Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Poly[lead(II)-μ_2-aqua-μ_4-terephthalato]

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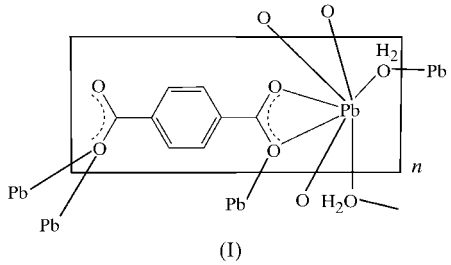
Received 9 December 2003
Accepted 22 December 2003
Online 31 January 2004

The title compound, $[Pb(C_8H_4O_4)(H_2O)]_n$, forms as an insoluble product in the reaction of sodium terephthalate(2−) with $Pb(NO_3)_2$ in water. Analysis has shown that the crystal structure is centrosymmetric, with the asymmetric unit containing one formula unit. The lead geometry is hemidirected seven-coordinate, with both monodentate and bidentate carboxylate coordination modes present. The combination of hydrogen bonds and coordination bonds produces a three-dimensional structure, including the first example, in a lead complex, of the common metal-coordinated carboxylate/water $R_1^1(6)$ graph-set motif.

Comment

As part of our recent study of monovalent and divalent metal salts of terephthalic acid (benzene-1,4-dicarboxylic acid, H_2TA; Dale & Elsegood, 2003*a*,*b*), we have investigated the complexation of the TA^{2-} anion to divalent lead, a known environmental pollutant (Shimoni-Livny *et al.*, 1998). Previously, the Pb^{II} salt of trimesic acid (Foreman *et al.*, 2000) was the only structurally characterized example of this cation complexed to the commonly used members of the benzene-polycarboxylic acid family, although Pb^{II} and Pb^{IV}–carboxylate complexes are well known in the literature, with 160 examples in the Cambridge Structural Database (CSD; Version 5.25, November 2003 update; Allen, 2002).



(I)

Attempts to produce single crystals of the desired coordination complex *via* the direct reaction of Pb^{II} with H_2TA are hindered by the low solubility of both H_2TA and the resulting Pb^{II} complex in water and organic solvents. However, the slow diffusion of separate aqueous solutions of $Pb(NO_3)_2$ and Na_2TA (formed from the reaction of H_2TA with two equivalents of NaOH) results in the formation of crystals of the title compound, $[Pb(TA)(H_2O)]$, (I).

The asymmetric unit of (I) contains one formula unit. The Pb^{II} cation is seven-coordinate (Fig. 1), having a hemidirected coordination sphere (Shimoni-Livny *et al.*, 1998). The water molecule asymmetrically bridges two symmetry-related Pb^{II} centres, and the remaining five coordination bonds on each Pb atom involve Pb–carboxylate interactions. Each Pb^{II} cation bonds to three symmetry-related TA^{2-} anions *via* monodentate coordination, while bidentate coordination is observed for a fourth TA^{2-} anion, having a bite angle of 51.07 (12)° [the CSD range for bidentate Pb^{II}/Pb^{IV}–carboxylate complexes is 45.82–58.33°, mean 51.3 (2)°]. The monodentate Pb–carboxylate bond lengths in (I) lie in the range 2.492 (3)–2.751 (4) Å [mean 2.658 Å; the CSD range for all Pb^{II}/Pb^{IV}–carboxylate interactions (monodentate and bidentate) is 2.148–3.075 Å, mean 2.582 (8) Å] and the bidentate Pb–carboxylate bond lengths in (I) are 2.434 (4) and 2.650 (4) Å [mean 2.542 Å; the CSD range for bidentate Pb^{II}/Pb^{IV}–carboxylate interactions is 2.177–2.968 Å, mean 2.532 (15) Å]. The mean bridging water–Pb bond length is 2.661 Å [the CSD range for $Pb^{II}/Pb^{IV}-OH_2$ bond lengths is 2.354–2.974 Å, mean 2.62 (2) Å].

The TA^{2-} anion bridges four symmetry-related Pb^{II} centres, utilizing three of its O atoms, the fourth (O2) being involved in hydrogen bonding. While the TA^{2-} anion bridges metal centres using both of its carboxylate groups in most of its divalent transition metal complexes [for example, Mg^{II}, Mn^{II} and Fe^{II} (Kaduk, 2002), Cd^{II} (Michaelides *et al.*, 1998), and Zn^{II} (Edgar *et al.*, 2001)], by contrast, in the structures of Cu^{II} (Kaduk, 2002), Ca^{II} (Dale & Elsegood, 2003*a*), and Sr^{II} and Ba^{II} (Groeneman & Atwood, 1999), the TA^{2-} anions utilize only one carboxylate group for coordination, while the second forms hydrogen bonds with included water molecules.

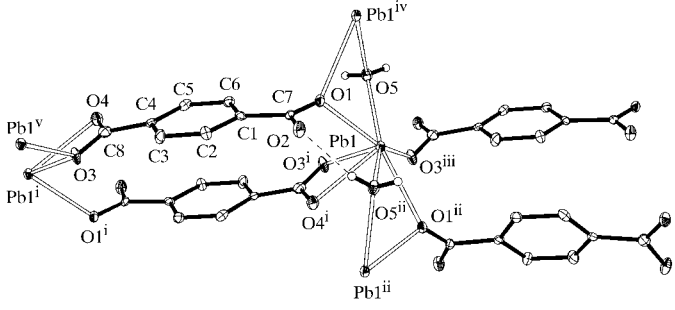


Figure 1
A view of (I), showing the atom-labelling scheme and the Pb^{II} coordination sphere. Displacement ellipsoids are drawn at the 50% probability level and C atoms are shown as unshaded ellipsoids. H atoms not involved in hydrogen bonding have been omitted for clarity and the O—H···O hydrogen bond is shown as a dashed line. Pb—O coordination bonds are highlighted as open bonds. [Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $1+x, y, z$; (iv) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $x-1, y, z$.]

  DOI: 10.1107/S0108270103029573

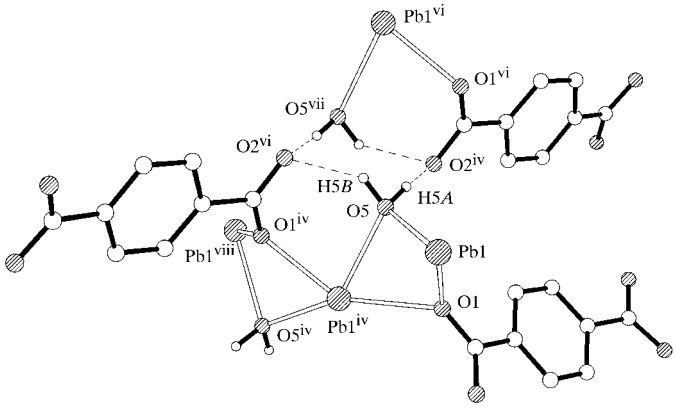


Figure 2
A view of the hydrogen-bonding motifs in (I). Aromatic H atoms have been omitted for clarity. Open circles represent C atoms, shaded circles O atoms and dotted circles Pb atoms. Pb—O coordination bonds are shown as open bonds. [Symmetry codes: (iv) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (vii) $2-x, 1-y, 1-z$; (viii) $x, y+1, z$.]

The bridging of two Pb^{II} centres each by the unique water molecule and carboxy atom O1 creates four-membered rings in which the O—Pb—O bond angles are 68.13 (11) and 62.12 (11)° (Fig. 2 and Table 1). The combination of Pb—O coordination bonds (Table 1) and a carboxy–water O—H···O hydrogen bond (Table 2) results in the formation of a six-membered ring, which can be described by the graph-set notation $R_1^1(6)$ (Etter, 1990; Etter & MacDonald, 1990; Bernstein *et al.*, 1995). While a search of the CSD shows that the $R_1^1(6)$ carboxylate/metal/water motif has not yet been characterized in complexes containing lead, a total of 494 structures (containing any metal cation other than lead) do contain the motif (the limits applied to the search were O···O = 2.0–3.5 Å, H···O = 1.0–2.5 Å and O—H···O = 120–180°). The results of this search are shown in Table 3, and it can be seen that the geometry of the $R_1^1(6)$ motif in (I) shows good agreement with the literature examples. O—H···O hydrogen bonds (Table 2) between the water molecules and carboxy groups also create $R_2^4(8)$ ring motifs (Fig. 2).

The three-dimensional network of coordination and hydrogen bonds in (I) (Fig. 3) results in a distance of ∼3.7 Å between the centroids of the aromatic rings of adjacent, slightly offset, TA^{2-} anions, which bridge the same two Pb^{II} centres. This conformation leads to the non-planar geometry of the TA^{2-} anions, the carboxy C atoms of which deviate (towards the Pb^{II} centres) from coplanarity with the aromatic ring by 0.080 (9) and 0.177 (9) Å for atoms C7 and C8, respectively.

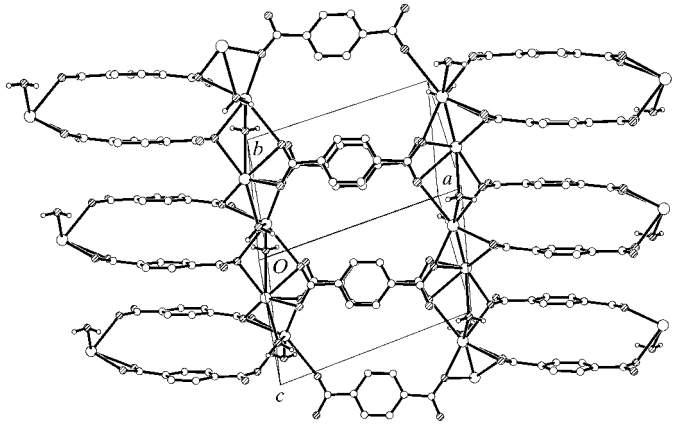


Figure 3
A packing plot of (I), viewed along the *bc* diagonal of the cell. Aromatic H atoms have been omitted for clarity. Open circles represent C atoms, shaded circles O atoms and dotted circles Pb atoms.

Experimental

X-Ray quality colourless crystals of (I) were obtained in quantitaive yield by diffusing together separate aqueous solutions (1:1 ratio) of lead(II) nitrate and sodium terephthalate (Na_2TA; formed from the reaction of H_2TA with two equivalents of NaOH in water). IR (KBr, cm^{-1}): ν_{max} 3425 (*br*, OH), 3063 and 2924 (aromatic C—H), 1524 (asymmetric CO_2^-), 1358 (symmetric CO_2^-), 818 and 748 (aromatic C—H), 521.

Crystal data

$[Pb(C_8H_4O_4)(H_2O)]$
M_r = 389.32
Monoclinic, $P2_1/c$
a = 10.6661 (7) Å
b = 7.5042 (5) Å
c = 11.1260 (8) Å
β = 109.404 (2)°
V = 839.95 (10) Å^3
Z = 4
D_x = 3.079 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3310 reflections
θ = 3.3–28.9°
μ = 20.08 mm^{-1}
T = 150 (2) K
Column, colourless
0.24 × 0.09 × 0.06 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.068, T_{max} = 0.300
4408 measured reflections
1637 independent reflections
1496 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.0°
$h = -8 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.057
S = 1.04
1637 reflections
134 parameters
H atoms treated by a mixture of restrained and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.2788P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.63 e Å^{-3}
$\Delta\rho_{min}$ = −2.11 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0017 (2)

Table 1
Selected geometric parameters (Å, °).

Pb1—O1	2.492 (3)	Pb1—O4^{i}	2.650 (4)
Pb1—O1^{ii}	2.731 (4)	Pb1—O5	2.563 (4)
Pb1—O3^{i}	2.434 (4)	Pb1—O5^{ii}	2.759 (4)
Pb1—O3^{iii}	2.751 (4)		
O1—Pb1—O5	68.13 (11)	O1—Pb1—O5^{ii}	76.97 (11)
O3^{i}—Pb1—O4^{i}	51.07 (12)	O1^{ii}—Pb1—O5^{ii}	62.12 (11)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O2^{iv}	0.90 (2)	1.97 (2)	2.728 (5)	140 (2)
O5—H5A···O2^{vi}	0.92 (2)	1.79 (2)	2.678 (5)	160 (2)

Symmetry codes: (iv) $2-x,\frac{1}{2}+y,\frac{3}{2}-z$; (vi) $x,\frac{1}{2}-y,z-\frac{1}{2}$.

Table 3
Comparison of molecular geometry (Å, °) for $R_1^1(6)$ motifs containing carboxylate and water ligands on any metal cation.

Limits applied to the search of the CSD (November 2003 update): O···O = 2.0–3.5 Å, $H_{water}\cdots O_{carboxy}$ = 1.0–2.5 Å and O—H···O = 120–180°. Redeterminations were included. Where more than one population range was obvious within the limits applied, the range and mean for each population are given.

	Range (CSD)	Mean (CSD)	(I)
O···O	2.429–2.983	2.680 (4)	2.728 (5)
$H_{water}\cdots O_{carboxy}$	1.280–2.458	1.871 (8)	1.97 (2)
O—H···O	130.29–179.74	157.0 (4)	140 (2)
M—carboxylate	1.929–2.290	2.123 (4)	
	2.291–2.637	2.438 (7)	2.492 (3)
	2.693–3.094	2.82 (3)	
M—OH_2	1.903–2.428	2.160 (5)	
	2.467–3.049	2.814 (19)	2.759 (4)
O—M—O	65.75–81.80	74.6 (3)	76.97 (11)
	82.78–106.20	91.0 (2)	

Aromatic H atoms were placed geometrically (C—H = 0.95 Å) and treated using a riding model, while the coordinates of the water H atoms were found in a difference Fourier map and subsequently refined using geometric restraints. U_{iso}(H) values were set at $1.2U_{eq}$(C) for aryl H atoms and at $1.5U_{eq}$(O) for O-bound H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

The authors would like to acknowledge the EPSRC for the provision of a studentship (SHD).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1557). Services for accessing these data are described at the back of the journal.

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