

Poly[bis(μ_3 -5'-carboxy-2,2'-bipyridine-5-carboxylato- κ^4 O:N,N':O')lead(II)]

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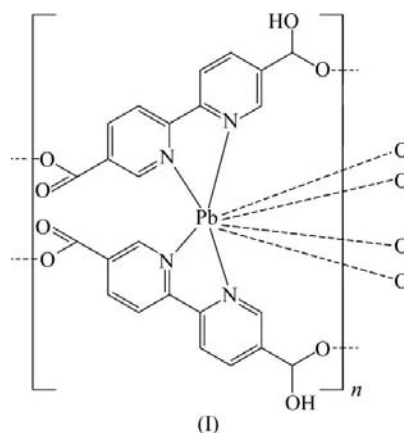
The title compound, $[\text{Pb}(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_4)_2]_n$, obtained by reaction of $\text{Pb}(\text{NO}_3)_2$ and 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bptc) under hydrothermal conditions, has a structure in which the unique Pb^{II} cation sits on a twofold axis and is octa-coordinated by four O-atom donors from four Hbptc^- ligands and four N-atom donors from two Hbptc^- ligands in a distorted dodecahedral geometry. With each Pb^{II} cation connected to six Hbptc^- ligands and each Hbptc^- ligand bridging three Pb^{II} cations, a three-dimensional polymeric structure is formed. From a topological point of view, the three-dimensional net is binodal, with six-connected (the Pb^{II} cation) and three-connected (the Hbptc^- ligand) nodes, resulting in a distorted rutile $(4^2.8)_2(4^4 8^9 12^2)$ topology.

Comment

The design and synthesis of high-dimensional metal-organic framework (MOF) structures is becoming an increasingly popular field of research due to their formation of interesting structures and their potentially useful ion-exchange, adsorption, catalytic, fluorescence and magnetic properties (Leininger *et al.*, 2000; Seo *et al.*, 2000; Swiegers & Malefetse, 2000; Wu *et al.*, 2005; Spencer *et al.*, 2006). The construction of coordination networks with different topological structures has attracted significant attention from chemists (Delgado Friedrichs *et al.*, 2003). Consequently, a variety of three-dimensional MOFs have been prepared by taking certain factors into account, such as the coordination nature of the metal ion and the shape, functionality, flexibility and symmetry of the organic ligand (Reger *et al.*, 2001; Kitaura *et al.*, 2002, 2003). The key step in forming extended structures with particular architectures is to select appropriate bridging ligands, with rigid multidentate ligands being particularly advantageous. 2,2'-Bipyridine-5,5'-dicarboxylic acid (H_2bptc) is an effective ligand which contains a number of N- and O-coordination sites and rich coordination modes. They have shown not only strong chelating ability, but also a bridging tendency, yielding mono- or polynuclear one-, two- or three-dimensional structures, depending on the metal ion and the

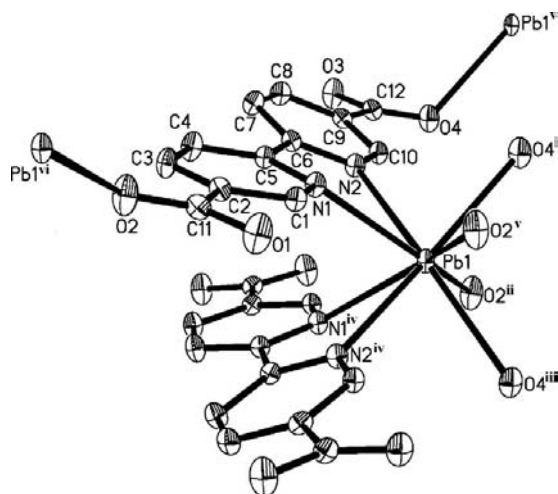
coligand used (Desmartin *et al.*, 1995; Finn & Zubieta, 2000; Min *et al.*, 2002; Tynan *et al.*, 2003; Lee & Suh, 2004; Matthews *et al.*, 2004; Schoknecht & Kempe, 2004; Szeto *et al.*, 2006, 2008; Tsai & Liu, 2008). Among the reported structures, only that containing neodymium is three-dimensional (Schoknecht & Kempe, 2004). The greater dimensionality can be attributed to the high coordination numbers of lanthanides, which provide more opportunities to extend in different directions. Furthermore, the published metal compounds are limited to transition and lanthanide metals, while complexes with main group metals are still absent.

The hydrothermal method has been a promising technique in preparing highly stable extended metal-ligand frameworks (Yaghi & Li, 1995; Gutschke *et al.*, 1996; Chui *et al.*, 1999; Gerrard & Wood, 2000). Taking advantage of the bridging ability of H_2bptc in the chemical design of metal-organic molecular assemblies and the potentially high coordination number of Pb^{II} , we have synthesized the title novel three-dimensional coordination polymer, (I), under hydrothermal conditions.

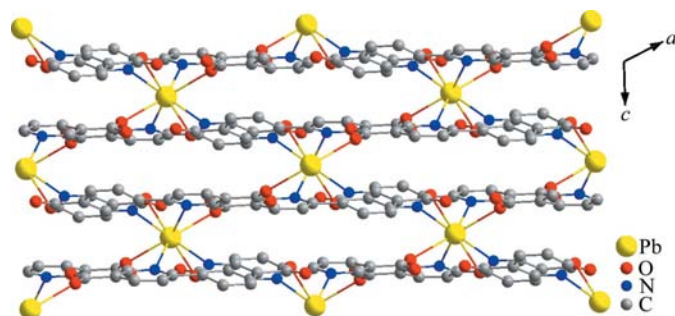


Compound (I) represents a rare example of a three-dimensional framework with three- and six-connected nodes which exhibits a rutile-related $(4^2.8)_2(4^4 8^9 12^2)$ topology. The structure of (I) is distinctly different from the three-dimensional structure of the previously reported neodymium complex $[\text{Nd}_2(\text{bpdcc})_3(\text{H}_2\text{O})_4]_n$, in which the lanthanide centres act as five-connectors and two types of ligand cross-linkers as three- and four-connectors (Schoknecht & Kempe, 2004).

The asymmetric unit of (I) contains one-half of a Pb^{II} cation, located on a twofold rotation axis, and an Hbptc^- anion (Fig. 1). Thus, the carboxyl groups of H_2bptc are partly deprotonated to produce Hbptc^- , which is in agreement with the IR data where strong absorption peaks were observed around 1700 cm^{-1} for $-\text{COOH}$. The two pyridyl rings of the ligand are rotated about the C—C single-bond axis with a dihedral angle between the planes of $12.83(16)^\circ$. The carboxylate groups have different twists relative to their attached pyridine ring, with dihedral angles of $2.7(5)$ and $16.6(4)^\circ$. Each Pb^{II} cation has a distorted dodecahedral coordination environment with four N atoms from two chelating Hbptc^- anions (N1 , N2 , N1^{iv} and N2^{iv} ; all symmetry


Figure 1

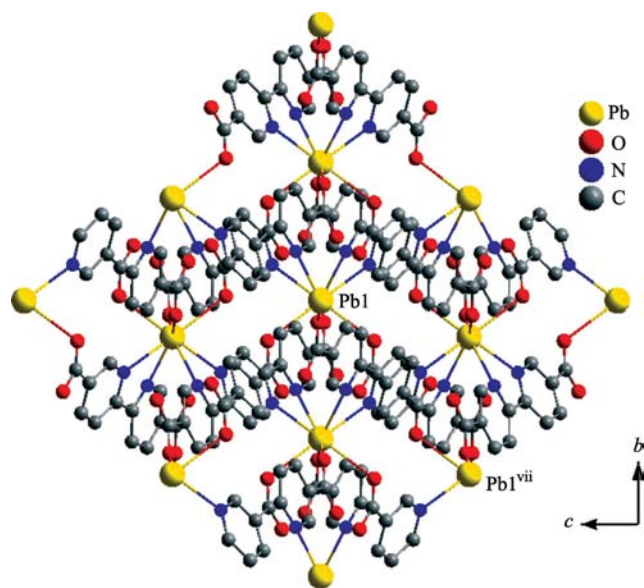
A view of the local coordination of the Pb^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 2, y, -z + \frac{1}{2}, z$; (v) $-x + \frac{3}{2}, -y - \frac{1}{2}, -z$; (vi) $x + \frac{1}{2}, y + \frac{1}{2}, z$.]


Figure 2

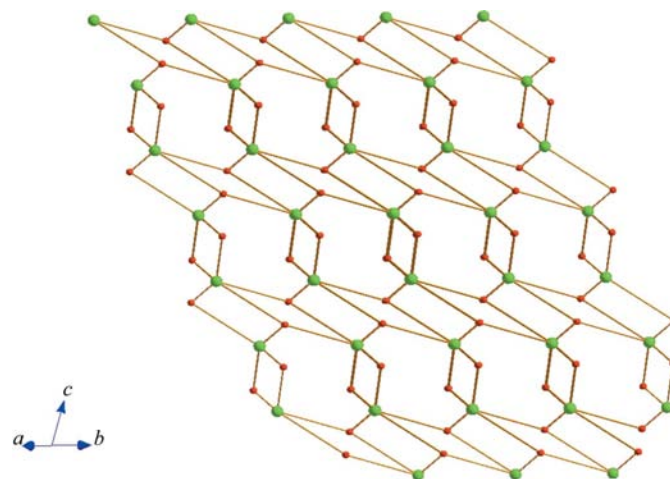
The packing of (I), viewed along the *b* axis, showing the connection mode of the mononuclear units within the *ac* plane.

codes as in Figs. 1 and 3) and four O atoms from four other Hbptc⁻ anions (O2ⁱⁱ, O2^v, O4ⁱ and O4ⁱⁱⁱ). In total, each Pb^{II} cation is connected to six Hbptc⁻ ligands, defining a six-connected node within the structure. The C—O distances (Table 1) involving uncoordinated oxygen are slightly longer than the C—O distances involving coordinated oxygen [O1—C11 = 1.269 (5) Å and O3—C12 = 1.298 (4) Å *versus* O2—C11 = 1.247 (5) Å and O4—C12 = 1.219 (4) Å]. Obvious peaks adjacent to atoms O3 and O1 can be seen in the difference electron-density maps. All these observations suggest that the H atom is actually disordered between the noncoordinated O atoms. The Hbptc⁻ anion coordinates to three Pb^{II} centres, *viz.* to Pb1 in a bidentate chelating mode and to Pb1^v and Pb1^{vi} in a monodentate bridging mode. Thus, each Hbptc⁻ ligand affords a three-connected node.

Each mononuclear Pb unit is linked to eight neighbouring mononuclear units to form a three-dimensional framework through the Hbptc⁻ ligands. Four neighbouring Pb^{II} cations are linked at two different distances through C₅H₃NCOO⁻


Figure 3

Packing view showing the connected mode of mononuclear units along the *bc* plane. H atoms have been omitted for clarity. [Symmetry code: (vii) $-x + 1, -y - 1, -z$.]


Figure 4

A schematic representation of the distorted rutile $(4^2.8)_2(4^48^9 12^2)$ topology of (I). Pb^{II} cations are shown as large spheres and Hbptc⁻ anions as small spheres.

spacers (half of the Hbptc⁻ ligand) [Pb1[·]··Pb1^v = 7.840 (1) Å and Pb1[·]··Pb1^{vi} = 9.485 (1) Å], while four other Pb^{II} cations are linked through ⁻OOC(C₅H₃N)₂COOH spacers (the whole Hbptc⁻ ligand) [Pb1[·]··Pb1^{vii} = 15.471 (2) Å; Fig. 3]. The connecting mode of the mononuclear units within the *ac* and *bc* planes are shown in Figs. 2 and 3, respectively.

A better insight into the nature of this intricate framework can be achieved by the application of a topological approach, *i.e.* reducing multidimensional structures to simple node and connection nets. As discussed above, the structure of (I) is binodal with six- (Pb^{II}) and three-connected (Hbptc⁻) nodes. The framework can be rationalized by considering the shortest circuits starting and ending at Pb^{II} and Hbptc⁻, leading to the formation of a distorted rutile $(4^2.8)_2(4^48^9 12^2)$ topology (Fig. 4) (Blatov *et al.*, 2005).

Experimental

A mixture of $\text{Pb}(\text{NO}_3)_2$ (0.2 mmol, 66 mg), H_2bptc (0.4 mmol, 98 mg) and H_2O (18.0 ml) in a molar ratio of 1:2:5000 was sealed in a 25 ml stainless steel reactor with a Teflon liner. The reactor was directly heated to 453 K, held at that temperature for 72 h and then cooled slowly to 303 K at a rate of 4 K h^{-1} . Green block-shaped crystals of the title complex were collected by filtration and washed with ethanol (yield 35%).

Crystal data

| | |
|--|---|
| $[\text{Pb}(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_4)_2]$ | $V = 2110.2 (4) \text{ \AA}^3$ |
| $M_r = 693.58$ | $Z = 4$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a = 15.1836 (17) \text{ \AA}$ | $\mu = 8.06 \text{ mm}^{-1}$ |
| $b = 11.3719 (13) \text{ \AA}$ | $T = 291 \text{ K}$ |
| $c = 13.5342 (16) \text{ \AA}$ | $0.20 \times 0.12 \times 0.08 \text{ mm}$ |
| $\beta = 115.447 (1)^\circ$ | |

Data collection

| | |
|---|--|
| Bruker SMART CCD area-detector diffractometer | 7034 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 1977 independent reflections |
| $T_{\min} = 0.296$, $T_{\max} = 0.565$ | 1909 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.026$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.020$ | 169 parameters |
| $wR(F^2) = 0.049$ | H-atom parameters constrained |
| $S = 1.09$ | $\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$ |
| 1977 reflections | $\Delta\rho_{\text{min}} = -1.44 \text{ e \AA}^{-3}$ |

Table 1

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

| | | | |
|--|-------------|--|-------------|
| Pb1—O2 ⁱ | 2.644 (3) | O1—C11 | 1.269 (5) |
| Pb1—N1 | 2.667 (3) | O2—C11 | 1.247 (5) |
| Pb1—N2 | 2.694 (3) | O3—C12 | 1.298 (4) |
| Pb1—O4 ⁱⁱ | 2.758 (3) | O4—C12 | 1.219 (4) |
| O2 ⁱ —Pb1—O2 ⁱⁱⁱ | 141.03 (13) | N2 ^{iv} —Pb1—N2 | 113.75 (12) |
| O2 ⁱ —Pb1—N1 | 139.69 (9) | O2 ⁱ —Pb1—O4 ^v | 76.46 (10) |
| O2 ⁱⁱⁱ —Pb1—N1 | 75.17 (9) | O2 ⁱⁱⁱ —Pb1—O4 ^v | 80.46 (9) |
| N1 ^{iv} —Pb1—N1 | 81.17 (12) | N1—Pb1—O4 ^v | 100.65 (9) |
| O2 ⁱ —Pb1—N2 | 81.58 (9) | N2—Pb1—O4 ^v | 72.90 (9) |
| O2 ⁱⁱⁱ —Pb1—N2 | 120.73 (10) | N1—Pb1—O4 ⁱⁱ | 136.50 (8) |
| N1 ^{iv} —Pb1—N2 | 70.89 (9) | N2—Pb1—O4 ⁱⁱ | 161.64 (9) |
| N1—Pb1—N2 | 59.82 (8) | O4 ^v —Pb1—O4 ⁱⁱ | 106.36 (12) |

Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 2, y, -z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, -y - \frac{1}{2}, -z$.

Although evidence of possible disorder was found in the difference electron-density map, carboxyl atom H3 on O3 was included at full occupancy and treated as a riding atom, with $\text{O—H} = 0.82 \text{ \AA}$. The aromatic H atoms were placed at calculated positions, with $\text{C—H} = 0.93 \text{ \AA}$. All H atoms were assigned fixed isotropic displacement parameters, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg & Berndt, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3226). Services for accessing these data are described at the back of the journal.

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