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# SOME STRUCTURAL CHEMISTRY OF ORGANOLEAD(IV) COMPOUNDS CONTAINING LEAD–SULPHUR BONDS. THE CRYSTAL AND MOLECULAR STRUCTURES OF TRIPHENYLLEAD BENZENETHIOLATE, $Ph_3PbSPh$, TRIPHENYLLEAD *O,O'*-DIETHYLDITHIOPHOSPHATE, $Ph_3PbS_2P(OEt)_2$, AND DIPHENYLLEAD BIS(*O,O'*-DIBENZYLDITHIOPHOSPHATE), $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$

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## Summary

The crystal and molecular structures of three organolead compounds containing lead–sulphur bonds are described. Crystals of triphenyllead benzenethiolate (I, $C_{24}H_{20}PbS$) are in the monoclinic space group $P2_1/c$, with $a$ 7.657, $b$ 16.427, $c$ 16.239 Å, $\beta$ 93.781°, $Z=$ 4; crystals of triphenyllead *O,O'*-diethyldithiophosphate (II, $C_{22}H_{25}O_2PPbS_2$), and diphenyllead bis(*O,O'*-dibenzyldithiophosphate) (III, $C_{40}H_{38}O_4PbS_4$) are both in triclinic space group $P\bar{1}$, with $a$ 9.579, $b$ 10.602, $c$ 12.710 Å, $\alpha$ 101.623, $\beta$ 99.554, $\gamma$ 100.719°, $Z=$ 2, and $a$ 11.760, $b$ 12. 532, $c$ 16.263 Å, $\alpha$ 80.14, $\beta$ 111.46, $\gamma$ 112.41°, $Z=$ 2, respectively. Structures were determined by the heavy atom method using 2820, 2752, and 3084 independent, non-zero reflections with $I > 3\sigma(I)$ for compounds I, II and III, respectively, collected using an automated four-circle diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). The refinements converged at conventional $R$-values of 3.44%, 7.40% and 7.68% for I, II, and III, respectively. Both $Ph_3PbSPh$ and $Ph_3PbS_2(OEt)_2$ form lattices comprising non-interacting molecules with geometries at lead only slightly distorted from tetrahedral. The distortion in the dithiophosphate is somewhat greater than in the benzenethiolate, and is accompanied by a marginally longer lead–sulphur distance (2.554(6) Å vs. 2.515(2) Å). The lead in $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ are coordinated in a distorted octahedral fashion by two mutually *trans* phenyl groups (angle CPbC 165.0(9)°) and two anisobidentate dithiophosphate ligands, each forming one short bond (2.723(6), 2.679(6) Å) and one long bond (2.940(7) , 2.957(6) Å) to lead. In the crystal lattice, adjacent pairs of molecules are linked by long (3.69(2) Å) lead–sulphur contacts to give an overall equatorial $[PbS_5]$ arrangement.

## Introduction

Little appears to be known concerning the structural chemistry of organolead(IV) compounds containing lead–sulphur bonds. Structural data has been reported for

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the two triphenyllead arenethiolate derivatives, triphenyllead 2,6-dimethylbenzenethiolate and triphenyllead 2-bromobenzenethiolate [1]. In the former, the lead atom enjoys slightly distorted tetrahedral geometry, whilst in the latter a weak intermolecular lead-bromine interaction of 3.77 Å causes severe distortion of the stereochemistry towards trigonal bipyramidal. The facility with which this distortion occurs even with weakly nucleophilic bromine reflects the ease with which lead achieves coordination numbers greater than four. Five coordination might also be expected in triorganolead(IV) thiolates as a result of [Pb–S–Pb] thiolate bridges, and its absence in the former example could possibly be just due to the steric requirements of the rather esoteric 2,6-dimethylphenyl residue. In order to clarify some of the coordination chemistry of lead in its derivatives with sulphur ligands, in particular to examine the ease, or otherwise, of the formation of coordination numbers greater than four, we have determined the crystal and molecular structures of three compounds triphenyllead benzenethiolate, in which the thiolate ligand is less sterically demanding, triphenyllead *O,O′*-diethyldithiophosphate, in which five coordination at lead could be achieved either by intramolecular *S,S*-chelation or by intermolecular *S,S*-bridging, and diphenyllead bis-(*O,O′*-dibenzyldithiophosphate), where unidentate and *S,S*-chelation or -bridging bidentate behaviour of the sulphur ligands are all possible. Results of these studies are reported in this paper.

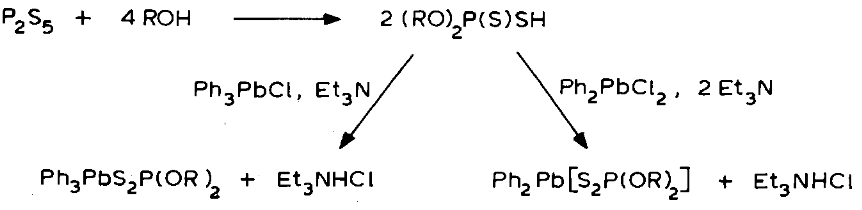
## Experimental

Triphenyllead benzenethiolate was prepared by the reaction of triphenylcyclopentadienyllead and thiophenol as reported previously [2]. The two dithiophosphate derivatives were synthesised according to Scheme 1.

The intermediate *O,O′*-dialkylphosphorodithioic acids, $(RO)_2P(S)SH$, were prepared in situ from phosphorous pentasulphide (1.1 g, 0.005 mol) with excess of the appropriate alcohol (0.02 mol) under an atmosphere of dry nitrogen, and used immediately without isolation.

### *Triphenyllead O,O′-diethyldithiophosphate,* $Ph_3PbS_2P(OEt)_2$

To a solution of *O,O′*-diethylphosphorodithioic acid obtained as above was added triphenyllead chloride (4.8 g, 0.01 mol) and excess triethylamine (3 ml). The mixture was refluxed for 15 min, and then extracted with a 1/1 toluene/water mixture (40 ml). The toluene layer was separated and dried over calcium sulphate. White crystals of the product were obtained on concentration, which could be recrystallised from dichloromethane or hexane (1.75 g, 28%). M.p. 102–104°C; dec. 195°C. Found: C, 42.3; H, 4.19. $C_{22}H_{25}O_2PPbS_2$ calcd.: C, 42.4; H, 4.01%. The



SCHEME 1

TABLE 1
CRYSTAL DATA

| | $Ph_3PbSPh$ | $Ph_3PbS_2P(OEt)_2$ | $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ |
|---|---|---|---|
| Formula | $C_{24}H_{20}SPb$ | $C_{22}H_{25}O_2PPbS_2$ | $C_{40}H_{38}O_4P_2PbS_4$ |
| Form. Wt. | 547.19 | 623.74 | 980.13 |
| Crystal System | Monoclinic | Triclinic | Triclinic |
| Space Group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 7.657(3) | 9.579(4) | 11.760(5) |
| $b$, Å | 16.427(6) | 10.602(4) | 12.532(5) |
| $c$, Å | 16.239(6) | 12.710(5) | 16.263(1) |
| $\alpha$, deg | | 101.623(4) | 80.14(3) |
| $\beta$, deg | 93.781(4) | 99.554(4) | 111.46(4) |
| $\gamma$, deg | | 100.719(4) | 112.41(4) |
| $V$, Å$^3$ | 2038.1 | 1142 | 1772 |
| $Z$ | 4 | 2 | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.784 | 1.81 | 1.834 |
| $\mu$(Mo-$K_\alpha$), cm$^{-1}$ | | 75.3 | 50.5 |
| No. of reflections [a] | 2820 | 2752 | 3084 |
| Final $R$-value | 3.44 | 7.40 | 7.68 |
| Weighted $R$ | 5.21 | 9.29 | 9.20 |
| $F(000)$ | 1048 | 604 | 1036 |
| Crystal size, mm$^3$ | 0.3×0.3×0.2 | 0.25×0.3×0.4 | 0.2×0.3×0.55 |
| $\lambda$(Mo-$K_\alpha$), Å | 0.71069 | 0.71069 | 0.71069 |

[a] $I > 3\sigma(I)$.

same compound may also be obtained by refluxing an equimolecular mixture of triphenyllead hydroxide and *O,O'*-diethylphosphorodithoic acid in ethanol for 3 h.

*Diphenyllead bis(O,O'-dibenzyldithiophosphate),* $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$

To a solution of *O,O'*-dibenzylphosphorodithioic acid obtained as above was added diphenyllead dichloride (4.2 g, 0.01 mol) and triethylamine (3 ml). The mixture was then extracted with a 1/1 toluene/water mixture (40 ml) followed by toluene (10 ml), the toluene layer separated, dried using calcium sulphate, and the volatile material removed using a rotary evaporator. The oily liquid which remained crystallised overnight, and was washed with hexane to afford an off-white product (4.2 g, 43%). M.p. 105–107°C dec. 175°C. Found: C, 49.6; H, 4.08. $C_{40}H_{38}O_4P_2PbS_4$ calcd.: C, 49.0; H, 3.88%.

*Structure determinations*

Pertinent crystal data for all three compounds is collected in Table 1. The structure determination and refinement was similar for all three crystals. The position of the lead atom was located from an initial Patterson synthesis, and those of the non-hydrogen light atoms from a series of difference Fourier syntheses. Both structures were refined by series of full-matrix, least-squares refinement, in which the thermal parameters were allowed to vary isotropically initially, and anisotropically in the later stages. In the structure determination of triphenyllead benzenethiolate a further difference Fourier synthesis at this stage allowed the location of the hydrogen atoms, which were included at fixed positions in the final stages of the refinement. The value of the isotropic thermal parameter, $U_{iso}$, was fixed at 0.050.

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES FOR $Ph_3PbSPh$ [a]

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Pb | 0.11419(4) | 0.18244(2) | 0.03936(1) |
| C(1) | 0.1723(9) | 0.1239(4) | 0.1606(4) |
| C(2) | 0.110(1) | 0.0.472(4) | 0.1791(4) |
| C(3) | 0.150(1) | 0.0158(5) | 0.2577(5) |
| C(4) | 0.246(1) | 0.0609(6) | 0.3154(4) |
| C(5) | 0.306(1) | 0.1362(6) | 0.2968(5) |
| C(6) | 0.270(1) | 0.1674(4) | 0.2195(4) |
| C(7) | 0.211(1) | 0.3090(4) | 0.0501(4) |
| C(8) | 0.386(1) | 0.3243(5) | 0.0465(5) |
| C(9) | 0.449(1) | 0.4036(6) | 0.0599(6) |
| C(10) | 0.339(1) | 0.4646(5) | 0.0748(5) |
| C(11) | 0.163(1) | 0.4505(5) | 0.0783(5) |
| C(12) | 0.097(1) | 0.3736(4) | 0.0660(4) |
| C(13) | 0.2107(9) | 0.1144(4) | −0.0643(4) |
| C(14) | 0.197(1) | 0.1449(4) | −0.1437(4) |
| C(15) | 0.263(1) | 0.1012(5) | −0.2082(4) |
| C(16) | 0.344(1) | 0.0275(5) | −0.1933(5) |
| C(17) | 0.358(1) | −0.0044(5) | −0.1144(5) |
| C(18) | 0.291(1) | 0.0384(5) | −0.0496(4) |
| S | 0.7879(3) | 0.1973(1) | 0.0151(1) |
| C(19) | 0.7715(9) | 0.2266(4) | −0.0910(4) |
| C(20) | 0.825(1) | 0.3011(4) | −0.1162(5) |
| C(21) | 0.814(1) | 0.3215(6) | −0.1982(6) |
| C(22) | 0.741(1) | 0.269(7) | −0.2545(5) |
| C(23) | 0.682(1) | 0.1934(6) | −0.2303(6) |
| C(24) | 0.694(1) | 0.1714(5) | −0.1482(6) |
| H(2) | 0.040 | 0.014 | 0.136 |
| H(3) | 0.109 | −0.041 | 0.271 |
| H(4) | 0.268 | 0.037 | 0.373 |
| H(5) | 0.378 | 0.168 | 0.341 |
| H(6) | 0.323 | 0.222 | 0.205 |
| H(8) | 0.471 | 0.277 | 0.034 |
| H(9) | 0.582 | 0.414 | 0.060 |
| H(10) | 0.386 | 0.523 | 0.083 |
| H(11) | 0.084 | 0.498 | 0.090 |
| H(12) | −0.035 | 0.361 | 0.071 |
| H(14) | 0.142 | 0.199 | −0.156 |
| H(15) | 0.251 | 0.123 | −0.266 |
| H(16) | 0.393 | −0.003 | −0.240 |
| H(17) | 0.414 | −0.060 | −0.104 |
| H(18) | 0.298 | 0.014 | 0.008 |
| H(20) | 0.877 | 0.341 | −0.074 |
| H(21) | 0.855 | 0.379 | −0.217 |
| H(22) | 0.728 | 0.285 | −0.316 |
| H(23) | 0.632 | 0.155 | −0.274 |
| H(24) | 0.658 | 0.116 | −0.132 |

[a] Estimated standard deviations in parentheses.

Corrections were made for the anomalous dispersion of the lead, suphur and phosphorous atoms, and Lorentz, polarisation and adsorption effects. The scattering factors used were those for neutral atoms [3]. All calculations were performed using the CRYSTALS suite of programs [4].

Final fractional atomic coordinates for $Ph_3PbSPh$ are listed in Table 2, and intramolecular bond distances and angles in Table 3. Atomic numbering is shown in Fig. 1. Similar data for $Ph_3PbS_2P(O\ Et)_2$ are given in Tables 4 and 5 and Fig. 2, and for $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ in Tables 6 and 7 and Fig. 3. Tables of thermal parameters and structure factors are available from the authors.

(*Continued on p. 288*)

TABLE 3

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (deg) FOR $Ph_3PbSPh$[a]

| | | | |
|---|---|---|---|
| Pb-C(1) | 2.210(6) | C(17)-C(18) | 1.39(1) |
| Pb-C(13) | 2.189(6) | C(18)-C(13) | 1.40(1) |
| Pb-C(7) | 2.210(7) | C(19)-C(20) | 1.36(1) |
| Pb-S | 2.515(2) | C(20)-C(21) | 1.36(1) |
| S-C(19) | 1.785(7) | C(2 )-C(22) | 1.34(1) |
| C(1)-C(2) | 1.38(1) | C(22)-C(23) | 1.39(1) |
| C(2)-C(3) | 1.39(1) | C(23)-C(24) | 1.37(1) |
| C(3)-C(4) | 1.36(1) | C(24)-C(19) | 1.40(1) |
| C(4)-C(5) | 1.36(1) | | |
| C(5)-C(6) | 1.36(1) | | |
| C(6)-C(1) | 1.37(1) | | |
| C(7)-C(8) | 1.37(1) | C(2)-H(2) | 1.013(7) |
| C(8)-C(9) | 1.39(1) | C(3)-H(3) | 1.020(8) |
| C(9)-C(10) | 1.34(1) | C(4)-H(4) | 1.021(7) |
| C(10)-C(11) | 1.37(1) | C(5)-H(5) | 1.020(8) |
| C(11)-C(12) | 1.37(1) | C(6)-H(6) | 1.024(7) |
| C(12)-C(7) | 1.40(1) | C(8)-H(8) | 1.034(8) |
| C(13)-C(14) | 1.38(1) | C(9)-H(9) | 1.036(9) |
| C(14)-C(15) | 1.39(1) | C(10)-H(10) | 1.033(8) |
| C(15)-C(16) | 1.37(1) | C(11)-H(11) | 1.015(8) |
| C(16)-C(17) | 1.38(1) | C(12)-H(12) | 1.039(8) |
| C(14)-H(14) | 1.004(7) | C(20)-H(20) | 1.018(8) |
| C(15)-H(15) | 1.006(7) | C(21)-H(21) | 1.039(9) |
| C(16)-H(16) | 1.007(7) | C(22)-H(22) | 1.023(8) |
| C(17)-H(17) | 1.013(8) | C(23)-H(23) | 1.008(9) |
| C(18)-H(18) | 1.010(7) | C(24)-H(24) | 0.990(8) |
| C(7)-Pb-C(13) | 114.4(3) | C(18)-C(13)-C(14) | 119.0(6) |
| C(1)-Pb-C(7) | 107.0(3) | C(13)-C(14)-C(15) | 120.5(7) |
| C(1)-Pb-C(13) | 113.9(3) | C(14)-C(15)-C(16) | 120.2(7) |
| C(1)-Pb-S | 108.8(2) | C(15)-C(16)-C(17) | 120.3(7) |
| C(7)-Pb-S | 104.2(2) | C(16)-C(17)-C(18) | 120.0(7) |
| C(13)-Pb-S | 108.2(2) | C(17)-C(18)-C(13) | 120.0(7) |
| C(19)-S-Pb | 100.6(3) | C(24)-C(19)-C(20) | 120.3(7) |
| C(6)-C(1)-C(2) | 119.9(6) | C(19)-C(20)-C(21) | 120.8(8) |
| C(1)-C(2)-C(3) | 118.5(7) | C(20)-C(21)-C(22) | 120.0(8) |
| C(2)-C(3)-C(4) | 120.2(7) | C(21)-C(22)-C(23) | 120.3(8) |
| C(3)-C(4)-C(5) | 120.9(7) | C(22)-C(23)-C(24) | 120.4(8) |
| C(4)-C(5)-C(6) | 119.8(7) | C(23)-C(24)-C(19) | 118.0(8) |
| C(5)-C(6)-C(1) | 120.7(7) | | |
| C(12)-C(7)-C(8) | 119.3(7) | | |
| C(7)-C(8)-C(9) | 119.3(8) | | |
| C(8)-C(9)-C(10) | 120.8(8) | | |
| C(9)-C(10)-C(11) | 120.7(8) | | |
| C(10)-C(11)-C(12) | 120.2(8) | | |
| C(11)-C(12)-C(7) | 119.7(7) | | |

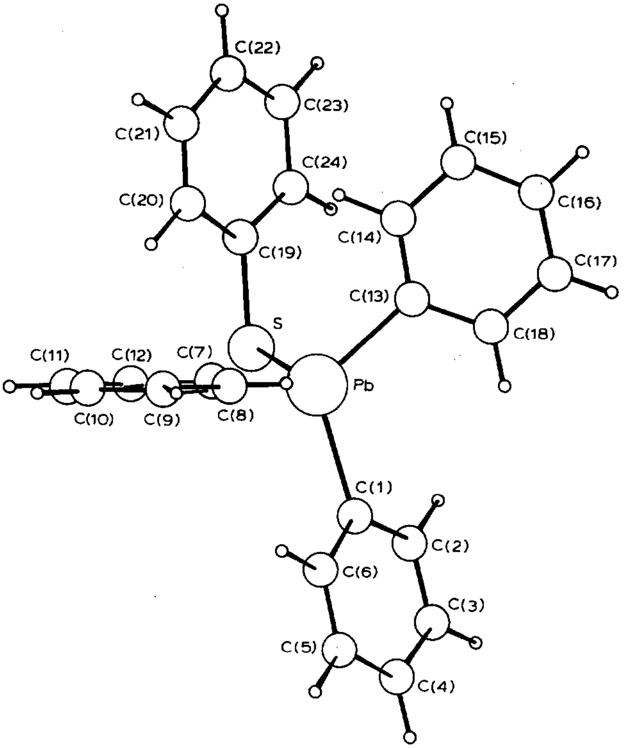


Fig. 1. View of the molecular geometry of triphenyllead benzenethiolate showing the atomic numbering.

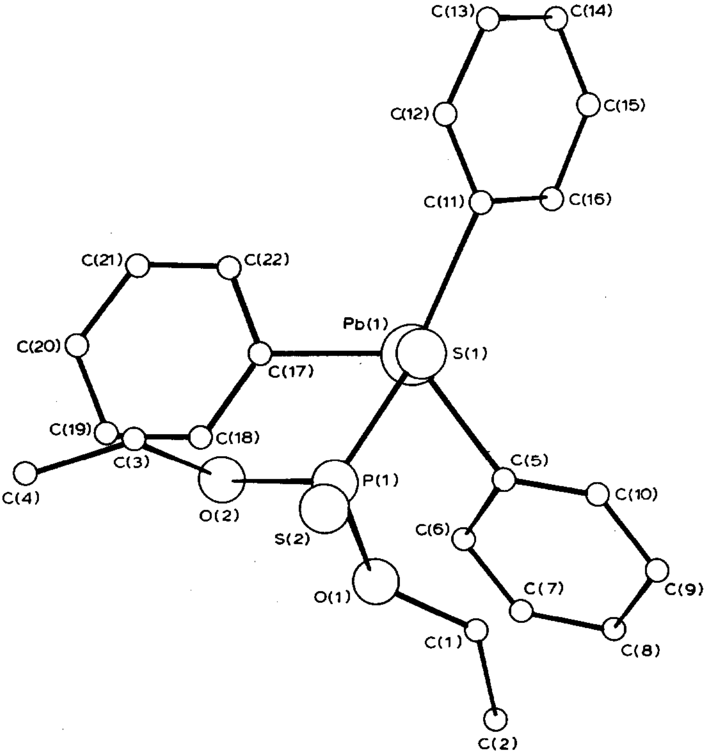


Fig. 2. The molecular geometry of triphenyllead *O,O′*-diethyldithiophosphate viewed down the lead–sulphur bond showing the atomic numbering.

TABLE 4

FINAL FRACTIONAL ATOMIC COORDINATES FOR $Ph_3PbS_2P(OEt)_2$ [a]

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Pb(1) | 0.09756(9) | 0.20352(8) | 0.39631(6) |
| S(1) | 0.2181(7) | 0.3864(6) | 0.3153(4) |
| S(2) | 0.2246(7) | 0.4436(5) | 0.0732(5) |
| P(1) | 0.1482(7) | 0.3165(5) | 0.1499(4) |
| O(1) | 0.980(2) | 0.269(1) | 0.124(1) |
| O(2) | 0.178(2) | 0.177(2) | 0.119(2) |
| C(1) | 0.893(3) | 0.368(3) | 0.131(2) |
| C(2) | 0.737(3) | 0.296(3) | 0.096(3) |
| C(3) | 0.289(4) | 0.147(4) | 0.088(4) |
| C(4) | 0.324(6) | 0.078(7) | −0.007(5) |
| C(5) | 0.866(2) | 0.198(2) | 0.370(2) |
| C(6) | 0.768(2) | 0.077(2) | 0.326(2) |
| C(7) | 0.617(2) | 0.070(2) | 0.314(2) |
| C(8) | 0.569(2) | 0.186(3) | 0.338(3) |
| C(9) | 0.673(3) | 0.310(2) | 0.381(3) |
| C(10) | 0.821(2) | 0.313(2) | 0.396(2) |
| C(11) | 0.217(2) | 0.283(2) | 0.567(1) |
| C(12) | 0.367(2) | 0.327(2) | 0.592(2) |
| C(13) | 0.443(3) | 0.373(2) | 0.701(2) |
| C(14) | 0.367(3) | 0.370(2) | 0.781(2) |
| C(15) | 0.219(3) | 0.331(3) | 0.760(2) |
| C(16) | 0.138(3) | 0.283(2) | 0.649(2) |
| C(17) | 0.151(2) | 0.017(2) | 0.330(1) |
| C(18) | 0.087(2) | −0.060(2) | 0.224(2) |
| C(19) | 0.122(3) | −0.184(2) | 0.187(2) |
| C(20) | 0.221(3) | −0.225(2) | 0.253(2) |
| C(21) | 0.278(3) | −0.152(2) | 0.363(2) |
| C(22) | 0.244(2) | −0.030(2) | 0.400(1) |

[a] Estimated standard deviations in parentheses.

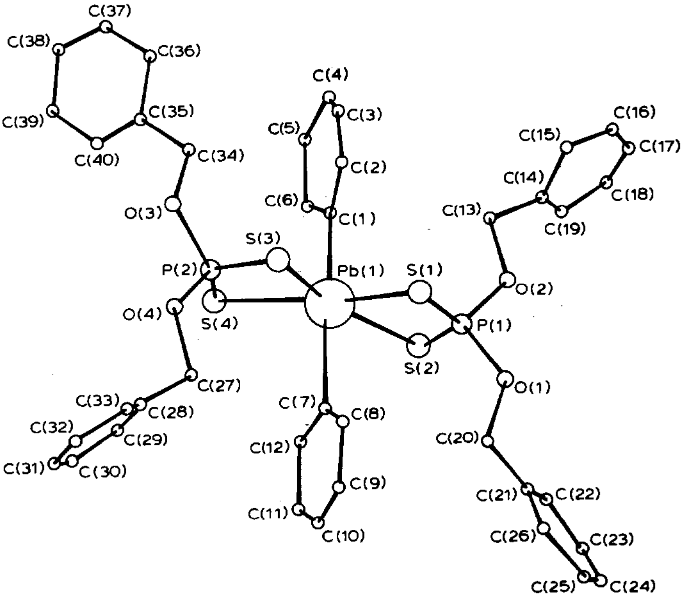


Fig. 3. View of the molecular geometry of diphenyllead bis(*O,O'*-dibenzyldithiophosphate) showing the atomic numbering.

TABLE 5

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (deg) for $Ph_3PbS_2P(OEt)_2$ [a]

| Distances | | Angles | |
|---|---|---|---|
| Pb(1)-S(1) | 2.554(6) | S(1)-Pb(1)-C(5) | 108.0(5) |
| Pb(1)-C(5) | 2.18(2) | S(1)-Pb(1)-C(11) | 97.8(5) |
| Pb(1)-C(11) | 2.20(2) | S(1)-Pb(1)-C(17) | 110.6(5) |
| Pb(1)-C(17) | 2.18(2) | C(5)-Pb(1)-C(11) | 115.0(7) |
| | | C(5)-Pb(1)-C(17) | 114.6(7) |
| S(1)-P(1) | 2.035(7) | C(11)-Pb(1)-C(17) | 109.5(7) |
| S(2)-P(1) | 1.923(7) | | |
| P(1)-O(1) | 1.56(2) | Pb(1)-S(1)-P(1) | 104.6(3) |
| P(1)-O(2) | 1.55(2) | S(1)-P(1)-S(2) | 111.0(4) |
| O(1)-C(1) | 1.45(3) | S(1)-P(1)-O(1) | 108.4(6) |
| C(1)-C(2) | 1.50(3) | S(1)-P(1)-O(2) | 107.5(8) |
| O(2)-C(3) | 1.26(4) | S(2)-P(1)-O(1) | 115.5(6) |
| C(3)-C(4) | 1.41(4) | S(2)-P(1)-O(2) | 117.4(8) |
| | | O(1)-P(1)-O(2) | 95.8(9) |
| C(5)-C(6) | 1.39(2) | P(1)-O(1)-C(1) | 118(1) |
| C(6)-C(7) | 1.41(3) | O(1)-C(1)-C(2) | 107(2) |
| C(7)-C(8) | 1.39(3) | P(1)-O(2)-C(3) | 127(2) |
| C(8)-C(9) | 1.43(3) | O(2)-C(3)-C(4) | 138(2) |
| C(9)-C(10) | 1.39(3) | | |
| C(10)-C(5) | 1.37(3) | Pb(1)-C(5)-C(6) | 119(1) |
| | | Pb(1)-C(5)-C(10) | 199(1) |
| C(11)-C(12) | 1.39(3) | C(6)-C(5)-C(10) | 122(1) |
| C(12)-C(13) | 1.40(3) | C(5)-C(10)-C(9) | 120(1) |
| C(13)-C(14) | 1.35(3) | C(10)-C(9)-C(8) | 120(1) |
| C(14)-C(15) | 1.37(4) | C(9)-C(8)-C(7) | 120(1) |
| C(15)-C(16) | 1.42(3) | C(8)-C(7)-C(6) | 119(1) |
| C(16)-C(11) | 1.39(3) | C(7)-C(6)-C(5) | 120(1) |
| C(17)-C(18) | 1.40(2) | Pb(1)-C(11)-C(12) | 121(1) |
| C(18)-C(19) | 1.42(3) | Pb(1)-C(11)-C(16) | 118(1) |
| C(19)-C(20) | 1.35(3) | C(12)-C(11)-C(16) | 121(2) |
| C(20)-C(21) | 1.41(3) | C(11)-C(12)-C(13) | 121(2) |
| C(21)-C(22) | 1.41(3) | C(12)-C(13)-C(14) | 118(2) |
| C(22)-C(17) | 1.38(2) | C(13)-C(14)-C(15) | 123(2) |
| | | C(14)-C(15)-C(16) | 120(2) |
| | | C(15)-C(16)-C(11) | 117(2) |
| | | Pb(1)-C(17)-C(18) | 123(1) |
| | | Pb(1)-C(17)-C(22) | 117(1) |
| | | C(18)-C(17)-C(22) | 120(1) |
| | | C(17)-C(18)-C(19) | 120(1) |
| | | C(18)-C(19)-C(20) | 120(1) |
| | | C(19)-C(20)-C(21) | 120(1) |
| | | C(20)-C(21)-C(22) | 120(1) |
| | | C(21)-C(22)-C(17) | 119(1) |

[a] Estimated standard deviations in parentheses.

## Results and discussion

Crystals of both triphenyllead benzenethiolate and triphenyllead *O,O'*-diethyldithiophosphate comprise isolated molecular units with approximately tetrahedral geometry (Fig. 1 and 2, respectively). In the case of the thiolate compound, the

*(Continued on p. 291)*

TABLE 6

FINAL FRACTIONAL ATOMIC COORDINATES FOR $Ph_2Pb[S_2O(OCH_2Ph)_2]_2$ [a]

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Pb(1) | 0.2752(1) | 0.09968(7) | 0.03732(5) |
| S(1) | 0.3107(6) | 0.0945(5) | 0.8819(4) |
| S(2) | 0.0226(6) | −0.0046(6) | 0.9103(4) |
| S(3) | 0.5352(6) | 0.1937(4) | 0.1044(4) |
| S(4) | 0.3468(7) | 0.1371(7) | 0.2271(4) |
| P(1) | 0.1205(7) | 0.0218(5) | 0.8226(4) |
| P(2) | 0.5231(6) | 0.1966(5) | 0.2240(4) |
| O(1) | 0.911(2) | 0.091(1) | 0.226(1) |
| O(2) | 0.072(2) | 0.092(1) | 0.735(1) |
| O(3) | 0.601(2) | 0.323(1) | 0.259(1) |
| O(4) | 0.614(1) | 0.139(1) | 0.2954(9) |
| C(1) | 0.242(2) | 0.263(2) | 0.009(1) |
| C(2) | 0.311(5) | 0.350(2) | 0.965(3) |
| C(3) | 0.286(5) | 0.456(3) | 0.950(3) |
| C(4) | 0.208(3) | 0.477(3) | 0.970(2) |
| C(5) | 0.137(5) | 0.393(3) | 0.022(4) |
| C(6) | 0.153(4) | 0.282(3) | 0.034(4) |
| C(7) | 0.729(2) | 0.079(2) | 0.920(1) |
| C(8) | 0.661(2) | 0.121(2) | 0.945(2) |
| C(9) | 0.655(3) | 0.231(2) | 0.915(2) |
| C(10) | 0.732(3) | 0.294(2) | 0.865(2) |
| C(11) | 0.807(4) | 0.256(3) | 0.845(3) |
| C(12) | 0.807(3) | 0.142(2) | 0.870(3) |
| C(13) | 0.083(4) | 0.207(3) | 0.737(2) |
| C(14) | −0.003(3) | 0.237(2) | 0.643(2) |
| C(15) | 0.075(3) | 0.309(4) | 0.598(2) |
| C(16) | 0.007(5) | 0.334(5) | 0.504(3) |
| C(17) | 0.868(5) | 0.309(4) | 0.484(3) |
| C(18) | 0.798(3) | 0.241(3) | 0.536(3) |
| C(19) | 0.859(3) | 0.200(3) | 0.618(2) |
| C(20) | 0.884(3) | 0.192(2) | 0.175(2) |
| C(21) | −0.011(3) | 0.297(2) | 0.232(2) |
| C(22) | 0.124(2) | 0.319(2) | 0.256(2) |
| C(23) | 0.212(3) | 0.418(3) | 0.305(2) |
| C(24) | 0.168(4) | 0.490(3) | 0.316(2) |
| C(25) | 0.029(4) | 0.472(2) | 0.292(2) |
| C(26) | 0.934(3) | 0.370(2) | 0.247(2) |
| C(27) | 0.595(3) | 0.019(2) | 0.288(2) |
| C(28) | 0.354(3) | 0.029(2) | 0.613(1) |
| C(29) | 0.435(3) | 0.070(2) | 0.560(2) |
| C(30) | 0.380(5) | 0.111(3) | 0.478(2) |
| C(31) | 0.256(5) | 0.114(3) | 0.449(3) |
| C(32) | 0.180(4) | 0.081(4) | 0.499(3) |
| C(33) | 0.235(3) | 0.034(3) | 0.588(2) |
| C(34) | 0.550(4) | 0.419(3) | 0.224(3) |
| C(35) | 0.435(3) | 0.514(2) | 0.708(3) |
| C(36) | 0.453(3) | 0.406(3) | 0.746(2) |
| C(37) | 0.442(4) | 0.335(3) | 0.691(3) |
| C(38) | 0.442(5) | 0.363(4) | 0.605(4) |
| C(39) | 0.396(4) | 0.465(4) | 0.566(3) |
| C(40) | 0.590(4) | 0.457(5) | 0.375(2) |

[a] Estimated standard deviations in parentheses.

TABLE 7

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLS (deg) for $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ [a]

| Distances | | Angles | |
|---|---|---|---|
| Pb(1)–C(1) | 2.176(21) | C(1)–Pb(1)–S(1) | 96.3(6) |
| Pb(1)–C(7) | 2.215(19) | C(1)–Pb(1)–S(2) | 88.8(6) |
| Pb(1)–S(1) | 2.723(6) | C(1)–Pb(1)–S(3) | 95.3(7) |
| Pb(1)–S(2) | 2.940(7) | C(1)–Pb(1)–S(4) | 87.7(6) |
| Pb(1)–S(3) | 2.679(6) | C(1)–Pb(1)–C(7) | 165.0(9) |
| Pb(1)–S(4) | 2.957(6) | S(1)–Pb(1)–S(2) | 69.9(2) |
| | | S(1)–Pb(1)–C(7) | 94.5(6) |
| C(1)–C(2) | 1.35(3) | S(1)–Pb(1)–S(3) | 86.3(2) |
| C(2)–C(3) | 1.43(4) | | |
| C(3)–C(4) | 1.20(4) | S(1)–Pb(1)–S(4) | 157.9(2) |
| C(4)–C(5) | 1.44(4) | S(2)–Pb(1)–C(7) | 86.5(6) |
| C(5)–C(6) | 1.44(4) | S(2)–Pb(1)–S(3) | 156.2(2) |
| C(6)–C(1) | 1.35(3) | S(2)–Pb(1)–S(4) | 132.0(2) |
| | | C(7)–Pb(1)–S(3) | 94.3(6) |
| C(7)–C(8) | 1.31(3) | C(7)–Pb(1)–S(4) | 85.7(6) |
| C(8)–C(9) | 1.39(3) | S(3)–Pb(1)–S(4) | 71.7(2) |
| C(9)–C(10) | 1.38(4) | | |
| C(10)–C(11) | 1.30(4) | Pb(1)–S(1)–P(1) | 91.4(3) |
| C(11)–C(12) | 1.41(4) | Pb(1)–S(2)–P(1) | 86.3(3) |
| C(12)–C(7) | 1.38(3) | S(1)–P(1)–O(2) | 110.8(8) |
| | | S(1)–P(1)–O(1) | 110.7(8) |
| S(1)–P(1) | 1.98(1) | S(2)–P(1)–O(1) | 113.5(8) |
| S(2)–P(1) | 1.93(1) | S(2)–P(1)–O(2) | 113.3(9) |
| P(1)–O(2) | 1.59(2) | S(2)–P(1)–S(1) | 112.4(4) |
| P(1)–O(1) | 1.58(1) | O(2)–P(1)–O(1) | 95.1(9) |
| O(2)–C(13) | 1.40(3) | | |
| C(13)–C(14) | 1.57(4) | P(1)–O(2)–C(13) | 121(2) |
| C(14)–C(15) | 1.36(4) | O(2)–C(13)–C(14) | 105(2) |
| C(15)–C(16) | 1.48(5) | C(13)–C(14)–C(15) | 109(3) |
| C(16)–C(17) | 1.45(6) | C(14)–C(15)–C(16) | 115(3) |
| C(17)–C(18) | 1.36(6) | C(15)–C(16)–C(17) | 114(4) |
| C(18)–C(19) | 1.38(4) | C(16)–C(17)–C(18) | 124(3) |
| C(19)–C(14) | 1.42(4) | C(17)–C(18)–C(19) | 121(3) |
| | | C(18)–C(19)–C(14) | 115(3) |
| O(1)–C(20) | 1.46(3) | C(19)–C(14)–C(13) | 122(3) |
| C(20)–C(21) | 1.57(3) | | |
| C(21)–C(22) | 1.42(3) | P(1)–O(1)–C(20) | 120(2) |
| C(22)–C(23) | 1.41(4) | O(1)–C(20)–C(21) | 104(2) |
| C(23)–C(24) | 1.27(5) | C(20)–C(21)–C(22) | 122(2) |
| C(24)–C(25) | 1.47(5) | C(21)–C(22)–C(23) | 118(3) |
| C(25)–C(26) | 1.43(4) | C(22)–C(23)–C(24) | 119(3) |
| C(26)–C(21) | 1.40(3) | C(23)–C(24)–C(25) | 124(3) |
| | | C(24)–C(25)–C(26) | 120(3) |
| S(3)–P(2) | 2.01(1) | C(25)–C(26)–C(21) | 113(3) |
| S(4)–P(2) | 1.93(1) | C(26)–C(21)–C(20) | 113(2) |
| P(2)–O(3) | 1.58(2) | | |
| P(2)–O(4) | 1.55(1) | Pb(1)–C(3)–P(2) | 90.3(3) |
| | | Pb(1)–S(4)–P(2) | 84.0(3) |
| O(4)–C(27) | 1.45(3) | S(3)–P(2)–O(3) | 108.7(8) |
| C(27)–C(28) | 1.60(3) | S(3)–P(2)–O(4) | 110.4(7) |
| C(28)–C(29) | 1.40(3) | O(3)–P(2)–O(4) | 96.3(8) |
| C(29)–C(30) | 1.36(4) | S(3)–P(2)–S(4) | 114.0(4) |
| C(30)–C(31) | 1.37(5) | S(4)–P(2)–O(3) | 112.7(8) |

TABLE 7 (continued)

| Distances | | Angles | |
|---|---|---|---|
| C(31)–C(32) | 1.32(5) | S(4)–P(2)–O(4) | 113.3(7) |
| C(32)–C(33) | 1.47(4) | | |
| C(33)–C(28) | 1.33(3) | P(2)–O(4)–C(27) | 119(1) |
| | | O(4)–C(27)–C(28) | 106(2) |
| O(3)–C(34) | 1.47(4) | C(27)–C(28)–C(29) | 122(3) |
| C(34)–C(35) | 1.43(5) | C(28)–C(29)–C(30) | 115(3) |
| C(35)–C(36) | 1.44(4) | C(29)–C(30)–C(31) | 123(3) |
| C(36)–C(37) | 1.30(4) | C(30)–C(31)–C(32) | 123(4) |
| C(37)–C(38) | 1.34(6) | C(31)–C(32)–C(33) | 115(4) |
| C(38)–C(39) | 1.42(6) | C(32)–C(33)–C(28) | 120(3) |
| C(39)–C(40) | 1.40(7) | C(33)–C(28)–C(27) | 115(3) |
| C(40)–C(35) | 1.30(4) | | |
| | | P(2)–O(3)–C(34) | 122(2) |
| | | O(3)–C(34)–C(35) | 113(3) |
| | | C(34)–C(35)–C(36) | 110(4) |
| | | C(35)–C(36)–C(37) | 117(3) |
| | | C(36)–C(37)–C(38) | 112(4) |
| | | C(37)–C(38)–C(39) | 121(5) |
| | | C(38)–C(39)–C(40) | 116(4) |
| | | C(39)–C(40)–C(35) | 120(5) |
| | | C(40)–C(35)–C(34) | 126(5) |
| | | Pb(1)–C(1)–C(2) | 120(2) |
| | | C(1)–C(2)–C(3) | 118(3) |
| | | C(2)–C(3)–C(4) | 127(4) |
| | | C(3)–C(4)–C(5) | 119(3) |
| | | C(4)–C(5)–C(6) | 115(3) |
| | | C(5)–C(6)–C(1) | 123(3) |
| | | C(6)–C(1)–P(1) | 122(2) |
| | | Pb(1)–C(7)–C(8) | 119(2) |
| | | C(7)–C(8)–C(9) | 121(2) |
| | | C(8)–C(9)–C(10) | 116(3) |
| | | C(9)–C(10)–C(11) | 123(3) |
| | | C(10)–C(11)–C(12) | 121(3) |
| | | C(11)–C(12)–C(7) | 116(3) |
| | | C(12)–C(7)–Pb(1) | 118(2) |

[a] Estimated standard deviations in parentheses.

deviation from ideal tetrahedral geometry is only slight, the direction of the distortion being towards a closing of the valence angles involving sulphur and an opening of those involving just carbon, in line with conventional isovalent hybridization arguments. Consistent with the somewhat greater electronegativity of the dithiophosphate group, the distortion is more pronounced, in the case of triphenyllead *O,O′*-diethyldithiophosphate, with the SPbC valence angle opposite the phosphorus–sulphur bond being closed to 97.8(5)° (mean angle SPbC 105.5(5)°; mean angle CPbC 113.0(7)°). Concomitantly, the lead–sulphur distance is longer in the dithiophosphate (2.554(6) Å) than in the benzenethiolate (2.515(2) Å) (cf. that in $Ph_3PbSC_6H_3Me_2$-2,6 [1] (2.512(6) Å)). No chelation or bridging by the dithiophosphate group is apparent. However, the formally multiply-bonded P=S distance (1.923(7) Å), although slightly shorter than that in the tin analogue

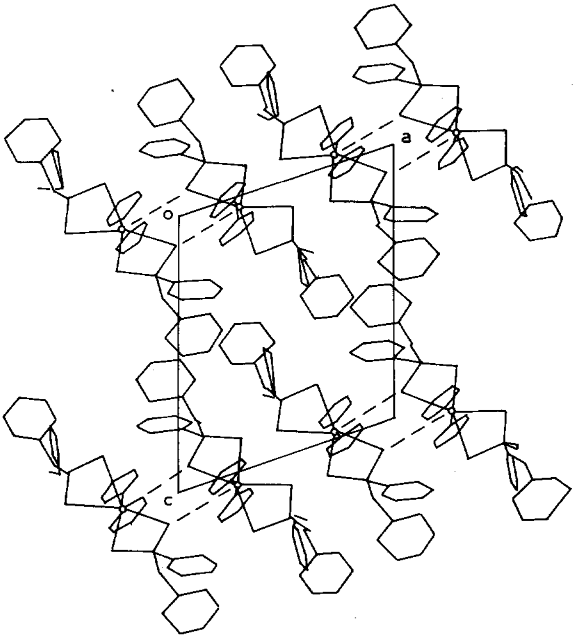


Fig. 4. Projection of the unit cell of diphenyllead bis(*O*,*O*′-dibenzyldithiophosphate) onto the *ac* plane. The short intermolecular lead–sulphur contacts are represented by dashed lines.

(1.931(1) Å) [5], in which the dithiophosphate group is also unidentate, is longer than those in compounds with "authentic" P=S double bonds such as $(i\text{-PrO})_2(S)PS\text{-}SP(S)(OPr\text{-}i)_2$ (1.908 Å) [6]. The P–S single bond distance (2.035(7) Å) and the two P–O distances (1.55(2) and 1.56(2) Å) are all marginally shorter than those observed for the tin analogue [5], probably reflecting a more anionic nature of the dithiophosphate ligand as a whole in the present case.

In contrast to the unidentate behaviour of the dithiophosphate group in $Ph_3PbS_2P(OEt)_2$, both *O*,*O*′-dibenzyldithiophosphate residues function as anisobidentate ligands in $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ resulting in distorted *trans*-$Ph_2PbS_4$ coordination for the lead atom (Fig. 3) The two short, mutually *cis*, lead–sulphur bonds are significantly longer (2.679(6), 2.723(6) Å) than in either of the two triphenyllead derivatives described above, whilst the CPbC is closed to 165.0(9)° along the bisector of the two longer lead–sulphur distances. The geometry at the metal in this compound is, therefore, intermediate between the octahedral geometry observed for $Ph_2Sn[S_2P(OPr\text{-}i)_2]_2$ (angle CSnC 180°, crystallographically imposed) [7] and the distorted tetrahedral geometry of its ethyl homologue, $Ph_2Sn[S_2P(OEt)_2]_2$, (angle CSnC 135(1)°) [8]. Examination of the molecular stacking in the crystal, however, reveals that adjacent pairs of molecules are held together by weak intermolecular Pb...S contacts (3.69(1) Å), thus completing a distorted equatorial $[PbS_5]$ arrangement.

In both of the two anisobidentate dithiophosphate ligands, each shorter lead–sulphur bond is associated with a longer phosphorus–sulphur bond, and vice versa, whereas the phosphorus–oxygen distances are the same within experimental error. Surprisingly, in view of the differing nature of the bonding in the two cases, the bond distance and angle data for the dithiophosphate residues in both $Ph_3PbS_2P(OEt)_2$ and $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ are remarkably similar, demonstrating that the electronic distribution in this type of ligand is rather insensitive to changes in the mode of bonding to the metal.

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