and two carbon atoms of the PNC_2 groups. In both the $(OMPA)_2$ and $(OMPA)_3$ complexes of Cu(II)[2,24] the PNC_2 groups which are coplanar with the P–O (donor) bond are more nearly planar than the other PNC_2 groups. In CuPCP, this tendency, if present, is much less pronounced. Instead, there is a correlation between the planarity of the nitrogen bonds and the presence of the PNC_2 group in axial or equatorial positions (see Table VI). In every case except one (N(20) and N(24)), the axial PNC_2 groups are more nearly planar than the corresponding equatorial group involving the same phosphorus atom. On the average, the nitrogen atom deviates 0.056 Å from the PC_2 plane for axial and 0.113 Å for equatorial groups.

The average bond distances and mean deviations for CuPCP are as follows: phosphoryl P–O, 1.483 (5) Å; bridging P–C–(P), 1.798 (13) Å; P–N, 1.623 (12) Å; N–C, 1.443 (30) Å.[25] The P–O distance is nearly identical with the corresponding distance in CuOMPA[2] and the $(OMPA)_2$ complex;[24] the short distance has been accounted for in terms of multiple bonding.[26,27] The P–C–(P) bond distances are consistent with literature values of 1.83 Å for $P\text{–}CH_2$[28] and 1.80–1.83 Å for $P\text{–}CH_3$[29–31] single bonds. The P–N bond distances are comparable to values of 1.56–1.63 Å which have been reported for delocalized systems involving P–N linkages.[32] The accepted value for a P–N single bond is 1.77–1.78 Å.[33,34]

In CuPCP the Cu–O distances range from 2.023 to 2.134 Å and the O–Cu–O angles are in the range 87.2–93.6°. In CuOMPA[2] the Cu–O distances are equal (2.065 Å) and the angles about Cu(II) are in the range 88.4–90.6°. Thus, the symmetry of Cu(II) in CuPCP is definitely lower than that of Cu(II) in CuOMPA, although the distortion from octahedral symmetry is not large.

At present, it is not possible to say whether the distortions of CuPCP from octahedral geometry arise because of the Jahn–Teller effect or because of steric effects. It is conceivable that the several short intra- and intermolecular atomic distances, through the distortions they introduce, affect the Cu–O distances. The present work, however, provides additional evidence that tris chelates of Cu(II) possess either trigonal symmetry or approximate octahedral geometry.

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CONTRIBUTION FROM THE MOBIL RESEARCH AND DEVELOPMENT CORPORATION, RESEARCH DEPARTMENT,
PAULSBORO, NEW JERSEY 08066

The Crystal Structure of *catena*-Bis[μ-(*O,O'*-diisopropyldithiophosphato)-digold(I)](*Au–Au*), $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$, a Polymeric Complex Containing Weak Gold–Gold Interactions

BY STEPHEN L. LAWTON,* WAYNE J. ROHRBAUGH, AND GEORGE T. KOKOTAILO

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The crystalline compound *catena*-bis[μ-(*O,O'*-diisopropyldithiophosphato)-digold(I)](*Au–Au*), $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$, forms yellow needles in the triclinic space group $P\bar{1}$ (C_i^1) with unit cell parameters $a = 12.495 \pm 0.004$, $b = 17.251 \pm 0.004$, $c = 12.167 \pm 0.004$ Å, $\alpha = 99.33 \pm 0.03°$, $\beta = 102.17 \pm 0.05°$, $\gamma = 72.79 \pm 0.02°$. The observed and calculated densities are 2.21 and 2.238 ± 0.002 g/cm³ (for $Z = 4$ formula weights/unit cell), respectively. A full-matrix anisotropic–isotropic least-squares refinement has resulted in a discrepancy index of 0.062 using three-dimensional X-ray diffraction counter data. The crystal structure is comprised of two crystallographically independent dimers each of which contains one gold–gold bond bridged through sulfur by two bidentate $S_2P(OC_3H_7)_2$ ligands. These dimers are joined together through the metal atoms in a staggered arrangement to form linear chains of weak gold–gold bonds extending the full length of the crystal. The gold–gold separations along the chain *within* and *between* the $[Au(dtp)]_2$ dimers range from 2.914 (5) to 3.109 (6) Å, with the average, 3.04 Å, being equivalent to $c/4$. Each gold atom is therefore surrounded by four atoms, two of which are sulfur and two are gold, in a slightly distorted square-planar configuration. The Au–S bonds average 2.28 (rms, 0.03) Å in length, a value which is comparable with that in gold(III) sulfur-ligated complexes. This material has been found to be dimeric in benzene solution by vapor pressure osmometry.

Introduction

The development of oil-soluble compounds which will deposit soft metallic films on rubbing metal surfaces for the reduction of wear has long been an objective in lubricant science. Investigation of metal *O,O'*-dialkylphosphorodithioates in this laboratory has resulted in the finding that gold derivatives exhibit excellent lubrication performance in this regard. These gold complexes are attractive because of their ability to deposit soft metallic films on the rubbing surfaces *in situ*. Wear studies, utilizing a four-ball machine and a pin-on-disk machine with *n*-hexadecane as the solvent, have demonstrated that any gold loss due to wear is replenished by further deposition for as long as additive is present in solution.[1] These results are significant since they provide the first demonstration of this novel mode of lubrication.

The mechanism of gold deposition on the rubbing metal surfaces is not fully understood. In an effort to shed light on this aspect, we have undertaken elucidation of the molecular structure of one of these gold compounds. The *O,O'*-diisopropylphosphorodithioate derivative, $Au(i\text{-}C_3H_7O)_2PS_2$, was selected for crystallographic study to enable direct comparisons to be made with other metal compounds having the same ligand and alkyl group.[2-5]

Experimental Section

Preparation.—Crystalline $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$, hereafter $\{[Au(dtp)]_2\}_n$, was prepared by treating an aqueous solution of ammonium *O,O'*-diisopropylphosphorodithioate (0.3 mol in 25 to 50 ml of water) with an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.1 mol in 25 to 50 ml of water).[1b] The ammonium salt was initially prepared by the procedure of Wystrach, *et al.*[6] The $\{[Au(dtp)]_2\}_n$ precipitate, formed as a result of exchange and reduction reactions, was isolated by filtration. Yellow acicular crystals (mp 109–110.5°) suitable for use in the X-ray investigation were obtained by recrystallization of the compound from acetone.

Crystal Data.—$\{[Au(dtp)]_2\}_n$, formula weight 820.49 per $[Au(dtp)]_2$ group, is triclinic with space group $P\bar{1}$ (C_i^1). The lattice parameters at 25° are $a = 12.495$ (4), $b = 17.251$ (4), $c = 12.167$ (4) Å, $\alpha = 99.33$ (3)°, $\beta = 102.17$ (5)°, and $\gamma = 72.79$ (2)°, $V = 2435$ (2) Å^3; $d_{obsd} = 2.21$ g/cm^3 (by flotation); and $d_{calcd} = 2.238$ (2) g/cm^3 for four formula weights/unit cell.

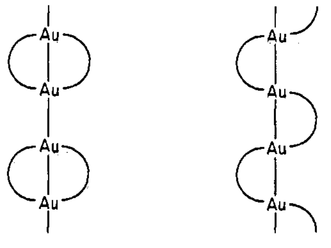
The triclinic symmetry was initially indicated by Weissenberg and precession X-ray photographs and the choice of $P\bar{1}$ as the probable space group was confirmed by the satisfactory refinement of the derived structure. The lattice parameters were determined by a least-squares fit[7] to 187 high angle Kα reflections measured from zero-level Weissenberg zones taken with copper radiation [$\lambda(K\alpha_1) = 1.54050$ Å and $\lambda(K\alpha_2) = 1.54434$ Å] using crystals mounted in three different orientations; each film was calibrated with superimposed aluminum powder lines ($a_0 = 4.0331$ Å). The Nelson–Riley extrapolation function was employed in the refinement. Indicated errors are 2σ. The observed lattice parameters correspond to the Niggli reduced cell. No symmetry higher than primitive triclinic was detected; the lack of higher symmetry was verified by the computer program TRACER II.[8]

Collection and Reduction of X-Ray Intensity Data.—Complete three-dimensional X-ray diffraction intensity data were taken at room temperature (23 ± 4°) with zirconium-filtered molybdenum radiation from a needle-like crystal 0.157 mm long and of cross-section 0.08 × 0.10 mm. The crystal was mounted in a 0.3 mm Lindemann glass capillary parallel with its longest dimension (c axis) and mounted on the diffractometer with c^* coincident with the ϕ axis. The half-widths of a number of narrow source–open counter 2θ scans[9] ranged from 0.05 to 0.13° θ, indicating that the crystal mosaicity was 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° take-off angle. The crystal–source and crystal–counter distances were 17 and 18.5 cm, respectively. The dimensions of the counter aperture were 5.0 × 5.0 mm. 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. Collection of the data covered the range $2\theta \leq 55°$ to include all possible observed reflections. A total of 11,218 independent reflections, as well as 516 Friedel pairs of reflections ($hk0$ and $\bar{h}\bar{k}0$, $\bar{h}k0$ and $h\bar{k}0$), were measured. Three standard reflections were monitored periodically as a check on crystal and electronic stability and a linear 26% decrease in intensities was observed.

The raw intensity of each reflection was corrected for background, crystal decomposition, Lorentz, polarization and absorption effects; equivalent forms were averaged. Transmission factors were calculated by the program ACACA.[10] The crystal was defined as an ellipsoidal cylinder with minor and major diameters 0.0808 and 0.1124 mm, respectively; these diameters represented a modification of those obtained by optical measurement and were determined by utilizing a method previously described.[3] Transmission factors for the full set of three-dimensional data ranged from 0.250 to 0.394, based on a linear absorption coefficient of 128.73 cm^{-1} for Mo Kα radiation. Estimated standard deviations in the intensities were computed as described elsewhere,[11] using a value of 0.04 for p. The estimated standard deviation in each structure factor was calculated by the method of finite-differences.[12] A total of 2725 independent reflections were observed above the background level of which 2194 had $F_o \geq 3\sigma(F_o)$. The remaining 531 reflections were considered as unobserved and thus omitted from the refinements.

Solution and Refinement of the Structure

Solution of the structure was achieved by standard heavy-atom techniques. A three-dimensional Patterson function[13] yielded a consistent set of trial x, y coordinates for the gold, sulfur, and phosphorus atoms, with an indication that each gold atom was separated by a distance equivalent to one-fourth the unit cell c parameter, ~3.0 Å, yielding an infinite –Au–Au– chain positioned at $\pm(^1/_4, ^1/_4)$. This gold repetition was initially indicated by the presence of very strong hkl reflections satisfying the condition $l = 4n$. The z coordinates of the atoms relative to the origin were derived by performing a series of structure factor calculations assuming, initially, structure I [⊃ represents $S_2P(OC_3H_7)_2$].



I II

The enantiomorph was first determined utilizing $l = 4n$ reflections only, by placing a reference gold atom, *viz.*, Au(1), at $z = \pm 1/40$.

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TABLE I

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

Atom	x	y	z	β_{11}′ or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv[c] B, Å^2
Au(1)	0.25802 (37)	0.24954 (26)	0.40135 (30)	0.01163 (51)	0.00535 (26)	0.00521 (36)	−0.00421 (29)	0.00161 (34)	−0.00010 (24)	4.73
Au(2)	0.24911 (34)	0.25101 (27)	0.65414 (29)	0.00680 (38)	0.00664 (27)	0.00467 (38)	−0.00245 (25)	0.00187 (31)	0.00038 (25)	4.36
Au(3)	0.24880 (38)	0.25033 (25)	0.90463 (28)	0.01249 (51)	0.00456 (24)	0.00399 (30)	−0.00350 (28)	0.00177 (32)	0.00053 (21)	4.40
Au(4)	0.25113 (35)	0.25203 (24)	1.14502 (28)	0.00793 (41)	0.00441 (23)	0.00528 (32)	−0.00198 (25)	0.00135 (31)	−0.00023 (22)	4.01
S(1)	0.4366 (15)	0.1623 (11)	0.4121 (12)	0.0062 (15)	0.0058 (9)	0.0033 (11)	−0.0007 (9)	0.0003 (10)	−0.0004 (7)	4.12
S(2)	0.4252 (20)	0.1663 (15)	0.6922 (19)	0.0115 (22)	0.0107 (14)	0.0059 (16)	−0.0031 (14)	0.0037 (15)	−0.0013 (12)	7.09
S(3)	0.0754 (16)	0.3371 (12)	0.3709 (14)	0.0071 (16)	0.0055 (9)	0.0068 (16)	−0.0011 (10)	0.0023 (12)	0.0019 (9)	4.44
S(4)	0.0740 (22)	0.3334 (16)	0.6490 (15)	0.0171 (28)	0.0120 (16)	0.0036 (13)	−0.0072 (17)	0.0006 (15)	−0.0004 (11)	7.77
S(5)	0.3043 (18)	0.3667 (9)	0.9290 (12)	0.0235 (27)	0.0049 (8)	0.0079 (13)	−0.0053 (12)	0.0094 (16)	−0.0025 (8)	6.91
S(6)	0.1835 (14)	0.3915 (9)	1.1644 (11)	0.0111 (17)	0.0047 (7)	0.0082 (13)	−0.0017 (9)	0.0046 (12)	−0.0003 (7)	5.15
S(7)	0.1873 (20)	0.1357 (12)	0.8546 (10)	0.0311 (34)	0.0104 (12)	0.0031 (10)	−0.0148 (18)	0.0009 (15)	−0.0011 (8)	8.71
S(8)	0.3176 (15)	0.1122 (8)	1.1303 (12)	0.0151 (20)	0.0034 (7)	0.0090 (13)	−0.0041 (13)	0.0009 (13)	0.0007 (7)	5.45
P(1)	0.5048 (13)	0.1853 (10)	0.5741 (11)	0.0084 (16)	0.0058 (9)	0.0054 (11)	−0.0031 (10)	0.0010 (10)	−0.0006 (7)	5.59
P(2)	0.0007 (13)	0.3169 (9)	0.4840 (12)	0.0070 (14)	0.0051 (8)	0.0084 (13)	−0.0030 (9)	0.0013 (11)	0.0004 (8)	4.48
P(3)	0.2867 (13)	0.4220 (9)	1.0816 (11)	0.0103 (16)	0.0037 (7)	0.0071 (12)	−0.0027 (9)	0.0023 (11)	−0.0002 (7)	4.38
P(4)	0.2129 (14)	0.0803 (9)	0.9955 (11)	0.0103 (16)	0.0047 (8)	0.0065 (11)	−0.0029 (9)	0.0015 (11)	−0.0007 (7)	4.73
O(1)	0.6307 (31)	0.1276 (20)	0.5927 (26)	5.2 (8)						
O(2)	0.5131 (31)	0.2754 (21)	0.5893 (27)	5.5 (8)						
O(3)	−0.0137 (31)	0.2295 (21)	0.4565 (26)	5.6 (8)						
O(4)	−0.1259 (30)	0.3658 (20)	0.4660 (25)	5.1 (8)						
O(5)	0.4032 (33)	0.4191 (22)	1.1597 (29)	6.7 (9)						
O(6)	0.2426 (27)	0.5146 (19)	1.0864 (24)	4.3 (7)						
O(7)	0.0975 (33)	0.0866 (22)	1.0249 (29)	6.6 (9)						
O(8)	0.2502 (27)	−0.0170 (19)	0.9735 (24)	4.6 (7)						

Group	x_c[d]	y_c	z_c	δ	ϵ	η	B,[e] Å^2
C_3H_7(1)	0.7025 (40)	0.0202 (26)	0.5880 (39)	−1.24 (16)	−1.86 (4)	−1.13 (18)	9.5 (11)
C_3H_7(2)	0.5703 (69)	0.3406 (43)	0.7187 (45)	1.08 (8)	3.12 (7)	−0.12 (16)	17.7 (20)
C_3H_7(3)	−0.0834 (55)	0.1682 (34)	0.5100 (43)	1.29 (6)	2.81 (5)	−2.85 (13)	12.6 (15)
C_3H_7(4)	−0.1929 (40)	0.4797 (25)	0.4858 (43)	−0.69 (12)	1.99 (4)	−2.72 (14)	9.2 (12)
C_3H_7(5)	0.5300 (38)	0.3418 (24)	1.2064 (40)	2.18 (8)	−2.13 (4)	1.74 (12)	9.1 (10)
C_3H_7(6)	0.1202 (33)	0.5903 (22)	1.0189 (33)	−1.19 (7)	2.08 (4)	3.16 (12)	7.4 (9)
C_3H_7(7)	−0.0395 (48)	0.1359 (30)	1.0386 (56)	−0.84 (12)	2.88 (5)	1.46 (7)	12.2 (16)
C_3H_7(8)	0.3784 (33)	−0.0890 (23)	0.9218 (33)	1.32 (9)	1.98 (4)	−2.63 (13)	7.7 (9)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter. [b] 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, η (in radians) are those described in ref 19. The origin of the internal system was taken at the group center with $\mathbf{a}_3$ normal to the plane and $\mathbf{a}_1$ ($\mathbf{a}_2$ for C_3H_7(7)) bisecting the C–C–C angle. [e] B is the refined isotropic thermal parameter for the group.

Of the two sets, the lower R value was obtained for $+1/40$. Utilizing $l \neq 4n$ reflections next, the value of z for the set $z = (1 + 5n)/40$, where $n = 0,1,2$, or 3, was then obtained by computing R for each n. Minimum R was obtained for $n = 3$, requiring Au(1) to assume a z coordinate of $\sim 16/40$. A subsequent series of full three-dimensional Fourier syntheses and isotropic–anisotropic least-squares refinements led to the location of the remaining 32 nonhydrogen atoms in the structure. Structure II was eventually ruled out as a candidate.

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 Au, S, P, O, and C tabulated by Hanson, *et al.*,[14] were used. Effects of anomalous scattering were included in F_c;[15] the values of $\Delta f'$ and $\Delta f''$ given in ref 16 were used for Au, S, and P. The initial 15 cycles, first with all atoms isotropic, then with Au, S, and P anisotropic, plus the scale factor, resulted in reliability indices of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.059$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.029$. For these initial cycles only reflections in the region $2\theta \leq 37.5°$ were used, 1350 in number and representing 62% of the total data, since those with larger scattering angles were not expected to significantly improve the positional parameters of the atoms at this stage.

Examination of the positional parameters of the isopropyl groups suggested that some constraint should be applied, since some carbon–carbon distances were as small as 1.33 Å and as large as 1.76 Å. These variations correlated with evidence from a difference electron density map which strongly suggested that some of the isopropyl groups were undergoing extensive librations. A rigid-body model having C_{2v} symmetry with C–C bonds 1.48 Å in length[17] and a C–C–C angle of 113°[18] was therefore introduced, using the least-squares group refinement procedure described by Ibers, *et al.*[19] The variable parameters for a group included an overall isotropic thermal parameter, the coordinates of the group center, and three orientation angles which have been described elsewhere.[19] In order to approximate the librational motions of these groups, a percentage correction was applied to the individual thermal parameter of each carbon atom; a value of 28% was subtracted from the refined overall thermal parameter for the vertex carbon and 14% was added for each methyl carbon. Analysis of mean $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ and of scattering angle was also carried out, revealing a trend in which the strong reflections were being overweighted. The weights were subsequently modified to remove this dependency. Ten cycles of refinement, now using all 2194 reflections above 3σ, resulted in convergence of the structure to $R_1 = 0.062$ and $R_2 = 0.037$. Substantial improvements in all bond lengths and angles involving O and C were noted by using these new weights since, in effect, greater emphasis was now being placed on the relatively weak, yet *important*, reflections of the type $l \neq 4n$. The final error-of-fit based on the 233 variables was 1.14. During the final cycle the shift in each positional parameter of the nongroup atoms averaged 4% of its corresponding standard deviation and those of the group atoms averaged 15%. A final difference electron density map contained residuals no larger than 0.3 e/Å^3, or at most 20% of a carbon atom.

The final positional, thermal, and group parameters are given in Table I, along with the associated standard deviations as esti-

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

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(18) Based on the average value observed in the molecule $[i\text{-}C_3H_7O)_2PS_2]_2$: S. L. Lawton, *Inorg. Chem.*, **9**, 2269 (1970).

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TABLE II

DERIVED POSITIONAL PARAMETERS FOR GROUP ATOMS IN $\{(Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$

Atom	x	y	z
	$C_3H_7(1)$		
C(1)	0.6580 (42)	0.0342 (73)	0.5918 (46)
C(2)	0.6967 (58)	0.0009 (41)	0.4826 (39)
C(3)	0.7526 (55)	0.0255 (68)	0.6895 (39)
	$C_3H_7(2)$		
C(4)	0.5486 (79)	0.3178 (50)	0.7202 (74)
C(5)	0.6738 (75)	0.3006 (64)	0.7360 (96)
C(6)	0.4885 (85)	0.4034 (59)	0.6997 (97)
	$C_3H_7(3)$		
C(7)	−0.0754 (65)	0.1980 (36)	0.5237 (56)
C(8)	0.0080 (66)	0.1201 (50)	0.5533 (72)
C(9)	−0.1828 (59)	0.1866 (53)	0.4531 (73)
	$C_3H_7(4)$		
C(10)	−0.1493 (45)	0.4628 (54)	0.5009 (51)
C(11)	−0.2421 (56)	0.4816 (60)	0.5674 (49)
C(12)	−0.1873 (67)	0.4946 (41)	0.3892 (53)
	$C_3H_7(5)$		
C(13)	0.4938 (47)	0.3354 (47)	1.1765 (44)
C(14)	0.5938 (55)	0.3479 (54)	1.1421 (47)
C(15)	0.5025 (55)	0.3421 (40)	1.3007 (46)
	$C_3H_7(6)$		
C(16)	0.1383 (59)	0.5577 (23)	1.0225 (44)
C(17)	0.0635 (50)	0.6129 (35)	1.0985 (45)
C(18)	0.1589 (60)	0.6001 (35)	0.9357 (45)
	$C_3H_7(7)$		
C(19)	−0.0061 (59)	0.1484 (43)	1.0326 (66)
C(20)	−0.0286 (80)	0.1422 (62)	1.1451 (55)
C(21)	−0.0838 (81)	0.1172 (72)	0.9381 (55)
	$C_3H_7(8)$		
C(22)	0.3683 (71)	−0.0558 (23)	0.9290 (37)
C(23)	0.4242 (61)	−0.1099 (34)	1.0194 (36)
C(24)	0.3428 (60)	−0.1012 (37)	0.8170 (35)

TABLE III

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

Atom	Min	Med	Max
Au(1)	0.190 (7)	0.223 (8)	0.306 (6)
Au(2)	0.168 (7)	0.216 (7)	0.302 (6)
Au(3)	0.161 (6)	0.225 (7)	0.301 (6)
Au(4)	0.189 (6)	0.231 (6)	0.252 (6)
S(1)	0.150 (26)	0.209 (24)	0.301 (21)
S(2)	0.180 (29)	0.286 (28)	0.394 (26)
S(3)	0.187 (24)	0.228 (25)	0.285 (23)
S(4)	0.157 (28)	0.310 (29)	0.417 (28)
S(5)	0.161 (21)	0.243 (21)	0.422 (24)
S(6)	0.201 (19)	0.260 (20)	0.296 (21)
S(7)	0.134 (25)	0.224 (22)	0.513 (26)
S(8)	0.182 (22)	0.252 (19)	0.333 (21)
P(1)	0.188 (20)	0.232 (22)	0.291 (21)
P(2)	0.192 (23)	0.244 (20)	0.272 (22)
P(3)	0.205 (20)	0.221 (19)	0.275 (22)
P(4)	0.199 (19)	0.250 (20)	0.279 (22)

TABLE V

INTERATOMIC DISTANCES (Å) IN $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$[a]

Atoms	Type	Dist	Atoms	Type	Dist
Au(1)—Au(2)	a	3.097 (6)	S(5)—P(3)	e	1.970 (18)
Au(2)—Au(3)	b	3.050 (6)	S(6)—P(3)	e	2.019 (21)
Au(3)—Au(4)	a	2.914 (5)	S(7)—P(4)	e	2.017 (23)
Au(4)—Au(1′)	b	3.109 (6)	S(8)—P(4)	e	1.983 (22)
Au(1)—S(1)	c	2.284 (18)	P(1)—O(1)	f	1.59 (4)
Au(1)—S(3)	c	2.326 (19)	P(1)—O(2)	f	1.57 (4)
Au(2)—S(2)	c	2.253 (25)	P(2)—O(3)	f	1.55 (4)
Au(2)—S(4)	c	2.223 (27)	P(2)—O(4)	f	1.54 (4)
Au(3)—S(5)	c	2.267 (16)	P(3)—O(5)	f	1.55 (4)
Au(3)—S(7)	c	2.276 (16)	P(3)—O(6)	f	1.52 (3)
Au(4)—S(6)	c	2.292 (16)	P(4)—O(7)	f	1.53 (4)
Au(4)—S(8)	c	2.297 (15)	P(4)—O(8)	f	1.60 (3)
S(1)···S(2)	d	3.430 (27)	O(1)—C(1)	g	1.54 (13)
S(3)···S(4)	d	3.398 (31)	O(2)—C(4)	g	1.67 (10)
S(5)···S(6)	d	3.422 (18)	O(3)—C(7)	g	1.49 (8)
S(7)···S(8)	d	3.436 (21)	O(4)—C(10)	g	1.61 (10)
S(1)—P(1)	e	2.001 (20)	O(5)—C(13)	g	1.56 (8)
S(2)—P(1)	e	2.028 (24)	O(6)—C(16)	g	1.43 (8)
S(3)—P(2)	e	1.944 (22)	O(7)—C(19)	g	1.42 (9)
S(4)—P(2)	e	2.036 (25)	O(8)—C(22)	g	1.60 (9)

Averages of Chemically Equivalent Bond Lengths (Å)

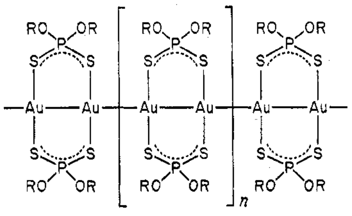
Bond	Type	Av (rms dev)	Bond	Type	Av (rms dev)
Au—Au	a	3.00 (12)	S—P	e	2.00 (3)
Au—Au	b	3.08 (4)	P—O	f	1.56 (3)
Au—S	c	2.28 (3)	O—C	g	1.53 (9)
S···S	d	3.42 (2)			

[a] Atomic coordinates for primed atoms in Tables V–VII are defined as follows: singly primed occur at $x, y, -1 + z$; doubly primed occur at $x, y, 1 + z$.

mated 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 1. The values of $|F_o|$ and F_c (in electrons ×10) for all 2194 observations are included in Table IV.[20] Tables V and VI give the final bond lengths and angles, with Figure 2 summarizing selected values in the inner coordination sphere. Standard deviations were derived from the variance–covariance matrix for functions involving nongroup atoms and from variances alone for those involving group atoms.[21]

Description of the Structure

Crystalline $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$ is comprised of an indefinite extension of [Au(dtp)]$_2$ units linked together through the metal atoms.[22] The resulting one-dimensional polymers, having structure III (R = $i\text{-}C_3H_7$),



III

contain chains of weak gold–gold bonds extending the full length of the crystal parallel with the needle axis. Metal–metal bonds linking dimeric units are formed by virtue of the tendency of monovalent gold to use all its valence orbitals (*i.e.*, to form a "closed-shell" electronic configuration). The square-planar configuration achieved by each gold atom is consistent with geometry usually displayed by trivalent gold. The five atoms defining each plane are coplanar within 5σ, as shown by Table VII for planes 1–4, and the four equatorial angles within each plane do not deviate by more than 6° from 90° (Figure 2).

The gold–gold bonds range in length from 2.914 (5)

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(20) Table IV will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number INORG-72-2227. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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

(22) Molecular weight vapor pressure osmometry data indicate that in benzene with weight per cent concentrations of 4% or less at 37° these chains dissociate into its dimeric units: J. J. Dickert, private communication, 1971.

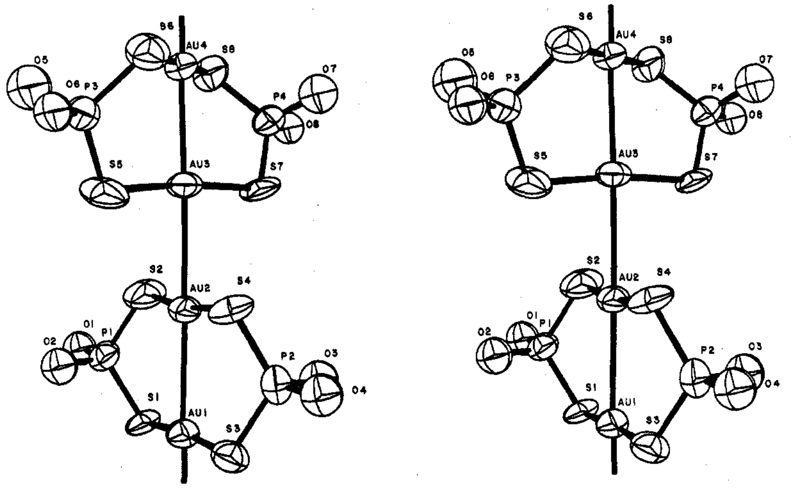

Figure 1.—A stereographic view of the two crystallographically independent $[\mathrm{Au(dtp)}]_2$ dimers per unit cell along the infinite Au–Au chain. Dimer 1 contains Au(1) and Au(2); dimer 2 contains Au(3) and Au(4). For simplicity, the isopropyl groups are not shown. Ellipsoidal boundaries are at the 63% probability level.

TABLE VI
INTERATOMIC ANGLES (DEG) IN $\{[\mathrm{Au}(i\text{-}\mathrm{C_3H_7O})_2\mathrm{PS_2}]_2\}_n$

Atoms	Type	Angle
Gold Coordination		
Au(1)–Au(2)–Au(3)	a	178.1 (2)
Au(2)–Au(3)–Au(4)	a	178.9 (2)
Au(3)–Au(4)–Au(1′)	a	178.6 (2)
Au(4)–Au(1′)–Au(2′)	a	176.6 (2)
Au(2)–Au(1)–S(1)	b	94.1 (4)
Au(2)–Au(1)–S(3)	b	91.5 (4)
Au(4)–Au(1′)–S(3′)	c	85.2 (4)
Au(4)–Au(1′)–S(5′)	c	89.1 (4)
Au(1)–Au(2)–S(2)	b	94.3 (5)
Au(1)–Au(2)–S(4)	b	96.1 (5)
Au(3)–Au(2)–S(2)	c	83.9 (5)
Au(3)–Au(2)–S(4)	c	85.7 (5)
Au(2)–Au(3)–S(5)	c	85.3 (4)
Au(2)–Au(3)–S(7)	c	87.1 (4)
Au(4)–Au(3)–S(5)	b	93.6 (4)
Au(4)–Au(3)–S(7)	b	94.0 (4)
Au(1′)–Au(4)–S(6)	c	90.3 (4)
Au(1′)–Au(4)–S(8)	c	88.2 (4)
Au(3)–Au(4)–S(6)	b	91.1 (4)
Au(3)–Au(4)–S(8)	b	90.4 (4)
S(1)–Au(1)–S(3)	d	174.3 (5)
S(2)–Au(2)–S(4)	d	169.6 (6)
S(5)–Au(3)–S(7)	d	172.2 (6)
S(6)–Au(4)–S(8)	d	178.4 (5)
Sulfur Coordination		
Au(1)–S(1)–P(1)	e	102.2 (8)
Au(2)–S(2)–P(1)	e	103.0 (12)
Au(1)–S(3)–P(2)	e	104.7 (10)
Au(2)–S(4)–P(2)	e	103.4 (10)
Au(3)–S(5)–P(3)	e	109.2 (8)
Au(4)–S(6)–P(3)	e	100.7 (7)
Au(3)–S(7)–P(4)	e	107.8 (7)
Au(4)–S(8)–P(4)	e	101.6 (8)

Averages of Chemically Equivalent Bond Angles (Deg)

Angle	Type	Av (rms dev)	Angle	Type	Av (rms dev)
Au–Au–Au	a	178 (1)	S–P–S	f	118 (1)
Au–Au–S	b	93 (2)	S–P–O	g	109 (3)
Au–Au–S	c	87 (2)	O–P–O	h	99 (5)
S–Au–S	d	174 (4)	P–O–C	i	120 (7)
Au–S–P	e	104 (3)	O–C–C	j	103 (5)

Atoms	Type	Angle
Phosphorus Coordination		
S(1)–P(1)–S(2)	f	116.7 (11)
S(3)—P(2)–S(4)	f	117.3 (11)
S(5)–P(3)–S(6)	f	118.1 (10)
S(7)–P(4)–S(8)	f	118.4 (10)
S(1)–P(1)–O(1)	g	107.1 (13)
S(1)–P(1)–O(2)	g	106.5 (15)
S(2)–P(1)–O(1)	g	107.3 (15)
S(2)–P(1)–O(2)	g	111.4 (14)
S(3)–P(2)–O(3)	g	108.9 (15)
S(3)–P(2)–O(4)	g	110.0 (15)
S(4)–P(2)–O(3)	g	109.4 (16)
S(4)–P(2)–O(4)	g	110.6 (15)
S(5)–P(3)–O(5)	g	112.1 (16)
S(5)–P(3)–O(6)	g	114.1 (14)
S(6)–P(3)–O(5)	g	109.8 (15)
S(6)–P(3)–O(6)	g	103.5 (14)
S(7)–P(4)–O(7)	g	108.8 (18)
S(7)–P(4)–O(8)	g	113.4 (13)
S(8)–P(4)–O(7)	g	111.2 (16)
S(8)–P(4)–O(8)	g	107.3 (14)
O(1)–P(1)–O(2)	h	107.4 (21)
O(3)–P(2)–O(4)	h	99.2 (22)
O(5)–P(3)–O(6)	h	96.9 (20)
O(7)–P(4)–O(8)	h	95.5 (20)
Oxygen Coordination		
P(1)–O(1)–C(1)	i	123 (3)
P(1)–O(2)–C(4)	i	118 (4)
P(2)–O(3)–C(7)	i	122 (3)
P(2)–O(4)–C(10)	i	115 (3)
P(3)–O(5)–C(13)	i	120 (3)
P(3)–O(6)–C(16)	i	125 (3)
P(4)–O(7)–C(19)	i	137 (5)
P(4)–O(8)–C(22)	i	115 (2)
Carbon Coordination		
O(1)–C(1)–C(2)	j	104 (6)
O(1)–C(1)–C(3)	j	97 (7)
O(2)–C(4)–C(5)	j	104 (7)
O(2)–C(4)–C(6)	j	97 (7)
O(3)–C(7)–C(8)	j	102 (6)
O(3)–C(7)–C(9)	j	110 (5)
O(4)–C(10)–C(11)	j	103 (6)
O(4)–C(10)–C(12)	j	102 (5)
O(5)–C(13)–C(14)	j	102 (5)
O(5)–C(13)–C(15)	j	96 (4)
O(6)–C(16)–C(17)	j	111 (4)
O(6)–C(16)–C(18)	j	112 (5)
O(7)–C(19)–C(20)	j	103 (6)
O(7)–C(19)–C(21)	j	101 (6)
O(8)–C(22)–C(23)	j	97 (4)
O(8)–C(22)–C(24)	j	107 (5)

TABLE VII

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

Plane 1	$0.3510X + 0.9106Y + 0.2185Z - 5.8736 = 0$
Plane 2	$0.3422X + 0.9131Y + 0.2217Z - 5.8948 = 0$
Plane 3	$0.9478X - 0.2978Y + 0.1140Z - 1.2295 = 0$
Plane 4	$0.9181X + 0.3422Y + 0.1998Z - 4.3164 = 0$
Plane 5	$0.3495X + 0.9089Y + 0.2273Z - 5.9233 = 0$

Plane 1	Au(1), 0.020 (4);	Au(2), −0.010 (4);	Au(4′), −0.009 (4);	S(1), −0.001 (17);	S(3), 0.014 (19)	
Plane 2	Au(2), −0.010 (4);	Au(1), 0.006 (4);	Au(3), 0.006 (4);	S(2), −0.026 (25);	S(4), −0.018 (24)	
Plane 3	Au(3), −0.004 (4);	Au(2), 0.004 (4);	Au(4), 0.004 (4);	S(5), −0.036 (18);	S(7), −0.041 (19)	
Plane 4	Au(4), −0.008 (4);	Au(3), 0.006 (4);	Au(1″), 0.006 (4);	S(6), −0.015 (16);	S(8), −0.018 (16)	
Plane 5	Au(1), 0.002 (4);	Au(2), 0.001 (4);	S(1), −0.020 (17);	S(2), 0.005 (25);	S(3), −0.006 (19);	S(4), −0.027 (24)

[a] The coordinate system used for the least-square planes was $X = xa \sin\gamma + zc(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma$; $Y = xa\cos\gamma + by + cz\cos\alpha$; $Z = zV/ab\sin\gamma$.

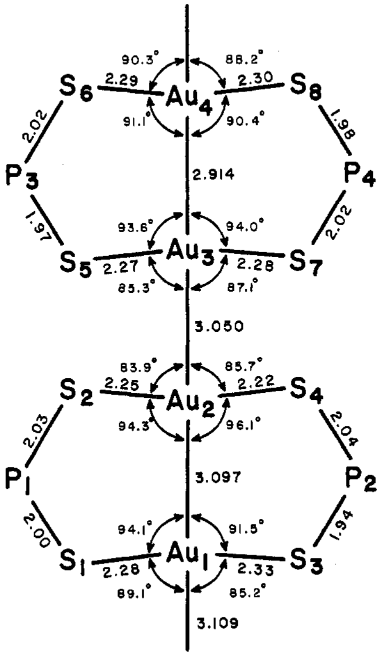

Figure 2.—The gold–sulfur–phosphorus skeleton of dimers 1 and 2 with selected bond lengths and angles.

to 3.109 (6) Å and average 3.04 Å ($c/4$). As shown in Figure 2 and Table V, despite the individual standard deviations, the lengths of the gold–gold bonds *within* the dimers cannot be considered to be significantly different from those *between* the dimers; the bond lengths in the "average" structure lead one to conclude that these slight perturbations are probably introduced by the molecular packing and associated van der Waals forces. Other gold complexes and their average gold–gold distances which may be compared with this structure are as follows: (i) the dithiocarbamate dimers, $[Au(n\text{-}C_3H_7)_2NCS_2]_2$ and $[Au(i\text{-}C_4H_9)_2NCS_2]_2$, 2.76 Å;[23,24] (ii) the chain structure, $\{[(i\text{-}C_3H_7NH_2)Au^I\text{-}(C{\equiv}CC_6H_5)]_2\}_n$, 3.27 Å within dimeric units and 3.72 Å between these units;[25] (iii) the infinite linear –Au(III)–Au(I)–dimethylglyoxime (HDMG) chain complex, $[Au^{III}(DMG)_2]^+\cdot[Au^ICl_2]^-$, 3.26 Å;[26] (iv) the gold cluster complexes $Au_{11}(SCN)_3[P(C_6H_5)_3]_7$, 2.67 (2) Å,[27] and $Au_{11}I_3[P(C_6H_4Cl)_3]_7$, 2.98 Å.[28] The distance in metallic gold is 2.884 Å.[29] A Raman study of the metal–metal bond in the gold(I) diisobutyldithiocarbamate dimer suggests that the 2.76-Å Au–Au interaction is fairly weak.[30] It does not seem unreasonable to assume, therefore, that in $\{[Au(dtp)]_2\}_n$, a 3.0-Å Au–Au separation is indicative of a very weak interaction.

The gold–sulfur bond averages 2.28 (3) Å in length, a value consistent with those in square-planar gold(III) complexes.[31] Pauling has suggested the value 1.40 Å for the square-planar radius of gold.[32a] The sum of this value and the covalent radius of sulfur[32b] gives 2.44 Å, suggesting that the Au–S bonds assume some multiple bond character.

The various phosphorus–sulfur bonds are chemically equivalent within one standard deviation, averaging 2.00 (3) Å. A similar statement applies to the 1.56 (3) Å phosphorus–oxygen bonds. These bond lengths are entirely comparable with those in other metal phosphorodithioates, phosphinothionates, and dithiophosphinates.

The two crystallographically independent dimers link together in a staggered conformation relative to the chain axis, as shown in Figure 1. According to Table V the intradimeric nonbonded S···S separation within each ligand [averaging 3.42 (2) Å] exceeds the associated Au–Au interaction (averaging 3.04 Å). This difference, clearly displayed in Figure 2, introduces the observed nonorthogonality in the S–Au–Au angles. It is reasonable to attribute the main driving force leading to the staggered conformation to *inter*dimeric S···S repulsion which would be severe in the eclipsed arrangement (with distances approaching 2.7 Å).

The laterally stacked chains are held together in the crystal primarily by methyl···sulfur and methyl···methyl van der Waals interactions. These interactions were found to be normal when compared with the expected values 3.85 and 4.0 Å, respectively.[32c]

Packing forces have interesting consequences upon the conformations of the various groups. In discussing

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(23) (a) S. Akerstrom, *Ark. Kemi*, **14**, 387 (1959); (b) R. Hesse, *Proc. Int. Conf. Coord. Chem.*, *6th*, 314 (1961).

(24) Though these dimers exhibit relatively short Au–Au separations, X-ray studies[23a] indicate that they join together in pairs similar to that found for $\{[Au(dtp)]_2\}_n$ (structure III), resulting in polymerization and gold chains. The Au···Au separations between the dimers are not available, however, so that we are unable to compare the relative strengths with ours.

(25) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **23**, 156 (1967).

(26) R. E. Rundle, *J. Amer. Chem. Soc.*, **76**, 3101 (1954).

(27) M. McPartlin and R. Mason, *J. Chem. Soc. D*, 334 (1969).

(28) V. G. Albano, P. L. Bellon, M. Manassero, and M. Sansoni, *ibid.*, 1210 (1970).

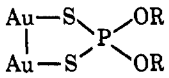
(29) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11**, S3 (1958).

(30) F. J. Farrell and T. G. Spiro, *Inorg. Chem.*, **10**, 1606 (1971).

(31) P. T. Beurskens, H. J. A. Blaaw, J. A. Cras, and J. J. Steggerda, *ibid.*, **7**, 805 (1968); P. T. Beurskens, J. A. Cras, and J. J. Steggerda, *ibid.*, **7**, 810 (1968); J. H. Enemark and J. A. Ibers, *ibid.*, **7**, 2636 (1968).

(32) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960: (a) pp 249, 252; (b) p 246; (c) p 260.

these it is helpful to view the dimers as consisting of two fused



five-membered rings sharing their Au–Au bonds. Both the five-ring configurations and the P–OR conformations are worthy of comment. First, it appears that the five-membered rings are all decidedly puckered. Whether this puckering is intrinsically associated with electron-pair avoidance in the five-ring itself (as it commonly is in the case of small rings which pucker spontaneously in the absence of external forces) or whether it is induced by the packing forces is not known. In either event, two puckering coordinates are possible which can be designated as A_2 (leading to C_2 symmetry) and B_1 (leading to C_s symmetry) relative to a planar C_{2v} reference structure.[33] It is evident that the interdimeric repulsion between isopropoxy groups leads to A_2 twisting deformations of the five-membered rings in dimer 2, and that the intrinsic linearity of S–Au–S bonds in the joined rings of the dimer makes the individual A_2 deformations cooperative, leading to a local C_2 symmetry of the dimer skeleton.[34] The two rings in dimer 1 pucker cooperatively, also, but the twist of dimer 2 provides holes in the cell for the isopropoxy groups of dimer 1 to enter *via* a B_1 bend (envelope flap) preserving local C_s symmetry of the dimer skeleton.[35]

A consequence of the above ring puckerings is that two of the isopropoxy groups in dimer 1 [namely, $C_3H_7(2)$ and $C_3H_7(3)$] but none of them in dimer 2 are compressed toward the –Au–Au– chain. The isopropoxy groups suffering this compression undergo hindered rotation about their P–O bonds to relieve their steric problem. They adopt what we may refer to as gauche locations when compared with the $(CH_3)_2$-C–O–P–O reference conformations. All other isopropoxy groups are found in trans locations.

In conclusion, we find that the material $\{[Au(dtp)]_2\}_n$ is strikingly different in structure from its copper analog,[5] $Cu_4(dtp)_4$, which exists as a discrete tetramer. On the other hand, both the gold and the copper derivatives display striking similarities in structure with the respective gold(I)[23] and copper (I)[36] *N*,*N*-dialkyldithiocarbamate complexes. A characteristic feature of each of these compounds is the presence of metal–metal bonding, albeit weak, which forms the nuclei or backbones of the molecular clusters or chains. A logical extension of this series of structural investigations to silver(I) *O*,*O*′-dialkylphosphorodithioates would now be of worthwhile interest in order to examine their polymerization tendencies and, specifically, to determine if hexamers form as in the case of silver(I) *N*,*N*-diethyldithiocarbamate, $[Ag(C_2H_5)_2NCS_2]_6$.[37]

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(33) Notation corresponding to conventional group theoretical tables with the out-of-plane axis taken in the *x* direction.

(34) The S(6)–Au(4)–S(8) twist about the –Au–Au– axis relative to S(5)–Au(3)–S(7) corresponds to 38°.

(35) The dihedral angles in dimer 1 formed by the flaps average 123.7°, compared with 180° if the dimer skeleton were strictly planar.

(36) R. Hesse, *Ark. Kemi*, **20**, 481 (1963).

(37) R. Hesse and L. Nilson, *Acta Chem. Scand.*, **23**, 825 (1969).

CONTRIBUTION FROM THE TRANSURANIUM RESEARCH LABORATORY,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

Crystal Structure of Americium Sulfate Octahydrate[1]

BY JOHN H. BURNS* AND RUSSELL D. BAYBARZ

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The structure of $Am_2(SO_4)_3\cdot 8H_2O$ has been determined by single-crystal X-ray diffraction methods. All nonhydrogen atomic positions were deduced from 3035 diffractometer-measured intensities by means of Patterson and Fourier methods. Refinement by the method of least squares with anisotropic thermal motion for each atom resulted in an agreement index, R_F, of 0.035. The monoclinic unit cell has dimensions of a = 13.619 (7), b = 6.837 (2), c = 18.405 (4) Å, and β = 102° 40 (5)′; it contains four formula units. The space group is $C2/c$. Each americium atom is coordinated by four oxygen atoms belonging to sulfate ions at 2.382–2.509 Å and by four water molecules at 2.406–2.553 Å. These eight oxygen atoms form a polyhedron which is intermediate between an antiprism and a dodecahedron. Cross-linking of americium atoms occurs through sharing of sulfate ions, and extensive hydrogen bonding involving the water molecules is indicated.

Introduction

Important questions in the study of aqueous solutions of lanthanide and actinide ions are those of hydration number and of which anions form inner-sphere and which form outer-sphere complexes. Evidence for the hydration number in solution is provided by such methods as proton magnetic resonance[2] and absorption

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(2) A. Fratiello, V. Kubo, S. Peak, B. Sanchez, and R. E. Schuster, *Inorg. Chem.*, **10**, 2552 (1971).