Poly[aqua(μ3-benzene-1,2-dicarboxylato)bis(μ3-hydroxido)bis(μ2-isonicotinato)dierbium(III) monohydrate] and the thulium analogue

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The two isomorphous lanthanide coordination polymers, $\{[Ln_2(C_6H_4NO_2)_2(C_8H_4O_4)(OH)_2(H_2O)]\cdot H_2O\}_n$ (Ln = Er and Tm), contain two crystallographically independent Ln ions which are both eight-coordinated by O atoms, but with quite different coordination environments. In both crystal structures, adjacent Ln atoms are bridged by μ_3-OH groups and carboxylate groups of isonicotinate and benzene-1,2-dicarboxylate ligands, forming infinite chains in which the Er···Er and Tm···Tm distances are in the ranges 3.622 (3)–3.894 (4) and 3.599 (7)–3.873 (1) Å, respectively. Adjacent chains are further connected through hydrogen bonds and π–π interactions into a three-dimensional supramolecular framework.

Comment

In recent years, the rational design and construction of metal coordination polymers has aroused great interest owing to their intriguing topological architectures and their potential application as functional materials (Meares & Wensel, 1984; Scott & Horrocks, 1992; Reineke *et al.*, 1999; Eddaoudi *et al.*, 2001). In constructing coordination polymers, multifunctional connectors such as a variety of carboxylate ligands are usually utilized as bridging groups, forming one-, two- and three-dimensional networks (Choi & Suh, 1998; MacGillivray *et al.*, 1998; Evans *et al.*, 1999; Chen *et al.*, 2001; Suresh *et al.*, 2001; Kumagai *et al.*, 2002; Lu & Babb, 2003; Song *et al.*, 2003; Zhang *et al.*, 2004). So far, numerous architectures have been assembled from the particular combination of appropriate metal centers and versatile ligands. Our interest in the area is to explore the possible construction of coordination polymers involving two types of different ligands simultaneously in a system, and to understand the co-operativity of both ligands. To the best of our knowledge, this area remains under-developed (Cheng *et al.*, 2006). Selecting nicotinic acid (HIN)

and benzene-1,2-dicarboxylic acid (H_2BDC) as mixed ligands and adopting the hydrothermal technique, we obtained the title compounds, (I) and (II), which display novel one-dimensional chain-like coordination features.

(I) Ln=Er
(II) Ln=Tm
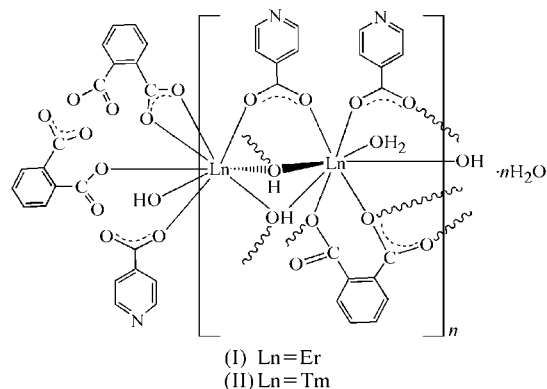
As shown in Fig. 1, the asymmetric unit contains two unique erbium(III) [or thulium(III)] atoms, two hydroxide ions, one BDC ligand, two IN ligands and one aqua ligand, as well as one uncoordinated water molecule. All the Ln^{III} ions are eight-coordinate, but with markedly different coordination environments. Atom Er1 (or Tm1) is surrounded by three OH groups, two carboxylate O atoms from two IN ligands, two carboxylate O atoms from a BDC ligand and an aqua ligand. Atom Er2 (or Tm2), on the other hand, is coordinated by three OH groups, two carboxylate O atoms from two IN ligands and three carboxylate O atoms from two BDC ligands. The Er—O and Tm—O distances span the ranges 2.278 (4)–2.499 (4) and 2.266 (3)–2.482 (3) Å, respectively (Tables 1 and 3).

The Ln^{III} centers are bridged by hydroxide and oxo groups to form an infinite wave-like chain, with Er···Er distances in
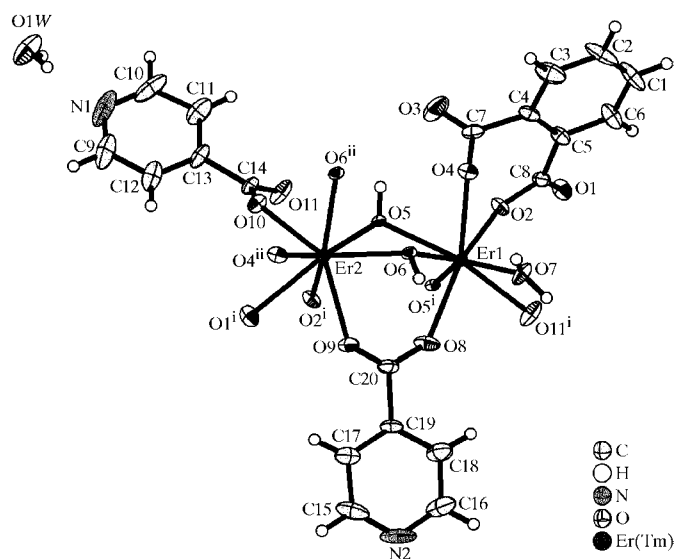

Figure 1
The molecular structure of (I) (as representative of both compounds), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.]

metal-organic compounds

the range 3.622 (3)–3.894 (4) Å [Tm···Tm = 3.599 (7)–3.873 (1) Å]. The BDC and IN ligands, coordinating the metal centers through the carboxylate O atoms, protrude outside of the above chain (Fig. 2). Despite the abundant and versatile coordination modes often found in IN and BDC ligands, only a single bidentate (for IN) and a unique pentadentate bridging (for BDC) mode are adopted in the crystal structures of the title compounds (Fig. 3). This suggests a high co-operativity between the IN and BDC ligands in the formation of (I) and (II). Adjacent chains are further connected into a three-dimensional supramolecular framework through hydrogen bonds and π–π stacking interactions. The former, described in Tables 2 and 4, exhibit O/N···O distances in the range
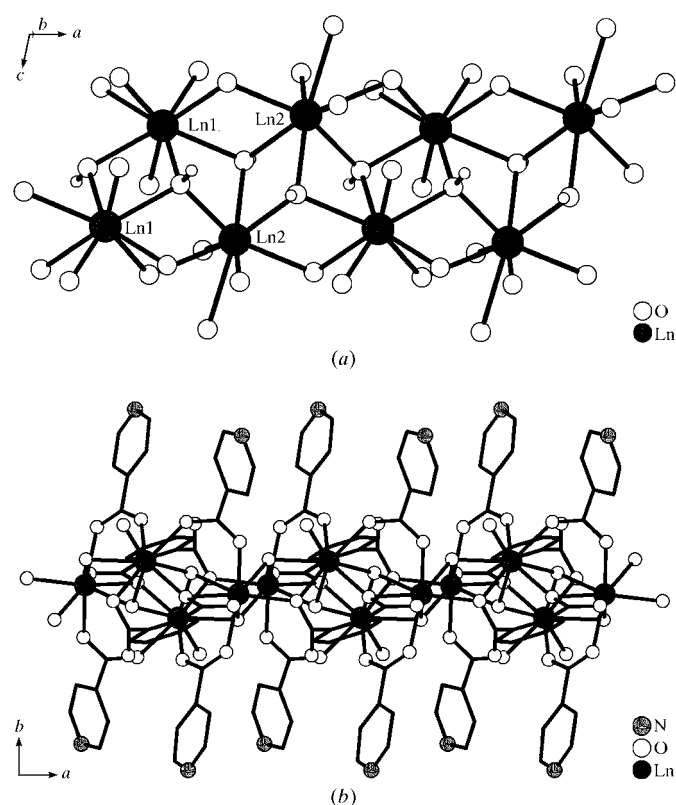

Figure 2
Different views of the one-dimensional infinite chains in (I) and (II), viz. (a) along b (aromatic rings have been omitted for clarity) and (b) along c.
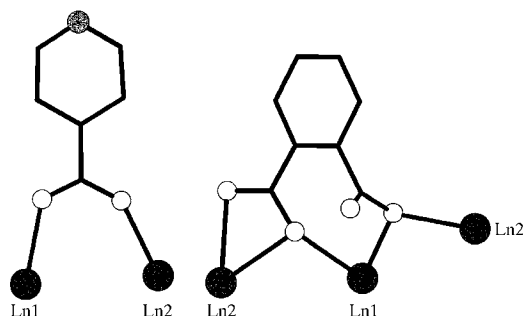

Figure 3
Coordination modes of the IN and BDC ligands in (I) (left) and (II) (right).
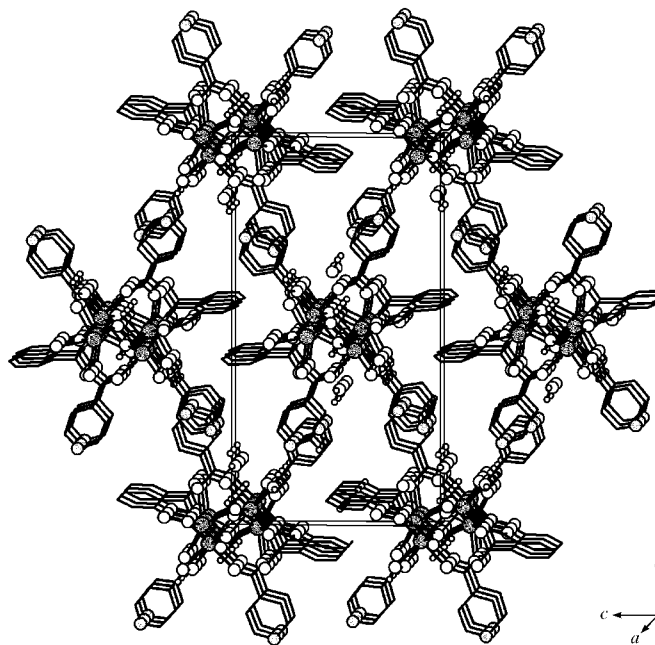

Figure 4
The packing of (I) and (II), projected along the chain direction. Note the interdigitation of the IN groups.

2.716 (5)–3.170 (6) Å for (I) and 2.702 (4)–3.1723 (5) Å for (II); the latter, in turn, lead to an interplanar distance between neighboring IN ligands of 3.546 (1) Å for (I) and 3.540 (2) Å for (II) (Fig. 4).

Experimental

The title compounds were synthesized under hydrothermal conditions. Typically, a mixture of Ln_2O_3 (0.5 mmol; Er 0.192 g, Tm 0.193 g), HIN (2.00 mmol, 0.247 g), H_2BDC (1.00 mmol, 0.167 g) and water (10 ml), in a ratio of 1:4:2:1112, was sealed in a 25 ml Teflon-lined steel autoclave and heated under autogenous pressure at 443 K for 6 d. The resulting prism-like crystals were recovered by filtration, washed with distilled water and dried in air.

Compound (I)

Crystal data

$[Er_2(C_6H_4NO_2)_2(C_8H_4O_4)(OH)_2(H_2O)]\cdot H_2O$	$\beta = 100.708\ (4)°$
$M_r = 812.88$	$V = 2318.36\ (17)$ Å^3
Monoclinic, $P2_1/c$	$Z = 4$
$a = 7.2706\ (5)$ Å	Mo $K\alpha$ radiation
$b = 24.2780\ (4)$ Å	$\mu = 7.26$ mm^{-1}
$c = 13.3668\ (2)$ Å	$T = 295\ (2)$ K
	$0.45 \times 0.10 \times 0.09$ mm

Data collection

Siemems SMART CCD diffractometer	18413 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996) $T_{min} = 0.399$, $T_{max} = 0.511$	4769 independent reflections
	4563 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	325 parameters
$wR(F^2) = 0.067$	H-atom parameters constrained
$S = 1.19$	$\Delta\rho_{max} = 1.76$ e Å^{-3}
4769 reflections	$\Delta\rho_{min} = -1.41$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Er1—O8	2.278 (4)	Er2—O5	2.315 (3)
Er1—O2	2.325 (3)	Er2—O4^{ii}	2.318 (3)
Er1—O7	2.326 (3)	Er2—O10	2.322 (3)
Er1—O11^{i}	2.331 (4)	Er2—O6^{ii}	2.329 (3)
Er1—O5	2.346 (3)	Er2—O6	2.341 (3)
Er1—O5^{i}	2.372 (3)	Er2—O9	2.342 (4)
Er1—O6	2.373 (3)	Er2—O2^{i}	2.461 (3)
Er1—O4	2.445 (3)	Er2—O1^{i}	2.499 (4)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$W\cdots$N1	0.93	1.95	2.834 (8)	160
O5—H5$\cdots$O3	0.85	2.42	3.170 (6)	147
O6—H6$\cdots$O1W^{iii}	0.87	1.98	2.826 (6)	164
O7—H7$W\cdots$N2^{iv}	0.86	1.96	2.788 (6)	161
O7—H8$W\cdots$O10^{ii}	0.87	1.87	2.716 (5)	165

Symmetry codes: (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Compound (II)

Crystal data

[Tm2(C6H4NO2)2(C8H4O4)(OH)2(H2O)]·H2O	$\beta = 100.700 (3)°$
$M_r = 816.22$	$V = 2302.97 (11)$ Å^3
Monoclinic, $P2_1/c$	$Z = 4$
$a = 7.2434 (2)$ Å	Mo $K\alpha$ radiation
$b = 24.2180 (6)$ Å	$\mu = 7.72$ mm^{-1}
$c = 13.3606 (4)$ Å	$T = 295 (2)$ K
	$0.35 \times 0.09 \times 0.07$ mm

Data collection

Siemems SMART CCD diffractometer	18502 measured reflections
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)	4754 independent reflections
	4602 reflections with $I > 2\sigma(I)$
$T_{min} = 0.373, T_{max} = 0.577$	$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	325 parameters
$wR(F^2) = 0.060$	H-atom parameters constrained
$S = 1.17$	$\Delta\rho_{max} = 1.11$ e Å^{-3}
4754 reflections	$\Delta\rho_{min} = -1.31$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Tm1—O8	2.266 (3)	Tm2—O5	2.303 (3)
Tm1—O7	2.311 (3)	Tm2—O10	2.308 (3)
Tm1—O2	2.314 (3)	Tm2—O4^{ii}	2.308 (3)
Tm1—O11^{i}	2.315 (3)	Tm2—O6^{ii}	2.315 (3)
Tm1—O5	2.332 (3)	Tm2—O9	2.326 (3)
Tm1—O6	2.364 (3)	Tm2—O6	2.327 (3)
Tm1—O5^{i}	2.366 (3)	Tm2—O2^{i}	2.447 (3)
Tm1—O4	2.439 (3)	Tm2—O1^{i}	2.482 (3)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$W\cdots$N1	0.92	1.94	2.822 (7)	160
O5—H5$\cdots$O3	0.85	2.42	3.172 (5)	148
O6—H6$\cdots$O1W^{iii}	0.87	1.99	2.830 (5)	165
O7—H7$W\cdots$N2^{iv}	0.86	1.97	2.798 (6)	161
O7—H8$W\cdots$O10^{ii}	0.86	1.86	2.702 (4)	165

Symmetry codes: (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

H atoms bound to C atoms were positioned geometrically, with C—H distances of 0.93 Å, and constrained to ride on their parent atoms [U_{iso}(H) = 1.2U_{eq}(C)]. H atoms bound to O atoms were located in a difference Fourier map and treated as riding, with U_{iso}(H) = 1.2U_{eq}(O)].

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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