O36'''—Ca3—O32^{iv}	82.1 (2)	O310—Ca8—O12	70.72 (13)
O31—Ca3—O32^{iv}	78.14 (13)	O312^v—Ca8—O12	64.89 (11)
O36'''—Ca3—O23	79.42 (15)	O22—Ca8—O12	56.42 (11)
O31—Ca3—O23	87.72 (13)		

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

The Kuma diffractometer system (Kuma, 1989) was used for data collection, cell refinement and data reduction. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990) and refined on F^2 with *SHELXL*93 (Sheldrick, 1993). Most of the non-H atoms were located from an *E* map. The remaining non-H atoms were revealed from a subsequent $\Delta\rho$ synthesis. In the final least-squares cycle non-H atoms were refined anisotropically. H atoms were included in geometrically calculated positions with C—H = 0.93 Å and each with an isotropic displacement coefficient 1.5 times that of its parent C atom. The atomic coordinates and the β angle of 90.40 (3)° suggested the possibility of orthorhombic symmetry (*Pbcn*). However, the higher symmetry is ruled out by (*a*) too many systematic absence violations and (*b*) the R_{int} values (0.09 and 0.43 for monoclinic and orthorhombic, respectively). Nonetheless, the structure can be interpreted as a pseudo-orthorhombic *Pbcn* structure, where atoms Ca1 and Ca3, Ca2 and Ca4, Ca5 and Ca6, Ca7 and Ca8 are symmetrically equivalent counterparts. The same is true for the respective furancarboxylate pairs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(o-benzoylbenzoato-O,O')lead(IV) Dichloromethane Solvate

Keith Prout,[a] David Vaughan-Lee,[a] Mark G. Moloney[b] and S. C. Prottey[b]

[a]*Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, England, and* [b]*Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, England*

Abstract

In the title complex, $[Pb(C_{14}H_9O_3)_4].CH_2Cl_2$, the Pb atom is located at a point of symmetry ($\bar{4}$) and is coordinated by eight carboxylate O atoms of four benzoylbenzoate anions at the corners of a somewhat distorted trigonal dodecahedron [Pb—O 2.317 (9) and 2.235 (9) Å]. The dichloromethane solvent molecule is disordered in holes in the crystal structure, on the fourfold inversion axis between the Pb atoms.

Comment

Lead(IV) reagents find considerable application in organic synthesis and have been found to mediate both oxidative processes (Rubottom, 1982) and C—C bond-forming reactions (Pinhey, 1991; Abramovitch, Barton & Finet, 1988; Barton, 1990). We have been interested in extending the synthetic applications of lead(IV) reagents and to this end are investigating the synthesis, characterization and reactivity of a wide range of lead(IV) tetracarboxylates. These compounds can be readily prepared by metathesis of tetrakis(acetato)-lead(IV) and another suitable carboxylic acid (Buston, Coop, Keady, Moloney & Thompson, 1994). Although most lead(IV) tetracarboxylates have been isolated as amorphous powders, tetrakis(o-benzoylbenzoato)-lead(IV), (I), prepared from tetrakis(acetato)lead(IV) and o-benzoylbenzoic acid using the literature procedure (Buston *et al.*, 1994), could be readily crystallized from a dichloromethane/light petroleum mixture, to give yellow crystals from which a limited diffraction pattern could be obtained.

(I)
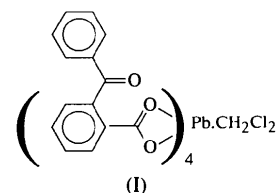
The crystal structure is composed of disordered solvent and tetrakis(o-benzoylbenzoato)lead(IV) complex molecules at fourfold inversion axes, with one crystallographically independent o-benzoylbenzoato ligand. The complexes form stacks parallel to the c axis, with large voids containing solvent between the complexes. The tetrakis(o-benzoylbenzoato)lead(IV) complex is shown in Fig. 1(a), with only one asymmetric unit represented as atomic displacement ellipsoids. The conformation of the ligand is defined by three planes, that of the carboxylate group, which makes an angle of 13.6° with the plane of the benzene ring of the benzoate group, which in turn makes an angle of 72.2° with the plane of the benzoyl group. The relevant torsion angles are O(2)—C(1)—C(2)—C(3) 14 (2), C(2)—C(7)—C(8)—C(9) 74 (3) and C(7)—C(8)—C(9)—C(10) −8 (3)°. The carboxylate group coordinates the Pb atom with two almost equal Pb—O syn contacts [Pb—O 2.317 (9)

and 2.235 (9) Å] to give an asymmetric planar four-membered ring. The planes of the four chelate rings of the complex intersect in the line of the c axis although this is not a requirement of the crystal symmetry. The Pb coordination sphere is shown in projection, firstly, down the a axis in Fig. 1(b), with the carboxylate C atoms included and Pb—O bonds drawn to emphasize the chelate rings, and, secondly, in Fig. 1(c), also down the a axis, with the coordination polyhedron edges drawn and the Pb—O bonds omitted to emphasize the form of the coordination polyhedron. The trigonal dodecahedron has 18 edges and with $\bar{4}$ symmetry only five are independent. Of these, one, within the chelate ring, is short [2.19 (1) Å] and the remaining four are longer [2.87 (1)–3.30 (1) Å].

A search of the Cambridge Structural Database (1994) produced no lead(IV) tetracarboxylates, but the structure of tetrakis(acetato)tin(IV) (Alcock & Tracy, 1979) has been shown to have a very similar coordination polyhedron to that of tetrakis(o-benzoylbenzoato)lead(IV), with four-membered chelate rings having unequal Sn—O bond lengths. The trigonal dodecahedral theme extends to tris(acetato)(2-methylphenyl)lead(IV) and tris-(acetato)(2-chlorophenyl)lead(IV) (Huber, Preut, Scholz & Schurmann, 1992) in which the phenyl group replaces one of the acetate ligands. In contrast, tris(acetato)diphenyllead(IV) (Alcock, 1972) and aquabis(acetato)diphenyllead(IV) benzene solvate (Gaffney, Harrison & King, 1982) are based on a trigonal bipyramidal coordination polyhedron. The former has the two phenyl groups at the apexes and the three acetato ligands around the equator. In the latter, the equatorial groups are two bidentate acetato ligands, one of which forms an extra syn Pb—O bond to a neighbouring lead complex resulting in a dimer which completes the coordination polyhedron, while the coordination polyhedron of the first Pb atom is completed by the water molecule. The mean Pb—O bond length in the dodecahedral complexes [2.286 Å in tetrakis(o-benzoylbenzoato)lead(IV)] is markedly shorter than that found in the trigonal bipyramidal complexes [2.556 Å in tris-(acetato)diphenyllead(IV)].
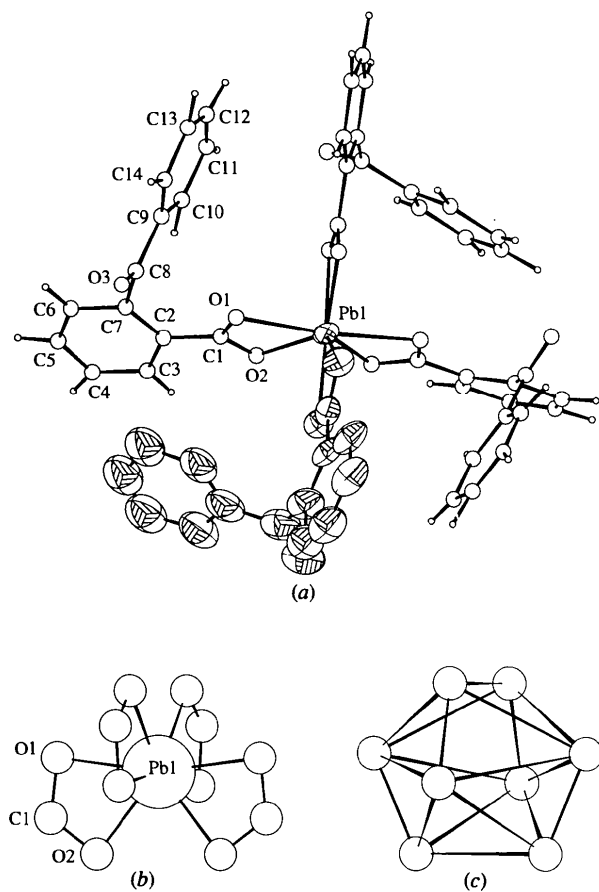

(a)

(b)   (c)

Fig. 1. (a) The four asymmetric units that comprise the complex showing the atom numbering for one asymmetric unit and 50% atomic displacement ellipsoids for a second. In (b), the Pb coordination sphere is redrawn with only the carboxylate groups of the ligand and in (c) the same view is shown to emphasize the shape of the coordination polyhedron.

Experimental

Crystal data

[Pb(C₁₄H₉O₃)₄].CH₂Cl₂	Mo $K\alpha$ radiation
$M_r = 1193.024$	$\lambda = 0.71073$ Å
Tetragonal	Cell parameters from 25
$I4_1/a$	reflections
$a = 13.818$ (1) Å	$\theta = 10$–14°
$c = 27.285$ (3) Å	$\mu = 3.424$ mm⁻¹
$V = 5209.7$ (8) Å³	$T = 295$ K
$Z = 4$	Brick-shaped
$D_x = 1.521$ Mg m⁻³	0.18 × 0.13 × 0.09 mm
	White

Data collection

Enraf–Nonius CAD-4 diffractometer	729 observed reflections $[F > 2.5\sigma(F)]$
$\omega/2\theta$ scans	$R_{int} = 0.0513$
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)	$\theta_{max} = 25°$ $h = -8 \rightarrow 9$ $k = 0 \rightarrow 13$ $l = 0 \rightarrow 30$
3750 measured reflections	3 standard reflections
2294 independent reflections	frequency: 60 min intensity decay: 12%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.13$
$R = 0.0447$	$\Delta\rho_{max} = 0.69$ e Å^{-3}
$wR = 0.0464$	$\Delta\rho_{min} = -0.48$ e Å^{-3}
$S = 1.21$	Extinction correction:
729 reflections	Larson (1970)
238 parameters	Extinction coefficient:
H-atom parameters not refined	40 (24)
Weighting scheme: three-term Chebychev polynomial; coefficients 3.02, −2.03, 2.18 (Carruthers & Watkin 1979)	Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)*

U_{iso} for C(102) and Cl; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{eq}/U_{iso}
Pb(1)	0	1/4	5/8	0.0532
O(1)	−0.1549 (6)	0.3104 (7)	0.6142 (3)	0.0739
O(2)	−0.0947 (8)	0.2930 (7)	0.6877 (4)	0.0821
O(3)	−0.361 (1)	0.392 (1)	0.5712 (6)	0.1440
C(1)	−0.165 (1)	0.316 (1)	0.6603 (6)	0.0703
C(2)	−0.256 (1)	0.3482 (9)	0.6824 (6)	0.0717
C(3)	−0.256 (1)	0.373 (1)	0.7326 (7)	0.0921
C(4)	−0.343 (2)	0.405 (1)	0.7538 (8)	0.1052
C(5)	−0.421 (2)	0.407 (1)	0.725 (1)	0.1167
C(6)	−0.425 (1)	0.385 (1)	0.6749 (9)	0.1164
C(7)	−0.339 (1)	0.354 (1)	0.6534 (9)	0.1012
C(8)	−0.350 (2)	0.330 (1)	0.601 (1)	0.1210
C(9)	−0.352 (1)	0.227 (2)	0.586 (1)	0.1216
C(10)	−0.333 (1)	0.153 (2)	0.618 (1)	0.1227
C(11)	−0.335 (1)	0.053 (2)	0.603 (1)	0.1413
C(12)	−0.360 (1)	0.040 (2)	0.555 (1)	0.1511
C(13)	−0.378 (1)	0.107 (2)	0.523 (1)	0.1499
C(14)	−0.374 (1)	0.203 (2)	0.539 (1)	0.1407
Cl(101)†	0.966 (3)	0.375 (3)	0.124 (3)	0.23 (2)
Cl(102)†	0.965 (9)	0.32 (1)	0.085 (5)	0.17 (4)
Cl(103)†	1.076 (5)	0.267 (5)	0.098 (2)	0.29 (3)

† Partial occupancy (see below).

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Pb(1)—O(1)	2.317 (9)	C(6)—C(7)	1.39 (2)
Pb(1)—O(2)	2.235 (9)	C(7)—C(8)	1.49 (3)
O(1)—C(1)	1.27 (2)	C(8)—C(9)	1.48 (3)
O(2)—C(1)	1.27 (2)	C(9)—C(10)	1.36 (3)
O(3)—C(8)	1.19 (2)	C(9)—C(14)	1.36 (3)
C(1)—C(2)	1.45 (2)	C(10)—C(11)	1.44 (3)
C(2)—C(3)	1.41 (2)	C(11)—C(12)	1.38 (3)
C(2)—C(7)	1.40 (2)	C(12)—C(13)	1.29 (4)
C(3)—C(4)	1.40 (2)	C(13)—C(14)	1.40 (3)
C(4)—C(5)	1.33 (3)	Cl(101)—C(102)	1.3 (1)
C(5)—C(6)	1.41 (3)	C(102)—Cl(103)	1.7 (1)

O(1)—Pb(1)—O(1^i)	90.93 (6)	C(4)—C(5)—C(6)	126 (2)
O(1)—Pb(1)—O(1^{ii})	165.3 (5)	C(5)—C(6)—C(7)	116 (2)
O(1)—Pb(1)—O(2)	57.4 (4)	C(2)—C(7)—C(6)	119 (2)
O(1^i)—Pb(1)—O(2)	82.4 (4)	C(2)—C(7)—C(8)	128.1 (19)
O(1^{ii})—Pb(1)—O(2)	137.3 (4)	C(6)—C(7)—C(8)	113 (2)
O(2)—Pb(1)—O(2^i)	125.9 (3)	O(3)—C(8)—C(7)	120 (2)
O(2)—Pb(1)—O(2^{ii})	80.0 (6)	O(3)—C(8)—C(9)	121 (3)
Pb(1)—O(1)—C(1)	90.0 (10)	C(7)—C(8)—C(9)	119 (2)
Pb(1)—O(2)—C(1)	93.7 (9)	C(8)—C(9)—C(10)	123 (3)
O(1)—C(1)—O(2)	118.8 (15)	C(8)—C(9)—C(14)	120 (3)
O(1)—C(1)—C(2)	121.9 (16)	C(10)—C(9)—C(14)	118 (3)
O(2)—C(1)—C(2)	119.3 (14)	C(9)—C(10)—C(11)	123 (3)
C(1)—C(2)—C(3)	119.1 (17)	C(10)—C(11)—C(12)	113 (3)
C(1)—C(2)—C(7)	119.2 (16)	C(11)—C(12)—C(13)	127 (3)
C(3)—C(2)—C(7)	121.7 (17)	C(12)—C(13)—C(14)	118 (3)
C(2)—C(3)—C(4)	119.1 (19)	C(9)—C(14)—C(13)	122 (3)
C(3)—C(4)—C(5)	118 (2)	Cl(101)—C(102)—Cl(103)	94 (8)

Symmetry codes: (i) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{5}{4} - z$; (ii) $-x, \frac{1}{2} - y, z$.

For space group $I4_1/a$ origin choice 2, *i.e.* with the origin at an inversion centre, the Patterson function confirmed that the Pb atoms were located at points with symmetry $\bar{4}$. The *o*-benzoylbenzoato ligands were then located from successive electron-density maps and refined by the full-matrix least-squares method with isotropic displacement parameters. The tetrakis(*o*-benzoylbenzoato)lead(IV) complex molecules stacked in columns parallel to **c** with large voids at the other $\bar{4}$ centre (Wyckoff *a*). These voids contained electron density that was attributed to dichloromethane solvent. Although the voids are large there is insufficient space for the four solvent molecules required by the crystal symmetry and a partial site occupancy model is proposed. The inclusion of a 25% occupancy dichloromethane molecule and the application of a *DIFABS* absorption correction (Walker & Stuart, 1983) reduced the residual from 23 to 7%. The *DIFABS* correction most probably corrects for overall anisotropic variations in the diffraction pattern over reciprocal space rather than acting as a true absorption correction. The C and O atoms of the *o*-benzoylbenzoato ligand and the Pb atom were refined with anisotropic displacement parameters with the following restraints within the ligand: that the two benzene rings should each be planar with an e.s.d. of 0.02 Å, that the difference in the mean-square displacements along the bond direction of a bonded pair of atoms should not exceed 0.01 Å^2, with an e.s.d. of 0.02 Å^2, and that the difference in the displacement parameters of a bonded pair of atoms should not exceed 0.01 Å^2, with an e.s.d. of 0.02 Å^2. H atoms were added, based on molecular geometry, before the final refinement.

CAD-4 *Software* (Enraf–Nonius, 1989) was used to collect the data. *SHELXS*86 (Sheldrick, 1990) was used to solve the structure. *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) was used for calculations and *CAMERON* (Pearce, Watkin & Prout, 1994) for the diagrams.

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A 1:1 Adduct of Aquachlorotriphenyltin with 3,4,7,8-Tetramethyl-1,10-phenanthroline

Seik Weng Ng

Institute of Advanced Studies, University of Malaya, 59100 Kuala Lumpur, Malaysia

Abstract

The aquaorganotin moiety in the title adduct, [SnCl-$(C_6H_5)_3(H_2O)].C_{16}H_{16}N_2$, is linked by hydrogen bonds through its axially bonded water molecule to the substituted 1,10-phenanthroline moiety. The Sn atom has *trans*-trigonal bipyramidal coordination, with aqua and chloro ligands in the axial positions.

Comment

With 1,10-phenanthroline, triphenyltin chloride forms a dimeric hydrated complex in which the coordinated water molecule [Sn—O = 2.42 Å] is linked by hydrogen bonds (O···N = 2.96 and 3.02 Å) to two

1,10-phenanthroline bases. Each base is further linked, although much more weakly (O···N = 3.31 and 3.42 Å), to the water molecule of another aquachlorotriphenyltin moiety (Gabe, Lee & Smith, 1984).

Addition of four methyl substituents to the 1,10-phenanthroline ligand increases the basicity of its N atoms, enhancing the propensity for hydrogen bonding with the water of the aquachlorotriphenyltin molecule. Thus, as shown by this present study, 3,4,7,8-tetramethyl-1,10-phenanthroline forms much shorter hydrogen bonds [2.661 (3) and 2.767 (3) Å] with aquachlorotriphenyltin than does 1,10-phenanthroline. The complex, (I), exists as a monomeric molecule and the

(I)
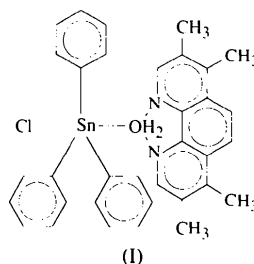
shortest water–water O···O distance exceeds 3.5 Å. Bond dimensions involving the Sn atom are similar to those found in the 1,10-phenanthroline and 2,2′:6′,2″-terpyridyl complexes. However, the hydrogen bonds are shorter and the Sn—O bond longer than those [O···N = 2.766 (2) and 2.807 (2); Sn—O = 2.317 (2) Å] found in the terpyridyl complex, which is monomeric. In the terpyridyl complex, the water molecule binds the 1- and 1″-N atoms of the base (Prasad, Lee, Le Page & Smith, 1982).

The Sn atom has essentially regular trigonal bipyramidal coordination geometry, with the three phenyl groups equatorial and the aqua and chloro ligands in the axial positions.
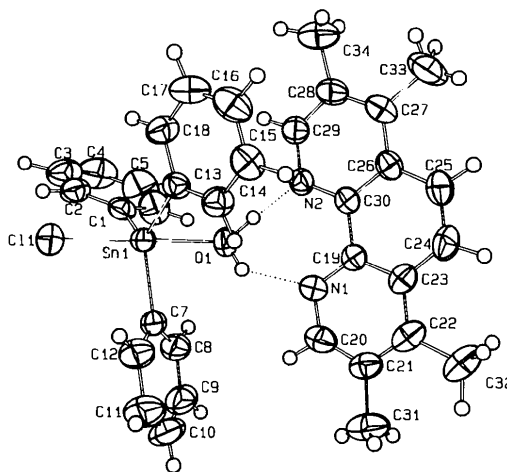

Fig. 1. Atomic labelling scheme for the title compound. Ellipsoids are drawn at the 50% probability level.