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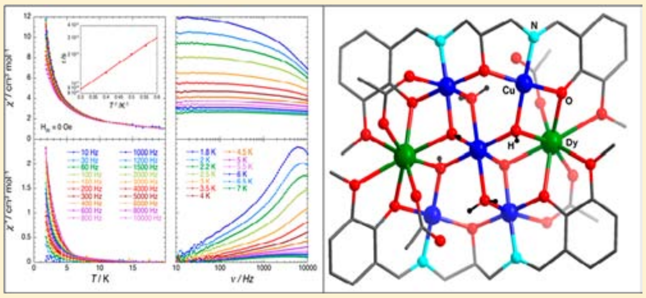
Syntheses, Structures, and Magnetic Properties of a Family of Heterometallic Heptanuclear $[Cu_5Ln_2]$ (Ln = Y(III), Lu(III), Dy(III), Ho(III), Er(III), and Yb(III)) Complexes: Observation of SMM behavior for the Dy(III) and Ho(III) Analogues

Vadapalli Chandrasekhar,*[†,‡] Atanu Dey,[†] Sourav Das,[†] Mathieu Rouzières,[§,∥] and Rodolphe Clérac*[§,∥]

[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India
[‡]Tata Institute of Fundamental Research, Centre for Interdisciplinary Sciences, 21 Brundavan Colony, Narsingi, Hyderabad-500075, India
[§]CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[∥]Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

S *Supporting Information*



ABSTRACT: Sequential reaction of the multisite coordination ligand (LH_3) with $Cu(OAc)_2·H_2O$, followed by the addition of a rare-earth(III) nitrate salt in the presence of triethylamine, afforded a series of heterometallic heptanuclear complexes containing a $[Cu_5Ln_2]$ core {Ln = Y(**1**), Lu(**2**), Dy(**3**), Ho(**4**), Er(**5**), and Yb(**6**)}. Single-crystal X-ray crystallography reveals that all the complexes are dicationic species that crystallize with two nitrate anions to compensate the charge. The heptanuclear aggregates in **1**−**6** are centrosymmetrical complexes, with a hexagonal-like arrangement of six peripheral metal ions (two rare-earth and four copper) around a central Cu(II) situated on a crystallographic inversion center. An all-oxygen environment is found to be present around the rare-earth metal ions, which adopt a distorted square-antiprismatic geometry. Three different Cu(II) sites are present in the heptanuclear complexes: two possess a distorted octahedral coordination sphere while the remaining one displays a distorted square-pyramidal geometry. Detailed static and dynamic magnetic properties of all the complexes have been studied and revealed the single-molecule magnet behavior of the Dy(III) and Ho(III) derivatives.

■ INTRODUCTION

Polynuclear metal complexes are attracting considerable attention in view of their wide range of potential applications in many fields, including physics,[1] chemistry,[2] biology,[3] nanotechnology,[4] and materials science.[5] For example, homo- and heteropolynuclear complexes are of interest because of their importance as magnetic materials, such as single-molecule and single-chain magnets,[6] which offer the possibility of testing fundamental questions in physics, such as low-dimensional magnetic properties, slow relaxation of the magnetization, quantum tunneling, or quantum interference.[7] From a practical point of view, these molecule-based magnets could be used for new and exciting applications, such as data storage, information processing,[8] quantum computing,[9] spintronics,[10] and low-temperature magnetic refrigerants.[11]

Initially, most of the SMMs were polynuclear metal complexes containing Mn(III) ions, which bring the magnetic anisotropy to the different molecular species.[12] This latter ingredient is fundamental to obtaining the SMM properties that are induced by combination of a high-spin ground state (S_T) and a large uniaxial magnetic anisotropy, D (considering the following Hamiltonian $H = DS_{T,z}^2$). These two characteristics create an energy barrier between the two ± m_{sT} ground states that is able to trap the magnetization in one of two energy minima at low enough temperature. In zero-dc field, slow relaxation of the magnetization is thus observed. Subsequent investigations revealed that, apart from other polynuclear 3d metal complexes, such as those containing Fe(II/III),[13] Co(II),[14] or Ni(II),[15] heterometallic complexes containing 3d/4f ions[16] are also promising systems to obtain SMM behavior. More recently, some mononuclear complexes have also reported to display SMM properties.[6a−g]

Among the 3d/4f systems, those containing Cu(II) metal ions[17] are particularly interesting in view of the favorable magnetic properties of such systems, including often ferromagnetic Cu(II)−Ln(III) interactions. The assembly of 3d/4f systems is facilitated by the use of appropriate compartmental ligands that contain different pockets to bind different metal ions. Recently, compartmental ligands, such as

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Table 1. Details of the Data Collection and Refinement Parameters for Compounds 1−3

	1	2	3
formula	$C_{46}H_{62}Cu_5Y_2N_6O_{34}$	$C_{46}H_{58}Cu_5Lu_2N_6O_{36}$	$C_{46}H_{62}Cu_5Dy_2N_6O_{34}$
MW/g·mol^{-1}	1738.54	1938.67	1885.77
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
unit cell dimensions (Å, deg)	a = 10.739(5)	a = 14.296(5)	a = 10.592(5)
	b = 12.555(5)	b = 15.466(5)	b = 12.485(5)
	c = 12.667(5)	c = 15.159(5)	c = 12.674(5)
	α = 102.406(5)		α = 101.990(5)
	β = 99.272(5)	β = 106.283(5)	β = 98.698(5)
	γ = 105.208(5)		γ = 105.724(5)
V/Å^3	1566.1(11)	3217.2(19)	1539.3(11)
Z	1	2	1
ρ_c/g cm^{-3}	1.843	2.001	2.034
μ/mm^{-1}	3.594	4.759	4.190
F(000)	875	1902	929
crystal size (mm^3)	0.16 × 0.13 × 0.10	0.16 × 0.13 × 0.09	0.16 × 0.12 × 0.08
θ range (deg)	2.32−25.50	2.63−26.50	2.09−26.50
limit hkl indices	$-12 \leq h \leq 12$	$-15 \leq h \leq 17$	$-11 \leq h \leq 13$
	$-13 \leq k \leq 15$	$-19 \leq k \leq 12$	$-15 \leq k \leq 13$
	$-15 \leq l \leq 11$	$-19 \leq l \leq 18$	$-12 \leq l \leq 15$
reflns. collected	8168	17 716	8656
ind. reflns.	5667 [R(int) = 0.0455]	6578 [R(int) = 0.0736]	6106 [R(int) = 0.0284]
completeness to θ (%)	97.3	98.5	95.8
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params.	5667/14/446	6578/9/450	6106/8/449
GOF on F^2	0.967	1.049	1.081
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0595	R_1 = 0.0498	R_1 = 0.0498
	wR_2 = 0.1453	wR_2 = 0.1219	wR_2 = 0.1174
R indices (all data)	R_1 = 0.0928	R_1 = 0.0667	R_1 = 0.0595
	wR_2 = 0.1662	wR_2 = 0.1358	wR_2 = 0.1239
largest diff. peak and hole (e·Å^{-3})	1.481 and −1.282	4.148 and −2.651	2.080 and −0.986

(S)P[N(Me)N=CH-C_6H_3-2-OH-3-OMe]$_3$, have allowed us to assemble several heterometallic trinuclear complexes like [Co-Ln-Co],[16n,o] (Ln = Gd(III), Dy(III), Tb(III), Ho(III), and Eu(III)), [Ni-Ln-Ni][16m] (Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), and Er(III)), and [Mn-Ln-Mn],[18] (Ln = Eu(III), Gd(III), and Dy(III)) derivatives possessing interesting magnetic properties. On the basis of this work, we designed ligands based on inorganic heterocyclic cyclo- and carbophosphazenes rings: [{$N_2P_2(O_2C_{12}H_8)_2$}{NP{N(CH_3)N=CH-C_6H_3-(2-OH)(3-OCH_3)}$_2$}] and [{NC(N(CH_3)$_2$)}$_2${NP{N(CH_3)N=CH-C_6H_3-(2-OH)(3-OCH_3)}$_2$}],[19] which lead to the isolation of magnetically interesting compounds. Both types of ligands, however, did not allow us to increase the nuclearity of the complexes beyond three. To assemble larger heterometallic polynuclear complexes, we oriented our research efforts toward a Schiff-base ligand, *N,N*′-bis(3-methoxysalicylidene)-1,3-diamino-2-propanol (H_3L). Although some homometallic complexes based H_3L were previously reported in the literature,[20] a series of 3d−4f heptanuclear complexes were synthesized for the first time with this ligand. Accordingly, herein, we report the synthesis and structural characterization of a new family of heterometallic heptanuclear [Cu_5Ln_2] complexes (Ln stands for rare-earth metal ions): [$Cu_5Y_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2$]$(NO_3)_2(H_2O)_2$ (**1**), [$Cu_5Lu_2(L)_2(\mu_3\text{-}OH)_4(\mu_3\text{-}OAc)_2(\mu\text{-}OAc)_2$]$(NO_3)_2(H_2O)_8$ (**2**), [$Cu_5Dy_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}H_2O)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2$]$(NO_3)_2(H_2O)_2$ (**3**), [$Cu_5Ho_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2$]$(NO_3)_2(H_2O)_2$ (**4**), [$Cu_5Er_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(HOEt)_2$]$(NO_3)_2$ (**3**), and [$Cu_5Yb_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(HOEt)_2$]$(NO_3)_2(H_2O)_2$ (**4**). The detailed magnetic properties of these complexes are also reported, including the SMM properties of the Dy(III) (**5**) and Ho(III) (**6**) analogues.

■ EXPERIMENTAL SECTION

Reagents and General Procedures. All the reagents and the chemicals were purchased from commercial sources and were used without further purification. The compound *N,N*′-bis(3-methoxysalicylidene)-1,3-diamino-2-propanol (H_3L) was prepared following a literature procedure.[20b] 1,3-Diaminopropan-2-ol, $Cu(OAc)_2{\cdot}H_2O$, and 3-methoxysalicylaldehyde (Fluka, Switzerland) were used as purchased. $Dy(NO_3)_3{\cdot}5H_2O$, $Ho(NO_3)_3{\cdot}5H_2O$, $Er(NO_3)_3{\cdot}5H_2O$, $Yb(NO_3)_3{\cdot}5H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, and $Lu(NO_3)_3{\cdot}H_2O$ were obtained from Sigma Aldrich Chemical Co. and were used as received.

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating at 400−4000 cm^{-1}. Elemental analyses of the compounds were obtained from a Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer.

Magnetic Measurements. The magnetic susceptibility measurements were obtained with the use of a MPMS-XL Quantum Design SQUID magnetometer and a PPMS-9 susceptometer. These magnetometer and susceptometer work between 1.8 and 400 K for dc applied fields ranging from −7 to 7 T (MPMS-XL). Measurements were

Table 2. Details of the Data Collection and Refinement Parameters for Compounds 4−6

	4	5	6
formula	$C_{46}H_{62}Cu_5Ho_2N_6O_{34}$	$C_{50}H_{70}Cu_5Er_2N_6O_{32}$	$C_{50}H_{70}Cu_5Yb_2N_6O_{32}$
MW/g·mol^{-1}	1890.58	1919.34	1930.90
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions (Å, deg)	a = 10.617(5)	a = 10.660(5)	a = 10.668(5)
	b = 12.461(5)	b = 12.466(5)	b = 12.440(5)
	c = 12.655(5)	c = 12.645(5)	c = 12.597(5
	α = 100.576(5)	α = 100.396(5)	α = 100.290(5)
	β = 98.813(5)	β = 98.948(5)	β = 98.910(5)
	γ = 106.441(5)	γ = 106.541(5)	γ = 106.710(5)
V/Å^3	1540.7(11)	1545.8(11)	1537.2(11)
Z	1	1	1
ρ_c/g cm^{-3}	2.038	2.062	2.086
μ/mm^{-1}	4.329	4.469	4.806
F(000)	931	949	953
crystal size (mm^3)	0.18 × 0.14 × 0.11	0.18 × 0.13 × 0.11	0.14 × 0.12 × 0.07
θ range (deg)	2.35−26.50	2.77−25.50	2.92−25.50
limit hkl indices	$-13 \leq h \leq 13$	$-12 \leq h \leq 12$	$-12 \leq h \leq 12$
	$-15 \leq k \leq 9$	$-15 \leq k \leq 8$	$-12 \leq k \leq 15$
	$-15 \leq l \leq 14$	$-15 \leq l \leq 15$	$-14 \leq l \leq 15$
reflns. collected	8746	8246	8188
ind. reflns.	6091 [R(int) = 0.0273]	5605 [R(int) = 0.0276]	5574 [R(int) = 0.0221]
completeness to θ (%)	95.3	97.2	97.1
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params.	6091/5/449	5605/17/455	5574/35/450
GOF on F^2	1.038	1.019	1.050
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0456	R_1 = 0.0369	R_1 = 0.0348
	wR_2 = 0.1202	wR_2 = 0.0920	wR_2 = 0.0855
R indices (all data)	R_1 = 0.0499	R_1 = 0.0418	R_1 = 0.0397
	wR_2 = 0.1239	wR_2 = 0.0962	wR_2 = 0.0890
largest diff. peak and hole (e·Å^{-3})	2.536 and −2.810	1.536 and −1.211	1.453 and −1.153

performed on polycrystalline samples of 13.48, 28.49, 10.58, 19.58, 25.69, and 25.04 mg for **1**−**6**, respectively, introduced in a polyethylene bag (3 × 0.5 × 0.02 cm). ac susceptibility measurements were measured with an oscillating ac field of 1 Oe with a frequency between 10 and 10 000 Hz (PPMS). M versus H measurements were performed at 100 K to check for the presence of ferromagnetic impurities that have been found absent. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

Synthesis. *Preparation of the Heptanuclear Complexes **1**−**6**.* The six metal complexes have been synthesized using the following general procedure: LH_3 (0.14 g, 0.4 mmol) was dissolved in a mixture of ethanol (20 mL) and acetonitrile (20 mL). $Cu(OAc)_2 \cdot H_2O$ (0.16 g, 0.8 mmol) and triethylamine (0.16 mL, 0.12 mmol) were added to this solution. The reaction mixture was refluxed for 12 h. At this stage, $Ln(NO_3)_3 \cdot nH_2O$ (0.4 mmol) was added, and the reaction mixture was stirred for a further period of 6 h at room temperature to afford a clear solution. The deep green-colored solution was evaporated to dryness, and the residue was washed with n-hexane and dissolved in a methanol/chloroform mixture (1:1) and kept for crystallization. After about a week, block-shaped green-colored crystals, suitable for X-ray crystallography were obtained. The characterization data for these complexes are given below.

*$[Cu_5Y_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2](NO_3)_2(H_2O)_2$ (**1**).* Yield: 0.12 g, 43% (based on Cu). mp: 192 °C (d). IR (KBr) cm^{-1}: 3384 (b), 2938 (m), 2678 (m), 2491 (w), 1649 (s), 1561 (s), 1468 (s), 1441 (s), 1384 (s), 1299 (w), 1242 (s), 1222 (s), 1168 (w), 1074 (w), 1037 (w) 987 (s), 951 (w), 856 (w), 826 (w), 786 (s), 747 (w), 685 (w), 612 (w), 557 (w), 480 (w). ESI-MS m/z, ion: 801.38, $[C_{46}H_{62}O_{26}N_4Cu_5Y_2]^{2+}$. Anal. Calcd for $C_{46}H_{66}Cu_5N_6O_{34}Y_2$ (1742.58): C, 31.71; H, 3.82; N, 4.82. Found: C, 31.21; H, 3.78; N, 4.80.

*$[Cu_5Lu_2(L)_2(\mu_3\text{-}OH)_4(\mu_3\text{-}OAc)_2(\mu\text{-}OAc)_2](NO_3)_2(H_2O)_8$ (**2**).* Yield: 0.13 g, 42% (based on Cu). mp: 187 °C (d). IR (KBr) cm^{-1}: 3434 (b), 2937 (m), 2677 (s), 2491 (w), 1640 (s), 1561 (s), 1471 (s), 1438 (s), 1384 (s), 1243 (w), 1221 (s), 1169 (s), 1116 (s), 1078 (w), 1036 (w), 967 (s), 856 (w), 833 (w), 785 (s), 740 (w), 684(s), 647 (w), 556 (w). ESI-MS m/z, ion: 842.42, $[C_{46}H_{54}O_{22}N_4Cu_5Lu_2]^{2+}$. Anal. Calcd for $C_{46}H_{70}Cu_5Lu_2N_6O_{36}$ (1950.73): C, 28.32; H, 3.62; N, 4.31. Found: C, 28.21; H, 3.78; N, 4.12.

*$[Cu_5Dy_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2](NO_3)_2(H_2O)_2$ (**3**).* Yield: 0.12 g, 40% (based on Cu). mp: 200 °C (d). IR (KBr) cm^{-1}: 3422 (b), 2938 (m), 2678 (w), 1649 (s), 1607 (s), 1561 (s), 1462 (s), 1441 (s), 1384 (s), 1296 (s), 1240 (s), 1220 (s), 1167 (w), 1069 (w), 1043 (w) 985 (s), 952 (w), 855 (w), 827 (w), 785 (s), 744 (w), 681 (w), 611 (w), 582 (w), 476 (w). ESI-MS m/z, ion: 865.91, $[C_{46}H_{62}O_{26}N_4Cu_5Dy_2]^{2+}$. Anal. Calcd for $C_{46}H_{66}Cu_5Dy_2N_6O_{34}$ (1889.77): C, 29.24; H, 3.52; N, 4.45. Found: C, 29.21; H, 3.48; N, 4.42.

*$[Cu_5Ho_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2](NO_3)_2(H_2O)_2$ (**4**).* Yield: 0.11 g, 36% (based on Cu). mp: 210 °C (d). IR (KBr) cm^{-1}: 3385 (b), 2974 (m), 2738 (s), 1637 (s), 1605 (s), 1561 (s), 1471 (s), 1440 (s), 1383 (s), 1317 (w), 1241 (s), 1221 (s), 1169 (w), 1079 (w), 1036 (w) 987 (s), 967 (w), 856 (w), 826 (w), 785 (s), 682 (w), 646 (w), 446 (w). ESI-MS m/z, ion: 874.94, $[C_{46}H_{62}O_{26}N_4Cu_5Ho_2]^{2+}$. Anal. Calcd for $C_{46}H_{66}Cu_5Ho_2N_6O_{34}$ (1894.63): C, 29.16; H, 3.51; N, 4.44. Found: C, 29.21; H, 3.38; N, 4.22.

*$[Cu_5Er_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(HOEt)_2](NO_3)_2$ (**5**).* Yield: 0.13 g, 42% (based on Cu). mp: 197 °C (d). IR (KBr) cm^{-1}: 3444 (b), 2938 (m), 2846 (w), 1651 (s), 1561 (s), 1465 (s), 1440 (s), 1397 (s), 1331 (s), 1237 (w), 1167 (s), 1112 (s), 1044 (w) 987 (s), 950 (w), 856 (w), 826 (w), 785 (s), 647 (w), 557 (w), 481 (w). ESI-MS m/z, ion: 898.46, $[C_{50}H_{70}O_{26}N_4Cu_5Er_2]^{2+}$. Anal. Calcd for

$C_{50}H_{70}Cu_5Er_2N_6O_{32}$ (1919.36): C, 31.29; H, 3.68; N, 4.38. Found: C, 31.11; H, 3.78; N, 4.17.

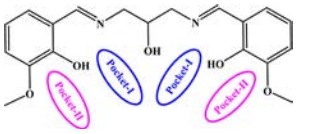
$[Cu_5Yb_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(HOEt)_2](NO_3)_2(H_2O)_2$ ***(6)***. Yield: 0.11 g, 36% (based on Cu). mp: 220 °C (d). IR (KBr) cm^{-1}: 3447 (b), 2975 (m), 2677 (m), 1652 (s), 1609 (s), 1562 (s), 1467 (s), 1440 (s), 1384 (s), 1332 (s), 1297 (m), 1242 (m), 1222 (s), 1167 (s), 1113 (s), 1074 (w), 1043 (w), 987 (s), 951 (w), 890 (w), 857 (w), 827 (w), 786 (s), 748 (w), 647 (w), 613 (w), 585 (w), 557 (w), 481 (w). ESI-MS *m/z*, ion: 904.48, $[C_{50}H_{70}O_{26}N_4Cu_5Yb_2]^{2+}$. Anal. Calcd for $C_{50}H_{70}Cu_5N_6O_{32}Yb_2$ (1930.92): C, 31.10; H, 3.65; N, 4.35. Found: C, 31.21; H, 3.78; N, 4.21.

X-ray Crystallography. Single-crystal X-ray diffraction data and the unit cell parameters for **1**−**6** are given in Tables 1 and 2. Crystals suitable for single-crystal X-ray analyses were obtained by slow evaporation of the reaction mixture. The diffraction data for **1**−**6** have been collected on a Bruker SMART CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å). The program SMART[21a] was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT[21a] for integration of the intensity of reflections and scaling, SADABS[21b] for absorption correction, and SHELXTL[21c,d] for space group, structure determination, and least-squares refinements on F^2. All the structures were solved by direct methods using the programs SHELXS-97[21e] and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[21e] Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The figures in the text have been generated using Diamond 3.1e software.[21f] Complexes **1**, **3**, **4**, **5**, and **6** crystallized in the triclinic $P\bar{1}$ space group, whereas **2** crystallized in the monoclinic $P2_1/n$ space group. The asymmetric unit of these complexes contains half of a molecule and a nitrate as the counteranion.

■ RESULTS AND DISCUSSION

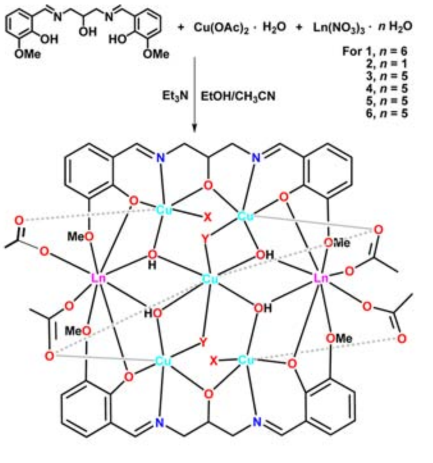
Synthetic Aspects. The LH_3 ligand possesses seven coordination sites, including two imino nitrogen atoms, two phenolic oxygen atoms, one alcoholic oxygen atom, and two oxygen atoms of the methoxy group (Scheme 1). On the basis of our recent results on the *N,N*′-(2-hydroxypropane-1,3-diyl)bis-(salicylaldimine) ligand,[22] one can anticipate that the compartmental LH_3 ligand containing two distinct coordination pockets, two O,N,O compartments suitable to accommodate 3d metal ions (pocket I, Scheme 1) and two O,O pockets able to accommodate rare-earth metal ions (pocket II, Scheme 1), should be able to stabilize 3d−4f complexes.

Scheme 1. Structure of the Ligand LH_3 Consisting of Two Distinct Coordination Pockets to Accommodate 3d (Pocket I) and 4f (Pocket II) Metal Ions



Accordingly, LH_3 reacts sequentially with $Cu(OAc)_2{\cdot}H_2O$ and $Ln(NO_3)_3{\cdot}nH_2O$ in a 1:2:1 stoichiometric ratio in the presence of triethylamine to afford heterometallic heptanuclear complexes $[Cu_5Y_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2](NO_3)_2(H_2O)_2$ (**1**), $[Cu_5Lu_2(L)_2(\mu_3\text{-}OH)_4(\mu_3\text{-}OAc)_2(\mu\text{-}OAc)_2](NO_3)_2(H_2O)_8$ (**2**), $[Cu_5Dy_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}H_2O)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2](NO_3)_2(H_2O)_2$ (**3**), $[Cu_5Ho_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(OH_2)_2](NO_3)_2(H_2O)_2$ (**4**), $[Cu_5Er_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(HOEt)_2](NO_3)_2$ (**5**), and $[Cu_5Yb_2(L)_2(\mu_3\text{-}OH)_4(\mu\text{-}OH_2)_2(\mu\text{-}OAc)_2(OAc)_2(HOEt)_2](NO_3)_2(H_2O)_2$ (**6**) in good yields (Scheme 2).

Scheme 2. Schematic Synthesis of the Heptanuclear Heterometallic Complexes 1−6



Ln = Dy, Ho and Y, X = Y = H_2O
Ln = Er and Yb X = EtOH, Y = H_2O
Ln = Lu, X = Y = None

The dashed Cu-O bonds between the terminal acetate and the central copper ion represent long Cu-O bonds found only in the case of the Cu_5Lu_2 (2)

Electrospray ionization mass spectrometry (ESI-MS) spectra of **1**−**6** reveal that they retain their molecular integrity in solution, as indicated by the presence of molecular ion peaks (see the Experimental Section). Thermogravimetric analyses were performed for complexes **1**−**6**, in order to investigate their thermal stability (Figure S4, Supporting Information). All the complexes show a similar type of thermal stability and decompose within 180−220 °C. The molecular structures of **1**−**6** were confirmed by single-crystal X-ray crystallography studies.

Molecular Structures of 1−6. X-ray crystallographic analysis of **1**−**6** reveals that all these complexes are dicationic species possessing a nearly similar structural arrangement (Figures 1−3 and Figures S1−S3, Supporting Information; Table 3 and Tables S1−S7, Supporting Information) with only minor structural variations, as indicated in Scheme 2. The heptanuclear aggregates **1**−**6** possess a centrosymmetrical molecular structure, as shown for the Cu_5Dy_2 analogue, **3**, in Figure 1. The central Cu3 site is lying on a crystallographic inversion center. The heptanuclear complexes of **1**−**6** are assembled together by the cumulative coordination action of two $[L]^{3-}$ symmetrically binding ligands (Scheme 2, Figure 1). The two fully deprotonated ligands utilize *all* their coordination sites to gather together the polynuclear heterometallic assembly. The deprotonated alcoholic oxygen of the Schiff-base ligands adopts a μ-coordination mode between Cu1 and Cu2 ions (Cu−O = 1.938−1.966 Å; Table 3). The deprotonated phenolate oxygen atoms form a μ-bridge between Cu1 and Cu2 sites and the lanthanide metal ions (Cu−O = 1.93−1.964 Å and Ln−O = 2.288−2.327 Å; Table 3). The six-coordinated central copper (Cu3) is linked to four Cu and two Ln ions via four μ_3-OH and two μ-OH_2 in the case of Cu_5Y_2 (**1**), Cu_5Dy_2 (**3**), Cu_5Ho_2 (**4**), Cu_5Er_2 (**5**), and Cu_5Yb_2 (**6**) complexes. In the case of the Cu_5Lu_2 derivative (**2**), the central hexacoordinated copper site is connected to the six surrounded metal ions (Cu1, Cu2, and Lu1) by four μ_3-OH bridges and two μ_3-OAc ligands (Scheme 2). The bond distances involving

Table 3. Selected Bond Distances (Å) for 1−6

	Ln = Y (**1**)	Ln = Lu (**2**)	Ln = Dy (**3**)	Ln = Ho (**4**)	Ln = Er (**5**)	Ln = Yb (**6**)
Ln−$O_{phenolate}$	2.327(5)	2.288(1)	2.320(2)	2.320(4)	2.323(4)	2.299(1)
	2.318(5)	2.288(1)	2.332(2)	2.31 (5)	2.296(4)	2.28(1)
Ln−O_{OMe}	2.525(5)	2.469(2)	2.526(2)	2.519(4)	2.514(4)	2.494(1)
	2.566(5)	2.532(1)	2.568(2)	2.557(4)	2.566(4)	2.567(1)
Ln−OH	2.353(3)	2.323(1)	2.41(2)	2.342(3)	2.333(3)	2.331(1)
	2.393(4)	2.277(1)	2.358(1)	2.396(4)	2.38(4)	2.357(1)
Ln−$OAc_{bridging}$	2.239(6)	2.227(1)	2.256(2)	2.25(5)	2.237(5)	2.216(1)
		2.251(1)				
Ln−$OAc_{terminal}$	2.236(6)		2.259(2)	2.26(4)	2.234(4)	2.214(1)
Cu−$O_{phenolate}$	1.952(4)	1.93(1)	1.98(2)	1.974(4)	1.957(3)	1.962(1)
	1.96(4)	1.93(1)	1.949(1)	1.957(3)	1.968(4)	1.964(1)
Cu−$O_{alcoholic}$	1.947(4)	1.938(1)	1.96(2)	1.962(4)	1.96(3)	1.966(1)
	1.954(4)	1.947(1)	1.959(1)	1.959(3)	1.956(4)	1.951(1)
Cu−$OH_{2\ bridging}$	2.457(6)		2.41(2)	2.411(5)	2.413(4)	2.299(1)
	2.337(7)		2.312(2)	2.302(6)	2.305(4)	2.408(1)
Cu−N	1.919(6)	1.959(2)	1.915(2)	1.92(6)	1.92(5)	1.921(1)
	1.921(7)	1.922(1)	1.923(2)	1.944(6)	1.94(5)	1.937(1)
Cu−OH	1.967(5)	1.967(1)	1.968(2)	1.966(5)	1.963(4)	1.962(1)
	1.962(4)	1.939(1)	2.026(1)	1.976(4)	1.974(4)	1.967(1)
	2.006(3)	1.952(1)	1.965(2)	2.025(3)	2.021(3)	2.021(1)
	1.96(5)	2.011(1)	1.957(2)	1.961(5)	1.967(4)	1.97(1)
Cu−OH_2/$EtOH_{terminal}$	2.554(8)		2.41(2)	2.433(5)	2.473(5)	2.477(1)
Cu−$OAc_{bridging}$	2.495(6)	2.345(2)	2.496(2)	2.484(5)	2.489(4)	2.457(1)
		2.37(1)				
		2.761(2)				

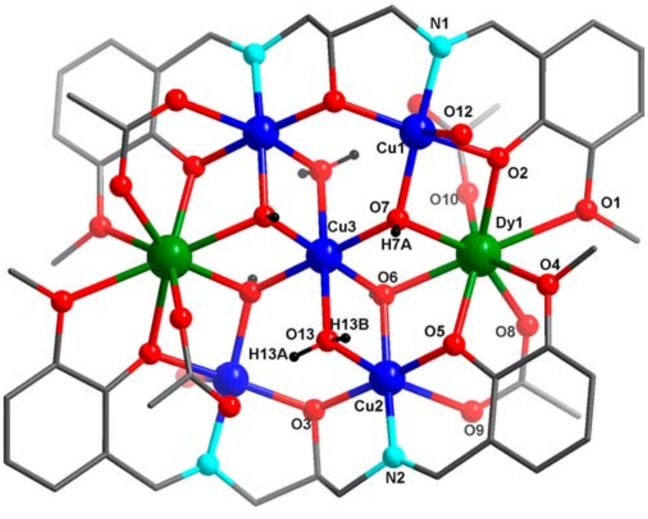


Figure 1. Dicationic part of the single-crystal X-ray structure of **3**. All hydrogen atoms (except hydroxy and bridging water) and solvent molecules have been omitted for clarity.

the μ_3-OH are Ln−O = 2.277−2.410 Å and Cu−O = 1.939−2.026 Å. On the other hand, the Cu−O bond distances involving the μ-OH_2 bridge are in the range of 2.302−2.457 Å (Table 3). BVS calculations were carried out to confirm the nature of hydroxide and water ligands (Table 4).[23] Whereas in complexes **1**, **3**, and **4**, one of the copper atoms (Cu1) is bound to a terminal water molecule (Cu−O = 2.41−2.554 Å), in **5** and **6**, this coordinated solvent is replaced by an ethanol molecule. Thus, in **1**, **3**, **4**, **5**, and **6**, copper ions are in three different coordination spheres: two are six-coordinate, while one is five-coordinate [see Figure 2: Cu2(6O), Cu3(5O,1N); Cu1(4O,1N)].

Table 4. BVS Calculation Values for Selected Oxygen Atoms

atom	BVS value	assignment
O6	1.35	OH^-
O7	1.22	OH^-
O13	0.31	OH_2

The coordination environment around the lanthanide ion is fulfilled by one terminal acetate (complexes **1**, **3**−**6**; Ln−O = 2.214−2.26 Å) as well as by two μ-OAc groups (complexes **1**, **3**−**6**; Ln−O = 2.216−2.256 Å and Cu−O = 2.457−2.496 Å; see Table 3), as shown by Scheme 2 and Figures 1 and 2. Complex **2** is structurally slightly different from the other analogues, as it does not possess a μ-bridging OH_2 molecule. Also, instead of the terminal acetate seen in the other complexes, two μ_3-OAc (to bridge together Cu3, Cu2, and Lu1) are present in **2** along with two μ-OAc bridges (see the Supporting Information). In this compound, long Cu−O bonds between terminal acetate and the central copper ion are present (Cu3−O8, 2.761(2) Å; Scheme 2, Table 3; Table S3 in the Supporting Information).

In all the compounds, the eight-coordinated lanthanide ion (Figure 2a) adopts a geometry that is far-removed from any idealized geometry and is a mixture of five ideal geometries (SAPR-8, TDD-8, JBTPR-8, BTPR-8, and JSD-8), which has been confirmed by the program SHAPE[24] (see the Supporting Information). The core of the heptanuclear assembly contains eight four-membered and two six-membered rings. The core is also characterized by the presence of two incomplete cubes (one missing vertex) that are joined to each other through the central copper (Figure 3a). The five copper atoms present in the heptanuclear core are in a perfect planar geometry with the two lanthanide ions being present above and below the Cu(II) plane with a distance of 1.055(1) Å (Figure 3b).

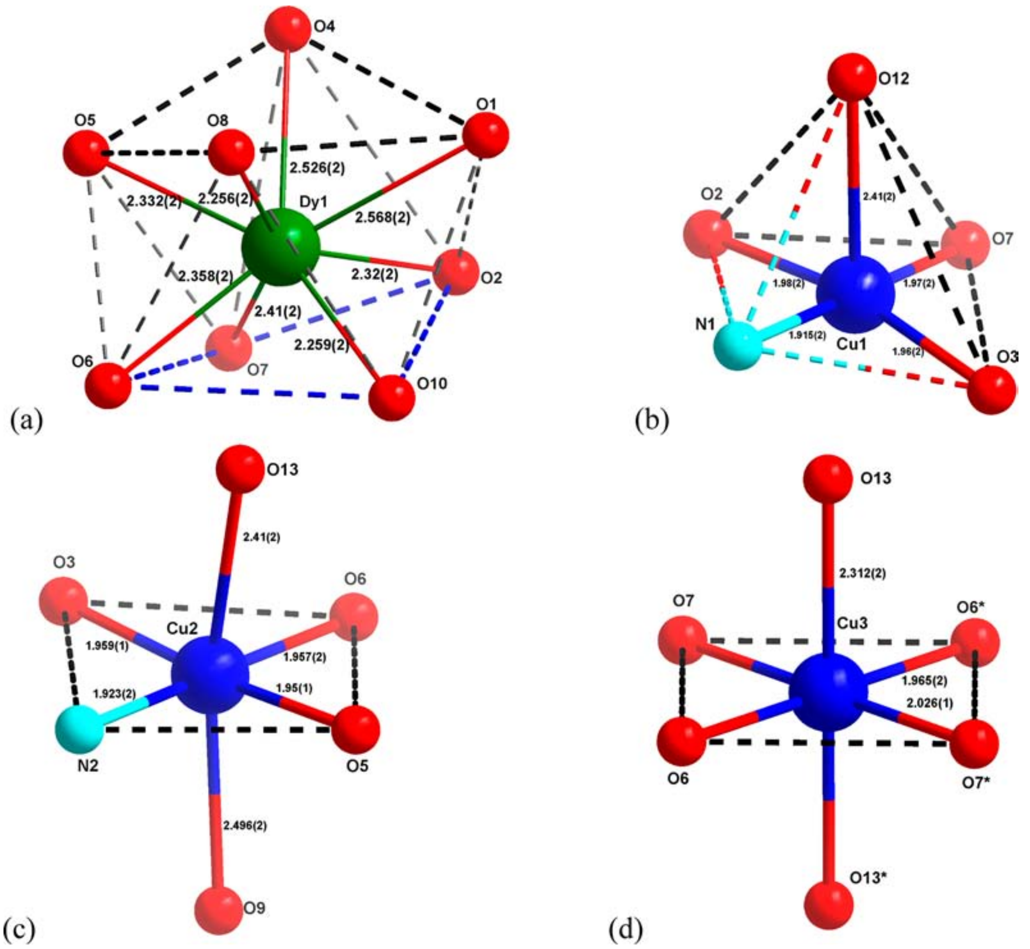


Figure 2. (a) Coodination environment around dysprosium in **3**. (b) Square-pyramidal geometry around Cu1 in **3**. (c) Distorted octahedral geometry around Cu2 in **3**. (d) Distorted octahedral geometry around the central copper ion (Cu3) in **3**. In all the cases, the Dy−O and Cu−O bond distances are also indicated.

It is also interesting to compare the present Cu_5Ln_2 series with a Cu_5Gd_2 complex previously reported by Powell and coworkers (Figure 4).[25] Unlike the present family of complexes, the example reported in the literature contains two well separated Cu−Gd−Cu motifs linked by a central Cu(II) through μ_3-OH and μ_3-Br bridging ligands. All the Cu_5Ln_2 species described in this work are better viewed as a hexanuclear Cu_4Ln_2 wheel accommodating a central Cu(II) ion (Figure 3a).

Static Magnetic Properties. Magnetic susceptibility measurements were carried out on polycrystalline samples of **1**−**6** in the 1.8−300 K temperature range at 1000 Oe. The room-temperature χT products estimated as 1.3 (**1**), 1.5 (**2**), 23.9 (**3**), 23.2 (**4**), 24.1 (**5**), and 5.3 (**6**) cm^3 K/mol are in relative good agreement with the presence of five Cu^{II} ions ($S = 1/2$, $g = 2$, $C = 0.375$ cm^3 K/mol) and two lanthanide metal ions: two diamagnetic Y^{III} metal ions for **1**, two diamagnetic Lu^{III} metal ions for **2**, two Dy^{III} metal ions ($S = 5/2$, $L = 5$, $^6H_{15/2}$, $g = 4/3$: $C = 14.1667$ cm^3 K/mol) for **3**, two Ho^{III} metal ions ($S = 2$, $L = 6$, $^5I_8$, $g = 5/4$: $C = 14.0625$ cm^3 K/mol) for **4**, two Er^{III} metal ions ($S = 3/2$, $L = 6$, $^4I_{15/2}$, $g = 6/5$: $C = 11.475$ cm^3 K/mol) for **5**, and two Yb^{III} metal ions ($S = 1/2$, $L = 3$, $^2F_{7/2}$, $g = 8/7$: $C = 2.5714$ cm^3 K/mol) for **6** (Table S8, Supporting Information).[26]

As shown in Figure 5, the magnetic properties of **1**−**6** are relatively different. Except for **1** and **2**, the lack of a χT product saturation at low temperatures suggests the absence of a well-defined ground state for these complexes. For **1** and **2**, upon decreasing the temperature, the χT product decreases down to 0.40 cm^3 K/mol at 1.8 K, indicating the presence of dominant antiferromagnetic interactions between the five magnetic centers leading to an $S_T = 1/2$ spin ground state. The χT product for **3**−**6** is also decreasing with the temperature, but it exhibits a clear minimum at ca. 10−20 K around 19.5, 18.1, 18.3, and 3.3 cm^3 K/mol, respectively, before increasing at lower temperatures up to 21.5, 25.6, 23.4, and 3.8 cm^3 K/mol at 1.8 K (Figure 5). For these complexes, it is difficult to conclude on the sign of the magnetic interactions between Ln(III) and Cu(II) spin carriers. Even knowing the presence of dominating antiferromagnetic interactions between Cu(II) spins on the basis of the magnetic properties of **1** and **2** (vide infra), the observed temperature dependence of the χT product could be induced by either weak ferromagnetic or antiferromagnetic Ln(III)···Cu(II) interactions combined with the thermal depopulation of the magnetic excited states of the lanthanide ions.[26]

Considering the number of magnetic pathways between spin carriers (Figure 1 and inset of Figure 5) and the difficulty to model magnetic complexes based on Dy(III) (**3**), Ho(III) (**4**), Er(III) (**5**), or Yb(III) (**6**) lanthanide ions, only **1** and **2** for which the Y(III) and Lu(III) ions are diamagnetic, could be analyzed and discussed. To model the temperature dependence

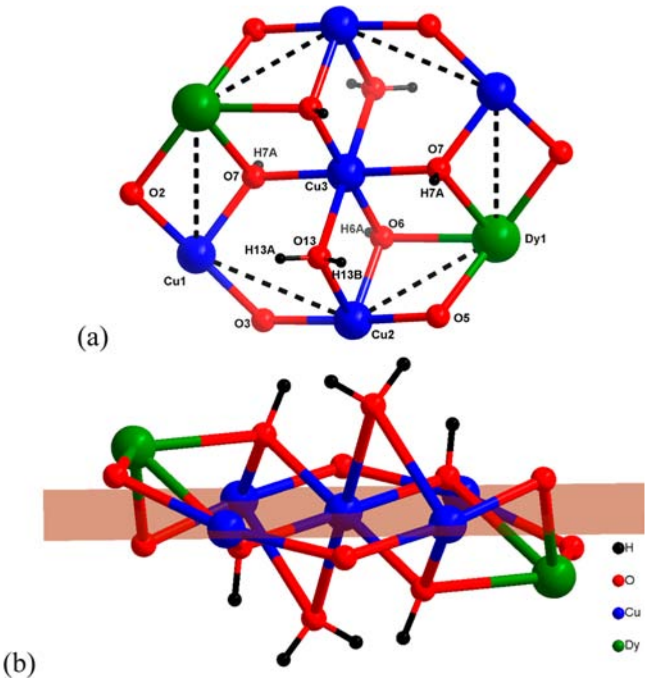


Figure 3. (a) Simplified view of the heptanuclear core in **3**, showing the hexagonal arrangement of six peripheral metal ions (four copper and two dysprosium) around the central copper ion. (b) Planar arrangement of the five copper atoms with the two dysprosium ions being present above and below the plane by 1.055(1) Å.

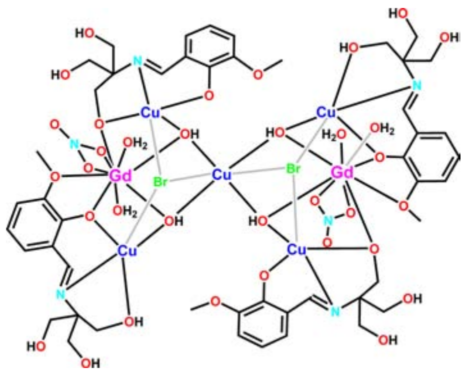


Figure 4. Dicationic portion of the heterometallic heptanuclear Cu_5Gd_2 complex known in the literature.[25]

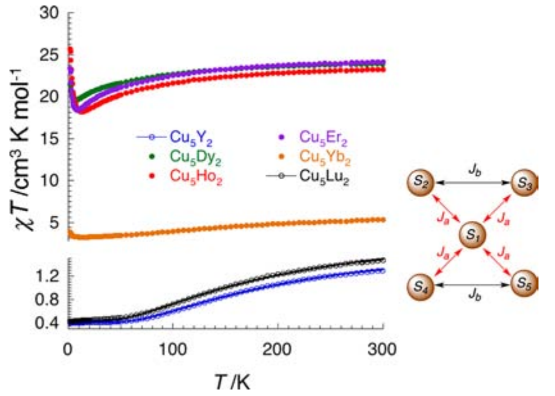


Figure 5. Temperature dependence of the χT product of compounds **1**−**6** (where $\chi = M/H$ per complex) measured at $H = 0.1$ T. The solid lines superposed to the magnetic properties of complexes **1** and **2** are the best fit of the experimental data to the Heisenberg model described in the text. Inset: Scheme of the spin and magnetic interaction topologies.

of the magnetic susceptibility for these latter complexes, we have used an isotropic Heisenberg model of five $S = 1/2$ spins with the following spin Hamiltonian:

$$H = -2J_a\{S_1\cdot(S_2 + S_3 + S_4 + S_5)\} - 2J_b(S_2\cdot S_3 + S_4\cdot S_5)$$

The J_a and J_b magnetic interactions are, respectively, between the central Cu(II) metal ion and the peripheral ones and between peripheral ones, as illustrated in Figure 5 (inset). J_b is mediated by a single alkoxide bridge, whereas J_a is the average magnetic interactions mediated by a μ_3-hydroxide/μ-OH_2 bridge. The application of the van Vleck equation[27] to the Kambe's vector coupling scheme[28] allows the determination of the low-field analytical expression of the magnetic susceptibility.[29] This Heisenberg model was able to reproduce relatively well the experimental data from 300 to 1.8 K for both compounds based on diamagnetic lanthanide ions (Figure 5; Figures S5 and S6, Supporting Information). The best set of parameters found are the following: $J_a/k_B = -78(3)$ K, $J_b/k_B = -134(2)$ K, and $g = 2.07(6)$ for **1** and $J_a/k_B = -79(3)$ K, $J_b/k_B = -121(2)$ K, and $g = 2.18(5)$ for **2**. The sign and magnitude of the estimated magnetic interactions imply an $S_T = 1/2$ ground state for these two complexes with an $S = 1/2$ first excited state lying in energy at +112 and +84 K above the ground state, for **1** and **2**, respectively. This result is confirmed by the field dependence of magnetization for **1** and **2** that has been measured at low temperatures below 8 K (Figures S7 and S8, Supporting Information). In both cases, the magnetization displays a clear saturation with the applied dc field above 6 T reaching 0.96 and 1.02 μ_B at 1.8 K and 7 T for **1** and **2**, respectively. This behavior indicates without ambiguity the absence of field-induced population of the excited states and also the presence of a negligible magnetic anisotropy in these systems. These conclusions are supported by the M versus H/T plots (Figures S7 and S8, Supporting Information), for which all the magnetization data can be superposed on a single master curve below 8 K, as expected for isotropic systems with a well-defined ground state. Furthermore the $S_T = 1/2$ spin ground state for these complexes is confirmed by the fitting of the M versus H/T single master curves to an $S = 1/2$ Brillouin function with $g = 2.00(3)$ for **1** and $g = 2.08(3)$ for **2** (Figures S7 and S8, Supporting Information).

Among the other complexes (Figures S9−S12, Supporting Information), **6** is the only one to display a clear saturation of the magnetization (above 4 T; with $M = 4.3$ μ_B at 1.8 K and 7 T; Figure S12, Supporting Information), indicating the absence of low-lying excited states (that could be populated with the applied magnetic field) and the presence of a negligible magnetic anisotropy. On the other hand, the field dependence of the magnetization for **3**−**5** exhibits (Figures S9−S11, Supporting Information) the following: (i) A rapid increase of the magnetization at low fields without an inflection point (S-shaped curve). This result, also valid for **3**, suggests the absence of weak Ln(III)···Cu(II) intracomplex antiferromagnetic interactions and the presence, if any, of ferromagnetic Ln(III)···Cu(II) interactions, and (ii) a linear increase without clear saturation even at 1.8 K under 7 T. These high-field behaviors reveal the presence of magnetic anisotropy in these Dy-, Ho-, and Er-based systems that might be combined with the field-induced population of low-lying magnetic excited

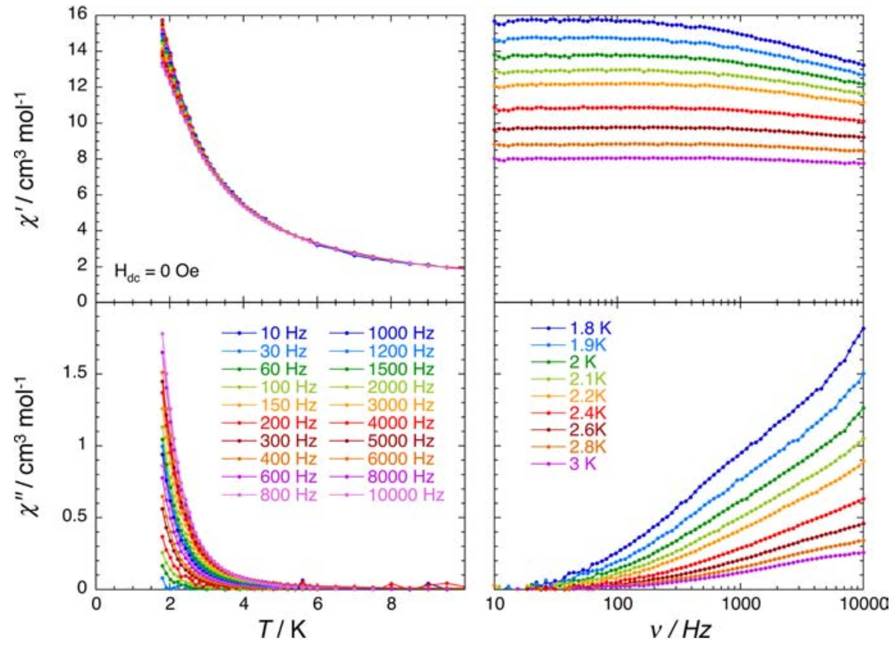


Figure 6. Temperature (left) and frequency (right) dependence of the real (χ', top) and imaginary (χ'', bottom) parts of the ac susceptibility at different ac frequencies between 10 and 10 000 Hz and different temperatures between 1.8 and 3 K, respectively, with a 1 Oe ac field for a polycrystalline sample of **4** in zero-dc field. Solid lines are guides.

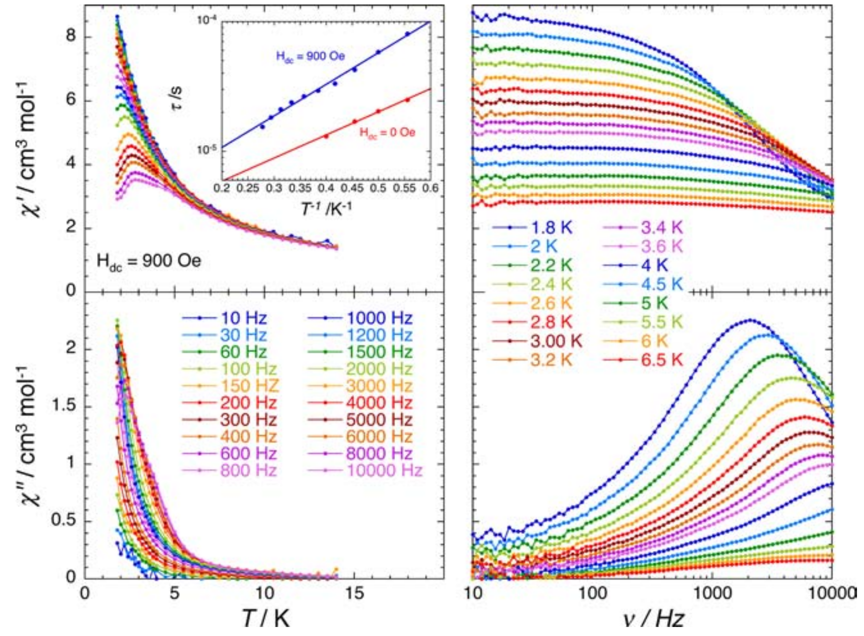


Figure 7. Temperature (left) and frequency (right) dependence of the real (χ', top) and imaginary (χ'', bottom) parts of the ac susceptibility at different ac frequencies between 10 and 10 000 Hz and different temperatures between 1.8 and 6.5 K, respectively, with a 1 Oe ac field for a polycrystalline sample of **3** in a 900 Oe dc field. Solid lines are guides. Inset: τ vs T^{-1} plot for **3** in zero (in red) and 900 Oe (in blue) dc fields. Solid lines are the best fits to the Arrhenius law discussed in the text.

states. At 1.8 K, the magnetization reaches 10.0, 9.5, and 11.6 μ_B under 7 T for **3**−**5**, respectively.

Dynamic Magnetic Properties: Single-Molecule Magnet Properties of 3 and 4. Although, at the lowest temperature available (1.8 K), the *M* versus *H* data do not show any sign of hysteresis effects, ac susceptibility measurements were performed in zero-dc field as a function of the temperature at different ac frequencies and also as a function of the ac frequency at different temperatures. Whereas **1**, **2**, **5**, and **6** do not exhibit any out-of-phase ac signal, **3** and **4** display below 5 K (for a frequency around 1000 Hz) an out-of-phase signal (Figure S13, Supporting Information; Figure 6, respectively).

The temperature and frequency dependence of the in-phase and out-of phase ac susceptibility measured in zero-dc field for **3** and **4** suggest that these complexes display SMM properties. However, only in the case of the Dy analogue, **3**, a clear maximum of the out-of-phase ac susceptibility is observed above 1.8 K in the experimentally available frequency and temperature ranges. From the data reported in Figure S13

(Supporting Information), the temperature dependence of the characteristic relaxation time has been extracted between 1.8 and 2.5 K. As shown in the insets of Figure 7 and Figure S13 (Supporting Information), this relaxation time was found to follow an Arrhenius law ($\tau(T) = \tau_0 \exp(\Delta/k_BT)$), with Δ/k_B = 4 K and $\tau_0 = 3 \times 10^{-6}$ s. It is worth mentioning that the obtained energy gap should be taken with caution, as it was determined in a small temperature domain due to the relatively fast relaxation of the magnetization above 1.8 K and also because the quantum relaxation pathway might be efficient at these temperatures. Indeed, the relatively high value of the pre-exponential factor ($>10^{-9}$ s) of the Arrhenius law further supports this assumption.

To explore the possibility to minimize the effects of the quantum relaxation pathway, the ac susceptibility for both complexes **3** and **4** was measured applying small dc fields (up to 1 T; Figures S14−S16, Supporting Information). In the case of **4**, the relaxation mode at 1.9 K seems to move toward higher frequencies (Figure S16, Supporting Information), suggesting a weak or negligible effect of the quantum relaxation. Accordingly, it was not possible to extract the relaxation time of the magnetization even under dc fields. On the other hand and as expected when quantum relaxation is effective, the characteristic frequency of **3** at 2 K first decreases at low fields (i.e., the relaxation time increases) and then increases as expected due to resonant quantum tunneling of the magnetization (Figure S15, Supporting Information). The optimum dc field that minimizes the effect of the quantum tunneling of the magnetization was estimated at 900 Oe (Figure S15). At this dc field, a maximum of the out-of-phase ac susceptibility was observed and the associated relaxation time was determined on a broader range of temperatures from 1.8 to 3.6 K (Figure 7). As shown in the inset of Figure 7, the relaxation time of **3** at 900 Oe follows an Arrhenius law with Δ_τ/k_B = 6 K and $\tau_0 = 3 \times 10^{-6}$ s.

■ CONCLUSIONS

In this work, we have demonstrated that the Schiff-base ligand, *N*,*N*′-bis(3-methoxysalicylidene)-1,3-diamino-2-propanol (H_3L), can be used to prepare, in good yields, a series of heptanuclear heterometallic complexes containing a $[Cu_5Ln_2]$ {M = Y(**1**), Lu(**2**), Dy(**3**), Ho(**4**), Er(**5**), and Yb(**6**)} core. These dicationic complexes are centrosymmetrical, with a central Cu(II) situated on a crystallographic inversion center. Around this central Cu(II), the other metal ions are situated in a hexagonal arrangement containing two lanthanide ions and four Cu(II) metal ions. Detailed magnetic studies on these compounds revealed the SMM properties of the Dy(III) and Ho(III) derivatives with energy barriers of the order of a few kelvins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vc@iitk.ac.in (V.C.), clerac@crpp-bordeaux.cnrs.fr (R.C.).

Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Prof. R. N. Mukherjee on the occasion of his 60th birthday.

■ REFERENCES

(1) (a) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, U.K., 2006, and references therein. (b) Affronte, M.; Carretta, S.; Timco, G. A.; Winpenny, R. E. P. *Chem. Commun.* **2007**, 1789. (c) Ikeda, N.; Oshumi, H.; Ohwada, K.; Ishii, K.; Inami, T.; Kakurai, T. *Nature* **2005**, *436*, 1136. (d) Kanatzidis, M. G.; Pöttgen, R.; Jeitschko, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2.

(2) (a) Kar, P.; Haldar, R.; Gómez-García, C. J.; Ghosh, A. *Inorg. Chem.* **2012**, *51*, 4265−4273. (b) Mandal, S. K.; Roesky, H. W. *Acc. Chem. Res.* **2010**, *43*, 248. (c) Huang, J.; Fu, X.; Wang, G.; Geb, Y.; Miaoa, Q. *Catal. Sci. Technol.* **2012**, *2*, 1040. (d) Sanchez-Delgado, R. A.; Puga, J.; Rosales, M. *J. Mol. Catal.* **1984**, *24*, 221. (e) Gates, B. C. *Chem. Rev.* **1995**, *95*, 511. (f) Pignolet, L. H.; Aubart, M. A.; Craighead, K. L.; Gould, R. A. T.; Krogstad, D. A.; Wiley, J. S. *Coord. Chem. Rev.* **1995**, *143*, 219.

(3) (a) Bertini, I. G. H. B.; Lippard, S. J.; Valentine, J. S. *Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994. (b) Barber, J.; Murray, J. W. *Philos. Trans. R. Soc., B* **2008**, *363*, 1129. (c) Basu, U.; Khan, I.; Hussain, A.; Kondaiah, P.; Chakravarty, A. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2658. (d) Chandrasekhar, V.; Nagarajan, L.; Hossain, S.; Gopal, K.; Ghosh, S.; Verma, S. *Inorg. Chem.* **2012**, *51*, 5605.

(4) Ozin, G. A.; Arsenault, A. C. *Nanochemistry: A Chemical Approach to Nanomaterials*; RSC Publishing: Cambridge, U.K., 2005.

(5) (a) Kimura, T. *Annu. Rev. Mater. Res.* **2007**, *37*, 387. (b) Ida, H.; Okazawa, A.; Kojima, N.; Shimizu, R.; Yamada, Y.; Enomoto, M. *Inorg. Chem.* **2012**, *51*, 8989. (c) Okawa, H.; Shigematsu, A.; Sadakiyo, M.; Miyagawa, T.; Yoneda, K.; Ohba, M.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 13516. (d) Coronado, E.; Martí-Gastaldo, C.; Navarro-Moratalla, E.; Ribera, A.; Blundell, S. J.; Baker, P. J. *Nat. Chem.* **2010**, *2*, 1031. (e) Clemente-León, M.; Coronado, E.; López-Jordà, M.; Desplanches, C.; Asthana, S.; Wang, H.; Létard, J. F. *Chem. Sci.* **2011**, *2*, 1121. (f) Chen, C. T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.

(6) (a) Liu, J. L.; Yuan, K.; Leng, J. D.; Ungur, L.; Wernsdorfer, W.; Guo, F. S.; Chibotaru, L. F.; Tong, M. L. *Inorg. Chem.* **2012**, *51*, 8538. (b) Feng, X.; Liu, J.; Harris, T. D.; Hill, S.; Long, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 7521. (c) Rinehart, J. D.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 12558. (d) Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1224. (e) Jiang, S.-D.; Wang, B.-W.; Su, G.; Wang, Z.-M.; Gao, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7448. (f) Jiang, S.-D.; Wang, B.-W.; Sun, H.-L.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2011**, *133*, 4730. (g) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.-y.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694. (h) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot. *J. Am. Chem. Soc.* **1991**, *113*, 5873. (i) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406. (j) Yang, E.-C.; Kirman, C.; Lawrence, J.; Zakharov, L. N.; Rheingold, A. L.; Hill, S.; Hendrickson, D. N. *Inorg. Chem.* **2005**, *44*, 3827. (k) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145.

(l) Jurca, T.; Farghal, A.; Lin, P. H.; Korobkov, I.; Murugesu, M.; Richeson, D. S. *J. Am. Chem. Soc.* **2011**, *133*, 15814. (m) Feng, P. L.; Hendrickson, D. N. *Inorg. Chem.* **2010**, *49*, 6393.

(7) (a) Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054. (b) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133. (c) Tejada, J.; Ziolo, R. F.; Zhang, X. X. *Chem. Mater.* **1996**, *8*, 1784. (d) Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830. (e) Gunther, L.; Barbara, B., Eds. *Quantum Tunneling of Magnetization: QTM '94*; NATO ASI Series E, Applied Sciences; Kluwer Academic Publishers: Boston, MA, 1995; Vol. *301*. (f) Waldmann, O.; Stamatatos, T. C.; Christou, G.; Güdel, H. U.; Sheikin, I.; Mutka, H. *Phys. Rev. Lett.* **2009**, *102*, 157202. (g) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (h) Ramsey, C. M.; del Barco, E.; Hill, S.; Shah, S. J.; Beedle, C. C.; Hendrickson, D. N. *Nat. Phys.* **2008**, *4*, 277. (i) Wernsdorfer, W.; Soler, M.; Christou, G.; Hendrickson, D. N. *J. Appl. Phys.* **2002**, *91*, 7164. (j) Lecren, L.; Wernsdorfer, W.; Li, Y. G.; Roubeau, O.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 11311.

(8) (a) Rogez, G.; Donnio, B.; Terazzi, E.; Gallani, J. L.; Kappler, J. P.; Bucher, J. P; Drillon, M. *Adv. Mater.* **2009**, *21*, 4323. (b) Chudnovsky, E. M. *Science* **1996**, *274*, 938. (c) Ardavan, A.; Blundell, S. J. *J. Mater. Chem.* **2009**, *19*, 1754.

(9) (a) Troiani, F.; Affronte, M. *Chem. Soc. Rev.* **2011**, *40*, 3119. (b) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789. (c) Meier, F.; Levy, J.; Loss, D. *Phys. Rev. Lett.* **2003**, *90*, 047901. (d) Tejada, J.; Chudnovsky, E. M.; del Barco, E.; Hernandez, J. M.; Spiller, T. P. *Nanotechnology* **2001**, *12*, 181. (e) Wernsdorfer, W. *Nat. Nanotechnol.* **2009**, *4*, 145.

(10) (a) del Carmen Giménez-López, M.; Moro, F.; La Torre, A.; Gómez-García, C. J.; Brown, P. D.; van Slageren, J.; Khlobystov, A. N. *Nat. Commun.* **2011**, *2*, 407. (b) Bogani, L.; Wernsdorfer, W. *Nat. Mater.* **2008**, *7*, 179. (c) Roch, N.; Florens, S.; Bouchiat, V.; Wernsdorfer, W.; Balestro, F. *Nature* **2008**, *453*, 633. (d) Sanvito, S. *Chem. Soc. Rev.* **2011**, *40*, 3336. (e) Jo, M. H.; Grose, J. E.; Baheti, K.; Deshmukh, M. M.; Sokol, J. J.; Rumberger, E. M.; Hendrickson, D. N.; Long, J. R.; Park, H.; Ralph, D. C. *Nano Lett.* **2006**, *6*, 2014.

(11) (a) Sessoli, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 43. (b) Karotsis, G.; Kennedy, S.; Teat, S. J.; Beavers, C. M.; Fowler, D. A.; Morales, J. J.; Evangelisti, M.; Daigamo, S. J.; Brechin, E. K. *J. Am. Chem. Soc.* **2010**, *132*, 12983. (c) Langley, S. K.; Chilton, N. F.; Moubaraki, B.; Hooper, T.; Brechin, E. K.; Evangelisti, M.; Murray, K. S. *Chem. Sci.* **2011**, *2*, 1166. (d) Hosoi, A.; Yukawa, Y.; Igarashi, S.; Teat, S. J.; Roubeau, O.; Evangelisti, M.; Cremades, E.; Ruiz, E.; Barrios, L. A.; Aromí, G. *Chem.—Eur. J.* **2011**, *17*, 8264. (e) Cremades, E.; Gómez-Coca, S.; Aravena, D.; Alvarez, S.; Ruiz, E. *J. Am. Chem. Soc.* **2012**, *134*, 10532. (f) Zheng, Y. Z.; Evangelisti, M.; Winpenny, R. E. P. *Chem. Sci.* **2011**, *2*, 99. (g) Zheng, Y.-Z.; Evangelisti, M.; Tuna, F.; Winpenny, R. E. P. *J. Am. Chem. Soc.* **2012**, *134*, 1057.

(12) (a) Christou, G. *Polyhedron* **2005**, *24*, 2065. (b) Milios, C. J.; Vinslava, A.; Wernsdorfer, W.; Moggach, S.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2007**, *129*, 2754. (c) Milios, C. J.; Inglis, R.; Vinslava, A.; Bagai, R.; Wernsdorfer, W.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2007**, *129*, 12505. (d) Taguchi, T.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2010**, *49*, 10579. (e) Alexandropoulos, D. I.; Papatriantafyllopoulou, C.; Aromi, G.; Roubeau, O.; Teat, S. J.; Perlepes, S. P.; Christou, G.; Stamatatos, T. C. *Inorg. Chem.* **2010**, *49*, 3962. (f) Lampropoulos, C.; Redler, G.; Data, S.; Abboud, K. A.; Hill, S.; Christou, G. *Inorg. Chem.* **2010**, *49*, 1325. (g) Taguchi, T.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2010**, *49*, 199. (h) Li, Y.-G.; Wernsdorfer, W.; Clérac, R.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2006**, *45*, 2376.

(13) (a) Mossin, S.; Tran, B. L.; Adhikari, D.; Pink, M.; Heinemann, F. W.; Sutter, J.; Szilagyi, R. K.; Meyer, K.; Mindiola, D. J. *J. Am. Chem. Soc.* **2012**, *134*, 13651. (b) Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1224. (c) Bagai, R.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2007**, *129*, 12918. (d) Ako, A. M.; Mereacre, V.; Lan, Y. H.; Wernsdorfer, W.; Clérac, R.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2010**, *49*, 1. (e) Hoshino, N.; Ako, A. M.; Powell, A. K.; Oshio, H. *Inorg. Chem.* **2009**, *48*, 3396. (f) Boudalis, A. K.; Sanakis, Y.; Clemente-Juan, J. M.; Donnadieu, B.; Nastopoulos, V.; Mari, A.; Coppel, Y.; Tuchagues, J. P.; Perlepes, S. P. *Chem.—Eur. J.* **2008**, *14*, 2514. (g) Prasad, T. K.; Poneti, G.; Sorace, L.; Rodriguez-Douton, M. J.; Barra, A. L.; Neugebauer, P.; Costantino, L.; Sessoli, R.; Cornia, A. *Dalton Trans.* **2012**, *41*, 8368. (h) Zhu, Y. Y.; Guo, X.; Cui, C.; Wang, B. W.; Wang, Z. M.; Gao, S. *Chem. Commun.* **2011**, *47*, 8049. (i) Weismann, D.; Sun, Y.; Lan, Y.; Wolmershäuser, G.; Powell, A. K.; Sitzmann, H. *Chem.—Eur. J.* **2011**, *17*, 4700. (j) Schlegel, C.; Burzurí, E.; Luis, F.; Moro, F.; Manoli, M.; Brechin, E. K.; Murrie, M.; Slageren, J. V. *Chem.—Eur. J.* **2010**, *16*, 10178.

(14) (a) Murrie, M. *Chem. Soc. Rev.* **2010**, *39*, 1986, and references therein. (b) Ibrahim, M.; Lan, Y.; Bassil, B. S.; Xiang, Y.; Suchopar, A.; Powell, A. K.; Kortz, U. *Angew. Chem., Int. Ed.* **2011**, *50*, 4708. (c) Zeng, M. H.; Yao, M. X.; Liang, H.; Zhang, W. X.; Chen, X. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1832. (d) Moubaraki, B.; Murray, K. S.; Hudson, T. A.; Robson, R. *Eur. J. Inorg. Chem.* **2008**, 4525. (e) Galloway, K. W.; Whyte, A. M.; Wernsdorfer, W.; Sanchez-Benitez, J.; Kamenev, K. V.; Parkin, A.; Peacock, R. D.; Murrie, M. *Inorg. Chem.* **2008**, *47*, 7438. (f) Ferguson, A.; Parkin, A.; Sanchez-Benitez, J.; Kamenev, K.; Wernsdorfer, W.; Murrie, M. *Chem. Commun.* **2007**, 3473.

(15) (a) Petit, S.; Neugebauer, P.; Pilet, G.; Chastanet, G.; Barra, A. L.; Antunes, A. B.; Wernsdorfer, W.; Luneau, D. *Inorg. Chem.* **2012**, *51*, 6645. (b) Serna, Z.; De la Pinta, N.; Urtiaga, M. K.; Lezama, L.; Madariaga, G.; Clemente-Juan, J. M.; Coronado, E.; Cortes, R. *Inorg. Chem.* **2010**, *49*, 11541. (c) Ferguson, A.; Lawrence, J.; Parkin, A.; Sanchez-Benitez, J.; Kamenev, K. V.; Brechin, E. K.; Wernsdorfer, W.; Hill, S.; Murrie, M. *Dalton Trans.* **2008**, 6409. (d) Aromi, G.; Bouwman, E.; Burzuri, E.; Carbonera, C.; Krzystek, J.; Luis, F.; Schlegel, C.; van Slageren, J.; Tanase, S.; Teat, S. J. *Chem.—Eur. J.* **2008**, *14*, 11158. (e) Bell, A.; Aromi, G.; Teat, S. J.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. Commun.* **2005**, 2808. (f) Bouldalis, A. K.; Pissas, M.; Raptopoulou, C. P.; Psycharis, V.; Abarca, B.; Ballesteros, R. *Inorg. Chem.* **2008**, *47*, 10674.

(16) (a) Colacio, E.; Ruiz, J.; Mota, A. J.; Palacios, M. A.; Cremades, E.; Ruiz, E.; White, F. J.; Brechin, E. K. *Inorg. Chem.* **2012**, *51*, 5857. (b) Mereacre, V.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem.—Eur. J.* **2008**, *14*, 3577. (c) Langley, S. K.; Moubaraki, B.; Murray, K. S. *Dalton Trans.* **2010**, *39*, 5066. (d) Holyńska, M.; Premužić, D.; Jeon, I.-R.; Wernsdorfer, W.; Clérac, R.; Dehnen, S. *Chem.—Eur. J.* **2011**, *17*, 9605. (e) Mereacre, V. M.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Filoti, G.; Bartolomé, J.; Anson, C. E.; Powell, A. K. *J. Am. Chem. Soc.* **2007**, *129*, 9248. (f) 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. (g) Chilton, N. F.; Langley, S. K.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2010**, *46*, 7787. (h) Colacio, E.; Ruiz-Sanchez, J.; White, F. J.; Brechin, E. K. *Inorg. Chem.* **2011**, *50*, 7268. (i) Efthymiou, C. G.; Stamatatos, T. C.; Papatriantafyllopoulou, C.; Tasiopoulos, A. J.; Wernsdorfer, W.; Perlepes, S. P.; Christou, G. *Inorg. Chem.* **2010**, *49*, 9737. (j) Ke, H.; Zhao, L.; Guo, Y.; Tang, J. K. *Inorg. Chem.* **2012**, *51*, 2699. (k) Pasatoiu, T. D.; Etienne, M.; Madalan, A. M.; Andruh, M.; Sessoli, R. *Dalton Trans.* **2010**, *39*, 4802. (l) Schray, D.; Abbas, G.; Lan, Y.; Mereacre, V.; Sundt, A.; Dreiser, J.; Waldmann, O.; Kostakis, G. E.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5185. (m) Chandrasekhar, V.; Pandian, B. M.; Boomishankar, R.; Steiner, A.; Vittal, J. J.; Houri, A.; Clérac, R. *Inorg. Chem.* **2008**, *47*, 4918. (n) Chandrasekhar, V.; Pandian, B. M.; Vittal, J. J.; Clérac, R. *Inorg. Chem.* **2009**, *48*, 1148. (o) Chandrasekhar, V.; Pandian, B. M.; Azhakar, R.; Vittal, J. J.; Clérac, R. *Inorg. Chem.* **2007**, *46*, 5140. (p) Andruh, M.; Costes, J.-P.; Diaz, C.; Gao, S. *Inorg. Chem.* **2009**, *48*, 3342.

(17) (a) Novitchi, G.; Pilet, G.; Ungur, L.; Moshchalkov, V. V.; Wernsdorfer, W.; Chibotaru, L. F.; Luneau, D.; Powell, A. K. *Chem. Sci.* **2012**, *3*, 1169. (b) Novitchi, G.; Wernsdorfer, W.; Chibotaru, L. F.; Costes, J.-P.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2009**,

48, 1614. (c) Langley, S. K.; Ungur, L.; Chilton, N. F.; Moubaraki, B.; Chibotaru, L. F.; Murray, K. S. *Chem.—Eur. J.* **2011**, *17*, 9209. (d) Iasco, O.; Novitchi, G.; Jeanneau, E.; Wernsdorfer, W.; Luneau, D. *Inorg. Chem.* **2011**, *50*, 7373. (e) Osa, S.; Kido, T.; Matsumoto, N.; Re, N.; Pochaba, A.; Mrozinski, J. *J. Am. Chem. Soc.* **2004**, *126*, 420. (f) Baskar, V.; Gopal, K.; Helliwell, M.; Tuna, F.; Wernsdorfer, W.; Winpenny, R. E. P. *Dalton Trans.* **2010**, *39*, 4747. (g) Mori, F.; Nyui, T.; Ishida, T.; Nogami, T.; Choi, K.-Y.; Nojiri, H. *J. Am. Chem. Soc.* **2006**, *128*, 1440. (h) Costes, J.-P.; Shova, S.; Wernsdorfer, W. *Dalton Trans.* **2008**, 1843. (i) Aronica, C.; Pilet, G.; Chastanet, G.; Wernsdorfer, W.; Jacquot, J.-F.; Luneau, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 4659.

(18) Chandrasekhar, V.; Pandian, B. M.; Boomishankar, R.; Steiner, A.; Clérac, R. *Dalton Trans.* **2008**, *38*, 5143.

(19) Chandrasekhar, V.; Senapati, T.; Dey, A.; Das, S.; Kalisza, M.; Clérac, R. *Inorg. Chem.* **2012**, *51*, 2031.

(20) (a) Liao, S.; Yang, X.; Jones, R. A. *Cryst. Growth Des.* **2012**, *12*, 970. (b) Lan, Y.; Novitchi, G.; Clérac, R.; Tang, J.; Madhu, N. T.; Hewitt, I. J.; Anson, C. E.; Brooker, S.; Powell, A. K. *Dalton Trans.* **2009**, 1721. (c) Elmali, A.; Zeyrek, C. T.; Elerman, Y. *J. Mol. Struct.* **2004**, *693*, 225.

(21) (a) *SMART & SAINT Software Reference Manuals*, version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003. (b) Sheldrick, G. M. *SADABS: A Software for Empirical Absorption Correction*, Version 2.05; University of Göttingen: Göttingen, Germany, 2002. (c) *SHELXTL Reference Manual*, version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000. (d) Sheldrick, G. M. *SHELXTL v.6.12*; Bruker AXS Inc.: Madison, WI, 2001. (e) Sheldrick, G. M. *SHELXL97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997. (f) Bradenburg, K. *Diamond*, version 3.1e; Crystal Impact GbR: Bonn, Germany, 2005.

(22) Chandrasekhar, V.; Senapati, T.; Dey, A.; Sañudo, C. E. *Inorg. Chem.* **2011**, *50*, 1420.

(23) (a) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192. (b) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (c) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226–3229. (d) Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585. (e) Mukherjee, S.; Abboud, A. K.; Wernsdorfer, W.; Christou, G. *Inorg. Chem.* **2013**, *52*, 873.

(24) (a) Pinsky, M.; Avnir, D. *Inorg. Chem.* **1998**, *37*, 5575. (b) Casanova, D.; Cirera, J.; Llunell, M.; Alemany, P.; Avnir, D.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1755. (c) Cirera, J.; Ruiz, E.; Alvarez, S. *Chem.—Eur. J.* **2006**, *12*, 3162.

(25) Wu, G.; Hewitt, I. J.; Mameri, S.; Lan, Y.; Clérac, R.; Anson, C. E.; Qiu, S.; Powell, A. K. *Inorg. Chem.* **2007**, *46*, 7229.

(26) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.

(27) van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibility*; Oxford University Press: Oxford, U.K., 1932.

(28) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48.

(29) Nellutla, S.; van Tol, J.; Dalal, N. S.; Bi, L.-H.; Kortz, U.; Keita, B.; Nadjo, L.; Khitrov, G. A.; Marshall, A. G. *Inorg. Chem.* **2005**, *44*, 9795.