TABLE VII

RMS RADIAL THERMAL DISPLACEMENTS AND COMPONENTS ALONG THE PRINCIPAL AXES R_1, R_2, AND R_3 OF THE VIBRATIONAL ELLIPSOIDS

Atom	Rms radial displacements, Å	Principal axes, Å		
		R_1	R_2	R_3
U(1)	0.228	0.124	0.132	0.138
U(2)	0.245	0.156	0.137	0.159
O(1)	0.293	0.136	0.174	0.193
O(3)	0.311	0.160	0.185	0.192
N(1)	0.263	0.138	0.155	0.162
O(11)	0.284	0.140	0.153	0.194
O(12)	0.327	0.140	0.179	0.235
O(13)	0.299	0.142	0.163	0.207
N(2)	0.311	0.145	0.164	0.222
O(21)	0.309	0.138	0.156	0.229
O(22)	0.440	0.142	0.213	0.358
O(23)	0.343	0.152	0.160	0.262
O(2)	0.291	0.131	0.159	0.205
H(21)	0.400	0.180	0.237	0.268
H(22)	0.413	0.180	0.206	0.310
O(4)	0.314	0.131	0.166	0.233
H(41)	0.401	0.172	0.226	0.283
H(42)	0.493	0.182	0.212	0.406

participate in hydrogen bonding since it is much larger than the motion of the corresponding oxygen of the other molecule.

Conclusion

All attempts to resolve the differences between this study and the X-ray study of Vdovenko, *et al.*,[2] have failed. The neutron study does indicate a face-centered symmetry with respect to the uranium atoms, and the β angles are similar when the usual convention is applied to the X-ray results, but the large differences with respect to the unique "*b*" axis cannot be reconciled. Also, the bond lengths are considerably different. It must be concluded, in light of the neutron study, that the abnormal U–O distances found by Vdovenko, *et al.*,[2] are in error and that the correct distances for such a structure are near those predicted by Zachariasen and Plettinger.[4]

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The Crystal and Molecular Structure of the Polymeric Complex Mercuric *O,O'*-Diisopropylphosphorodithioate, Hg$[(i\text{-}C_3H_7O)_2PS_2]_2$

BY STEPHEN L. LAWTON

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Mercuric *O,O'*-diisopropylphosphorodithioate, Hg$[(i\text{-}C_3H_7O)_2PS_2]_2$, crystallizes in the monoclinic space group $C2/c$ with unit cell parameters $a = 31.70 \pm 0.02$, $b = 8.66 \pm 0.01$, $c = 22.34 \pm 0.01$ Å, and $\beta = 129.34 \pm 0.02°$. The observed and calculated densities are 1.74 ± 0.02 and 1.758 ± 0.004 g/cm^3 (for $Z = 8$ molecules/unit cell), respectively. The structure was refined by least-squares methods to a final conventional R index of 0.057 using three-dimensional X-ray diffraction counter data. Unlike the zinc(II) and cadmium(II) *O,O'*-diisopropylphosphorodithioate complexes which exist as dimers, this complex polymerizes into helical chains around the unit cell twofold screw axis aligned parallel with the crystal needle axis. One of the $(RO)_2PS_2$ groups functions as a chelating group and the other as a bridging group linking two mercury atoms together. Each mercury atom is surrounded by five sulfur atoms: two at relatively short distances of 2.388 ± 0.005 and 2.391 ± 0.006 Å, two at intermediate distances of 2.748 ± 0.005 (the polymeric bridge) and 2.888 ± 0.005 Å, and one making a van der Waals contact at 3.408 ± 0.006 Å. The –S–Hg–S– angle involving the two short Hg–S bonds is $149.7 \pm 0.2°$. There are no Hg–S interactions with neighboring chains. The P–S bonds within each ligand are unequal in length, averaging 2.01 ± 0.01 and 1.94 ± 0.01 Å; sulfur atoms forming the shorter bonds are associated with the longer (and weaker) Hg–S interactions. The P–O bonds within the nonbridging ligand average 1.62 ± 0.03 Å and those within the bridging ligand average 1.54 ± 0.02 Å.

Introduction

Recently the structures of zinc *O,O'*-diisopropylphosphorodithioate, $Zn_2[(i\text{-}C_3H_7O)_2PS_2]_4$, and of cadmium *O,O'*-diisopropylphosphorodithioate, $Cd_2[(i\text{-}C_3H_7O)_2PS_2]_4$, were reported.[1] These two complexes were found to exist in the crystalline state as isomorphous dimers in which each metal atom is coordinated with four sulfur atoms in a somewhat distorted tetrahedral environment. The two phosphorodithioate groups per metal were found to serve two independent functions: one acting as a chelating group and the other as a bridging group linking two metal atoms together to form the dimer. The four phosphorus–sulfur bonds were found to be essentially equivalent.

It is well known that mercury, the third member of the group IIb elements, exhibits a strong tendency to form complexes with considerably different coordination characteristics than are found for zinc and cadmium. For example, in the divalent state mercury often forms compounds with linear HgX_2 coordination as well as with tetrahedral HgX_4 coordination (X = monovalent ligands) whereas compounds with ZnX_2 and CdX_2 coordination are quite rare. Mercuric compounds with the HgX_2 coordination, however, often exhibit weak $Hg\cdots X$ interactions in addition to the two strong short Hg–X bonds, resulting in polymeric structures. It was of interest to extend our investigation of the metal O,O'-dialkylphosphorodithioates to mercury(II) to determine which type of coordination, MX_2 or MX_4, this metal atom would assume when chelated by the $(RO)_2PS_2$ ligand. Crystals of the mercury(II) diisopropyl derivative of empirical formula

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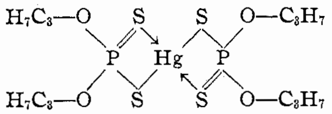
(1) S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, **8**, 2410 (1969).



were therefore synthesized. The crystal morphology and X-ray photographs of this complex indicated that the structure of this material differed considerably from that of its zinc(II) and cadmium(II) analogs. Its crystal and molecular structure was subsequently determined and the results of this investigation are reported here.

Experimental Section

Preparation.—Mercuric O,O'-diisopropylphosphorodithioate, $Hg(dtp)_2$, where dtp = $(i\text{-}C_3H_7O)_2PS_2$, was prepared by a method described elsewhere.[2] Soft, light gray needles for use in the X-ray investigation were obtained by recrystallization of the compound from warm absolute ethanol.

Crystal Data.—Mercuric O,O'-diisopropylphosphorodithioate, $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$ (formula weight 627.15), is monoclinic, with space group $C2/c$ (C_{2h}^6). The lattice parameters at 24° are a = 31.70 ± 0.02, b = 8.65 ± 0.01, c = 22.34 ± 0.01 Å, β = 129.34 ± 0.02°, V = 4739 ± 12 Å^3; d_{obsd} = 1.74 ± 0.02 g/cm^3 (by flotation), d_{calcd} = 1.758 ± 0.004 g/cm^3 for Z = 8 formula units/unit cell. The crystal habit is acicular and elongated along the b direction.

The crystal symmetry was determined from Weissenberg photographs which yielded systematic extinctions hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with the space groups Cc and $C2/c$. The centrosymmetric choice, $C2/c$, was initially indicated on the basis of intensity statistics.[3] The Patterson synthesis also revealed a set of vectors consistent with $C2/c$. The centrosymmetric space group was subsequently confirmed by the successful refinement of the derived structure. The lattice parameters were determined by a least-squares fit[4] to 55 independent unresolved Cu Kα reflections (λ 1.5418 Å) measured on zero-level Weissenberg zones in the 2θ range 77–120° 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. The observed lattice constants were checked with the computer program TRACER II[5] to verify that no symmetry higher than C-centered monoclinic was present.

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 0.230 mm long and of cross section 0.092 × 0.130 mm, parallel with b^*, c^*, and approximately $[\bar{2}01]^*$, respectively. Owing to its fragile character, the crystal was mounted in a 0.3-mm Lindemann glass capillary with the needle axis coincident with the ϕ axis of the diffractometer. The half-widths of a number of narrow-source, open-counter 2θ scans[6] ranged from 0.07 to 0.09° in θ, indicating that the crystal mosaicity was acceptably small. 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 receiving aperture size selected to minimize extraneous background was 4.2 mm wide by 2.5 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 3093 independent reflections in the range $2\theta \leq 45°$ were collected. No attenuators other than the β filter were necessary. Three standard reflections were measured periodically as a check on crystal decomposition and a total 7% decrease in intensities was observed.

The raw intensity of each reflection was corrected for background, crystal decomposition, Lorentz, polarization, and absorption effects. The transmission factors were computed by the program ACACA.[7] Owing to the moderately large linear absorption coefficient (71.1 cm^{-1}), refined crystal dimensions normal to the needle axis, rather than those obtained by optical measurement, were used in the absorption correction to reduce possible errors in the calculated transmission factors. Pursuant to this refinement, the shape, or profile, of the crystal normal to the needle axis was first carefully examined by measuring the intensity of a strong low-order $0k0$ reflection, in this case 020, at χ = 90° in 10° intervals of ϕ from 0 to 360°. These intensities were used to prepare a plot of I_n/I_{av} *vs.* ϕ, where I_n (corrected for background) was the intensity at $\phi = n$ and I_{av} was the average intensity over the full range of ϕ. By systematically adjusting the shape and optically measured crystal thickness, a "best fit" of the transmission factor curve A_n/A_{av} with that of I_n/I_{av} plotted against ϕ was obtained by defining the crystal as an ellipsoidal cylinder with *minor* diameter 0.1034 mm and *major* diameter 0.1150 mm. The maximum deviation in F_o from the mean, defined as $(|F_{\max} - F_{\min}|/F_{\text{av}}) \times 100$, for the 36 measurements was subsequently reduced from 6.3% with no applied correction to 0.3% with this correction. (The corresponding factor based on an absorption correction using the optically measured shape was 7.1%. This value was sufficiently large to indicate that refraction problems arising from the capillary walls and crystal adherent interfered strongly with the optical measurement of the crystal, thereby rendering the observed dimensions unreliable.) The calculated ratio of the minimum and maximum transmission factors for the full set of three-dimensional data was 0.867. Standard deviations in the intensities were computed as described elsewhere,[8] using a value of 0.05 for p. The estimated standard deviation in each F_o was determined by employing the

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(2) J. J. Dickert and C. N. Rowe, *J. Org. Chem.*, **32**, 647 (1967).

(3) (a) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, England, 1957, pp 32–41; (b) L. Guggenberger, "WSTAT, a Fortran Crystallographic Intensity Statistical Analysis Program," Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del., 1967.

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

(5) S. L. Lawton, "TRACER II, a Fortran Lattice Transformation–Cell Reduction Program," Mobil Research and Development Corp., Research Department., Paulsboro, N. J., 1967.

(6) In the region examined, $2\theta < 11°$, the 2θ-scan and ω-scan techniques yield comparable results: T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

(7) (a) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr.*, **122**, 24 (1965); (b) C. T. Prewitt, "ACACA, a Fortran Polyhedral Absorption Correction Program," Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del., 1966.

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

method of finite differences.[9] A total of 1649 reflections were observed above the background level, of which 1533 had $F_o^2 \geq \sigma(F_o^2)$. Those with $F_o^2 < \sigma(F_o^2)$ were considered as unobserved and thus omitted from the refinements.

Solution and Refinement of the Structure

An unsharpened Patterson function was first calculated using all observed reflections, from which the mercury and phosphorus atoms were located.[10] The positional and isotropic thermal parameters of these seven atoms plus the scale factor were refined by least-squares to an R index $[R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|]$ of 0.17 in the centrosymmetric space group $C2/c$. A series of three-dimensional electron density functions (F_o and $F_o - F_c$) and isotropic least-squares refinements led to the location of all remaining nonhydrogen atoms in the molecule.

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 structure amplitudes, respectively, and w is the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral S, P, O, and C tabulated by Hanson, *et al.*,[11] and those for neutral Hg tabulated by Doyle and Turner[12] were used. Effects of anomalous scattering of Hg, P, and S were included in the structure factor calculations,[13] using values for $\Delta f'$ and $\Delta f''$ given in ref 14. The best fully weighted isotropic refinement of all 23 atoms plus the scale factor resulted in $R_1 = 0.117$ and $R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2} = 0.083$ for the reflections above $\sigma(F_o^2)$. Further refinement with anisotropic thermal factors introduced for Hg, S, and P reduced R_1 and R_2 to 0.064 and 0.040, respectively. A subsequent three-dimensional difference map revealed vibrational patterns of the isopropyl groups which seemed physically reasonable. Extending anisotropic thermal refinement to the oxygen and carbon atoms reduced the R values still further. All thermal ellipsoids were well-behaved during all stages of the refinement. A second difference map was then computed to locate hydrogen atoms, but because of the large thermal motions of the carbon atoms, none could be readily located.

Convergence was reached with $R_1 = 0.058$ and $R_2 = 0.034$ for the 1533 observed reflections. Corresponding values for all 1649 reflections were $R_1 = 0.066$ and $R_2 = 0.037$. The final standard deviation for an observation of unit weight (*i.e.*, the "error of fit") based on the 208 variables was 1.40. Variation in the value of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) for different ranges of $|F_o|$ and $(\sin \theta)/\lambda$ was small and was considered to be satisfactory.[15] On the final cycle the shift in each positional and thermal parameter averaged 0.004 times its own σ. A final difference map calculated on an absolute scale showed no peaks greater than 0.3 e$^-$/Å^3, consistent with good refinement. Comparison of the final values of $|F_o|$ and $|F_c|$ indicated that a correction for secondary extinction was not necessary.

The question of the correct space group arose in the refinement with the appearance of generally large thermal parameters for all atoms, particularly those of the light atoms in the outer coordination sphere. Derived magnitudes of these parameters indicated the possible existence of *two* crystallographically independent molecules of slightly dissimilar molecular geometry and group orientations such as would be allowed in the noncentrosymmetric space group Cc. This seemed unlikely, however, because of the low R values obtained in the $C2/c$ refinement, the lack of any convergence difficulties, the featureless difference Fourier synthesis at the conclusion of this refinement, and a statistical analysis of the observed intensities. It was therefore concluded that the $C2/c$ space group adequately describes the structure.

The final refined positional and anisotropic thermal parameters are given in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. Table II gives the root-mean-square amplitudes of vibrations of the atoms. Table III lists the observed and calculated structure factors, excluding contributions in F_c due to hydrogen. Four reflections—200, 002, $\bar{1}11$, and $\bar{2}02$—were too close to the direct beam to be measured accurately and so only their calculated structure factors are indicated. Data with $F_o^2 < \sigma(F_o^2)$ are not included in Table III; of these, none had $F_o^2 > 2\sigma(F_o^2)$.

Description of the Structure

Crystals of mercuric O,O'-diisopropylphosphorodithioate contain eight Hg(dtp)$_2$ molecules per unit cell. These molecules polymerize into infinite zigzag chains around the crystallographic screw diad axes parallel with the needle axis of the crystal, as illustrated in Figures 1 and 2. Tables IV and V list the final interatomic

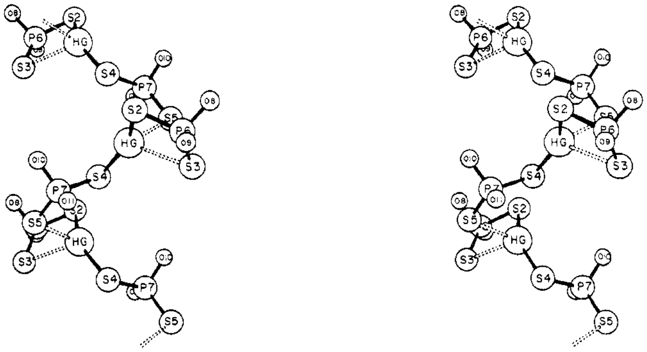

Figure 1.—A stereographic view of three Hg[$(i\text{-}C_3H_7O)_2PS_2$]$_2$ molecules within the infinite chain. Dotted bonds represent the "long" Hg–S interactions. The carbon atoms are not shown.

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

[10] 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 this structure: Guggenberger's FOUR Fourier program; Busing, Martin, and Levy's ORFLS crystallographic least-squares program; Busing and Levy's ORFFE function and error program; and Johnson's ORTEP thermal ellipsoid plotting program.

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

[12] P. A. Doyle and P. S. Turner, *ibid.*, **22**, 153 (1967).

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

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

[15] D. W. J. Cruickshank and D. E. Pilling, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Roberts, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961.

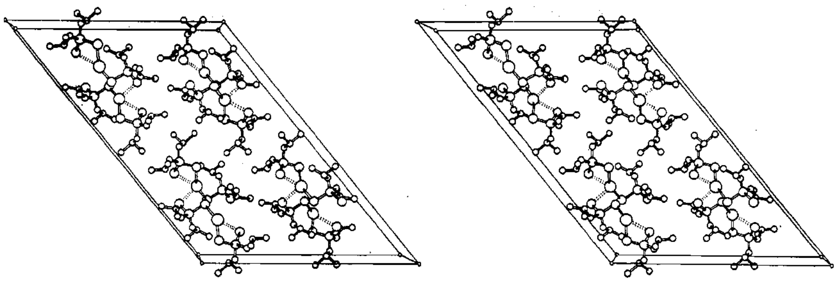

Figure 2.—Stereographic illustration of the molecular packing of the $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$ helical chains in the unit cell. View is along the *b* axis with the origin in the lower left corner below the plane of the paper. Dotted bonds represent the "long" Hg–S interactions.

TABLE I

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

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv, B, Å^2
Hg(1)	0.31437 (3)	0.53349 (8)	0.26431 (5)	37.1 (0.2)	200.7 (1.3)	80.0 (0.4)	6.8 (0.6)	39.7 (0.3)	28.8 (0.9)	7.55
S(2)	0.3973 (2)	0.6786 (6)	0.3350 (3)	39 (2)	304 (12)	67 (3)	−22 (4)	35 (2)	−25 (5)	8.51
S(3)	0.3679 (2)	0.4199 (6)	0.2060 (3)	40 (2)	258 (13)	73 (3)	24 (4)	39 (2)	14 (5)	8.10
S(4)	0.2545 (2)	0.3637 (5)	0.2633 (3)	28 (1)	226 (10)	46 (3)	−9 (3)	22 (2)	11 (4)	6.49
S(5)	0.2570 (2)	0.1495 (5)	0.3834 (3)	35 (1)	182 (9)	45 (2)	−17 (3)	28 (2)	−5 (4)	6.14
P(6)	0.4182 (3)	0.5812 (8)	0.2747 (4)	31 (2)	346 (17)	70 (3)	15 (4)	30 (2)	26 (6)	8.71
P(7)	0.2972 (2)	0.3053 (6)	0.3749 (3)	26 (1)	132 (9)	39 (2)	−2 (3)	21 (2)	−1 (4)	4.92
O(8)	0.4274 (7)	0.7186 (20)	0.2365 (11)	59 (5)	451 (41)	105 (10)	−19 (12)	66 (7)	18 (17)	11.5
O(9)	0.4825 (7)	0.5309 (25)	0.3347 (11)	51 (5)	411 (43)	111 (11)	24 (14)	39 (6)	24 (20)	13.8
O(10)	0.3104 (4)	0.4525 (13)	0.4238 (5)	22 (2)	165 (19)	47 (5)	3 (7)	16 (3)	16 (10)	5.8
O(11)	0.3563 (5)	0.2676 (13)	0.4131 (7)	30 (3)	152 (21)	70 (7)	8 (7)	30 (4)	5 (10)	6.5
C(12)	0.3873 (13)	0.8191 (40)	0.1800 (17)	67 (10)	532 (95)	52 (15)	32 (26)	33 (11)	90 (31)	13.8
C(13)	0.4128 (15)	0.9717 (35)	0.2144 (22)	120 (15)	318 (67)	247 (33)	−48 (28)	133 (20)	−56 (41)	20.2
C(14)	0.3823 (14)	0.7958 (39)	0.1121 (16)	97 (13)	804 (111)	82 (17)	8 (29)	67 (13)	30 (37)	18.5
C(15)	0.5001 (15)	0.4065 (39)	0.3726 (20)	74 (13)	432 (83)	111 (22)	73 (26)	64 (15)	146 (35)	14.0
C(16)	0.5406 (11)	0.4306 (52)	0.4590 (17)	49 (8)	1340 (173)	97 (16)	88 (34)	38 (10)	143 (54)	21.8
C(17)	0.5382 (15)	0.3356 (47)	0.3625 (18)	76 (12)	1220 (163)	104 (19)	142 (36)	53 (14)	65 (43)	22.9
C(18)	0.2704 (9)	0.5627 (28)	0.4107 (12)	44 (6)	268 (53)	74 (12)	33 (16)	37 (8)	−14 (22)	9.1
C(19)	0.3002 (11)	0.7179 (21)	0.4369 (14)	86 (10)	70 (33)	133 (18)	4 (15)	73 (12)	6 (20)	12.3
C(20)	0.2625 (11)	0.5243 (31)	0.4711 (17)	97 (10)	353 (59)	207 (23)	−17 (23)	120 (14)	−91 (34)	15.9
C(21)	0.3694 (9)	0.1230 (29)	0.3999 (13)	36 (6)	324 (56)	78 (13)	16 (15)	40 (8)	42 (23)	8.4
C(22)	0.3982 (13)	0.1383 (26)	0.3700 (17)	125 (13)	325 (55)	204 (24)	94 (22)	148 (17)	95 (29)	15.8
C(23)	0.4063 (13)	0.0379 (34)	0.4747 (17)	98 (12)	499 (79)	139 (20)	143 (28)	80 (13)	86 (36)	17.7

[a] All atoms are in the general symmetry position (8f). Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter. [b] The form of the anisotropic temperature factor expression is exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β's and their estimated standard deviations have been multiplied by 10^4. [c] Calculated from the anisotropic thermal parameters and unit cell parameters by the equation $B \cong (4/3)(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab \cos\gamma + 2\beta_{13}ac \cos\beta + 2\beta_{23}bc \cos\alpha)$: W. C. Hamilton, *Acta Crystallogr.*, **12,** 609 (1959).

TABLE II

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

Atom	Min	Med	Max
Hg(1)	0.249 (1)	0.306 (1)	0.362 (1)
S(2)	0.296 (8)	0.309 (7)	0.375 (7)
S(3)	0.269 (7)	0.311 (7)	0.372 (7)
S(4)	0.247 (7)	0.278 (7)	0.330 (7)
S(5)	0.226 (7)	0.256 (7)	0.342 (6)
P(6)	0.298 (9)	0.316 (8)	0.377 (9)
P(7)	0.224 (8)	0.238 (7)	0.284 (7)
O(8)	0.25 (2)	0.42 (2)	0.44 (2)
O(9)	0.36 (3)	0.42 (2)	0.47 (2)
O(10)	0.24 (2)	0.26 (2)	0.31 (1)
O(11)	0.23 (2)	0.30 (2)	0.32 (2)
C(12)	0.21 (4)	0.48 (4)	0.50 (4)
C(13)	0.33 (4)	0.49 (3)	0.64 (4)
C(14)	0.29 (4)	0.55 (4)	0.56 (4)
C(15)	0.23 (4)	0.43 (4)	0.54 (4)
C(16)	0.33 (4)	0.42 (3)	0.74 (5)
C(17)	0.38 (4)	0.41 (4)	0.74 (5)
C(18)	0.24 (3)	0.34 (3)	0.42 (3)
C(19)	0.16 (4)	0.42 (3)	0.51 (3)
C(20)	0.26 (4)	0.42 (3)	0.60 (3)
C(21)	0.26 (3)	0.31 (3)	0.39 (3)
C(22)	0.23 (3)	0.32 (3)	0.66 (3)
C(23)	0.27 (4)	0.43 (3)	0.64 (4)

distances, angles, and corresponding standard deviations. Important distances and angles within the inner coordination sphere are summarized in Figure 3. Owing to the complexity of thermal motion within the molecule, no corrections in the bond lengths were made.

The Mercury(II) Coordination.—The three ions Zn^{2+}, Cd^{2+}, and Hg^{2+} each have a filled d^{10} shell. All three form stable compounds with covalent bonds when the metal (M) is attached to four ligands (X) to form an MX_4 group of tetrahedral symmetry. However, unlike Zn^{2+} and Cd^{2+}, Hg^{2+} exhibits a *strong* tendency also to form MX_2 compounds in which the two bonds are shorter than the four found in the MX_4 compounds. These two classes, MX_2 and MX_4, are summarized in Table VI for known mercury(II) complexes with sulfur ligands.

In Table VI the following observed structural features may be noted. (i) In the MX_2 group the two short mercury–sulfur bonds vary in length from 2.36 to 2.49 Å. In the MX_4 group the mercury–sulfur bond varies in length from 2.49 to 2.66 Å. (ii) In the MX_2 group, the two short bonds are linear in some cases but significantly nonlinear in others; the X–M–X angle ranges from 129 to 180° with no apparent effect on the

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS × 10) FOR MERCURIC *O,O'*-DIISOPROPYLPHOSPHORODITHIOATE, $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$

H	L	FO	FC
**** K = 0 ****			
0	2		-8860
0	4	3278	3370
0	6	5121	-5109
0	8	3557	3549
0	10	1200	-1264
0	12	604	464
0	14	437	-442
2	0		-5967
-2	2		6278
2	4	2198	-2147
-2	4	2683	-2746
2	6	3339	3298
-2	6	5609	5559
2	8	1106	-1100
-2	8	4450	-4505
-2	10	2049	2036
2	12	808	827
-2	12	1711	-1753
2	14	611	-417
-2	14	1604	1663
-2	16	1199	-1140
4	2	3611	3644
-4	2	1331	-1419
4	4	515	-579
-4	4	1302	-1109
-4	6	2470	-2458
4	8	616	-528
-4	8	5221	5138
4	10	951	946
-4	10	3336	-3359
4	12	1088	-903
-4	12	1343	1410
-4	14	1285	-1173
-4	16	1232	1236
-4	18	757	-745
6	0	645	799
6	2	3067	-3055
6	4	2630	2593
-6	4	439	386
6	6	1926	-1973
-6	6	451	-406
6	8	1450	1453
-6	8	2659	-2527
6	10	1163	-1252
-6	10	1450	1370
-6	12	654	-472
-6	16	534	-426
-6	18	468	351
8	0	2440	-2428
8	2	4036	4029
-8	2	1759	1996
8	4	3106	-3066
-8	4	5942	-5864
8	6	1476	1565
-8	6	4934	5043
8	8	959	-831
-8	8	3663	-3598
8	10	928	916
-8	10	2132	2133
-8	12	1016	-1141
10	0	2598	2622
10	2	1561	-1494
-10	2	2930	-2890
10	4	395	-332
-10	4	3429	3447
10	6	961	1003
-10	6	4104	-4107
-10	8	4126	4119
-10	10	4487	-4466
-10	12	3163	3129
-10	14	1368	-1278
-10	16	878	914
12	0	606	817
12	2	1709	-1764
12	4	1783	1759
-12	4	647	-565
12	6	1076	-1115
-12	6	1108	1135
12	8	610	535
-12	8	456	395
12	10	447	-353
-12	10	1241	1238
-12	12	2402	-2382
-12	14	1574	1576
-12	16	1464	-1440
-12	18	1226	1353
-12	20	551	-609
14	0	2244	-2245
14	2	1506	1495
-14	2	2404	2435
14	4	853	-758
-14	4	2772	-2728
-14	6	1777	1823
-14	8	1321	-1279
-14	10	1670	1693
-14	14	613	534
-14	18	1063	-1232
-14	20	726	796
16	0	2467	2423
16	2	1612	-1588
-16	2	2350	-2406
16	4	689	677
-16	4	3382	3390
16	6	700	-573
-16	6	4416	-4412
-16	8	3181	3214
-16	10	1946	-1908
-16	12	1158	1190
-16	14	1533	-1514
-16	16	1079	1183
18	0	1736	-1755
18	2	688	744
-18	2	1572	1597
-18	4	1654	-1632
-18	6	3485	3545
-18	8	3533	-3536
-18	10	2423	2474
-18	12	1882	-1869
-18	14	2190	2129
-18	16	1916	-1952
-18	18	849	971
-18	22	630	576
-20	4	701	-733
-20	6	611	-531
-20	8	2337	2349
-20	10	2220	-2205
-20	12	1733	1779
-20	14	2681	-2637
-20	16	2539	2613
-20	18	1573	-1509
-20	20	476	612
-20	22	628	-799
-20	24	594	696
22	0	594	437
22	2	599	-572
-22	4	913	1011
-22	6	832	-937
-22	14	817	820
-22	16	1248	-1335
-22	18	565	698
24	0	469	-272
-24	4	575	-644
-24	6	837	947
-24	10	768	813
-24	12	1934	-1882
-24	14	1367	1305
-26	4	443	483
-26	6	749	-999
-26	8	809	702
-26	10	553	-587
-26	12	1220	1313
-26	14	1275	-1360
-26	16	452	663
-26	18	672	-455
-26	20	585	451
-28	6	427	409
-28	8	622	-435
-28	12	618	-598
-28	14	717	820
-28	20	704	-775
-28	22	535	653
-30	20	467	517
-30	22	728	-620
-32	10	538	-647
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1	3	1237	1301
-1	3	2939	2778
1	4	3015	3119
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1	5	2571	-2542
-1	5	1971	1983
1	6	3402	-3430
-1	6	980	1114
1	7	563	557
-1	7	1170	-1216
1	8	2489	2552
-1	8	1264	-1337
1	9	654	587
-1	9	980	-1099
1	10	1777	-1789
-1	10	813	733
1	11	617	327
-1	11	497	492
1	12	1547	1627
-1	12	1662	-1558
1	13	650	-683
1	14	908	-949
-1	14	1323	1318
1	16	627	396
-1	16	785	-652
-1	18	573	504
3	0	5535	-5610
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3	2	5420	5440
-3	2	5099	5029
3	3	554	388
-3	3	3156	-3144
3	4	3613	-3683
-3	4	6598	-6245
-3	5	847	873
3	6	4018	4060
-3	6	2911	2929
-3	7	1184	1175
3	8	2017	-2041
-3	8	1217	-1151
-3	9	801	917
3	10	1160	1187
-3	10	540	475
-3	11	1055	-1182
3	12	816	-794
-3	14	560	-365
5	0	5953	6000
5	1	1057	973
-5	1	1666	1562
5	2	2567	-2617
-5	2	3366	-3432
-5	3	1588	1649
5	4	2662	2571
-5	4	2705	2774
5	5	692	-713
-5	5	3373	-3327
5	6	2484	-2406
-5	6	3340	-3373
-5	7	465	414
5	8	1052	1184
-5	8	3189	3134
5	9	720	817
-5	9	556	-661
5	10	438	-442
-5	10	2556	-2541
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-5	12	1421	1488
-5	14	717	-728
-5	16	738	779
-5	19	495	325
7	0	1820	-1841
7	1	644	458
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-7	2	2451	2624
7	3	582	-580
-7	3	1389	-1382
-7	4	2749	-2829
7	5	724	746
-7	5	1192	1434
-7	6	3648	3677
7	7	581	512
-7	7	647	-865
-7	8	4183	-4204
7	9	845	-864
-7	9	980	986
-7	10	3299	3355
-7	11	1457	-1479
-7	12	2321	-2312
-7	13	428	342
-7	14	1004	1098
-7	16	803	-756
-7	18	528	561
9	0	1577	-1519
9	1	928	783
9	2	2514	2599
-9	2	579	-540
9	3	688	-698
-9	3	712	-428
9	4	1921	-1879
9	5	624	541
-9	5	1066	954
9	6	1691	1555
9	7	911	-979
-9	7	571	-464
9	8	1279	-1270
-9	8	2058	1996
9	9	501	482
9	10	866	726
-9	10	1802	-1865
-9	11	738	789
-9	12	1573	1627
-9	13	1399	-1381
-9	14	805	-692
-9	15	789	889
-9	16	808	758
-9	18	668	-689
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11	1	1834	-1791
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11	2	3014	-3005
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11	3	725	692
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11	4	1485	1383
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11	8	628	590
-11	8	3407	3329
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-11	14	735	-691
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13	2	778	855
-13	2	2839	2869
-13	3	511	-702
-13	4	3912	-4010
-13	6	4941	4987
-13	8	3903	-3828
-13	10	3070	2999
-13	11	416	-298
-13	12	2734	-2749
-13	13	1224	1177
-13	14	2250	2232
-13	15	584	-499
-13	16	1132	-1269
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15	0	863	759
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-15	2	834	-846
15	3	413	325
-15	3	535	552
-15	4	1163	1147
-15	5	1195	-1159
-15	6	2588	-2560
-15	7	744	768
-15	8	2641	2603
-15	9	639	-527
-15	10	1792	-1725
-15	12	1724	1702
-15	13	590	-619
-15	14	1946	-1995
-15	15	438	403
-15	16	1798	1904
-15	18	1177	-1254
-15	20	734	764
-15	22	612	-620
17	0	713	588
-17	1	544	-645
17	2	621	-644
-17	2	652	-704
17	4	607	576
-17	4	1008	1075
-17	5	789	773
-17	10	868	944
-17	11	399	-454
-17	12	1537	-1550
-17	14	1759	1716
-17	16	1498	-1472
-17	18	1154	1151
-17	20	957	-936
-17	22	511	608
19	0	1401	-1340
19	2	1076	1014
-19	2	1572	1689
-19	3	534	-585
19	4	795	-718
-19	4	2185	-2190
19	6	490	408
-19	6	1786	1865
-19	8	807	-865
-19	9	1167	1175
-19	10	920	927
-19	12	505	-219
-19	13	729	-642
-19	16	550	404
-19	17	436	394
-19	20	444	441
-19	22	520	-431
21	0	677	741
21	2	603	-431
-21	2	919	-847
-21	4	1386	1290
-21	6	1770	-1803
-21	8	1886	1872
-21	9	1088	-1248
-21	10	2222	-2205
-21	11	1266	1208
-21	12	2305	2245
-21	14	1539	-1513
-21	16	880	1045
-21	18	866	-967
-23	6	751	704
-23	7	615	494
-23	8	1011	-964
-23	9	484	263
-23	10	1261	1245
-23	11	760	-807
-23	12	1898	-1904
-23	13	487	355
-23	14	1830	1805
-23	16	1349	-1282
-23	18	1101	1081
-23	20	516	-669
-25	18	561	-649
-25	19	481	529
-25	22	514	-290
-27	6	443	-581
-27	8	610	443
-27	12	615	533
-27	14	505	-416
-29	6	562	676
-29	8	556	-778
-29	10	748	796
-29	12	923	-893
-29	14	743	835
-29	16	659	-686
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-31	14	681	-692
-31	16	756	755
-31	18	709	-684
-31	20	549	659
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0	4	5752	5795
0	5	496	-680
0	6	2912	-2962
0	7	909	882
0	8	1351	1333
0	10	980	-1014
0	12	679	650
2	0	2297	-2400
2	1	1128	-1034
-2	1	2189	1999
2	2	3043	3059
-2	2	2653	2742
2	3	2680	2694
-2	3	1586	-1627
2	4	2399	-2429
-2	4	4327	-4337
2	5	1632	-1581
-2	5	2118	2132
2	6	608	637
-2	6	3775	3891
2	7	651	539
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2	8	516	422
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2	9	722	-608
-2	9	909	989
-2	10	2241	2266
2	11	712	687
-2	12	2002	-2033
-2	13	495	410
2	14	642	-448
-2	14	885	916
-2	18	505	321
-4	1	1684	1603
4	2	711	831
-4	2	967	790
4	3	818	-689
-4	3	1377	-1347
4	4	1449	-1574
4	5	1132	1112
-4	5	431	-429
4	6	1795	1807
-4	6	1719	-1716
4	7	850	-986
-4	7	1100	969
4	8	1419	-1414
-4	8	1055	1105
4	9	974	1063
4	10	457	407
-4	10	1083	-1094
4	11	794	-742
-4	12	2043	2060
4	13	465	303
4	14	632	473
-4	14	1457	-1431
-4	15	588	592
-4	16	476	438
6	0	3319	3372
-6	1	657	-739
6	2	3708	-3720
-6	2	3322	-3312
6	3	1298	1354
-6	3	4202	4105
6	4	2541	2523
-6	4	665	899
6	5	1324	-1377
-6	5	2163	-2108
6	6	2261	-2287
6	7	716	643
6	8	1386	1529
6	10	487	-577
-6	10	1073	-1061
6	11	697	529
6	12	731	637
-6	13	428	208
6	14	502	-493
-6	14	809	716
-6	15	690	-512
8	0	3660	-3600
8	1	2297	2266
-8	1	2034	1995
8	2	2399	2368
-8	2	4327	4308
8	3	3062	-3041
-8	3	4206	-4124
8	4	1653	-1665
-8	4	4717	-4691
8	5	1700	1648
-8	5	3472	3365
8	6	1844	1920
-8	6	3250	3155
8	7	450	-300
-8	7	1226	-1150
8	8	835	-919
-8	8	1907	-1915
-8	9	1018	955
-8	10	1940	1946
-8	11	957	-1032
-8	12	1862	-1989
-8	14	510	520
-8	15	695	696
10	0	1909	1869
10	1	1575	-1623
-10	1	928	-1026
10	2	1033	-893
-10	2	2877	-2864
10	3	1591	1583
-10	3	2513	2526
10	4	816	806
-10	4	4105	3973
-10	5	2948	-2949
10	6	489	-413
-10	6	5225	-5221
-10	7	475	769
-10	8	4311	4308
-10	9	1591	-1527
-10	10	3165	-3104
-10	11	2752	2788
-10	12	3128	3105
-10	13	1750	-1692
-10	14	1639	-1660
-10	16	870	882
-10	18	675	-707
-10	19	562	478
12	0	618	614
12	1	721	-715
-12	1	1138	-1130
12	2	674	-619
-12	2	538	433
-12	3	749	-790
-12	4	653	-746
-12	5	1776	1757
12	6	610	-661
-12	6	1463	1500
12	7	510	233
12	8	671	654
-12	8	2041	-1939
-12	10	1452	1517
-12	11	2221	-2306
-12	12	1887	-1944
-12	13	2201	2218
-12	14	1660	1665
-12	15	1175	-1007
-12	16	960	-896
-12	17	702	552
-12	18	960	854
-12	19	741	-689
-12	20	729	-792
14	0	1605	-1584
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14	2	809	770
-14	2	1627	1632
14	4	644	-742
-14	4	1909	-1887
-14	5	1410	-1290
14	6	826	809
-14	6	2178	2160
-14	7	605	515
-14	8	910	-850
-14	10	985	917
-14	11	746	736
-14	13	877	-886
-14	14	807	-820
-14	16	570	630
-14	19	556	445
-14	20	545	441
16	0	1551	1578
-16	1	591	-597
16	2	861	-828
-16	2	2030	-2108
-16	3	552	556
16	4	601	729
-16	4	1716	1675
-16	5	418	313
16	6	584	-506
-16	6	1946	-1981
-16	8	2173	2132
-16	9	647	-594
-16	10	2091	-2029
-16	12	1363	1199
18	0	696	-646
-18	2	1691	1639
-18	3	551	-592
18	4	487	-311
-18	4	1737	-1715
-18	6	1548	1440
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-18	8	1651	-1593
-18	9	1707	1803
-18	10	2257	2236
-18	11	495	-563
-18	12	2468	-2406
-18	14	1837	1809
-18	16	1016	-1181
-18	18	1003	1031
-18	20	595	-649
20	0	640	-543
20	1	527	409
-20	4	431	452
-20	6	570	-502
-20	8	714	676
-20	9	891	-862
-20	10	1429	-1371
-20	11	790	847
-20	12	1780	1687
-20	14	1497	-1554
-20	15	638	580
-20	16	1078	1177
-20	18	1281	-1278
-20	20	933	947
-20	21	522	-316
22	0	775	736
-22	1	537	-388
22	2	425	-325
-22	2	857	-781
-22	4	477	642
-22	6	585	-618
-22	7	845	1024
-22	8	818	798
-22	9	824	-791
-22	11	600	383
-22	20	737	-645
-24	4	685	-612
-24	6	692	816
-24	8	1115	-1163
-24	9	654	732
-24	10	1204	1243
-24	11	554	-653
-24	12	714	-801
-24	13	517	500
-24	14	638	633
-24	16	923	-927
-24	18	495	523
-26	6	450	-587
-26	8	994	897
-26	10	1305	-1270
-26	12	1020	1149
-26	14	784	-723
-26	16	720	928
-26	18	937	-922
-26	19	505	478
-28	10	529	509
-28	12	664	-803
-28	14	665	626
-28	17	557	492
-28	18	877	853
-30	10	436	261
-30	18	490	-407
-32	14	473	-302
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1	2	1430	-1476
-1	2	634	-704
1	3	2402	2431
1	4	1226	1317
-1	4	1035	1076
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-16	7	1196	1207
-16	8	648	713
-16	9	1240	-1264
-16	11	1162	951
-16	13	475	-574
-16	14	801	-867
-18	3	864	-991
-18	5	1071	1052
-18	7	1029	-918
-18	8	698	-809
-18	9	1195	1281
-18	11	1328	-1311
-18	13	951	964
-18	15	655	-639
-18	17	574	432
-20	9	513	-524
-20	11	915	1009
-20	13	783	-931
-20	17	504	-510
-22	13	537	486
-24	9	485	620
**** K = 7 ****			
1	0	428	-400
1	1	773	-712
-1	1	756	-810
1	2	930	737
-1	2	556	-603
1	3	806	813
1	5	919	-1002
-1	5	654	392
1	7	902	853
-1	7	752	-481
1	11	617	510
3	1	1263	1199
-3	1	1615	1612
3	3	1164	-1277
-3	3	1627	-1634
3	5	1274	1394
-3	5	721	758
3	7	1062	-929
5	1	812	-827
-5	1	1178	-1182
-5	2	516	-638
5	3	1019	1052
-5	3	1832	1803
-5	4	732	634
5	5	812	-863
-5	5	1415	-1457
-5	7	1032	1116
-5	9	935	-1040
-5	11	599	681
-7	3	965	-879
-7	5	1108	1099
-7	6	565	-457
-7	7	1022	-902
-7	9	986	1117
-7	11	998	-986
-7	13	708	704
-9	1	565	669
9	5	611	680
-9	6	709	529
-9	13	643	-510
-11	1	857	-1004
11	3	887	782
-11	3	958	1106
11	5	527	-514
-11	5	715	-606
-11	9	732	-780
-11	11	474	496
13	1	578	450
-13	1	669	751
-13	3	1329	-1393
-13	5	1184	1210
-13	7	786	-959
-13	9	1057	1077
-13	11	1005	-1082
-13	13	694	784
-13	14	525	493
-15	5	893	-933
-15	7	738	729
-15	9	881	-825
-15	11	1075	1001
-15	13	866	-869
-17	13	634	596
-17	15	630	-461
-19	9	732	561
-19	10	587	479
-21	7	629	480
-21	9	566	-707
-21	11	676	637
**** K = 8 ****			
0	1	1127	-1238
0	3	800	761
0	7	662	718
2	1	660	724
-2	1	921	924
-2	3	693	-819
-2	5	795	585
-2	7	829	-792
-2	9	742	709
4	2	566	-543
4	3	563	-456
-4	8	526	-259
-4	9	799	-718
6	1	850	-736
6	3	1096	1040
-6	3	604	743
6	5	567	-728
8	1	612	690
-8	1	545	714
8	3	655	-841
-8	3	1126	-1050
-8	5	861	871
-8	7	687	-923
-8	9	647	719
-10	3	990	906
-10	5	793	-855
-10	7	846	848
-10	8	528	-471
-10	9	844	-1005
-12	5	617	517
-12	9	537	509
-12	11	720	-617
-14	1	515	470
-14	10	481	386
-16	5	589	-587
-16	7	776	739
-16	9	597	-551
**** K = 9 ****			
3	1	731	736
-3	3	514	-521
5	1	616	-619
-5	1	580	-729
-5	2	540	258
-7	5	506	262

length of the two bonds. The MX_4 group, on the other hand, exhibits tetrahedral or near-tetrahedral symmetry. Metacinnabarite, for example, crystallizes in the zinc blende (wurtzite) structure in which each atom is surrounded tetrahedrally by four other atoms.[16] (iii) In the MX_2 group mercury often exhibits a tendency to form *weak* interactions with additional atoms, thus increasing its sphere of nearest neighbors in some cases to as high as six. These additional interactions often result in the formation of polymers. Cinnabar, for example, is hexagonal with mercury surrounded by six sulfur atoms: two at 2.36 Å and making an angle with mercury of 172 (2)°, two at 3.10 Å, and two at 3.30 Å.[17] The structure consists of zigzag –Hg–S–Hg– helical chains which are bound to neighboring chains through weak Hg···S interactions to produce a pseudopolymeric compound.

Molecules of $Hg(dtp)_2$ in the present investigation exhibit features fully consistent with those found in the MX_2 group. Each mercury atom is surrounded by five sulfur atoms: two at relatively short distances of 2.388 (5) and 2.391 (6) Å, two at intermediate distances of 2.748 (5) and 2.888 (5) Å, and one at 3.408 (6) Å. The two short distances are well within the range 2.36–2.49 Å observed for the structures of this

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TABLE IV

INTERATOMIC DISTANCES IN $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$

Intrachelating ligand		Interchelating ligand	
Atoms[a]	Dist, Å	Atoms[a]	Dist, Å
Hg(1)-S(2)	2.391 (6)	Hg(1)-S(4)	2.388 (5)
Hg(1)-S(3)	2.888 (5)	Hg(1)-S(5')	2.748 (5)
S(2)···S(3)	3.284 (8)	S(4)···S(5)	3.221 (6)
P(6)-S(2)	2.023 (8)	P(7)-S(4)	2.006 (6)
P(6)-S(3)	1.935 (8)	P(7)-S(5)	1.946 (6)
P(6)-O(8)	1.60 (2)	P(7)-O(10)	1.55 (1)
P(6)-O(9)	1.64 (2)	P(7)-O(11)	1.52 (1)
O(8)-C(12)	1.39 (3)	O(10)-C(18)	1.46 (2)
O(9)-C(15)	1.26 (3)	O(11)-C(21)	1.41 (2)
C(12)-C(13)	1.48 (4)	C(18)-C(19)	1.53 (3)
C(12)-C(14)	1.44 (3)	C(18)-C(20)	1.56 (3)
C(15)-C(16)	1.51 (4)	C(21)-C(22)	1.44 (3)
C(15)-C(17)	1.49 (4)	C(21)-C(23)	1.49 (3)
		Hg(1)···S(4')	3.408 (6)

[a] Bonds signified by dashes and nonbonds by dots.

TABLE V

INTERATOMIC ANGLES IN $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$

Atoms	Angle, deg	Atoms	Angle, deg
	Mercury Coordination		
S(2)-Hg(1)-S(3)	76.3 (2)	S(3)-Hg(1)···S(4')	134.1 (1)
S(2)-Hg(1)-S(4)	149.7 (2)	S(3)-Hg(1)-S(5')	81.6 (1)
S(2)-Hg(1)···S(4')	89.4 (2)	S(4)-Hg(1)···S(4')	95.8 (1)
S(2)-Hg(1)-S(5')	109.0 (2)	S(4)-Hg(1)-S(5')	99.7 (2)
S(3)-Hg(1)-S(4)	118.5 (2)	S(4')···Hg(1)-S(5')	62.0 (1)
	Sulfur Coordination		
Hg(1)-S(2)-P(6)	91.6 (3)	Hg(1)-S(5')-P(7')	103.2 (2)
Hg(1)-S(3)-P(6)	79.7 (3)	Hg(1)···S(4')-Hg(1')	158.7 (2)
Hg(1)-S(4)-P(7)	103.7 (3)		
	Phosphorus Coordination		
S(2)-P(6)-S(3)	112.1 (4)	S(4)-P(7)-O(10)	109.6 (5)
S(4)-P(7)-S(5)	109.2 (3)	S(4)-P(7)-O(11)	111.9 (5)
S(2)-P(6)-O(8)	107.1 (7)	S(5)-P(7)-O(10)	113.6 (5)
S(2)-P(6)-O(9)	109.2 (7)	S(5)-P(7)-O(11)	116.5 (5)
S(3)-P(6)-O(8)	116.8 (7)	O(8)-P(6)-O(9)	94.6 (11)
S(3)-P(6)-O(9)	115.4 (8)	O(10)-P(7)-O(11)	95.5 (6)
	Oxygen Coordination		
P(6)-O(8)-C(12)	126 (2)	P(7)-O(10)-C(18)	126 (1)
P(6)-O(9)-C(15)	125 (2)	P(7)-O(11)-C(21)	120 (1)
	Carbon Coordination		
O(8)-C(12)-C(13)	102 (3)	O(11)-C(21)-C(22)	112 (2)
O(8)-C(12)-C(14)	107 (3)	O(11)-C(21)-C(23)	109 (2)
O(9)-C(15)-C(16)	113 (4)	C(13)-C(12)-C(14)	109 (3)
O(9)-C(15)-C(17)	108 (3)	C(16)-C(15)-C(17)	98 (3)
O(10)-C(18)-C(19)	104 (2)	C(19)-C(18)-C(20)	105 (2)
O(10)-C(18)-C(20)	106 (2)	C(22)-C(21)-C(23)	107 (2)

type. They are equal in length within one standard deviation. If the van der Waals radius of mercury(II) is assumed to be at least half of the interatomic distance in crystalline mercury,[18] 1.5025 Å, and if that of sulfur[19] is taken as 1.85 Å, then their sum (3.35 Å or greater) suggests that an appreciable interaction also exists in the ~2.8 Å set. In this set the bridging Hg–S interaction (2.748 (5) Å) appears to be slightly stronger than the nonbridging interaction (2.888 (5) Å). These sulfur atoms form essentially double bonds with phosphorus. The fifth sulfur atom (that which also forms the Hg–S bridge) occurs at a distance slightly greater than 3.35 Å, revealing no appreciable interaction. The angle formed by the two short Hg–S covalent bonds is 149.7 (2)° which, being considerably less than 180°, lends further evidence that in mercury(II) compounds of this type the bicovalent angle is quite flexible. As with most other members of this group a pseudopolymeric structure exists. As shown in Figures 1 and 2 the molecules arrange themselves into helical chains with no Hg–S linkages existing between the chains. Cleavages of the crystals parallel with the needle axis are readily explained by this molecular packing.

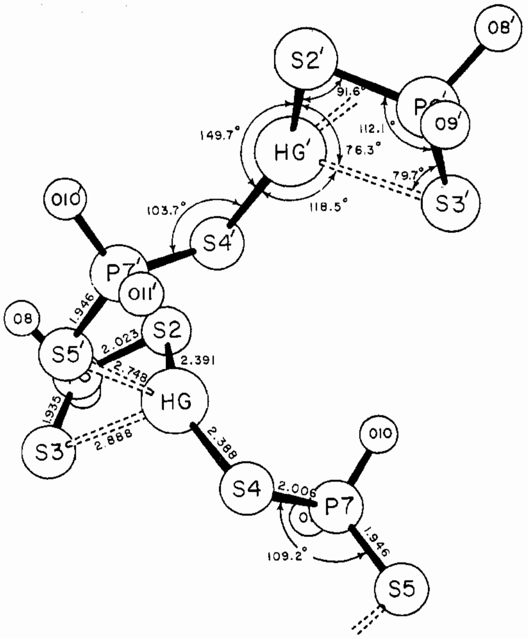

Figure 3.—Selected bond distances and angles in $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$. The carbon atoms are not shown.

In a nonpolar solvent such as benzene (38°) $Hg(dtp)_2$ dissociates into monomers. In a study of divalent zinc, cadmium, mercury, and lead *O,O'*-diisopropylphosphorodithioates, vapor pressure lowering data have shown[20] that the mercury(II) derivative has the smallest association constant (order: Cd > Zn > Pb > Hg), indicating that the metal–sulfur interaction linking the molecules together is the weakest of the four compounds studied.

The Phosphorodithioate Ligands.—As was found in the molecules of $Zn_2(dtp)_4$ and $Cd_2(dtp)_4$ previously determined,[1] the two phosphorodithioate groups per metal atom serve the *same two* independent functions with one acting as a chelating group and the other as a bridging group linking two metal atoms together. However, unlike those in the zinc and cadmium derivatives, no two bridging groups in $Hg(dtp)_2$ are associated with the same two metal atoms; consequently, polymeric chains, rather than dimers, result. This same type of chain was recently shown to form in crystals of $Zn[(C_2H_5O)_2PS_2]_2$.[21]

The lengths of the two P–S bonds within each ligand vary inversely with the lengths of the adjoining Hg–S bonds, as required by bond order conservation around sulfur. The two sets of P–S distances average 1.94

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[20] I. J. Heilweil, *Amer. Chem. Soc., Div. Petroleum Chem., Preprints*, **10**, No. 4-D, 19 (1965).

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TABLE VI

SUMMARY OF KNOWN MERCURY(II) COMPOUNDS WITH MERCURY–SULFUR INTERACTIONS[a]

Compound	Mercury environment	Hg–S contacts,[b] Å	S–Hg–S angles,[b,c] deg	Ref
		A. Two Short Bonds (MX_2)		
HgS (cinnabar)	6S	2 at 2.36 2 at 3.10 2 at 3.30	1 at 172.4 (17)	*d*
$Hg(SCH_3)_2$	5S	2 at 2.36 (5) 3 at 3.25 (5)	1 at 180.0 (25)	*e*
$Hg(SC_2H_5)_2$	6S	2 at 2.45 2 at 3.53 2 at 3.56	1 at 180	*f*
$Hg_3S_2Cl_2$	2S, 2Cl, 2Cl	2 at 2.45 (2)	1 at 166 (1)	*g*
$2HgCl_2\cdot(C_2H_5)_2S$	S, 3Cl, 2Cl⁻	1 at 2.41 (2)	...	*h*
$HgCl_2\cdot C_4H_8S$	2S, Cl, 3Cl⁻	1 at 2.40 (2)	...	*i*
$Hg[SC(NH_2)_2]_2Cl_2$	Not available	2 at 2.37	1 at 128.75	*j*
$Hg[SC(NH_2)_2]_2(SCN)_2$	6S	1 at 2.360 (6) 1 at 2.488 (6) 4 at 3.100–3.392 (6)	1 at 180 (8)	*k*
$Hg(C_{13}H_{11}N_4S)_2\cdot 2C_2H_5N$	4S, 2N	2 at 2.4 2 at 2.8	1 at 155	*l*
$Hg[(C_6H_5)NC(OCH_3)S]_2$	2S	1 at 2.317 (7) 1 at 2.343 (7)	1 at 174.7 (2)	*m*
$CoHg_2(SCN)_6\cdot C_6H_6$	4S, 2C	1 at 2.424 1 at 2.455 1 at 2.719 1 at 2.855	1 at 140	*n*
$Hg[(i\text{-}C_3H_7O)_2PS_2]_2$	5S	1 at 2.388 (5) 1 at 2.391 (6) 1 at 2.748 (5) 1 at 2.888 (5) 1 at 3.408 (6)	1 at 149.7 (2)	This study
		B. Four Short Bonds (MX_4)		
HgS (metacinnabarite)	4S	4 at 2.54	6 at 109.47	*o*
$Cu[Hg(SCN)_4]$	4S	2 at 2.520 (14) 2 at 2.620 (14)	6 at 93.33–143	*p*
$Hg[Co(NCS)_4]$	4S	4 at 2.558 (4)	6 at 105.1–118.7 (1)	*q*
$[Hg(SCN)_4][Cu(C_2H_8N_2)_2]$	4S	4 at 2.49–2.61	6 at 100.017–120.2	*r*
$Hg[SC(NH_2)_2]_4Co(SCN)_4$	4S	4 at 2.590 (7)	6 at 109.47 (150)	*s*
$Hg(tert\text{-}C_4H_9S)_2$	4S	2 at 2.590 (25) 2 at 2.660 (25)	6 at 87.0–121.0 (15)	*t*
$Hg(SC_4H_8O)_2Cl_2$	2S, 2Cl	1 at 2.540 (22) 1 at 2.590 (22)	1 at 115.0 (8)	*u*
$C_8H_{12}S_2Hg_2Cl_4$	2S, 2Cl	2 at 2.53	1 at 109	*v*
$Hg(S_3C_3H_6)Cl_2$	2S, 2Cl	2 at 2.61 (1)	1 at 113.0 (3)	*w*

[a] Structural features of a number of these compounds have been reviewed by C.-I. Bränden, *Ark. Kemi*, **22**, 501 (1964). [b] Numbers given in parentheses represent standard deviations occurring in the least significant digits of the parameters as quoted by the respective authors. [c] The indicated angles refer only to those formed by the two short Hg–S bonds in the MX_2 group and to all Hg–S bonds in the MX_4 group. [d] See ref 17. [e] D. C. Bradley and N. R. Kunchur, *J. Chem. Phys.*, **40**, 2258 (1964). [f] D. C. Bradley and N. R. Kunchur, *Can. J. Chem.*, **43**, 2786 (1965); a reference to earlier work is cited therein. [g] A. J. Frueh and N. Gray, *Acta Crystallogr., Sect. B*, **24**, 156 (1968). [h] C.-I. Bränden, *Ark. Kemi*, **22**, 83 (1963). [i] C.-I. Branden, *ibid.*, **22**, 495 (1964). [j] K. K. Cheung, R. S. McEwen, and G. A. Sim, *Nature (London)*, **205**, 383 (1965). [k] A. Korczynski, *Rocz. Chem.*, **40**, 547 (1966). [l] M. M. Harding, *J. Chem. Soc.*, 4136 (1958); a reference to earlier work is cited therein. [m] R. S. McEwen and G. A. Sim, *J. Chem. Soc. A*, 1552 (1967). [n] R. Grønbaek and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 1889 (1964). [o] See ref 16. [p] A. Korczynski, *Rocz. Chem.*, **36**, 1539 (1962). [q] J. W. Jeffery and K. M. Rose, *Acta Crystallogr., Sect. B*, **24**, 653 (1968). [r] H. Scouloudi, *ibid.*, **6**, 651 (1953). [s] A. Korczynski and M. A. Porai-Koshits, *Rocz. Chem.*, **36**, 1567 (1965). [t] N. R. Kunchur, *Nature (London)*, **204**, 468 (1964). [u] R. S. McEwen and G. A. Sim, *J. Chem. Soc. A*, 271 (1967). [v] K. K. Cheung and G. A. Sim, *ibid.*, 5988 (1965). [w] W. R. Costello, A. T. McPhail, and G. A. Sim, *ibid.*, *A*, 1190 (1966).

(1) and 2.01 (1) Å. The P–O bonds are also nonequivalent. Those within the nonbridging ligand average 1.62 (3) Å in length whereas those within the bridging ligand average 1.54 (2) Å in length, the averages differing by at most three standard deviations. Both deviate from the average length 1.57 (2) Å observed within this series.[22] The relative importance of π bonding within the PS_2O_2 groups is difficult to assess directly because of the paucity of data on M←SPO bond lengths. We therefore offer no formal explanation for the P–O bond length differences at this time. The S–P–S and O–P–O bond angles in the distorted PS_2O_2 tetrahedron are consistent

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(22) The weighted average, plus associated rms deviation, was based on the lengths of P–O bonds present in $-PS_2(OR)_2$ ligands reported in ref 1 and 21 and the following: (a) V. Kastalsky and J. F. McConnell, *Acta Crystallogr., Sect. B*, **25**, 909 (1969); (b) J. F. McConnell and V. Kastalsky, *ibid.*, **22**, 853 (1967); (c) S. Ooi and Q. Fernando, *Inorg. Chem.*, **6**, 1558 (1967); (d) S. Husebye, *Acta Chem. Scand.*, **20**, 24 (1966); (e) S. L. Lawton, *Inorg. Chem.*, **9**, 2269 (1970). (f) Bond lengths used include corrections for thermal motion of the atoms when available. The 1.62 (3) Å average bond length in $Hg(dtp)_2$ is within one standard deviation of the P–O bond length 1.64 (5) Å reported in ionic $KS_2P(OCH_3)_2$: P. Coppens, C. H. MacGillavry, S. G. Hovenkamp, and H. Douwes, *Acta Crystallogr.*, **15**, 765 (1962).

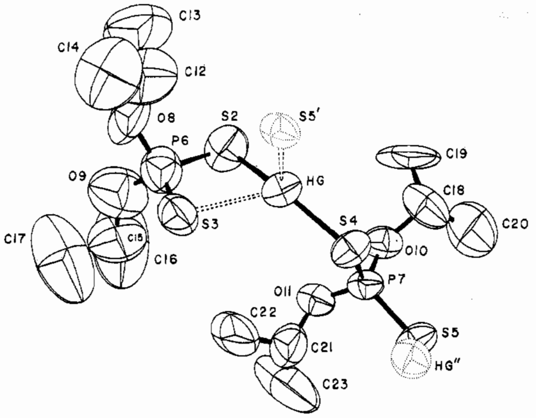

Figure 4.—A parallel projection of the $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$ molecule illustrating the principal root-mean-square thermal displacements. Ellipsoidal boundaries are at the 60% probability level. Atoms S(5′) at $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$ and Hg″ at $^1/_2 - x, -^1/_2 + y, {}^1/_2 - z$ are related by symmetry to the parent molecule at x, y, z and are indicated by dotted lines.

with those in other phosphorodithioates.[1,21,22a-22f,23]

The two multidentate PS_2 ligands each form a nearly planar array of linkages with the mercury atom, the maximum deviation from planarity not exceeding 0.08 Å. Expressed in unit cell coordinates, the equation of the weighted plane[24] for the chelating ligand with mercury is $0.844x - 6.028y + 12.011z - 0.225 = 0$; distances of the defining atoms from this plane are as follows (Å): Hg(1), −0.0006 (8); S(2), 0.044 (6); S(3), 0.028 (5); P(6), −0.076 (7). The equation of the weighted plane for the bridging ligand with mercury is $19.836x - 6.634y - 11.351z - 0.305 = 0$; distances of the defining atoms from this plane are as follows (Å): Hg(1), 0.0012(8); S(4), −0.048(5); S(5), 0.059(5); P(7), −0.080 (5). The mercury atom Hg(1) is substantially out of the plane defined by atoms S(2), S(3), and S(4), however, by an amount 0.480 (1) Å. This deviation may be due to the presence of the Hg(1)–S(5′) bridge as well as to crystal packing.

Thermal Motion.—As can be seen in Figure 4, atoms within the inner coordination sphere appear to undergo normal vibrational motions. The relative sizes and orientations of the derived thermal ellipsoids for the isopropyl groups, however, are so excessively large that it is doubtful the ellipsoidal model adequately describes actual motions of the atoms in these groups. It is more reasonable to expect that these groups undergo extensive libration. Significantly, the principal rms thermal displacements of the Hg, S, and P atoms range from 0.22 to 0.38 Å (Table II), indicating the presence of large lattice vibrations as well; such vibrations would be anticipated in a low-melting material (99.5°).

As was found in crystals of polymeric $Zn[(C_2H_5O)_2PS_2]_2$, the bridging group exhibits generally smaller thermal parameters than does the chelating group, reflecting the tight binding of atoms within the chains.

van der Waals Contacts.—The laterally stacked chains are held together by methyl···sulfur, methyl···oxygen, and methyl···methyl interactions, the latter being the most prevalent. All the distances are normal when compared with the expected values of 3.85, 3.4, and 4.0 Å, respectively.

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The Crystal and Molecular Structure of Chlorotris(N,N'-dimethylthiourea)copper(I)

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The crystal structure of chlorotris(N,N'-dimethylthiourea)copper(I) has been determined from counter diffractometer data at room temperature from 240 crystallographically independent reflections. The compound crystallizes in the rhombohedral space group $R3m$ with $a = b = c = 8.867 \pm 0.002$ Å, $\alpha = \beta = \gamma = 112.43 \pm 0.08°$ (hexagonal cell: $a = b = 14.741$ (3) Å, $c = 7.471$ (2) Å, $d_m = 1.44$ (3) g/cm³, and $d_c = 1.46$ g/cm³ with one molecule in the rhombohedral cell. The structure was solved by conventional heavy-atom techniques and refined by full-matrix least squares to a final conventional R of 0.030. The structure is composed of discrete "tetrahedral" molecules separated by ordinary van der Waals distances. The space group requires the molecule to have $3m$ (C_{3v}) symmetry. The Cu–S and Cu–Cl distances are 2.360 ± 0.001 and 2.406 ± 0.005 Å, respectively, while the S–Cu–S and S–Cu–Cl angles are 106.4 ± 0.1 and $112.4 \pm 0.1°$, respectively. The Cu–S–C angle is $111.1 \pm 0.3°$ and the metal–sulfur bond involves the sulfur sp² orbital. The analogous Ag complex has a cell six times as large.

Introduction

It has been shown that the Cu(I) and Ag(I) complexes with thiourea, $SC(NH_2)_2$, hereafter tu, give rise to a multiplicity of stoichiometries and some unusual and unexpected bonding as well. $Cu(tu)_3Cl$[2] is a chain structure made up of almost regular tetrahedrally co-

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[2] (a) Y. Okaya, C. B. Knobler, and R. Pepinsky, *Z. Kristallogr., Kristallgeometrie, Kristallophys., Kristallchem.*, **111**, 385 (1959); (b) Y. Okaya and C. Knobler, *Acta Crystallogr.*, **17**, 928 (1964).