

# Poly[bis( $\mu$ -benzene-1,4-dicarboxylato)bis[ $\mu$ -6-(4-pyridyl)-5*H*-imidazolo[4,5-*f*][1,10]phenanthroline]-dilead(II)]: an interpenetrating $\alpha$ -Po net

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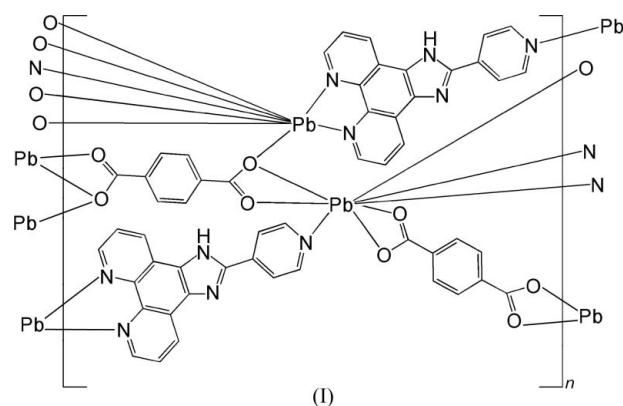
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The asymmetric unit of the title compound,  $[\text{Pb}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{18}\text{H}_{11}\text{N}_5)_2]_n$ , contains two  $\text{Pb}^{\text{II}}$  atoms, two benzene-1,4-dicarboxylate (1,4-bdc) dianions and two 6-(4-pyridyl)-5*H*-imidazolo[4,5-*f*][1,10]phenanthroline (*L*) ligands. Each  $\text{Pb}^{\text{II}}$  atom is eight-coordinated by three N atoms from two different *L* ligands and five carboxylate O atoms from three different 1,4-bdc dianions. The two 1,4-bdc dianions (1,4-bdc<sub>1</sub> and 1,4-bdc<sub>2</sub>) show different coordination modes. Each 1,4-bdc<sub>1</sub> coordinates to two  $\text{Pb}^{\text{II}}$  atoms in a chelating bis-bidentate mode. Each carboxylate group of the 1,4-bdc<sub>2</sub> anion connects two  $\text{Pb}^{\text{II}}$  atoms in a chelating-bridging tridentate mode to form a dinuclear unit. Neighbouring dinuclear units are connected together by the aromatic backbone of the 1,4-bdc dianions and the *L* ligands into a three-dimensional six-connected  $\alpha$ -polonium framework. The most striking feature is that two identical three-dimensional single  $\alpha$ -polonium nets are interlocked with each other, thus leading directly to the formation of a twofold interpenetrated three-dimensional  $\alpha$ -polonium architecture. The framework is held together in part by strong N—H...O hydrogen bonds between the imidazole NH groups of the *L* ligands and the carboxylate O atoms of 1,4-bdc dianions within different  $\alpha$ -polonium nets.

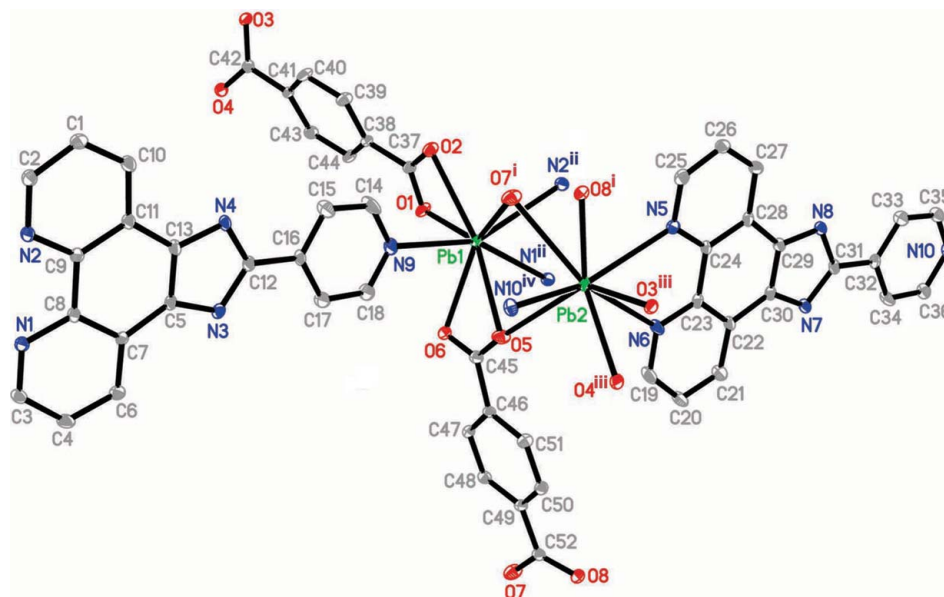
## Comment

The design and synthesis of coordination polymers with infinite three-dimensional framework structures has been an area of rapid growth in recent years, owing to the potential of these polymers in various applications such as catalysis, electrical conductivity, host-guest chemistry and magnetism (Ockwig *et al.*, 2005; O'Keefe *et al.*, 2008; Yang *et al.*, 2008). In this regard, a great many coordination polymers with mineral topologies, including  $\text{CdSO}_4$  (cds),  $\text{NbO}$  (nbo),  $\text{Pt}_3\text{O}_4$  (pto), pyrite (pyr), quartz (qtz), rutile (rto), diamond (diaz) and sodalite (sod),

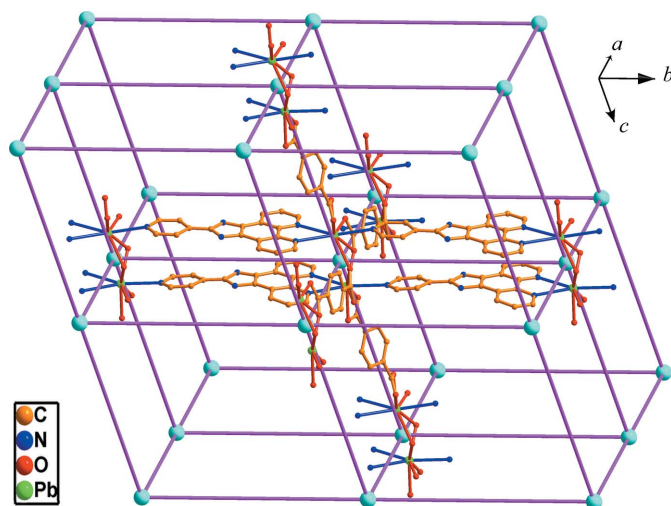
have provided experimental examples of these theoretical topologies (Batten, 2001; Batten & Robson, 1998; Carlucci *et al.*, 2003). As a result, the design and construction of diverse topological networks has received much attention (Eddaoudi *et al.*, 2001). The topologies of coordination polymers can often be controlled and modified by the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand (Long *et al.*, 2002). It is well known that careful selection of a suitable organic ligand with certain features is helpful for constructing coordination polymers with desirable properties. So far, the combination of bridging carboxylates, 1,10-phenanthroline-like (phen-like) chelating ligands and metal ions has generated many interesting coordination architectures (Wang *et al.*, 2008; Qiao *et al.*, 2008; Kong *et al.*, 2009). Unfortunately, owing to the termination effect of chelating phen-like ligands, such coordination polymers containing both polycarboxylates and phen-like ligands are usually only one- or two-dimensional (Wang *et al.*, 2009, 2010; Qiao *et al.*, 2009). High-dimensional complexes based on dicarboxylate and phen-like ligands have rarely been reported (Yang *et al.*, 2007). Here, we have selected the benzene-1,4-dicarboxylate dianion (1,4-bdc) as an organic linker and 6-(4-pyridyl)-5*H*-imidazolo[4,5-*f*][1,10]phenanthroline (*L*) as an *N*-donor ligand, generating a new twofold interpenetrating coordination polymer with an  $\alpha$ -Po topology, *viz.*  $[\text{Pb}_2(1,4\text{-bdc})_2(L)_2]_n$  (I).



The asymmetric unit of (I) contains two  $\text{Pb}^{\text{II}}$  atoms, two 1,4-bdc dianions and two *L* ligands (Fig. 1). Each  $\text{Pb}^{\text{II}}$  atom is eight-coordinated by three N atoms from two different *L* ligands and five carboxylate O atoms from three different 1,4-bdc dianions. The Pb—O distances (Table 1) are comparable with those observed for  $[\text{Pb}(\text{eedb})(L')(\text{DMF})]$  (eedb is 4,4'-ethylenedibenzoate and *L'* is pyrazino[2,3-*f*][1,10]phenanthroline and DMF is dimethylformamide) (Qiao *et al.*, 2009). The two independent 1,4-bdc dianions show different coordination modes. For convenience, the 1,4-bdc anions containing atoms O1–O4 and O5–O8 are designated 1,4-bdc<sub>1</sub> and 1,4-bdc<sub>2</sub>, respectively. Each 1,4-bdc<sub>1</sub> anion coordinates to two  $\text{Pb}^{\text{II}}$  atoms in a chelating bis-bidentate mode. Carboxylate atoms O1 and O2 chelate Pb1, while atoms O3 and O4 chelate Pb2<sup>v</sup> [symmetry code: (v) *x*, *y*, *z* – 1]. Each carboxylate group of the 1,4-bdc<sub>2</sub> anion connects two  $\text{Pb}^{\text{II}}$  atoms in a chelating-bridging tridentate mode to form a dimer. Carboxylate atoms O5 and



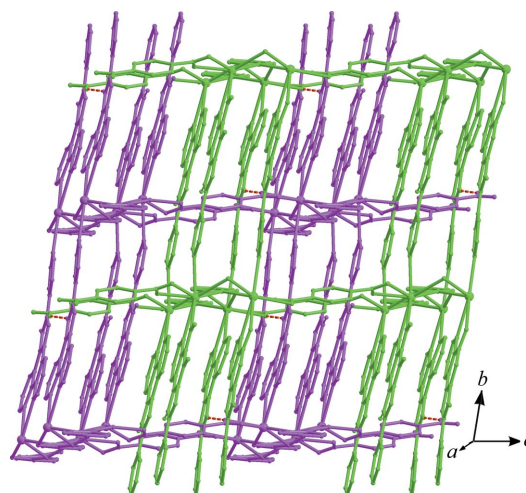
**Figure 1**  
A view of the local coordination of the Pb<sup>II</sup> atoms in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $x, y, 1 + z$ ; (iv)  $x, y - 1, z$ .]



**Figure 2**  
A view of the three-dimensional  $\alpha$ -polonium net of (I). Large balls represent the six-connected nodes.

O6 chelate Pb1, while atom O5 bridges simultaneously to Pb2. The other O atoms, O7 and O8, chelate Pb2<sup>vi</sup>, while atom O7 bridges simultaneously to Pb1<sup>vi</sup> [symmetry code: (vi)  $1 + x, y, z$ ]. The distance between the Pb<sup>II</sup> atoms in the dinuclear unit is 3.751 (3) Å.

Neighbouring dinuclear units are connected together by the aromatic backbone of both 1,4-bdc dianions and the *L* ligands. Each dinuclear Pb<sup>II</sup> unit is surrounded by eight organic ligands, *viz.* four bridging 1,4-bdc dianions and four bridging *L* ligands. Although each dinuclear Pb<sup>II</sup> unit is ligated by eight bridging ligands, it is essentially linked to six nearest neighbours, because two pairs of *L* ligands form two 'double bridges' (Fig. 2). Each dinuclear unit therefore acts as a six-



**Figure 3**  
A view of the twofold interpenetrated  $\alpha$ -polonium structure of (I). Hydrogen-bonding interactions between the nets are shown as dashed lines.

connecting node, and the overall three-dimensional framework topology is that of  $\alpha$ -polonium (Fig. 2).

The most striking feature of (I) is that two identical three-dimensional single  $\alpha$ -polonium nets are interlocked with each other, thus leading directly to the formation of a twofold interpenetrated three-dimensional  $\alpha$ -Po architecture (Fig. 3).

There are strong N—H...O hydrogen bonds between the imidazole NH groups of the *L* ligands (N3 and N8) and the carboxylate O atoms of the 1,4-bdc ligands within different  $\alpha$ -Po nets (Table 2). Each  $\alpha$ -Po net is hydrogen bonded to its neighbour through these hydrogen bonds, which further consolidates the twofold interpenetrated framework.

To date, although a number of  $\alpha$ -Po frameworks have been reported, we are not aware of any other example of a Pb<sup>II</sup>

coordination polymer with this motif (O'Keeffe *et al.*, 2008; Wang *et al.*, 2010). As far as we know, only one  $\alpha$ -Po framework based on a 1,10-phen-like ligand,  $[\text{Cd}(1,4\text{-ndc})(L')]_n$  ( $L'$  is pyrazino[2,3-*f*][1,10]phenanthroline (1,4-ndc is naphthalene-1,4-dicarboxylate), has been reported so far (Qiao *et al.*, 2008). In that structure, four  $\text{Cd}^{\text{II}}$  atoms are bridged by the carboxylate groups of the 1,4-ndc ligands to form tetranuclear cadmium carboxylate clusters. These tetranuclear cadmium carboxylate clusters are further connected together by the aromatic backbone of the dicarboxylate ligands to generate a three-dimensional non-interpenetrating  $\alpha$ -Po net.

Notably, although the very recently reported compound  $\{[\text{Pb}(1,4\text{-bdc})(L)] \cdot 2\text{H}_2\text{O}\}_n$  (Wang *et al.*, 2010) is constructed from the same mixed organic ligands and  $\text{Pb}^{\text{II}}$  atoms, its structure is entirely different from that of (I). In that compound, each carboxylate group of the 1,4-bdc anion chelates one  $\text{Pb}^{\text{II}}$  atom in a bidentate mode. All 1,4-bdc anions assume one kind of coordination mode, namely bridging bis(bidentate). Adjacent  $\text{Pb}^{\text{II}}$  atoms are bridged by 1,4-bdc dianions to form a one-dimensional zigzag chain. The  $L$  ligands are attached on both sides of the chains in chelating modes. Clearly, the topological difference between (I) and the previously reported compound is mainly attributed to the different coordination modes of the 1,4-bdc dianions and the  $L$  ligands. The water molecules are not coordinated to any of the metal atoms, and are in the voids between the chains. It should be pointed out that the previously reported compound was synthesized at 443 K, while (I) was prepared at 468 K in the presence of  $\text{Pb}^{\text{II}}$ , 1,4-bdc and  $L$ . Thus, the synthesis of the two structures can apparently be controlled through variation of the reaction temperature.

## Experimental

A mixture of  $\text{Pb}(\text{NO}_3)_2$  (0.5 mmol), 1,4- $\text{H}_2\text{bdc}$  (0.5 mmol) and  $L$  (1 mmol) was dissolved in distilled water (12 ml). The resulting solution was stirred for about 2 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 468 K for 7 d under autogenous pressure, then cooled slowly to room temperature. Pale-yellow block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 35% based on  $\text{Pb}^{\text{II}}$ ).

### Crystal data

$[\text{Pb}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{18}\text{H}_{11}\text{N}_5)_2]$	$\gamma = 81.399$ (1) $^\circ$
$M_r = 1337.24$	$V = 2299.2$ (3) $\text{\AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 10.9066$ (7) $\text{\AA}$	Mo $K\alpha$ radiation
$b = 15.0537$ (10) $\text{\AA}$	$\mu = 7.38$ $\text{mm}^{-1}$
$c = 15.0663$ (10) $\text{\AA}$	$T = 293$ K
$\alpha = 75.890$ (1) $^\circ$	$0.27 \times 0.22 \times 0.16$ mm
$\beta = 74.199$ (1) $^\circ$	

### Data collection

Bruker APEX diffractometer	12743 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	7984 independent reflections
$T_{\text{min}} = 0.56$ , $T_{\text{max}} = 0.77$	6315 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

**Table 1**

Selected bond lengths ( $\text{\AA}$ ).

Pb1—O1	2.508 (4)	Pb2—O3 <sup>iii</sup>	2.424 (4)
Pb1—O2	2.691 (4)	Pb2—O4 <sup>iii</sup>	2.651 (4)
Pb1—O5	2.772 (4)	Pb2—O5	2.761 (4)
Pb1—O6	2.591 (4)	Pb2—O7 <sup>i</sup>	2.836 (4)
Pb1—O7 <sup>i</sup>	2.555 (4)	Pb2—O8 <sup>i</sup>	2.545 (4)
Pb1—N1 <sup>ii</sup>	2.824 (4)	Pb2—N5	2.853 (4)
Pb1—N2 <sup>ii</sup>	2.829 (4)	Pb2—N6	2.852 (4)
Pb1—N9	2.681 (5)	Pb2—N10 <sup>iv</sup>	2.662 (5)

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

**Table 2**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H3A $\cdots$ O1 <sup>v</sup>	0.86	1.93	2.720 (6)	151
N8—H8A $\cdots$ O3 <sup>vi</sup>	0.86	2.02	2.822 (6)	155

Symmetry codes: (v)  $-x + 1, -y, -z$ ; (vi)  $-x, -y + 1, -z$ .

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.070$

$S = 0.98$

7984 reflections

649 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 1.27 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$

All H atoms were positioned geometrically, with  $\text{N-H} = 0.86 \text{ \AA}$  and  $\text{C-H} = 0.93 \text{ \AA}$ , and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3261). Services for accessing these data are described at the back of the journal.

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