

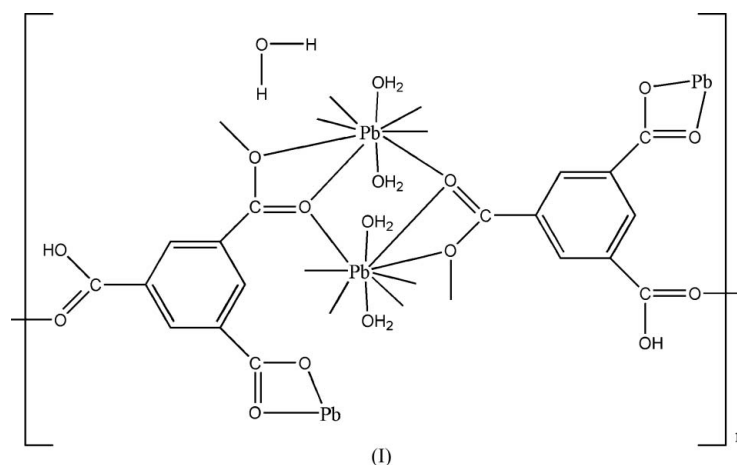
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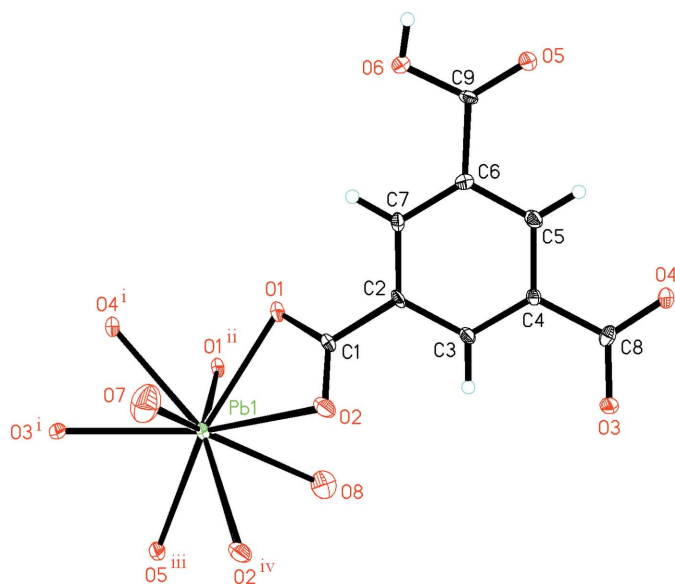
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Key indicators

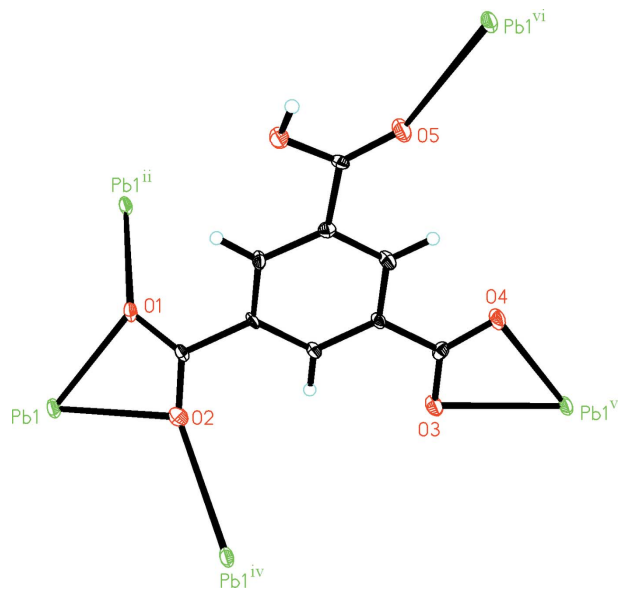
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$
 R factor = 0.034
 wR factor = 0.083
Data-to-parameter ratio = 11.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Poly[[tetraaquabis(μ_5 -1-carboxybenzene-3,5-dicarboxylato)dilead(II)] monohydrate]Crystals of the title compound, $\{[\text{Pb}_2(\text{C}_9\text{H}_4\text{O}_6)_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$, were obtained from an aqueous solution. In the crystal structure, each Pb^{II} cation is nine-coordinated by seven O atoms from five carboxylate groups of five 1-carboxybenzene-3,5-dicarboxylate (TBC) dianions and two water molecules. Pairs of Pb atoms are bridged by two tridentate carboxylate groups of two TBC dianions, yielding centrosymmetric dinuclear complexes. These are connected by TBC dianions, forming a three-dimensional network.Received 26 July 2006
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Comment

Lead(II) is capable of accommodating different coordination numbers and geometries with or without a stereochemically active lone pair (Wang & Vittal, 2003). Of these, a number of polymeric Pb^{II} compounds have been structurally characterized (Ceconi *et al.*, 2003; Bridgewater & Parkin, 2000; Ying *et al.*, 2003). The absence of crystal field stabilization energy effects also allows Pb^{II} cations to adopt a range of different coordination geometries not restricted to octahedral, tetrahedral or square planar (Foreman *et al.*, 2000). The benzene-1,3,5-tricarboxylic acid (TBCA) ligand binds to metal atoms in a variety of bonding modes. When TBCA binds to lead ions, various coordination modes and conformations can be obtained, making this ligand particularly useful for the study of the coordination chemistry of Pb^{2+} . Thus, we have selected the Pb–TBCA system to extend this research and we present here the crystal structure of the title compound, (I).Compound (I) crystallizes with one Pb^{2+} and one TBC dianion in the asymmetric unit (Fig. 1). The Pb atom has a coordination number of nine. Each Pb ion is coordinated by seven O atoms from five carboxylate groups from five TBC anions. Two O atoms from water molecules complete the

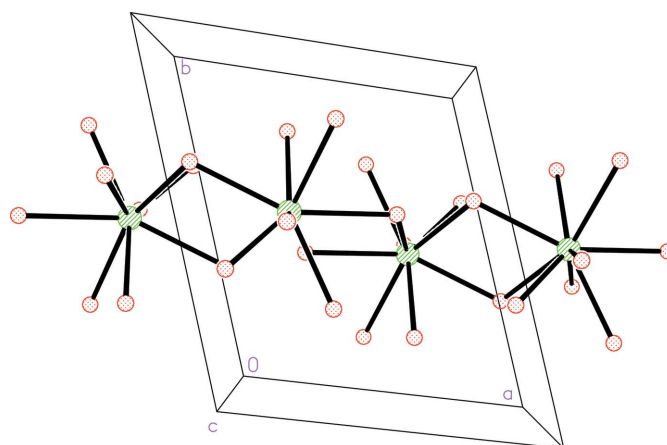

Figure 1

The contents of the asymmetric unit of (I), together with symmetry-equivalent atoms to complete the coordination of Pb1. Symmetry codes as in Table 1.


Figure 2

Coordination mode of the TBC dianion. Symmetry operations as in Table 1, plus (v) $x, y, 1 + z$; (vi) $1 + x, 1 + y, 1 + z$.

coordination environment. The coordination geometry about Pb cannot be derived from a simple polyhedron. The geometry of the TBC dianion is unexceptional, and two of its three carboxylate groups are deprotonated. Each dianion coordinates to five Pb^{2+} ; Fig. 2 shows the coordination mode. One of the deprotonated carboxylate groups coordinates to three Pb: O1 and O2 chelate a Pb cation, and both O1 and O2 coordinate to one Pb cation. The second carboxylate group (O3 and O4) coordinates to one Pb. The protonated carboxylate group is monodentate. Hence, pairs of Pb^{II} ions are bridged by two tridentate carboxylate groups, forming centrosymmetric dinuclear units with the inversion centre halfway between the


Figure 3

Chains derived from edge-sharing PbO_9 polyhedra.

two Pb. These units form polymeric chains that run along the a axis (Fig. 3). The chains are linked together by the TBC anions, yielding a three-dimensional framework.

There are also $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2), which connect the coordination polymer and water molecules and help to stabilize the crystal structure.

Experimental

The title compound was synthesized by adding a solution of benzene-1,3,5-tricarboxylic acid (0.04 g, 0.2 mmol) and 2,2'-dithiosalicic acid (0.06 g, 0.2 mmol) in dimethylformamide (10 ml) dropwise to a stirred solution of lead nitrate (0.07 g, 0.2 mmol) in water (10 ml) at 298 K. The reaction mixture was filtered and the filtrate allowed to stand for about six weeks until colourless prismatic crystals of (I) were obtained. Crystals suitable for X-ray diffraction were collected by filtration, washed with water and ethanol and dried in air.

Crystal data

$[\text{Pb}_2(\text{C}_9\text{H}_4\text{O}_6)_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$
 $M_r = 910.64$
 Triclinic, $P\bar{1}$
 $a = 7.4106$ (6) Å
 $b = 8.2178$ (7) Å
 $c = 10.1424$ (9) Å
 $\alpha = 94.694$ (10)°
 $\beta = 105.165$ (10)°
 $\gamma = 108.024$ (9)°

$V = 557.91$ (10) Å³
 $Z = 1$
 $D_x = 2.710$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 15.16$ mm⁻¹
 $T = 298$ (2) K
 Prism, colourless
 $0.10 \times 0.06 \times 0.05$ mm

Data collection

Bruker APEX area-detector diffractometer
 ω scans
 Absorption correction: numerical (SADABS; Bruker, 2002)
 $T_{\text{min}} = 0.344$, $T_{\text{max}} = 0.465$

3941 measured reflections
 1949 independent reflections
 1896 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.083$
 $S = 1.29$
 1949 reflections
 171 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.017P)^2 + 3.5615P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.57$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0066 (8)

Table 1
Selected bond lengths (Å).

Pb1—O4 ⁱ	2.562 (6)	Pb1—O1 ⁱⁱ	2.745 (6)
Pb1—O1	2.617 (6)	Pb1—O5 ⁱⁱⁱ	2.782 (6)
Pb1—O2	2.641 (6)	Pb1—O2 ^{iv}	2.815 (6)
Pb1—O7	2.652 (9)	Pb1—O8	2.875 (8)
Pb1—O3 ⁱ	2.702 (6)		

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

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6 ^v ···O3 ^v	0.82	1.83	2.629 (8)	164

Symmetry code: (v) $x + 1, y + 1, z$.

H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C—H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and O—H = 0.82 Å, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Water H atoms appear to be disordered and were not considered in the structure model. The highest peak and deepest hole of the residual electron density are 1.06 and 0.92 Å, respectively, from Pb1.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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References

- Bridgewater, B. & Parkin, G. (2000). *Inorg. Chem. Commun.* **3**, 534–536.
- Bruker (2002). *SMART* (Version 5.62), *SAINTE* (Version 6.02), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Cecconi, F., Ghilardi, C. A., Midollini, S. & Orlandini, A. (2003). *Inorg. Chem. Commun.* **6**, 546–548.
- Foreman, M. R. St. J., Gelbrich, T., Hursthouse, M. B. & Plater, M. J. (2000). *Inorg. Chem. Commun.* **3**, 234–238.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Wang, X. B. & Vittal, J. J. (2003). *Inorg. Chem. Commun.* **6**, 1074–1077.
- Ying, S. M., Mao, J. G., Yang, B. P. & Sun, Z. M. (2003). *Inorg. Chem. Commun.* **6**, 1319–1322.