniv.nl.

(1) Gatteschi, D. *Adv. Mater*. **1994**, *6*, 635–645.
(2) Kahn, O. *Acc. Chem. Res*. **2000**, *33*, 647–657.
(3) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789–793.
(4) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc*. **1991**, *113*, 5873–5874.
(5) Aromi, G.; Brechin, E. K. Synthesis of 3d metallic single-molecule magnets. In *Single-Molecule Magnets and Related Phenomena*; Springer-Verlag Berlin: Berlin, 2006; Vol. *122*, pp 1−67.
(6) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull*. **2000**, *25*, 66–71.
(7) Long, J. R. *Molecular Cluster Magnets*; World Scientific Publishing: Hong Kong, 2003.
(8) Sorace, L.; Sangregorio, C.; Figuerola, A.; Benelli, C.; Gatteschi, D. *Chem. Eur. J*. **2009**, *15*, 1377–1388.
(9) Sessoli, R.; Powell, A. K. *Coord. Chem. Rev*. **2009**, *253*, 2328–2341.
(10) Benelli, C.; Gatteschi, D. *Chem. Rev*. **2002**, *102*, 2369–2387.
(11) Osa, S.; Kido, T.; Matsumoto, N.; Re, N.; Pochaba, A.; Mrozinski, J. *J. Am. Chem. Soc*. **2004**, *126*, 420–421.
(12) Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L. *Angew. Chem., Int. Ed*. **2004**, *43*, 3912–3914.
(13) Mishra, A.; Wernsdorfer, W.; Parsons, S.; Christou, G.; Brechin, E. K. *Chem. Commun*. **2005**, 2086–2088.
(14) Mereacre, V. M.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Filoti, G.; Bartolome, J.; Anson, C. E.; Powell, A. K. *J. Am. Chem. Soc*. **2007**, *129*, 9248–9249.
(15) Mereacre, V.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem. Eur. J*. **2008**, *14*, 3577–3584.
(16) Ako, A. M.; Mereacre, V.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem. Commun*. **2009**, 544–546.
(17) Stamatatos, T. C.; Teat, S. J.; Wernsdorfer, W.; Christou, G. *Angew. Chem., Int. Ed*. **2009**, *48*, 521–524.

Scheme 1. Schiff-Base Ligand (H_3L) Used in Synthesis of Compound **1**



complexes contain Mn−Ln or Cu−Ln cores.[18] All the other transition metals have rarely been used and investigated in such bimetallic systems. Among those, few compounds with a Fe-Ln cluster core have been reported, and only four of them have been characterized as SMMs.[19−23]

In the present paper, the synthesis, structure determination, and magnetic properties of a family of isostructural heterobimetallic Fe-Ln complexes of general formula $[Fe^{III}{}_4Ln^{III}{}_2(H_2L)_2(HL)_2L_2(CH_3OH)_2((CH_3)_3CCOO)_2(NO_3)_2][Ln^{III}(NO_3)_4(H_3L)(CH_3OH)]\cdot NO_3\cdot H_2O$ is described, hereafter abbreviated as $[Fe_4Ln_2][Ln]$, where H_3L is a trihydroxy Schiff-base ligand (Scheme 1) and Ln is Nd, Gd, Tb, Dy, and Ho, for compounds **1**, **2**, **3**, **4**, and **5**, respectively. The oxidation states of the metal ions were estimated by using bond valence sum (BVS) calculations.[24,25] Among these five new coordination compounds, only **4** shows a slow relaxation of the magnetization at low temperatures, which may be indicative of SMM behavior.

Experimental Section

Physical Measurements. Elemental analyses (for C, H, and N) were carried out on a Perkin-Elmer 2400 series II analyzer. Infrared spectra were recorded using reflectance technique over the range of 4000−300 cm^{-1} on a Perkin-Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device. X-ray powder diffraction data were collected on a Philips X'Pert diffractometer, using the monochromatic Cu Kα radiations.

Crystallography. X-ray Structure Determinations of **1** & **4**: Crystals were mounted in the 90(2) K nitrogen cold stream provided by a Oxford Cryosystems Cryostream 700 Plus low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a Platinum200 CCD detector on beamline 11.3.1 at the Advanced Light Source in Berkeley, CA. Diffraction data were collected using synchrotron radiation, monochromated using silicon(111) to a wavelength of 0.77490(1) Å. An approximate full sphere of data was collected using 0.3° ω scans. The data were integrated using the program SAINT V7.56A. A multiscan correction for absorption was applied using the program SADABS-2008/1. The structures were solved by direct methods (SHELXS-97), refined by full-matrix least-squares on F^2 (SHELXL-97) and determined to be isostructural.[26,27] The lanthanide complex ion sits slightly off an inversion center, creating a significant amount of disorder, which required modeling with restraints. The hydrogen atoms on carbon atoms were generated geometrically and refined as riding atoms with C−H = 0.95−0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH and CH_2 groups and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 groups. Crystal Data for **1**: $C_{41.50}H_{54.70}N_7O_{25.84}Fe_2Nd_{1.50}$, M_w = 1393.12, monoclinic, *C*2/*c*, *a* = 28.436(2) Å, *b* = 15.4647(13) Å, *c* = 25.171(2) Å, β = 92.1510(10)°, *V* = 11061.3(16) $Å^3$. A total of 105860 reflections were collected, of which 12225 were unique [*R*(int) = 0.0534], and 9807 were observed [$I > 2\sigma(I)$]. Refinement was completed using 861 parameters and 341 restraints. The maximum and minimum peaks in the final difference Fourier map were 2.646 and −1.261 $eÅ^{-3}$. *T* = 150(2) K, *Z* = 8, R_1 [$I > 2\sigma(I)$] = 0.0533, wR_2 (all data) = 0.1657, GOF (on F^2) = 1.018. Crystal Data for **4**: $C_{41.50}H_{54.70}N_7O_{25.84}Fe_2Dy_{1.50}$, M_w = 1420.51, monoclinic, *C*2/*c*, *a* = 28.325(2) Å, *b* = 15.4176(11) Å, *c* = 24.9861(18) Å, β = 92.5940(10)°, *V* = 10900.2(13) $Å^3$. A total of 59461 reflections were collected, of which 11174 were unique [R(int) = 0.0591], and 8929 were observed [$I > 2\sigma(I)$]. Refinement was completed using 856 parameters and 337 restraints. The maximum and minimum peaks in the final difference Fourier map were 1.635 and −1.423 $eÅ^{-3}$. *T* = 150(2) K, *Z* = 8, R_1 [$I > 2s(I)$] = 0.0497, wR_2 (all data) = 0.1592, GOF (on F^2) = 1.079. CCDC reference numbers for **1** and **4** are 743082 and 743083, respectively.

Magnetic Measurements. Both dc and ac magnetic susceptibilities were measured on a Quantum Design MPMS-XL-5 SQUID magnetometer down to 2 K. Diamagnetic corrections were applied for the sample holder, determined experimentally, and for the complexes, evaluated through Pascal's constants of all the constituent atoms, respectively.[28]

Synthesis. All the syntheses were carried out in air with commercially available reagents as A. R. grade (Fluka), without performing any further purification. Preparation of $[Fe_3(\mu_3\text{-}O)(piv)_6(H_2O)_3]piv$: The trinuclear iron compound was prepared by a slight modification of an early reported procedure.29 Fe(NO3)3·9H2O (10 g, 24.8 mmol) and pivalic acid (Hpiv, 28.0 g, 290 mmol) were heated slowly under stirring to 160 ± 5 °C over 3 h until the elimination of brown NO_2 gas had stopped. Upon the solution being cooled to 75−80 °C, ethanol (85 mL) and water (15 mL) were added slowly under stirring. Upon standing overnight, red-brown hexagonal prism-shaped crystals of $[Fe_3(\mu_3\text{-}O)(piv)_6(H_2O)_3]piv$ were obtained. The crystals were filtered off, washed with benzene and hexane, and dried in air.

General Synthetic Procedure for Complexes 1−5. A solution of 2-amino-1,3-propanediol (0.091 g, 1 mmol) and salicylaldehyde (0.122 g, 1 mmol) in methanol:acetonitrile solution (5 mL + 20 mL) was stirred for 10 min at 70 °C, followed by the addition of 0.5 mmol of $Ln(NO_3)_3\cdot xH_2O$. To the resulting yellow solution, 110 mg (0.12 mmol) of $[Fe_3(\mu_3\text{-}O)(piv)_6(H_2O)_3]piv$ were added. The resulting dark solution was refluxed for 1 h and then filtered while still hot. The filtrate was kept undisturbed for the slow evaporation of the solvent. Dark-red crystals were formed after 1 week. Yield: 49% (1), 42% (2), 39% (3), 42% (4), 41% (5). Elemental analysis for the general formula $C_{83}H_{111}N_{14}O_{50}Fe_4Ln_3$ corresponding to the formula $[Fe^{III}{}_4Dy^{III}{}_2(H_2L)_2(HL)_2L_2(CH_3OH)_2((CH_3)_3CCOO)_2(NO_3)_2]$-$[Dy^{III}(NO_3)_4(H_3L)(CH_3OH)]\cdot NO_3\cdot H_2O)$, and excluding possible small amounts of disordered water. (1) Calcd: C, 36.10; H, 4.05; N, 7.10. Found: C, 35.60; H, 4.00; N, 7.00. (2) Calcd: C, 35.55; H, 3.99; N, 6.99. Found: C, 34.67; H, 3.78; N, 6.79. (3) Calcd: C, 35.53; H. 3.99; N. 6.99. Found: C, 34.97; H, 3.78; N, 6.88. (4) Calcd: C, 35.40; H, 3.97; N, 6.96. Found: C, 35.13; H, 3.79; N, 6.68. (5) Calcd: C, 35.31; H, 3.96; N, 6.95. Found: C, 34.87; H, 3.97; N, 6.98. FTIR (neat, cm^{-1}): (1) 1640 (s), 1621 (s),

---

(18) Andruh, M.; Costes, J. P.; Diaz, C.; Gao, S. *Inorg. Chem.* **2009**, *48*, 3342–3359.

(19) Ferbinteanu, M.; Kajiwara, T.; Choi, K. Y.; Nojiri, H.; Nakamoto, A.; Kojima, N.; Cimpoesu, F.; Fujimura, Y.; Takaishi, S.; Yamashita, M. *J. Am. Chem. Soc.* **2006**, *128*, 9008–9009.

(20) Abbas, G.; Lan, Y.; Mereacre, V.; Wernsdorfer, W.; Clérac, R.; Buth, G.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2009**, *48*, 9345–9355.

(21) Akhtar, M. N.; Mereacre, V.; Novitchi, G.; Tuchagues, J. P.; Anson, C. E.; Powell, A. K. *Chem. Eur. J.* **2009**, *15*, 7278–7282.

(22) Murugesu, M.; Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Polyhedron* **2006**, *25*, 613–625.

(23) Pointillart, F.; Bernot, K.; Sessoli, R.; Gatteschi, D. *Chem. Eur. J.* **2007**, *13*, 1602–1609.

(24) Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585–1588.

(25) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247.

(26) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

(27) Tvaroska, I.; Rochas, C.; Taravel, F. R.; Turquois, T. *Biopolymers* **1992**, *32*, 551–560.

(28) Kahn, O., *Molecular Magnetism*; Wiley-VCH: Weinheim, Germany, 1993.

1601 (m), 1538 (s), 1471 (s), 1417 (s), 1290 (s), 1278 (s), 1117 (m), 1062 (s), 991 (m), 754 (s); (2) 1643 (s), 1621 (s), 1602 (m), 1538 (s), 1471 (s), 1417 (s), 1292 (s),1278 (s), 1117 (m), 1062 (s), 994 (m), 754 (s); (3) 1645 (s), 1621 (s), 1601 (m), 1548 (s), 1472 (s), 1418 (s), 1292 (s), 1278 (s), 1117 (m), 1063 (s), 992 (m), 754 (s); (4) 1644 (s), 1621 (s), 1601 (m), 1547 (s), 1479 (s), 1418 (s), 1293 (s), 1278 (s), 1116 (m), 1064 (s), 991 (m), 755 (s); (5) 1645 (s), 1621 (s), 1601 (m), 1549 (s), 1480 (s), 1418 (s),1294 (s), 1278 (s), 1117 (m), 1064 (s), 996 (m), 754 (s).

Results and Discussion

Synthesis and Crystal Structures. The starting trinuclear iron(III) compound $[Fe_3(\mu_3\text{-}O)(piv)_6(H_2O)_3]piv$ (piv = pivalate) was synthesized applying a slightly modified literature procedure.[29] Compounds **1**−**5** were synthesized by the following way. The Schiff-base ligand was prepared in situ in a methanol/acetonitrile solution (1:4), prior to the addition of $Ln(NO_3)_3\cdot xH_2O$. As a source of Fe^{III} ion, $[Fe_3(\mu_3\text{-}O)(piv)_6(H_2O)_3](piv)$ was then added to the resulting solution, and the resulting reaction mixture was refluxed. Dark crystals were obtained by slow evaporation of the filtered solution during 1 week. The single-crystal structures of compounds **1** and **4** have been determined by X-ray diffraction. These isostructural compounds crystallize in the monoclinic space group C_2/c, their structure being built up from a hexanuclear $[Fe_4Ln_2]^{2+}$ cation, an anionic $[Ln]^-$ mononuclear complex and a lattice nitrate anion, as was some disordered lattice water. The hexanuclear $[Fe_4Dy_2]^{2+}$ unit of **4** is depicted in Figure 1 (and that of **1** is given in Figure S1). The metal atoms are organized in an "S" shape along the backbone of the cluster and are connected by the deprotonated μ-phenoxide and μ-alkoxide groups of the Schiff-base ligand. In this hexanuclear unit, the two Dy^{III} ions are located at the two terminal positions of the "S"-shape chained cluster, while the four Fe^{III} ions comprise the central part of the chain (Figure 1a). The complex is centrosymmetric and each half consists of one Dy^{III} (Dy1) and two Fe^{III} (Fe1, Fe2) ions. The Dy^{III} ion in the chain is nine coordinated by one bidentate nitrate anion (oxygen atoms O53 and O54), one methanol molecule (oxygen atom O91), two Schiff-base ligands and one pivalate. The singly deprotonated Schiff-base ligand (H_2L) coordinates with four donor atoms, i.e., the oxygen atoms O22 and O23 from terminal neutral hydroxyl groups, one imino nitrogen atom (N21), and one phenoxido oxygen atom (O21), which acts as a bridge between the metal centers Dy1 and Fe1. The Dy1 and Fe1 ions are separated by a distance of 3.392 Å and the ∠Fe(1)—O(21)—Dy(1) is 102.86°. The coordination sphere of Dy1 is completed by one carboxylate oxygen atom (O52) from a bridging pivalate group, and the terminal phenoxide bridging oxygen atom (O32) from another Schiff-base (HL). The latter also connects Fe(1) and Dy(1) with an ∠Fe(1)—O(32)—Dy(1) of 103.17°. The other oxygen atom (O51) of the bridging carboxylate group coordinates Fe1. Fe1 exhibits an octahedral coordination environment consisting of a doubly deprotonated Schiff-base ligand (HL) occupying three equatorial sites with one imino nitrogen (N31) and two oxygen atoms (O31 and O32). The deprotonated phenoxy oxygen atom (O31) further coordinates to Fe(2), thus forming a bridge between the iron ions, with an ∠Fe(1)—O(31)—Fe (2) of 100.84° and a separation distance of 3.192 Å. Two Fe2 atoms are sitting in the middle of the "S-shape cluster chain", bridged by two μ-oxygen atoms (O12) with an ∠Fe(2)—O(12)—Fe(2) of 100.00° and a separation distance of 3.074 Å. A triply deprotonated Schiff-base (L) coordinates equatorially to Fe2 through three donor atoms (N11, O11, O12).

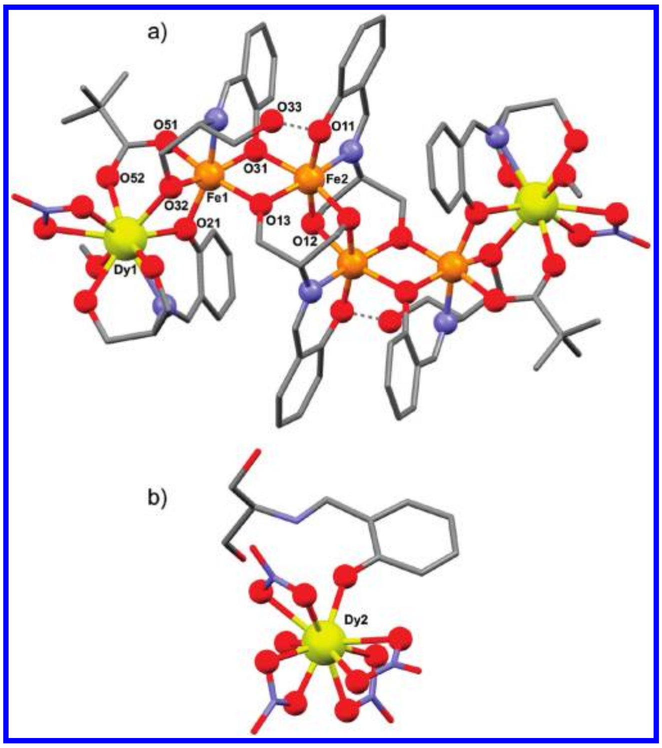


Figure 1. (a) Projection of the centrosymmetric hexanuclear $[Fe_4Dy_2]^{2+}$ unit of compound **4**, highlighting its S-shaped core. (b) View of one of the component of the disordered mononuclear anionic unit of compound **4**. Metal ions and their coordination sphere, as well as oxygen atoms involved in bridging or intramolecular H-bonds (dashed lines), are shown as balls and sticks. Hydrogen atoms are omitted for clarity. Color code: Dy, yellow; Fe, orange; O, red; N, blue; C, gray.

Table 1. Selected Bond Lengths (Å) and Angles (°) for Compound **4**

Fe(1)−O(13)	2.010(4)	Dy(1)−O(32)	2.349(4)
Fe(1)−O(21)	1.998(4)	Dy(1)−O(52)	2.332(4)
Fe(1)−O(31)	2.020(4)	Dy(1)−O(53)	2.453(4)
Fe(1)−O(32)	1.969(4)	Dy(1)−O(54)	2.571(4)
Fe(1)−O(51)	2.021(4)	Dy(1)−O(91)	2.390(5)
Fe(1)−N(31)	2.121(5)	Dy(1)−N(21)	2.475(5)
Fe(2)−O(11)	1.951(4)	Dy(1)−O(21)	2.332(4)
Fe(2)−O(12)	1.973(4)	Dy(1)−O(22)	2.399(4)
Fe(2)−O(13)	1.989(4)		
Fe(2)−O(31)	2.120(4)	Fe(1)—O(31)—Fe(2)	100.84(18)
Fe(2)−N(11)	2.089(5)	Fe(1)—O(13)—Fe(2)	105.91(19)
Dy(1)−O(21)	2.332(4)	Fe(1)—O(32)—Dy(1)	103.17(17)
Dy(1)−O(22)	2.399(4)	Fe(1)—O(21)—Dy(1)	102.86(17)
Dy(1)−O(23)	2.455(4)	Fe(2)—O(12)—Fe(2′)	100.00(18)

Selected bond distances and angles are listed in Table 1. The mononuclear anionic $[Dy^{III}(NO_3)_4(H_3L)(CH_3OH)]^-$ unit is strongly disordered over a crystallographic inversion center (Figure 1b shows one of the forms). In this mononuclear unit, the lanthanide ion is ten coordinate. Eight coordination sites are satisfied by four nitrate ions,

---

[29] Batsanov, A. S.; Struchkov, Y. T.; Timko, G. A. *Koord. Khim.* **1988**, *14*, 266–270.

one site is occupied by a methanol and the remaining position is occupied by one phenolic oxygen atom belonging to one neutral Schiff-base ligand. This mononuclear anionic unit is hydrogen bonded to the hexanuclear unit *via* the terminal hydroxy groups of the ligand, generating a zigzag framework (see the Supporting Information, Figures S5 and S6).

X-ray powder diffraction studies for all five compounds reveal comparable patterns, thus indicating an isomorphous character (see Figure S3 in the Supporting Information). The infrared spectra of all compounds are very similar as well (see Figure S4 in the Supporting Information), further confirming the isostructural nature of the five compounds.

Magnetic Properties. dc magnetization measurements were carried out on polycrystalline samples of compounds **1-5** in the temperature range 2−300 K. The derived χT vs T plots are shown in Figure 2, where χ is the molar magnetic susceptibility per $[Fe_4Ln_2][Ln]$ formula unit. At 300 K, the product χT is 17.44, 33.45, 43.78, 49.53, and 50.19 cm^3K/mol, respectively, for **1**−**5**. On lowering the temperature, a similar steady decrease of χT is observed for all five compounds down to, respectively, ca. 6.3, 24.7, 35.2, 37.7, and 39.5 cm^3K/mol at 50 K. At lower temperatures, χT decreases further in a more abrupt manner in the case of the Ho compound **5**, down to 9.7 cm^3K/mol at 2 K. On the other hand, a plateau is slowly reached at low temperatures for the four other compounds, respectively at ca. 1.8, 21, 28.3, and 29.7 cm^3K/mol for **1**−**4** (see Figure S6 in the Supporting Information). In the case of the Tb and Dy compounds **3** and **4**, a further decrease sets in below 5 K, down to 22.8 and 26.9 cm^3K/mol at 2 K.

The experimental data of all compounds can be fitted satisfactorily to a Curie−Weiss law, i.e., down to 30 K for the Nd compound **1** and down to 100 K for **2**−**5**, leading to the following Curie and Weiss constants: $C = 26.91$ cm^3K/mol and $\theta = -163.34$ K for **1**; $C = 37.28$ cm^3K/mol and $\theta = -36.36$ K for **2**; $C = 47.68$ cm^3K/mol and $\theta = -29.40$ K for **3**; $C = 53.86$ cm^3K/mol and $\theta = -28.14$ K for **4**; and $C = 53.74$ cm^3K/mol and $\theta = -24.09$ K for **5** (full lines given in Figure 2 and Figure S6 in the Supporting Information). These Curie constants are in reasonably good agreement with the expected values for four Fe^{III} ($S = 5/2$) and three Ln^{III} noninteracting ions: 22.42 cm^3K/mol for **1** (Nd^{III}: $^4I_{9/2}$, $S = 3/2$, $L = 3$, $g = 8/11$, $C = 1.64$ cm^3K/mol), 41.12 cm^3K/mol for **2** (Gd^{III}: $^8S_{7/2}$, $S = 7/2$, $L = 0$, $C = 7.875$ cm^3K/mol for $g = 2$), 52.93 cm^3K/mol for **3** (Tb^{III}: $^7F_6$, $S = 3$, $L = 3$, $g = 3/2$, $C = 11.81$ cm^3K/mol), 60.01 cm^3K/mol for **4** (Dy^{III}: $^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17$ cm^3K/mol) and 59.68 cm^3K/mol for **5** (Ho^{III}: $^5I_8$, $S = 2$, $L = 6$, $g = 5/4$, $C = 14.06$ cm^3K/mol). The observed lowering of χT is typical of dominant antiferromagnetic (AF) interactions, but the thermal depopulation of the Stark sublevels of the Ln^{III} ion ground states may also participate to it, except for the Gd compound, **2**. Indeed, similar Weiss negative constants are derived for compounds **2**−**5**, whereas a larger negative Weiss constant is obtained for the Nd compound **1**. Given the known weak interactions between lanthanide and 3d metal ions, the dominant AF interaction has to be ascribed to one of the two Fe−Fe interactions within the $[Fe_4]$ unit, most likely that between Fe1 and Fe2, since it shows larger Fe−O−Fe angles, thus providing a stronger overlap among magnetic orbitals.

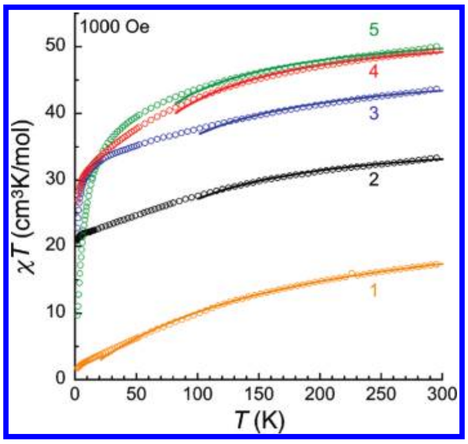


Figure 2. Temperature dependence of the χT product for compounds **1**−**5**. χ is the molar magnetic susceptibility per $[Fe_4Ln_2][Ln]$ formula unit. Full lines are Curie−Weiss fits of the high temperature data (see text).

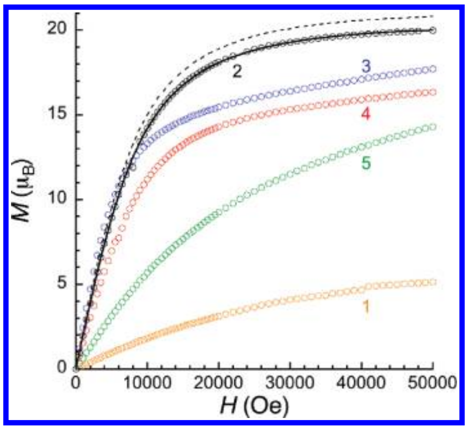
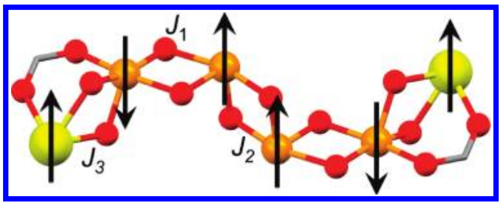


Figure 3. Field dependence of the magnetization for compounds **1**−**5** at 2 K. The dashed line is the Brillouin function for three spin 7/2 with $g = 2$, whereas the full line is the best fit of the data of compound **2** to a Brillouin function for three spin 7/2, yielding a g value of 1.94.

Field-dependence measurements of the magnetization up to 5 T were performed at 2 K for compounds **1**−**5**, and are shown in Figure 3. Saturation is almost reached at 5 T at ca. 20 μ_B in the case of the Gd compound **2**, close to the value expected for three isolated $S = 7/2$ spins, 21 μ_B. On the other hand, a lack of saturation is observed for the four other compounds, and in a more pronounced manner for the Ho compound **5**. This behavior is likely related to thermal and/or field-induced population of excited states, but also to the intrinsic magnetic anisotropy of the Ln^{III} ions, especially in the case of Tb and Dy. The experimental data for the Gd compound **2** is perfectly reproduced by a Brillouin function for 3 isolated 7/2 spins with a g value of 1.94 (see full line in Figure 3), in agreement with the presence of only three Gd^{III} spins. Given the isostructural nature of the five compounds, the most likely situation at low temperatures corresponds to only three Ln^{III} spins in all five compounds: the isolated Ln^{III} ion and the two weakly coupled Ln^{III} ions belonging to the centrosymmetric $[Fe_4Ln_2]$ unit. For these two latter Ln^{III} spins to have the same orientation, independent of the Ln−Fe interaction (J_3 in Scheme 2, J_3 can be expected to change sign along the Ln series), the central Fe−Fe

Scheme 2. Topology of the Intra-Complex Interactions in **1**−**5**, with J_1 and $J_3 < 0$ (AF) and $J_2 > 0$ (F), the dominant interaction being J_1



coupling (J_2 in Scheme 2) needs to be ferromagnetic (F), whereas the outer Fe−Fe coupling (J_1 in Scheme 2) should then be AF. As mentioned above, this behavior is in good agreement with the smaller Fe2−O12−Fe2 angle of 99.99° and the shorter Fe2−Fe2 separation of 3.074 Å with respect to the Fe1−O−Fe2 angles (105.93 and 100.83°) and Fe1−Fe2 separation (3.192 Å), and the magneto-structural correlations for known Fe(III) oxido, hydroxido and/or alkoxido complexes.[30−32] With this coupling scheme, in which the dominant AF interaction is J_1, the spin topology within the [Fe_4Ln_2] moieties can be depicted as shown in Scheme 2. The presence of slow dynamics in these molecular systems was systematically probed through ac susceptibility measurements, carried out in the frequency range 100−1500 Hz and at temperatures between 2 and 10 K. At zero dc applied field, no out-of-phase component of the susceptibility was detected down to 2 K for all five compounds. Because quantum tunneling effects can produce fast zero-field relaxation, small dc fields between 0 and 1 T were applied while monitoring ac susceptibilities of **1**−**5**. Only in the case of the Dy compound 4, this resulted in the onset of a frequency-dependent out-of-phase susceptibility, the optimum field range being 1000−1500 Oe. Thus ac data were collected at variable temperature in a 1000 Oe dc field (see Figure 4), now showing a clear frequency-dependent out-of-phase signal, suggesting that **4** is indeed behaving as a SMM.[33] Unfortunately, the maximum in χ'' is not reached in the accessible range of frequencies and temperatures of our equipment, thus impeding the determination of the corresponding relaxation times τ, and indicating a rather small energy gap. SMM properties of lanthanide-containing polynuclear complexes are known to be modulated by the metal ions used, the largest energy barriers being mostly observed for Dy(III) compounds.[15] Nonetheless, it is now well-established that mononuclear lanthanide complexes may behave as SMM, when their coordination environment results in highly anisotropic situations. In particular, the highest anisotropy barriers have been found in mononuclear bis-phtalocyanine-based lanthanide complexes of Tb(III).[34]

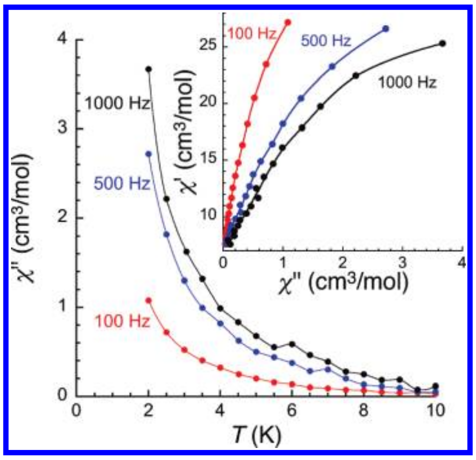


Figure 4. Temperature dependence of out-of-phase (χ'') ac susceptibility component at different frequencies and 1000 Oe applied dc field and Cole−Cole plot (inset) for compound **4**. Lines are only guides to the eye.

In this family of compounds, the Dy(III) complex exhibits slow relaxation of magnetization at much smaller temperatures, rather close to what we observe for compound **4**.[35] Therefore, it is a valid hypothesis that the observed slow relaxation of magnetization in compound 4 arises from the isolated mononuclear $[Dy]^-$ anion, and not from the $[Dy_2Fe_4]^+$ cation.[36] Indeed, the environment of the isolated Dy ion does present some axial anisotropy (two much shorter Dy−O bond distances, e.g., with O41 and O99). Although the fact that we do not observe any slow relaxation of magnetization in the Tb compound would then be surprising, it is still a plausible hypothesis since even tiny variations in the lanthanide ion environment have been shown to have strong effects on the spin dynamics.[37] Lower temperature experiments on single crystals would be necessary to ascertain the origin of the slow dynamics in compound **4** and its potential presence in the other compounds of the present series.

Conclusions

A new family of five isomorphous complexes containing a $[Fe^{III}{}_4Ln^{III}{}_2]^{2+}$ cation and separate $[Ln^{III}]^-$ species has been synthesized from a Schiff-base ligand bearing two hydroxyalkyl arms, a trinuclear iron precursor complex and lanthanide nitrates. The $[Fe_4Ln_2]^{2+}$ complexes present a S-shaped linear arrangement of the metal ions with a central Fe_4 core, and are connected in a zigzag fashion in the crystal lattice, through intermolecular hydrogen bonds. Comprehensive magnetic studies and magnetostructural analysis were performed suggesting the presence of both a dominant antiferromagnetic and a weak ferromagnetic interactions among the iron ions. Among the five compounds, compound **4** was found to show frequency-dependent ac-susceptibility,

---

(30) Cañada-Vilalta, C.; O'Brien, T. A.; Brechin, E. K.; Pink, M.; Davidson, E. R.; Christou, G. *Inorg. Chem.* **2004**, *43*, 5505–5521.

(31) Khanra, S.; Konar, S.; Clearfield, A.; Helliwell, M.; McInnes, E. J. L.; Tolis, E.; Tuna, F.; Winpenny, R. E. P. *Inorg. Chem.* **2009**, *48*, 5338–5349.

(32) Weihe, H.; Gudel, H. U. *J. Am. Chem. Soc.* **1997**, *119*, 6539–6543.

(33) It should be noted that nevertheless the SMM character would need to be confirmed by lower temperatures measurements to evidence the presence of hysteresis, because under an applied external dc field a non-SMM high-spin complex may show slow relaxation of magnetization. See Aromi, G.; Knapp, M. J.; Claude, J. P.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1999**, *121*, 5489–5499.

(34) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694–8695.

(35) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2931–2935.

(36) Note that the quantum processes in mononuclear lanthanide SMM is due to a fundamentally different mechanism from that of transition-metal-based SMMs, e.g., to resonant quntum tunneling between entangled states of the electronic and nuclear spin systems. See Giraud, R.; Wernsdorfer, W.; Tkachuk, A. M.; Mailly, D.; Barbara, B. *Phys. Rev. Lett.* **2001**, *87*, 4.

(37) Branzoli, F.; Carretta, P.; Filibian, M.; Zoppellaro, G.; Graf, M. J.; Galan-Mascaros, J. R.; Fuhr, O.; Brink, S.; Ruben, M. *J. Am. Chem. Soc.* **2009**, *131*, 4387–4396.

which suggests that the compound behaves as a SMM at low temperature.

Acknowledgment. Financial support and help from the FP6 Network of Excellence "Magmanet" is kindly acknowledged, (contract number 515767). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231.

Supporting Information Available: X-ray crystallographic data in CIF format of complexes **1** and **4**; additional crystallographic figures and comparison of XRPD and IR spectra for the five compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.