

A unique two-dimensional coordination network of 1-benzofuran-2,3-dicarboxylate with lanthanum(III) obtained by solvothermal synthesis

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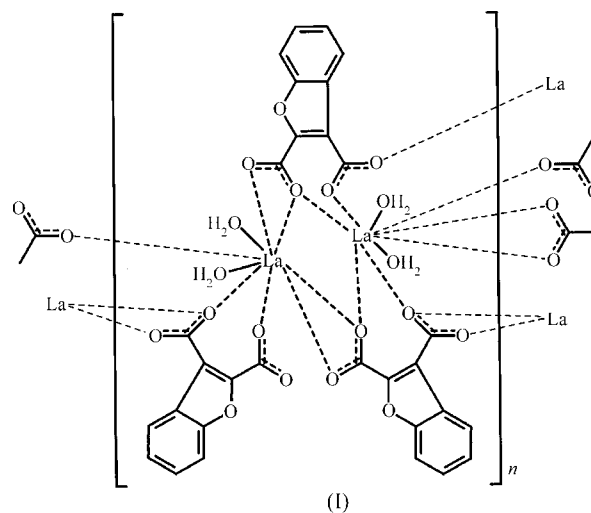
The title compound, poly[bis[*diaqualanthanum(III)*]-tris(μ -1-benzofuran-2,3-dicarboxylato)], $[\text{La}_2(\text{C}_{10}\text{H}_4\text{O}_5)_3(\text{H}_2\text{O})_4]_n$, was obtained under solvothermal conditions by reacting lanthanum trinitrate hexahydrate with 1-benzofuran-2,3-dicarboxylic acid in a strongly basic environment. It forms an extended two-dimensional coordination network, wherein every lanthanum ion links to four deprotonated diacid ligands, while two of the latter bridge between adjacent metal cations. The component species are additionally linked to one another by hydrogen bonds. The polymeric arrays are tightly stacked one on top of the other, without incorporating any solvent in the interface zones between them, which are lined with the lipophilic benzofuran residues. This study provides the first example of coordination networking with the aid of the 1-benzofuran-2,3-dicarboxylate ligand.

Comment

This report is part of our recent effort to evaluate the supramolecular reactivity of 1-benzofuran-2,3-dicarboxylic acid (BFDC), a previously unexplored ligand that can readily coordinate to various metal ions (Koner & Goldberg, 2009*a,b*). We have characterized the molecular structure of this species and revealed that under mild conditions it tends to react with various cations as a monoanion, while maintaining an intramolecular hydrogen bond between the two carboxylic acid substituents (Koner & Goldberg, 2009*a,b*). As a result, in neutral or weakly basic environments, the coordination potential of this bis-bidentate ligand (with four carboxylate O sites) to metal ions could not fully materialize, in contrast with earlier observations with related bifunctional anions, such as benzene-1,4-dicarboxylate (*e.g.* Guilera & Steed, 1999; Reineke *et al.*, 2000; Chen *et al.*, 2006; Hu *et al.*, 2007; Pham *et al.*, 2008). We anticipated that possible application of the BFDC unit, as a bidentate or polydentate bridging ligand, in the synthesis of extended coordination networks might

require more extreme experimental conditions. Correspondingly, in order to extend the supramolecular functional reactivity of BFDC, we changed the synthetic approach in the following ways. First, we applied stronger basic conditions by introducing sodium hydroxide into the reaction mixture to assure complete deprotonation of BFDC. Then, the latter was reacted preferably with lanthanide ions, as these provide a very attractive interface to promote the formation of coordination networks owing to their large size, the spatial divergence of the valence orbitals, their high coordination numbers and their high affinity for oxo ligands due to their 'hard' nature (Lipstman *et al.*, 2007; Muniappan *et al.*, 2007). Finally, the reaction was carried out under solvothermal conditions, which were found to promote the formation of high-nuclearity coordination products (Low *et al.*, 2003; Eddaoudi *et al.*, 2002).

In this study, we report the first coordination network constructed from doubly deprotonated BFDC (BFDC^{2-}) and *diaqualanthanum(III)*, with a 3:2 ratio to account for charge balance. The molecular structure of the title compound, (I), is depicted in Fig. 1. The basic structural unit involves the binuclear $[\text{La}_2(\text{COO})_6]$ motif frequently found in coordination



frameworks of lanthanide ions and dicarboxylate bridging ligands (Reineke *et al.*, 2000; Chen *et al.*, 2006; Hu *et al.*, 2007; Pham *et al.*, 2008). The asymmetric unit contains two La^{III} ions, three BFDC^{2-} ligands and four molecules of water (Fig. 1). Every metal cation is coordinated by two water molecules and seven O atoms from four BFDC^{2-} anions. The La—O coordination bonds are in the range 2.430 (3)–2.677 (3) Å (Table 1), in agreement with earlier observations (Muniappan *et al.*, 2007). Compound (I) exhibits two-dimensional coordination networks (Fig. 2). The three crystallographically independent BFDC^{2-} units bridge between adjacent lanthanide ions in different coordination geometries (none of the carboxylate groups exhibits solely a μ_2 -chelating binding to a single metal ion). Atom La1 coordinates to the three ligands of the asymmetric unit (Fig. 1), as well as to atom O36 ($-x, -y + 1, -z$). Atom La2 links to two ligands of the asymmetric unit (containing atoms O7 and O21, and atoms O37 and O50), as well as to O51 at ($-x, -y, -z$) and O20 at ($-x + 1, -y, -z$). Of the 12 carboxylate O atoms, only O23 is not coordinated to

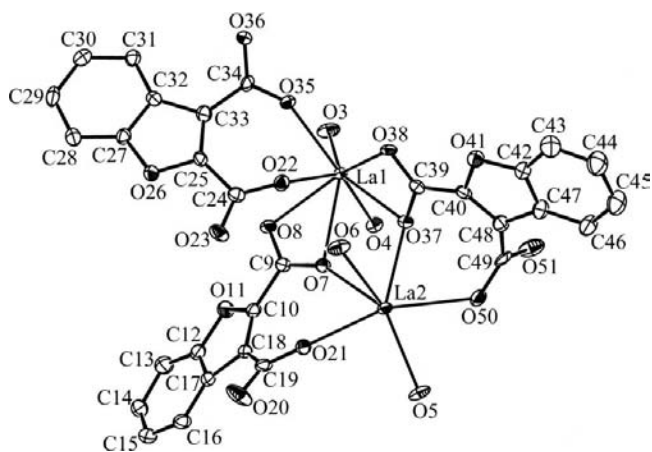


Figure 1
The asymmetric unit of (I), showing the atom-labeling scheme of the asymmetric unit. The atom ellipsoids represent displacement parameters at the 50% probability level at *ca* 110 K. H atoms have been omitted.

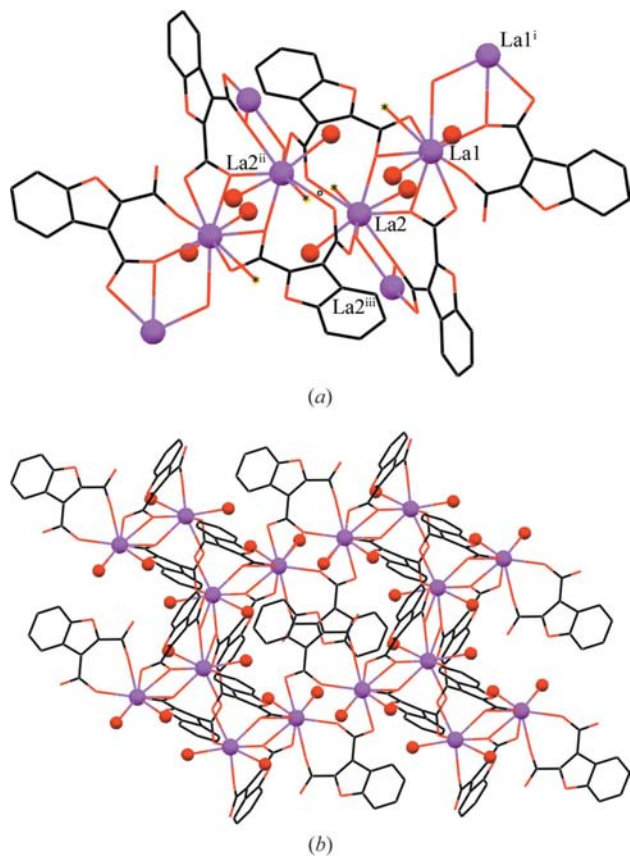


Figure 2
The coordination pattern in (I). Lanthanum ions and water O atoms are depicted as small spheres. (a) A fragment of the coordination network around the marked inversion center at (0, 0, 0). O atoms marked with an asterisk belong to neighboring dicarboxylate entities. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x, -y, -z$; (iii) $-x + 1, -y, -z$.] (b) An extended face-on view of the coordination network, aligned parallel to the *ab* plane and centered at $z = 0$. H atoms have been omitted.

a metal ion. The distances between adjacent La atoms within the network are as follows: $\text{La1} \cdots \text{La2} = 4.332(1) \text{ \AA}$, $\text{La1} \cdots \text{La1}(-x, -y + 1, -z) = 4.432(1) \text{ \AA}$ and $\text{La2} \cdots \text{La2}(-x + 1, -y, -z) = 4.340(1) \text{ \AA}$ (Fig. 2a). Additional hydrogen bonds

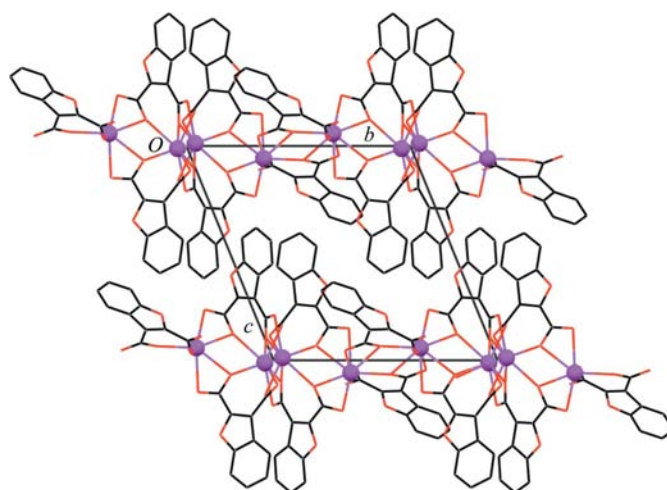


Figure 3
The crystal packing of (I) projected down the *a* axis. Two coordination networks at $z = 0.0$ and $z = 1.0$ are shown edge-on. Note the tight fit between the networks and between the outward-oriented lipophilic benzofuran residues of adjacent layers in the interface zone centered at $z = \frac{1}{2}$. Lanthanum ions and water O atoms are depicted as small spheres and H atoms have been omitted.

involving the aqua ligands as H-atom donors and the carboxylate groups, furan O atoms and water molecules of the same network as H-atom acceptors provide further links between the constituent components (Table 2).

The coordination networks are aligned parallel to the *ab* plane of the crystal and are centered at $z = 0$. The metal ions, aqua ligands and carboxylate binding sites are located in the interior of the polymeric array, while the lipophilic benzofuran residues are oriented outward, lining the upper and lower surface of the coordination network. In the crystal structure, the networks are tightly stacked one on top of the other along the *c* axis. The concave surface areas of one layer fit into the convex surface areas of adjacent layers from above and below without leaving any voids in between (Fig. 3). Typical parallel and T-type orientations between the benzene rings of adjacent networks characterize the intermolecular organization in the interface zone.

In summary, this study reports a unique two-dimensional coordination polymer of lanthanum ions with BFDC^{2-} bridging ligands. It demonstrates for the first time the utility of BFDC in the formation of extended coordination networks. In BFDC, the *ortho*-substituted carboxylic acid functions are positioned on one end of the organic ligand, while the other end consists of the aromatic benzene ring. This appears to limit the coordination functionality of this molecule to one or two dimensions (Koner & Goldberg, 2009a,b), as opposed to the three-dimensional coordination frameworks that could be obtained with other ligands, such as benzene-1,4-dicarboxylate, that bear *trans*-related coordinating functions (Reineke *et al.*, 2000; Chen *et al.*, 2006; Hu *et al.*, 2007; Pham *et al.*, 2008). Within a wider context of our crystal engineering program to design functional metal-organic frameworks, further studies are underway to construct extended coordination polymers with BFDC and related dicarboxylic acid ligands, and various lanthanide ions.

Experimental

All the reactants and solvents (see below) were obtained commercially. A mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.13 g, 0.3 mmol), 1-benzofuran-2,3-dicarboxylic acid (0.124 g, 0.6 mmol) and NaOH (0.05 g, 1.2 mmol) was sealed in a stainless steel reactor, heated at 433 K for 3 d and then cooled slowly to room temperature. Colorless crystals of (I) were recovered from the reactor, washed with distilled water and dried in air. IR (KBr, cm^{-1}): 3440 (*br*, water stretching), 1718 (ν of COOH), 1602 and 1559 (ν_{as} of OCO^-), 1417 and 1362 (ν_{s} of OCO^-).

Crystal data

$[\text{La}_2(\text{C}_{10}\text{H}_4\text{O}_5)_3(\text{H}_2\text{O})_4]$	$\gamma = 84.8788$ (10°)
$M_r = 962.28$	$V = 1499.76$ (5) \AA^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.1011$ (2) \AA	Mo $K\alpha$ radiation
$b = 13.1771$ (2) \AA	$\mu = 2.90$ mm^{-1}
$c = 13.7172$ (3) \AA	$T = 110$ K
$\alpha = 67.3835$ (9°)	$0.35 \times 0.20 \times 0.10$ mm
$\beta = 81.1791$ (9°)	

Data collection

Nonius KappaCCD diffractometer	16461 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	7169 independent reflections
$T_{\text{min}} = 0.430$, $T_{\text{max}} = 0.760$	5523 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	460 parameters
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 2.68$ e \AA^{-3}
7169 reflections	$\Delta\rho_{\text{min}} = -1.67$ e \AA^{-3}

Table 1

Selected bond lengths (\AA).

La1—O35	2.430 (3)	La2—O21	2.470 (3)
La1—O22	2.535 (3)	La2—O37	2.515 (3)
La1—O37	2.570 (3)	La2—O7	2.517 (3)
La1—O8	2.580 (3)	La2—O5	2.528 (3)
La1—O4	2.586 (3)	La2—O51 ⁱⁱ	2.542 (4)
La1—O3	2.596 (3)	La2—O6	2.551 (4)
La1—O7	2.618 (3)	La2—O50	2.594 (4)
La1—O36 ⁱ	2.622 (3)	La2—O20 ⁱⁱⁱ	2.607 (4)
La1—O38	2.644 (3)	La2—O21 ⁱⁱⁱ	2.677 (3)
La1—O35 ⁱ	2.787 (3)		

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

H atoms bound to C atoms were located in calculated positions and were constrained to ride on their parent atoms, with C—H distances of 0.95 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bound to O atoms were either located in difference Fourier maps or positioned to optimize intermolecular hydrogen bonding. All the O—H bond lengths were first restrained to 0.90 (2) \AA , but were then kept fixed in the final least-squares cycles with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*;

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3A \cdots O38 ⁱ	0.90	2.01	2.865 (4)	159
O3—H3B \cdots O26 ^{iv}	0.90	2.21	3.008 (5)	148
O4—H4A \cdots O50 ⁱⁱ	0.90	1.93	2.816 (5)	168
O4—H4B \cdots O5 ⁱⁱ	0.90	2.39	2.963 (5)	122
O5—H5A \cdots O36 ^v	0.90	1.84	2.705 (5)	162
O5—H5B \cdots O23 ⁱⁱⁱ	0.90	1.95	2.750 (4)	148
O6—H6B \cdots O22	0.88	1.88	2.736 (4)	163

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

program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3297). Services for accessing these data are described at the back of the journal.

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