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The Crystal and Molecular Structure of Polymeric Lead(II) *O,O'*-Diisopropylphosphorodithioate, Pb[(*i*-$C_3H_7O)_2PS_2]_2$. Deformation of a Hexathiocoordinate Lead Group by a Stereochemically Active Lone Pair of Electrons

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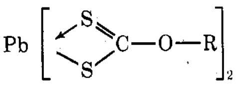
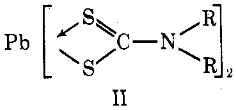
Lead(II) *O,O'*-diisopropylphosphorodithioate crystallizes as light gray needles in the monoclinic space group C_{2h}^5-$P2_1/n$ with $a = 25.290 \pm 0.004$, $b = 10.067 \pm 0.002$, $c = 9.335 \pm 0.002$ Å, $\beta = 95.97 \pm 0.02°$, $d_{obsd} = 1.77 \pm 0.02$ g/cm^3, and $d_{calcd} = 1.781 \pm 0.001$ g/cm^3 for $Z = 4$ formula weights/unit cell. The structure was refined by least-squares methods using three-dimensional X-ray diffraction data collected by counter methods. The final R index based on F for 2034 reflections above $2\sigma(F_o)$ was 0.056. In the solid material Pb[(*i*-$C_3H_7O)_2PS_2]_2$ units form polymeric chains extending along the needle axis. Nearly planar Pb$(S_2P)_2$ groups stack one above the other in a staggered arrangement joined by intergroup Pb–S bonds. Each lead atom is surrounded by six sulfur atoms: two at relatively short distances of 2.766 (8) Å, two at intermediate distances of 3.01 (3) Å, and two at 3.20 (4) Å. One S–Pb–S angle at 152.3 ± 0.1° and three in the range from 66.6 ± 0.2 to 75.5 ± 0.1° correspond to the largest angular deviations from 90° in the lead coordination sphere. The bending and stretching deformations of the PbS_6 group from O_h symmetry are consistent with the classical apportioning of fourteen electrons (seven pairs) in the valence shell of lead, of which six pairs are bonding and one is a stereochemically active lone pair, in accord with the Gillespie–Nyholm valence-shell electron-pair repulsion (VSEPR) model. The resulting configuration closely approximates an irregular pentagonal bipyramid in which the lone pair occupies an equatorial position and thus represents an authentic example of its type for a nontransition element in sixfold coordination. Extension of the VSEPR rules to other lead compounds with sulfur chelates reveals that the lead(II) alkylxanthates display molecular configurations, entailing coordination numbers less than 6, which can also be accounted for unequivocally by the presence of a lone pair of electrons.

Introduction

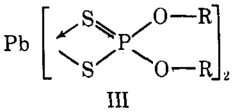
Dithiocoordinate chelates of lead have been the subjects of recent structural investigations. Those examined thus far have included the alkylxanthates, I, where R = C_2H_5,[1] *i*-C_3H_7,[2] and *n*-C_4H_9,[3] and the dialkyldithiocarbamate, II, where R = C_2H_5.[4] We now wish to report the structure of a third lead derivative, that of an *O,O'*-dialkylphosphorodithioate, III, where R = *i*-C_3H_7. The crystal structure was determined as part of a research program in our laboratory[5,6] related to the study of metal phosphorodithioates as lubricating oil additives.



I



II



III

Prior to our present study, vapor pressure osmometry data had revealed that in benzene at 38° in concentrations less than 0.035 g/cm^3 Pb[(*i*-$C_3H_7O)_2PS_2]_2$, hereafter referred to as Pb(dtp)$_2$, exists as monomers in equilibrium with dimers.[5] These data suggested that in the crystalline form the substance was likely to exist as a polymer of some sort, with a polymerization number, *n*, at least equal to 2. Accordingly, the probable molecular architecture would not resemble the monomeric alkylxanthates but rather would exhibit a configuration displayed by dimeric $Pb_2[(C_2H_5)_2NCS_2]_4$[4] or, alternatively, a bridged polymeric structure in which lead would possess a coordination number of 4 or greater.

Results of our structural investigation have revealed the presence of infinite polymeric chains in the solid material formed by two sulfur atoms in each Pb(dtp)$_2$ unit symmetrically bridging two lead atoms, expanding the coordination number of lead from 4 to 6. The significance of this type of inter-Pb(dtp)$_2$ interaction, in which the two bridging sulfur atoms *each* donate *two* extra electrons into the valence shell of lead, is to increase the number of valence electrons from ten to *fourteen*, thereby making the PbS_6 group "formally" isoelectronic with XeF_6. Assessment of the bond lengths and bond angles within this group revealed the striking discovery of a stereochemically "active" lone pair of electrons radiating from lead. A preliminary report of our findings has been published.[7] We now wish to give a full account of this structure.

Experimental Section

Preparation.—Lead *O,O'*-diisopropylphosphorodithioate was synthesized utilizing a method previously described.[5,6] Soft, light gray needles for use in the structure determination were obtained by recrystallization of the compound from warm absolute ethanol.

Crystal Data.—Pb(dtp)$_2$, formula weight 633.75, is monoclinic with space group $P2_1/n$ (C_{2h}^5). The lattice parameters at 24° are $a = 25.290$ (4), $b = 10.067$ (2), $c = 9.335$ (2) Å, $\beta = 95.97$ (2)°, and $V = 2364$ (2) Å^3; $d_{obsd} = 1.77$ (2) g/cm^3 (by flotation) and $d_{calcd} = 1.781$ (1) g/cm^3 for $Z = 4$ formula weights/

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(1) H. Hagihara and S. Yamashita, *Acta Crystallogr.*, **21**, 350 (1966).

(2) H. Hagihara, N. Yoshida, and Y. Watanabe, *ibid., Sect. B*, **25**, 1775 (1969).

(3) H. Hagihara, Y. Watanabe, and S. Yamashita, *ibid., Sect. B*, **24**, 960 (1968).

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(5) I. J. Heilweil, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **10**, No. 4-D, 19 (1965).

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(7) S. L. Lawton and G. T. Kokotailo, *Nature* (*London*), **221**, 550 (1969).

unit cell. The crystal habit is acicular and elongated along the *c* direction.

The crystal symmetry was determined from Weissenberg photographs which, initially, yielded systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) consistent with the space groups Cc and $C2/c$. Overexposed photographs, however, revealed the presence of additional weak reflections which destroyed the *C*-centering operation, indicating the correct space group to be $P2_1/n$, based on $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$. The lattice parameters were determined by a least-squares fit[8] to 117 high-angle Kα reflections measured from zero-level Weissenberg zones taken with copper radiation (λ_1 1.54050 Å, λ_2 1.54434 Å) using crystals mounted in three different orientations; each film was calibrated with superimposed aluminum powder lines ($a_0 = 4.0330$ Å). The Nelson–Riley extrapolation function was employed in the refinement. Indicated errors in the cell parameters are 2σ.

Collection and Reduction of X-Ray Intensity Data.—Complete three-dimensional X-ray diffraction intensity data were taken at room temperature with zirconium-filtered molybdenum Kα radiation from a needlelike crystal 0.34 mm long and of cross section 0.09 × 0.13 mm. The crystal was mounted in a 0.3-mm Lindemann glass capillary parallel with its longest dimension (*c* axis) and mounted on the diffractometer with c^* coincident with the ϕ axis. The half-widths of a number of narrow source-open counter 2θ scans[9] ranged from 0.07° (c^* vector) to 0.17° (a^* and b^* vectors) in θ, indicating that the crystal mosaicity was small though somewhat anisotropic. A General Electric quarter-circle Eulerian cradle mounted on a Siemens diffractometer equipped with a Siemens scintillation detector and pulse height discriminator was used to collect the intensity data with the moving-crystal–moving-counter measurement technique (θ, 2θ coupling) and a 3.5° takeoff angle. The crystal–source and crystal–counter distances were 17 and 18.5 cm, respectively. The receiving aperture size selected to minimize extraneous background was 5.0 mm wide by 5.0 mm high. The counter angle, 2θ, was scanned over 2° at a speed of 1°/min. Background counts of 24 sec were taken at each end of the 2θ scan. A total of 5747 independent reflections in the range $2\theta \leq 55°$ were collected. Three standard reflections were measured periodically as a check on electronic and crystal stability and a total 9.6% decrease in intensities was observed.

The raw intensity of each reflection was corrected for background, crystal decomposition, Lorentz, polarization, and absorption effects. Transmission factors were calculated by the program ACACA.[10] The crystal was defined as an ellipsoidal needle with minor and major diameters 0.0926 mm and 0.1360 mm, respectively; these diameters were a modification of those obtained by optical measurement and were determined by utilizing a method previously described.[11] The transmission factors for the full set of three-dimensional data ranged from 0.397 to 0.557, based on a linear absorption coefficient of 75.20 cm^{-1} for Mo Kα radiation. Estimated standard deviations in the intensities were computed as described elsewhere,[12] using a value of 0.05 for p. The estimated standard deviation of each structure factor was calculated by employing the finite-difference method of Williams and Rundle.[13] A total of 2298 independent reflections were observed above the background level of which 2034 (1883 of type $h + k = 2n$, 151 of type $h + k = 2n + 1$) had $F_o > 2\sigma(F_o)$. The remaining 264 reflections were considered as unobserved and therefore omitted from the refinements.

Solution and Refinement of the Structure

Solution of the structure was achieved by standard heavy-atom techniques. A three-dimensional Patterson function yielded a consistent set of trial coordinates for the lead and two of the four sulfur atoms.[14] A subsequent series of three-dimensional electron density functions (F and ΔF) and isotropic least-squares refinements led to the location of all but three of the remaining nonhydrogen atoms in the structure. Of the four isopropyl groups, only three were readily located.

The structure was refined by using a full-matrix least-squares procedure. The function minimized was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$, with $|F_o|$ and $|F_c|$ being the observed and calculated structure amplitudes, respectively, and w the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral atoms tabulated by Hanson, *et al.*,[15] were used. Real and imaginary dispersion corrections for Pb, S, and P[16] were applied to the calculated structure factors.[17] The best fully weighted isotropic refinement of all 20 atoms plus the scale factor resulted in $R_1 = \Sigma|\Delta|/\Sigma|F_o| = 0.080$ and $R_2 = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2} = 0.071$ for the reflections above $2\sigma(F_o)$. Additional least-squares cycles with anisotropic thermal parameters assigned to Pb, S, and P reduced R_1 and R_2 to 0.068 and 0.064, respectively.

A three-dimensional difference Fourier synthesis calculated at this stage now revealed the location of the previously unresolved isopropyl group. This group was found to be statistically disordered in two major conformations, such that three of the six carbon peaks overlapped to produce one large peak and three small peaks; from these peaks plausible coordinates of the six carbon positions were determined. A meaningful refinement of the atoms was achieved by treating the disordered group as two rigid bodies constrained to C_{2v} symmetry using the least-squares group refinement procedure described by Ibers, *et al.*[18] In this refinement C–C bond lengths of 1.48 Å and C–C–C bond angles of 113° were assumed. The bond length was derived from the average length observed in isopropyl groups 2 and 4 of the present investigation[19] and the bond angle from the average value observed in the molecule $[(i\text{-}C_3H_7O)_2PS_2]_2$.[21] Each group was assigned a single, variable isotropic thermal parameter, six variable positional parameters, and a fixed population parameter of 0.5. This initial refinement of the isopropyl groups, together with the other atoms and the scale factor, converged rapidly to discrepancy values of $R_1 = 0.061$ and $R_2 = 0.042$. Three additional cycles of least-squares refinement were then run with the disordered group given multiplicities of α (for group 3A) and $(1 - \alpha)$ (for group 3B) with the parameter α being treated as a variable. These least-squares calculations yielded a value of $\alpha = 0.54$ (2) indicating that we have approximately a 50% disorder in this group. The disorder was fixed at 50% during all remaining cycles of refinement.

Up to this point the refinement had proceeded with one overall isotropic thermal parameter per rigid isopropyl group. In other structures containing these groups in which the carbon atoms were allowed to refine with individual isotropic thermal parameters the methyl carbons were generally found to exhibit larger thermal parameters than do the vertex carbons. In order to approximate more closely this motion, a percentage correction was applied to the individual thermal parameters of each carbon in the two groups. A value of 28% was subtracted from the refined overall thermal parameter for the vertex carbon and 14% was added for each methyl carbon. These percentage corrections were average values derived from other diisopropylphosphorodithioate structures refined in this laboratory. In subsequent calculations only the overall value was refined.

In the final round of calculations the three ordered isopropyl groups were also treated as rigid bodies constrained to C_{2v} sym-

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[8] D. E. Williams, "LCR-2, A Fortran Lattice Constant Refinement Program," Report IS-1052, Ames Laboratory, Iowa State University, Ames, Iowa, 1964.

[9] In the region examined, $2\theta < 19°$, the 2θ-scan and ω-scan techniques yield comparable results: T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

[10] B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **122**, 24 (1965); C. T. Prewitt, "ACACA, A Fortran Polyhedral Absorption Correction Program," Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del., 1966.

[11] S. L. Lawton, *Inorg. Chem.*, **10**, 328 (1971).

[12] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *ibid.*, **6**, 197 (1967).

[13] D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

[14] In addition to various local programs for the CDC 1604B computer, local modifications of the following programs were used in the solution and refinement of the structure: Guggenberger's FOUR Fourier program; Doedens and Ibers' NUCLS crystallographic least-squares group refinement program; Busing and Levy's ORFFE function and error program; Johnson's ORTEP thermal ellipsoid plotting program.

[15] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

[16] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

[17] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

[18] S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

[19] The value 1.48 Å, compared to the expected value of 1.54 Å for a C–C single bond, represents a foreshortening of the bond due to thermal and librational effects.[20]

[20] D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 757 (1965); **14**, 896 (1961); W. R. Busing and H. A. Levy, *ibid.*, **17**, 142 (1964); V. Schomaker and K. N. Trueblood, *ibid., Sect. B*, **24**, 63 (1968).

[21] S. L. Lawton, *Inorg. Chem.*, **9**, 2269 (1970).

TABLE I

FINAL POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Atom	x[b]	y	z	β_{11} or B[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv, B,[d] Å^2
Pb	0.49961 (9)	0.52870 (5)	0.24930 (30)	0.00170 (1)	0.01038 (6)	0.01061 (6)	−0.00002 (7)	0.00002 (2)	−0.00034 (20)	4.08
S(1)	0.5561 (4)	0.7379 (7)	0.3809 (13)	0.0029 (2)	0.0116 (8)	0.0154 (17)	−0.0007 (3)	−0.0010 (4)	0.0004 (9)	5.86
S(2)	0.5768 (4)	0.4388 (7)	0.5302 (13)	0.0020 (2)	0.0092 (8)	0.0180 (16)	0.0003 (2)	0.0003 (4)	0.0035 (7)	5.06
S(3)	0.4517 (4)	0.7536 (7)	0.1229 (14)	0.0034 (2)	0.0116 (9)	0.0175 (19)	0.0014 (4)	−0.0013 (5)	−0.0018 (9)	6.57
S(4)	0.4205 (4)	0.4660 (7)	−0.0293 (11)	0.0020 (2)	0.0143 (9)	0.0101 (11)	0.0002 (3)	0.0008 (3)	−0.0017 (8)	4.73
P(1)	0.6008 (4)	0.6260 (8)	0.5230 (11)	0.0017 (1)	0.0170 (10)	0.0099 (12)	0.0000 (3)	0.0006 (3)	−0.0016 (9)	4.82
P(2)	0.4054 (4)	0.6550 (8)	−0.0210 (12)	0.0020 (2)	0.0139 (9)	0.0113 (13)	0.0018 (3)	−0.0003 (3)	0.0005 (8)	4.88
O(1)	0.6020 (6)	0.6796 (13)	0.6829 (17)	5.6 (4)						
O(2)	0.6620 (4)	0.6317 (11)	0.5018 (12)	4.1 (3)						
O(3)	0.4056 (5)	0.7160 (14)	−0.1741 (16)	4.9 (3)						
O(4)	0.3464 (5)	0.6866 (12)	0.0107 (14)	5.4 (3)						

Group	x_c[e]	y_c	z_c	δ	ϵ	η
$C_3H_7(1)$	0.6115 (9)	0.8400 (15)	0.7725 (20)	1.400 (17)	−3.154 (18)	1.251 (45)
$C_3H_7(2)$	0.7014 (5)	0.5873 (13)	0.3529 (16)	−2.965 (14)	−2.717 (14)	−2.817 (33)
$C_3H_7(3A)$	0.4002 (9)	0.8921 (22)	−0.2499 (26)	1.123 (38)	−2.243 (23)	−1.417 (66)
$C_3H_7(3B)$	0.3904 (18)	0.8839 (34)	−0.2429 (49)	1.974 (47)	2.579 (40)	−0.967 (112)
$C_3H_7(4)$	0.3069 (5)	0.6470 (13)	0.1579 (16)	2.799 (14)	2.746 (15)	0.417 (35)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter. [b] Coordinates are based on positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] B's are isotropic thermal parameters equivalent to the anisotropic tensors: W. C. Hamilton, *Acta Crystallogr.*, **12,** 609 (1959). [e] x_c, y_c, z_c are fractional coordinates of the centroids. The angles δ, ϵ, η (in radians) are those described in ref 18. The origin of the internal system was taken at the group centroid with a_3 normal to the plane and a_1 bisecting the C–C–C angle.

TABLE II

DERIVED POSITIONAL AND THERMAL PARAMETERS FOR GROUP ATOMS IN $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$

Atom	x	y	z	B, Å^2
		$C_3H_7(1)$		
C(1)	0.6106 (10)	0.8232 (25)	0.7169 (21)	8.0 (8)
C(2)	0.6603 (9)	0.8275 (28)	0.8156 (33)	11.8 (9)
C(3)	0.5636 (8)	0.8693 (30)	0.7851 (31)	12.5 (9)
		$C_3H_7(2)$		
C(4)	0.6807 (5)	0.5853 (16)	0.3640 (21)	5.7 (5)
C(5)	0.7039 (8)	0.6983 (15)	0.2906 (25)	8.1 (6)
C(6)	0.1796 (8)	0.4783 (16)	0.4040 (26)	8.9 (6)
		$C_3H_7(3A)$		
C(7A)	0.4138 (12)	0.8665 (38)	−0.2101 (29)	4.5[a]
C(8A)	0.4209 (14)	0.8718 (37)	−0.3654 (32)	7.2
C(9A)	0.3658 (14)	0.9379 (42)	−0.1741 (36)	7.2
		$C_3H_7(3B)$		
C(7B)	0.3864 (26)	0.8463 (50)	−0.2034 (57)	9.0[b]
C(8B)	0.4305 (23)	0.9434 (62)	−0.1814 (63)	14.3
C(9B)	0.3542 (24)	0.8620 (60)	−0.3440 (69)	14.3
		$C_3H_7(4)$		
C(10)	0.3267 (6)	0.6383 (17)	0.1417 (22)	6.0 (5)
C(11)	0.3122 (8)	0.7579 (17)	0.2213 (25)	8.5 (6)
C(12)	0.2818 (8)	0.5448 (17)	0.1108 (29)	9.6 (7)

[a] Average refined group B = 6.3 (5) Å^2. [b] Average refined group B = 12.5 (13) Å^2.

metry; in addition to the variable coordinates of the group centroid and the three group orientation angles, each carbon atom was assigned an individual variable isotropic thermal parameter. Positions of the hydrogen atoms were then computed[22] and their contributions to F_c were included in subsequent calculations as fixed atoms. A single overall isotropic thermal parameter was refined for the 35 hydrogens.

Convergence was reached with R_1 = 0.056 and R_2 = 0.037 for the 2034 observed reflections. Corresponding values for all 2298 reflections were R_1 = 0.072 and R_2 = 0.044. The final error of fit based on the 122 variables was 1.50. The relative correctness of the weighting scheme, as judged by the variation of mean $w\Delta^2$ with $|F_o|$ and $(\sin \sigma)/\lambda$, was satisfactory. A final difference Fourier synthesis indicated that all electron density had been correctly accommodated.[23]

TABLE III

CALCULATED POSITIONAL PARAMETERS (×10^3) FOR HYDROGEN IN $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Atom[b]	x	y	z	Atom[b]	x	y	z
C(1)H(1)	614	873	629	C(9A)H(19A)	335	904	−231
C(2)H(2)	656	777	902	C(9A)H(20A)	362	927	−071
C(2)H(3)	689	789	766	C(9A)H(21A)	370	1034	−195
C(2)H(4)	669	920	840	C(7B)H(15B)	361	869	−130
C(3)H(5)	561	818	874	C(8B)H(16B)	456	924	−253
C(3)H(6)	568	964	810	C(8B)H(17B)	417	1033	−193
C(3)H(7)	531	858	719	C(8B)H(18B)	449	931	−084
C(4)H(8)	651	550	301	C(9B)H(19B)	377	842	−422
C(5)H(9)	734	735	353	C(9B)H(20B)	324	800	−353
C(5)H(10)	716	668	200	C(9B)H(21B)	341	953	−357
C(5)H(11)	677	768	270	C(10)H(22)	356	592	199
C(6)H(12)	750	515	467	C(11)H(23)	283	805	165
C(6)H(13)	702	409	456	C(11)H(24)	301	731	314
C(6)H(14)	732	442	317	C(11)H(25)	343	816	238
C(7A)H(15A)	446	900	−153	C(12)H(26)	252	589	054
C(8A)H(16A)	389	837	−422	C(12)H(27)	293	468	058
C(8A)H(17A)	427	964	−393	C(12)H(28)	270	514	202
C(8A)H(18A)	452	818	−384				

[a] Coordinates are based on C–H = 0.98 Å. The final refined overall isotropic temperature factor for hydrogen is B = 9.4 (13) Å^2. [b] C(m)H(n) is hydrogen n of carbon m.

TABLE IV

FINAL ROOT-MEAN-SQUARE THERMAL AMPLITUDES OF VIBRATION (Å) IN $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$

Atom	Min	Med	Max
Pb	0.2102 (9)	0.2313 (9)	0.2397 (8)
S(1)	0.236 (11)	0.246 (10)	0.326 (11)
S(2)	0.199 (9)	0.257 (11)	0.294 (11)
S(3)	0.231 (10)	0.256 (13)	0.362 (12)
S(4)	0.203 (11)	0.251 (10)	0.275 (8)
P(1)	0.203 (12)	0.231 (9)	0.298 (9)
P(2)	0.196 (11)	0.234 (12)	0.303 (10)

The final positional, thermal, and group parameters are given in Table I, along with the associated standard deviations as derived from the inverse matrix, while Table II lists the final positional parameters of the isopropyl atoms derived from the group parameters. The calculated hydrogen positions are listed in Table III. Root-mean-square thermal displacements along the directions of the principal axes for those atoms refined anisotropically are given in Table IV. Table V[24] lists the observed

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(22) Idealized hydrogen coordinates were computed assuming C–H bond lengths of 0.98 Å, H–C–H bond angles of 109° 28′, and the methyl groups rotated to give perfect staggered conformations with respect to the C–H bonds radiating from the vertex carbon atoms.[21]

(23) This compound was originally reported to contain 1 mol of water per metal atom, as determined by the Karl Fischer method.[5,6] The final results of the present structural investigation, based on this difference Fourier synthesis, *strongly* indicate the complete absence of water of crystallization in the crystal.

(24) Table V will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, be referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche. Included in the listing (F_c only) is the strong first-order 110 reflection excluded from the refinement; its 2θ value of 4.36° brought the reflection too close to the main X-ray beam to be accurately measured.

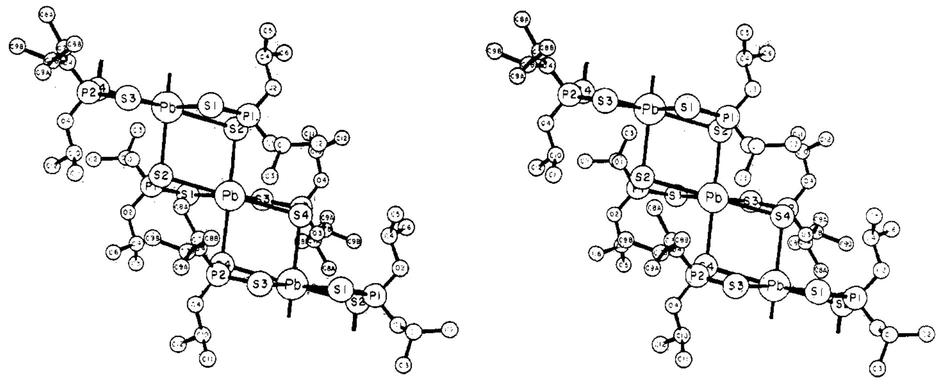

Figure 1.—A stereographic view of three $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$ units within the infinite chain. View is along the pseudo-C_2 symmetry axis.

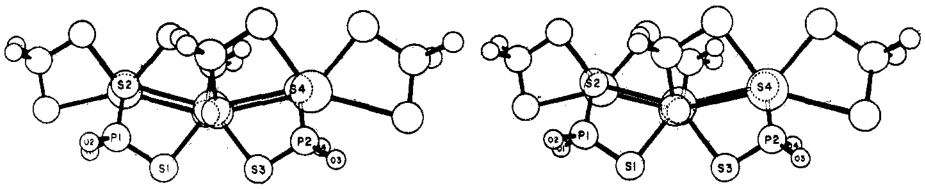

Figure 2.—A stereographic view of three $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$ units along the infinite chain. For clarity, the isopropyl groups are not shown.

TABLE VI
INTERATOMIC DISTANCES AND ANGLES IN
$Pb[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Bond Lengths, Å[b]

Pb···Pb′	4.714 (6)	P(1)–S(2)	1.982 (13)
Pb···Pb″	4.692 (6)	P(2)–S(3)	1.958 (13)
Pb–S(1)	2.761 (7)	P(2)–S(4)	1.944 (12)
Pb–S(3)	2.772 (7)	P(1)–O(1)	1.584 (17)
Pb–S(2′)	2.985 (12)	P(1)–O(2)	1.582 (14)
Pb–S(4″)	3.027 (11)	P(2)–O(3)	1.556 (17)
Pb–S(2)	3.232 (10)	P(2)–O(4)	1.584 (16)
Pb–S(4)	3.175 (9)	O(1)–C(1)	1.49 (3)
S(1)···S(2)	3.336 (10)	O(2)–C(4)	1.49 (2)
S(1)···S(3)	3.387 (7)	O(3)–C(7A)	1.57 (4)
S(3)···S(4)	3.284 (10)	O(3)–C(7B)	1.41 (5)
P(1)–S(1)	2.000 (14)	O(4)–C(10)	1.45 (2)

Bond Angles, Deg

S(1)–Pb–S(2)	67.1 (2)	S(2)–P(1)–O(1)	105.5 (8)
S(1)–Pb–S(2′)	87.3 (3)	S(2)–P(1)–O(2)	110.2 (7)
S(1)–Pb–S(3)	75.5 (1)	S(3)–P(2)–O(3)	111.8 (9)
S(1)–Pb–S(4″)	86.4 (3)	S(3)–P(2)–O(4)	106.2 (8)
S(2)–Pb–S(2′)	81.4 (3)	S(4)–P(2)–O(3)	109.3 (8)
S(2)–Pb–S(4)	152.3 (1)	S(4)–P(2)–O(4)	113.4 (7)
S(2)–Pb–S(4″)	99.5 (3)	O(1)–P(1)–O(2)	110.5 (9)
S(2′)–Pb–S(3)	85.3 (3)	O(3)–P(2)–O(4)	100.7 (8)
S(2′)–Pb–S(4)	100.9 (3)	P(1)–O(1)–C(1)	121.3 (12)
S(2′)–Pb–S(4″)	172.6 (2)	P(1)–O(2)–C(4)	119.9 (9)
S(3)–Pb–S(4)	66.6 (2)	P(2)–O(3)–C(7A)	126.2 (15)
S(3)–Pb–S(4″)	89.4 (3)	P(2)–O(3)–C(7B)	120.7 (26)
S(4)–Pb–S(4″)	81.7 (2)	P(2)–O(4)–C(10)	120.2 (10)
Pb–S(2)–Pb′	98.6 (3)	O(1)–C(1)–C(2)	105 (2)
Pb-S(4)–Pb″	98.3 (2)	O(1)–C(1)–C(3)	107 (2)
Pb–S(1)–P(1)	95.5 (4)	O(2)–C(4)–C(5)	110 (1)
Pb–S(2)–P(1)	82.4 (4)	O(2)–C(4)–C(6)	106 (1)
Pb–S(3)–P(2)	94.7 (4)	O(3)–C(7A)–C(8A)	106 (2)
Pb–S(4)–P(2)	83.3 (4)	O(3)–C(7A)–C(9A)	107 (2)
S(1)–P(1)–S(2)	113.8 (6)	O(3)–C(7B)–C(8B)	110 (4)
S(3)–P(2)–S(4)	114.6 (6)	O(3)–C(7B)–C(9B)	115 (4)
S(1)–P(1)–O(1)	112.8 (8)	O(4)–C(10)–C(11)	106 (1)
S(1)–P(1)–O(2)	112.9 (8)	O(4)–C(10)–C(12)	112 (1)

[a] Primed atoms correspond to the following symmetry positions: Pb′ and S(2′) at $1 - x, 1 - y, 1 - z$; Pb″ and S(4″) at $1 - x, 1 - y, \bar{z}$. These positions are illustrated in Figure 4.
[b] Bonds are signified by dashes and nonbonds by dots.

and calculated structure factors (in electrons × 10) for all reflections above $2\sigma(F_o)$. Selected bond lengths and angles are given in Table VI together with their standard deviations as derived from the variance–covariance matrix for functions involving nongroup atoms and from variances alone for those involving group atoms.[25] The bond lengths have not been corrected for thermal effects. In view of the disorder, distances and angles involving C_3H_7 (3A) and C_3H_7 (3B) should not be taken seriously.

Description of the Structure

Lead(II) *O,O′*-diisopropylphosphorodithioate exists in the crystalline form as polymeric chains. Nearly planar $Pb(S_2P)_2$ groups stack one above the other in a staggered arrangement joined by intergroup Pb–S bonds. These bonds may be considered as "axial bonds" in the resultant sixfold coordination of sulfur around lead(II). Of the four "equatorial" sulfurs within a $Pb(S_2P)_2$ group only two, cis to each other, are involved in the intergroup bonding. Figures 1 and 2 show stereographic views of three $Pb(dtp)_2$ units within the chain and Figure 3 portrays the packing of these chains in the crystal. Each unit is related to its associated neighbor by a center of symmetry. There are no Pb–S linkages between chains. Results of least-squares analyses of the planarity of the ligands are given in Table VII.[26] By virtue of the relatively strong binding between adjacent $Pb(dtp)_2$ units, the two "equatorial" ligands are twisted out of coplanarity; the dihedral angle between the two planes is 17.1°.

Within the polymeric chain the closest methyl··· methyl approaches occur between $C_3H_7(1)$ at x, y, z and $C_3H_7(3''')$ at $x, y, 1 + z$. Corresponding distances less than a normal value of 4.0 Å are C(3)···C(8B‴) at 3.5 Å, C(3)···C(8A‴) at 3.7 Å, and C(3)···C(7A‴) at 3.8 Å. All other intermolecular contacts, including methyl···sulfur and methyl···oxygen, assume normal van der Waals distances.

Of particular interest is the arrangement of sulfur atoms about any given lead atom. The striking dis-

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(25) F. R. Ahmed and D. W. Cruickshank, *Acta Crystallogr.*, **6**, 385 (1953).

(26) Weights were based on the variance–covariance matrix as obtained from the final cycle of least-squares refinement: W. C. Hamilton, *ibid.*, **14**, 185 (1961).

TABLE VII

WEIGHTED LEAST-SQUARES PLANES AND DISTANCES (Å) OF THE ATOMS FROM THEIR RESPECTIVE PLANES[a]

Plane A: $0.7830X - 0.1805Y - 0.5952Z - 7.3640 = 0$

Plane B: $0.8027X + 0.1165Y - 0.5849Z - 9.2160 = 0$

Plane A	Pb	0.002 (2)	S(1)	−0.087 (10)	S(2)	−0.071 (9)	P(1)	0.109 (9)
Plane B	Pb	−0.002 (2)	S(3)	0.075 (10)	S(4)	0.049 (9)	P(2)	−0.088 (9)

[a] The orthogonal coordinate system (X, Y, Z) used for each least-squares plane is $X = xc \cos \beta$, $Y = by$, $Z = zc \sin \beta$.

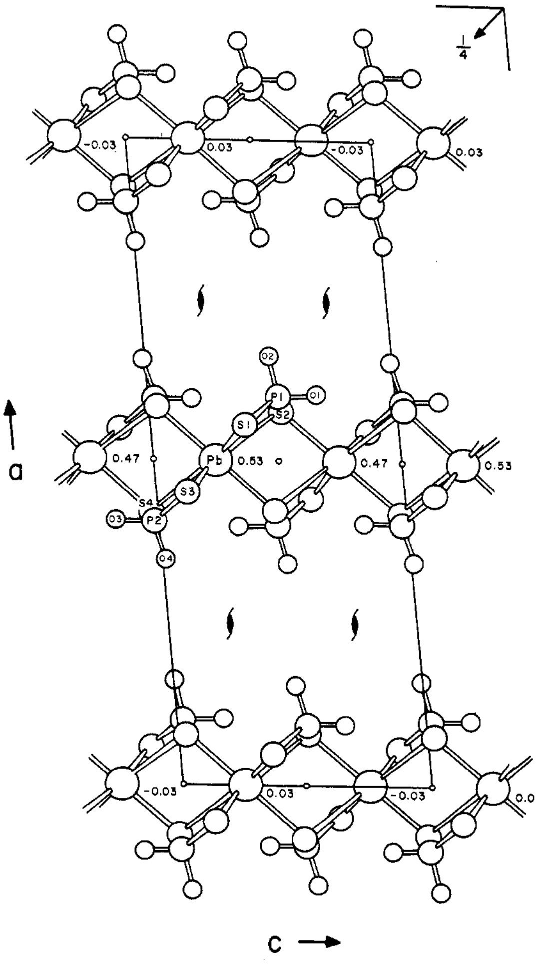

Figure 3.—[010] projection of the primitive unit cell of Pb[$(i\text{-}C_3H_7O)_2PS_2]_2$. The numbered atoms define the asymmetric unit (Table I). Numbers adjacent to the Pb atoms represent the fractional unit cell y coordinate (elevation) of these atoms, where the plane of the paper is $y = 0.0$. For clarity, the isopropyl groups are not shown.

placement of sulfurs from the vertices of a regular octahedron might be interpreted in terms of the steric requirements of the bulky isopropyl groups when $Pb(S_2P)_2$ units in adjacent planes come together to form the "axial" Pb–S bonds. One edge of each octahedron may open up to accommodate these groups. The resulting space provides room for one ordered isopropyl group, $C_3H_7(1)$, and, at the same time, rather more than enough room for the other group, $C_3H_7(3)$, which is disordered and equally distributed between two conformations.

It is enlightening to examine not only the deformation of the PbS_6 group from O_h symmetry but also the detailed Pb–S bond lengths and angles, some of which are summarized in Figure 4. These bond lengths and angles are fully consistent with the apportionment of fourteen electrons (seven pairs) in the valence shell of lead, of which six pairs are bonding and one is a lone pair.

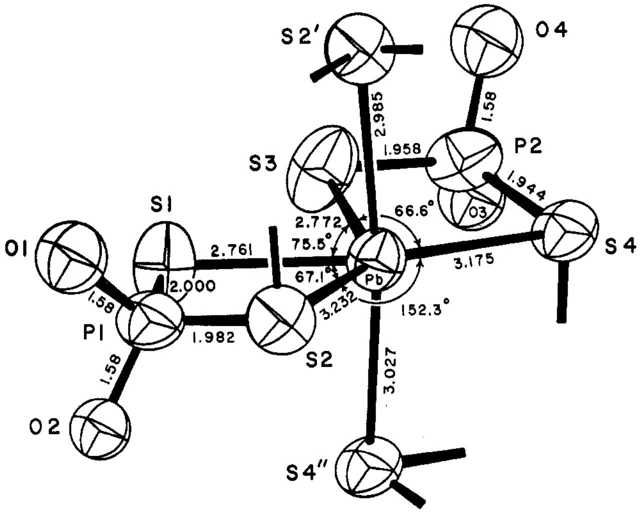

Figure 4.—A parallel projection of a Pb[$(i\text{-}C_3H_7O)_2PS_2]_2$ unit illustrating the principal root-mean-square thermal displacements of atoms in the inner coordination sphere. The ellipsoidal boundaries are at the 60% probability level.

The mean Pb–S bond length, 2.95 Å, is nearly the same as the value 2.97 Å in cubic PbS (NaCl lattice) in which lead contains a delocalized lone pair of electrons.[27] The sulfur atoms along one edge of the distorted octahedron may be envisioned as being pushed apart (as if by a protruding lone pair of electrons) concomitantly compressing the sulfur atoms on the opposite edge together (152.3° *vs.* 75.5°). The two bonds adjacent to the lone pair (forming the 152.3° angle) are then lengthened to an average 3.20 (4) Å, whereas those most remote from the lone pair shrink inward to an average 2.766 (8) Å. The bonds essentially normal to this plane are affected only slightly in comparison to those in cubic PbS, averaging 3.01 (3) Å in length. The PbS_6E group (where E denotes an unshared pair of electrons) may therefore be considered to approximate an irregular pentagonal bipyramid in which the lone pair occupies an equatorial position as shown in Figure 5. The bending and stretching deformations are just those expected on the basis of the valence-shell electron-pair repulsion (VSEPR) model of Sidgwick and Powell[28] and Gillespie and Nyholm.[29] Alternately, and more or less equivalently, the deformations may be described as "pseudo-Jahn–Teller" effects corresponding to the perturbation of an octahedral structure by a seventh valence shell electronic pair.[30] It is noteworthy that the backside S···S nonbonded distance, 3.387 (7) Å, is virtually as short as the S···S distances in the bidentate ligands which are constrained to be

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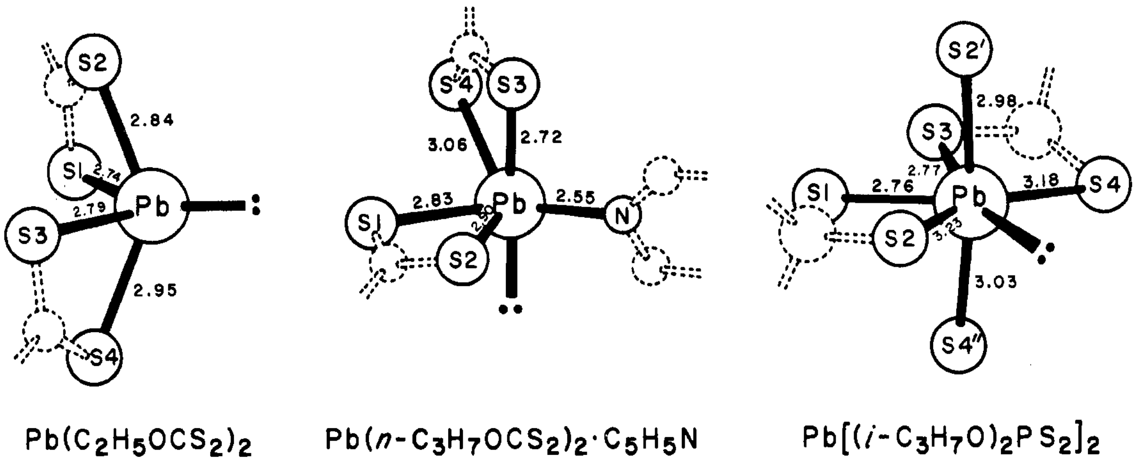
[27] A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, England, 1962, p 527.

[28] N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940).

[29] R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

[30] L. S. Bartell, *ibid.*, **45**, 754 (1968).



$Pb(C_2H_5OCS_2)_2$ $Pb(n\text{-}C_3H_7OCS_2)_2\cdot C_5H_5N$ $Pb[(i\text{-}C_3H_7O)_2PS_2]_2$

Figure 5.—Molecular configurations of lead(II) ethylxanthate, lead(II) *n*-propylxanthate–pyridine, and lead(II) diisopropylyphosphorodithioate, showing the proposed locations of the stereochemically active lone pair of electrons. For clarity, atoms in the outer coordination sphere are not shown.

short (3.284 (10) and 3.336 (10) Å) and is markedly shorter than the 3.70-Å van der Waals radius sum.

Relatively few examples of complexes of nontransition elements are presently known with seven valence-shell electron pairs. These include IF_7, XeF_6, $SeCl_6^{2-}$, $SeBr_6^{2-}$, $TeCl_6^{2-}$, and $SbBr_6^{3-}$. Of the more symmetrical configurations possible for seven-coordination (D_{5h}, C_2, C_s, C_{2v}, and C_{3v}),[31] two are exhibited by the structures of gaseous IF_7 and XeF_6. IF_7 executes a pseudorotational oscillation about a mean pentagonal-bipyramidal structure[32] while XeF_6 occurs as an irregular octahedron exhibiting a preference toward C_{3v} symmetry, though it is less distorted than predicted solely by the VSEPR model.[33] Each of the five ions above has a *regular* octahedral structure[34] and thus fails to conform to the simplest variant of the VSEPR model, perhaps because of crowding in the coordination sphere of the central atom and perhaps because of electrostatic interactions.[35] The structure of $Pb(dtp)_2$ reported here may therefore be regarded as a truly authentic example of a seven electron pair case in which a lone pair of electrons behaves as a static Gillespie–Nyholm pseudo ligand.[36,36a]

Reinforcing our interpretation of the PbS_6 molecular geometry in $Pb(dtp)_2$ are certain features common to other sulfur chelates of lead(II). In these chelates the coordination about lead, which at first glance is irregular and chaotic, may be understood in terms of the VSEPR theory as illustrated in Figure 5. Four-coordinate PbS_4E in lead ethylxanthate[1] assumes the trigonal-bipyramidal arrangement of five electron pairs displayed by SF_4[37] with the lone pair of electrons occupying an equatorial position. Five-coordinate PbS_4NE in lead isopropylxanthate–pyridine[2] assumes a structure based on the octahedral arrangement of six electron pairs similar to that in BrF_5[38] with the lone pair of electrons occupying the axial site. All show the expected qualitative affect of lone-pair–bond-pair interactions on the Pb–S bond lengths; bonds most remote from the lone pair tend to be shorter than the adjacent bonds. Thus, in the xanthate possessing the trigonal-bipyramidal configuration, the axial bonds are longer than the equatorial bonds, whereas in the octahedral structure, the equatorial bonds are the longest.

Acknowledgments.—We thank J. J. Dickert and C. N. Rowe for supplying the purified crystals of this compound and for helpful discussions. We are also indebted to Professor L. S. Bartell for his stimulating assistance in the interpretation of the interesting stereochemistry of the lead coordination sphere. Finally, we thank Mrs. J. C. Mahley for her assistance with the data collection.

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(31) H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, **7**, 488 (1968).

(32) W. J. Adams, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **53**, 4040 (1970).

(33) R. M. Gavin and L. S. Bartell, *ibid.*, **48**, 2460 (1968); L. S. Bartell and R. M. Gavin, *ibid.*, **48**, 2466 (1968).

(34) G. Engel, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **90**, 341 (1935); J. L. Hoard and B. N. Dickenson, *ibid.*, **84**, 436 (1933); A. C. Hazell, *Acta Chem. Scand.*, **20**, 165 (1966); I. D. Brown, *Can. J. Chem.*, **42**, 2758 (1964); A. K. Das and I. D. Brown, *ibid.*, **44**, 939 (1966); S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **5**, 743 (1966); C. R. Hubbard and R. A. Jacobson, *Iowa Acad. Sci.*, **75**, 85 (1968).

(35) R. J. Gillespie, *Advan. Chem. Ser.*, **No. 62**, 221 (1967).

(36) In the absence of supporting evidence we are unable to assess the relative importance of the stereochemically active lone pair of electrons and the steric repulsion by the isopropyl groups. It is not known, for example, the extent to which the PbS_6E octahedron would deform if the isopropyl repulsion were removed. Examination of the methyl derivative of this material might offer potential information in this regard. It is quite possible that as the polymeric chains form during crystallization, the *a priori* steric interactions by the isopropyl groups enable the lone pair to become stereochemically active by providing a convenient opening through which they may emerge. Irrespective of the original source of the driving force, it is quite clear that the observed variations of Pb–S bond lengths in the coordination sphere provide plausible evidence that a lone pair of electrons does indeed protrude through the S(2)–Pb–S(4) opening.

(36a) NOTE ADDED IN PROOF.—Following acceptance of this paper for publication, examples of three other structures containing bidentate ligands which elegantly display a stereochemically active lone pair of electrons in six-coordination were found to have been reported. These include $[Sb(C_2O_4)_3]^{3-}$ [M. C. Poore and D. R. Russell, *Chem. Commun.*, 18 (1971)], $As(S_2COC_2H_5)_3$ [G. Carrai and G. Gottardi, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **113**, 373 (1960)], and $As[S_2CN(C_2H_5)_2]_3$ [M. Colapietro, A. Domenicano, L. Scaramuzza, and A. Vaciago, *Chem. Commun.*, 302 (1968)]. The trisoxalatoantimonate(III) anion exhibits a pentagonal bipyramidal arrangement of seven electron pairs but with the lone pair occupying an axial site. The axial Sb–O bond is 0.2 Å shorter than the five equatorial bonds and the antimony atom is displaced 0.35 Å out of the equatorial plane away from the axial oxygen atom. The arsenic(III) complexes display distorted trigonal antiprismatic structures (C_{3v} symmetry) with the unshared electron pair orbital at the apex. The three As–S bonds nearest the lone pair are longer than those furthest from the lone pair, differing by 0.7 Å in the xanthate and 0.5 Å in the carbamate.

(37) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

(38) R. D. Burbank and F. N. Bensey, *ibid.*, **27**, 982 (1957).