Novel lanthanide(III) coordination networks based on 1,2-bis(4-pyridyl)ethane-*N,N′*-dioxide and *trans*-1,2-bis(4-pyridyl)ethene-*N,N′*-dioxide†

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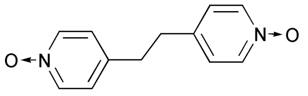
Received (in New Haven, CT, USA) 19th December 2001, Accepted 11th February 2002
First published as an Advance Article on the web 13th May 2002

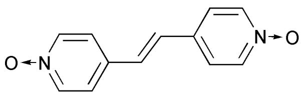
The new ligand 1,2-bis(4-pyridyl)ethane-*N,N′*-dioxide (L) was used to generate five lanthanide(III) coordination networks of three structural types: (i) the isomorphous pair $\{[Ln(L)_3]\cdot(ClO_4)_3\cdot(H_2O)\}_\infty$ (Ln = Er, **1**; Yb, **2**) comprises two interpenetrating α-polonium nets in which each lanthanide(III) ion is in a rare homoleptic distorted octahedral coordination environment; (ii) an unprecedented mat-like pattern of three interwoven (6,3) nets is found in isomorphous $\{[Ln(NO_3)_3(L)_{1.5}]\cdot H_2O\}_\infty$ (Ln = Er, **3**; Yb, **4**); (iii) $\{[La(NO_3)_3(L)\ (CH_3OH)]\cdot CH_3OH\cdot CH_2Cl_2\}_\infty$, **5**, is built of an offset stacking of distorted square grids. The complex $[Er(L')_{0.5}(H_2O)_3(C_2O_4)](ClO_4)\cdot L'\cdot 6H_2O\cdot(dioxane)_{0.5}$ (L′ = *trans*-1,2-bis(4-pyridyl)ethene-*N,N′*-dioxide), **6**, is composed of (6,3) nets in which the Er(III) ions are bridged by both L′ ligands and oxalate ions.

Introduction

The crystal engineering of coordination polyhedra and networks with different geometrical and topological characteristics has developed rapidly for the past decade.[1] In particular, the "node and spacer" methodology has proven to be remarkably successful in the rational design of metal-organic architectures. In this context, the most utilized linear spacer ligand by far for linking metal centers is 4,4′-bipyridine, bipy. More recently, bifunctional analogs with an extended backbone such as 1,2-bis(4-pyridyl)ethane,[2] *trans*-1,2-bis(4-pyridyl)ethene,[3] 1,2-bis(4-pyridyl)ethyne,[4] bis(4-pyridyl)disulfide[5] and 1,4-bis[(4-pyridyl)methyl]-2,3,5,6-tetrafluorophenylene[6] have been employed as nucleophilic linkers in self-assembly reactions with various labile metal moieties. Another alternative strategy to lengthen a linear bis-pyridine ligand is to convert its terminal nitrogen donors to *N*-oxide groups. A typical example is 4,4′-bipyridine-*N,N′*-dioxide (bpdo), of which several transition metal[7] and lanthanide[8,9] complexes have been reported. Several salient points are noteworthy: (a) the coordination preference between the ligand sites in bpdo and bipy is different, as oxygen is harder than nitrogen; (b) each oxygen atom in bpdo may link to two or more metal centers while the nitrogen donor in bipy is always coordinated to only one metal center; (c) bpdo is a longer spacer than its parent bipy, which allows for the formation of more porous structures. The strategy of using the $Ln(NO_3)_3$ moiety as a three- or four-connected node and bpdo as a bridging ligand has led to the coordination polymers $\{[Sm(bpdo)_2(NO_3)_3]\cdot 0.5H_2O\}_\infty$ and $\{[Er_2(bpdo)_3(NO_3)_6]\cdot 2CH_3OH\}_\infty$, which exhibit two-fold interpenetrating three-dimensional $CdSO_4$-like networks and a two-dimensional network of 4.8^2 topology, respectively.[9] Our recent studies on the design of coordination networks with lanthanide metal salts and polydentate ligands[10] prompted us to develop 1,2-bis(4-pyridyl)ethane-*N,N′*-dioxide (L) and *trans*-1,2-bis(4-pyridyl)ethene-*N,N′*-dioxide (L′) as new spacer ligands for inorganic network assembly. We now report four kinds of their lanthanide(III) complexes displaying very different network structures, namely $\{[Ln(L)_3]\cdot(ClO_4)_3\cdot(H_2O)\}_\infty$ (Ln = Er, **1**; Yb, **2**), $\{[Ln(NO_3)_3(L)_{1.5}]\cdot H_2O\}_\infty$ (Ln = Er, **3**; Yb, **4**), $[La(NO_3)_3(L)\ (CH_3OH)]\cdot CH_3OH\cdot CH_2Cl_2\}_\infty$, **5**, and $[Er(L')_{0.5}(H_2O)_3(C_2O_4)](ClO_4)\cdot L'\cdot 6H_2O\cdot(dioxane)_{0.5}$, **6**.



L



L′

Experimental

Synthesis

1,2-Bis(4-pyridyl)ethane-*N,N′*-dioxide (L). A mixture of 1,2-bis(4-pyridyl)ethane (10 g, 54.3 mmol), acetic acid (40 ml), and 35% hydrogen peroxide (20 ml) was heated at 70–80 °C for 3 h. An additional portion of hydrogen peroxide (15 ml) was added, and heating was continued for a further 9 h. The excess acetic acid and water were removed under vacuum, water (20 ml) was added, and the mixture then concentrated to dryness under vacuum. Acetone (150 ml) was added to the remaining oil to yield a pale-yellow precipitate, which was filtered off and washed twice with hot acetone to remove unreacted 1,2-bis(4-pyridyl)ethane. The crude product was recrystallized from ethanol and dried in vacuum to give 10 g of the adduct $L\cdot H_2O_2$. Yield 85%. Anal. found: C, 57.09; H, 5.57; N, 11.04. Calcd for $C_{12}H_{12}N_2O_2\cdot H_2O_2$: C, 57.59; H, 5.64; N, 11.19%. ^1H NMR (300 MHz, D_2O): $\delta = 7.99$ (4H, d, $J = 6.6$ Hz, py-2,6), 7.24 (4H, d, $J = 6.6$ Hz, py-3,5), 2.56 (4H, s, $-CH_2-CH_2-$), 1.83 (2H, m, H_2O_2).

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† In memory of Prof. Charles A. McDowell (1918–2001).

DOI: 10.1039/b111660f

$\{[Er(L)_3]\cdot(ClO_4)_3\cdot(H_2O)\}_\infty$, 1. A solution of L·$H_2O_2$ (50 mg, 0.2 mmol) in MeOH (8 cm^3) was carefully layered over a solution of $Er(ClO_4)_3$ (46 mg, 0.1 mmol) in H_2O (0.5 cm^3), MeOH (2 cm^3) and CH_2Cl_2 (5 cm^3). Pale pink crystals of **1** were deposited after several days. Yield xx%. Anal. found: C, 38.41; H, 3.40; N, 7.57. Calcd for the empirical formula $Er(ClO_4)_3\cdot3L\cdot H_2O$: C, 38.19; H, 3.38; N, 7.42%.

$\{[Yb(L)_3]\cdot(ClO_4)_3\cdot(H_2O)\}_\infty$, 2. Colorless compound **2** was prepared in the same manner as **1** using $Yb(ClO_4)_3$ in place of $Er(ClO_4)_3$. Yield xx%. Anal. found: C, 38.22; H, 3.40; N, 7.56. Calcd for $Yb(ClO_4)_3\cdot$ 3L·H_2O: C, 37.99; H, 3.37; N, 7.38%.

$\{[Er(NO_3)_3(L)_{1.5}]\cdot H_2O\}_\infty$, 3. A solution of L·$H_2O_2$ (50 mg, 0.2 mmol) in MeOH (7 ml) was carefully layered over a slurry of powdered $Er(NO_3)_3\cdot6H_2O$ (46 mg, 0.1 mmol) and CH_2Cl_2 (5 ml) in a test tube. Over a period of several days, pale pink crystals gradually appeared on the wall of the test tube. Yield xx%. Anal. found: C, 31.07; H, 2.92; N, 11.78. Calcd for $Er(NO_3)_3\cdot1.5L\cdot H_2O$: C, 31.08; H, 2.90; N, 12.08%.

$\{[Yb(NO_3)_3(L)_{1.5}]\cdot H_2O\}_\infty$, 4. Colorless crystals of **4** were obtained as for **3** using the corresponding Yb(III) nitrate. Yield xx%. Anal. found: C, 30.90; H, 2.89; N, 12.24. Calcd for $Yb(NO_3)_3\cdot1.5L\cdot H_2O$: C, 30.82; H, 2.87; N, 11.98%.

$[La(NO_3)_3(L)\ (CH_3OH)]\cdot CH_3OH\cdot CH_2Cl_2\}_\infty$, 5. The synthetic procedure used for **3** was repeated using La(III) nitrate. However, compound **5** with an entirely different stoichiometry from that of **3** was obtained. Yield xx%. Anal. found: C, 26.21; H, 3.23; N, 10.40. Calcd for $La(NO_3)_3\cdot L\cdot2CH_3OH\cdot CH_2Cl_2$: C, 26.10; H, 3.21; N, 10.15%.

***trans*-1,2-Bis(4-pyridyl)ethylene-*N*,*N'*-dioxide (L′).** Synthesized by the same method as for L using *trans*-1,2-bis(4-pyridyl)ethylene instead of 1,2-bis(4-pyridyl)ethane. The adduct L′·H_2O_2 was obtained in 85% yield. Anal. found: C, 58.29; H, 4.90; N, 11.49. Calcd for $C_{12}H_{10}N_2O_2\cdot$ H_2O_2: C, 58.06; H, 4.87; N, 11.28%.

$[Er(L')_{0.5}(H_2O)_3(C_2O_4)](ClO_4)\cdot L'\cdot6H_2O\cdot(dioxane)_{0.5}$, 6. A solution containing $(NH_4)_2C_2O_4$ (14 mg, 0.1 mmol) and L′·H_2O_2 (50 mg, 0.2 mmol) in dioxane (2 cm^3) and MeOH (8 cm^3) was carefully layered over a solution of $Er(ClO_4)_3$ (46 mg, 0.1 mmol) in H_2O (0.5 cm^3), MeOH (2.0 cm^3) and CH_2Cl_2 (5.0 cm^3). The two layers were allowed to diffuse into each other, and pale pink crystals appeared after several days. Yield xx%. Anal. found: C, 30.12; H, 4.26; N, 4.87. Calcd for $[Er(ClO_4)(C_2O_4)]\cdot$ $1.5L'\cdot9H_2O\cdot(C_4H_8O_2)_{0.5}$: C, 29.95; H, 4.23; N, 4.76%.

X-Ray crystallography

Selected single crystals of **1**–**6** sealed inside Lindemann glass capillaries were used for data collection on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Intensity data was obtained in the range $1.5 < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[11] The structures were solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL program package.[12] Selected data are given in Table 1.

CCDC reference numbers 170489–170493 and 175817. See http://www.rsc.org/suppdata/nj/bi/b111660f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Pale pink crystals of **1**, and colorless crystals of **2**, were prepared by slow diffusion of $Er(ClO_4)_3$ or $Yb(ClO_4)_3$ and L in a MeOH–CH_2Cl_2–H_2O mixture. Crystalline compounds **3**, **4** and **5** were prepared in a similar manner with $Ln(NO_3)_3\cdot6H_2O$ O (Ln = Er, Yb, La). Pale pink crystals of **6** were prepared by slow diffusion of $Er(ClO_4)_3$, $(NH_4)_2C_2O_4$ and L′ in a MeOH–CH_2Cl_2–dioxane–H_2O mixture. The crystal structures of **1**–**6** were determined from single crystal X-ray analysis. Selected bond lengths and angles are given in Table 2.

In **1**, the Er(III) ion, water molecule, ligand L and perchlorate group occupy special positions of site symmetry 32, $\bar{3}$, 2 and 2, respectively. The CH_2CH_2 chain of L exhibits twofold disorder, and the pyridyl rings make a dihedral angle of 2.3°. The Er(III) ion is in a rare homoleptic octahedral environment, being coordinated by *N*-oxide groups from six L ligands with Er–O = 2.232(6) Å and O–Er–O = 88.0(3)°, generating a three-dimensional α-polonium (or NaCl) (4,6) net (Fig. 1).[13] The crystal structure, which comprises two independent interpenetrating nets related by a *c* glide, is further consolidated by

Table 1 Crystallographic data of complexes **1**–**6**

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{36}H_{38}Cl_3N_6O_{19}Er$	$C_{36}H_{38}Cl_3N_6O_{19}Yb$	$C_{18}H_{23}N_6O_{13}Er$	$C_{18}H_{23}N_6O_{13}Yb$	$C_{30}H_{42}Cl_6N_{10}O_{13}La$	$C_{22}H_{37}ClErN_3O_{21}$
Formula weight	1132.33	1138.12	698.68	704.46	1449.26	882.26
Crystal system	Hexagonal	Hexagonal	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$R\ \bar{3}\ c$ (no. 167)	$R\ \bar{3}\ c$ (no. 167)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P\ \bar{1}$ (no. 2)	$P\ \bar{1}$ (no.2)
a/Å	24.03(1)	23.993(1)	8.331(1)	8.332(2)	9.609(2)	10.101(2)
b/Å	24.03(1)	23.993(1)	15.243(3)	15.215(3)	10.801(3)	11.282(2)
c/Å	12.81(1)	12.8101(8)	19.580(4)	19.602(4)	13.566(3)	16.313(3)
α/°	90	90	90	90	73.380(5)	79.512(3)
β/°	90	90	94.797(4)	94.882	82.011(5)	88.198(3)
γ/°	120	120	90	90	89.895(5)	66.963(3)
U/Å^3	6409.0(9)	6386.7(6)	2472.0(9)	2476.3(8)	1365.2(6)	1680.6(5)
Z	6	6	4	4	1	2
μ(Mo-Kα)/mm^{-1}	2.238	2.471	3.473	3.854	1.925	2.665
Reflections collected	14135	13995	16642	16387	9333	11459
Independent reflections	1759	1720	5963	5968	6474	7914
R_{int}	0.0756	0.0574	0.0833	0.0676	0.0417	0.0296
Observed reflections [$I > 2\sigma(I)$]	1060	1060	3023	3819	4154	6160
R_1 [$I > 2\sigma(I)$][a]	0.0568	0.0549	0.0470	0.0496	0.0627	0.0421
wR_2 (all data)[b]	0.1844	0.1863	0.1310	0.1232	0.1782	0.0919

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $wR_2 = [\Sigma[w\ (F_o{}^2 - F_c{}^2)^2]/\ \Sigma[w(F_o{}^2)^2]^{1/2}$

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**6**

Complex **1**			
Er(1)–O(1)	2.232(6)		
O(1)#1–Er(1)–O(1)#2	166.7(3)	O(1)–Er(1)–O(1)#4	83.6(3)
O(1)#1–Er(1)–O(1)	102.0(3)	O(1)#3–Er(1)–O(1)#4	166.7(3)
O(1)#2–Er(1)–O(1)	88.0(3)	O(1)#1–Er(1)–O(1)#5	88.0(3)
O(1)#1–Er(1)–O(1)#3	83.6(3)	O(1)#2–Er(1)–O(1)#5	83.6(3)
O(1)#2–Er(1)–O(1)#3	88.0(3)	O(1)–Er(1)–O(1)#5	166.7(3)
O(1)–Er(1)–O(1)#3	88.0(3)	O(1)#3–Er(1)–O(1)#5	102.0(3)
O(1)#1–Er(1)–O(1)#4	88.0(3)	O(1)#4–Er(1)–O(1)#5	88.0(3)
O(1)#2–Er(1)–O(1)#4	101.9(3)		
Complex **2**			
Yb(1)–O(1)	2.213(6)		
O(1)#1–Yb(1)–O(1)#2	167.1(3)	O(1)–Yb(1)–O(1)#4	84.0(3)
O(1)#1–Yb(1)–O(1)	101.7(3)	O(1)#3–Yb(1)–O(1)#4	167.2(3)
O(1)#2–Yb(1)–O(1)	87.9(3)	O(1)#1–Yb(1)–O(1)#5	87.9(3)
O(1)#1–Yb(1)–O(1)#3	84.0(3)	O(1)#2–Yb(1)–O(1)#5	84.0(3)
O(1)#2–Yb(1)–O(1)#3	87.9(3)	O(1)–Yb(1)–O(1)#5	167.1(3)
O(1)–Yb(1)–O(1)#3	87.9(3)	O(1)#3–Yb(1)–O(1)#5	101.7(3)
O(1)#1–Yb(1)–O(1)#4	87.9(3)	O(1)#4–Yb(1)–O(1)#5	87.9(3)
O(1)#2–Yb(1)–O(1)#4	101.7(3)		
Complex **3**			
Er(1)–O(1)#1	2.302(6)	Er(1)–O(7)	2.461(7)
Er(1)–O(2)	2.254(6)	Er(1)–O(8)	2.448(7)
Er(1)–O(3)	2.278(6)	Er(1)–O(10)	2.431(7)
Er(1)–O(5)	2.446(7)	Er(1)–O(11)	2.445(7)
Er(1)–O(4)	2.419(6)		
O(2)–Er(1)–O(3)	84.4(3)	O(4)–Er(1)–O(5)	51.2(3)
O(2)–Er(1)–O(1)#1	85.3(2)	O(10)–Er(1)–O(5)	144.4(3)
O(3)–Er(1)–O(1)#1	149.6(2)	O(11)–Er(1)–O(5)	145.8(2)
O(2)–Er(1)–O(4)	130.4(3)	O(2)–Er(1)–O(8)	149.9(3)
O(3)–Er(1)–O(4)	84.7(2)	O(3)–Er(1)–O(8)	121.7(3)
O(1)#1–Er(1)–O(4)	80.4(2)	O(1)#1–Er(1)–O(8)	78.1(2)
O(2)–Er(1)–O(10)	80.7(3)	O(4)–Er(1)–O(8)	71.5(3)
O(3)–Er(1)–O(10)	130.1(2)	O(10)–Er(1)–O(8)	71.1(3)
O(1)#1–Er(1)–O(10)	75.9(2)	O(11)–Er(1)–O(8)	93.9(3)
O(4)–Er(1)–O(10)	138.9(3)	O(5)–Er(1)–O(8)	118.7(3)
O(2)–Er(1)–O(11)	76.4(3)	O(2)–Er(1)–O(7)	145.1(2)
O(3)–Er(1)–O(11)	77.5(2)	O(3)–Er(1)–O(7)	70.8(2)
O(1)#1–Er(1)–O(11)	127.3(2)	O(1)#1–Er(1)–O(7)	128.1(2)
O(4)–Er(1)–O(11)	146.3(3)	O(4)–Er(1)–O(7)	72.6(3)
O(10)–Er(1)–O(11)	52.7(2)	O(10)–Er(1)–O(7)	96.5(3)
O(2)–Er(1)–O(5)	79.2(3)	O(11)–Er(1)–O(7)	74.5(2)
O(3)–Er(1)–O(5)	76.6(2)	O(5)–Er(1)–O(7)	116.6(3)
O(1)#1–Er(1)–O(5)	73.4(2)	O(8)–Er(1)–O(7)	51.7(2)
Complex **4**			
Yb(1)–O(1)#1	2.268(5)	Yb(1)–O(7)	2.467(6)
Yb(1)–O(2)	2.241(5)	Yb(1)–O(8)	2.443(6)
Yb(1)–O(3)	2.246(5)	Yb(1)–O(10)	2.432(7)
Yb(1)–O(4)	2.403(6)	Yb(1)–O(11)	2.450(6)
Yb(1)–O(5)	2.437(6)		
O(2)–Yb(1)–O(3)	84.7(2)	O(4)–Yb(1)–O(8)	71.5(2)
O(2)–Yb(1)–O(1)#1	85.6(2)	O(10)–Yb(1)–O(8)	71.0(2)
O(3)–Yb(1)–O(1)#1	149.5(2)	O(5)–Yb(1)–O(8)	119.0(2)
O(2)–Yb(1)–O(4)	130.6(3)	O(2)–Yb(1)–O(11)	76.5(2)
O(3)–Yb(1)–O(4)	84.3(2)	O(3)–Yb(1)–O(11)	77.9(2)
O(1)#1–Yb(1)–O(4)	80.3(2)	O(1)#1–Yb(1)–O(11)	127.3(2)
O(2)–Yb(1)–O(10)	80.5(3)	O(4)–Yb(1)–O(11)	146.1(2)
O(3)–Yb(1)–O(10)	130.4(2)	O(10)–Yb(1)–O(11)	52.7(2)
O(1)#1–Yb(1)–O(10)	75.9(2)	O(5)–Yb(1)–O(11)	146.0(2)
O(4)–Yb(1)–O(10)	138.9(2)	O(8)–Yb(1)–O(11)	93.6(2)
O(2)–Yb(1)–O(5)	78.9(3)	O(2)–Yb(1)–O(7)	145.1(2)
O(3)–Yb(1)–O(5)	76.7(2)	O(3)–Yb(1)–O(7)	71.1(2)
O(1)#1–Yb(1)–O(5)	73.2(2)	O(1)#1–Yb(1)–O(7)	127.6(2)
O(4)–Yb(1)–O(5)	51.7(2)	O(4)–Yb(1)–O(7)	72.8(2)
O(10)–Yb(1)–O(5)	143.8(3)	O(10)–Yb(1)–O(7)	96.2(2)
O(2)–Yb(1)–O(8)	149.6(3)	O(5)–Yb(1)–O(7)	117.5(2)
O(3)–Yb(1)–O(8)	121.9(2)	O(8)–Yb(1)–O(7)	51.6(2)
O(1)#1–Yb(1)–O(8)	77.6(2)	O(11)–Yb(1)–O(7)	74.2(2)
Complex **5**			
La(1)–O(1)	2.559(5)	La(1)–O(1)#1	2.623(5)
La(1)–O(2)	2.449(5)	La(1)–O(7)	2.608(7)
La(1)–O(3)	2.629(7)	La(1)–O(9)	2.661(6)

Table 2 (continued)

La(1)–O(4)	2.595(7)	La(1)–O(10)	2.637(6)
La(1)–O(6)	2.665(6)	La(1)–O(12)	2.541(6)
O(2)–La(1)–O(12)	147.6(2)	O(1)–La(1)–O(10)	77.4(2)
O(2)–La(1)–O(1)	80.0(2)	O(4)–La(1)–O(10)	80.5(2)
O(12)–La(1)–O(1)	131.3(2)	O(7)–La(1)–O(10)	153.5(2)
O(2)–La(1)–O(4)	77.5(2)	O(1)#1–La(1)–O(10)	70.5(2)
O(12)–La(1)–O(4)	72.9(2)	O(3)–La(1)–O(10)	123.8(2)
O(1)–La(1)–O(4)	136.5(2)	O(2)–La(1)–O(9)	68.9(2)
O(2)–La(1)–O(7)	66.5(2)	O(12)–La(1)–O(9)	110.3(2)
O(12)–La(1)–O(7)	121.7(2)	O(1)–La(1)–O(9)	69.6(2)
O(1)–La(1)–O(7)	77.6(2)	O(4)–La(1)–O(9)	67.7(2)
O(4)–La(1)–O(7)	124.5(2)	O(7)–La(1)–O(9)	128.0(2)
O(2)–La(1)–O(1)#1	138.5(2)	O(1)#1–La(1)–O(9)	107.1(2)
O(12)–La(1)–O(1)#1	73.8(2)	O(3)–La(1)–O(9)	113.2(2)
O(1)–La(1)–O(1)#1	61.2(2)	O(10)–La(1)–O(9)	48.2(2)
O(4)–La(1)–O(1)#1	141.3(2)	O(2)–La(1)–O(6)	108.5(2)
O(7)–La(1)–O(1)#1	89.8(2)	O(12)–La(1)–O(6)	73.4(2)
O(2)–La(1)–O(3)	78.6(2)	O(1)–La(1)–O(6)	107.4(2)
O(12)–La(1)–O(3)	72.2(2)	O(4)–La(1)–O(6)	114.9(2)
O(1)–La(1)–O(3)	155.3(2)	O(7)–La(1)–O(6)	48.4(2)
O(4)–La(1)–O(3)	48.8(2)	O(1)#1–La(1)–O(6)	72.8(2)
O(7)–La(1)–O(3)	82.6(2)	O(3)–La(1)–O(6)	68.4(2)
O(1)#1–La(1)–O(3)	133.9(2)	O(10)–La(1)–O(6)	134.2(2)
O(2)–La(1)–O(10)	117.0(2)	O(9)–La(1)–O(6)	176.2(2)
O(12)–La(1)–O(10)	70.8(2)		
Complex **6**			
Er(1)–O(1)	2.326(3)	Er(1)–O(7)#2	2.401(3)
Er(1)–O(4)	2.361(3)	Er(1)–O(1W)	2.303(4)
Er(1)–O(5)#1	2.369(3)	Er(1)–O(2W)	2.341(4)
Er(1)–O(6)	2.307(3)	Er(1)–O(3W)	2.315(4)
O(1W)–Er(1)–O(6)	99.0(1)	O(3W)–Er(1)–O(4)	73.9(1)
O(1W)–Er(1)–O(3W)	147.9(1)	O(1)–Er(1)–O(4)	141.6(1)
O(6)–Er(1)–O(3W)	88.6(1)	O(2W)–Er(1)–O(4)	138.2(1)
O(1W)–Er(1)–O(1)	86.2(1)	O(1W)–Er(1)–O(5)#1	76.9(1)
O(6)–Er(1)–O(1)	143.6(1)	O(6)–Er(1)–O(5)#1	142.5(1)
O(3W)–Er(1)–O(1)	106.0(1)	O(3W)–Er(1)–O(5)#1	78.2(1)
O(1W)–Er(1)–O(2W)	140.7(1)	O(1)–Er(1)–O(5)#1	73.8(1)
O(6)–Er(1)–O(2W)	83.0(1)	O(2W)–Er(1)–O(5)#1	123.8(1)
O(3W)–Er(1)–O(2W)	71.0(1)	O(4)–Er(1)–O(5)#1	68.6(1)
O(1)–Er(1)–O(2W)	71.3(1)	O(1W)–Er(1)–O(7)#2	69.6(1)
O(1W)–Er(1)–O(4)	78.2(1)	O(6)–Er(1)–O(7)#2	69.0(1)
O(6)–Er(1)–O(4)	74.1(1)	O(3W)–Er(1)–O(7)#2	141.1(1)
O(4)–Er(1)–O(7)#2	125.3(1)	O(1)–Er(1)–O(7)#2	79.5(1)
O(5)#1–Er(1)–O(7)#2	138.1(1)	O(2W)–Er(1)–O(7)#2	74.8(1)

[a] Symmetry codes for **1** and **2**: #1: $-x+2/3$, $-x+y+1/3$, $-z+5/6$; #2: $-x+y$, $-x+1$, z; #3: $-y+1$, $x-y+1$, z; #4: $y-1/3$, $x+1/3$, $-z+5/6$; #5: $x-y+2/3$, $-y+4/3$, $-z+5/6$; for **3** and **4**: #1: $x+1/2$, $-y+1/2$, $z+1/2$; for **5**: #1: $-x+1$, $-y+1$, $-z+1$; for **6**: #1: $-x+1$, $-y+1$, $-z+1$; #2: $-x+1$, $-y$, $-z+1$.

six donor hydrogen bonds [O1W···O1 = 2.595 Å] from each water molecule to two ErO_6 octahedra belonging to different nets and aligned parallel to the *c* axis. The cavities of the resulting framework accommodate the ClO_4^- anions, each forming weak O···H–C interactions with the pyridyl rings of three neighboring L ligands; the C···O distances of 3.218–3.488 Å lie in the normal range.[14] Compound **1** provides a rare example of six equivalent 2-connected ligands arranged about an octahedral lanthanide center. In contrast, the analogous twofold interpenetrating α-polonium nets in the recently reported complex $\{[La(4,4'\text{-bpdo})_4]\cdot[Co(C_2H_{11}B_9)_2]_3\cdot0.5CH_3OH\}_\infty$ have eight 4,4′-bpdo ligands around each La(III) node, which is linked to only six nearest neighbors with two pairs of 4,4′-bpdo ligands forming two *trans*-disposed "double-bridges".[15]

Of the two independent L ligands in **3**, one is located at an inversion center, while the other has its pyridyl rings making a dihedral angle of 14.7°. The Er(III) ion is coordinated by three *N*-oxide groups (2.254–2.302 Å) and three terminal bidentate nitrate groups (2.419–2.461 Å), forming an ErO_9 distorted tricapped trigonal prism [Fig. 2(a)]. The 3-connected $Er(NO_3)_3$ nodes and 2-connected L ligands generate a nonplanar, two-dimensional (6,3) net exhibiting a herringbone or "parquet floor" tiling pattern.[16] Three independent nets are interwoven to form a mat-like composite layer, which to our knowledge is unprecedented (Fig. 3). The crystal structure comprises a snug stacking of such layers parallel to the $(10\bar{1})$ plane, and the disordered water molecules, each occupying two equally populated sites, are accommodated in the cavities.

It is well known that counterions may play a crucial role in coordination network construction. A recent example is [Ag(2-AMPDPN)X] (X = $CF_3SO_3^-$, ClO_4^-, NO_3^-; 2-AMPDPN = 2-aminomethylpyridinedipropionitrile), where profound changes in the polymeric structures are caused by a simple variation of the counteranion.[17] In the present report, from **1** to **3** (or **2** to **4**), quite different structures are formed by changing the counterion from perchlorate to nitrate. In addition, the metal ion employed may also influence the structure of the coordination network. When a late lanthanide ion such as

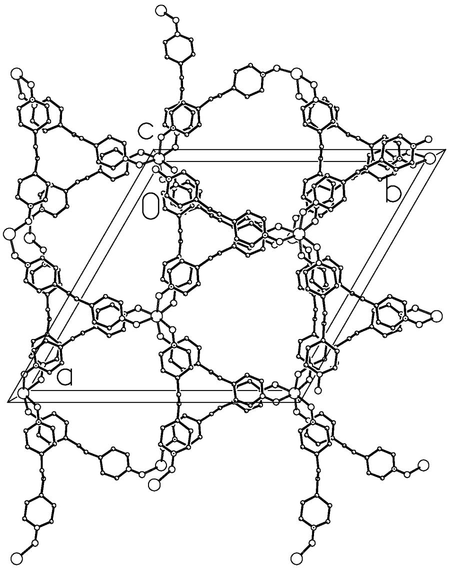


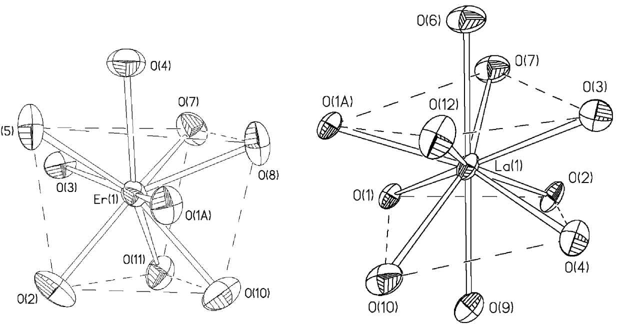
Fig. 1 A porous α-polonium coordination network in $\{[Ln(L)_3]\cdot(ClO_4)_3\cdot(H_2O)\}_\infty$ (Ln = Er, **1**; Yb, **2**). The crystal structure consists of two interpenetrating networks.

Er^{3+} in **3** (or Yb^{3+} in **4**) was replaced by the early lanthanide ion La^{3+} in **5** to generate the corresponding complex by the same synthetic method, structural variation also occurred.

Of the two independent L ligands in **5** that occupy $\bar{1}$ sites, one acts as a normal end-to-end linker, whereas the other functions in a μ_4 mode with each *N*-oxide group bridging a pair of La(III) ions. Each La(III) center is surrounded by *N*-oxide groups from three L ligands, three terminal bidentate nitrate groups, and one of the two independent CH_3OH molecules to form a bicapped square antiprism [Fig. 2(b)]. The centrosymmetric dimeric La_2O_2 moiety can be considered as a 4-connected node, and the resulting distorted square grid has its mean plane oriented approximately normal to [$\bar{1}1\bar{1}$] (Fig. 4). The crystal structure consists of an offset stacking of grids between which the uncoordinated CH_3OH and highly disordered CH_2Cl_2 solvate molecules are accommodated.

Single crystal X-ray analysis revealed that the Er(III) center in **6** is in an eight-coordinate square antiprismatic environment surrounded by two chelating oxalates, one L′ and three aqua ligands with Er–O distances in the range between 2.303(4) and 2.401(3) Å. The Er(III) atoms are alternately bridged by oxalates to form a zigzag chain along the *b* direction, and such chains are further crosslinked by L′ ligands to generate a cationic brick-like net $[Er(L')_{0.5}(H_2O)_3(C_2O_4)]_\infty{}^+$ parallel to the (100) plane (Fig. 5). The perchlorate anions are accommodated in the cavities. An interesting feature is that a pair of L′ guests are located in each rectangular void bounded by adjacent two-dimensional nets (Fig. 6). In addition, the dioxane and water solvate molecules are accommodated between adjacent layers. Hydrogen bonds play a key role in stabilizing these molecules in the crystal structure, linking the two-dimensional coordination networks to generate a three-dimensional structure (Fig. 7).

It is noteworthy that our attempt to prepare crystalline analogs of compounds **1**–**5** using L′ in place of L has not been successful thus far. Complex **6** was obtained only in the presence of oxalate ions. The flexible spine of L and the rigidity of L′ may account for this. It is found that the dihedral angles of the two pyridyl moieties of L are 2.3, 14.7 and 0.0° in **1** (or



(a) (b)

Fig. 2 (a)Tricapped trigonal-prismatic coordination environment of the Er(III) ion in $\{[Er(NO_3)_3\ (L)_{1.5}]\cdot H_2O\}_\infty$, **3**. The trigonal prism is indicated by broken lines. The atom pairs (O4, O5), (O7, O8) and (O10, O11) belong to bidentate nitrate groups. Symmetry code: A $(\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$. (b) Bicapped square-antiprismatic coordination environment of the La(III) ion in $\{[La(NO_3)_3(L)(CH_3OH)]\cdot CH_3OH\cdot CH_2Cl_2\}_\infty$, **5**. The atom pairs (O3, O4), (O6, O7)and (O9, O10) belong to nitrate groups, and O12 comes from the methanol ligand. The top and bottom faces of the square antiprism are outlined by broken lines. Symmetry code: A $(1-x,\ 1-y,\ 1-z)$.

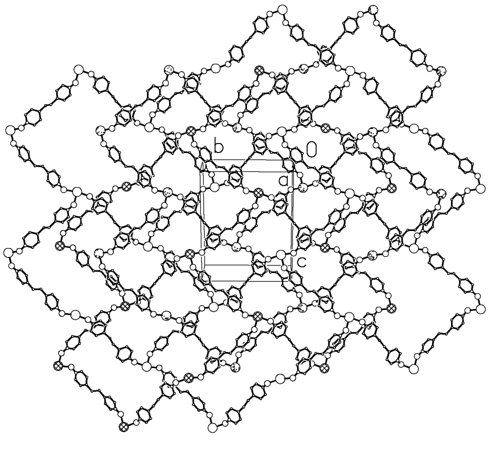


Fig. 3 Interpenetrating weave pattern of 3 two-dimensional (6,3) nets in the crystal structure of $\{[Ln(NO_3)_3\ (L)_{1.5}]\cdot H_2O\}_\infty$ (Ln = Er, **3**; Yb, **4**). The 3-connected Ln(III) nodes belonging to independent nets are represented by large spheres of different styles (open, filled, or cross-hatched). The terminal bidentate nitrate groups of each $Ln(NO_3)_3$ node have been omitted for clarity.

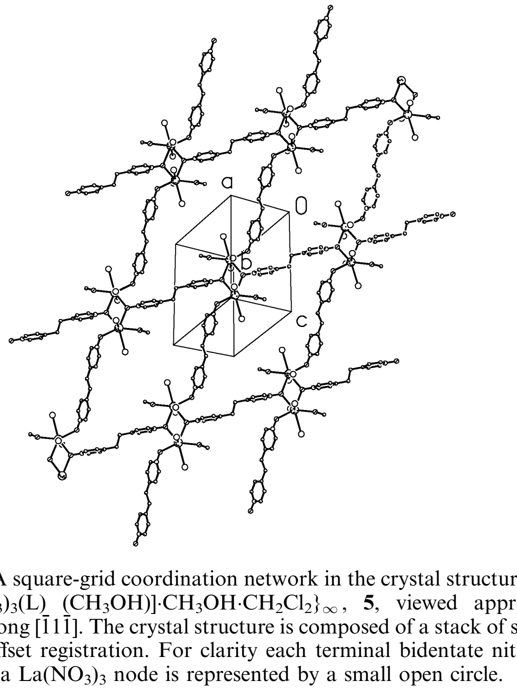


Fig. 4 A square-grid coordination network in the crystal structure of $\{[La(NO_3)_3(L)\ (CH_3OH)]\cdot CH_3OH\cdot CH_2Cl_2\}_\infty$, **5**, viewed approximately along [$\bar{1}1\bar{1}$]. The crystal structure is composed of a stack of such nets in offset registration. For clarity each terminal bidentate nitrate group of a $La(NO_3)_3$ node is represented by a small open circle.

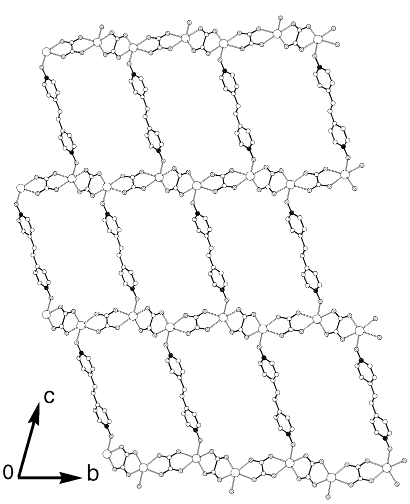


Fig. 5 A (6,3) net parallel to the (100) plane in **6**. The aqua ligands have been omitted for clarity.

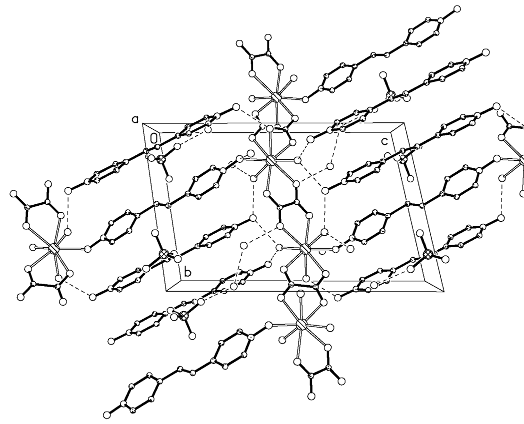


Fig. 6 Hydrogen-bonded inclusion pattern in the crystal structure of **6** viewed along the *a* direction.

2), **3** (or **4**) and **5**, respectively. In contrast, the two pyridyl moieties of L′ always lie in the same plane.

This study has demonstrated the versatility of 1,2-bis(4-pyridyl)ethane-*N,N*′-dioxide (L) as a bridging ligand for coordination network assembly. The *N*-oxide group serves as a donor to one or two lanthanide(III) centers, and its potential to coordinate three metal centers may be further explored. The structures of **3**–**5** substantiate previous finding that the $Ln(NO_3)_3$ moiety is a useful 3- or 4-connected node for the construction of coordination networks.[9] The fact that compounds **3** and **5** with very different structures can be formed in the same kind of preparation highlights the role of solvent control as well as the inherent difficulty and exciting challenge in coordination network design.

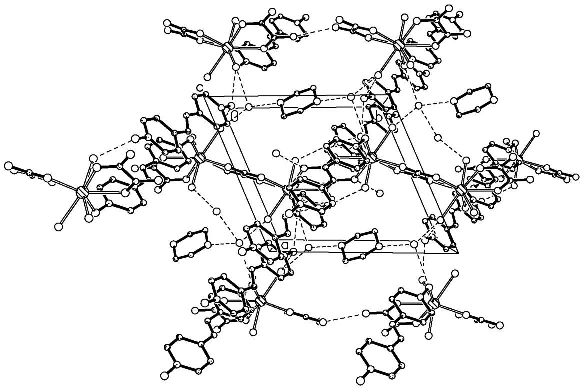


Fig. 7 Hydrogen-bonded inclusion pattern in the crystal structure of **6** viewed along the *c* direction.

Acknowledgements

This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 4268/00P and a Croucher Visiting Scholarship to W.-J. L.

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