The Crystal and Molecular Structure of *adamanta*-(μ_4-oxo-hexakis(μ-triphenylsiloxy)-tetralead(II)

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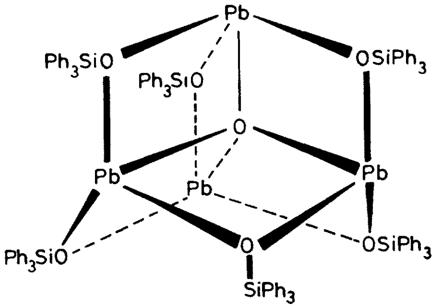
Summary The crystal and molecular structure of the title compound, $[Pb_4(OSiPh_3)_6O]$, obtained from the reaction of triphenylsilanol and bis(cyclopentadienyl)lead(II), is described.

There are isolated reports of siloxy-lead(II) compounds in the literature. An early patent[1] describes the preparation of bis(trimethylsiloxy)lead(II), a white crystalline solid decomposing at 180 °C, by the reaction of trimethylsilanol and dry lead(II) oxide in anhydrous ether at room temperature. Later, Andrianov *et al.*[2] employed a lead(II) silanolate of composition $[2Pb(OSiEt_3)_2 \cdot Pb(OH)_2]$ in the preparation of $[(Et_3SiO)_3VO]$.



(1)

The reaction of triphenylsilanol with bis(cyclopentadienyl)lead(II) in ether at room temperature resulted in the immediate precipitation of a white solid which analysed correctly for bis(triphenylsiloxy)lead(II). However, when the reaction mixture was refluxed for 0·5 h, and the product recrystallised from benzene–ether (1 : 1) at room temperature, colourless crystals of a condensation product, *adamanta*-$[Pb_4(OSiPh_3)_6O]$ (**1**), as a (1 : 1) benzene solvate [m.p. 212—215 °C (decomp.); ν(SiOPb) 885 cm^{-1}], formed by the elimination of hexaphenyldisiloxane, were obtained; its structure is reported herein.

Crystal Data: $C_{114}H_{96}O_7Pb_4Si$, $M = 2575{\cdot}29$; monoclinic, space group $P2_1/n$, $a = 14{\cdot}7931$, $b = 29{\cdot}5659$, $c = 23{\cdot}4745$ Å, $\beta = 92{\cdot}1830°$, $Z = 4$, $U = 10{,}259{\cdot}6$ Å^3, $D_c = 1{\cdot}667$ g cm^{-3}, $F(000) = 1248$.†

The structure was solved by three-dimensional Fourier and Patterson syntheses using 7357 independent, non-zero

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

reflections obtained on a Hilger and Watts Y290 four-circle diffractometer. Block-diagonal, least-squares refinement, with the lead and silicon atoms varying anisotropically and the remaining atoms isotropically, was carried out to a final *R*-value of 0·0494.

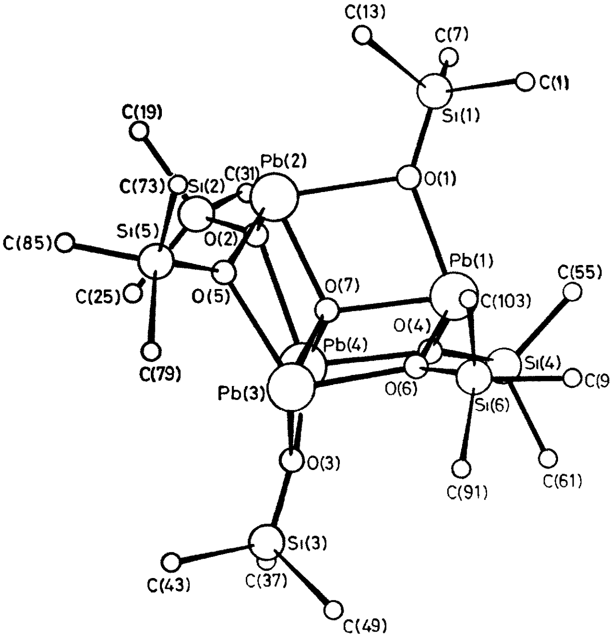

FIGURE Crystal structure of $[Pb_4(OSiPh_3)_6O]$ (**1**), omitting all carbon atoms except those bonded directly to silicon. C(67) is hidden below Si(6).

The skeleton of the molecule, omitting all the carbon atoms save for those bonded directly to silicon, is shown in the Figure. The central feature of the structure comprises a (Pb_4O_6) unit with the adamantane framework. At the centre of this unit is an oxygen atom, which is essentially equidistant from all four lead atoms [Pb–O(7) 2·25(1)—2·31(1) Å]. The other six oxygen atoms are part of the triphenylsiloxy-groups which bridge adjacent lead atoms in an unsymmetrical fashion, each lead forming one short bond [2·28(1)—2·32(1) Å] and two longer bonds [2·36(1)—2·49(1) Å] to three oxygens. The lead atoms, therefore, have a distorted trigonal bipyramidal electronic environment in which the lone pair of electrons and the central oxygen atom occupy axial sites. Bond distances from silicon to carbon [1·85(2)—1·90(2) Å] and to oxygen [1·58(1)—1·62(1) Å] are normal, although the latter are shorter than in (triphenylsiloxy)triphenyl-lead(IV) [1·87(3) Å].[3]

The structure of the present compound thus bears some resemblance to those of the two very similar oxolead(II) cations α- and β-$[Pb_6O(OH)_6]^{4+}$,[4,5] obtained by the hydrolysis of lead(II) perchlorate. Both clusters comprise three distorted Pb_4-tetrahedra connected by common faces. The central tetrahedron of each cluster, like the structure reported here, contains an oxygen atom at its centre (Pb–O 2·22—2·33 Å), whilst the lead atoms of the two outer tetrahedra are triply bridged by the six hydroxy-groups, usually also with two short and one long Pb–O bonds.

Subsequent recrystallisation of the title compound results in further condensation *via* hexaphenyldisiloxane elimination yielding crystalline $[Pb_8(OSiPh_3)O_5]$.

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[1] U.S.P. 2,455,880, *C.A.*, 1949, **43**, 2032d.
[2] K. A. Andrianov, A. A. Zhdanov, and E. A. Kashutina, *Dokl. Akad. Nauk SSSR*, 1959, **126**, 1261.
[3] P. G. Harrison, T. J. King, J. A. Richards, and R. C. Phillips, *J. Organomet. Chem.*, 1976, **116**, 307.
[4] T. G. Spiro, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1969, **8**, 856.
[5] A. Olin and R. Soderquist, *Acta Chem. Scand.*, 1972, **26**, 3505.