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Stereochemical Consequences of Electron Lone Pairs. An Examination of Certain Sulfosalts and Chelates of Trivalent Arsenic, Antimony, and Bismuth and the Crystal and Molecular Structure of Bismuth(III) *O,O'*-Diisopropylphosphorodithioate, $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$[1]

STEPHEN L. LAWTON,*[2] CARL J. FUHRMEISTER,[3a] RAYMOND G. HAAS,[3a] CLAUDE S. JARMAN, Jr.,[3b] and FRANK G. LOHMEYER[3b]

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The compound bismuth(III) *O,O'*-diisopropylphosphorodithioate, $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$, crystallizes as yellow prismatic crystals in the monoclinic space group $C_{2h}{}^5\text{-}P2_1/c$ with $a = 20.096 \pm 0.002$, $b = 9.086 \pm 0.002$, $c = 21.619 \pm 0.003$ Å; $\beta = 114.71 \pm 0.01°$; $d_{\text{obsd}} = 1.54 \pm 0.03$ g/cm^3 and $d_{\text{calcd}} = 1.572 \pm 0.001$ g/cm^3 for $Z = 4$ molecules/unit cell. Three-dimensional X-ray data were collected on a three-circle diffractometer equipped with a scintillation detector using the θ–2θ scan technique and zirconium-filtered Mo Kα radiation. The structure was solved by reiterative application of the Sayre equation and Fourier methods and refined by full-matrix least-squares techniques to a final discrepancy index (based on F) of 0.076 for the 2734 independent reflections above $3\sigma(F_o)$. The bismuth ion is coordinated to three ligands in a pseudo trigonally distorted octahedral environment displaying C_3 symmetry. Stretching and bending deformations within the $:BiS_6$ group are consistent with the apportioning of fourteen electrons (seven pairs) in the valence shell of bismuth, 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 seven-coordinate arrangement of the electron pairs has approximate C_{3v} symmetry in which the lone pair assumes a position in one of the triangular octahedral faces. The three Bi–S bonds adjacent to the lone pair are longer (averaging 2.874 Å) than the three (averaging 2.702 Å) most remote from the lone pair. Interligand angles between the longer bonds are greater (at 99.9°) than those between the shorter bonds (91.2°), whereas intraligand S–Bi–S angles average only 72.0° as dictated by the ligand bite. The relatively small size of this bite (3.28 Å), which is markedly shorter than the 3.70-Å van der Waals radius sum, leaves enough interligand room to allow the stereochemical activity of the lone pair of electrons to be felt. The structural features of the $:BiS_6$ group turn out to be related to those in a large class of minerals and synthetic compounds in which a stereochemically active lone pair of electrons occurs.

Introduction

By virtue of its elegant simplicity, the valence-shell electron-pair repulsion (VSEPR) model of Sidgwick and Powell[4] and of Gillespie and Nyholm[5] has emerged as a popular theory in accounting for observed trends in molecular stereochemistry. According to this scheme the stereochemistry of nontransition elements is governed by repulsions between pairs of valence electrons. While there are numerous examples of four-, five-, and six-electron pair cases, there have been relatively few authentic seven-electron pair examples, particularly those in which one of the electron pairs is a stereochemically active lone pair.

According to the VSEPR model, hexacoordinate $:ML_6$ complexes (M = nontransition metal, L = ligand, ":" = lone pair) are not expected, as a rule, to possess a regular octahedral structure but rather one based on seven-coordination with a lone pair of electrons occupying the seventh position. Energy calculations, based on a model of mutually repulsive points on a spherical surface, have given a crude comparison of the stabilities of various geometries.[6] These calculations dictate that the favored geometry of seven groups about a common point depends upon the hardness of the pair repulsion force law, *i.e.*, the power of n appearing in the energy expression $E = \Sigma r_{ij}{}^{-n}$. For high n a C_{3v} structure is most stable, for intermediate values of n C_{2v}, C_s, and C_2 symmetries gain importance, and for n less than 2.0 D_{5h} symmetry is favored.

Until recently the only recognized examples of $:ML_6$ coordination involving isolated units have been the hexahalide complexes of xenon in the vapor phase[7] and of tellurium(IV),[8] antimony(III),[9] and bismuth(III)[10] in the crystalline phase. Except for XeF_6, each of these complexes has failed to display deformations from O_h symmetry which would conform to the simplest variant of the VSEPR model, perhaps because of crowding in the coordination sphere of the central atoms or because of electrostatic interactions.[5d] Gillespie has pointed out that when ligand· · ·ligand distances approach the sum of their normal van der Waals radii, repulsive forces may override the stereochemical influence of the lone pair.[5d] Thus, in the case of XeF_6 in the vapor phase, with nearest-neighbor F· · ·F distances slightly *greater* than the sum of their normal van der Waals radii, the molecule is a distorted octahedron exhibiting a preference toward C_{3v} symmetry, though the region associated with the lone pair is not as large as that predicted by the VSEPR model for less crowded molecules.[7] Obviously, only limited success can be achieved in isolated units.

If full stereochemical activity of the lone pair is to be

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[2] Mobil Research and Development Corp., Research Department, Paulsboro, N. J. 08066.

[3] (a) Student, Paulsboro High School, Paulsboro, N. J. (b) Student, Woodstown High School, Woodstown, N. J.

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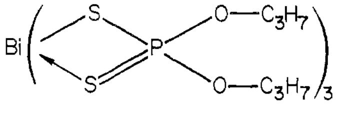
achieved in the seven-coordination case, it would appear that interligand repulsions must somehow be overriden. One approach to achieving this is *via* chelation of the coordinating atoms, *i.e.*, by use of bidentate groups. Evidence supporting this proposal is furnished by such bidentate ligands as $S_2CNR_2^-$,[11] $S_2COR_2^-$,[12,13] $S_2P(OR)_2^-$,[14] and $C_2O_4^{2-}$.[15] Of the more symmetrical configurations possible for seven-coordination, two are exhibited by structures with these ligands, as shown in Figure 1 in which the coordinating atoms and the lone pair are represented as points on a sphere. In the dithiocarbamate[11] and xanthate[12,13] complexes the central $:ML_6$ groups display C_{3v} symmetry with the lone pair in the face of the trigonally distorted octahedron emanating from the central atom along the threefold symmetry axis. Stoichiometry allows three bidentate ligands to belong uniquely to a given M ion and to provide the six coordinate bonds to L atoms. In the polymeric lead *O,O'*-diisopropylphosphorodithioate complex,[14] stoichiometry forces M ions to share ligands. This is accomplished by pseudo-D_{5h} symmetry in which four equatorial M-L bonds are provided by two ligands and two axial bonds by yet two other ligands. The lone pair ends up in an equatorial site. In the antimony oxalate anion,[15] stoichiometry allows hexacoordination without ligand sharing. Unlike the thio-chelated complexes, a pseudo-D_{5h} symmetry is favored in this case with five tightly grouped equatorial M-L bonds and an axial M-L bond, leaving the lone pair in the remaining axial site. Nuclear and electron repulsion energies, steric requirements of the ligands, bite size perhaps, all become important in controlling the overall geometry of the $:ML_6$ groups. Regardless of the driving force, once a natural site is provided for the lone pair and it arrives there, the lone pair will significantly influence the distribution of bond lengths and bond angles.

In an effort to explore in more detail the stereochemical consequences of lone pairs in $:ML_6$ groups with different chelating ligands, the complex bismuth(III) *O,O'*-diisopropylphosphorodithioate having empirical formula



was selected for crystallographic study. Bismuth, because of its large size (relative to arsenic and antimony), and the phosphorodithioate ligand, because it incorporates tetrahedral S_2PO_2 rather than planar S_2CN or S_2CO, were considered as logical candidates suitable for augmenting those already studied. Moreover, an important consideration in determining the suitability of systems for a quantitative study of the stereochemical effect of the lone pair in $:ML_6$ groups is the opportunity that all six coordinate bonds may be equivalent before deformation from an octahedral configuration. In many potential examples of distortions attributable to lone pairs the interpretation is clouded because of competing factors, such as space requirements associated with ligand sharing in polymeric structures. This complication is absent in the tris-bidentate complexes, including the $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$ complex whose structure has now been determined.

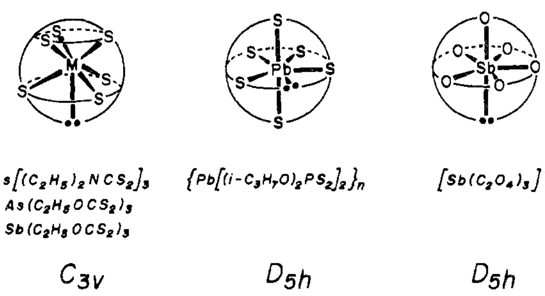


Figure 1. Points-on-a-sphere representation of $:ML_6$ groups in complexes derived from bidentate ligands. Indicated symmetries refer to ML_7-type geometries in which all seven points are hypothetically equivalent.

Experimental Section

Preparation. Crystalline $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$, hereafter $Bi(dtp)_3$, was prepared by treating an aqueous solution of ammonium *O,O'*-diisopropylphosphorodithioate (0.2 mol in 100 ml of water) with an aqueous solution of $BiCl_3$ (0.067 mol in 30 ml of concentrated HCl and made up to total volume of 80 ml with water), using a procedure previously described.[16] Yellow prismatic crystals (mp 67-68°) suitable for use in the X-ray investigation were obtained by recrystallization of the compound from *n*-decane.

Crystal Data. $Bi(dtp)_3$, formula weight 848.81, is monoclinic with space group $P2_1/c$ (C_{2h}^5). The lattice parameters at 25 ± 3° are $a = 20.096$ (2), $b = 9.086$ (2), $c = 21.619$ (3) Å, and $\beta = 114.71$ (1)°, $V = 3586$ (2) Å^3, $d_{obsd} = 1.54$ (3) g/cm^3 (by flotation in a mixture of 1,2-dichloropropane and 1,2-dibromoethane), and $d_{calcd} = 1.572$ (1) g/cm^3 for $Z = 4$ molecules/unit cell.

The monoclinic symmetry was initially indicated by Weissenberg and precession X-ray photographs which yielded systematic extinctions ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with the space group $P2_1/c$. The lattice parameters and their estimated standard deviations were obtained by a least-squares refinement[17] of 30 independent reflection angles measured in the angular region $24° < 2\theta < 31°$ on a Siemens diffractometer using Mo Kα radiation (λ 0.7107 Å) and a takeoff angle of 2°. Each measurement consisted of determining the 2θ value at half peak height on both sides of the peak in both the positive and the negative 2θ regions and averaged. These lattice parameters were examined by the computer program TRACER II[18] for the presence of hidden symmetry higher than primitive monoclinic; none was found.

Collection and Reduction of X-Ray Intensity Data. Complete three-dimensional X-ray diffraction intensity data were taken at room temperature (25 ± 3°) with zirconium-filtered molybdenum radiation from a prismatic crystal of length 0.459 mm and of cross section measuring 0.12 × 0.18 mm. The crystal was sealed in a thin-walled Lindemann glass capillary and mounted on the diffractometer with b^* (the 0.459-mm axis) coincident with the ϕ axis. Half-widths of a number of narrow-source, open-counter 2θ scans[19] ranged from 0.07° (b^* and c^* vectors) to 0.15° (d^*_{011} vector) in θ, indicating that the crystal mosaicity was acceptably small albeit anisotropic. A General Electric quarter-circle Eulerian cradle mounted on a Siemens diffractometer equipped with a Siemens scintillation detector and a pulse height discriminator was used 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 17.0 and 18.5 cm, respectively. Dimensions of the counter aperture were 5.0 mm × 5.0 mm. The counter angle, 2θ, was scanned over 2° at a speed of 2°/min. Background counts of 12 sec were taken at each end of the 2θ scan. Collection of the data covered the range $2\theta \leqslant 50°$ to include all possible observed reflections. A total of 6119 independent reflections, as well as 190 Friedel pairs of reflections ($hk0$ and $\bar{h}\bar{k}0$), were measured. Intensities of three standard reflections were monitored periodically as a

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(11) M. Colapietro, A. Domenicano, L. Scaramuzza, and A. Vaciago, *Chem. Commun.*, 302 (1968).

(12) G. Carrai and G. Gottardi, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 113, 373 (1960).

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(17) D. E. Williams, "LCR-2, a Fortran Lattice Constant Refinement Program," Report IS-1052, Ames Laboratory, Iowa State University, Ames, Iowa, 1964.

(18) S. L. Lawton, "TRACER II, a Fortran Lattice Transformation–Cell Reduction Program," *J. Appl. Crystallogr.*, 6, 309 (1973).

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

check on crystal and electronic stability and were found to remain essentially constant throughout the data collection.

The raw intensity of each reflection was corrected for background, Lorentz, polarization, and absorption effects; equivalent forms were averaged. In making the absorption correction the crystal was defined as an ellipsoidal cylinder with minor and major diameters 0.120 and 0.181 mm, respectively, cross sections which were determined by utilizing a method previously described.[20] Transmission factors for the full set of three-dimensional data ranged from 0.430 to 0.594, based on a linear absorption coefficient of 51.72 cm^{-1} for Mo Kα radiation.[21] Estimated standard deviations in the intensities were computed as described elsewhere, using a value of 0.05 for the ignorance factor p.[22] The estimated standard deviation in each structure factor was calculated by the method of finite difference.[23] A total of 2968 independent reflections were observed above the background level of which 2827 had $F_o \geqslant 3\sigma(F_o)$. The remaining 141 reflections were considered as unobserved and thus omitted from the refinements.

Solution and Refinement of the Structure. Coordinates of atoms in the inner coordination sphere were determined by direct methods. Normalized structure factors (E's) were calculated and 230 reflections with $E > 1.49$ were phased by use of Long's program for reiterative application of the Sayre equation. The program's algorithm for selecting a starting set of phases was used. Three linearly independent reflections were chosen to fix the origin and the signs of four additional reflections were assumed to initiate phasing to yield 16 possible solutions. An E map based on the 230 phased reflections from the solution with the fewest number of cycles (five) and the highest consistency index ($C = 0.998$ for $+++$)[24] with NBACK > 0 readily revealed eight of the ten atoms in the BiS_6P_3 fragment. Successive structure factor calculations and electron density (F and ΔF) syntheses revealed all remaining nonhydrogen atoms.

The structure was refined by using a full-matrix least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated amplitudes, respectively, and w is the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral Bi, S, P, O, and C tabulated by Hanson, *et al.*,[25] were used. Effects of anomalous scattering were included in F_c,[26] using values of $\Delta f'$ and $\Delta f''$ for Bi, S, and P given in ref 27. Initially only reflections in the range $2\theta \leqslant 37.5°$ and satisfying the condition $F_o \geqslant 6\sigma(F_o)$ were used, representing 57% of the data. Using this data set the best fully weighted isotropic refinement of all 34 nonhydrogen atoms plus the scale factor resulted in $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.091$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.082$. Additional least-squares cycles with anisotropic thermal parameters assigned to Bi, S, and P further reduced R_1 and R_2 to 0.056 and 0.052, respectively.

Examination of the positional parameters of the isopropyl groups revealed a range of 1.40-1.64 Å (with a mean of 1.48 Å) for the C-C distances and a range of 100-121° (with a mean of 112.1°) for the C-C-C angles. These variations were not unexpected in view of the rather large thermal and, perhaps, librational motions of the group atoms suggested by the magnitudes of their isotropic B values. A rigid-body model having C_{2v} symmetry with C-C bonds of length 1.48 Å[28] and a C-C-C angle of 113°[29] was therefore introduced for the isopropyl groups using the least-squares group refinement procedure described by Ibers, *et al.*[30] The variable parameters for a group included individual isotropic thermal parameters, the coordinates of the group centers, and three orientation angles which have been described elsewhere.[30] Several iterations of refinement resulted in no net change in R_1 but a slight decrease of R_2 to 0.051.

Continuation of the refinement, now using all 2827 reflections above 3σ, led to $R_1 = 0.086$ and $R_2 = 0.059$. Analysis of mean $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ revealed that the weighting scheme was essentially constant. However, two reflections (004 and $\bar{6}29$) satisfied the condition $||F_o| - |F_c||/\sigma(F_o) > 3$ and so their weights were arbitrarily adjusted to give corresponding values of 3.0; in addition, 93 very weak reflections satisfying the condition $|F_o| > 2|F_c|$ were given zero weight, suggesting that perhaps the arbitrarily assigned threshold of $F_o \geqslant 3\sigma(F_o)$ for an observed reflection may have been a little low. Two subsequent iterations of least-squares refinement resulted in convergence of the structure to $R_1 = 0.076$ and $R_2 = 0.053$. The final error-of-fit based on the 169 variables and 2734 reflections was 1.65. During the final cycle the shift in each positional and thermal parameter of the nongroup atoms averaged 4.3% of its corresponding standard deviation and those of the groups averaged 14.1%. A final difference electron density map was essentially featureless, thus validating the results of the least-squares refinement and confirming the essential correctness of the determined molecular structure.

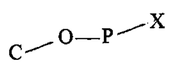
The final positional, thermal, and group parameters are given in Table I, along with the associated standard deviations as estimated from the inverse matrix, while Table II lists the final positional parameters of the isopropyl atoms derived from the group parameters. Root-mean-square thermal displacements along the directions of the principal axes for those atoms refined anisotropically are given in Table III. An indication of the directions of these principal axes of vibration is given in Figure 2. The values of $|F_o|$ and F_c for all 2734 observations used in the final stages of refinement are also available.[31]

Description of the Structure

The structure consists of discrete Bi(dtp)_3 molecules in which bismuth assumes a pseudo trigonally distorted octahedral environment of six sulfur atoms. Figure 2 shows a stereographic view of the molecule while Figure 3 portrays the packing in the unit cell. Selected bond lengths and angles are given in Table IV together with their standard deviations as derived from the variance-covariance matrix for functions involving nongroup atoms and from variances alone[32] for those involving group atoms.

By virtue of t_{1u} stretch-t_{1u} bend "pseudo-Jahn-Teller interactions"[33] and in accord with the VSEPR model, lone pair-bond pair repulsions in the bismuth coordination sphere result in longer bond lengths for those bonds adjacent to the lone pair and shorter lengths for those more remote, as well as an opening of the bond angles straddling the lone pair. Owing to steric interactions between interligand isopropyl groups, however, the lone pair is inhibited from achieving its full stereochemical activity. The closest nonbonded contacts occur among C(2)· · ·C(10) at 4.3 Å, C(2)· · ·C(12) at 4.0 Å, and C(9)· · ·C(15) at 4.1 Å, indicating that normal (*ca.* 4.0 Å) van der Waals interactions prevail.

All six isopropoxy groups adopt what may be referred to as trans locations when compared with the planar



reference conformation (C = vertex carbon, X = O or S), as shown by Table V. Five of these groups are trans to oxygen;

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(20) S. L. Lawton, *Inorg. Chem.*, 10, 328 (1971).

(21) In addition to various local programs for the IBM 360/67 computer, local modifications of the following programs were used in the solution and refinement of the structure: Prewitt's ACACA polyhedral absorption correction program; Stone and Dewar's FAME program for F to normalized $F(E)$ conversion; Long's REL direct method program; Guggenberger's FOUR Fourier summation program, a modification of a program written by C. J. Fritchie, Jr.; Doedens and Ibers' NUCLS crystallographic least-squares group refinement program based upon Busing and Levy's ORFLS; Busing and Levy's ORFFE function and error program; and Johnson's ORTEP thermal ellipsoid plotting program.

(22) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

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(24) Signs refer, in turn, to phases of the following origin-determining reflections: 123 ($E = 3.65$), 035 ($E = 2.94$), and 429 ($E = 1.94$).

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

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

(27) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

(28) The value 1.48 Å, compared with the expected value of 1.54 Å for a C-C single bond, was used to account for some foreshortening of the bond due to thermal and librational effects.

(29) Based on the average value observed in the molecule $[(i\text{-C}_3\text{H}_7\text{O})_2\text{PS}_2]_2$: S. L. Lawton, *Inorg. Chem.*, 9, 2269 (1970).

(30) S. H. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

(31) See paragraph at end of paper regarding supplementary material.

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

(33) L. S. Bartell, *J. Chem. Educ.*, 45, 754 (1968).

Table I. Final Positional, Thermal, and Group Parameters for $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$[a]

Atom	x	y	z	β_{11}[b] or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv[c] B, Å^2
Bi	0.74466 (5)	0.86635 (11)	0.48815 (4)	0.00434 (3)	0.02196 (15)	0.00293 (2)	−0.00159 (9)	0.00117 (2)	−0.00028 (8)	6.02
S(1)	0.79868 (34)	1.04952 (74)	0.59719 (28)	0.00650 (30)	0.01987 (131)	0.00308 (20)	0.00179 (49)	0.00133 (20)	0.00089 (40)	6.96
S(2)	0.83445 (40)	0.69465 (74)	0.60592 (30)	0.00860 (36)	0.01664 (130)	0.00381 (23)	0.00013 (53)	0.00213 (23)	−0.00149 (41)	7.81
S(3)	0.70172 (27)	1.10830 (86)	0.40853 (26)	0.00388 (21)	0.02341 (134)	0.00416 (20)	0.00111 (50)	0.00160 (17)	−0.00002 (50)	6.48
S(4)	0.84715 (30)	0.91653 (72)	0.42903 (30)	0.00461 (23)	0.01988 (132)	0.00525 (24)	0.00070 (44)	0.00191 (20)	−0.00050 (46)	7.01
S(5)	0.61535 (34)	0.83576 (76)	0.49615 (32)	0.00711 (30)	0.02047 (142)	0.00578 (25)	−0.00210 (53)	0.00388 (23)	−0.00282 (54)	7.80
S(6)	0.65910 (32)	0.66121 (81)	0.38547 (27)	0.00557 (26)	0.02185 (146)	0.00462 (22)	−0.00101 (55)	0.00253 (19)	−0.00109 (51)	7.06
P(1)	0.85087 (29)	0.88004 (79)	0.65643 (24)	0.00544 (24)	0.01707 (108)	0.00267 (16)	−0.00006 (51)	0.00178 (16)	−0.00026 (47)	5.61
P(2)	0.79040 (29)	1.09337 (70)	0.38974 (25)	0.00444 (22)	0.01855 (129)	0.00271 (18)	−0.00024 (43)	0.00127 (16)	−0.00039 (39)	5.51
P(3)	0.58308 (33)	0.69212 (70)	0.41830 (34)	0.00461 (26)	0.01595 (127)	0.00570 (27)	−0.00073 (43)	0.00211 (22)	0.00021 (46)	6.77
O(1)	0.93451 (61)	0.9195 (14)	0.69591 (55)	5.86 (31)						
O(2)	0.82633 (56)	0.8616 (16)	0.71569 (55)	5.81 (28)						
O(3)	0.76861 (62)	1.1080 (18)	0.31007 (63)	7.33 (34)						
O(4)	0.83801 (64)	1.2377 (15)	0.41283 (64)	6.01 (33)						
O(5)	0.50797 (77)	0.7414 (19)	0.36280 (73)	8.70 (41)						
O(6)	0.55615 (90)	0.5442 (22)	0.43743 (86)	10.28 (51)						

Group	x_c[d]	y_c	z_c	δ	ϵ	η
$C_3H_7(1)$	1.0116 (8)	0.9485 (21)	0.6748 (6)	0.165 (16)	−3.093 (16)	0.185 (43)
$C_3H_7(2)$	0.8249 (8)	0.9656 (15)	0.7886 (7)	−1.643 (15)	−3.059 (14)	1.334 (41)
$C_3H_7(3)$	0.7191 (10)	1.0169 (19)	0.2289 (8)	−1.297 (29)	2.440 (20)	−2.273 (56)
$C_3H_7(4)$	0.8926 (7)	1.3179 (17)	0.4925 (6)	1.012 (15)	−2.821 (13)	−0.001 (37)
$C_3H_7(5)$	0.4739 (9)	0.8974 (22)	0.3108 (11)	0.697 (53)	−2.002 (22)	−2.270 (82)
$C_3H_7(6)$	0.5871 (9)	0.3678 (19)	0.4729 (9)	2.139 (22)	2.577 (18)	1.984 (49)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter, unless otherwise indicated. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] B's are isotropic thermal parameters equivalent to the anisotropic tensors: W. C. Hamilton, *Acta Crystallogr.*, 12, 609 (1959). [d] x_c, y_c, and z_c are the fractional coordinates of the group centers. The angles δ, ϵ, and η (in radians) are those described in ref 30. The origin of the internal system was taken at the group center with a_3 normal to the plane and a_1 bisecting the C–C–C angle.

Table II. Derived Positional and Refined Thermal Parameters for Group Atoms in $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
		$C_3H_7(1)$					$C_3H_7(4)$		
C(1)	0.9826 (8)	0.9393 (25)	0.6589 (11)	9.3 (7)	C(10)	0.8768 (9)	1.2671 (18)	0.4864 (11)	6.7 (5)
C(2)	1.0150 (12)	1.0869 (21)	0.6812 (12)	10.5 (7)	C(11)	0.8461 (11)	1.4117 (24)	0.4924 (12)	11.3 (8)
C(3)	1.0372 (14)	0.8192 (21)	0.6843 (13)	13.5 (10)	C(12)	0.9549 (9)	1.2749 (24)	0.4987 (11)	9.2 (7)
		$C_3H_7(2)$					$C_3H_7(5)$		
C(4)	0.8278 (10)	0.9793 (26)	0.7653 (7)	7.2 (6)	C(13)	0.5019 (11)	0.8903 (57)	0.3297 (13)	13.4 (9)
C(5)	0.8906 (8)	0.9490 (27)	0.8310 (9)	8.5 (6)	C(14)	0.4417 (19)	0.9446 (52)	0.3461 (14)	19.8 (15)
C(6)	0.7562 (8)	0.9686 (32)	0.7694 (11)	12.8 (9)	C(15)	0.4781 (16)	0.8574 (42)	0.2565 (15)	16.5 (11)
		$C_3H_7(3)$					$C_3H_7(6)$		
C(7)	0.7385 (13)	0.9876 (33)	0.2511 (12)	11.6 (9)	C(16)	0.5930 (14)	0.4039 (28)	0.4557 (10)	10.1 (7)
C(8)	0.7592 (14)	1.0595 (35)	0.2002 (16)	16.8 (12)	C(17)	0.5360 (15)	0.2881 (32)	0.4322 (11)	14.3 (11)
C(9)	0.6598 (14)	1.0035 (45)	0.2353 (15)	18.2 (14)	C(18)	0.6323 (14)	0.4115 (30)	0.5307 (11)	13.5 (10)

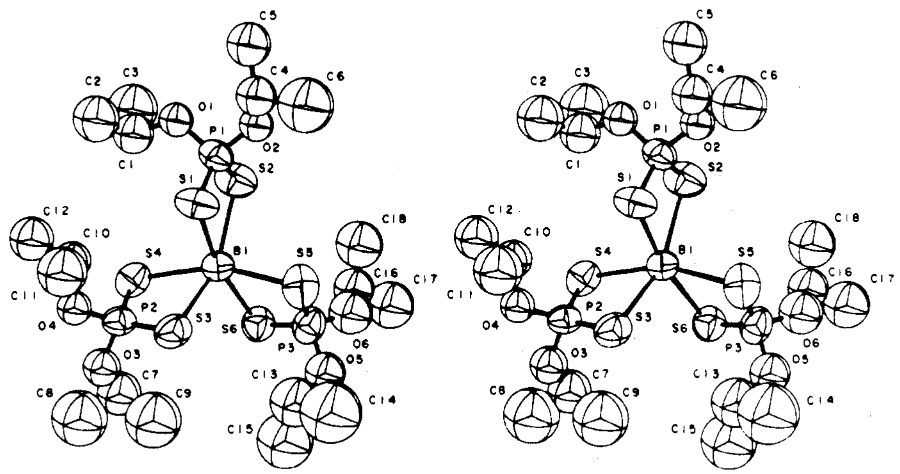

Figure 2. A stereographic view of the $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$ molecule parallel with the pseudo-triad axis, illustrating the principal root-mean-square thermal displacements of the nonhydrogen atoms. Ellipsoidal boundaries are at the 65% probability level.

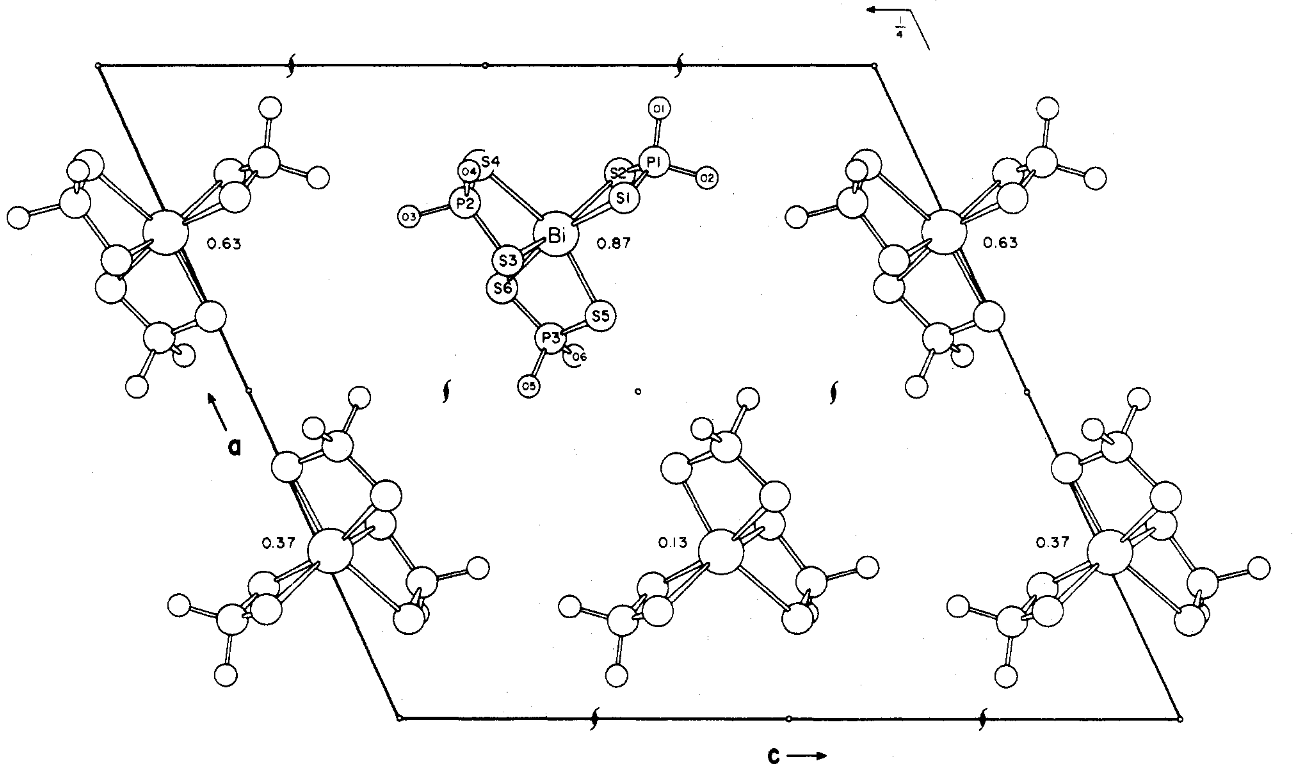

Figure 3. [010] projection of the primitive unit cell of $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$. The numbered atoms define the asymmetric unit (Table I). A number adjacent to each molecule represents the fractional unit cell y coordinate (elevation) of the bismuth atom, where the plane of the paper is $y = 0.0$. For clarity the isopropyl groups are not shown.

Table III. Final Root-Mean-Square Thermal Amplitudes of Vibration (Å) in $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$

Atom	Min	Med	Max
Bi	0.237 (1)	0.268 (2)	0.317 (2)
S(1)	0.239 (8)	0.286 (9)	0.354 (8)
S(2)	0.239 (10)	0.293 (9)	0.392 (9)
S(3)	0.250 (8)	0.287 (8)	0.318 (9)
S(4)	0.270 (8)	0.293 (8)	0.328 (8)
S(5)	0.261 (10)	0.292 (9)	0.378 (8)
S(6)	0.280 (9)	0.290 (11)	0.325 (9)
P(1)	0.220 (8)	0.268 (8)	0.305 (7)
P(2)	0.229 (8)	0.278 (10)	0.282 (9)
P(3)	0.251 (10)	0.283 (8)	0.338 (8)

the remaining, $i\text{-}C_3H_7(2)$, is trans to a sulfur atom. Presumably $i\text{-}C_3H_7(2)$ has undergone hindered rotation about its P-O bond from a C-O-P-O trans position to allow greater efficiency in molecular packing; *a priori* steric interference between this group and $i\text{-}C_3H_7(6)$ does not appear to have been the driving force in this case since the C_3 symmetry-related groups $i\text{-}C_3H_7(4)$ and $i\text{-}C_3H_7(5)$ in the other two ligands failed to adopt the same C-O-P-S conformation as that adopted by $i\text{-}C_3H_7(2)$.

The approximately C_{3v} configuration of the $:BiS_6$ nucleus of $Bi(dtp)_3$ turns out to be isostructural with $:MS_6$ nuclei in the ethyl xanthate (ex) and diethyldithiocarbamate (dtc) molecules $As(ex)_3$, $As(dtc)_3$, and $Sb(ex)_3$. Displacements of the sulfurs from the vertices of an octahedron (Figure 4) vary appreciably among the four structures, as can be seen from Table VI. Useful gauges for measuring the extent of deformation of the central $:MS_6$ groups are the ratios R_α and R_β defined in Table VI. Based on these ratios stretching deformations are largest in $As(ex)_3$ whereas bending defor-

Table IV. Interatomic Distances and Angles in $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$[a,b]

	Bond Lengths, Å		
Bi-S(1)	2.714 (6)	S(1)-P(1)	1.997 (8)
Bi-S(3)	2.702 (6)	S(3)-P(2)	1.991 (7)
Bi-S(5)	2.690 (6)	S(5)-P(3)	2.011 (8)
Av (rms)	2.702 (12)	Av (rms)	1.999 (10)
Bi-S(2)	2.886 (6)	S(2)-P(1)	1.959 (9)
Bi-S(4)	2.878 (6)	S(4)-P(2)	1.948 (8)
Bi-S(6)	2.858 (6)	S(6)-P(3)	1.955 (8)
Av (rms)	2.874 (15)	Av (rms)	1.954 (6)
S(1)· · ·S(2)	3.292 (8)	P(1)-O(1)	1.576 (11)
S(3)· · ·S(4)	3.270 (8)	P(1)-O(2)	1.562 (12)
S(5)· · ·S(6)	3.282 (9)	P(2)-O(3)	1.595 (12)
Av (rms)	3.281 (11)	P(2)-O(4)	1.576 (13)
S(1)· · ·S(3)	3.751 (7)	P(3)-O(5)	1.551 (14)
S(1)· · ·S(5)	3.923 (9)	P(3)-O(6)	1.568 (18)
S(3)· · ·S(5)	3.935 (9)	Av (rms)	1.572 (15)
Av (rms)	3.85 (11)	O(1)-C(1)	1.50 (2)
S(2)· · ·S(4)	4.424 (9)	O(2)-C(4)	1.51 (2)
S(2)· · ·S(6)	4.603 (8)	O(3)-C(7)	1.60 (3)
S(4)· · ·S(6)	4.192 (9)	O(4)-C(10)	1.47 (3)
Av (rms)	4.42 (21)	O(5)-C(13)	1.51 (5)
		O(6)-C(16)	1.44 (3)
		Av (rms)	1.50 (5)
	Bond Angles, Deg		
S(1)-Bi-S(2)	71.9 (2)	S(2)-P(1)-O(1)	113.0 (6)
S(3)-Bi-S(4)	71.7 (2)	S(2)-P(1)-O(2)	109.1 (7)
S(5)-Bi-S(6)	72.5 (2)	S(4)-P(2)-O(3)	112.7 (6)
Av (rms)	72.0 (4)	S(4)-P(2)-O(4)	112.4 (5)
S(1)-Bi-S(3)	87.7 (2)	S(6)-P(3)-O(5)	114.6 (7)
S(1)-Bi-S(5)	93.1 (2)	S(6)-P(3)-O(6)	112.4 (8)
S(3)-Bi-S(5)	93.7 (2)	Av (rms)	112.4 (18)
Av (rms)	91 (3)	O(1)-P(1)-O(2)	102.2 (6)
S(2)-Bi-S(4)	100.2 (2)	O(3)-P(2)-O(4)	97.4 (8)
S(2)-Bi-S(6)	106.5 (2)	O(5)-P(3)-O(6)	96.9 (10)
S(4)-Bi-S(6)	93.9 (2)	Av (rms)	100 (3)
Av (rms)	100 (6)	P(1)-O(1)-C(1)	121.2 (11)
Bi-S(1)-P(1)	89.8 (3)	P(1)-O(2)-C(4)	126.1 (9)
Bi-S(3)-P(2)	90.0 (3)	P(2)-O(3)-C(7)	130.3 (14)
Bi-S(5)-P(3)	89.7 (3)	P(2)-O(4)-C(10)	118.0 (10)
Av (rms)	89.8 (1)	P(3)-O(5)-C(13)	119.0 (16)
Bi-S(2)-P(1)	85.7 (3)	P(3)-O(6)-C(16)	129.4 (15)
Bi-S(4)-P(2)	85.8 (3)	Av (rms)	124 (5)
Bi-S(6)-P(3)	86.1 (3)	O(1)-C(1)-C(2)	103.2 (14)
Av (rms)	85.9 (2)	O(1)-C(1)-C(3)	104.8 (15)
S(1)-P(1)-S(2)	112.6 (3)	O(2)-C(4)-C(5)	107.8 (15)
S(3)-P(2)-S(4)	112.2 (4)	O(2)-C(4)-C(6)	105.4 (16)
S(5)-P(3)-S(6)	111.7 (4)	O(3)-C(7)-C(8)	99.2 (20)
Av (rms)	112.2 (5)	O(3)-C(7)-C(9)	97.4 (20)
S(1)-P(1)-O(1)	109.1 (6)	O(4)-C(10)-C(11)	101.8 (17)
S(1)-P(1)-O(2)	110.3 (6)	O(4)-C(10)-C(12)	104.2 (15)
S(3)-P(2)-O(3)	110.4 (5)	O(5)-C(13)-C(14)	95.6 (23)
S(3)-P(2)-O(4)	110.8 (6)	O(5)-C(13)-C(15)	104.6 (28)
S(5)-P(3)-O(5)	109.2 (7)	O(6)-C(16)-C(17)	107.4 (22)
S(5)-P(3)-O(6)	111.2 (8)	O(6)-C(16)-C(18)	103.7 (18)
Av (rms)	110.2 (9)	Av (rms)	103 (4)

[a] Average (weighted) distances and angles, plus rms deviations, in all tables and in the text were computed by expressions appearing in footnote *b* of Table V in the following reference: S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 8, 2410 (1969). [b] Bonds are signified by dashes and nonbonds by dots.

mations are greatest in $Sb(ex)_3$. Both types of deformations are smallest in $Bi(dtp)_3$ for reasons discussed above. Taking into account the constraint imposed on the geometry of the molecules by the rigid nature of the COR, CNR_2, and $P(OR)_2$ ligands and by the size of the "bite" angles at the metal, mean interligand S-M-S angles of 98-99° would occur if the structures were unperturbed and had overall D_3 symmetry. The *observed* S-M-S angles on the backside of the $:M(S_2X)_3$ molecules, *including* $Bi(dtp)_3$, are about 8° smaller than the corresponding angles would be in the undistorted D_3 refer-

Table V. Selected Dihedral Angles in $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$[a]

Bond array	Deg	Bond array	Deg
C(1)-O(1)-P(1)-O(2)	176	C(10)-O(4)-P(2)-O(3)	−175
C(4)-O(2)-P(1)-S(2)	−178	C(13)-O(5)-P(3)-O(6)	176
C(7)-O(3)-P(2)-O(4)	162	C(16)-O(6)-P(3)-O(5)	151

[a] Computed by QCPE program 215, written by R. A. Wohl, School of Chemistry, Rutgers University, New Brunswick, N. J., May 1971. The dihedral angle for the sequence L1-L2-L3-L4 corresponds to the angle necessary to rotate (+ for clockwise, − for anticlockwise) the directed plane L1-L2-L3 into coincidence with the directed plane L2-L3-L4. View is down the L2→L3 bond.

Table VI. Dimensions of $:MS_6$ Groups Involving Trivalent As, Sb, and Bi in Thio-Chelated Complexes

	Av M-S distances,[a] Å					Av S-M-S angles,[a] deg					Av S· · ·S separations,[a] Å		
	a	*b*	(*a* + *b*)/2	*b* − *a*	R_α = *a*/*b*	*aa*	*bb*	*bb* − *aa*	R_β = *aa*/*bb*	*ab* (intra)	$S_a\cdots S_b$ (intra)	$S_a\cdots S_a$ (inter)	Ref
$As(C_2H_5OCS_2)_3$	2.28	2.94	2.61	0.66	0.78	92.0	107.6[b]	15.6	0.86	67.8[b]	2.99[b]	3.28[b]	*e*
$As[(C_2H_5)_2NCS_2]_3$[c,d]	2.35	2.84	2.55	0.49	0.83	89.7	104.2	14.5	0.86	68.9	2.97	3.32	*f*
$Sb(C_2H_5OCS_2)_3$	2.52	3.00	2.76	0.48	0.84	87.5	113.1[b]	25.6	0.77	64.8[b]	2.99[b]	3.48[b]	*g*
$Bi[(i\text{-}C_3H_7O)_2PS_2]_3$[d]	2.70	2.87	2.79	0.17	0.94	91.2	99.9	8.7	0.91	72.0	3.28	3.85	*h*

[a] Distances and angles, denoted by letters, are identified in Figure 4. S_a and S_b refer to sulfur atoms forming M-S bonds *a* and *b*, respectively. [b] Computed by the present authors from the positional parameters. [c] Individual values entering into the tabulated averages were computed by the present authors from the final positional parameters kindly supplied by A. Vaciago in a communication dated Nov 6, 1971. [d] All entries are weighted averages. [e] See ref 12. [f] See ref 11. [g] See ref 13. [h] This study.

Table VII. Dimensions of $:MS_3$ Pyramids for Trivalent Metal Atoms in Various Sulfosalts[a, b]

Mineral	Compn	Av M-S length, Å	Av S-M-S angle, deg	Av S· · ·S sepn, Å	Total no. of independent pyramids used in av	Ref
		$:AsS_3$ Pyramids				
Baumhauerite[c]	$Pb_{12}As_{16}S_{36}$	2.29[e,f]	97.8[e,f]	3.45[e,f]	14	*g*
Binnite	$Cu_{12}As_4S_{13}$	2.25	98.4	3.40	1	*h*
Dufrenoysite	$Pb_8As_8S_{20}$	2.30[f]	97.8[f]	3.47[e,f]	8	*i*
Gratonite	$Pb_9As_4S_{15}$	2.29	98.8	3.48	2	*j*
Hatchite	$PbTlAgAs_2S_5$	2.27	98.8	3.45[e,f]	2	*k*
Hutchinsonite	$(Pb,Tl)_2As_5S_9$	2.29	98.0	3.44	5	*l*
Marrite	$PbAgAsS_3$	2.27	98.3	3.43	1	*m*
Nowackiite	$Cu_6Zn_3As_4S_{12}$	2.25	101.6	3.49	2	*n*
Rathite-I	$(Pb,Tl)_3As_4(As,Ag)S_{10}$	2.28	98.2	3.45	3	*o*
Rathite-II[d]	$Pb_{6.5}Pb_{12}As_{25}S_{56}$	2.29	97.7	3.46[e,f]	22	*p*
Seligmannite	$PbCuAsS_3$	2.28	97.1	3.44	2	*q*
Trechmannite	$AgAsS_2$	2.27	95.2	3.36	1	*r*
Wallisite	$PbTlCuAs_2S_5$	2.28	98.4	3.46[e,f]	2	*s*
Xanthoconite	Ag_3AsS_3	2.25[f]	99.0[f]	3.41[f]	1	*t*
		Av 2.28	97.7	3.45	66	
		$:SbS_3$ Pyramids				
Bournonite	$PbCuSbS_3$	2.46	93.3	3.48	2	*q*
Miargyrite	$AgSbS_2$	2.53[f]	92.8[e,f]	3.68[e,f]	2	*u*
Stephanite	Ag_5SbS_4	2.47[e,f]	94.3[f]	3.62[f]	1	*v*
Stibnite	Sb_2S_3	2.54	91.0	3.61[e,f]	1	*w*
Tetrahedrite	$Cu_{12}Sb_4S_{13}$	2.45	95.1	3.61[e,f]	1	*x*
		Av 2.51	92.3	3.55	7	
		$:BiS_3$ Pyramids				
Aikinite	$PbCuBiS_3$	2.72	86.5	3.75	1	*y*
Aikinite	$PbCuBiS_3$	2.74	87.8	3.75[e,f]	1	*z*
Bismuthinite	Bi_2S_3	2.68	88.1	3.68[e,f]	1	*aa*
Galenobismutite	$PbBi_2S_4$	2.74[f]	91.1[e,f]	3.86[e,f]	2	*bb*
		Av 2.73	88.7	3.78	5	

[a] Tabulation includes only those structures which were based on intensity data corrected for absorption and which were well refined, *viz.*, had acceptably low reliability *R* values, and all metal atoms were properly identified. [b] Average distances and angles were computed in accordance with footnote *a* of Table IV. [c] Pyramids involving As(3′), As(4), and As(5) were not included in the averages. [d] Pyramids involving As(4), As(5), As(6a), As(6b), As(23a), and As(23b) were not included in the averages. [e] Individual values of M–S, S–M–S, or S· · ·S entering into the averages were computed by the present authors from the published positional coordinates. [f] Individual standard deviations, σ_i, in M–S, S–M–S, or S· · ·S were estimated by the present authors from the published standard deviations in the positional coordinates using expressions appearing in the following reference: F. R. Ahmed and D. W. Cruickshank, *Acta Crystallogr.*, 6, 385 (1953). [g] P. Engel and W. Nowacki, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **129**, 178 (1969). [h] B. J. Wuensch, Y. Takeuchi, and W. Nowacki, *ibid.*, **123**, 1 (1966). [i] B. Ribar, Ch. Nicca, and W. Nowacki, *ibid.*, **130**, 15 (1969). [j] B. Ribar and W. Nowacki, *ibid.*, **128**, 321 (1969). [k] F. Marumo and W. Nowacki, *ibid.*, **125**, 249 (1967). [l] Y. Takeuchi, S. Ghose, and W. Nowacki, *ibid.*, **121**, 321 (1965). [m] B. J. Wuensch and W. Nowacki, *ibid.*, **125**, 459 (1967). [n] F. Marumo, *ibid.*, **124**, 352 (1967). [o] F. Marumo and W. Nowacki, *ibid.*, **122**, 433 (1965). [p] P. Engel and W. Nowacki, *ibid.*, **131**, 356 (1970). [q] A. Edenharter, W. Nowacki, and Y. Takeuchi, *ibid.*, **131**, 397 (1970). [r] T. Matsumoto and W. Nowacki, *ibid.*, **129**, 163 (1969). [s] Y. Takeuchi, M. Ohmasa, and W. Nowacki, *ibid.*, **127**, 349 (1968). [t] P. Engel and W. Nowacki, *Acta Crystallogr., Sect. B*, **24**, 77 (1968). [u] C. R. Knowles, *Acta Crystallogr.*, **17**, 847 (1964). [v] B. Ribar and W. Nowacki, *Acta Crystallogr., Sect. B*, **26**, 201 (1970). [w] See ref 36. [x] B. J. Wuensch, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **119**, 437 (1964). [y] See ref 38. [z] See ref 39. [aa] See ref 37. [bb] See ref 40.

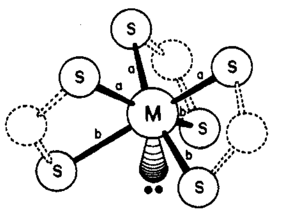

Figure 4. Molecular configuration of the $:MS_6$ inner coordination sphere (M = As, Sb, Bi) in structures of arsenic(III) and antimony(III) ethyl xanthate, arsenic(III) *N,N*-diethyldithiocarbamate, and bismuth(III) *O,O′*-diisopropylphosphorodithioate. The stereochemically active lone pair of electrons radiating from the central metal atom is shown. Distances and angles involving the M–S bonds are summarized in Table VI. In all four structures the $:MS_6$ group has C_{3v} or pseudo-C_{3v} symmetry.

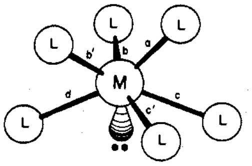

Figure 5. Molecular configuration of the $:ML_6$ coordination sphere (M = trivalent Sb or Bi and L = S or Se) in structures of stibnite, bismuthinite, aikinite, galenobismutite, and antimony selenide (Sb_2Se_3). The stereochemically active lone pair of electrons radiating from the central metal atom is shown. Distances and angles involving the M–S and M–Se bonds are summarized in Table VIII. In all five structures the $:ML_6$ group has crystallographic C_s symmetry.

ence structures. It is striking to note that, in the xanthate and dithiocarbamate complexes, the lone pair forces the backside S· · ·S nonbonded distances between ligands to be markedly shorter (3.28–3.48 Å) than the 3.70-Å[34] van der Waals radius sum. Apparently the absence of strong repulsive interactions between ethyl groups of neighboring ligands

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(34) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

Table VIII. Dimensions of $:MS_6$ and $:MSe_6$ Groups in a Series of Related Sulfosalts[a]

Identification (Fig 5)	Sb_2S_3 (stibnite[b]) M = Sb	Bi_2S_3 (bismuthinite[c]) M = Bi	$PbCuBiS_3$ (aikinite[d]) M = Bi	$PbCuBiS_3$ (aikinite[e]) M = Bi	$PbBi_2S_4$ (galenobismutite[f]) M = Bi	Sb_2Se_3[g] M = Sb
			M-S(Se) Bond Lengths, Å			
Short bonds $\{a$	2.521 (3)	2.686 (13)	2.658 (6)	2.663 (11)	2.634 (11)	2.658 (10)
$b = b'$	2.539 (2)	2.674 (9)	2.755 (4)	2.734 (8)	2.727 (7)	2.665 (7)
Long bonds $\{c = c'$	3.111 (3)	3.067 (10)	2.948 (4)	2.966 (9)	2.986 (8)	3.220 (8)
d	3.167 (3)	3.045 (14)	3.163 (6)	3.117 (13)	3.122 (11)	3.261 (11)
Av of 3 short bonds (I)[h]	2.54	2.68	2.74	2.72	2.71	2.66
Av of 3 long bonds (II)[h]	3.13	3.06	2.99	3.00	3.01	3.23
Av of all 6 bonds[h]	2.75	2.85	2.86	2.84	2.85	2.91
Diff between I and II	0.59	0.38	0.25	0.28	0.30	0.57
$R_\alpha = I/II$	0.81	0.88	0.92	0.91	0.90	0.82
			S(Se)-M-S(Se) Bond Angles, Deg			
bb'	98.13 (8)	95.9 (3)	94.27 (13)	94.9 (4)	97.5 (2)	96.1 (2)
cc'	76.14 (5)	80.7 (3)	86.46 (11)	85.6 (3)	86.7 (2)	75.9 (2)
$ab = ab'$	87.49 (8)	84.2 (3)	83.43 (15)	84.2 (3)	92.7 (3)	86.5 (3)
$ac = ac'$	77.95 (8)	78.1 (3)	83.07 (15)	81.7 (3)	87.5 (3)	79.7 (3)
$bc = b'c'$	91.22 (7)	89.2 (3)	88.05 (12)	88.1 (2)	87.9 (2)	92.5 (2)
$bd = b'd$	79.65 (8)	79.9 (10)[i]	77.46 (14)	77.3 (3)	85.0 (3)	81.1 (3)
$cd = c'd$	116.93 (9)	119.0 (11)[i]	116.53 (15)	117.5 (3)	95.1 (3)	114.4 (2)
ad	160.2 (3)	154.7 (26)[i]	151.7 (3)	152.4 (6)	177 (5)	161.5 (8)
$bc' = b'c$	162.4 (2)	161.0 (26)[i]	166.0 (5)	165.2 (9)	175 (2)	163.3 (7)

[a] Distances and angles presented in this table which were not directly available from the papers cited were computed by the present authors from the positional parameters. In these cases the standard deviations were estimated by an expression due to Ahmed and Cruickshank in ref *f* of Table VII. [b] See ref 36. [c] See ref 37. [d] See ref 38. [e] See ref 39. [f] See ref 40. [g] See ref 41. [h] Weighted average. [i] The estimated standard deviation includes an arbitrary uncertainty factor of 3.0.

allows perturbation of the $:MS_6$ group by the stereochemically active lone pair to proceed with relative ease. It would be interesting to find whether less crowded molecules of $Bi[(RO)_2PS_2]_3$, such as those with R = H, CH_3, or C_2H_5, would likewise allow the lone pair to exert a greater influence on the sulfur atoms within the bismuth coordination sphere.

In view of the conspicuous variability induced in the $:MS_6$ deformations, it is worthwhile examining sulfur derivatives of As(III), Sb(III), and Bi(III) which do not employ bidentate ligands, namely, the sulfosalts. These comprise a special group of minerals having the general structural formula $A_lA_mM_nL_p$, where A_l = metal atoms with coordination number (CN) 2, 3, or 4 (*viz.*, Cu, Ag, Zn, Hg, Tl), A_m = metal atoms with CN = 6, 7, 8, or 9 (*viz.*, Fe, Co, Ni, Hg, Tl, Pb), M = trivalent As, Sb, or Bi, and L = S (Se, Te).[35] This class differs from sulfides by the presence of $:ML_3$ units which assume a distorted tetrahedral arrangement of four electron pairs analogous to that displayed by $:NH_3$, where a lone pair of electrons occupies one of the tetrahedral sites. These trigonal pyramids often share sulfur atoms and form a finite or infinite network. A compilation of M-S and S· · ·S distances and S-M-S angles within these $:AsS_3$, $:SbS_3$, and $:BiS_3$ pyramids is presented in Table VII.

Four of the sulfosalts,[36-40] as well as a synthetic selenium analog,[41] contain $:ML_3$ (L = S or Se) units which, through ligand sharing, form $:ML_6$ units of pseudo-C_{3v} symmetry having three short and three long bonds together with an avoided region ascribable to a lone pair of electrons. Sulfur (or selenium) atoms forming these long bonds approach the $:MS_3$ (or $:MSe_3$) units on the side containing the lone pair. Although these contacts are long, they appear to represent a significant interaction entirely comparable to those in the previously discussed thio bidentate chelates of trivalent arsenic and antimony. The compounds in which these resulting $:ML_6$ units occur are summarized in Table VIII and and Figure 5. All may be viewed as derivatives of the stibnite, Sb_2S_3, structure with Sb sites replaced by Bi or Pb and with tetrahedral holes filled by Cu (aikinite) or Pb (galenobismutite). Agreement between the average values of the six bonds—2.76 Å in $Sb(ex)_3$[13] and 2.75 Å in Sb_2S_3,[36] 2.79 Å in $Bi(dtp)_3$ and 2.84-2.86 Å in Bi_2S_3,[37] $PbCuBiS_3$,[38,39] and $PbBi_2S_4$[40]—is rather remarkable, considering the complexity of the sulfosalt structures and their extensive ligand sharing. The average Bi-S bond length, *ca.* 2.85 Å in the sulfosalts, exactly parallels that, 2.97 Å, found in cubic PbS[42] and the average value, 2.95 Å, found in polymeric $\{[Pb(i\text{-}C_3H_7O)_2PS_2]_2\}_n$.[14] The seventh coordination site occupied by the nonbonded electron pair in the $:ML_6$ groups in the sulfosalts (Table VIII) appears not to be equidistant between the three adjacent M-L bonds. Two of the L ligands, while forming crystallographically equivalent long bonds (c and c'), also form two short bonds (b and b') with a neighboring M atom. Accordingly, the angle cc' is constrained to be small (76-87°). Nevertheless, more than enough room is provided for the lone pair, as witnessed by the rather large equivalent angles cd and $c'd$ of 95° in galenobismutite and 114-119° in the other sulfosalts.

Unlike the alkyl xanthate and dialkyldithiocarbamate ligands which are planar, the *O,O'*-dialkylphosphorodithioate ligand incorporates tetrahedral phosphorus, which is surrounded by two sulfur and two oxygen atoms. In $Bi(dtp)_3$ the bond lengths and bond angles involving these atoms are

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unexceptional. The lengths of the two independent P-S bonds within each ligand vary inversely with the lengths of the adjoining Bi-S bonds, as is plausible to maintain bond order conservation around sulfur. The two sets of distances average 1.999 and 1.954 Å, differing by about five standard deviations. The six P-O bonds are equivalent within two standard deviations of the average 1.572 Å. In agreement with those in other structures containing this ligand, the S-P-S angles (averaging 112°) are larger than the O-P-O angles (averaging 100°).

Conclusion

We have shown that $Bi(dtp)_3$ adopts a configuration consistent with the VSEPR theory, a valence-bonding scheme which accounts for observed trends in molecular architecture of nontransition elements. Owing to *a priori* equivalency of the sulfur atoms, discrete molecules of the type $:M(S_2X)_3$, where M is trivalent As, Sb, or Bi and S_2X represents thio bidentate ligands, have emerged as an excellent source of complexes for studying seven-coordination in which a nonbonding electron pair occupies a coordination site. There exists a wide range of as yet unexplored ligands suitable for further study of $:ML_6$ coordination, including L_2COR, L_2CNR_2, $L_2P(OR)_2$, $L_2P(R)(OR)$, and L_2PR_2, where L = S or Se and R = H, CH_3, F, Cl, Br, or I, just to name a few. Krishnan and Zingaro, for example, have reported the preparation of $As[(C_2H_5O)_2PSe_2]_3$, $Sb[(C_2H_5O)_2PSe_2]_3$, and $Bi[(C_2H_5O)_2PSe_2]_3$.[43] A definitive resolution of $:ML_6$ coordination might sharpen our overall understanding of lone pair-bond pair interactions in the more crowded seven-coordination spheres.

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Registry No. $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$, 42294-79-1; $(i\text{-}C_3H_7O)_2PSSH \cdot {}^1/_3Bi$, 42282-62-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-135.

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Contribution from the William Rand Kenan, Jr., Laboratories of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Molecular Structure of Diperchloratobis[2-(2-aminoethyl)pyridine]copper(II)

DAVID L. LEWIS and DEREK J. HODGSON*

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The crystal structure of diperchloratobis[2-(2-aminoethyl)pyridine]copper(II), $Cu(AEP)_2(ClO_4)_2$, has been determined from three-dimensional X-ray data obtained from a four-circle automatic diffractometer using Mo Kα radiation. The complex crystallizes in the space group $P\bar{1}$ of the triclinic system with cell constants $a = 8.275$ (3), $b = 9.772$ (4), $c = 7.894$ (4) Å; $\alpha = 126.88$ (2), $\beta = 82.20$ (3), $\gamma = 111.22$ (3)°. The observed and calculated densities for one molecule per unit cell are 1.75 (3) and 1.779 g cm^{-3}, and the structure was refined by full-matrix least-squares methods to a final value of the R factor of 0.030 for 2275 independent reflections whose intensities were greater than 3 times their estimated standard deviations. The molecule is a six-coordinate monomer with tetragonally distorted octahedral geometry at the copper atom; four nitrogen atoms from two AEP ligands form the equatorial plane and oxygen atoms from two perchlorate groups occupy the axial sites. The perchlorate groups are weakly coordinated with a Cu-O bond length of 2.883 (2) Å, as compared to the Cu-N bond lengths of 2.005 (2) and 2.024 (2) Å for the AEP coordination.

Introduction

The preparation of complexes of the formulation $Cu(AEP)_2X_2$ where AEP is 2-(2-aminoethyl)pyridine and X is a halogen was first reported by Uhlig and Maaser,[1] who assumed their conformation to be six-coordinate and monomeric. Recently, the structural determinations of $Cu(AEP)_2Br_2$[2] and $Cu(AEP)_2I_2$[3] have shown this assumption to be incorrect as these complexes have been demonstrated to be five- and four-coordinate, respectively. This change in coordination with diverse anions is not unique as Hathaway and coworkers[4] and McWhinnie and coworkers[5,6] have postulated similar trends in other copper complexes. Hathaway, *et al.*,[4] have shown that from electronic and epr spectra several diverse conformations would be anticipated for various $Cu(bipy)_2X_2$ and $Cu(bipy)_2XY$ complexes (where bipy is 2,2′-bipyridine). Similarly, McWhinnie, *et al.*, have concluded that complexes of the type $Cu(bipyam)_2X_2$ (where bipyam is 2,2′-bipyridylamine) may assume at least three different geometries depending upon the choice of anion.[5,6] Confirmation of these trends by three-dimensional crystal structure determination has not yet been completed.

As an extention of the recently compiled data on $Cu(AEP)_2I_2$ and $Cu(AEP)_2Br_2$, characterization of other AEP complexes with the remaining halogens or pseudohalogens would be valuable. Also, recent work with the pseudohalogen perchlo-

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