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

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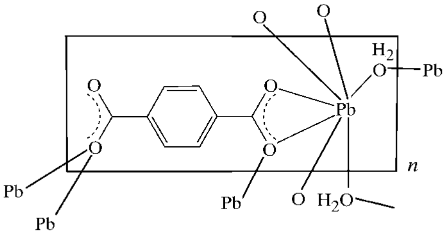
The title compound, $[\mathrm{Pb}(\mathrm{C_8H_4O_4})(\mathrm{H_2O})]_n$, forms as an insoluble product in the reaction of sodium terephthalate(2−) with $\mathrm{Pb(NO_3)_2}$ in water. Analysis has shown that the crystal structure is centrosymmetric, with the asymmetric unit containing one formula unit. 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, $\mathrm{H_2TA}$; Dale & Elsegood, 2003*a*,*b*), we have investigated the complexation of the $\mathrm{TA^{2-}}$ anion to divalent lead, a known environmental pollutant (Shimoni-Livny *et al.*, 1998). Previously, the $\mathrm{Pb^{II}}$ 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 $\mathrm{Pb^{II}}$ and $\mathrm{Pb^{IV}}$–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 $\mathrm{Pb^{II}}$ with $\mathrm{H_2TA}$ are hindered by the low solubility of both $\mathrm{H_2TA}$ and the resulting $\mathrm{Pb^{II}}$ complex in water and organic solvents. However, the slow diffusion of separate aqueous solutions of $\mathrm{Pb(NO_3)_2}$ and $\mathrm{Na_2TA}$ (formed from the reaction of $\mathrm{H_2TA}$ with two equivalents of NaOH) results in the formation of crystals of the title compound, $[\mathrm{Pb(TA)(H_2O)}]$, (I).

The asymmetric unit of (I) contains one formula unit. The $\mathrm{Pb^{II}}$ cation is seven-coordinate (Fig. 1), having a hemidirected coordination sphere (Shimoni-Livny *et al.*, 1998). The water molecule asymmetrically bridges two symmetry-related $\mathrm{Pb^{II}}$ centres, and the remaining five coordination bonds on each Pb atom involve Pb–carboxylate interactions. Each $\mathrm{Pb^{II}}$ cation bonds to three symmetry-related $\mathrm{TA^{2-}}$ anions *via* monodentate coordination, while bidentate coordination is observed for a fourth $\mathrm{TA^{2-}}$ anion, having a bite angle of 51.07 (12)° [the CSD range for bidentate $\mathrm{Pb^{II}/Pb^{IV}}$–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 $\mathrm{Pb^{II}/Pb^{IV}}$–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 $\mathrm{Pb^{II}/Pb^{IV}}$–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 $\mathrm{Pb^{II}/Pb^{IV}{-}OH_2}$ bond lengths is 2.354–2.974 Å, mean 2.62 (2) Å].

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

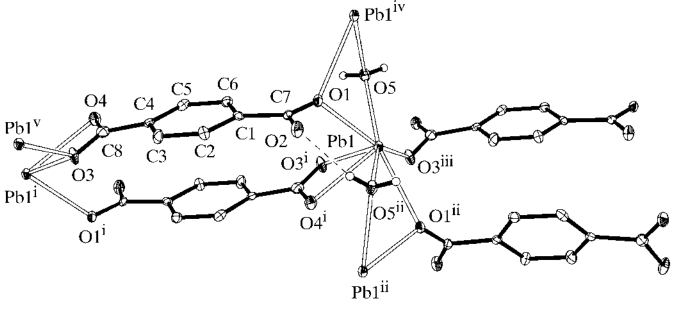


Figure 1
A view of (I), showing the atom-labelling scheme and the $\mathrm{Pb^{II}}$ coordination sphere. Displacement ellipsoids are drawn at the 50% probability level and C atoms are shown as unshaded ellipsoids. H atoms not involved in hydrogen bonding have been omitted for clarity and the O—H···O 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) $x-1, y, z$.]

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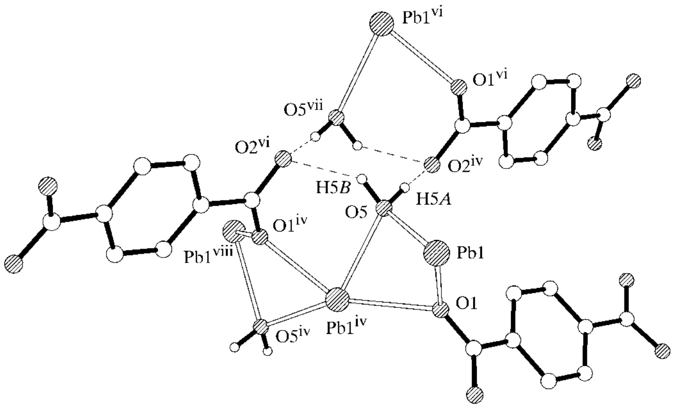

Figure 2
A view of the hydrogen-bonding motifs in (I). Aromatic H atoms have been omitted for clarity. Open circles represent C atoms, shaded circles O atoms and dotted circles Pb atoms. Pb—O coordination bonds are shown as open bonds. [Symmetry codes: (iv) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$;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

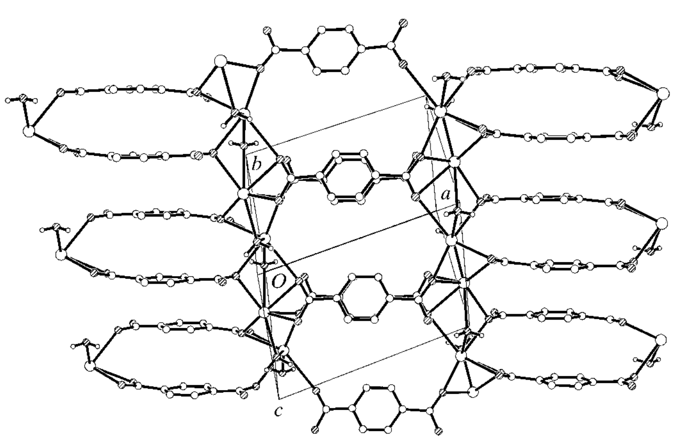

Figure 3
A packing plot of (I), viewed along the *bc* diagonal of the cell. Aromatic H atoms have been omitted for clarity. Open circles represent C atoms, shaded circles O atoms and dotted circles Pb atoms.

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.

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
$\beta = 109.404$ (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
$\theta = 3.3$–28.9°
$\mu = 20.08$ 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 $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 26.0°$
$h = -8 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 10$

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$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$B\cdots$O2$^{\rm iv}$	0.90 (2)	1.97 (2)	2.728 (5)	140 (2)
O5—H5$A\cdots$O2$^{\rm vi}$	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$\cdots$O = 2.0–3.5 Å, H$_{\rm water}\cdots$O$_{\rm carboxy}$ = 1.0–2.5 Å and O—H$\cdots$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$\cdots$O	2.429–2.983	2.680 (4)	2.728 (5)
H$_{\rm water}\cdots$O$_{\rm carboxy}$	1.280–2.458	1.871 (8)	1.97 (2)
O—H$\cdots$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. $U_{\rm iso}$(H) values were set at 1.2$U_{\rm eq}$(C) for aryl H atoms and at 1.5$U_{\rm eq}$(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.

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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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