Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetramethylammonium dichlorotriphenylplumbate

R. Alan Howie* and James L. Wardell†

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

† Present address: Departamento de Química Inorgânica, Instituto de Química, Universidad Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil.

Correspondence e-mail: r.a.howie@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.011 Å
R factor = 0.031
wR factor = 0.079
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

© 2001 International Union of Crystallography
Printed in Great Britain – all rights reserved

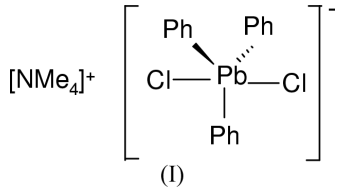
The title compound, an unexpected reaction product formulated $[NMe_4]^+[Cl_2Ph_3Pb]^-$ or $(C_4H_{12}N)[PbCl_2(C_6H_5)_3]$, is isostructural with the corresponding tin compound as reported by Ng [*Acta Cryst*. (1995), C**51**, 1124–1125]. Both cation and anion occupy special positions on the twofold axes.

Received 5 February 2001
Accepted 16 May 2001
Online 22 May 2001

Comment

A search of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) at the Chemical Database Service of the EPSRC at Daresbury (Fletcher *et al.*, 1996) readily revealed the entry with refcode YUHSOJ, corresponding to the compound $[NMe_4]^+[Cl_2Ph_3Sn]^-$, (II), as reported by Ng (1995), with a C-centred monoclinic cell very similar to that determined for the title compound, (I). Analysis of the structure of (I) demonstrated conclusively that the two compounds are isostructural although the extremely obtuse angle of 132.4763 (10)° of the C-centred cell of (I) prompted the adoption of the alternative near-orthogonal I-centred cell and the space group $I2$, as indicated below.

Both cation and anion in (I) and (II) have crystallographic twofold axial symmetry. In particular, the Pb1, C1 and C4 atoms of the anion (Fig. 1) and the N1 atom of the cation of (I) occupy special positions on the twofold axes.



(I)

The structures of (I) and (II) are compared in terms of bond lengths and angles involving the central metal atom (M = Pb or Sn) in Table 1. The bond lengths are entirely consistent with the replacement of Sn in (II) by Pb in (I) and the bond angles wholly compatible with the isostructural nature of the compounds.

The Pb1 atom in (I) has a trigonal-bipyramidal coordination with the propeller-like arrangement of phenyl substituents in the equatorial plane. The dihedral angles formed by the planes of the Ph rings C1/C2/C3/C4/C3^{i}/C2^{i} and C5–C10 with the equatorial plane Pb1/C1/C5/C5^{i} are equal to 59.9 (2)° and 49.3 (2)° respectively [symmetry code: (i) $1-x, y, 1-z$]; the three phenyl-ring planes are pairwise roughly orthogonal with interplanar angles C1/C2/C3/C4/C3^{i}/C2^{i}^C5–C10 and C5–C10^C5^{i}–C10^{i} being equal to 88.2 (2) and 85.3 (2)°, respectively.

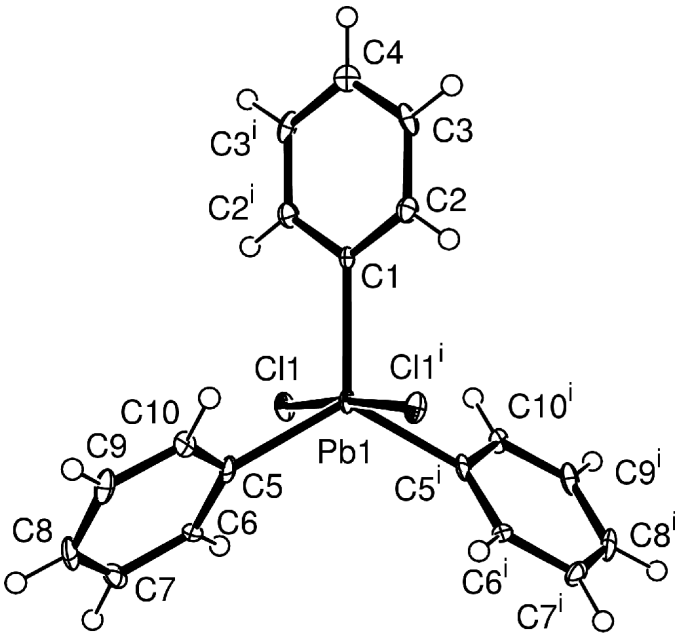


Figure 1
The anion of (I) showing the labelling scheme. Non-H atoms are shown as 50% ellipsoids and H atoms are shown as open circles. [Symmetry code: (i) $1-x, y, 1-z$.]

The isolation of (I) from the reaction mixture described below is in complete contrast to the formation of $[Q][R_2X\mathrm{Sn(dmit)}]$, where Q = monovalent cation, R = alkyl or phenyl, X = halide or pseudohalide and dmit represents the 1,3-dithiole-2-thione-4,5-dithiolate dianion $(C_3S_5)^{2-}$, which can be achieved by reaction of R_2Sn(dmit) with $[Q]X$ (Aupers *et al.*, 1998). Although other Pb containing species in the residue from the reaction have not been identified, it is clear that the formation of I has involved a disproportionation reaction according to the following scheme:

Unlike $[Q][R_2X\mathrm{Sn(dmit)}]$, the Pb analogues have proved to be elusive and are also not available from reactions between R_2MX_2 (M = Pb) and $[Q]_2[\mathrm{Zn(dmit)_2}]$ (Doidge-Harrison *et al.*, 1996). Disproportionation reactions as the scheme are known in organotin chemistry, especially where X_2 is a chelating unit (Blunden *et al.*, 1990). Specific examples are known for solutions or reaction mixtures containing tin and dmit species *e.g.* $[\mathrm{NEt_4}][\mathrm{Ph_3Sn(NCS)_2}]$ isolated from a mixture of $\mathrm{Na_2(dmit)}$, $\mathrm{Ph_2Sn(NCS)_2}$ and $[\mathrm{NEt_4}]\mathrm{Br}$ (Cox & Wardell, 1996). More complex disproportionation is indicated by the formation of $[1,4\text{–}\mathrm{Me_2pyridinium}]_2[\mathrm{Sn(dmit)_3}]$ during the attempted recrystallization of $[1,4\text{–}\mathrm{Me_2pyridinium}][\mathrm{Ph_2(SeCN)Sn(dmit)}]$ from acetone solution (de Assis *et al.*, 1999).

Experimental

Red crystals of the title compound, (I), were obtained from a solution of $\mathrm{Ph_2Pb(dmit)}$ (0.57 g, 1 mmol), where dmit represents the 1,3-dithiole-2-thione-4,5-dithiolate dianion $(C_3S_5)^{2-}$, and $[\mathrm{NMe_4}]\mathrm{Cl}$ (0.33 g, 3 mmol) in acetone (10 ml) which was left at ambient temperature (293 K) for 5 d. The crystals were isolated by filtration and dried but not manipulated further.

Crystal data

$(C_4H_{12}N)[PbCl_2(C_6H_5)_3]$
M_r = 583.54
Monoclinic, $I2$
a = 10.3759 (3) Å
b = 9.7074 (3) Å
c = 10.8400 (3) Å
β = 92.432 (1)°
V = 1090.85 (6) Å^3
Z = 2
D_x = 1.777 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3028 reflections
θ = 2.9–27.5°
μ = 7.98 mm^{-1}
T = 100 (2) K
Block, red
0.20 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.344, T_{max} = 0.625
3885 measured reflections
2200 independent reflections
2198 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 12$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.079
S = 1.08
2200 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 2.6404P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 3.21 e Å^{-3}
$\Delta\rho_{min}$ = −4.68 e Å^{-3}
Absolute structure: (Flack, 1983). 884 Friedel pairs
Flack parameter = −0.022 (12)

Table 1
Bond lengths and angles (Å,°) involving M in (I) and (II).

	(I) (M = Pb)	(II) (M = Sn)
M—Cl1	2.7312 (14)	2.5982 (13)
M—C1	2.215 (10)	2.144 (7)
M—C5	2.201 (7)	2.136 (4)
Cl1—M—C1	92.01 (10)	91.46 (7)
Cl1—M—C5	87.8 (2)	88.39 (14)
Cl1—M—Cl1^{i}	176.0 (2)	177.08 (9)
Cl1—M—C5^{i}	90.3 (2)	90.19 (14)
C1—M—C5	118.27 (14)	119.02 (13)
C1—M—Cl1^{i}	92.01 (10)	91.46 (7)
C1—M—C5^{i}	118.27 (19)	119.02 (13)
C5—M—Cl1^{i}	90.3 (2)	90.19 (14)
C5—M—C5^{i}	123.5 (4)	121.96 (18)
Cl1^{i}—M—C5^{i}	87.8 (2)	88.39 (14)

† Atom designations and symmetry code [(i) $1-x, y, 1-z$] are those of the structure of (I). Bond distances and angles for (II) generated by *PLATON* (Spek, 1990) from the CIF associated with CSD entry YUHSOJ (Ng, 1995).

The structure of (I) was refined initially on the basis of the cell with a = 14.6840 (3), b = 9.7074 (3), c = 10.3759 (3) Å, β = 132.4763 (10)° and space group $C2$, *i.e.* the cell originally used to index the intensity data. Refinement based on the atomic coordinates for (II), CSD refcode YUHSOJ (Ng, 1995), but with the absolute structure inverted, finally yielded R = 0.033, positive proof of the isostructural relationship of (I) and (II). The structure of (I) was then re-examined on the basis of the near-orthogonal alternative cell with space group $I2$ as indicated in the tabular data above. The solution of the structure, in this case, was simply to place Pb at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, the obvious conclusion for the space group $I2$ with Z = 2, and to extract positions for the remaining non-H atoms from a succession of difference-map

calculations. In the final stages, H atoms were placed in calculated positions and refined with a riding model. At the same time, isotropic refinement was adopted for C4 to deal with persistent and severe non-positive definite anisotropic refinement of this atom. All other non-H atoms were refined anisotropically as C4 had been prior to the inclusion of H atoms. The anisotropy of C10 is also rather extreme in this model which gave a final R of 0.0315 as noted in the table above. Features in the final difference map of 3.21 and -4.68 e Å^{-3} are respectively 0.82 and 0.89 Å distant from Pb and are attributed to ripple.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury. The use of the EPSRC X-ray crystallographic service at Southampton and the valuable assistance of the staff there is gratefully acknowledged. One of us, JLW, acknowledges the financial support of CNPq Brazil.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Assis, F. de, Chohan, Z. H., Howie, R. A., Khan, A., Low, J. N., Spencer, G. M., Wardell, J. L. & Wardell, S. M. S. V. (1999). *Polyhedron*, **19**, 3533–3544.
Aupers, J. H., Chohan, Z. H., Cox, P. J., Doidge-Harrison, S. M. S. V., Howie, R. A., Khan, A., Spencer, G. M. & Wardell, J. L. (1998). *Polyhedron*, **17**, 4475–4486.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Blunden, S. J., Harston, P., Hill, R. & Wardell, J. L. (1990). *Appl. Organomet. Chem.* **4**, 383–385.
Cox, P. J. & Wardell, J. L. (1996). *Acta Cryst.* C**52**, 317–319.
Doidge-Harrison, S. M. S. V, Irvine, J. T. S., Spencer, G. M., Wardell, J. L., Ganis, P., Valle, G. & Tagliavini, G. (1996). *Polyhedron*, **15**, 1807–1815.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Ng, S. W. (1995). *Acta* Cryts. C**51**, 1124–1125.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.