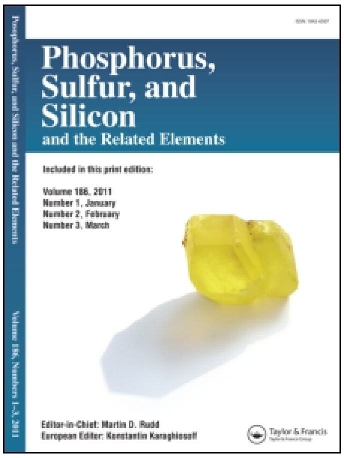

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# NOVEL CYCLIC PENTACOORDINATE AND PSEUDOPENTACOORDINATE LEAD COMPOUNDS

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# NOVEL CYCLIC PENTACOORDINATE AND PSEUDO-PENTACOORDINATE LEAD COMPOUNDS

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Dedicated to John Verkade on the occasion of his 60th birthday

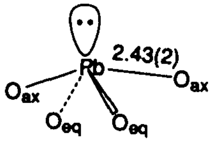
*(Received February 15, 1995; in final form March 5, 1996)*

The new bicyclic lead(II) phosphinate $[(t\text{-Bu})_2PO_2]_2Pb$ (**1**) was synthesized by the reaction of *p*-tolyllead triacetate with di-*t*-butylphosphinic acid and water. An X-ray study showed that it had a pseudo-trigonal bipyramidal geometry (*p*-TBP) with a stereochemically active lone pair of electrons occupying an equatorial site. Infrared data ruled out the possible presence of a Pb—H bond. A series of new monocyclic Pb(IV) compounds, $[Et_4N][(MeC_6H_3S_2)PbPh_2X]$ where X = Br (**2**), Cl (**3**), and F (**4**), was synthesized from the addition reaction of tetraethylammonium halide to 2,2-diphenyl-1,3,2-toluene dithiolato plumbole(IV), $(MeC_6H_3S_2)PbPh_2$ (**5**). An X-ray study of **3** revealed a monocyclic anionic TBP geometry which was compared with related dithiolato cyclic structures formed earlier by lighter elements of Group IVA. The lead(II) compound **1** crystallizes in the monoclinic space group C2/c with a = 15.594(4) Å, b = 16.889(3) Å, c = 12.642(2) Å, $\beta$ = 136.85(1)°, and Z = 4. The lead(IV) compound **3** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.245(5) Å, b = 12.049(3) Å, c = 19.048(4) Å, $\beta$ = 96.22(2)°, and Z = 4. The conventional unweighted residuals are 0.023(1) and 0.0387 (3).

*Key words:* Lead(II) phosphinate, lead(IV) plumbates, pentacoordinate, lone pair.

## INTRODUCTION

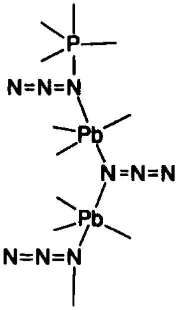
Not much attention has been directed toward the formation of molecular geometries for lead that assume pentacoordinate or pseudo-pentacoordinate structures. A recently reported example of a pseudo-pentacoordinate lead(II) compound is found in the "sawhorse" geometry of $Pb_4Zr_2(O\text{-}i\text{-}Pr)_{16}$ (**A**)[2a] where a lone electron pair is envisioned at an equatorial site. Thus, the local arrangement around the pseudo-pentacoordinated lead center is sketched in **A** in a trigonal bipyramidal framework where the longest Pb—O distance is 2.43(**2**) Å. The remaining ones fall in the range 2.23(**2**)–2.39(**2**) Å. A pseudo-trigonal bipyramidal geometry for Pb(II) also has been found in an X-ray study of a cyclodextrin complex with hexadecanuclear lead, $[Pb_{16}(\gamma\text{-}CDH_{16})_2]\cdot$ca. $20H_2O$, **B**,[2b] where $\gamma$-CD = cyclomaltooctaose. In **B**, the Pb—O distances for the pseudo-TBP geometry fall in the range 2.212(**15**)–2.502(**15**)



$A^{2a}$

Å. Closely related to **A** is the sawhorse structure of $Pb(OCH_2CH_2OMe)_2$ (**C**)[2c] which consists of a one-dimensional chain with the alkoxide ligands coordinating in a unidentate fashion and serving as a bridge between tetracoordinate lead(II) atoms. Unlike **A** and **C**, the sulfide formulation, $Pb[S_2P(OC_2H_5)_2]_2$ (**D**),[2d] exhibits a distorted tetragonal pyramidal structure. Presumably the lone pair would reside in an axial position of a pseudo-square pyramidal arrangement.[3]

Lead(IV), similar to silicon,[1b,4–6] germanium[4] and tin,[4] should be capable of forming anionic five-coordinated complexes. While these are well known for the lighter congeners, very few lead compounds have been structurally characterized in this coordination state. The organoazide derivative $Me_3PbN_3$ (**E**) proves to be interesting in that it has been shown to possess an almost perfect TBP geometry in a polymeric network where linear azide groups are linked to adjacent lead atoms that are in a planar $Me_3Pb$ arrangement.[7]



**E**[7]

To increase our knowledge about the structural nuances associated with lead(II) and lead(IV) compounds in pentacoordinate and pseudo-pentacoordinate geometries, particularly the effect of the so called "inert pair" for lead(II), we have examined synthetic approaches leading to their formation. Previously, in our studies in tin chemistry,[8] phosphinate ligands proved useful in forming polynuclear organooxotin compounds with interesting geometries. Prior to that, work on pentacoordinated tin[4,9] and germanium[4,11,12] proved particularly successful with the stabilizing effect of the toluene-3,4-dithiol ligand. In the present study, these two synthetic approaches were employed. Their use led to the synthesis of a pseudo-pentacoordinate derivative, $[(t\text{-}Bu)_2PO_2]_2Pb$ (**1**), and a series of toluene dithiolato plumboles, $[Et_4N](MeC_6H_3S_2)PbPh_2X$, where X = Br (**2**), Cl (**3**), and F (**4**). Molecular structures of **1** and **3** were established by X-ray analyses. $^1H$ NMR data were recorded for **1**–**4**.

## EXPERIMENTAL

Diphenyllead dichloride (Alfa) and toluene-3,4-dithiol (Aldrich), were used as received. Triethylamine (Aldrich) was distilled over KOH before use. The tetraethylammonium halides (Aldrich) were thoroughly pumped under vacuum for 6–8 h at room temperature before use. The other solvents were purified according to standard procedures.[13] *p*-Tolyllead triacetate[14] and di-*t*-butylphosphinic acid[15] were prepared according to literature procedures. All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[16] $^1H$ NMR spectra were recorded on a Varian Associates XL-300 FT-NMR spectrometer in $CDCl_3$ solution at 23°C. Chemical shifts are reported, downfield positive, in ppm relative to tetramethylsilane as an internal standard. The infrared spectra were recorded using KBr windows on a Perkin-Elmer Model 180 spectrometer.

*Syntheses*

*Lead(II) bis(di-t-butylphosphinate)* $[(t\text{-}Bu)_2PO_2]_2Pb$ (**1**). *p*-Tolyllead triacetate (0.165 g, 0.35 mmol) and di-*t*-butylphosphinic acid (0.062 g, 0.35 mmol) were heated together for 3 h in benzene (40 mL) with the azeotropic removal of acetic acid. The solvent was completely removed and more di-*t*-butylphosphinic acid (0.062 g, 0.35 mmol) was added to the residue dissolved in chloroform (30 mL). The mixture was heated at reflux for 2 h, the solvent was removed, and the residue was dissolved in a mixture of dichloromethane (15 mL) and diethylether (10 mL). Slow evaporation of solvent at 20°C (in air) gave lead(II) bis(di-*t*-butylphosphinate) (**1**) as rectangular blocks. $^{1}$H NMR: 1.21 ($^{3}J$(P—H) = 13.8 Hz). $^{31}$P NMR: 52.0 to 57.0 (br). The IR spectrum did not show any band in the region 1500–2500 cm$^{-1}$ which indicated the absence of any Pb—H bond. Strong absorptions at 1110 ($\nu_{P=O}$), 1005, and 825 cm$^{-1}$ were observed. Anal. Calcd. for $C_{16}H_{36}O_4P_2Pb$: C, 34.21; H, 6.41. Found: C, 34.14; H, 6.35.

*(4-Methylbenzene-1,2-dithiolato)diphenylplumbole(IV),* $(MeC_6H_3S_2)PbPh_2$ (**5**). This compound was reported earlier by Wieber and Baudis.[17] A modified procedure has been employed in the present preparation. Toluene-3,4-dithiol (0.81 g, 5.18 mmol) was dissolved in 20 mL of diethylether. Diphenylleaddichloride (2.24 g, 5.18 mmol) was added to the above solution and remained as a suspension. Triethylamine (1.05 g, 10.38 mmol) was dissolved in 30 mL of ether and added dropwise to the reaction mixture. A yellow color resulted. After the addition of amine was completed, the reaction mixture was stirred at room temperature for 18 h. The reaction flask was wrapped with aluminum foil to prevent reaction with light. The reaction mixture was filtered. Removal of the solvent from the filtrate yielded a very small amount of product. The precipitate obtained was treated with 50 mL of water to dissolve triethylamine hydrochloride. The insoluble material that was left behind after the water treatment was dissolved in a mixture of methylene chloride and acetonitrile (50 mL each) and dried ($Na_2SO_4$). Filtration, followed by removal of solvent yielded a bright yellow solid: mp (235°C, d). There was a change in color from yellow to tangerine at 130–140°C. Lit.[17] mp 163–165°C (yield 2.30 g, 86.0%). Anal. Calcd. for $C_{19}H_{16}S_2Pb$: C, 44.26; H, 3.13. Found: C, 44.24; H, 3.26. $^{1}$H NMR: 6.64–7.75 (m), 2.24 (s, C*H*$_3$ tolyl).

*Tetraethylammonium (4-Methylbenzene-1,2-dithiolato)diphenylbromoplumbate,* $[Et_4N][(MeC_6H_3S_2)PbPh_2Br]$ (**2**). To a solution of **5** (0.50 g, 0.97 mmol) in 40 mL of acetonitrile was added tetraethylammonium bromide (0.20 g, 0.95 mmol) at room temperature. The color of the reaction mixture changed from yellow to orange. The solution was stirred at room temperature for 4 h and the solvent removed *in vacuo* to yield a yellowish solid. It was recrystallized twice from methylene chloride/hexane (1:1) at 0°C to afford tangerine colored crystals: mp 160–165°C (d). The color of the compound changes from tangerine to a dark orange at 115°C and to yellow at 128°C (yield 0.40 g, 56.8%). Anal. Calcd. for $C_{27}H_{36}NBrS_2Pb$: C, 44.68; H, 5.00; N, 1.94. Found: C, 44.98; H, 5.16; N, 2.19. $^{1}$H NMR: 7.91 (m), 7.51 (m), 7.25 (m), 3.30 (q, N—C*H*$_2$), 2.22 (s, C*H*$_3$ tolyl), 1.27 (t, N—C—C*H*$_3$).

*Tetraethylammonium (4-Methylbenzene-1,2-dithiolato)diphenylchloroplumbate,* $[Et_4N][(MeC_6H_3S_2)PbPh_2Cl]$ (**3**). To a mixture of **5** (1.01 g, 1.96 mmol) and tetraethylammonium chloride (0.33 g, 1.99 mmol) was added 100 mL of acetonitrile. The mixture was stirred at room temperature for 14 h. Removal of solvent yielded a solid. It was dissolved in 20 mL of methylene chloride and 2 mL of acetonitrile and kept in a refrigerator for crystallization. After a week, tangerine colored crystals were isolated: mp 135–140°C (yield 0.90 g, 67.4%). Anal. Calcd. for $C_{27}H_{36}NClS_2Pb$: C, 47.60; H, 5.33; N, 2.06. Found: C, 47.46; H, 5.27; N, 2.07. $^{1}$H NMR: 7.90 (m), 7.55 (m), 7.35 (m), 3.40 (q, N—C*H*$_2$), 2.25 (s, C*H*$_3$ tolyl), 1.35 (t, N—C—C*H*$_3$).

*Tetraethylammonium (4-Methylbenzene-1,2-dithiolato)diphenylfluoroplumbate,* $[Et_4N][(MeC_6H_3S_2)PbPh_2F]$ (**4**). To a solution of **5** (1.0 g, 1.94 mmol) in acetonitrile (50 mL) was added tetraethylammonium fluoride (0.36 g, 1.94 mmol) and the reaction mixture was stirred at room temperature for 4 h. Removal of solvent yielded an oil. The oil was dissolved in methylene chloride (5 mL) and hexane (3 mL) and kept for crystallization at 5°C whereupon yellow crystals grew out of solution: mp 132°C (d) (yield 0.90 g, 69.8%). Anal. Calcd. for $C_{27}H_{36}NFS_2Pb$: C, 48.77; H, 5.46; N, 2.10. Found: C, 47.90; H, 5.50; N, 2.05. $^{1}$H NMR: 8.20 (m), 7.35 (m), 2.80 (q, N—C*H*$_2$), 2.20 (s, C*H*$_3$ tolyl), 0.90 (t, N—C—C*H*$_3$).

*X-ray Experimental.* The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation. The crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystal from atmosphere as a precaution. Details of the experimental procedures have been described previously.[18] Crystallographic data are summarized in Table I.

TABLE I

Crystallographic data for compounds 1 and 3

| Compound | 1 | 3 |
|---|---|---|
| formula | $C_{16}H_{36}O_4P_2Pb$ | $C_{27}H_{36}ClNPbS_2$ |
| formula weight | 561.60 | 681.33 |
| crystal system | monoclinic | monoclinic |
| space group | C2/c (No.15) | $P2_1/c$ (No.14) |
| a (Å) | 15.594(4) | 12.245(5) |
| b (Å) | 16.889(3) | 12.049(3) |
| c (Å) | 12.642(2) | 19.048(4) |
| α (°) | - | - |
| β (°) | 136.85(1) | 96.22(2) |
| γ (°) | - | - |
| V ($Å^3$) | 2277(2) | 2794(2) |
| Z | 4 | 4 |
| T (°C) | 23 ± 2 | 23 ± 2 |
| λ (Å) | 0.71073 | 0.71073 |
| $D_{calc}$ ($g/cm^3$) | 1.635 | 1.620 |
| $\mu_{MoK\alpha}$ ($cm^{-1}$) | 76.16 | 62.99 |
| $R^a$ | 0.023 | 0.0387 |
| $R_w$ | $0.030^b$ | $0.0616^c$ |

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

[b] $R_w(F_o) = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$

[c] $R_w(F_o^2) = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}^{1/2}$

*X-ray Study for $[(t\text{-}Bu)_2PO_2]_2Pb$* (**1**). The colorless crystal used for the study had approximate dimensions of 0.15 × 0.30 × 0.38 mm. Data were collected using the $\theta$-$2\theta$ scan mode with $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 50°$. A total of 1997 independent reflections (+h, +k, ±l) was measured. Empirical absorption corrections based on psi scans were applied ($T_{min}/T_{max} = 0.407$). The data with $I > 3\sigma_I$ (1771) were used in the calculations. The structure was solved by Patterson and difference Fourier techniques and was refined by full-matrix least-squares.[19] Refinements were based on F and computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers in ideal positions.

*X-ray Study for $[Et_4N][(MeC_6H_3S_2)PbPh_2Cl]$* (**3**). The orange needle crystal used for the study had approximate dimensions of 0.35 × 0.35 × 0.80 mm. Data were collected using the $\theta$-$2\theta$ scan mode with $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 43°$. A total of 3916 independent reflections (+h, +k, ±l) was measured. Empirical absorption corrections based on psi scans were applied ($T_{min}/T_{max} = 0.806$). All of the data were included in the refinement. The structure was solved by direct methods and difference Fourier techniques and was refined by full-matrix least-squares. Refinements were based on $F^2$ and computations were performed on a 486/66 computer using SHELXS-86 for solution[20] and SHELXL-93 for refinement.[21] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the 2515 reflections with $I \geq 2\sigma_I$.

## RESULTS AND DISCUSSION

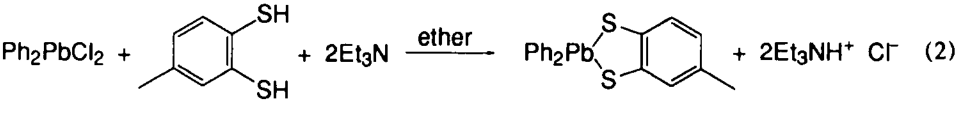
Atomic coordinates and bond lengths and angles are listed in Tables II and III, respectively, for **1** and in Tables IV and V for **3**. The atom labeling scheme is shown in the ORTEP plot for **1** in Figure 1 and in the SNOOPI diagram for **3**, Figure 2.

### *Syntheses*

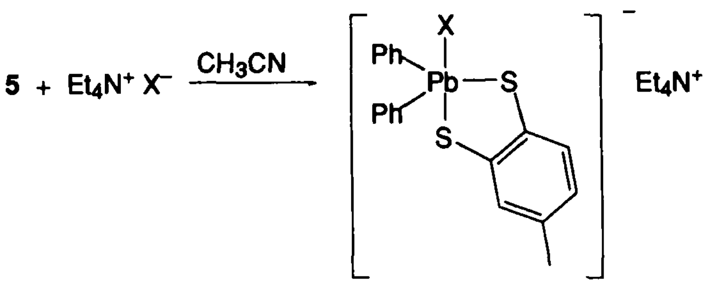
The bicyclic lead phosphinate, **1**, was prepared by the reaction of *p*-tolyllead triacetate with di-*t*-butylphosphinic acid and water according to Equation 1.

$$(p\text{-tol})Pb(CH_3CO_2)_3 + 2(t\text{-}Bu)_2PO_2H + H_2O \rightarrow \underset{\mathbf{1}}{[(t\text{-}Bu)_2PO_2]_2Pb} + p\text{-tol(OH)} + 3CH_3CO_2H \qquad (1)$$

The monocyclic dithiolato halo plumboles, **2–4**, were prepared by the condensation reaction of diphenyllead dichloride with toluene-3,4-dithiol in ether solution in the presence of $Et_3N$, followed by the addition of tetraethylammonium halide in acetonitrile solution. Yields in the range of 57–70% resulted. Equations 2 and 3 outline the reaction sequence.



**5**



(3)

X = Br (2), Cl (3), F (4)

TABLE II

Atomic coordinates in crystalline $[(t\text{-Bu})_2PO_2]_2Pb$ (1)[a]

| Atom[b] | x | y | z | B equiv[c] |
|---|---|---|---|---|
| Pb | 0.000 | 0.21643(1) | 0.250 | 3.229(5) |
| P | 0.22503(7) | 0.33222(7) | 0.32224(9) | 3.35(3) |
| O1 | 0.0951(2) | 0.3092(2) | 0.2424(3) | 5.09(9) |
| O2 | 0.3335(3) | 0.2877(2) | 0.4659(3) | 4.22(9) |
| C1 | 0.2261(4) | 0.3116(4) | 0.1803(4) | 5.1(1) |
| C2 | 0.2201(6) | 0.2197(4) | 0.1674(6) | 7.7(2) |
| C3 | 0.1103(5) | 0.3456(5) | 0.0192(5) | 7.4(2) |
| C4 | 0.3478(4) | 0.3407(6) | 0.2369(5) | 7.8(2) |
| C5 | 0.2390(4) | 0.4383(3) | 0.3733(5) | 5.2(2) |
| C6 | 0.2224(5) | 0.4377(4) | 0.4792(6) | 7.8(2) |
| C7 | 0.1356(6) | 0.4894(4) | 0.2316(7) | 8.8(3) |
| C8 | 0.3684(5) | 0.4722(4) | 0.4615(8) | 8.4(3) |

a. Numbers in parentheses are estimated standard deviations.

b. Atoms are labeled to agree with Figure 1.

c. Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

## *Structures*

The bicyclic lead phosphinate **1** has a local sawhorse geometry which may be regarded as a pseudo-trigonal bipyramid (*p*-TBP) with the bidentate phosphinate forming rings located at axial-equatorial positions coupling adjacent lead atoms in a

TABLE III

Bond lengths (Å) and angles (deg) for $[(t\text{-Bu})_2PO_2]_2Pb$ (1)[a]

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| Pb | O1 | 2.208(4) | C1 | C3 | 1.540(6) |
| Pb | O2 | 2.458(2) | C1 | C2 | 1.557(9) |
| P | O1 | 1.513(4) | C1 | C4 | 1.540(9) |
| P | O2 | 1.497(2) | C5 | C6 | 1.54(1) |
| P | C1 | 1.840(7) | C5 | C7 | 1.529(7) |
| P | C5 | 1.863(6) | C5 | C8 | 1.536(9) |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|
| O1 | Pb | O1 | 89.5(2) | Pb | O2 | P | 147.3(2) |
| [b]O1 | Pb | O2 | 93.3(1) | P | C1 | C2 | 104.4(5) |
| [c]O1 | Pb | O2 | 89.1(1) | P | C1 | C3 | 112.5(5) |
| [d]O2 | Pb | O2 | 176.7(1) | P | C1 | C4 | 111.8(4) |
| C2 | C1 | C4 | 109.1(6) | C2 | C1 | C3 | 108.0(4) |
| O1 | P | O2 | 117.3(2) | C3 | C1 | C4 | 110.8(6) |
| O1 | P | C1 | 105.2(2) | P | C5 | C6 | 104.1(4) |
| O1 | P | C5 | 103.8(2) | P | C5 | C7 | 112.3(4) |
| O2 | P | C1 | 106.4(2) | P | C5 | C8 | 111.6(5) |
| O2 | P | C5 | 108.6(2) | C6 | C5 | C7 | 108.7(6) |
| C1 | P | C5 | 116.0(3) | C6 | C5 | C8 | 109.7(5) |
| Pb | O1 | P | 140.2(2) | C7 | C5 | C8 | 110.2(6) |

a. Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 1.

b. Endocyclic.

c. Exocyclic.

d. Tipped toward lone pair.

polymeric network, Figure 1. The lead atom lies on a two-fold axis. The remaining equatorial site is envisioned to have a lone pair. The bond parameters are consistent with this view. The $O_{eq}$—Pb—$O_{eq}$ angle is 89.5(2)° which could possibly reflect the effect of the lone pair according to VSEPR theory. The $O_{ax}$—Pb—$O_{ax}$ angle is 176.7(1)° with the oxygen atoms slightly tipped toward the lone pair.

The possibility that a Pb—H bond was present in **1** but missed in the X-ray study was ruled out by the absence of any absorption in the infrared spectrum in the 1500–2500 $cm^{-1}$ region. Pb—H stretching vibrations are normally found in the

TABLE IV

Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for [Et$_4$N][(MeC$_6$H$_3$S$_2$)PbPh$_2$Cl] (3)[a]

| Atom[b] | x | y | z | U(eq) |
|---|---|---|---|---|
| Pb | 2974(1) | 392(1) | 1714(1) | 43(1) |
| Cl | 3578(3) | -1331(3) | 904(2) | 71(1) |
| S(1) | 1913(2) | 1821(2) | 2435(2) | 52(1) |
| S(2) | 1245(2) | -722(2) | 1752(2) | 52(1) |
| C(1) | 969(8) | 908(9) | 2765(5) | 38(3) |
| C(2) | 693(8) | -132(8) | 2487(6) | 40(3) |
| C(3) | -67(9) | -771(9) | 2797(6) | 53(3) |
| C(4) | -608(10) | -385(11) | 3350(7) | 64(3) |
| C(5) | -350(10) | 667(11) | 3633(6) | 63(4) |
| C(5M) | -963(12) | 1077(14) | 4234(8) | 93(5) |
| C(6) | 431(9) | 1281(10) | 3342(6) | 52(3) |
| C(7) | 2994(9) | 1491(9) | 777(5) | 43(3) |
| C(8) | 3866(9) | 1488(10) | 385(6) | 54(3) |
| C(9) | 3888(12) | 2210(12) | -173(7) | 72(4) |
| C(10) | 3007(13) | 2931(11) | -341(7) | 73(4) |
| C(11) | 2132(11) | 2943(11) | 54(7) | 67(4) |
| C(12) | 2122(9) | 2215(10) | 605(6) | 56(3) |
| C(13) | 4351(9) | 25(9) | 2531(6) | 42(3) |
| C(14) | 4459(10) | 680(11) | 3133(7) | 67(4) |
| C(15) | 5291(11) | 471(14) | 3682(7) | 81(4) |
| C(16) | 5965(12) | -413(15) | 3607(8) | 92(5) |
| C(17) | 5873(11) | -1069(12) | 3023(9) | 82(4) |
| C(18) | 5068(10) | -828(9) | 2476(7) | 58(3) |
| N | -2214(7) | 1586(7) | 1262(4) | 48(2) |
| C(19) | -2814(11) | 503(10) | 1121(7) | 67(4) |
| C(20) | -2281(13) | -486(11) | 1463(8) | 89(5) |
| C(21) | -2087(10) | 1841(10) | 2038(6) | 61(3) |
| C(22) | -3125(12) | 1916(13) | 2388(7) | 85(4) |
| C(23) | -2888(10) | 2470(10) | 854(6) | 66(4) |
| C(24) | -2465(12) | 3646(11) | 957(8) | 85(4) |
| C(25) | -1067(10) | 1543(11) | 1037(6) | 64(3) |
| C(26) | -1009(10) | 1180(14) | 301(7) | 81(4) |

[a] Numbers in parantheses are estimated standard deviations. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

[b] Atoms are labeled to agree with Figure 2.

2200–2500 cm$^{-1}$ region.[23] The TBP geometry also expresses itself in that the axial Pb—O bond lengths are over 0.2 Å longer compared to the Pb—O$_{eq}$ lengths, i.e., Pb—O$_{ax}$ = 2.458(2) Å relative to Pb—O$_{eq}$ = 2.208(4) Å.

The structural arrangement for **1** has a close analogy with the lead zirconium isopropoxide, Pb$_4$Zr$_2$(O-*i*-Pr)$_{16}$ (**A**),[2a] with the lead cyclodextrin complex, [Pb$_{16}$($\gamma$-CDH$_{16}$)$_2$]·ca 20H$_2$O (**B**),[2b] and with the lead dialkoxide, Pb(OCH$_2$CH$_2$OMe)$_2$ (**C**).[2c] For **A**, the sawhorse geometry reported has P—O bond lengths of 2.23(2)–2.43(2) Å, in a similar range to that of **1** and **C**. In the *p*-TBP geometry for **B**, the Pb—O distances are again in a comparable range as that for **1**, **A**, and **C**, i.e., 2.215(15)–2.502(15) Å, although the upper end of the Pb—O range is a little higher. Hence, even though lead(II) with a PbO$_4$ local bonding arrangement is found in widely

TABLE V

Bond lengths [Å] and angles [deg] for [$Et_4N$][($MeC_6H_3S_2$)$PbPh_2Cl$] (3)[a]

| | | | |
|---|---|---|---|
| Pb-C(13) | 2.212(11) | C(9)-C(10) | 1.40(2) |
| Pb-C(7) | 2.224(10) | C(10)-C(11) | 1.38(2) |
| Pb-S(2) | 2.515(3) | C(11)-C(12) | 1.37(2) |
| Pb-S(1) | 2.632(3) | C(13)-C(18) | 1.36(2) |
| Pb-Cl | 2.736(3) | C(13)-C(14) | 1.39(2) |
| S(1)-C(1) | 1.760(10) | C(14)-C(15) | 1.40(2) |
| S(2)-C(2) | 1.767(11) | C(15)-C(16) | 1.36(2) |
| C(1)-C(2) | 1.388(14) | C(16)-C(17) | 1.36(2) |
| C(1)-C(6) | 1.415(14) | C(17)-C(18) | 1.39(2) |
| C(2)-C(3) | 1.39(2) | N-C(21) | 1.50(2) |
| C(3)-C(4) | 1.38(2) | N-C(19) | 1.508(14) |
| C(4)-C(5) | 1.40(2) | N-C(23) | 1.510(14) |
| C(5)-C(6) | 1.37(2) | N-C(25) | 1.513(14) |
| C(5)-C(5M) | 1.52(2) | C(19)-C(20) | 1.47(2) |
| C(7)-C(8) | 1.368(14) | C(21)-C(22) | 1.50(2) |
| C(7)-C(12) | 1.39(2) | C(23)-C(24) | 1.51(2) |
| C(8)-C(9) | 1.38(2) | C(25)-C(26) | 1.48(2) |
| | | | |
| C(13)-Pb-C(7) | 127.6(4) | C(8)-C(7)-Pb | 120.9(8) |
| C(13)-Pb-S(2) | 116.9(3) | C(12)-C(7)-Pb | 119.2(8) |
| C(7)-Pb-S(2) | 115.1(3) | C(7)-C(8)-C(9) | 120.1(12) |
| C(13)-Pb-S(1) | 98.4(3) | C(8)-C(9)-C(10) | 119.4(12) |
| C(7)-Pb-S(1) | 94.5(3) | C(11)-C(10)-C(9) | 120.7(12) |
| S(2)-Pb-S(1) | 82.45(9) | C(12)-C(11)-C(10) | 119.0(12) |
| C(13)-Pb-Cl | 90.7(3) | C(11)-C(12)-C(7) | 120.8(12) |
| C(7)-Pb-Cl | 88.4(3) | C(18)-C(13)-C(14) | 119.2(11) |
| S(2)-Pb-Cl | 83.76(11) | C(18)-C(13)-Pb | 123.0(8) |
| S(1)-Pb-Cl | 165.84(10) | C(14)-C(13)-Pb | 117.7(8) |
| C(1)-S(1)-Pb | 99.1(3) | C(13)-C(14)-C(15) | 120.8(12) |
| C(2)-S(2)-Pb | 101.8(4) | C(16)-C(15)-C(14) | 117.4(14) |
| C(2)-C(1)-C(6) | 118.0(10) | C(17)-C(16)-C(15) | 122.9(13) |
| C(2)-C(1)-S(1) | 124.8(8) | C(16)-C(17)-C(18) | 118.8(13) |
| C(6)-C(1)-S(1) | 117.2(8) | C(13)-C(18)-C(17) | 120.8(12) |
| C(3)-C(2)-C(1) | 119.0(10) | C(21)-N-C(19) | 110.4(9) |
| C(3)-C(2)-S(2) | 116.5(8) | C(21)-N-C(23) | 110.8(9) |
| C(1)-C(2)-S(2) | 124.5(8) | C(19)-N-C(23) | 106.9(8) |
| C(4)-C(3)-C(2) | 122.4(11) | C(21)-N-C(25) | 106.6(9) |
| C(3)-C(4)-C(5) | 119.4(11) | C(19)-N-C(25) | 111.6(9) |
| C(6)-C(5)-C(4) | 118.0(12) | C(23)-N-C(25) | 110.6(9) |
| C(6)-C(5)-C(5M) | 123.5(13) | C(20)-C(19)-N | 115.9(10) |
| C(4)-C(5)-C(5M) | 118.5(12) | N-C(21)-C(22) | 116.6(10) |
| C(5)-C(6)-C(1) | 123.1(11) | N-C(23)-C(24) | 115.7(10) |
| C(8)-C(7)-C(12) | 119.9(10) | C(26)-C(25)-N | 114.9(10) |

[a] Estimated standard deviations are in parantheses. The atom labeling scheme is shown in Figure 2.

different environments, the *p*-TBP geometry is maintained and is consistent with the presence of a stereochemically active lone pair.

Lead(II) O,O'-diisopropylphosphorodithioate, Pb[(*i*-PrO)$_2$PS$_2$]$_2$ (F)[24] is an example of a higher coordinate structure with seven electron pairs in its valence shell that also exhibits the effect of a stereochemically active lone pair.[3]

It is noted that the nearly planar Pb(S$_2$P)$_2$ fragment shows a S4—Pb—S2 angle of 152.4° which is indicative of the presence of the lone pair. Overall, the geometry

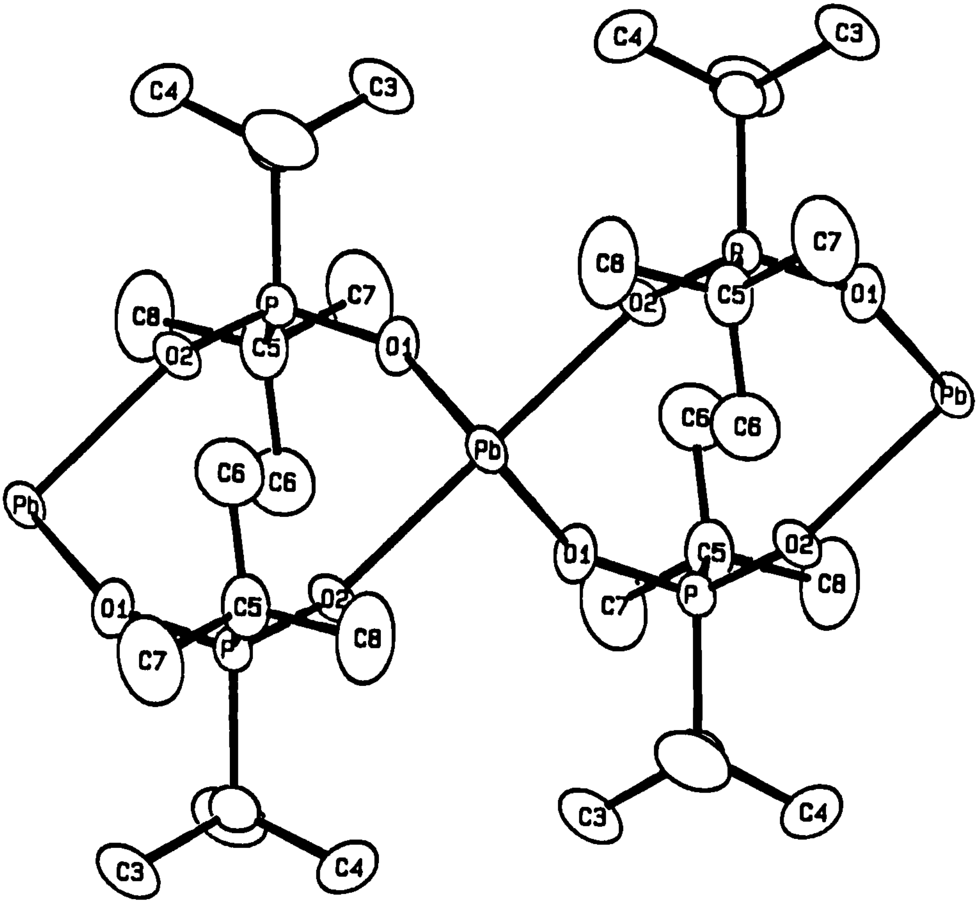


FIGURE 1 ORTEP plot of $[(t\text{-Bu})_2PO_2]_2Pb$ (**1**) with thermal ellipsoids at the 30% probability level, viewed down the crystallographic two-fold axis. Three symmetry related units are shown (−x, y, 1/2 − z; 1/2 − x, 1/2 − y, 1 − z; x − 1/2, 1/2 − y, z − 1/2) to complete the coordination sphere of the independent Pb atom. Hydrogen atoms are omitted for clarity.

closely approximates an irregular pentagonal bipyramid due to its polymeric nature consisting of staggered stacks with two out-of-plane sulfur atoms at each lead atom.

The monocyclic anionic dithiolato chloroplumbole **3** has a TBP geometry with the sulfur containing ring spanning axial-equatorial positions. The axial Pb—S distance (2.632(3) Å) is longer as expected compared to the equatorial Pb—S distance 2.515(3) Å, i.e., by 0.117 Å. An X-ray study of the bromo derivative **2** shows a TBP geometry with nearly the same bond parameters as the chloro plumbole **3**,[25] cf. Tables V and VI and Figures 2 and 3. Compared to **3**, the Pb—$S_{ax}$ distance for **2** is 2.627(3) Å and the Pb—$S_{eq}$ distance is 2.514(3) Å.

Consistent with the lower coordination geometry for **3** compared to **F**,[24] the Pb—S bond lengths are shorter on the average by 0.424 Å. The average Pb—S length for the pentacoordinated structure **3** is 2.574(3) Å and that for the pseudo-hepta-coordinate structure **F** is 2.997(9) Å. PbS itself has a NaCl lattice structure[26] with a

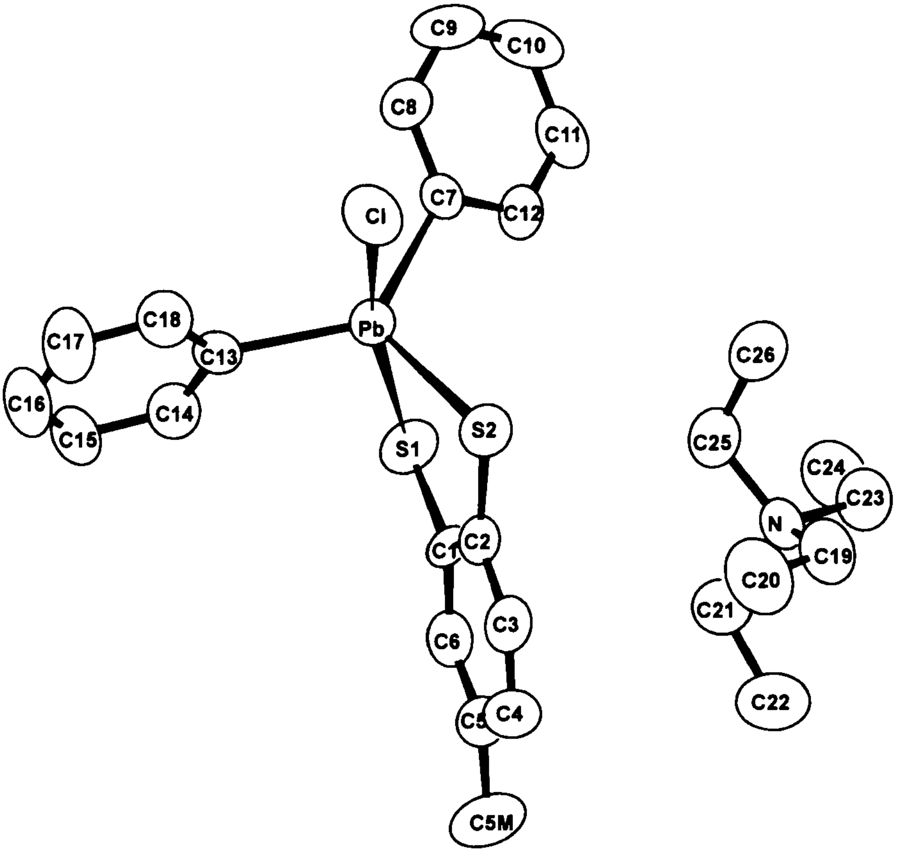
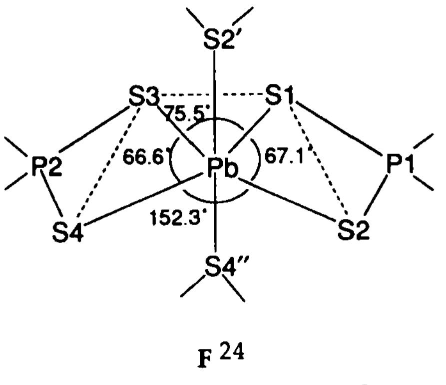


FIGURE 2 SNOOPI diagram of $[Et_4N][(MeC_6H_3S_2)PbPh_2Cl]$ (3) showing the molecular geometry and atom labeling scheme. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.



**F**[24]

lone pair and has an average Pb—S distance of 2.97 Å, comparable to that present in **F**.

The $^1H$ NMR spectra for the bromo and fluoro derivatives, **2** and **4**, respectively, are nearly the same as found for the same type of composition for **3**, thus implying similar structural forms in solution.

TABLE VI

Bond lengths [Å] and angles [deg] for $[Et_4N][(MeC_6H_3S_2)PbPh_2Br]$ (2)[a]

| | | | |
|---|---|---|---|
| Pb-C(13) | 2.22(1) | C(9)-C(10) | 1.37(2) |
| Pb-C(7) | 2.20(1) | C(10)-C(11) | 1.35(2) |
| Pb-S(2) | 2.514(3) | C(11)-C(12) | 1.40(2) |
| Pb-S(1) | 2.627(3) | C(13)-C(18) | 1.39(2) |
| Pb-Br | 2.898(3) | C(13)-C(14) | 1.38(2) |
| S(1)-C(1) | 1.76(1) | C(14)-C(15) | 1.39(2) |
| S(2)-C(2) | 1.77(1) | C(15)-C(16) | 1.39(2) |
| C(1)-C(2) | 1.41(1) | C(16)-C(17) | 1.35(2) |
| C(1)-C(6) | 1.40(2) | C(17)-C(18) | 1.41(2) |
| C(2)-C(3) | 1.36(2) | N-C(21) | 1.56(2) |
| C(3)-C(4) | 1.38(2) | N-C(19) | 1.50(1) |
| C(4)-C(5) | 1.40(2) | N-C(23) | 1.51(1) |
| C(5)-C(6) | 1.39(2) | N-C(25) | 1.52(2) |
| C(5)-C(5M) | 1.51(2) | C(19)-C(20) | 1.55(2) |
| C(7)-C(8) | 1.37(2) | C(21)-C(22) | 1.52(2) |
| C(7)-C(12) | 1.39(2) | C(23)-C(24) | 1.53(2) |
| C(8)-C(9) | 1.39(2) | C(25)-C(26) | 1.53(2) |
| C(13)-Pb-C(7) | 129.9(4) | C(5)-C(6)-C(1) | 124(1) |
| C(13)-Pb-S(2) | 116.3(2) | C(8)-C(7)-C(12) | 119(1) |
| C(7)-Pb-S(2) | 113.4(3) | C(7)-C(8)-C(9) | 120(1) |
| C(13)-Pb-S(1) | 97.1(3) | C(8)-C(9)-C(10) | 120(1) |
| C(7)-Pb-S(1) | 94.8(3) | C(11)-C(10)-C(9) | 121(1) |
| S(2)-Pb-S(1) | 82.91(9) | C(12)-C(11)-C(10) | 120(1) |
| C(13)-Pb-Br | 91.6(2) | C(11)-C(12)-C(7) | 120(1) |
| C(7)-Pb-Br | 87.7(2) | C(18)-C(13)-C(14) | 120(1) |
| S(2)-Pb-Br | 83.69(8) | C(13)-C(14)-C(15) | 122(1) |
| S(1)-Pb-Br | 166.25(7) | C(16)-C(15)-C(14) | 116(1) |
| C(1)-S(1)-Pb | 99.6(4) | C(17)-C(16)-C(15) | 124(1) |
| C(2)-S(2)-Pb | 102.2(4) | C(16)-C(17)-C(18) | 119(1) |
| C(2)-C(1)-C(6) | 117(1) | C(13)-C(18)-C(17) | 119(1) |
| C(2)-C(1)-S(1) | 125.1(8) | C(21)-N-C(19) | 110.2(8) |
| C(6)-C(1)-S(1) | 117.4(8) | C(21)-N-C(23) | 112.1(9) |
| C(3)-C(2)-C(1) | 120(1) | C(19)-N-C(23) | 107.4(8) |
| C(3)-C(2)-S(2) | 116.6(8) | C(21)-N-C(25) | 106.2(9) |
| C(1)-C(2)-S(2) | 123.7(8) | C(19)-N-C(25) | 111(1) |
| C(4)-C(3)-C(2) | 121(1) | C(23)-N-C(25) | 110.1(8) |
| C(3)-C(4)-C(5) | 122(1) | C(20)-C(19)-N | 117(1) |
| C(6)-C(5)-C(4) | 115(1) | N-C(21)-C(22) | 114.7(9) |
| C(6)-C(5)-C(5M) | 121(1) | N-C(23)-C(24) | 116(1) |
| C(4)-C(5)-C(5M) | 124(1) | C(26)-C(25)-N | 116(1) |

[a] Estimated standard deviations are in parantheses. The atom labeling scheme is shown in Figure 3.

In comparison with structural studies on lighter members of main Group IV elements, germanium ($[Ph_3PMe][MeC_6H_3S_2)_2GeF]\cdot CH_3CN$, G[11]) and tin ($[Et_4N][(MeC_6H_3S_2)Ph_2SnCl]$, H,[9] $[Me_4N][MeC_6H_3S_2)_2SnCl]$, I[9] and $[Ph_3PMe][(MeC_6H_3S_2)_2SnBr]$, J[27]) form anionic pentacoordinate geometries with the use of toluene-3,4-dithiol as a coordinating ligand. However, silicon does not. This was attributed[27] to the special stability of Sn—S bonding in these compounds provided by a proper balance of low tin atom electronegativity vs the tendency of tin to increase its co-

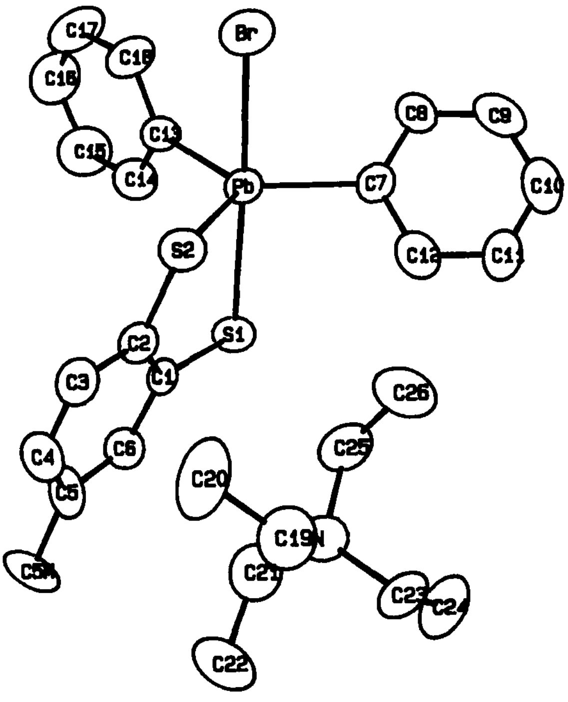
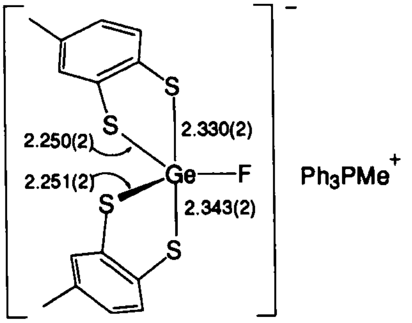


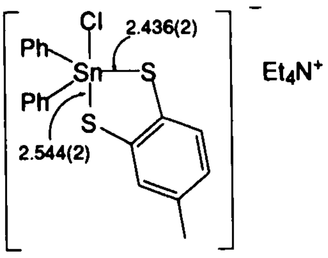
FIGURE 3 ORTEP plot of $[Et_4N][(MeC_6H_3S_2)PbPh_2Br]$ (2) showing the molecular geometry and atom labeling scheme. Hydrogen atoms are omitted for clarity.

ordination number toward hexacoordinate when Sn—O bonds are present due to the resultant greater tin acidity. In view of the anionic TBP geometry found for **3** and the pseudo-heptacoordinate geometry for **F**,[24] this same stabilizing effect appears to hold for the formation of Pb—S bonds in hypervalent compounds. It might be said that this is an application of the hard-soft acid-base concept[28,29] where relatively soft lead and sulfur give a preference to Pb—S bonding and hard silicon and oxygen give a preference to Si—O bonding.

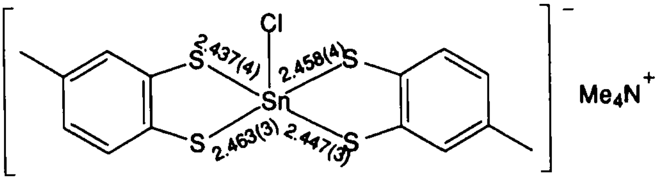
Metal-sulfur bond lengths in Å are shown in the schematics for **G–J**. Also the extent of geometrical change from a TBP to a square pyramid (SP) is given. As is usual for bicyclic derivatives of main group elements with unsaturated rings and having like atoms in each ring system bonded to the central atom, the resulting structure tends toward square pyramidal,[30–32] as is found for **I** and **J**. In contrast, monocyclic pentacoordinate derivatives like **H** tend to be close to TBP. All of the derivatives **G–J** lie along the Berry coordinate.[33] However, the monocyclic plumbole **3**, although near TBP, has a non-Berry geometry in that the equatorial C13—Pb—C7 angle is expanded to 127.6(4)° from the ideal 120° angle while the axial Cl—Pb—S1 angle of 165.8(1)° has deviated from 180° in the direction of the equatorial atom S2 rather than away from S2 (Figure 2). Similarly, the C13—Pb—C7 angle for the bromo derivative **2** is 129.9(4)° and the Br—Pb—S1 angle is 166.25(7)°, like **3**, with the axial atoms tipped toward the equatorial atom S2.



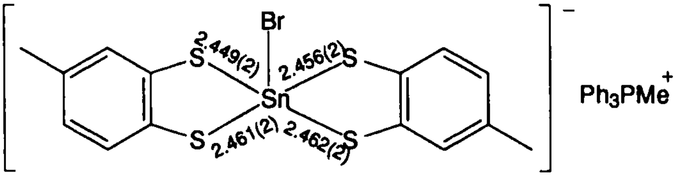
$G^{11}$ (TBP → SP, 40.3%)



$H^9$ (TBP → SP, 14.1%)



$I^9$ (TBP → SP, 76.9%)



$J^{27}$ (TBP → SP, 94.2%)

### *Structural Details for* 1

In **1**, the Pb atoms lie on crystallographic two-fold axes with the $(t\text{-Bu})_2PO_2$ ligands in general positions. The two-fold axes generate a second phosphinate ligand for every Pb atom, consistent with the formulation $[(t\text{-Bu})_2PO_2]_2Pb$. Pairs of n-glide related Pb atoms are bridged by two inversion related phosphinate groups, resulting in an extended chain structure containing four-coordinate Pb atoms in the solid.

## CONCLUSION

The formation of **1** extends our knowledge of the ability of Pb(II) to exert stereochemical lone pair effects in *p*-TBP geometries. Like the lighter cogeners in Group IVA, i.e., Ge and Sn, Pb(IV) is capable of forming an anionic TBP geometry with a dithiolato cyclic ligand. However, this is not observed for Si.

## ACKNOWLEDGEMENT

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