

# Poly[bis( $\mu_4$ -benzene-1,2-dicarboxylato)di- $\mu_3$ -isonicotinato-di-lanthanum(III)]

Guo-Ming Wang,\* Shu-Yun Xue, Hui Li and Hui-Luan Liu

Department of Chemistry, Teachers College of Qingdao University, Qingdao, Shandong 266071, People's Republic of China

Correspondence e-mail: gmwang\_pub@163.com

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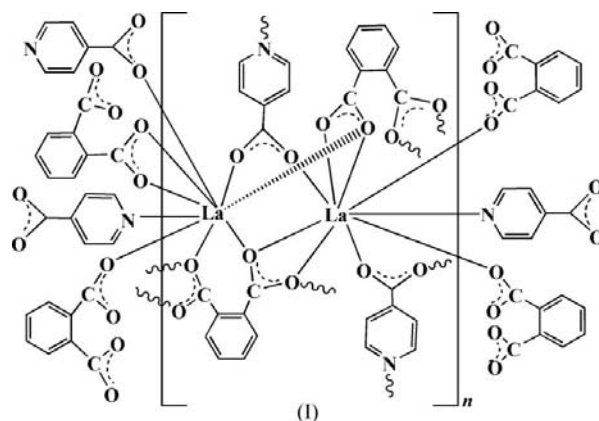
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In the title compound,  $[\text{La}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_6\text{H}_4\text{NO}_2)_2]_n$ , there are two crystallographically independent La centres, both nine-coordinated in tricapped trigonal prismatic coordination geometries by eight carboxylate O atoms and one pyridyl N atom. The La centres are linked by the carboxylate groups of isonicotinate ( $\text{IN}^-$ ) and benzene-1,2-dicarboxylate ( $\text{BDC}^{2-}$ ) ligands to form La–carboxylate chains, which are further expanded into a three-dimensional framework with nanometre-sized channels by La–N bonds. In the construction of the resultant architecture, in tricapped trigonal prismatic coordination geometries by eight carboxylate O atoms and one pyridyl N atom, while the BDC ligands link to four different cations each, displaying penta- and heptadentate chelating–bridging modes, respectively.

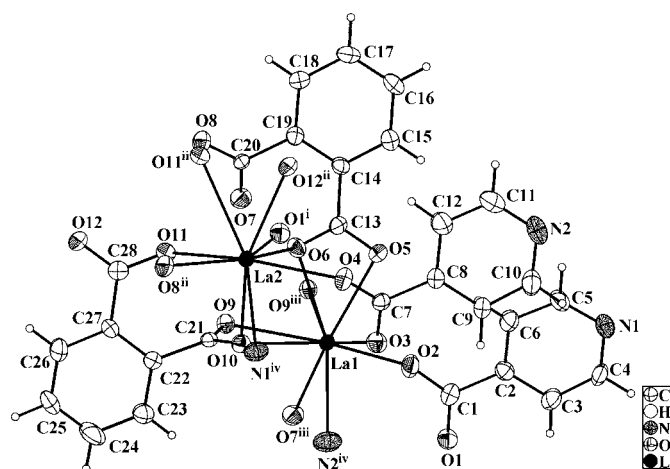
## Comment

The rational design and construction of metal–organic coordination networks have 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). Carboxylate lanthanide networks in particular have attracted increasing attention due to their ability to both chelate to a metal and simultaneously bridge to adjacent metals, especially with the larger and less rigid coordination spheres of rare earth elements. To design such coordination polymers, an effective synthetic approach is based on the deliberate combination of appropriate metal ions and multifunctional ligands. Up to now, a variety of multicarboxylate ligands, such as pyridinecarboxylate, imidazoledicarboxylic acid and pyrazinecarboxylic acid, *etc.*, have been successfully employed as bridging groups to construct one-, two- and three-dimensional networks (Choi *et al.*, 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). Our interest is to explore the co-operativity of mixed organic

ligands in coordinating metal centres and to construct novel coordination polymers with interesting and complicated architectures and topologies. As a continuation of our previous work (Wang, Li *et al.*, 2007; Wang, Huang *et al.*, 2007), we report here a new lanthanide coordination polymer, poly[bis( $\mu_4$ -benzene-1,2-dicarboxylato)di- $\mu_3$ -isonicotinato-di-lanthanum(III)], (I), which displays an interesting three-dimensional coordination framework with nanometre-sized channels.

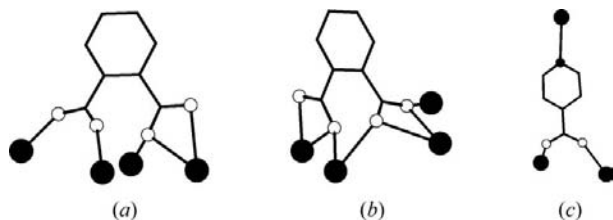


As shown in Fig. 1, the asymmetric unit contains two unique  $\text{La}^{\text{III}}$  centres, two benzene-1,2-dicarboxylate ( $\text{BDC}^{2-}$ ) ligands and two isonicotinate ( $\text{IN}^-$ ) ligands. The La1 and La2 centres are both nine-coordinate with a distorted tricapped trigonal prismatic geometry. Each La centre is surrounded by two carboxylate O atoms from two IN ligands, six carboxylate O atoms from four BDC ligands and one pyridyl N atom. Interestingly, there are no hydroxo or aqua ligands within the structure, despite the synthesis being carried out under aqueous conditions. The La–O bond distances range from

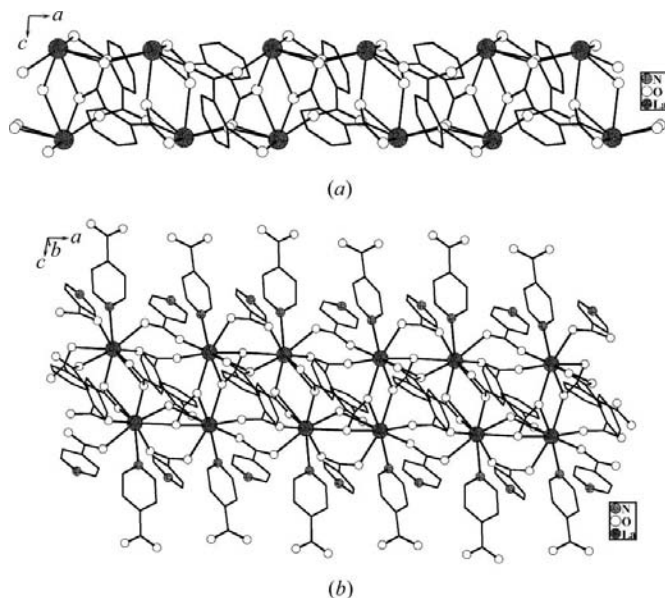


**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $1 + x, y, z$ ; (ii)  $2 - x, 1 - y, 1 - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ .]



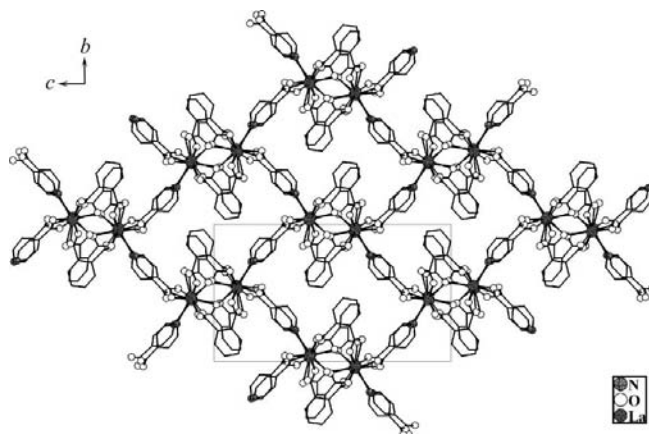
**Figure 2**  
Coordination modes of the IN and BDC ligands in (I).



**Figure 3**  
Different views of the one-dimensional chains, constructed (a) from the BDC ligands only or (b) from IN and BDC mixed ligands.

2.366 (3) to 2.811 (3) Å, while the La–N bond distances are 2.734 (4) or 2.782 (4) Å.

The BDC ligands in the asymmetric unit exhibit two types of coordination modes as depicted in Fig. 2: (i) coordinating four La<sup>III</sup> ions in a pentadentate chelating–bridging mode (Fig. 2a) or (ii) binding four La<sup>III</sup> ions in a heptadentate chelating–bridging mode (Fig. 2b). The IN ligands, however, adopt the same tridentate bridging mode with both carboxylate groups adopting a bimonodentate coordination mode, connecting two La<sup>III</sup> ions, while the N atom simultaneously coordinates a third La<sup>III</sup> centre (Fig. 2c). On the basis of these connection schemes of the BDC ligands, the La centres are bridged by carboxylate groups to form a ladder-like chain along the *a* axis, with separations between adjacent La<sup>III</sup> ions of 4.326 (3), 4.375 (1), 4.499 (7) and 5.572 (1) Å (Fig. 3a). The remaining coordination sites of La<sup>III</sup> ions, however, are filled by the IN ligands. Thus, an interesting one-dimensional La–carboxylate chain with mixed ligands is formed (Fig. 3b), which is somewhat similar to that of  $\{[\text{Ln}_2(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{C}_8\text{H}_4\text{O}_4)(\text{OH})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$  (Ln = Er and Tm) (Wang, Huang *et al.*, 2007). However, in that case the pyridyl N atom is free and noncoordinated, thus making no contribution to the expansion of such chains into a high-dimensional architecture, whereas the IN ligands in the



**Figure 4**  
A view of the three-dimensional La–carboxylate framework with one-dimensional channels.

present structure, acting as tri-connectors, not only afford the carboxylate groups as donor atoms, but also provide their pyridyl N atoms to covalently coordinate the La<sup>III</sup> ions. It is worth noting that carboxylate O atoms usually prefer to bind hard lanthanide ions while the softer N atom is ideally suited to bind soft transition metal ions such as Ag and Cu, according to the hard–soft acid–base theory. A search of the literature and the Cambridge Structural Database (CSD, Version of February 2009; Allen, 2002) reveals that, despite the existence of several *3d–4f* and *4d–4f* heterometallic Ln–TM (TM = transition metal) coordination polymers incorporating the IN ligand (for typical examples, see: Zhang *et al.*, 2005; Luo *et al.*, 2006; Gu & Xue, 2006; Liu *et al.*, 2006; Gu & Xue, 2007a; Cheng *et al.*, 2008; Wang *et al.*, 2008; Lian *et al.*, 2009), lanthanide frameworks directly assembled from the covalent N–Ln linkage mode are relatively rare (Gu & Xue, 2007b). In the title compound, however, adjacent La–carboxylate chains are directly interconnected by the covalent N–Ln linkages, forming a three-dimensional framework and leaving in between one-dimensional channels parallel to the chains, in part occupied by BDC ligands and with approximate dimensions 12 × 17 Å, as defined by the limiting La centres (Fig. 4).

## Experimental

The title compound was synthesized under mild hydrothermal conditions. Typically, La<sub>2</sub>O<sub>3</sub> (0.5 mmol, 0.163 g), HIN (2.30 mmol, 0.284 g), H<sub>2</sub>BDC (0.75 mmol, 0.122 g) and H<sub>2</sub>O (10 ml) were sealed in a 25 ml Teflon-lined steel autoclave and heated under autogenous pressure at 443 K for 9 d. The yellow prism-like crystals obtained were recovered by filtration, washed with distilled water and dried in air.

### Crystal data

$[\text{La}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_6\text{H}_4\text{NO}_2)_2]$	$V = 2658.80 (14) \text{ \AA}^3$
$M_r = 850.25$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.9357 (3) \text{ \AA}$	$\mu = 3.24 \text{ mm}^{-1}$
$b = 12.4348 (5) \text{ \AA}$	$T = 295 \text{ K}$
$c = 21.6047 (3) \text{ \AA}$	$0.25 \times 0.13 \times 0.12 \text{ mm}$
$\beta = 95.067 (4)^\circ$	

## Data collection

Bruker APEXII area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.498$ ,  $T_{\max} = 0.697$

20786 measured reflections  
 5502 independent reflections  
 4666 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.082$   
 $S = 1.03$   
 5502 reflections

397 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.08 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.02 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (Å).

La1—O2	2.366 (3)	La2—O1 <sup>iii</sup>	2.500 (3)
La1—O3	2.461 (3)	La2—O4	2.479 (3)
La1—O5	2.569 (3)	La2—O6	2.616 (3)
La1—O6	2.677 (3)	La2—O8 <sup>iv</sup>	2.416 (3)
La1—O7 <sup>i</sup>	2.449 (3)	La2—O10	2.652 (3)
La1—O9 <sup>i</sup>	2.551 (3)	La2—O11	2.574 (3)
La1—O9	2.601 (3)	La2—O11 <sup>iv</sup>	2.811 (3)
La1—O10	2.723 (3)	La2—O12 <sup>iv</sup>	2.513 (3)
La1—N2 <sup>ii</sup>	2.734 (4)	La2—N1 <sup>ii</sup>	2.782 (4)

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

All H atoms bound to C atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H atoms, and constrained to ride on their parent atoms [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

Data collection: APEX2 (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); 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: BG3111). Services for accessing these data are described at the back of the journal.

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