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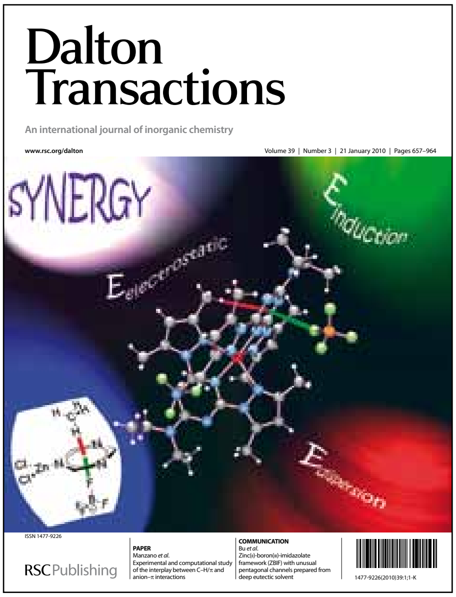

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ARTICLE TYPE

Family of dumbbell Ni_4Ln_2 (Ln = Pr, Sm, Eu, Gd, Tb, Ho, Er) complexes: syntheses, structures, luminescent and magnetic properties

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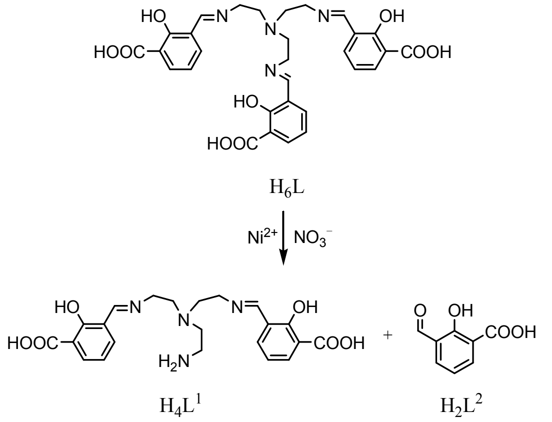
The synthesis and characterization of a family of heterometallic Ni_4Ln_2 complexes (Ln = Pr(**1**), Sm(**2**), Eu(**3**), Gd(**4**), Tb(**5**), Ho(**6**) and Er(**7**)) of formula $[Ni_2LnL^1 L^2(OH)(H_2O)]_2$ are reported, where H_4L^1 is 3,3'-(1E,1'E)-(2,2'-(2-aminoethylazanediyl)bis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-hydroxybenzoic acid), H_2L^2 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 novel $Ni_4Ln_2O_{10}$ core, 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 lanthanide contraction. The luminescent properties of all compounds have been studied. The magnetic susceptibility analysis demonstrate antiferromagnetic interaction within complex **4**.

Introduction

The chemistry of heterometallic 3d-4f complexes have attracted considerable attention due to their structural diversity,[1] and versatile applications in magnetic,[2] luminescent,[3] adsorptive,[4] and electrical materials.[5] Among all the heteronuclear edifice, most are about the 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-Ln[11] and Cr-Ln[12] systems are reported. We have recently joined ongoing efforts in this area and have initially focused primarily on Ni-Ln species. We were interested to discover 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 also can 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) 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 (H_6L = 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), (H_6L), 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 ligand H_6L is degraded into NH_2 group, giving the new ligand H_4L^1 (Scheme 1). It is the first example from hydrated Ni(II) salt promoting partial hydrolysis of the Schiff base ligand.

Herein, we reported 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**)].



Scheme 1 Proposed process for the formation of H_4L^1

Experimental Section

General

All chemicals and solvents were in 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}. ^{1}H NMR spectra was 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℃ at a heating rate of 10℃ min^{-1}. Magnetic measurement was carried out on polycrystalline samples with a MPMS-7SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all atoms.

Preparation of ligand H$_6$L.

The ligand H$_6$L 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) during 3 h. After cooling to room temperature, yellow precipitate were obtained, which were 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. ^{1}H 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).

Table 1 Crystallographic Data and Refinement for **1-4**

	1	**2**	**3**	**4**
Formula	$C_{60}H_{73}N_8Ni_4O_{32.5}Pr_2$	$C_{60}H_{75}N_8Ni_4O_{32.5}Sm_2$	$C_{60}H_{74}N_8Ni_4O_{33}Eu_2$	$C_{60}H_{74}N_8Ni_4O_{32}Gd_2$
Formula weight	1942.93	1963.82	1974.03	1968.61
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	12.770(4)	12.7048(6)	12.703(3)	12.6620(10)
b/Å	18.183(6)	18.1777(9)	18.339(5)	18.1513(14)
c/Å	15.616(5)	15.5866(8)	15.578(4)	15.5428(12)
α/°	90.00	90.00	90.00	90.00
β/°	100.262(5)	99.9870(10)	98.101(4)	99.7790(10)
γ/°	90.00	90.00	90.00	90.00
Volume/Å^3	3568(2)	3545.1(3)	3592.9(16)	3520.3(5)
T/K	296(2)	296(2)	296(2)	296(2)
Space group	*P*21/*n*	*P*21/*n*	*P*21/*n*	*P*21/*n*
Z	1	1	2	2
D_{calcd} (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	$C_{60}H_{74}N_8Ni_4O_{32}Tb_2$	$C_{61}H_{74}N_8Ni_4O_{32}Ho_2$	$C_{60}H_{73}N_8Ni_4O_{31.5}Er_2$
Formula weight	1971.95	1995.98	1979.63
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	12.6435(13)	12.636(4)	12.596(2)
b/Å	18.3018(19)	18.317(5)	18.121(3)
c/Å	15.4157(16)	15.566(5)	15.466(3)
α/°	90.00	90.00	90.00
β/°	96.424(2)	98.222(5)	99.104(3)
γ/°	90.00	90.00	90.00
Volume/Å^3	3544.8(6)	3565.8(18)	3485.7(11)
T/K	296(2)	296(2)	296(2)
Space group	*P*21/*n*	*P*21/*n*	*P*21/*n*
Z	2	2	1
D_{calcd} (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

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$_2$PrL^{1}L^2(OH)(H$_2$O)]$_2$·8H$_2$O (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 $Ni(OAc)_2\cdot4H_2O$ (0.25 g, 1 mmol) and $Pr(NO_3)_3\cdot6H_2O$ (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).

$[Ni_2SmL^1L^2(OH)(H_2O)]_2\cdot8.5H_2O$ (2). Yield: 0.44 g, 45% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{75}N_8Ni_4O_{32.5}Sm_2$: 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).

$[Ni_2EuL^1L^2(OH)(H_2O)]_2\cdot9H_2O$ (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).

$[Ni_2GdL^1L^2(OH)(H_2O)]_2\cdot8H_2O$ (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).

$[Ni_2TbL^1L^2(OH)(H_2O)]_2\cdot8H_2O$ (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).

$[Ni_2HoL^1L^2(OH)(H_2O)]_2\cdot7H_2O\cdot CH_3OH$ (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).

$[Ni_2ErL^1L^2(OH)(H_2O)]_2\cdot7.5H_2O$ (7). Yield: 0.51 g, 52% (based on the nickel salt). Anal. Calcd (%) for $C_{60}H_{73}N_8Ni_4O_{31.5}Er_2$: 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 Table 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 ($\lambda = 0.71073$ Å). The program SMART[20a] was used for collecting frames of data, indexing reflection, and determining lattice parameters, SAINT[20a] for integration of the intensity of reflections and scaling, SADABS[20b] for absorption correction, and SHELXTL[20c,d] for 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 refinement in a riding model along with attached carbon atoms.

Results and Discussion

IR and UV-vis spectra of complexes

In the IR spectra of ligand H_6L, the band at 1694 cm^{-1} can be ascribed to the stretching vibration of the ν(COOH) vibration band, the broad band at 3430 cm^{-1} can be assigned to the ν(OH) band[21] and the absorption band at 1658 cm^{-1} corresponds to the stretching vibration of the C=N(imine) band.[22] In the title complexes, the COO^- asymmetrical vibration band of ν_{as}(COO) exhibits one intense absorption band around 1560 cm^{-1}, which may be attributed to ν_{as}(COO) band of the monodentate coordination carboxyl group; while the other intense absorption band around 1410 cm^{-1} may be assigned to ν_s(COO), the symmetrical vibration band of 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 metal ions. The C=N(imine) band shifts to lower frequency about 10 cm^{-1} in the title complexes.

UV-vis spectra were recorded for all of the complexes in CH_3OH (5.0×10^{-4} mol L^{-1}) (Fig. S1). In the visible region, all of the complexes **1-7** show an absorption peak range from 547 to 594nm, which can be assigned to the spin-allowed d-d transition $^3A_{2g}$-$^3T_{2g}$[24] range from. This can also be seen from the molar absorption coefficient (ε/L·mol^{-1}·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 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 45% yield. The result reveals that one imine bond in the ligand H_6L is degraded into NH_2 group, giving the new ligand H_4L^1 like Zn^{2+}, Cu^{2+} and Cd^{2+} reported in the literature,[25] the Ni^{2+} catalyzed partial degradation of 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 was suggested in Scheme 1. Coordination and so deprotonation of one arm of the ligand H_6L to Ni^{2+} possibly forms small quantities of $H_3O^+NO_3^-$ *in situ*, which catalyses the hydrolysis of the remaining unbound 3-carboxylsalicylidene arms back to amine groups, then bind 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 entities $[Ni_2GdL^1L^2(OH)(H_2O)]_2$ 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 Table 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 group adopt a doubly bridged mode, and each connects one Ni ion and one Gd ion. Meanwhile, the hydroxyl group just adopts a triply bridged mode linking two Ni ions and one Gd ion.

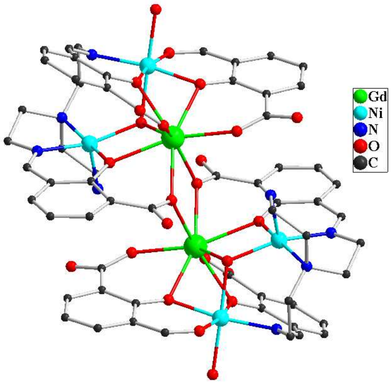


Fig. 1 Compound $[Ni_2GdL(OH)(H_2O)]_2$ (**4**); hydrogen atoms and solvent molecules omitted for clarity.

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]	2.008a	2.013[a]	2.0015[a]
Ni2-N	2.015(6)	2.021(3)	2.026(5)	2.025(3)	2.029(6)	2.022(3)	2.027(3)
Ni2-O	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)
	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]
Ln-O	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)
	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]
Ni1-Ln	3.5375(13)	3.5001(6)	3.5057(11)	3.4783(5)	3.4628(8)	3.4687(9)	3.4433(6)
Ni2-Ln	3.1902(12)	3.1617(5)	3.1672(10)	3.1449(5)	3.1506(8)	3.1352(9)	3.1209(6)
Ni1-Ni2	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.

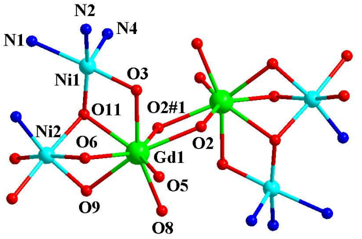
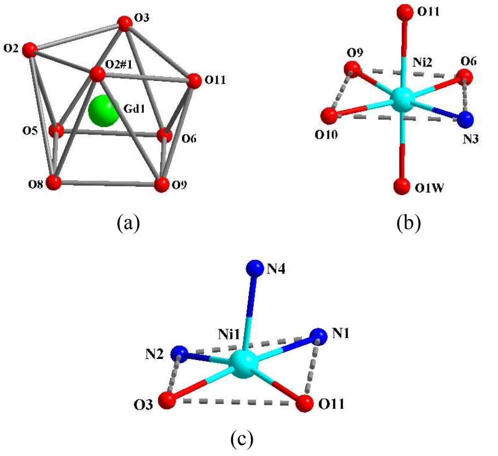


Fig. 2 Coordination environment of nickel and gadolinium in $[Ni_2GdL(OH)(H_2O)]_2$ (**4**); carbon and hydrogen atoms, and solvent

Two Ni ions exist in dissimilar environments. The Ni1 ion is five-coordinated with the N_3O_2 environment, and the coordination polyhedron can be viewed as distorted square pyramid geometry (Fig. 3). Two nitrogen atoms (N1, N2) and a 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 1.979(2)-2.036(2) Å and 1.960(3)-2.166(3) Å, 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 has adopted a slightly distorted octahedral geometry with an NO_5 donor set, (Fig. 3). The equatorial positions of Ni2 are occupied by NO_3 donor atoms from the ligand H_4L^1 and H_2L^2, 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 2.007(2)-2.068(2) Å. The Ni2-N bond length is 2.025(3) Å. They are comparable with the range 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 hydroxyl group. The value of Ni1···Ni2 separation is 3.4221(16) Å. The Ni1-O11-Ni2 angle is 116.4 (1)°.



(a) (b)

(c)

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**.

The Gd ion is coordinated by three phenolic oxygen atoms, four carboxyl oxygen atoms from both ligands and a hydroxyl 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 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 Ni_2GdO_4 core, these are further bridged by carboxyl groups to adjacent core, thus affording a $Ni_4Gd_2O_{10}$ 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.

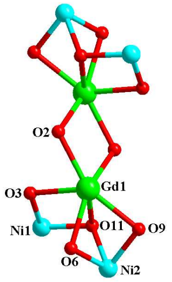


Fig. 4 View of the $[Ni_2Gd]_2$ dumbbell core

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 proceeding from **1** to **7** (Table 3).

Luminescence Properties

The luminescence spectra of the ligand H_6L and the complexes **1-7** were studied at room temperature in the solid state. When excited at 286 nm, ligand H_6L exhibits a broad strong peak 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 excitation wavelength. As some lanthanide ions was directly modulated by the presence of the *d*- metal ions.[26] Compound **6** appears red shift to 474 nm, which may be assigned to ligand-metal charge transfer.[27] As shown in Fig. 5, the emission intensity generally decrease in the order Tb(**5**) >Er(**7**) >Ho(**6**) >Gd(**4**) >Eu(**3**) >Sm(**2**) >Pr(**1**), in accord with the lanthanide contraction, except Tb(**5**).

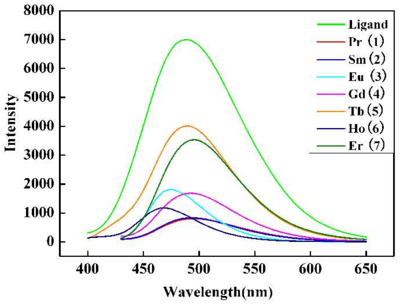


Fig. 5 Fluorescence spectra of ligand H_6L and complexes **1-7**

Thermogravimetric Analysis (TGA)

The TGA of 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 point five 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 point five free and two coordinated water molecules (calcd 8.64%).

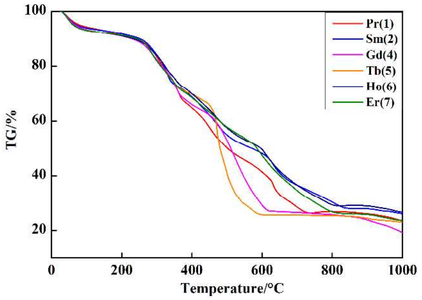


Fig. 6 TGA curves for **1-2** and **4-7**

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 χ_MT versus T are shown in Fig. 7 for **2** and **3**. For **2**, at 300 K, the observed χ_MT value of 4.11 cm^3 K mol^{-1} is close to the expected value of 4.18 cm^3 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 χ_MT value decrease regularly, approaching a minimum around 2 K with χ_MT = 1.64 cm^3 K mol^{-1}.The experimental χ_MT value for **3** at room temperature (9.39 cm^3 K mol^{-1}) is higher than the theoretical value (5.63 cm^3 K mol^{-1}) calculated for four uncoupled Ni^{II} ions (S = 1) and two Eu^{III} ions (S = 0) in the ground state $^7F_0$. 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 χ_MT product is higher than estimated. As shown in Figure 7, lowering the temperature induces a continuous decrease of the χ_MT product of **3** to a value of 0.16 cm^3 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 interactions of Ni···Ln and Ln···Ln in **2** and **3**, with lanthanide ions having intrinsic complicated magnetic characteristics, which include the presence of spin-orbit coupling and magnetic anisotropy.[28]

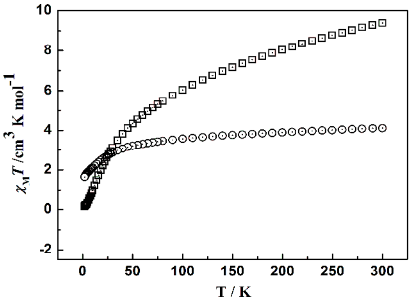
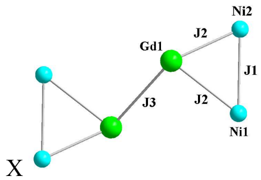


Fig. 7 $\chi_M T$ versus T plots for complex **2** (○) and **3** (□)



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

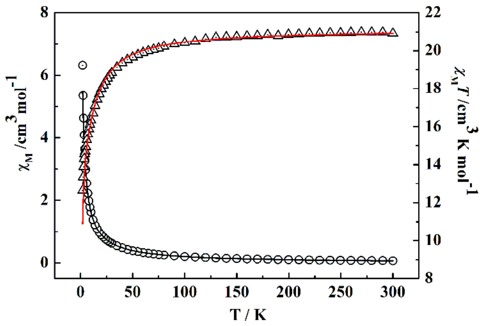


Fig. 8 $\chi_M T$ versus T plots for complex **4** (△), the red line is the simulation of the experimental data.

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 $\chi_M T$ value of 20.92 cm^3 K mol^{-1} is in good agreement with the expected value of 19.75 cm^3 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 $\chi_M T$ value decreases slowly up to 120 K, where it reaches a value of 20.62 cm^3 K mol^{-1}, and then decreases rapidly down to 2 K, reaching a minimum value of 12.62 cm^3 K mol^{-1}. To our knowledge, no formula in literatures is available to reproduce the magnetic susceptibility of such a complex system. Therefore, its magnetic properties was preliminarily investigated. We were able to successfully simulate the magnetic susceptibility data using the three-J models as shown in Scheme 2. Using the MAGPACK[29] program and employing the Hamiltonian in eq 1

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

afforded the parameters J_1 = −4.35 cm^{-1}, J_2 = −0.17 cm^{-1}, J_3 = −0.05 cm^{-1}, and g = 2.07. Previous literature reported that Ni-O-Ni angles between any two Ni^{II} ions that are smaller than 98° are expected to 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)°) 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 [H$_6$L = 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), containing N$_3$O$_3$ and O$_6$ inner and outer pockets, respectively, allows the synthesis of a new family of heterometallic hexanuclear Ni$_4$Ln$_2$ clusters. In all of these compounds, the six metal ions are held together to form novel Ni$_4$Ln$_2$O$_{10}$ core, exhibit a relatively rare dumbbell-type structure. From the 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 compounds are first constructed from in situ Ni^{II}-catalyzed partial degradation of tripodal ligand, which further expands 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 decrease in the order Tb(**5**) >Er(**7**) >Ho(**6**) >Gd(**4**) >Eu(**3**) >Sm(**2**) >Pr(**1**), in accord with the lanthanide contraction, except Tb(**5**). magnetic preperties of **2**, **3** and **4** have been also measured and analyzed.

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Notes and references

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† Electronic Supplementary Information (ESI) available: UV-vis spectra of the complexes **1**-**7**. CCDC reference numbers 898018-898024. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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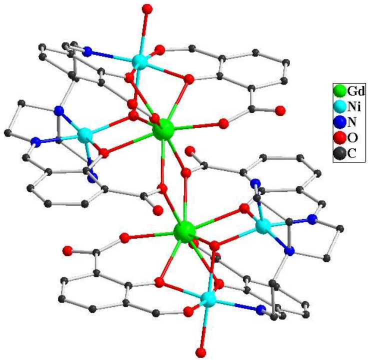	A family of dumbbell Ni_4Ln_2 complexes