The Crystal and Molecular Structure of Bis[diacetatodiphenyl-lead(IV)] Hydrate Benzene Solvate

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Crystals of the title compound are triclinic, space group $P\bar{1}$, with a = 17.3574, b = 11.3271, c = 12.9940 Å, α = 113.8404, β = 114.0116, γ = 103.7998°, and Z = 2, and comprise binuclear units of composition $Pb_2Ph_2(O_2CMe)_4{\cdot}H_2O$ with an additional molecule of benzene occupying a cleft position in the crystal lattice. The geometry at each of the lead atoms is that of a distorted pentagonal bipyramid, with the axial positions being occupied by the phenyl groups. The equatorial sites of one lead atom are occupied by oxygen atoms from two chelating acetate groups and the water molecule. The second lead atom is also chelated by two acetate groups, and the fifth equatorial position in the co-ordination sphere of this lead atom is occupied by a triply bridging oxygen atom of an acetate group chelating the other lead. In addition, the two halves of the binuclear unit are also held together by a hydrogen bond between the water molecule and a carbonyl oxygen of an acetate group chelating the second lead atom. The chelation of all four acetate groups is unsymmetrical, with Pb–O bond distances falling in the range 2.32(2)—2.72(2) Å. The Pb–O(H_2O) distance is 2.58(2) Å.

No structural data are available for diorganolead(IV) bis(carboxylates), although the structure of the $[PbPh_2(O_2CMe)_3]^-$ anion has been determined.[1] The title compound was isolated from the reaction of bis(cyclopentadienyl)diphenyl-lead(IV) with glacial acetic acid in benzene,[2] and an *X*-ray diffraction study was instituted in order to distinguish between the several structural possibilities as well as to investigate the role, if any, of the solvate molecules of this unusual stoicheiometry.

EXPERIMENTAL

Crystal Preparation.—Glacial acetic acid was added to a solution of bis(cyclopentadienyl)diphenyl-lead(IV) in benzene under anaerobic conditions.[2] Large colourless crystals of the product grew from the reaction mixture and were found to have the composition $Pb_2Ph_4(O_2CMe)_4{\cdot}H_2O{\cdot}C_6H_6$. The water of crystallisation appears to arise from the glacial acetic acid, which was not dried (Found: C, 43.25; H, 3.70. Calc. for $C_{38}H_{40}O_9Pb_2$: C, 43.25; H, 3.80%). On standing for several days, the crystals gradually effloresced, losing solvent and becoming powdery. A crystal was selected, cleaved to a suitable size, loaded into a 0.3-mm Lindemann capillary, and used to obtain the Weissenberg photographs and collect the intensity data.

Crystal Data.—$C_{38}H_{40}O_9Pb_2$, M = 1 055.08, Triclinic, space group $P\bar{1}$, with a = 17.3574, b = 11.3271, c = 12.9940 Å, α = 113.8404, β = 114.0116, γ = 103.7998°, U = 2 072,83 Å^3, Z = 2, D_c = 1.018 g cm^{-3}, $F(000)$ = 1 008, $\lambda(\text{Mo-}K_\alpha)$ = 0.7107 Å, $\mu(\text{Mo-}K_\alpha)$ = 15.65 cm^{-1}.

Structure determination and refinement was carried out by the usual Patterson and Fourier techniques using the intensity data of 6 290 independent reflections with $I > 3\sigma(I)$ on a Hilger and Watts four-circle diffractometer employing Mo-K_α radiation. Corrections were applied for Lorentz and polarisation effects, but not for absorption. Data reduction and subsequent calculations were performed using the CRYSTALS programs,[3] and the molecular structures drawn using the PLUTO package.[4] Atomic scattering factors used were those for neutral atoms.[5] The final R value was 0.0935.

Final fractional atomic co-ordinates are listed in Table 1, and intramolecular bond distances and angles in Tables 2 and 3, respectively. The atomic labelling can be seen in Figure 1.

TABLE 1

Final fractional atomic co-ordinates of the non-hydrogen atoms in $Pb_2Ph_4(O_2CMe)_4{\cdot}H_2O{\cdot}C_6H_6$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pb(1)	0.388 38(8)	0.152 1(1)	0.574 2(1)
O(5)	0.253(1)	0.076(2)	0.615(2)
O(4)	0.317(2)	0.289(2)	0.641(2)
C(4)	0.179(2)	0.228(3)	0.650(4)
C(3)	0.254(3)	0.199(4)	0.634(3)
O(3)	0.477(2)	0.364(2)	0.597(2)
O(2)	0.519(1)	0.204(2)	0.532(2)
C(1)	0.525(2)	0.322(4)	0.560(3)
C(2)	0.596(3)	−0.428(4)	0.556(4)
C(15)	0.296(3)	0.062(4)	0.373(4)
C(20)	0.199(2)	−0.095(4)	0.287(3)
C(16)	0.296(2)	0.107(4)	0.298(4)
C(18)	0.152(3)	−0.100(4)	0.080(4)
C(17)	0.234(3)	0.039(5)	0.155(5)
C(19)	0.138(3)	−0.160(4)	0.146(4)
C(9)	0.481(3)	0.207(3)	0.756(4)
C(14)	0.511(2)	0.318(3)	0.889(3)
C(13)	0.587(3)	0.371(4)	1.019(4)
C(12)	0.656(3)	0.321(4)	1.031(4)
C(11)	0.642(3)	0.218(4)	0.912(4)
C(10)	0.565(2)	0.172(4)	0.782(3)
O(1)	0.362(1)	−0.108(2)	0.509(2)
Pb(2)	0.815 66(9)	0.108 5(1)	0.323 2(1)
O(7)	0.919(2)	0.168(2)	0.259(2)
O(6)	0.919(2)	−0.003(3)	0.294(2)
C(5)	0.953(3)	0.083(4)	0.271(4)
C(6)	1.032(3)	0.082(4)	0.250(4)
O(8)	0.796(2)	0.300(2)	0.313(2)
O(9)	0.712(2)	0.225(2)	0.383(3)
C(7)	0.746(3)	0.315(3)	0.365(3)
C(8)	0.733(3)	0.451(4)	0.402(5)
C(27)	0.927(2)	0.245(3)	0.541(3)
C(28)	0.954(3)	0.208(4)	0.621(4)
C(29)	1.029(3)	0.302(4)	0.759(4)
C(30)	1.081(2)	0.456(4)	0.815(3)
C(31)	1.059(2)	0.501(4)	0.731(4)
C(32)	0.988(3)	0.407(4)	0.590(4)
C(21)	0.687(3)	−0.053(4)	0.116(3)
C(25)	0.594(5)	−0.300(4)	−0.094(5)
C(22)	0.630(3)	−0.024(4)	0.045(4)
C(23)	0.552(4)	−0.121(6)	−0.092(6)
C(24)	0.542(4)	−0.264(7)	−0.155(5)
C(26)	0.688(5)	−0.208(4)	0.053(5)
C(37)	0.786(3)	0.439(4)	0.822(5)
C(36)	0.845(3)	0.475(5)	0.778(4)
C(35)	0.884(3)	0.607(5)	0.802(4)
C(33)	0.820(4)	0.687(5)	0.928(5)
C(34)	0.874(4)	0.716(5)	0.878(5)
C(38)	0.774(3)	0.549(4)	0.901(4)

TABLE 2

Final interatomic bond distances (Å) for $Pb_2Ph_4(O_2CMe)_4 \cdot H_2O \cdot C_6H_6$ with estimated standard deviations in parentheses

Pb(1)–O(1)	2.58(2)	C(1)–O(2)	1.20(4)
Pb(1)–O(2)	2.53(2)	C(1)–O(3)	1.23(4)
Pb(1)–O(3)	2.34(2)	C(1)–C(2)	1.52(4)
Pb(1)–O(4)	2.32(2)	C(3)–O(4)	1.24(4)
Pb(1)–O(5)	2.64(2)	C(3)–O(5)	1.31$_5$(4)
Pb(1)–C(9)	1.94$_5$(4)	C(3)–C(4)	1.49$_5$(4)
Pb(1)–C(15)	2.02(4)	C(5)–O(6)	1.23(4)
Pb(2)–O(5)	2.72(2)	C(5)–O(7)	1.27(4)
Pb(2)–O(6)	2.49(2)	C(5)–C(6)	1.50$_5$(5)
Pb(2)–O(7)	2.33(2)	C(7)–O(8)	1.29(4)
Pb(2)–O(8)	2.32$_5$(2)	C(7)–O(9)	1.22(4)
Pb(2)–O(9)	2.65(2)	C(7)–C(8)	1.51$_5$(5)
Pb(2)–C(21)	2.18$_5$(3)	O(1)–O(9)	2.74(3)
Pb(2)–C(27)	2.17$_5$(3)		

TABLE 3

Final interatomic bond angles (°) for $Pb_2Ph_4(O_2CMe)_4 \cdot H_2O \cdot C_6H_6$ with estimated standard deviations in parentheses

O(1)–Pb(1)–O(2)	93.6(6)
O(2)–Pb(1)–O(3)	50.8(7)
O(3)–Pb(1)–O(4)	81.7(7)
O(4)–Pb(1)–O(5)	52.6(7)
O(5)–Pb(1)–O(1)	81.2(6)
C(15)–Pb(1)–C(18)	169.0$_5$(9)
C(15)–Pb(1)–O(1)	87.6(8)
C(15)–Pb(1)–O(2)	85.1(10)
C(15)–Pb(1)–O(3)	89.0(10)
C(15)–Pb(1)–O(4)	94.3(9)
C(15)–Pb(1)–O(5)	95.4(10)
C(9)–Pb(1)–O(1)	82.5(9)
C(9)–Pb(1)–O(2)	90.8(11)
C(9)–Pb(1)–O(3)	96.3(11)
C(9)–Pb(1)–O(4)	95.9(10)
C(9)–Pb(1)–O(5)	87.7(11)
O(2)–C(1)–O(3)	119(2)
O(3)–C(1)–C(2)	118(3)
O(2)–C(1)–C(2)	122(3)
O(5)–Pb(2)–O(6)	89.4(7)
O(6)–Pb(2)–O(7)	53.3$_5$(7)
O(7)–Pb(2)–O(8)	81.1(8)
O(8)–Pb(2)–O(9)	51.8(7)
O(9)–Pb(2)–O(5)	84.4(6)
C(27)–Pb(2)–C(21)	168.0(14)
C(27)–Pb(2)–O(5)	82.6(9)
C(27)–Pb(2)–O(6)	86.8(9)
C(27)–Pb(2)–O(7)	95.2(10)
C(27)–Pb(2)–O(8)	95.3(8)
C(27)–Pb(2)–O(9)	87.3(9)
C(21)–Pb(2)–O(5)	85.9(12)
C(21)–Pb(2)–O(6)	95.4(10)
C(21)–Pb(2)–O(7)	96.0(12)
C(21)–Pb(2)–O(8)	90.7(10)
C(21)–Pb(2)–O(9)	88.1$_5$(10)
O(6)–C(5)–O(7)	120(3)
O(6)–C(5)–C(6)	119(4)
O(7)–C(5)–C(6)	120(4)
O(8)–C(7)–O(9)	121(3)
O(8)–C(7)–O(8)	117(3)
O(9)–C(7)–C(8)	122(3)

Observed and calculated structure factors, anisotropic thermal parameters, and bond distances and angles involving the phenyl rings are available as Supplementary Publication No. SUP **23264** (50 pp.).[*]

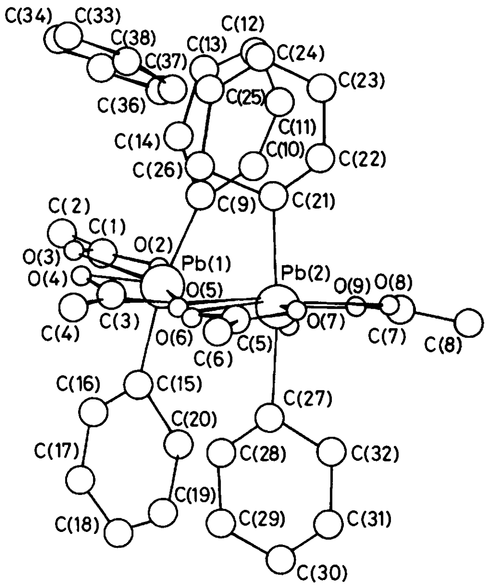

FIGURE 1 The molecular structure of the binuclear $Pb_2Ph_4(O_2CMe)_4 \cdot H_2O$ unit showing the benzene of solvation and the atomic numbering

DISCUSSION

Crystals of the title compound consist of discrete binuclear molecules of composition $Pb_2Ph_4(O_2CMe)_4 \cdot H_2O$ (Figure 1). The benzene molecule of solvation occupies a cleft position in the crystal lattice and has no interaction with either of the lead atoms. The geometry at each lead atom is that of a distorted pentagonal bipyramid, in which the apical sites are occupied by the phenyl groups. The lead–carbon bond distances involving Pb(1) are significantly shorter [1.94(4) and 2.02(4) Å] than those involving Pb(2) [2.17(3) and 2.18(3) Å], which are closer to those found in the $[PbPh_2(O_2CMe)_3]^-$ anion [2.16(3) Å][1] and other phenyl-lead(IV)

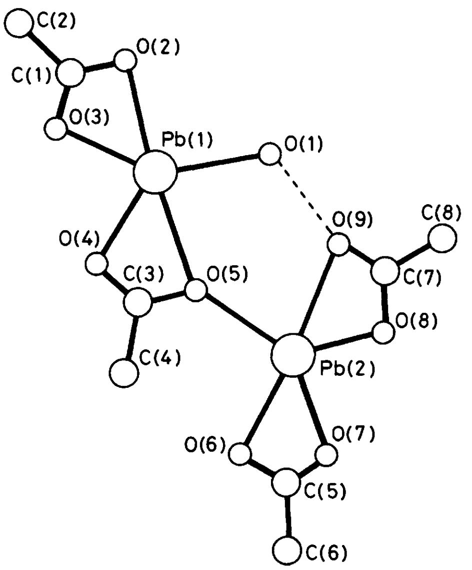

FIGURE 2 View of the equatorial plane of the $Pb_2Ph_4(O_2CMe)_4 \cdot H_2O$ unit

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[*] For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

compounds, which fall in the range 2.12—2.22 Å. The C–Pb–C bond angle deviates from linearity to 169(1) and 168(1)° for Pb(1) and Pb(2), respectively, with the phenyl groups bent towards the less hindered side of each lead atom, *i.e.* towards the long Pb–O bond in each case.

The equatorial sites on both lead atoms are occupied by oxygen atoms from the four acetate groups and the water molecule in a coplanar arrangement [summation of the angles around Pb(1) is 359.9° and around Pb(2) is 360.0°]. As can be seen from a projection of the equatorial plane (Figure 2), each lead atom is chelated unsymmetrically by two acetate groups. The fifth site on Pb(1) is occupied by the water molecule at a moderately long Pb–O distance [2.58(2) Å], whilst the equatorial co-ordination at Pb(2) is completed by a triply bridging oxygen at O(5) of an acetate group chelating Pb(2) at a much longer distance [2.72(2) Å]. The two halves of the molecule are thus held together by the triply bridging oxygen atom supplemented by a hydrogen bond between the water molecule [O(1)] and an oxygen atom [O(9)] of an acetate group chelating Pb(2). The shorter Pb–O bonds between the lead atoms and each of the four acetate groups vary only marginally [2.32(2)—2.34(2) Å]. The corresponding longer Pb–O bonds fall into two types: bonds to O(5) and O(9), which are involved in holding the two halves of the molecule together, to which the distances are 2.64(2) and 2.65(2) Å, respectively, and interactions with O(2) and O(6), which are much shorter [2.53(2) and 2.49(2) Å, respectively]. These distances are significantly longer than that in four-co-ordinate $PbPh_3(OSiPh_3)$ [2.01(3) Å] [6] but are similar to those observed in five-co-ordinate $PbPh_3(OH)$ [2.37(2), 2.44(2) Å],[7] $PbPh_3(O_2CMe)$ [2.36(2), 2.56(2) Å],[8] and the eight-co-ordinate $[PbPh_2(O_2CMe)_3]^-$ anion [2.48(2)—2.63(2) Å].[1]

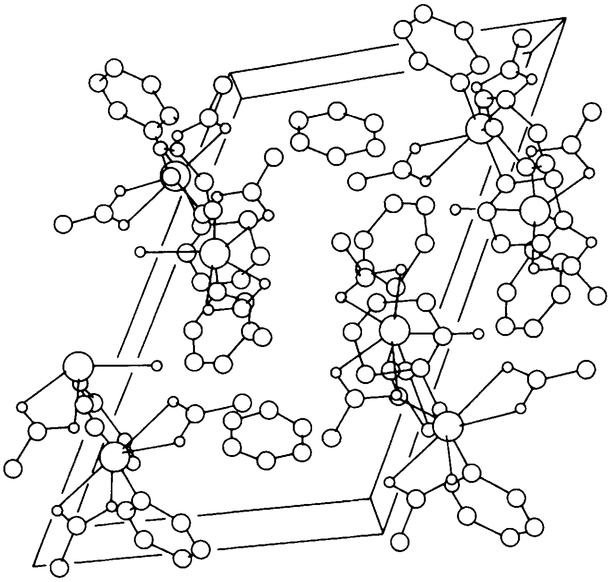

FIGURE 3 View of the unit cell showing the crystal packing

The projection of the unit cell in Figure 3 shows that the $Pb_2Ph_4(O_2CMe)_4{\cdot}H_2O$ units are well separated in the crystal lattice.

We thank the S.R.C. for a Research Studentship (to C. G.) and the Esso Petroleum Company Ltd. for financial support.

[1/1639 *Received, 22nd October*, 1981]

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