

Family of dumbbell Ni₄Ln₂ (Ln = Pr, Sm, Eu, Gd, Tb, Ho, Er) complexes: syntheses, structures, luminescent and magnetic properties†

Cite this: *Dalton Trans.*, 2013, **42**, 5047

Baolin Liu,^{a,b} Qingxia Liu,^a Hongping Xiao,^{*c} Wu Zhang^a and Ruojie Tao^{*a}

The synthesis and characterization of a family of heterometallic Ni₄Ln₂ complexes (Ln = Pr(1), Sm(2), Eu(3), Gd(4), Tb(5), Ho(6) and Er(7)) of the formula [Ni₂LnL¹L²(OH)(H₂O)]₂ are reported, where H₄L¹ is 3,3'-(1E,1'E)-(2,2'-(2-aminoethylazanediyl)bis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-hydroxybenzoic acid) and H₂L² is 3-formyl-2-hydroxybenzoic acid. The molecular structures of 1–7 were determined by single-crystal X-ray diffraction and reveal that they are isostructural. In all of these compounds, the six metal ions are held together to form a novel Ni₄Ln₂O₁₀ core and exhibit a relatively rare dumbbell-type structure. In these compounds, the Ni ions are in slightly distorted square-pyramidal or octahedral environments. An all-oxygen coordination environment (8O) is present around the central lanthanide ion, which is present in a distorted square antiprismatic geometry. The Ln–Ln and Ln–O_{avg} bond distances in 1–7 show a gradual reduction proceeding from 1 to 7, in accordance with the lanthanide contraction. The luminescent properties of all the compounds have been studied. The magnetic susceptibility analysis demonstrate antiferromagnetic interactions within complex 4.

Received 29th August 2012,
Accepted 7th January 2013

DOI: 10.1039/c3dt32935f

www.rsc.org/dalton

Introduction

The chemistry of heterometallic 3d–4f complexes has attracted considerable attention due to their structural diversity¹ and versatile applications in magnetic,² luminescent,³ adsorptive⁴ and electrical materials.⁵ Among all the heteronuclear edifices, most contain Cu–Ln systems,⁶ which contain one-dimensional chains,^{6a} two-dimensional layers^{6b} and three-dimensional networks,^{6c} while a few with Ni–Ln,⁷ Fe–Ln,⁸ Co–Ln,⁹ Zn–Ln,¹⁰ Mn–Ln¹¹ and Cr–Ln¹² systems are reported. We have recently joined ongoing efforts in this area and have initially focused primarily on Ni–Ln species. We were interested in discovering whether Ni–Ln combinations could be optimized to take advantage of the second order orbital angular momentum of Ni^{II} ions,¹³ which means that they can also provide large negative zero field splitting parameters. It is worth noting that

there are only a few reports centered on the synthesis of Ni–Ln heterometallic single molecule magnets (SMMs).¹⁴

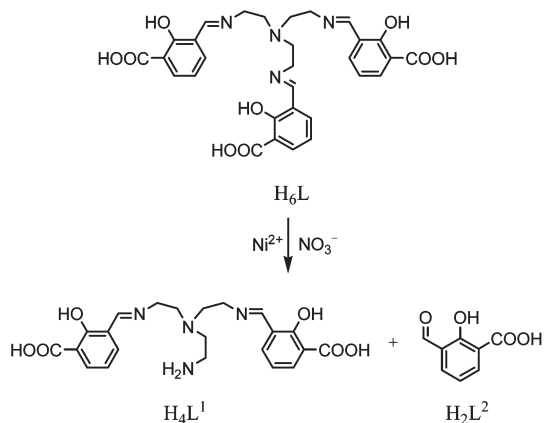
To facilitate the formation of 3d–4f clusters, many researchers have employed polydentate chelating ligands, such as Schiff bases,¹⁵ *N*-substituted diethanolamines,¹⁶ and tripodal ligands.¹⁷ All the ligands are appealing for mixed-metal systems because the chemical characteristics of the polydentate (N and O atoms) compounds can fulfill the coordination affinities to 3d and 4f metal ions for N and O atoms. Such polydentate ligands have led to the discovery of many interesting 3d–4f clusters, some of which display SMM behaviour. It is noteworthy that syntheses of Ni–Ln based SMMs remain relatively scarce. These Ni–Ln complexes have been less studied than the Cu–Ln examples, probably because there is no strict control over the coordination geometry of the 3d metal ion. Indeed, in some cases, Ni–Ln complexes containing diamagnetic square-planar Ni(II) ions were obtained.¹⁸ To avoid this, we have designed a new tripodal Schiff-base ligand (H₆L = 3,3',3''-(1E,1'E,1''E)-(2,2',2''-nitrilotris(ethane-2,1-diyl) tris(azan-1-yl-1-ylidene))tris(methan-1-yl-1-ylidene)tris(2-hydroxybenzoic acid), (H₆L), which was used in this study to build 3d–4f heterometallic coordination polymers. The main novelty of this work is that one imine bond in the H₆L ligand is degraded into an NH₂ group, giving the new ligand H₄L¹ (Scheme 1). This is the first example from a hydrated Ni(II) salt promoting partial hydrolysis of the Schiff base ligand.

^aInstitute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, China. E-mail: rjtao@henu.edu.cn

^bKey Laboratory of Advanced Energy Materials Chemistry, Nankai University, Tianjin, China

^cCollege of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, China. E-mail: hp_xiao@yahoo.com.cn

†Electronic supplementary information (ESI) available: UV-vis spectra of complexes 1–7. CCDC 898018–898024. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32935f



Scheme 1 Proposed process for the formation of H_4L^1 .

Herein, we report the syntheses, crystal structures, luminescent properties and magnetic properties of seven dumbbell coordination clusters formulated as $[Ni_2LnL^1L^2(OH)(H_2O)]_2$ [$Ln = Pr(1), Sm(2), Eu(3), Gd(4), Tb(5), Ho(6)$ and $Er(7)$].

Experimental section

General

All the chemicals and solvents were analytical grade and used as commercially available. 3-Formyl-2-hydroxybenzoic acid was prepared by the literature method.¹⁹ Elemental analyses for C, H and N were carried out on a Perkin-Elmer 2400II analyzer. The infrared spectra were recorded on an Avater-360 spectrometer using KBr pellets in a range of 400–4000 cm^{-1} . 1H NMR spectra were recorded on Bruker AC-400 spectrometer. The UV-vis spectra were recorded on a UV-550 spectrometer in a range of 400–800 nm. The fluorescence spectra were measured on a F-7000 Fluorometer. Thermogravimetric analysis was carried out on an TGA/SDTA851e analyzer in a nitrogen atmosphere and the complexes were heated to 1000 °C at a heating rate of 10 °C min^{-1} . Magnetic measurements were carried out on polycrystalline samples with a MPMS-7SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the atoms.

Preparation of ligand H_6L

The ligand H_6L was prepared by refluxing a solution of 3-formyl-2-hydroxybenzoic acid (4.98 g, 30 mmol), tris-(2-aminoethyl)amine (1.46 g, 10 mmol) in ethanol (50 mL) for 3 h. After cooling to room temperature, a yellow precipitate was obtained, which was filtered off, washed with cool ethanol and diethylether and air-dried. Yield, 5.13 g, 87%. Anal. Calcd (%) for $C_{30}H_{30}N_4O_9$: C, 61.02; H, 5.08; N, 9.49. Found: C, 60.68; H, 4.98; N, 9.39. 1H NMR (DMSO- d_6 , δ , ppm): 3.00 (6 H, t, 3 CH_2), 3.82 (6 H, t, 3 CH_2), 6.51 (3 H, t, 3 CH), 7.42 (3 H, dd, 3 CH), 7.95 (3 H, dd, 3 CH), 8.66 (3 H, br s, 3 CH), 10.33 (3 H, s, 3 OH), 12.84 (3 H, br s, 3 COOH). IR (KBr, cm^{-1}): 3430(b), 1694(s), 1658(s), 1600(s), 1530(s), 1470(s), 1320(s), 1240(s), 1180(m),

1150(s), 1070(s), 1010(w), 893(s), 858(m), 752(s), 739(m), 602(m), 550(s), 528(w), 471(m).

Complexes

All complexes 1–7 were prepared and isolated through the same experimental procedure, as described for complex 1. Using the appropriate salt yielded the desired complexes.

$[Ni_2PrL^1L^2(OH)(H_2O)]_2 \cdot 8H_2O$ (1). A water solution of NaOH (0.24 g, 6 mmol) was added to the Schiff-base H_6L ligand (0.590 g, 1 mmol) dissolved in 10 mL of water. The reaction mixture was stirred for 5 min. Then, a solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) and $Pr(NO_3)_3 \cdot 6H_2O$ (0.427 g, 1 mmol) in methanol (30 mL) was added dropwise and the mixture was kept stirring for another 2 h at room temperature. The resulting pale green solution was filtered and allowed to stand at room temperature. Green block single crystals, suitable for X-ray diffraction analysis, were formed after 1 month. Yield: 0.44 g, 45% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{73}N_8Ni_4O_{32.5}Pr_2$: C, 37.09; H, 3.79; N, 5.77. Found: C, 36.82; H, 3.54; N, 5.59. IR (KBr, cm^{-1}): 3430(b), 1640(s), 1600(s), 1556(s), 1440(s), 1410(s), 1310(s), 1230(s), 1190(m), 1150(m), 1140(m), 1080(s), 1039(w), 966(s), 874(s), 831(m), 804(m), 760(s), 669(s), 633(m).

$[Ni_2SmL^1L^2(OH)(H_2O)]_2 \cdot 8.5H_2O$ (2). Yield: 0.44 g, 45% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{73}N_8Ni_4O_{32.5}Sm_2$: C, 36.70; H, 3.85; N, 5.71. Found: C, 36.48; H, 3.61; N, 5.56. IR (KBr, cm^{-1}): 3428(b), 1642(s), 1600(s), 1553(s), 1440(s), 1417(s), 1310(s), 1230(s), 1190(m), 1150(m), 1140(m), 1080(s), 1038(w), 966(s), 874(s), 831(m), 806(m), 766(s), 669(s), 633(m).

$[Ni_2EuL^1L^2(OH)(H_2O)]_2 \cdot 9H_2O$ (3). Yield: 0.47 g, 48% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{74}N_8Ni_4O_{33}Eu_2$: C, 36.51; H, 3.78; N, 5.68. Found: C, 36.39; H, 3.57; N, 5.52. IR (KBr, cm^{-1}): 3412(b), 1627(s), 1592(s), 1558(s), 1442(s), 1409(s), 1301(s), 1234(s), 1201(m), 1177(m), 1157(m), 1082(s), 1041(w), 976(s), 879(s), 831(m), 806(m), 763(s), 669(s), 625(m).

$[Ni_2GdL^1L^2(OH)(H_2O)]_2 \cdot 8H_2O$ (4). Yield: 0.42 g, 43% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{74}N_8Ni_4O_{32}Gd_2$: C, 36.61; H, 3.79; N, 5.69. Found: C, 36.44; H, 3.59; N, 5.54. IR (KBr, cm^{-1}): 3430(b), 1640(s), 1600(s), 1562(s), 1450(s), 1410(s), 1311(s), 1233(s), 1197(m), 1168(m), 1146(m), 1082(s), 1032(w), 966(s), 876(s), 831(m), 798(m), 764(s), 671(s), 633(m).

$[Ni_2TbL^1L^2(OH)(H_2O)]_2 \cdot 8H_2O$ (5). Yield: 0.56 g, 57% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{74}N_8Ni_4O_{32}Tb_2$: C, 36.55; H, 3.78; N, 5.68. Found: C, 36.32; H, 3.57; N, 5.51. IR (KBr, cm^{-1}): 3426(b), 1641(s), 1600(s), 1556(s), 1452(s), 1408(s), 1309(s), 1232(s), 1198(m), 1169(m), 1148(m), 1081(s), 1031(w), 966(s), 874(s), 829(m), 800(m), 766(s), 669(s), 634(m).

$[Ni_2HoL^1L^2(OH)(H_2O)]_2 \cdot 7H_2O \cdot CH_3OH$ (6). Yield: 0.44 g, 44% (based on the nickel salt). Anal. Calcd (%) for $C_{61}H_{74}N_8Ni_4O_{32}Ho_2$: C, 36.71; H, 3.74; N, 5.61. Found: C, 36.56; H, 3.52; N, 5.49. IR (KBr, cm^{-1}): 3427(b), 1640(s), 1600(s), 1562(s), 1455(s), 1415(s), 1310(s), 1233(s), 1199(m), 1160(m), 1146(m), 1080(s), 1032(w), 968(s), 877(s), 831(m), 808(m), 766(s), 673(s), 634(m).

$[\text{Ni}_2\text{ErL}^1\text{L}^2(\text{OH})(\text{H}_2\text{O})]_2 \cdot 7.5\text{H}_2\text{O}$ (7). Yield: 0.51 g, 52% (based on the nickel salt). Anal. Calcd (%) for $\text{C}_{60}\text{H}_{73}\text{N}_8\text{Ni}_4\text{O}_{31.5}\text{Er}_2$: C, 36.40; H, 3.72; N, 5.66. Found: C, 36.23; H, 3.51; N, 5.53. IR (KBr, cm^{-1}): 3425(b), 1641(s), 1600(s), 1553(s), 1453(s), 1412(s), 1317(s), 1236(s), 1200(m), 1167(m), 1148(m), 1079(s), 1033(w), 968(s), 876(s), 831(m), 810(m), 760(s), 673(s), 636(m).

X-ray crystallography

The crystal data and the cell parameters for 1–7 are given in Tables 1 and 2. The crystal data for 1–7 have been collected on a Bruker SMART APEX CCD diffractometer with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The program SMART^{20a} was used for collecting frames of data, indexing reflection and determining lattice parameters. SAINT^{20a} was used for the integration of the intensity of the reflections and scaling, SADABS^{20b} was used for the absorption correction and SHELXTL^{20c,d} was used for the space group and

structure determination and least-squares refinements on F^2 . The hydrogen atom positions were calculated theoretically and included in the final cycles of the refinement in a riding model along with attached carbon atoms.

Results and discussion

IR and UV-vis spectra of the complexes

In the IR spectra of ligand H_6L , the band at 1694 cm^{-1} can be ascribed to the stretching vibration of the $\nu(\text{COOH})$ vibration band, the broad band at 3430 cm^{-1} can be assigned to the $\nu(\text{OH})$ band²¹ and the absorption band at 1658 cm^{-1} corresponds to the stretching vibration of the $\text{C}=\text{N}(\text{imine})$ band.²² In the title complexes, the COO^- asymmetrical vibration band of $\nu_{\text{as}}(\text{COO})$ exhibits one intense absorption band around 1560 cm^{-1} , which may be attributed to the $\nu_{\text{as}}(\text{COO})$ band of

Table 1 Crystallographic data and refinement for 1–4

	1	2	3	4
Formula	$\text{C}_{60}\text{H}_{73}\text{N}_8\text{Ni}_4\text{O}_{32.5}\text{Pr}_2$	$\text{C}_{60}\text{H}_{75}\text{N}_8\text{Ni}_4\text{O}_{32.5}\text{Sm}_2$	$\text{C}_{60}\text{H}_{74}\text{N}_8\text{Ni}_4\text{O}_{33}\text{Eu}_2$	$\text{C}_{60}\text{H}_{74}\text{N}_8\text{Ni}_4\text{O}_{32}\text{Gd}_2$
Formula weight	1942.93	1963.82	1974.03	1968.61
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
$a/\text{\AA}$	12.770(4)	12.7048(6)	12.703(3)	12.6620(10)
$b/\text{\AA}$	18.183(6)	18.1777(9)	18.339(5)	18.1513(14)
$c/\text{\AA}$	15.616(5)	15.5866(8)	15.578(4)	15.5428(12)
$\alpha/^\circ$	90.00	90.00	90.00	90.00
$\beta/^\circ$	100.262(5)	99.9870(10)	98.101(4)	99.7790(10)
$\gamma/^\circ$	90.00	90.00	90.00	90.00
Volume/ \AA^3	3568(2)	3545.1(3)	3592.9(16)	3520.3(5)
T/K	296(2)	296(2)	296(2)	296(2)
Space group	$P21/n$	$P21/n$	$P21/n$	$P21/n$
Z	1	1	2	2
$D_{\text{calcd}}(\text{g cm}^{-3})$	1.809	1.840	1.675	1.857
$F(000)$	1958	1974	1804	1972
R_{int}	0.0679	0.0436	0.0449	0.0361
$R_1/wR_2[I > 2\sigma(I)]$	0.0514/0.1070	0.0341/0.0794	0.0383/0.1074	0.0306/0.0666
R_1/wR_2 (all data)	0.0904/0.1175	0.0519/0.0856	0.0471/0.1123	0.0479/0.0710
GOF on F^2	0.971	1.026	1.069	1.011

Table 2 Crystallographic data and refinement for 5–7

	5	6	7
Formula	$\text{C}_{60}\text{H}_{74}\text{N}_8\text{Ni}_4\text{O}_{32}\text{Tb}_2$	$\text{C}_{61}\text{H}_{74}\text{N}_8\text{Ni}_4\text{O}_{32}\text{Ho}_2$	$\text{C}_{60}\text{H}_{73}\text{N}_8\text{Ni}_4\text{O}_{31.5}\text{Er}_2$
Formula weight	1971.95	1995.98	1979.63
Crystal system	Monoclinic	Monoclinic	Monoclinic
$a/\text{\AA}$	12.6435(13)	12.636(4)	12.596(2)
$b/\text{\AA}$	18.3018(19)	18.317(5)	18.121(3)
$c/\text{\AA}$	15.4157(16)	15.566(5)	15.466(3)
$\alpha/^\circ$	90.00	90.00	90.00
$\beta/^\circ$	96.424(2)	98.222(5)	99.104(3)
$\gamma/^\circ$	90.00	90.00	90.00
Volume/ \AA^3	3544.8(6)	3565.8(18)	3485.7(11)
T/K	296(2)	296(2)	296(2)
Space group	$P21/n$	$P21/n$	$P21/n$
Z	2	2	1
$D_{\text{calcd}}(\text{g cm}^{-3})$	1.848	1.859	1.886
$F(000)$	1976	1996	1978
R_{int}	0.0429	0.0441	0.0540
$R_1/wR_2[I > 2\sigma(I)]$	0.0378/0.1043	0.0313/0.0727	0.0369/0.0824
R_1/wR_2 (all data)	0.0513/0.1102	0.0454/0.0770	0.0619/0.0890
GOF on F^2	1.058	1.010	0.993

the monodentate coordination carboxyl group, while the other intense absorption band around 1410 cm^{-1} may be assigned to $\nu_s(\text{COO})$, the symmetrical vibration band of the monodentate coordination carboxyl group.²³ The differences between antisymmetric and symmetric stretching bands indicate that the carboxylate group coordinated to the metal ions in a bridging fashion. The absence of a characteristic absorption band in the range of 1700 cm^{-1} indicates the complete deprotonation of the ligands and coordination to the metal ions. The $\text{C}=\text{N}(\text{imine})$ band shifts to a lower frequency by about 10 cm^{-1} in the title complexes.

UV-vis spectra were recorded for all of the complexes in CH_3OH ($5.0 \times 10^{-4}\text{ mol L}^{-1}$) (Fig. S1, ESI†). In the visible region, all of the complexes 1–7 show an absorption peak range from 547 to 594 nm, which can be assigned to the spin-allowed d–d transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$.²⁴ This can also be seen from the molar absorption coefficient ($\epsilon/\text{L mol}^{-1}\text{ cm}^{-1}$), 94.4 (1), 109 (2), 117.2 (3), 153.2 (4), 41.4 (5), 276 (6), 80.8 (7). The similarity of the optical spectrum for all of the complexes is indicative of the invariance of the coordination environment around the Ni centers in these complexes.

Crystal structures of 1–7

The reaction of rare-earth nitrate salts and nickel acetate with H_6L in a mixture of water and methanol in a 1 : 3 molar ratio in the presence of NaOH leads to the formation of hexanuclear heterometallic Ni_4Ln_2 clusters 1–7 in about a 45% yield. The result reveals that one imine bond in the ligand H_6L is degraded into an NH_2 group, giving the new ligand H_4L^1 and like the Zn^{2+} , Cu^{2+} and Cd^{2+} compounds reported in the literature,²⁵ the Ni^{2+} catalyzed partial degradation of the imine-phenol ligand takes place, as reported here. According to the idea proposed earlier by J. Parr and co-workers,²⁵ a proposed process for the formation of H_4L^1 is suggested in Scheme 1. Coordination and therefore deprotonation of one arm of the ligand H_6L to Ni^{2+} possibly forms small quantities of $\text{H}_3\text{O}^+\text{NO}_3^-$ *in situ*, which catalyses the hydrolysis of the remaining unbound 3-carboxylsalicylidene arms back to amine groups and then binds to the metal centre.

Single-crystal X-ray diffraction analyses reveal that compounds 1–7 are isomorphous, crystallizing in the monoclinic space group $P2_1/n$. The structure of 4 will be described as representative of the whole series. The crystal structure consists of the entities $[\text{Ni}_2\text{GdL}^1\text{L}^2(\text{OH})(\text{H}_2\text{O})]_2$ and water molecules of crystallization. A perspective view of the hexanuclear portion is depicted in Fig. 1. Selected bond parameters of 1–7 are summarized in Tables 1 and 2. The complex core can be described as two Ni_2GdO_4 subunits held together by two carboxyl groups (Fig. 2). Each Ni_2GdO_4 subunit comprises two Ni ions and one Gd ion, in which the three metallic ions are connected to each other by means of three phenoxo groups and one hydroxyl group. In addition, three phenoxo groups adopt a doubly bridged mode and each connects one Ni ion and one Gd ion. Meanwhile, the hydroxyl group only adopts a triply bridged mode linking two Ni ions and one Gd ion.

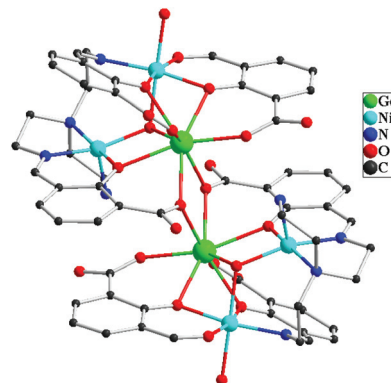


Fig. 1 Compound $[\text{Ni}_2\text{GdL}(\text{OH})(\text{H}_2\text{O})]_2$ (4); hydrogen atoms and solvent molecules omitted for clarity.

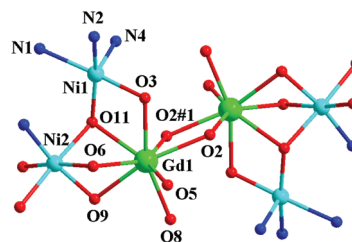


Fig. 2 Coordination environment of nickel and gadolinium in $[\text{Ni}_2\text{GdL}(\text{OH})(\text{H}_2\text{O})]_2$ (4); carbon, hydrogen atoms and solvent omitted for clarity.

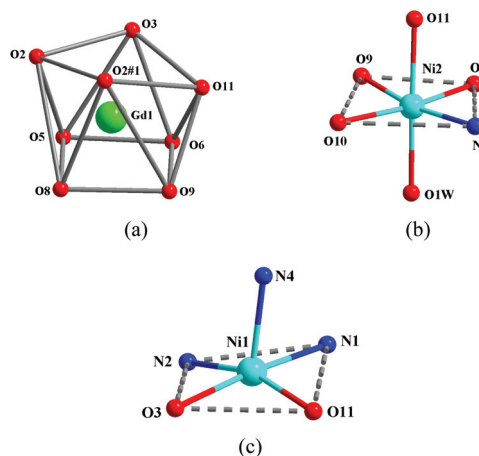


Fig. 3 (a) Distorted square antiprismatic environment around the gadolinium (III) metal ion in 4. (b) Distorted octahedral environment around the Ni2 atom in 4. (c) Distorted square pyramid environment around the Ni1 atom in 4.

Two Ni ions exist in dissimilar environments. The Ni1 ion is five-coordinate with the N_3O_2 environment and the coordination polyhedron can be viewed as a distorted square pyramid geometry (Fig. 3). Two nitrogen atoms (N1, N2) and an oxygen atom (O3) from the ligand H_4L^1 build the basal plane, whereas the apical position is occupied by a nitrogen atom (N4) from the ligand H_4L^1 . The Ni1–O and Ni1–N bond lengths cover ranges of $1.979(2)$ – $2.036(2)\text{ \AA}$ and $1.960(3)$ – $2.166(3)\text{ \AA}$, which are similar to the values reported in the literature.^{7e}

The Ni ion lies at about 0.2257 Å above the average basal plane. The dihedral angle formed by Ni1N1N2 and Ni1O3O11 is 161.275(87)°. The Ni2 ion adopts a slightly distorted octahedral geometry with an NO₅ donor set (Fig. 3). The equatorial positions of Ni2 are occupied by NO₃ donor atoms from the ligands H₄L¹ and H₂L² and the axial positions are occupied by two oxygen atoms arising from one water molecule and one hydroxyl group. The Ni2–O distances are in the range of 2.007(2)–2.068(2) Å. The Ni2–N bond length is 2.025(3) Å. These are comparable with the ranges found in the literature.^{7f} The Ni2 ion lies at about 0.0467 Å above the equatorial plane. The dihedral angle formed by Ni2N3O6 and Ni2N9O10 is 175.4(9)°. The two Ni ion pairs are connected through a hydroxyl group. The value of the Ni1...Ni2 separation is 3.4221(16) Å. The Ni1–O11–Ni2 angle is 116.4(1)°.

The Gd ion is coordinated by three phenolic oxygen atoms, four carboxyl oxygen atoms from both ligands and a hydroxyl

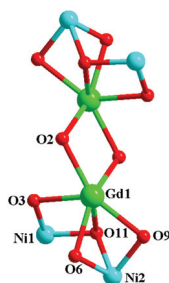


Fig. 4 View of the [Ni₂Gd]₂ dumbbell core.

group, resulting in an 8-fold coordinated geometry. The coordination polyhedron can be best described as a distorted square antiprism (Fig. 3). The Gd–O bond lengths fall in the range of 2.308(3)–2.413(2) Å, similar to the values reported previously.^{7e,f} Each Gd ion is linked through phenoxo groups and the hydroxyl group toward the two Ni ions, resulting in a Ni₂GdO₄ core. These are further bridged by carboxyl groups to an adjacent core, thus affording a Ni₄Gd₂O₁₀ dumbbell core (Fig. 4). The Ni...Gd distances range from 3.1449(5) to 6.6161(6) Å. The Gd...Gd distance is 3.9511(4) Å.

An inspection of Table 3 reveals that the Ni–O_{avg} and Ni–N_{avg} bond distances for all of the complexes are very similar and range from 2.002 to 2.054 Å for Ni–O_{avg} and from 2.014 to 2.063 Å for Ni–N_{avg} bonds. The Ln–O_{avg} bond distances generally decrease in the order Pr(2.433) > Sm(2.394) > Eu(2.393) > Gd(2.371) > Tb(2.359) > Ho(2.344) > Er(2.328), in accord with the lanthanide contraction. It is also interesting to note that the Ln–Ln distances found in 1–7 follow the lanthanide contraction and decrease from 1 to 7 (Table 3).

Luminescence properties

The luminescence spectra of the ligand H₆L and the complexes 1–7 were studied at room temperature in the solid state. When excited at 286 nm, the ligand H₆L exhibits a broad strong peak at around 489 nm. The spectra of 1–2, 4–5 and 7 were blue shifted from 490 to 495 nm along with an enhancement of the excitation wavelength as some lanthanide ions were directly modulated by the presence of the d-metal ions.²⁶ Compound 6 appears red shift to 474 nm, which may be

Table 3 Selected bond distances for 1–7

	1	2	3	4	5	6	7
Ni1–N	2.178(6)	2.166(3)	2.165(5)	2.166(3)	2.158(5)	2.171(3)	2.167(3)
	2.022(7)	2.019(3)	2.039(6)	2.026(3)	2.038(6)	2.032(3)	2.015(3)
	1.956(6)	1.954(3)	1.970(5)	1.960(3)	1.966(5)	1.972(3)	1.957(3)
	2.052 ^a	2.0463 ^a	2.058 ^a	2.0506 ^a	2.054 ^a	2.0583 ^a	2.0463 ^a
Ni1–O	2.036(5)	2.039(2)	2.057(4)	2.036(2)	2.035(4)	2.045(3)	2.035(2)
	1.986(5)	1.982(3)	1.994(4)	1.979(2)	1.981(4)	1.981(2)	1.968(2)
	2.011 ^a	2.0105 ^a	2.0255 ^a	2.0075 ^a	2.008 ^a	2.013 ^a	2.0015 ^a
	2.015(6)	2.021(3)	2.026(5)	2.025(3)	2.029(6)	2.022(3)	2.027(3)
Ni2–N	2.022(4)	2.010(3)	2.022(4)	2.052(3)	2.006(4)	2.005(3)	1.993(2)
	2.040(5)	2.031(2)	2.030(4)	2.007(2)	2.045(4)	2.028(2)	2.018(2)
Ni2–O	2.042(5)	2.046(2)	2.053(4)	2.028(2)	2.091(5)	2.046(2)	2.038(2)
	2.055(5)	2.053(3)	2.054(4)	2.047(2)	2.036(4)	2.054(3)	2.051(2)
	2.059(5)	2.064(3)	2.090(4)	2.068(2)	2.050(4)	2.087(3)	2.092(2)
	2.0436 ^a	2.0408 ^a	2.0498 ^a	2.0404 ^a	2.0456 ^a	2.0428 ^a	2.0384 ^a
	2.481(4)	2.440(2)	2.439(3)	2.410(2)	2.406(4)	2.393(2)	2.377(2)
	2.395(5)	2.357(2)	2.428(3)	2.332(2)	2.387(4)	2.303(2)	2.294(2)
	2.450(4)	2.415(2)	2.412(3)	2.389(2)	2.310(4)	2.374(3)	2.348(2)
	2.480(4)	2.433(2)	2.342(3)	2.407(2)	2.390(4)	2.375(2)	2.353(2)
Ln–O	2.357(5)	2.329(3)	2.331(4)	2.308(3)	2.292(4)	2.271(3)	2.261(2)
	2.372(5)	2.346(3)	2.391(3)	2.335(2)	2.320(4)	2.308(3)	2.287(2)
	2.435(4)	2.392(2)	2.363(4)	2.375(2)	2.403(4)	2.344(2)	2.337(2)
	2.491(4)	2.440(2)	2.438(3)	2.413(2)	2.367(4)	2.383(2)	2.365(2)
	2.4326 ^a	2.394 ^a	2.393 ^a	2.3711 ^a	2.3593 ^a	2.3438 ^a	2.3277 ^a
	3.5375(13)	3.5001(6)	3.5057(11)	3.4783(5)	3.4628(8)	3.4687(9)	3.4433(6)
	3.1902(12)	3.1617(5)	3.1672(10)	3.1449(5)	3.1506(8)	3.1352(9)	3.1209(6)
	3.4444(15)	3.4343(8)	3.4447(13)	3.4221(6)	3.4406(11)	3.4195(10)	3.4008(7)
Ln–Ln	4.0483(11)	3.9862(4)	3.9788(7)	3.9511(4)	3.9418(5)	3.9104(8)	3.8876(5)

^a Average bond distances.

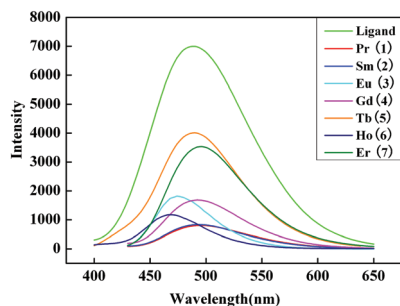


Fig. 5 Fluorescence spectra of the ligand H₆L and complexes 1–7.

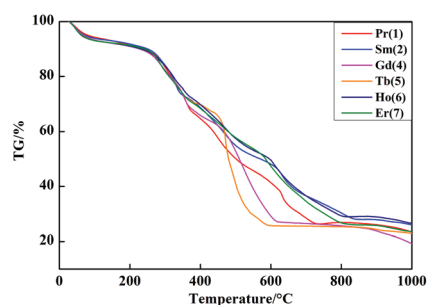


Fig. 6 TGA curves for 1–2 and 4–7.

assigned to ligand–metal charge transfer.²⁷ As shown in Fig. 5, the emission intensity generally decreases in the order Tb(5) > Er(7) > Ho(6) > Gd(4) > Eu(3) > Sm(2) > Pr(1), in accord with the lanthanide contraction, except for Tb(5).

Thermogravimetric analysis (TGA)

The TGA of the compounds are depicted in Fig. 6. For 1, the weight loss of 9.39% between 25 and 219 °C is attributed to the loss of two coordinated and eight free water molecules (calcd 9.30%). The decomposition of 1 occurs above 219 °C. For 2, the weight loss of 9.56% in the range of 25–242 °C corresponds to the loss of eight and a half free and two coordinated water molecules (calcd 9.62%). The weight loss above 242 °C indicates the decomposition of the framework. For 4, the weight loss of 9.22% in the range of 25–206 °C corresponds to the loss of eight free and two coordinated water molecules (calcd 9.14%). The residues decompose after 206 °C. For 5, the weight loss of 9.2% in the range of 25–220 °C corresponds to the loss of eight free and two coordinated water molecules (calcd 9.13%) and above 220 °C, complex 5 is gradually decomposed. For 6, the weight loss of 9.76% between 25 and 227 °C is attributed to the loss of one methanol molecule, two coordinated and seven free water molecules (calcd 9.71%). The decomposition of 6 occurs above 227 °C. For 7, the weight loss of 8.71% in the range of 25–201 °C corresponds to the loss of seven and a half free and two coordinated water molecules (calcd 8.64%).

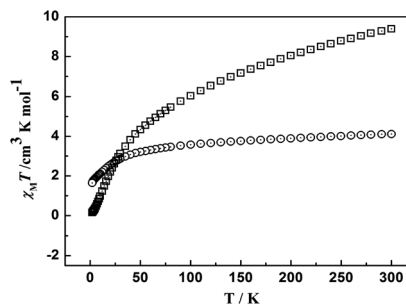
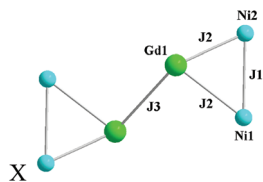


Fig. 7 $\chi_{\text{M}}T$ versus T plots for complex 2 (O) and 3 (□).

Magnetic properties

The temperature-dependent magnetic susceptibility data of polycrystalline samples of 2, 3 and 4 have been recorded at an applied magnetic field of 1000 Oe in the temperature range of 2–300 K. The curves of $\chi_{\text{M}}T$ versus T are shown in Fig. 7 for 2 and 3. For 2, at 300 K, the observed $\chi_{\text{M}}T$ value of 4.11 cm³ K mol⁻¹ is close to the expected value of 4.18 cm³ K mol⁻¹ for two uncoupled Sm^{III} ions (⁶H_{5/2}, $S = 5/2$, $L = 0$ and $g = 2/7$) and four uncoupled Ni^{II} ions ($S = 1$ and $g = 2$). Upon cooling, the $\chi_{\text{M}}T$ value decreases regularly, approaching a minimum around 2 K with $\chi_{\text{M}}T = 1.64$ cm³ K mol⁻¹. The experimental $\chi_{\text{M}}T$ value for 3 at room temperature (9.39 cm³ K mol⁻¹) is higher than the theoretical value (5.63 cm³ K mol⁻¹) calculated for four uncoupled Ni^{II} ions ($S = 1$) and two Eu^{III} ions ($S = 0$) in the ⁷F₀ ground state. This result is explained by the presence of the first excited states that are sufficiently low in energy to be thermally populated at 300 K. As these thermally populated levels are much more magnetic than the ground state, the experimental $\chi_{\text{M}}T$ product is higher than estimated. As shown in Fig. 7, lowering the temperature induces a continuous decrease of the $\chi_{\text{M}}T$ product of 3 to a value of 0.16 cm³ K mol⁻¹ at 2 K. This behavior is the expected result of the progressive and finally total depopulation of the magnetic excited states of the europium(III) metal ions. However, it is difficult to comment on the Ni...Ln and Ln...Ln interactions in 2 and 3 as lanthanide ions have intrinsic complicated magnetic characteristics, which include the presence of spin–orbit coupling and magnetic anisotropy.²⁸

In 4, the introduction of magnetically isotropic Gd^{III} ions allows us to estimate the magnetic interactions of Ni...Gd and Gd...Gd. For 4, at room temperature, the $\chi_{\text{M}}T$ value of 20.92 cm³ K mol⁻¹ is in good agreement with the expected value of 19.75 cm³ K mol⁻¹ for two uncoupled Gd^{III} ions (⁸S_{7/2}, $S = 7/2$, and $g = 2$) and four noninteracting Ni^{II} ions ($S = 1$ and $g = 2$). Upon cooling, the $\chi_{\text{M}}T$ value decreases slowly up to 120 K, where it reaches a value of 20.62 cm³ K mol⁻¹, and then decreases rapidly down to 2 K, reaching a minimum value of 12.62 cm³ K mol⁻¹. To our knowledge, no formula in the literature is available to reproduce the magnetic susceptibility of such a complex system. Therefore, its magnetic properties were preliminarily investigated. We were able to successfully simulate the magnetic susceptibility data using the three-J



Scheme 2 Magnetic exchange interactions from the three- J model employed to simulate the susceptibilities of compound **4**.

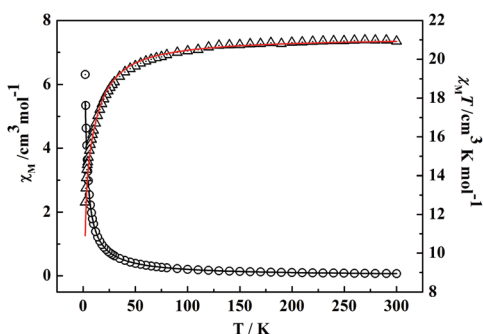


Fig. 8 $\chi_M T$ versus T plots for complex **4** (Δ), the red line is the simulation of the experimental data.

models, as shown in Scheme 2. Using the MAGPACK²⁹ program and employing the Hamiltonian in eqn (1)

$$\hat{H} = - \sum 2J_{ij} \hat{S}_i \hat{S}_j \quad (1)$$

afforded the parameters $J_1 = -4.35 \text{ cm}^{-1}$, $J_2 = -0.17 \text{ cm}^{-1}$, $J_3 = -0.05 \text{ cm}^{-1}$ and $g = 2.07$ (Fig. 8). Previous literature reported that Ni–O–Ni angles between any two Ni^{II} ions that are smaller than 98° are expected to show ferromagnetic coupling. Angles larger than 98° are expected to lead to antiferromagnetic coupling between Ni^{II} ions.³⁰ J_1 corresponds to the bridging angles larger than 98° and its value is negative. Obviously, our result ($116.4(1)^\circ$) is in very good agreement with the literature report.³⁰ As expected, the interactions between metal ions in the hexanuclear moiety are all antiferromagnetic.

Conclusions

The use of a specifically designed tripodal Schiff-base ligand [$\text{H}_6\text{L} = 3,3',3''\text{-(1E,1'E,1''E)-(2,2',2''-nitritoltris(ethane-2,1-diy) tris(azan-1-yl-1-ylidene))tris(methan-1-yl-1-ylidene)tris(2-hydroxybenzoic acid)}$], containing N_3O_3 and O_6 inner and outer pockets, respectively, allows for the synthesis of a new family of heterometallic hexanuclear Ni_4Ln_2 clusters. In all of these compounds, the six metal ions are held together to form a novel $\text{Ni}_4\text{Ln}_2\text{O}_{10}$ core, exhibiting a relatively rare dumbbell-type structure. From a structural point of view, the nickel ions involved in the hexanuclear complexes have different coordination spheres: distorted octahedrons and square-pyramids. The coordination geometry around the lanthanide metal ion is distorted icosahedral. To the best of our knowledge, all the compounds are first constructed from *in situ* Ni^{II}-catalyzed

partial degradation of tripodal ligand, which further expands the studying models of the hydrolysis of the imine–phenol Schiff base types. The Ln–Ln separation and Ln– O_{avg} bond distances follow the lanthanide contraction trend. The luminescent intensity generally decreases in the order $\text{Tb}(5) > \text{Er}(7) > \text{Ho}(6) > \text{Gd}(4) > \text{Eu}(3) > \text{Sm}(2) > \text{Pr}(1)$, in accord with the lanthanide contraction, except for Tb(5). The magnetic properties of **2**, **3** and **4** have been also measured and analyzed.

Acknowledgements

We acknowledge the generous financial support of the National Science Foundation of China (21271143), the Natural Science Foundation of Henan Province (092300410031), the Open Project of Key Lab Adv Energy Mat Chem (Nankai Univ) (KLAEMC-OP201201) and the Natural Science Foundation of Henan University (2010YBZR007 and 2010YBZR015).

References

- (a) A. D. C. Noord, J. W. Kampf and V. L. Pecoraro, *Angew. Chem., Int. Ed.*, 2002, **41**, 4667; (b) R. Gheorghe, P. Cucos, M. Andruh, J. P. Costes, B. Donnadieu and S. Shova, *Chem.–Eur. J.*, 2006, **12**, 187; (c) X. J. Kong, L. S. Long, Z. Zheng, R. B. Huang and L. S. Zheng, *Acc. Chem. Res.*, 2010, **43**, 201.
- (a) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *J. Am. Chem. Soc.*, 2004, **126**, 420; (b) C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk and V. L. Pecoraro, *Angew. Chem., Int. Ed.*, 2004, **43**, 3912; (c) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328.
- (a) J. C. G. Bunzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048; (b) M. D. Ward, *Coord. Chem. Rev.*, 2007, **251**, 1663.
- M. Shibusaki and N. Yoshikawa, *Chem. Rev.*, 2002, **102**, 2187.
- (a) J. J. Zhang, T. L. Sheng, S. Q. Xia, G. Leibelng, F. Meyer, S. M. Hu, R. B. Fu, S. C. Xiang and X. T. Wu, *Inorg. Chem.*, 2004, **43**, 5472; (b) G. L. Zhuang, Y. C. Jin, H. X. Zhao, X. J. Kong, L. S. Long, R. B. Huang and L. S. Zheng, *Dalton Trans.*, 2010, **39**, 5077.
- (a) H. Z. Kou, B. C. Zhou and R. J. Wang, *Inorg. Chem.*, 2003, **42**, 7658; (b) R. Calvo, R. E. Rapp, E. Chagas, R. P. Sartoris, R. Baggio, M. T. Garland and M. Pereg, *Inorg. Chem.*, 2008, **47**, 10389; (c) D. Y. Shi, J. W. Zhao, L. J. Chen, P. T. Ma, J. P. Wang and J. Y. Niu, *CrystEngComm*, 2012, **14**, 3108; (d) R. Gheorghe, M. Andruh, A. Muller and M. Schmidtman, *Inorg. Chem.*, 2002, **41**, 5314; (e) H. Z. Kou, Y. B. Jiang and A. L. Cui, *Cryst. Growth Des.*, 2005, **5**, 77; (f) K. F. Konidaris, C. N. Morrison, J. G. Servetas, M. Haukka, Y. Lan, A. K. Powell, J. C. Plakatouras and G. E. Kostakis, *CrystEngComm*, 2012, **14**, 1842; (g) J. X. Ma, X. F. Huang, Y. Song, X. Q. Song and W. S. Liu, *Inorg. Chem.*, 2009, **48**, 6326; (h) X. P. Yang,

- R. A. Jones, M. M. Oye, M. Wiester and R. J. Lai, *New J. Chem.*, 2011, **35**, 310; (i) X. F. Li, Y. B. Huang and R. Cao, *Cryst. Growth Des.*, 2012, **12**, 3549.
- 7 (a) J. P. Liu, D. W. Knoepfel, S. M. Liu, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 2001, **40**, 2842; (b) A. Q. Wu, G. H. Guo, F. K. Zheng and M. S. Wang, *Inorg. Chem. Commun.*, 2005, **8**, 1078; (c) P. Mahata, K. V. Ramya and S. Natarajan, *Inorg. Chem.*, 2009, **48**, 4942; (d) X. Hu, Y. F. Zeng, Z. Chen, E. C. Sanudo, F. C. Liu, J. Ribas and X. H. Bu, *Cryst. Growth Des.*, 2009, **9**, 421; (e) J. P. Costes, T. Yamaguchi, M. Kojima and L. Vendier, *Inorg. Chem.*, 2009, **48**, 5555; (f) H. S. Ke, L. Zhao, Y. Guo and J. K. Tang, *Inorg. Chem.*, 2012, **51**, 2699.
- 8 (a) J. P. Costes, J. M. Clemente-Juan, F. Dahan, F. Dumestre and J. P. Tuchagues, *Inorg. Chem.*, 2002, **41**, 2886; (b) T. Akitsu and Y. Einaga, *Polyhedron*, 2006, **25**, 2655; (c) W. T. Chen, G. C. Guo, M. S. Wang, G. Xu, L. Z. Cai, T. Akitsu, M. A. Tanaka, A. Matsushita and J. S. Huang, *Inorg. Chem.*, 2007, **46**, 2105; (d) S. Mukherjee, Y. Lan, G. Novitchi, G. E. Kostakis, C. E. Anson and A. K. Powell, *Polyhedron*, 2009, **28**, 1782.
- 9 (a) T. Shiga, H. O. Kawa, S. Kitagawa and M. Ohba, *J. Am. Chem. Soc.*, 2006, **128**, 16426; (b) Y. Wang, P. Cheng, J. Chen, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2007, **46**, 4530; (c) Y. G. Huang, X. T. Wang, F. L. Jiang, S. Gao, M. Y. Wu, Q. Gao, W. Wei and M. C. Hong, *Chem.-Eur. J.*, 2008, **14**, 10340; (d) J. P. Costes, L. Vendier and W. Wernsdorfer, *Dalton Trans.*, 2011, **40**, 1700.
- 10 (a) M. C. Yin, X. F. Lei, M. Li, L. J. Yuan and J. T. Sun, *J. Phys. Chem. Solids*, 2006, **67**, 1372; (b) H. L. Gao, B. Zhao, X. Q. Zhao, Y. Song, P. Cheng, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2008, **47**, 11057.
- 11 (a) B. Zhao, P. Cheng, Y. Dai, C. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang and G. L. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 934; (b) B. Zhao, P. Cheng, X. Y. Chen, C. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 3012; (c) B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394; (d) B. Zhao, H. L. Gao, X. Y. Chen, P. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *Chem.-Eur. J.*, 2006, **12**, 149; (e) T. K. Prasad, M. V. Rajasekharan and J. P. Costes, *Angew. Chem., Int. Ed.*, 2007, **46**, 2851; (f) C. M. Zaleski, J. W. Kampf, T. Mallah, M. L. Kirk and V. L. Pecoraro, *Inorg. Chem.*, 2007, **46**, 1954; (g) A. Mishra, A. J. Tasiopoulos, W. Wernsdorfer, E. E. Moushi, B. Moulton, M. J. Zaworotko, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2008, **47**, 4832; (h) T. C. Stamatatos, S. J. Teat, W. Wernsdorfer and G. Christou, *Angew. Chem., Int. Ed.*, 2009, **48**, 521.
- 12 (a) S. Decurtins, M. Gross, H. W. Schmalle and S. Ferlay, *Inorg. Chem.*, 1998, **37**, 2443; (b) A. Figuerola, C. Diaz, M. S. El Fallah, J. Ribas, M. Maestro and J. Mahia, *Chem. Commun.*, 2001, 1204; (c) B. Zhai, L. Yi, H. S. Wang, B. Zhao, P. Cheng, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2006, **45**, 8471; (d) J. Rinck, G. Novitchi, W. V. Heuvel, L. Ungur, Y. Lan, W. Wernsdorfer, C. E. Anson, L. F. Chibotaru and A. K. Powell, *Angew. Chem., Int. Ed.*, 2010, **49**, 7583.
- 13 (a) S. K. Singh, N. K. Tibrewal and G. Rajaraman, *Dalton Trans.*, 2011, **40**, 10897; (b) K. C. Mondal, G. E. Kostakis, Y. Lan, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2011, **50**, 11604.
- 14 (a) F. Pointillart, K. Bernot, R. Sessoli and D. Gatteschi, *Chem.-Eur. J.*, 2007, **13**, 1602; (b) C. G. Efthymiou, T. C. Stamatatos, C. Papatriantafyllopoulou, A. J. Tasiopoulos, W. Wernsdorfer, S. P. Perlepes and G. Christou, *Inorg. Chem.*, 2010, **49**, 9737; (c) T. D. Pasatou, M. Etienne, A. M. Madalan, M. Andruh and R. Sessoli, *Dalton Trans.*, 2010, **39**, 4802.
- 15 (a) A. Elmali and Y. Elerman, *J. Mol. Struct.*, 2005, **737**, 29; (b) C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J. F. Jacquot and D. Luneau, *Angew. Chem., Int. Ed.*, 2006, **45**, 4659; (c) C. Aronica, G. Chastanet, G. Pilet, B. L. Guennic, V. Robert, W. Wernsdorfer and D. Luneau, *Inorg. Chem.*, 2007, **46**, 6108.
- 16 (a) A. M. Ako, V. Mereacre, R. Clerac, I. J. Hewitt, Y. Lan, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2007, 5245; (b) V. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson and A. K. Powell, *Chem.-Eur. J.*, 2008, **14**, 3577; (c) V. Mereacre, D. Prodius, A. M. Ako, N. Kaur, J. Lipkowski, C. Simmons, N. Dalal, I. Geru, C. E. Anson, A. K. Powell and C. Turta, *Polyhedron*, 2008, **27**, 2459; (d) M. N. Akhtar, Y. Lan, V. Mereacre, R. Clerac, C. E. Anson and A. K. Powell, *Polyhedron*, 2009, **28**, 1698; (e) M. N. Akhtar, Y. Z. Zheng, Y. Lan, V. Mereacre, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2009, **48**, 3502; (f) A. M. Ako, V. Mereacre, R. Clerac, I. J. Hewitt, Y. Lan, G. Buth, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2009, **48**, 6713.
- 17 (a) A. Mishra, W. Wernsdorfer, S. Parsons, G. Christou and E. K. Brechin, *Chem. Commun.*, 2005, 2086; (b) M. Murugesu, A. Mishra, W. Wernsdorfer, K. A. Abboud and G. Christou, *Polyhedron*, 2006, **25**, 61313; (c) G. Wu, I. J. Hewitt, S. Mameri, Y. Lan, R. Clerac, C. E. Anson, S. Qium and A. K. Powell, *Inorg. Chem.*, 2007, **46**, 7229.
- 18 A. Jana, S. Majumder, L. Carrella, M. Nayak, T. Weyhermueller, S. Dutta, D. Schollmeyer, E. Rentschler, R. Koner and S. Mohanta, *Inorg. Chem.*, 2010, **49**, 9012.
- 19 C. A. Buehler, B. C. Bass and R. B. Darling, *et al.*, *J. Am. Chem. Soc.*, 1940, **62**, 890.
- 20 (a) *SMART & SAINT Software Reference manuals, version 6.45*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003; (b) G. M. Sheldrick, *SADABS a Software for Empirical Absorption Correction, Ver. 2.05*, University of Göttingen, Göttingen, Germany, 2002; (c) *SHELXTL Reference Manual, ver. 6.1*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2000; (d) G. M. Sheldrick, *SHELXTL ver. 6.12*, Bruker AXS Inc., Madison, WI, 2001; (e) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

- 21 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
- 22 O. Kahn, J. Galy and Y. Journaux, *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 2165.
- 23 (a) S. L. Johnson and K. A. J. Rumon, *J. Phys. Chem.*, 1965, **69**, 74; (b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 5th edn, 1997, vol. B.
- 24 (a) Z. Xu, P. W. Read, D. E. Hibbs, M. B. Hursthouse, K. M. A. Malik, B. O. Patrick, S. J. Rettig, M. Seid, D. A. Summers, M. Pink, R. C. Thompson and C. Orvig, *Inorg. Chem.*, 2000, **39**, 508; (b) S. R. Bayly, Z. Xu, B. O. Patrick, S. J. Rettig, M. Pink, R. C. Thompson and C. Orvig, *Inorg. Chem.*, 2003, **42**, 1576; (c) R. Koner, H. H. Lin, N. Ito, A. Hidaka, H. Okawa, S. Kitagawa and M. Ohba, *Inorg. Chem.*, 2007, **46**, 3492.
- 25 (a) P. Bhattacharyya, J. Parr and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1998, 3263; (b) X. X. Zhou, Y. P. Cai, S. Z. Zhu, Q. G. Zhan, M. S. Liu, Z. Y. Zhou and L. Chen, *Cryst. Growth Des.*, 2008, **8**, 2076.
- 26 (a) T. Gunnlaugsson, J. P. Leonard, K. Sénéchal and A. J. Harte, *Chem. Commun.*, 2004, 782; (b) A. M. Nonat, A. J. Harte, K. S. David, J. P. Leonard and T. Gunnlaugsson, *Dalton Trans.*, 2009, 4703.
- 27 (a) J. Tercero and C. Diaz, *Inorg. Chem.*, 2003, **42**, 3366; (b) R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, **51**, 33.
- 28 X. Q. Zhao, Y. H. Lan, B. Zhao, P. Cheng, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2010, **39**, 4911.
- 29 J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.*, 1999, **38**, 6081.
- 30 H. L. C. Feltham, R. Clérac and S. Brooker, *Dalton Trans.*, 2009, 2965.