Crystal and Molecular Structure of Tetramethylammonium Triacetatodiphenylplumbate(IV): An Eight-co-ordinate Lead Complex

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The crystal structure of the title complex has been determined. The crystals are orthorhombic, space-group *Pcan*, $a = 17{\cdot}772$, $b = 9{\cdot}397$, $c = 14{\cdot}324$ Å, $Z = 4$. 886 Intensities above background were measured by counter methods and refined to a final R of 0·037. The crystal contains discrete cations and anions. The lead atom is eight-co-ordinate with approximately hexagonal bipyramidal geometry. The Pb–C(axial) bonds are of normal length, 2·16(3) Å. The equatorial Pb–O bonds are very long, 2·55 Å (mean). The structure is compared with that of the uranyl triacetate anion. The unit cell of the corresponding caesium salt has been determined as cubic, $a = 13{\cdot}21$ Å.

As a ligand, the acetate ion can bind in three ways: unidentate, bidentate chelating, and bidentate bridging. This makes it very difficult to determine the co-ordination of a metal acetate from the formula. For this reason, and because it potentially shows a high co-ordination number, the structure of the triacetatodiphenylplumbate(IV) ion[1] has been determined by single-crystal *X*-ray methods.

EXPERIMENTAL

Crystal Data.—$C_{22}H_{31}NO_6Pb$, $M = 612{\cdot}2$, Orthorhombic, $a = 17{\cdot}772(6)$, $b = 9{\cdot}397(4)$, $c = 14{\cdot}324(6)$ Å, $U = 2392{\cdot}1$ Å^3, $D_m = 1{\cdot}5$ (by flotation), $Z = 4$, $D_c = 1{\cdot}6$, $F(000) = 1128$. Systematic absences: $hk0$ with $h + k = 2n + 1$, $h0l$ with $h = 2n + 1$, $0kl$ with $l = 2n + 1$ indicate space-group *Pcan* (No. 60, with x and y exchanged, positions $\pm [x, y, z;\ \tfrac{1}{2} + x, \tfrac{1}{2} + y, \tfrac{1}{2} - z;\ \tfrac{1}{2} + x, \tfrac{1}{2} - y, z;\ x, -y, \tfrac{1}{2} - z]$). Mo-$K_\alpha$ *X*-radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 69{\cdot}8$ cm^{-1}. There is a strong pseudo-systematic extinction with $h + k = 2n + 1$ generally weak. The well formed colourless chunky crystals show faces of form $\{110\}$ and $\{001\}$. The unit-cell constants and standard deviations were determined by least-squares fit to the reflecting positions of 12 high-angle reflections using the standard program of a Picker FACS-1. The final data set was collected on this instrument equipped with a graphite monochromator using θ—2θ scan, 4° take-off angle, no attenuators; the crystals were enclosed in a Lindemann glass tube. Data was collected to $2\theta = 50°$.

Data Collection.—The initial data were taken with a Stoe two-circle goniometer, and the structure was solved (see later) but could not be satisfactorily refined. The reason for this was probably crystal decomposition, because when the data were re-collected reflections were monitored more carefully, and very variable rates of decomposition were observed for different crystals at different times. During the final collection three crystals were used and the data were further grouped into 7 sections, in all, with a separate scale-factor for each, depending on the rate of decomposition. It should be noted that the subdivisions correspond approximately to increasing h, and so the anisotropic B_{11} temperature factors may not be as well determined as the others.

The decomposition seemed to show no angle dependence, was approximately linear within each group and was compensated for by multiplying the net intensity of the Nth reflection in the jth group by $(1{\cdot}0 + k_jN)$ where k_j was chosen to fit the rate of decomposition in the group. Lorentz and polarisation corrections were applied, assuming the monochromator to be perfectly mosaic, and the data were corrected for absorption with the program ABSCOR;[2] maximum and minimum transmission factors were 0·5 and 0·3. 886 Reflections with $I/\sigma(I) > 3{\cdot}0$ were taken to be observed.

Prelimimary investigations were also made on very small crystals of caesium triacetatodiphenylplumbate(IV) which were optically isotropic and usually formed as hexagonal prisms (forms $\{110\}$ and $\{111\}$) or dodecahedra ($\{110\}$). The data obtained were: $C_{18}H_{19}CsO_6Pb$, cubic, primitive, $a = 13{\cdot}21$ Å, $U = 2305$ Å^3, $D_m = 1{\cdot}9$ (by flotation), $Z = 4$, $D_c = 1{\cdot}93$.

The Laue group is probably $m3m$, but the weak photographs did not allow systematic absences to be identified. The anion must lie on a special position with the phenyl groups disordered, and the most likely choices of space-group are $P4_132$, $P4_232$, or $P4_332$, with special position symmetry 32.

Structure Solution.—In space-group *Pcan* both cation and anion lie on special positions on either a two-fold axis or an inversion centre; both the pseudo-systematic absence, $h + k \neq 2n$, and the formula of the anion indicate that the lead atom must be on the two-fold axis. With the original data set this atom was readily located by a Patterson synthesis. Although a Fourier synthesis phased on the lead atom shows false mirror symmetry (*i.e.* special position symmetry $2mm$ instead of 2) the other atoms of the anion were located without great difficulty, by assigning Fourier peaks either to phenyl ring atoms or to acetate atoms. The nitrogen of the tetramethylammonium group was also located, again on the two-fold axis, but the carbon atoms seemed to be disordered. Although the atomic positions were reasonable, least-squares refinement did not reduce R below 0·18. Because the data quality was suspect, data were then re-collected (see earlier). Starting from the previous positions, refinement with all atoms isotropic rapidly converged to R 0·066. The tetramethylammonium group was located, not ordered on the two-fold axis, but with one carbon atom on the axis and the other three occupying two alternative sets of positions. With all atoms anisotropic, R was reduced to 0·050. 22 Reflections which showed large discrepancies, perhaps due to extinction or the lack of attenuators were removed and final refinement gave R 0·037. Unit weights were found to be satisfactory (with the reflections including duplicate measurements of standard reflections in different scale groups). Scattering factors were from ref. 3 and anomalous dispersion was corrected for.[3] The only significant features on the final difference

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[1] F. Huber and E. Schönafinger, *Angew. Chem.*, 1968, **80**, 79.

[2] ABSCOR, an analytical absorption program in the '*X*-RAY 63' system.

[3] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

TABLE 1

Atomic co-ordinates and anisotropic * temperature factors ($\times 10^4$) with standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb	1487·1(6)	0	2500	21·2(8)	120·1(1·3)	39·3(4)	0	0	−4·2(3·7)
O(11)	2836(12)	810(22)	3044(15)	43(8)	270(37)	102(15)	12(14)	−5(10)	−64(19)
O(21)	369(10)	853(19)	3375(12)	35(6)	205(28)	68(11)	−17(11)	1(7)	−24(15)
O(22)	1384(10)	1551(21)	3957(16)	26(9)	216(32)	100(15)	1(13)	5(10)	−39(20)
N(1)	8385(12)	0	2500	22(9)	170(47)	68(16)	0	0	35(52)
C(11)	3177(20)	0	2500	21(10)	238(67)	46(17)	0	0	60(82)
C(12)	4009(20)	0	2500	39(13)	117(46)	339(64)	0	0	207(61)
C(21)	706(14)	1483(26)	3983(16)	40(10)	114(35)	55(13)	−8(15)	6(9)	9(18)
C(22)	278(15)	2141(27)	4802(15)	65(12)	153(40)	57(14)	24(17)	30(10)	−8(20)
C(31)	1490(15)	1835(28)	1596(17)	29(7)	166(39)	59(12)	−24(18)	−23(11)	17(19)
C(32)	1980(16)	1837(30)	862(17)	45(11)	185(46)	44(14)	−7(20)	14(11)	4(21)
C(33)	1978(15)	3052(33)	247(17)	45(10)	246(57)	49(13)	−24(20)	−2(9)	8(24)
C(34)	1466(17)	4160(27)	400(16)	42(9)	194(37)	55(12)	6(21)	6(12)	17(19)
C(35)	976(15)	4105(27)	1157(17)	40(10)	155(38)	65(14)	7(17)	4(11)	19(21)
C(36)	975(12)	2926(24)	1747(17)	30(8)	120(35)	70(15)	−4(15)	10(10)	15(18)
C(41)	7516(25)	0	2500	34(14)	535(123)	289(54)	0	0	313(83)
C(42)	8917(98)	745(90)	1753(55)	151(199)	300(136)	64(48)	34(120)	106(80)	−49(68)
C(43)	8555(40)	934(107)	3379(50)	65(27)	685(280)	124(44)	−79(75)	62(32)	−269(96)
C(44)	8744(30)	1331(63)	2226(32)	48(18)	252(88)	63(43)	−12(32)	−7(19)	125(48)

The acetate group on the two-fold axis contains atoms O(11), C(11), and C(12); the acetate group in a general position is O(21), O(22), C(21), C(22); the benzene ring is C(31)—(36); the tetramethylammonium group is N(1) and C(41)—(44) (disordered, 0·5 population parameter).

* In the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Fourier synthesis were a few ripples around the lead atom position; no hydrogen atom peaks could be found, and so these were not included in the calculations. The final atomic co-ordinates and temperature factors are given in Table 1, and the final structure factors are listed in Supplementary Publication No. SUP 20318 (5 pp., 1 microfiche).* In this listing scale-group changes occur after the following reflections: 6, 0, 10; 6, 0, 14; 8, 6, 11; 12, 2, 6; 15, 7, 5; 8, 0, 1. All computing was carried out with the 'X-RAY 63' system of programs [4] on an IBM 7094 or on the S.R.C. Atlas.

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses. A primed atom is related to the corresponding unprimed atom by the two-fold axis

(*a*) Lead environment

Pb–O(11)	2·63(2)	O(11)–Pb–O(11′)	48·9(7)
Pb–O(21)	2·48(2)	O(21)–Pb–O(22)	49·1(6)
Pb–O(22)	2·55(2)	O(11)–Pb–O(22)	70·0(6)
Pb–O(31)	2·16(3)	O(21)–Pb–O(21′)	73·7(6)
O(11) · · · O(22)	2·98(3)	C(31)–Pb–C(31′)	179·7(1·0)
		O(17)–Pb–C(31)	86·8(9)
O(21) · · · O(21′)	2·98(3)	O(21)–Pb–C(31)	92·7(8)
		O(22)–Pb–C(31)	92·0(8)

(*b*) Acetate groups

C(11)–O(11)	1·25(3)	O(11)–C(11)–O(11′)	121·7(3·2)
C(11)–C(12)	1·38(5)	O(11)–C(11)–C(12)	119·1(1·8)
C(21)–O(21)	1·21(3)	O(21)–C(21)–O(22)	119·8(2·4)
C(21)–O(22)	1·21(3)	O(21)–C(21)–C(22)	120·3(2·3)
C(21)–C(22)	1·53(3)	O(22)–C(21)–C(22)	119·9(2·3)

(*c*) Benzene ring

C(31)–C(32)	1·37(4)	C(36)–C(31)–C(32)	123(2)
C(32)–C(33)	1·44(4)	C(31)–C(32)–C(33)	118(3)
C(33)–C(34)	1·40(4)	C(32)–C(33)–C(34)	120(2)
C(34)–C(35)	1·40(4)	C(33)–C(34)–C(35)	120(2)
C(35)–C(36)	1·39(3)	C(34)–C(35)–C(36)	120(2)
C(36)–C(31)	1·39(4)	C(35)–C(36)–C(31)	120(2)

(*d*) Tetramethyl ammonium group

N(1)–C(41)	1·54(5)	Mean of six tetrahedral angles 108·6°, σ 2—5°; none departs significantly from the normal value.
N(1)–C(42)	1·59(12)	
N(1)–C(43)	1·57(8)	
N(1)–C(44)	1·46(6)	

RESULTS AND DISCUSSION

The structure determination shows that the crystal contains discrete tetramethylammonium and triacetatodiphenylplumbate ions. Both ions lie on the two-fold axis x, 0, $\frac{1}{4}$. In the environment of the lead atom, it bisects one acetate group and relates the second acetate group to the third and the two phenyl groups to each other. In the tetramethylammonium group the nitrogen and one carbon atom are on the axis and the other three carbon atoms have a two-fold disorder. Bond lengths and angles are given in Table 2. For all the organic moieties the values are normal.

Co-ordination of the Lead Atom.—The lead atom is eight-co-ordinate, with its ligands forming an approximate hexagonal bipyramid (Figure 1). Two phenyl groups are in the axial positions and three bidentate acetate groups take up the equatorial positions. The details of various mean planes are given in Table 3. The lead atom deviates by 0·04 Å from the plane of the phenyl carbon atoms, a value which is probably not statistically significant. One phenyl ring is rotated by 73° relative to the other, which excludes the possibility of π orbital conjugation through the lead atom. The acetate groups do not lie precisely in a plane. If their mean plane is defined by their central carbon atoms, the largest deviations are by O(11) and O(11′), (plus and minus 0·209 Å), while C(22) deviates by 0·13 Å. These deviations do not seem to be of chemical importance.

The lengths of the bonds from the lead atom do not all correspond to expected values. For Pb–C, the follow-

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[4] 'X-RAY 63' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

ing values (Å) have been reported:[5,6] 2·20 (±0·01) and 2·25 (±0·06) in $PbMe_4$ and Pb_2Me_6, 2·27 (±0·03) in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2PbMe_6$ (ref. 7), and in $[Ph_2PbBr]_4C$ 2·25 (mean) to the central carbon atom and 2·20 to the phenyl ring.[8] The observed distance of 2·16 Å is not significantly different from this last value, and reinforces the previous evidence that C(sp^2)–Pb is shorter than C(sp^3)–Pb. The only Pb^{IV}–O distances which have been determined [9] are in PbO_2 and range from 2·16 to 2·22 Å (octahedral co-ordination). This compares satisfactorily with estimates obtained by (i) subtracting from the Pb–C distances the difference between the covalent radius of carbon and that of oxygen,[10] or (ii) adding the difference between the covalent radii of tin and lead (*ca.* 0·06 Å) [10] to the Sn–O distances of 2·12 and 2·14 Å in two tin acetates.[11] However, in the triacetatodiphenylplumbate ion, the mean Pb–O distance is 0·35 Å longer than this (2·55 Å, with individual values rather scattered but at most 4σ from this value). The implications of this can be seen in relation to the overall geometry.

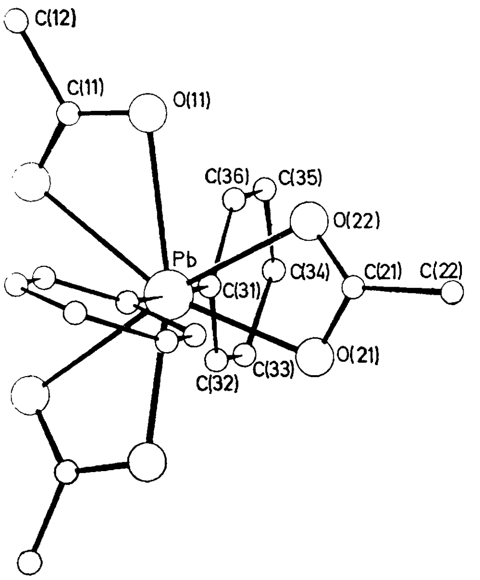

FIGURE 1 The anion viewed almost parallel to the C–Pb–C axis. The two-fold axis passes through C(11) and C(12).

TABLE 3

Equations of mean planes (in orthogonal Å co-ordinates) and deviations (Å) of relevant atoms from the planes

Plane (1): C(31)—(36) $0{\cdot}675X + 0{\cdot}459Y + 0{\cdot}578Z = 3{\cdot}89$
[C(31) −0·011, C(32) 0·008, C(33) −0·005, C(34) 0·006, C(35) −0·009, C(36) 0·012, Pb 0·035]

Plane (2): Pb, C(11), C(21) $-\,0{\cdot}836Y + 0{\cdot}549Z = 1{\cdot}965$
[O(11) 0·209, O(21) −0·017, O(22) 0·073, C(22) −0·127]

Angles (°) between planes:* (1)—(2) 86·2
(1)—(1′) 72·7

* Plane (1′) is related to plane (1) by the two-fold axis.

Acetate groups can be considered as either truly bidentate or as occupying only one co-ordination position. Taking the first view, the only other compounds with hexagonal bipyramidal co-ordination are uranyl (and neptunyl, plutonyl, and americyl) derivatives *e.g.* $UO_2(OAc)_3$ (ref. 12). Very similar bonding schemes are possible for both the lead and uranium compounds, the latter (U^{VI}) using two electrons for each U=O(axial) bond, and the former (Pb^{IV}) using one electron for each Pb–C(axial) bond. In the uranyl compounds, the equatorial are very much longer than the axial bonds,[12] longer than would be expected for the replacement of U=O with U–O. This is precisely the behaviour of the lead compound and clearly the two have a strong resemblance.

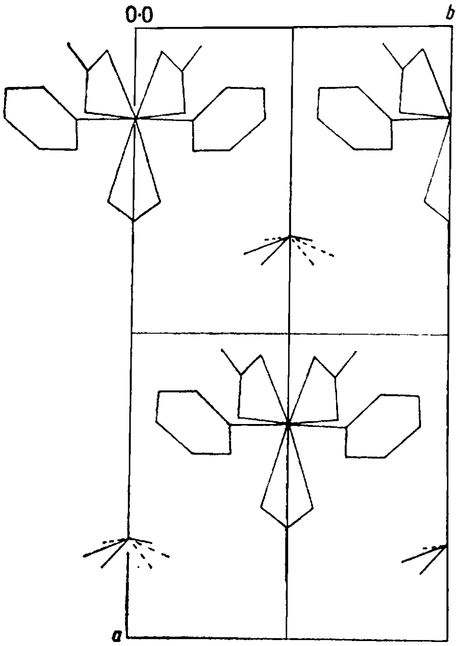

FIGURE 2 Packing of the molecule viewed down *c*, showing the layer with Pb and N atoms at *z* 0·25. One of the two orientations of the NMe_4^+ ion is shown dotted. There is a gap between this layer and that at *z* 0·75, which has Pb atoms close to the *x,y* positions of the N atoms in the *z* 0·25 layer and *vice versa*

If the acetate groups were considered to occupy only one co-ordination position, the compound would be five-co-ordinate with trigonal-bipyramidal geometry. However, in trigonal-bipyramidal species with some alkyl or aryl ligands, it is well established that these groups occupy the equatorial positions. A notable example is

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[5] C.-H. Wong and V. Schomaker, *J. Chem. Phys.*, 1958, **28**, 1007.

[6] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1940, **36**, 1209.

[7] B. P. Biryukov, Yu. T. Struchkov, R. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Zhur. strukt. Khim.*, 1968, **9**, 922.

[8] J. Kroon, J. B. Hulscher, and A. F. Peerdeman, *J. Organometallic Chem.*, 1970, **23**, 477.

[9] A. I. Zaslavskii and S. Tolkachev, *Zhur. fiz. Khim.*, 1952, **26**, 743.

[10] A. F. Wells, 'Structural Inorganic Chemistry,' 3rd edn., Oxford, 1962, p. 696.

[11] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1876.

[12] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 526.

Cl_3SbPh_2 which has two phenyl groups and one chlorine atom around the equator.[13] In triacetatodiphenylplumbate on this model the phenyl groups are in the axial positions. This implies that a five-co-ordinate model does not give a satisfactory representation of the structure.

Molecular Packing.—All significant intermolecular contacts are likely to be between unlocated hydrogen atoms and so cannot usefully be discussed. A general description of the packing can be given in terms of layers perpendicular to c with a centred arrangement in each layer (Figure 2). One layer has Pb and N atoms at height z 0·25 and there is a considerable gap to the next with z 0·75. Each ion has three neighbours of opposite charge in the same layer and two others above and below it.

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[13] T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem.*, 1961, **2**, 445.