

Poly[μ_8 -4,4'-bipyridine-2,2',6,6'-tetracarboxylato-dilead(II)]

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Received 1 November 2009

Accepted 14 December 2009

Online 8 January 2010

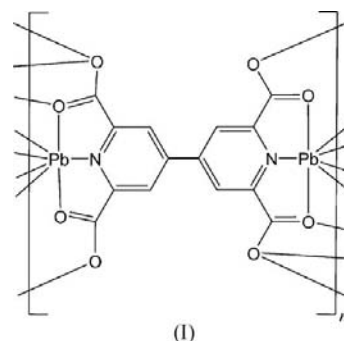
The Pb^{II} cation in the title compound, $[\text{Pb}_2(\text{C}_{14}\text{H}_4\text{N}_2\text{O}_8)]_n$, is seven-coordinated by one N atom and six O atoms from four 4,4'-bipyridine-2,2',6,6'-tetracarboxylate (BPTCA^{4-}) ligands. The geometric centre of the BPTCA^{4-} anion lies on an inversion centre. Each pyridine-2,6-dicarboxylate moiety of the BPTCA^{4-} ligand links four Pb^{II} cations *via* its pyridyl N atom and two carboxylate groups to form two-dimensional sheets. The centrosymmetric BPTCA^{4-} ligand then acts as a linker between the sheets, which results in a three-dimensional metal-organic framework.

Comment

A number of Pb^{II} -carboxylate complexes with layered or three-dimensional network structures have been reported in recent years (Ayyappan *et al.*, 1999; Fredoueil *et al.*, 2002; Drumel *et al.*, 1995; Bentiss *et al.*, 2004). This might be partly ascribed to the unique coordination chemistry of the Pb^{II} cation, due to its large radius, variable stereochemical activity and flexible coordination environment, which is different from those of the divalent transition metal ions (Zhang, Zhou *et al.*, 2008). To construct the targeted Pb^{II} network, nitrogen-containing polytopic organic acids (Liang *et al.*, 2007; Cheng *et al.*, 2006; Zhao *et al.*, 2003; Gao *et al.*, 2006; Wang *et al.*, 2007; Mahata & Natarajan, 2005) are usually selected as the linkers, due to their abundant coordination modes in bridging Pb^{II} cations into clusters or multidimensional frameworks (Ayyappan *et al.*, 1999; Fredoueil *et al.*, 2002). For further investigation of the coordination chemistry of Pb^{II} , 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid (H_4BPTCA) was used as the linker in this work, due to its versatile binding modes and its interesting skeleton (Lin *et al.*, 2006; Bai, Qi *et al.*, 2008; Bai, Liu *et al.*, 2008). Thus, we present here the synthesis and crystal structure of the title compound, $[\text{Pb}_2(\text{BPTCA})]_n$, (I).

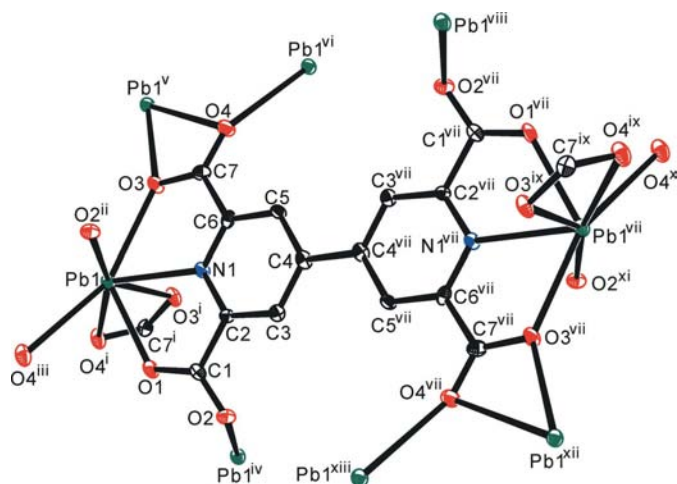
Compound (I) was obtained in the form of light-yellow pyramid-shaped crystals, which are stable at ambient temperature. Single-crystal structure analysis reveals that it

crystallizes in the monoclinic space group $C2/c$ with the H_4BPTCA ligand completely deprotonated, which is also indicated by IR spectroscopic data. As shown in Fig. 1, the Pb^{II} cation possesses a monocapped trigonal prismatic coordination geometry completed by two O atoms and one N atom from one BPTCA^{4-} ligand, two carboxylate O atoms from another BPTCA^{4-} ligand, and another two carboxylate O atoms from two different BPTCA^{4-} ligands. The Pb—O bond lengths are in the range 2.404 (6)–2.847 (7) Å and the Pb—N bond length is 2.459 (7) Å. The geometric centre of the BPTCA^{4-} anion lies on an inversion centre. Each pyridine-2,6-dicarboxylate moiety of the BPTCA^{4-} anion uses one *syn-anti* carboxylate group (O1—C1—O2) to connect adjacent Pb^{II} cations, forming one-dimensional chains along the *b* direction. The other carboxylate group of the pyridine-2,6-dicarboxylate moiety uses atom O3 to coordinate to two Pb^{II} cations from two neighbouring chains to form a ribbon (Fig. 2) and atom O4 to coordinate to two Pb^{II} cations from two neighbouring ribbons, leading to the construction of two-dimensional sheets parallel to the *bc* plane (Fig. 3). Neighbouring two-dimensional sheets are then bridged through the centrosymmetric BPTCA^{4-} ligands, which results in a three-dimensional metal-organic framework (Fig. 4).



As described above, one carboxylate group of the pyridine-2,6-dicarboxylate moiety of the BPTCA^{4-} ligand adopts a *syn-anti* coordination mode, while the other presents a μ_3, η^4 -bridging mode. Thus, each pyridine-2,6-dicarboxylate moiety of the BPTCA^{4-} ligand behaves as a μ_4, η^7 -bridge and each BPTCA^{4-} ligand acts as a μ_8, η^{14} -linker.

The structure of (I) is different from those of the related three-dimensional isostructural complexes $[\text{Mn}_2(\text{BPTCA})-(\mu_2\text{-H}_2\text{O})_2]_n$ (Bai, Qi *et al.*, 2008) and $[\text{Cd}_2(\text{BPTCA})-(\mu_2\text{-H}_2\text{O})_2]_n$ (Bai, Liu *et al.*, 2008), in which infinite $-M-O-$ ($M = \text{Mn}$ or Cd) zigzag chains built from the bridging water molecules and M^{II} ions are bridged by carboxylate groups to generate a two-dimensional network. These two-dimensional networks are further pillared by BPTCA^{4-} ligands to form a three-dimensional porous inorganic-organic polymer. Each pyridine-2,6-dicarboxylate moiety of the BPTCA^{4-} ligand in the two compounds adopts a μ_3 -bridging mode to link three metal ions with two carboxylate groups, presenting different coordination modes: one adopts a *syn-anti* $\mu_2, \eta^1: \eta^1$ -bridging mode to link two metal ions, and the other acts as a $\mu_2, \eta^1: \eta^2$ -bridge. The structure of (I) is also entirely different from that of the related three-dimensional complex $[\text{Zn}_2(\text{BPTCA})]_n$.


Figure 1

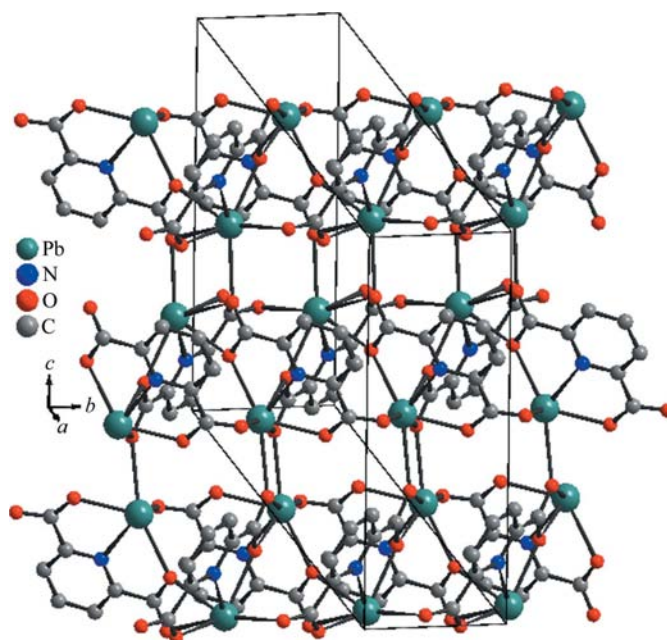
A view of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $x, -y, z - \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x, -y, z + \frac{1}{2}$; (vii) $-x + 1, -y + 1, -z + 1$; (viii) $-x + 1, -y, -z + 1$; (ix) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (x) $-x + 1, y + 1, -z + \frac{3}{2}$; (xi) $-x + 1, -y + 2, -z + 1$; (xii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (xiii) $-x + 1, y + 1, -z + \frac{1}{2}$.]


Figure 2

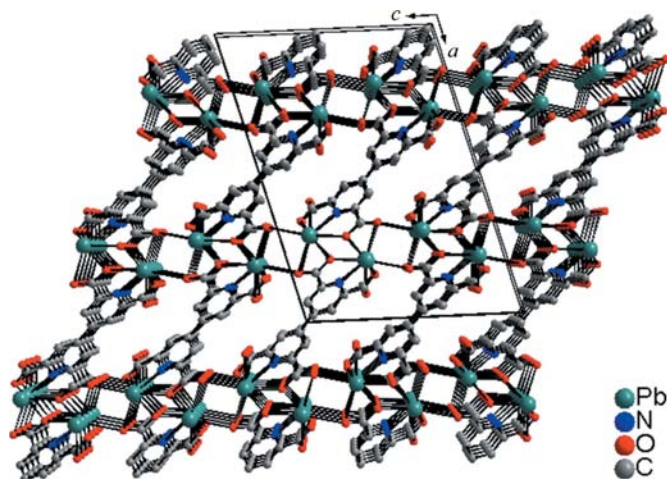
A view of the one-dimensional chain running along the *b* direction.

$4\text{H}_2\text{O}$) $_{\infty}$ (Lin *et al.*, 2006) with a 4^6_6 topology, which crystallizes in a chiral space group, $P4_22_12$, with the chirality generated by the helical chains of hydrogen-bonded guest water molecules rather than by the coordination framework. Another two two-dimensional Mn^{II} complexes (Bai, Qi *et al.*, 2008) and one two-dimensional Cu^{II} complex (Bai, Liu *et al.*, 2008) were also reported to be constructed from the BPTCA^{4-} ligand.

The geometries of Pb^{II} cations can be classified into hemidirectionality and holodirectionality. Hemidirectionality refers to a Pb^{II} cation which spreads the ligands within a single hemisphere to have its valence lone pair expanding within the other hemisphere (Gourlaouen *et al.*, 2008; van Severen *et al.*, 2009). In compound (I), the central Pb^{II} cation is seven-coordinated in a monocapped trigonal prism geometry by one N atom and six O atoms from four BPTCA^{4-} ligands. The seven atoms are located on one side of the Pb^{II} cation, which shows hemidirectionality, leaving the other side for the stereochemically active lone pair. This is similar to previously reported examples of Pb^{II} hemidirectionality, such as $[\text{Pb}(\text{INO})_2]_2 \cdot 7\text{H}_2\text{O}$ (Zhao *et al.*, 2007), $[\text{Pb}(\text{HIDC})]_n$ (H_3IDC is imidazole-4,5-dicarboxylic acid; Zhang, Song *et al.*, 2008), $[\text{Pb}(\text{fum})]_n$ (fum is fumarate; Zhang *et al.*, 2009), $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (ba is benzylacetylacetonate; Ahmadzadi *et al.*,


Figure 3

A view of the two-dimensional sheet parallel to the *bc* plane.


Figure 4

A view of the three-dimensional metal-organic framework of (I).

2009), $[\text{Pb}(\text{suc})(\text{H}_2\text{bbp})]_2$ [H_2suc is succinic acid and H_2bbp is 2,6-bis(2-benzimidazolyl)pyridine; Meng *et al.*, 2009], and $[\text{Pb}(\text{INA})_2]$ (INA is isonicotinate, $\text{NC}_5\text{H}_4\text{-4-CO}_2^-$; Zhang, Zhou *et al.*, 2008). The Pb^{II} cations in these compounds present different coordination numbers. The arrangement of the ligands around the Pb^{II} cations in these compounds suggest a vacant site in the coordination geometry around the metal ions, which is possibly occupied by a stereoactive lone electron pair on Pb^{II} . Therefore, the Pb^{II} cations in these compounds also adopt hemidirected geometry.

Experimental

H_4BPTCA (86 mg, 0.025 mmol) was dissolved in water (14 ml) and NaOH (66 mg, 0.165 mmol) was added to the solution. After stirring

for 30 min, PbCO₃ (108.1 mg, 0.028 mmol) was added to the mixture. The resulting solution was transferred to a 25 ml Teflon-lined stainless steel autoclave and heated at 373 K for 4 d. The autoclave was then allowed to cool to room temperature over a period of 24 h. Light-yellow pyramid-shaped crystals of (I) were obtained, washed with deionized water and dried at ambient temperature (yield 40%). IR (KBr, ν , cm⁻¹): 3440 (s), 2341 (w), 2274 (w), 1630 (s), 1615 (s), 1593 (s), 1568 (s), 1429 (s), 1401 (s), 1380 (s), 1376 (s), 1333 (s), 1188 (m), 1071 (m), 996 (w), 902 (w), 809 (m), 799 (w), 736 (w), 658 (w).

Crystal data

[Pb ₂ (C ₁₄ H ₄ N ₂ O ₈)]	$V = 1456.1(3) \text{ \AA}^3$
$M_r = 742.58$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 19.696(2) \text{ \AA}$	$\mu = 23.15 \text{ mm}^{-1}$
$b = 5.3916(8) \text{ \AA}$	$T = 298 \text{ K}$
$c = 14.2090(16) \text{ \AA}$	$0.18 \times 0.11 \times 0.07 \text{ mm}$
$\beta = 105.203(2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	3640 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1998)	1285 independent reflections
$T_{\min} = 0.103$, $T_{\max} = 0.294$	1116 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	118 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 1.46 \text{ e \AA}^{-3}$
1285 reflections	$\Delta\rho_{\text{min}} = -1.89 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Pb1—O1	2.404 (6)	Pb1—O2 ⁱⁱ	2.625 (6)
Pb1—N1	2.459 (7)	Pb1—O4 ⁱⁱⁱ	2.798 (7)
Pb1—O3 ⁱ	2.512 (6)	Pb1—O4 ⁱ	2.847 (7)
Pb1—O3	2.610 (6)		
O1—Pb1—N1	66.7 (2)	N1—Pb1—O4 ⁱⁱⁱ	124.5 (2)
O1—Pb1—O3 ⁱ	78.8 (2)	O3 ⁱ —Pb1—O4 ⁱⁱⁱ	127.40 (18)
N1—Pb1—O3 ⁱ	76.5 (2)	O3—Pb1—O4 ⁱⁱⁱ	153.23 (16)
O1—Pb1—O3	128.19 (18)	O2 ⁱⁱ —Pb1—O4 ⁱⁱⁱ	81.98 (18)
N1—Pb1—O3	63.0 (2)	O1—Pb1—O4 ⁱ	80.5 (2)
O3 ⁱ —Pb1—O3	78.39 (12)	N1—Pb1—O4 ⁱ	120.5 (2)
O1—Pb1—O2 ⁱⁱ	101.2 (2)	O3 ⁱ —Pb1—O4 ⁱ	48.36 (19)
N1—Pb1—O2 ⁱⁱ	73.3 (2)	O3—Pb1—O4 ⁱ	115.1 (2)
O3 ⁱ —Pb1—O2 ⁱⁱ	146.9 (2)	O2 ⁱⁱ —Pb1—O4 ⁱ	164.78 (19)
O3—Pb1—O2 ⁱⁱ	75.94 (19)	O4 ⁱⁱⁱ —Pb1—O4 ⁱ	84.4 (2)
O1—Pb1—O4 ⁱⁱⁱ	70.67 (18)		

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

H atoms were generated geometrically, with C—H = 0.93 \AA , and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In the final difference Fourier map, the positions of the highest peak (1.46 e \AA^{-3}) and deepest hole (−1.89 e \AA^{-3}) are at (0.2100, 0.2182, 0.8709) and (0.2723, 0.1024, 0.0412), which are 0.90 and 1.37 \AA from Pb1, respectively.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SHELXTL (Sheldrick, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL and DIAMOND (Brandenburg, 2004); software used to prepare material for publication: SHELXTL.

The authors are grateful for financial support from the National Natural Science Foundation of China (grant No. 20971029) and the New Century Ten Hundred Thousand Talents Programme of Guangxi Province.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3035). Services for accessing these data are described at the back of the journal.

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