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The first coordination polymer of lanthanum(III) with a naphthalene-1,4,5,8-tetracarboxylic 1,8-anhydride derivative

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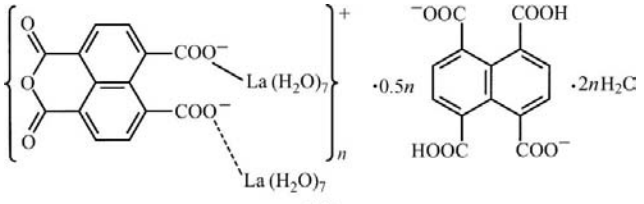
The title compound, *catena*-poly[[[heptaaqualanthanum(III)]-μ-1,3-dioxo-2-oxa-1*H*,3*H*-phenalene-6,7-dicarboxylato-κ^2O^6:O^7] hemi(4,8-dicarboxynaphthalene-1,5-dicarboxylate) dihydrate], $\{[La(C_{14}H_4O_7)(H_2O)_7](C_{14}H_6O_8)_{0.5}\cdot 2H_2O\}_n$, is a dihydrate of a coordination polymer between the dianion of naphthalene-1,4,5,8-tetracarboxylic 1,8-anhydride and the heptahydrated lanthanum(III) ion, charge balanced by an additional 4,8-dicarboxynaphthalene-1,5-dicarboxylate dianion that is located on an inversion centre and is not coordinated to the metal ion. The linear polymeric arrays adopt a comb-like structure, and these pack in pairs with one chain interpenetrating another, like two parts of a zip, to optimize stacking interactions between their ligand fragments. All the components of this compound are further interlinked by an extensive pattern of O—H$\cdots$O hydrogen bonds throughout the crystal structure. The main scientific significance of the results reported here is that they demonstrate for the first time the feasibility of coordination polymerization of the above organic ligand with lanthanide ions. The resulting polymer has a unique architecture. Finally, the reported structure is a rare example where the tetraacid and the diacid anhydride ligand species co-exist in the same crystal.

Comment

Naphthalene-1,4,5,8-tetracarboxylic acid, (I), and its anhydride derivative naphthalene-1,4,5,8-tetracarboxylic acid 1,8-anhydride, (II), are attractive ligands for the formulation of coordination polymers with metal ions and functional metal–organic complexes. They bear multiple functional groups and have a rigid molecular framework, allowing for simultaneous coordination of several metal ions in different directions. Usually, the metal–ligand interaction is associated with deprotonation of the carboxylic acid functions, and thus it is strengthened by electrostatic attraction. Not surprisingly, therefore, (I) and (II) have been the subject of considerable attention in this context in recent years. However, only a small number of extended coordination polymeric structures with rare earth and transition metal ions have been reported to date (Senkovska, 2006; Surble *et al.*, 2006; Chen *et al.*, 2005; Xu, Yuan, Wu *et al.*, 2005; Zhao & Tao, 2004), as the reactions of (I) and (II) with metal ions are often terminated with the formation of discrete complexes (Wang *et al.*, 2005; Fitzgerald & Gerkin, 1994; Fitzgerald *et al.*, 1993). The coordination features of these ligands with lanthanide ions have not been explored until now. The crystal structure of the free ligand, (II), has been reported only recently (Xu, Yuan, Zhou *et al.*, 2005). As part of our ongoing investigation of coordination polymers that involve organic carboxylic acid ligands and lanthanide ions (George *et al.*, 2006; Muniappan *et al.*, 2007; Lipstman *et al.*, 2007), we report here the title compound, (III), a new material and the first coordination polymer of (II) with an La^{3+} ion, which cocrystallized with (I).



(III)

The molecular structure of (III) is shown in Fig. 1. In the crystal structure, the metal ion is heptahydrated. The asymmetric unit consists of one La(H$_2$O)$_7$ moiety, one doubly deprotonated (II) ligand, one half of a doubly deprotonated (I) ligand which resides on an inversion centre at $(0, 0, \frac{1}{2})$, and two additional water molecules of hydration. The lanthanide ion bridges by coordination [to atoms O9 and O28 at $(x - 1, y, z)$] between the carboxylate groups of two adjacent ligands, revealing a total coordination number of 9 (which is common for La^{3+} ions). Its coordination geometry can be best described as a tricapped trigonal prism. Similarly, each ligand moiety links to two different metal ions at (x, y, z) and $(x + 1, y, z)$, leading to the formation of linear one-dimensional coordination polymers that extend parallel to the *a* axis of the crystal structure (Fig. 2). All the La—O coordination distances are within the range 2.495 (2)–2.647 (2) Å (Table 1). As the two carboxylate functions available for bonding are located on the same side of the ligand moiety, the polymeric arrays adopt a comb shape, with the planes of the ligands oriented nearly perpendicular to (and on the same side of) the propagation axis of the polymer. Moreover, the proximity of the two carboxylate groups and optimization of the polymeric coordination are associated with a slight deformation of the naphthalene backbone from planarity and a marked twist of the carboxylate groups in opposite directions with respect to the naphthalene ring. Thus, the dihedral angle between the two aryl rings (C12–C15/C25/C26 and C21–C26) is 4.84 (2)°, while the C11—C12$\cdots$C24—C27 pseudo-torsion angle is 29.16 (18)°.

A similar comb-type arrangement has only been observed before in the photoluminescent polymeric structure of (II) with Cd–phen ions (phen is 1,10-phenanthroline; Xu, Yuan,

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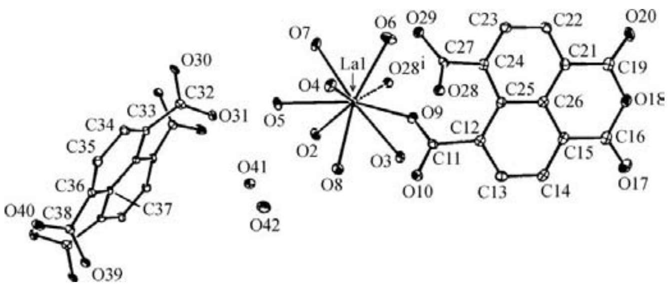

Figure 1

The molecular structure of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. The uncoordinated ligand is located on an inversion centre at $(0, 0, \frac{1}{2})$, and only atoms of the asymmetric unit are labelled. H atoms have been omitted. The coordination of La1 to O28^i is shown by a dashed line. [Symmetry code: (i) $x - 1, y, z$.]

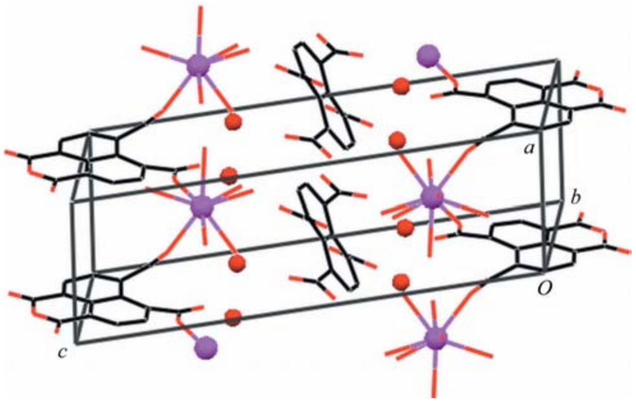

Figure 3

The crystal packing of (III), omitting the H atoms. The lanthanum ions and water molecules of crystallization are depicted as small spheres. Note that the double polymeric chains are centred at $z = 0$ (and $z = 1$), while layers of the uncoordinated naphthalenetetracarboxylic acid ligand are centred at $z = \frac{1}{2}$. The latter are hydrogen bonded to the former with the aid of interstitial water molecules (Table 2).

Wu *et al.*, 2005). In that case, the Cd-bound phen ligand is inserted between neighbouring moieties of (II) along the polymer, stabilizing the polymeric arrangement by stacking interactions. The reported distance between the phen and naphthalene planes is 3.739 Å. The situation is somewhat different in the present study. There are no aromatic fragments in the analysed compound other than (II), and an additional negative ion is needed to balance the 3+ charge of the lanthanide ion. Nature solved the first problem by an interpenetrating arrangement of inversion-related polymeric chains, where the ligand fragments of one polymeric chain penetrate between the ligands of another polymer (Fig. 2), as in a zip fastener. The distance between the mean planes of the overlapping fragments is 3.279 (2) Å [this value refers to the interplanar distance of the flat antiparallel fragments C15–C21 at (x, y, z) and $(1 - x, 2 - y, -z)$]. The charge-balance issue is resolved by the inclusion in the crystal structure of a doubly deprotonated (I) ligand, not coordinated to the metal ions, which is located on an inversion centre (Fig. 3). These species are arranged in planes which interface between the coupled polymeric chains. Further stabilization of the observed structure is provided by the very extensive array of crosslinking O—H···O hydrogen bonds, which involves the nine water molecules in the asymmetric unit, along with the carboxyl and carboxylate groups (Table 2 lists 19 unique hydrogen-bonding interactions). The rigidity of the resulting structure is well reflected in the negligible solubility of this solid in water and common organic solvents.

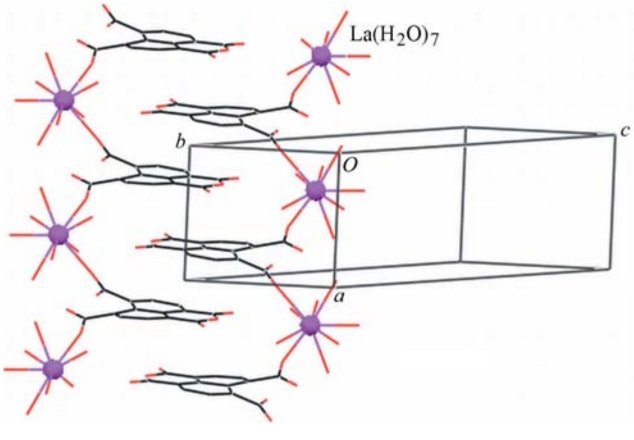

Figure 2

A stick diagram illustrating the coordination polymerization along the *a* axis in (III). H atoms have been omitted. Heptahydrated lanthanum ions are depicted as small spheres. Two interpenetrating polymeric chains are shown, exhibiting efficient stacking interactions between the aromatic ligands of the two chains.

In summary, we have demonstrated that the naphthalenetetracarboxylic acid ligand can form coordination polymers not only with transition metals but also with lanthanide ions. This first example represents a one-dimensional double-chain polymer, and further studies are underway to construct similar polymers with two- and three-dimensional architectures. Such materials may reveal features of microporosity (*e.g.* for gas sorption) and photoluminescence (*e.g.* for photophysical applications) (Xu, Yuan, Wu *et al.*, 2005; Surble *et al.*, 2006) and have considerable potential significance.

Experimental

Naphthalene-1,4,5,8-tetracarboxylic acid and lanthanum nitrate hexahydrate were purchased commercially and used without further purification. The tetrasodium salt of the acid was prepared according to the reported method of Fitzgerald *et al.* (1991). A mixture of $La(NO_3)_3 \cdot 6H_2O$ (0.044 g, 0.1 mmol) and tetrasodium naphthalene-1,4,5,8-tetracarboxylate (0.055 g, 0.1 mmol) was dissolved in water (15 ml). The mixture was allowed to stand in a capped vial for 10 d at room temperature. Needle-shaped crystals of (III) were deposited, collected by filtration, washed with water and air-dried. The product is insoluble in water and in common organic solvents. IR (KBr, cm^{-1}): 3454 and 3260 (water stretching vibrations), 1718 (COOH), 1608 and 1566 (COO^- asymmetric stretching), 1434 and 1391 (COO^- symmetric stretching). The solid IR spectrum confirms the presence of both carboxyl and carboxylate groups in the structure. Formation of the anhydride species (II) from (I) occurred during the crystallization process.

Table 1
Selected bond lengths (Å).

La1—O6	2.4948 (17)	La1—O7	2.6094 (17)
La1—O9	2.5039 (16)	La1—O4	2.6136 (17)
La1—O28^{i}	2.5138 (16)	La1—O2	2.6212 (16)
La1—O5	2.5180 (17)	La1—O3	2.6470 (17)
La1—O8	2.5491 (18)		

Symmetry code: (i) $x - 1, y, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*B*···O41	0.90	1.93	2.822 (2)	176
O2—H2*A*···O10^{i}	0.90	1.77	2.653 (2)	166
O3—H3*A*···O20^{ii}	0.90	1.97	2.857 (2)	167
O3—H3*B*···O10^{i}	0.90	1.99	2.862 (2)	165
O4—H4*A*···O30^{iii}	0.90	2.02	2.919 (2)	173
O4—H4*B*···O2^{iv}	0.90	2.09	2.984 (2)	178
O5—H5*A*···O31	0.90	1.89	2.751 (2)	161
O5—H5*B*···O40^{v}	0.90	1.82	2.705 (2)	167
O6—H6*A*···O29	0.90	1.88	2.777 (2)	175
O6—H6*B*···O42^{vi}	0.90	1.86	2.749 (3)	169
O7—H7*A*···O39^{vi}	0.90	2.04	2.902 (2)	160
O7—H7*B*···O29^{i}	0.90	1.97	2.810 (2)	155
O8—H8*A*···O42	0.90	1.86	2.723 (3)	160
O8—H8*B*···O10	0.90	2.27	3.027 (3)	141
O30—H30···O39^{vi}	0.90	1.60	2.494 (2)	171
O41—H41*A*···O29^{vii}	0.90	1.93	2.776 (2)	157
O41—H41*B*···O31	0.90	1.90	2.708 (2)	149
O42—H42*A*···O40^{v}	0.90	1.85	2.720 (3)	164
O42—H42*B*···O41	0.90	1.90	2.795 (3)	174

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y + 2, -z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x + 1, y, z$; (v) $-x + 1, -y, -z + 1$; (vi) $x, y + 1, z$; (vii) $x - 1, y - 1, z$.

Crystal data

$[La(C_{14}H_4O_7)(H_2O)_7]$-
$(C_{14}H_6O_8)_{0.5}\cdot 2H_2O$
$M_r = 736.32$
Triclinic, $P\overline{1}$
$a = 6.6222$ (2) Å
$b = 9.4831$ (2) Å
$c = 20.5543$ (7) Å
$\alpha = 91.3625$ (9)°
$\beta = 98.9233$ (12)°
$\gamma = 94.5506$ (14)°
$V = 1270.29$ (6) Å^3
$Z = 2$
Mo *Kα* radiation
$\mu = 1.78$ mm^{-1}
$T = 110$ (2) K
0.30 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.617$, $T_{max} = 0.842$
12656 measured reflections
5821 independent reflections
5404 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.058$
$S = 1.03$
5821 reflections
379 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.33$ e Å^{-3}
$\Delta\rho_{min} = -1.27$ e Å^{-3}

H atoms bound to C atoms were located in calculated positions and were constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. All H atoms bound to O atoms were located in a difference Fourier map. The corresponding O—H distances were modified and constrained to be 0.90 Å, with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3220). Services for accessing these data are described at the back of the journal.

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