$[XeF^+][Sb_2F_{11}^-]$. In $[BrF_4^+][Sb_2F_{11}^-]$ the atoms Br, Sb(1), Sb(2), F(1), F(2), F(4), F(5), F(7), F(8), F(9), F(12), and F(15) are all within 0.3 Å of being coplanar; their common plane is very nearly parallel to the 201 planes. This near coplanarity extends the whole length of any given chain. The planes of adjacent chains (see Figure 2) are parallel but are spaced $c/2$ or c apart along the c direction. The closest approaches of fluorine atoms bonded to different bromine and antimony atoms within the chains are 3.03, 3.24, and 3.47 Å, all of which are substantially greater than twice the van der Waals radius of fluorine.

The chains are approximately close packed. There is no bridging between chains. The minimum interchain F---F separation is 2.72 Å, which is approximately twice the van der Waals radius of fluorine. The minimum interchain Br---F and Sb---F distance is 3.56 Å, which is approximately the value expected for the sums of the van der Waals radii of the atom pairs.

In summary, this is the first direct evidence for the existence of the BrF_4^+ cation. Although the present experimental data do not allow very precise determinations of bond lengths and angles, valuable information about the structure of this interesting adduct was obtained.

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The Crystal and Molecular Structure of the Tetranuclear Metal Cluster Complex Copper(I) *O,O'*-Diisopropylphosphorodithioate, $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$

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Copper(I) *O,O'*-diisopropylphosphorodithioate, $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$, crystallizes as light yellow prisms in the orthorhombic space group $P2_12_12_1$ with unit cell parameters $a = 11.283 \pm 0.006$, $b = 12.380 \pm 0.004$, and $c = 33.825 \pm 0.008$ Å. The observed and calculated densities are 1.55 ± 0.02 and 1.556 ± 0.002 g/cm^3 (for $Z = 4$ molecules/unit cell), respectively. A full-matrix anisotropic–isotropic least squares refinement has resulted in a discrepancy index of 0.072 using three-dimensional X-ray diffraction counter data. The crystal structure is comprised of discrete tetrameric molecules, each containing a central tetrahedron of copper atoms. Chelated to this tetrahedron through sulfur atoms are four $(C_3H_7O)_2PS_2$ ligands, so arranged as to give the molecule a symmetry approaching S_4. One of the sulfur atoms in each ligand bridges two copper atoms almost symmetrically with average distances of 2.256 (9) and 2.272 (16) Å; the other forms a bond with a third copper atom at a distance of 2.272 (9) Å. Each phosphorus atom is thus centered more or less above a face of the copper tetrahedron. Of the six edges of the tetrahedron (the Cu–Cu bonds), the four which are bridged by sulfur average 2.74 (3) Å; the other two edges average 2.950 (6) Å. The two sulfurs in each ligand play different roles in the chelation and this difference is reflected in the lengths of the P–S bonds. Those associated with the Cu–S–Cu bridges average 2.036 (11) Å in length; those bonded to a single Cu are shorter, at 1.972 (8) Å. The average P–O bond length is 1.56 (2) Å, a value entirely comparable to those in previously determined metal phosphorodithioates.

Introduction

Structural investigations of organocopper(I) complexes have shown that the cuprous ion generally adopts a tetrahedral configuration. Recently, compounds containing clusters of four or more copper atoms, entailing coordination numbers greater than 4, have also been reported. These include the copper tetramer, hexamer, and octamer. The tetrameric compounds, *e.g.*, $Cu_4I_4[As(C_2H_5)_3]_4$[1] and $Cu_4[S_2CN(C_2H_5)]_4$[2] display a central tetrahedral configuration of copper atoms. The hexamer, *e.g.*, $Cu_6[SOCN(C_3H_7)_2]_6$,[3] and octamer, *e.g.*, the phenyltrimethylammonium salt of $Cu_8[S_2CC(CN)_2]_6^{4-}$,[4] exhibit a central octahedral and cubic cluster, respectively. Syntheses and characterizations of other copper clusters have also been reported.[5]

As part of a continuing investigation of metal phosphorodithioate complexes, the crystal structure of $Cu_4(dtp)_4$, where dtp = $S_2P(OC_3H_7)_2$, was undertaken. Initial evidence of a tetranuclear copper cluster in $Cu_4(dtp)_4$ was based on vapor pressure osmometry data[6] for benzene solutions at 37°. The present study examines the stereochemistry of this metal cluster complex in the crystalline form and the influence of the dtp ligand on the copper–copper interactions.

Experimental Section

Preparation.—Copper(I) *O,O'*-diisopropylphosphorodithioate was synthesized according to a method previously described.[7] Brittle, light yellow prismatic crystals for use in the X-ray investigation were obtained by recrystallization of the compound from a warm ethanol–acetone mixture.

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Crystal Data.—$Cu_4(dtp)_4$, of formula weight 1107.28, is orthorhombic with space group $P2_12_12_1$ ($D_2{}^4$). The lattice parameters at 27° are $a = 11.283$ (6), $b = 12.380$ (4), $c = 33.825$ (8) Å, and $V = 4724$ (5) Å^3; $d_{obsd} = 1.55$ (2) g/cm^3 (by flotation), $d_{calcd} = 1.556$ (2) g/cm^3 for $Z = 4$ formula units/unit cell.

The crystal symmetry was determined from Weissenberg and precession X-ray photographs which yielded systematic extinctions ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) consistent with the space group $P2_12_12_1$. The lattice parameters were determined by a least-squares fit[8] to 112 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 several different orientations; each film was calibrated with superimposed aluminum powder lines ($a_0 = 4.0332$ Å). The Nelson–Riley extrapolation function was employed in the refinement. Indicated errors are 2σ.

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 prismatic crystal of length 0.33 mm and of a cross section measuring 0.08 × 0.12 mm. The crystal was sealed in a thin-walled Lindemann glass capillary and mounted on the diffractometer with a^* (the 0.33-mm axis) coincident with the ϕ axis. The half-widths of a number of narrow-source, open-counter 2θ scans[9] ranged from 0.06 to 0.10° 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 a pulse height discriminator was used with the moving-crystal, moving-counter measurement technique (θ, 2θ coupling) and a 3.5° takeoff angle. The crystal–source and crystal–counter distances were 17 and 18.5 cm, respectively. The dimensions of the counter aperture were 5.0 mm × 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 4667 independent reflections were measured. Equivalent reflections were not measured. Three standard reflections were measured periodically as a check on crystal and electronic stability and a linear 4% decrease in intensities was observed.

The raw intensity of each reflection was corrected for background, crystal decomposition, and Lorentz and polarization effects. Transmission factors ranged from 0.83 to 0.87 based on a linear absorption coefficient of 23.5 cm^{-1}; no absorption corrections were therefore applied. Estimated standard deviations in the intensities were computed as described elsewhere,[10] using a value of 0.05 for p. The estimated standard deviation in each F_o was calculated by employing the finite-difference method. A total of 2093 reflections were observed above the background level of which 1904 had $F_o{}^2 \geq \sigma(F_o{}^2)$. The remaining 189 reflections were considered as unobserved and thus omitted from the refinements.

Solution and Refinement of the Structure

The structure was solved using Patterson superposition and Fourier techniques.[11] An unsharpened Patterson function was first calculated using all observed reflections. From the crystallographic data ($Z = 16$ formula units of Cu(dtp) in a space group of order 4) the molecule was initially assumed to exist as a tetramer in which four copper atoms formed a tetrahedron. Using this assumption a tetrahedron was readily located at the origin. A superposition along one of the three Cu–Cu vectors emanating from the origin revealed the three remaining Cu_4 tetrahedra in the unit cell generated by the three unit cell twofold screw axes. A series of three-dimensional electron density functions (F and ΔF) and isotropic least-squares refinements led to the location of all remaining atoms in the structure.

TABLE I

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR THE NONHYDROGEN ATOMS IN $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$[a]

Atom	x	y	z	B,[b] Å^2
Cu(1)	0.53887 (32)	0.58226 (32)	0.60472 (10)	. . .
Cu(2)	0.66224 (32)	0.39530 (34)	0.59980 (11)	. . .
Cu(3)	0.48817 (31)	0.39632 (31)	0.65677 (10)	. . .
Cu(4)	0.40907 (32)	0.40964 (34)	0.57923 (10)	. . .
S(1)	0.39551 (82)	0.69026 (64)	0.63082 (27)	. . .
S(2)	0.30055 (64)	0.42551 (66)	0.63519 (22)	. . .
S(3)	0.72136 (73)	0.38217 (70)	0.53595 (22)	. . .
S(4)	0.47552 (75)	0.54706 (65)	0.54194 (22)	. . .
S(5)	0.55631 (72)	0.49349 (74)	0.70877 (23)	. . .
S(6)	0.72462 (78)	0.55447 (70)	0.62723 (21)	. . .
S(7)	0.42129 (78)	0.23753 (64)	0.55531 (23)	. . .
S(8)	0.60093 (77)	0.25562 (62)	0.63722 (21)	. . .
P(1)	0.27829 (69)	0.58422 (73)	0.64977 (21)	. . .
P(2)	0.60644 (76)	0.47945 (64)	0.50959 (22)	. . .
P(3)	0.71128 (74)	0.53421 (68)	0.68706 (22)	. . .
P(4)	0.49266 (77)	0.16639 (63)	0.60175 (25)	. . .
O(1)	0.1492 (16)	0.6169 (16)	0.6367 (5)	4.9 (5)
O(2)	0.2628 (17)	0.5848 (17)	0.6954 (5)	4.9 (5)
O(3)	0.5367 (18)	0.4236 (16)	0.4765 (5)	5.1 (5)
O(4)	0.6726 (16)	0.5714 (15)	0.4865 (5)	4.2 (4)
O(5)	0.8014 (17)	0.4482 (15)	0.6997 (5)	4.5 (5)
O(6)	0.7662 (17)	0.6395 (15)	0.7065 (5)	4.6 (5)
O(7)	0.3874 (16)	0.1190 (15)	0.6266 (5)	4.5 (4)
O(8)	0.5632 (17)	0.0647 (15)	0.5903 (5)	5.0 (5)
C(1)	0.1244 (29)	0.6528 (25)	0.5951 (10)	5.7 (8)
C(2)	0.2866 (30)	0.6782 (27)	0.7210 (10)	5.8 (8)
C(3)	0.5951 (31)	0.3504 (27)	0.4472 (10)	6.3 (9)
C(4)	0.7754 (34)	0.6259 (30)	0.4998 (10)	7.2 (10)
C(5)	0.9324 (31)	0.4559 (27)	0.6893 (10)	6.1 (9)
C(6)	0.7040 (33)	0.7388 (29)	0.7014 (10)	6.4 (9)
C(7)	0.4031 (30)	0.0777 (28)	0.6684 (9)	6.2 (8)
C(8)	0.6757 (33)	0.0764 (32)	0.5676 (11)	7.9 (10)
C(9)	0.0467 (38)	0.5603 (32)	0.5781 (12)	9.1 (12)
C(10)	0.0638 (38)	0.7533 (33)	0.5960 (12)	8.7 (11)
C(11)	0.2918 (35)	0.6396 (31)	0.7609 (12)	7.9 (11)
C(12)	0.1914 (37)	0.7567 (33)	0.7159 (11)	8.0 (11)
C(13)	0.5332 (45)	0.2513 (39)	0.4460 (14)	11.2 (14)
C(14)	0.5998 (42)	0.4121 (42)	0.4103 (14)	11.2 (13)
C(15)	0.7464 (36)	0.7294 (33)	0.5164 (11)	7.7 (11)
C(16)	0.8684 (43)	0.6261 (39)	0.4680 (15)	11.4 (14)
C(17)	0.9542 (39)	0.3484 (35)	0.6689 (13)	9.7 (13)
C(18)	0.9956 (40)	0.4710 (34)	0.7244 (13)	9.6 (12)
C(19)	0.6656 (38)	0.7799 (34)	0.7403 (13)	8.7 (12)
C(20)	0.7935 (47)	0.8153 (39)	0.6872 (14)	11.2 (14)
C(21)	0.2761 (40)	0.0740 (37)	0.6828 (12)	9.8 (12)
C(22)	0.4496 (38)	−0.0255 (35)	0.6692 (12)	9.1 (12)
C(23)	0.6544 (41)	0.0380 (36)	0.5285 (14)	10.2 (13)
C(24)	0.7538 (60)	−0.0024 (51)	0.5890 (17)	14.5 (18)

[a] All atoms are in the general symmetry position 4(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 final anisotropic thermal parameters for Cu, S, and P are given in Table II.

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 atoms were those tabulated by Hanson, *et al.*[12] Effects of anomalous scattering were included in the structure factor calculations,[13] using values of $\Delta f'$ and $\Delta f''$ for Cu, S, and P given in ref 14. The best fully weighted isotropic refinement of all 48 nonhydrogen atoms plus the scale factor resulted in $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.086$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.084$ for the reflections above $\sigma(F_o{}^2)$. Additional least-squares cycles with anisotropic thermal parameters assigned to Cu, S, and P further reduced R_1 and R_2 to 0.077 and 0.075, respectively. A three-dimensional difference synthesis at this stage provided evidence of slight anisotropic motion of the lighter oxygen and carbon atoms but due to the paucity of data (seven reflections per variable at this point) no attempt was made to refine them anisotropically.

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TABLE II

FINAL ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv,[b] B, Å^2
Cu(1)	0.00774 (38)	0.00777 (33)	0.00084 (4)	0.00061 (35)	0.00023 (11)	−0.00008 (11)	4.31
Cu(2)	0.00866 (41)	0.00845 (36)	0.00077 (4)	0.00019 (35)	−0.00006 (11)	−0.00004 (12)	4.50
Cu(3)	0.00760 (39)	0.00711 (32)	0.00085 (4)	−0.00121 (34)	0.00017 (11)	−0.00013 (11)	4.15
Cu(4)	0.00770 (37)	0.00738 (33)	0.00084 (4)	0.00049 (35)	−0.00006 (11)	−0.00030 (11)	4.21
S(1)	0.0100 (10)	0.0054 (7)	0.00133 (11)	−0.0005 (7)	0.0005 (3)	−0.0005 (2)	4.92
S(2)	0.0057 (7)	0.0068 (7)	0.00095 (8)	−0.0004 (6)	0.0000 (2)	−0.0002 (2)	3.90
S(3)	0.0081 (8)	0.0080 (8)	0.00094 (9)	0.0029 (7)	0.0007 (2)	0.0000 (2)	4.57
S(4)	0.0085 (9)	0.0080 (7)	0.00076 (8)	0.0008 (7)	0.0001 (2)	0.0003 (2)	4.37
S(5)	0.0079 (9)	0.0102 (8)	0.00074 (8)	−0.0019 (7)	−0.0001 (2)	−0.0007 (2)	4.71
S(6)	0.0097 (9)	0.0095 (8)	0.00054 (8)	−0.0033 (7)	0.0002 (2)	−0.0000 (2)	4.55
S(7)	0.0099 (10)	0.0060 (7)	0.00093 (9)	−0.0010 (7)	−0.0006 (3)	0.0001 (2)	4.42
S(8)	0.0100 (9)	0.0057 (6)	0.00069 (8)	0.0002 (7)	−0.0004 (3)	−0.0001 (2)	4.00
P(1)	0.0074 (8)	0.0068 (7)	0.00076 (8)	0.0013 (7)	0.0004 (2)	−0.0006 (2)	3.91
P(2)	0.0072 (8)	0.0055 (7)	0.00076 (8)	0.0009 (7)	−0.0002 (2)	0.0001 (2)	3.57
P(3)	0.0064 (8)	0.0073 (7)	0.00065 (8)	−0.0012 (7)	−0.0004 (2)	0.0001 (2)	3.68
P(4)	0.0092 (9)	0.0052 (6)	0.00085 (9)	0.0005 (7)	0.0002 (3)	−0.0000 (2)	4.00

[a] The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] 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 III

CALCULATED POSITIONAL PARAMETERS ($\times 10^4$) FOR HYDROGEN IN $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$[a]

Atom[b]	x	y	z	Atom[b]	x	y	z
C(1)H(1)	1984	6592	5802	C(15)H(29)	8181	7625	5274
C(2)H(2)	3626	7110	7138	C(16)H(30)	8404	6687	4454
C(3)N(3)	6764	3364	4560	C(16)H(31)	9416	6578	4783
C(4)N(4)	8075	5825	5215	C(16)H(32)	8837	5517	4595
C(5)H(5)	9465	5159	6710	C(17)H(33)	9397	2895	6876
C(6)H(6)	6376	7317	6829	C(17)H(34)	9005	3413	6463
C(7)H(7)	4509	1276	6843	C(17)H(35)	10365	3452	6597
C(8)H(8)	7069	1503	5681	C(18)H(36)	9804	4103	7423
C(9)H(9)	−0268	5549	5934	C(18)H(37)	10805	4748	7185
C(9)H(10)	0279	5758	5504	C(18)H(38)	9701	5384	7369
C(9)H(11)	0902	4919	5798	C(19)H(39)	7344	7858	7578
C(10)H(12)	−0099	7455	6111	C(19)H(40)	6292	8513	7370
C(10)H(13)	1141	8078	6086	C(19)H(41)	6077	7301	7518
C(10)H(14)	0453	7759	5689	C(20)H(42)	8581	8200	7065
C(11)H(15)	2157	6068	7680	C(20)H(43)	8249	7904	6618
C(11)H(16)	3548	5854	7632	C(20)H(44)	7573	8867	6838
C(11)H(17)	3086	7000	7788	C(21)H(45)	2307	0236	6664
C(12)H(18)	1157	7235	7232	C(21)H(46)	2744	0498	7104
C(12)H(19)	2062	8194	7329	C(21)H(47)	2411	1463	6809
C(12)H(20)	1885	7799	6882	C(22)H(48)	4001	−0734	6531
C(13)H(21)	4516	2640	4373	C(22)H(49)	5303	−0244	6585
C(13)H(22)	5726	2021	4276	C(22)H(50)	4514	−0519	6965
C(13)H(23)	5325	2191	4725	C(23)H(51)	6235	−0359	5297
C(14)H(24)	5190	4267	4011	C(23)H(52)	5965	0849	5155
C(14)H(25)	6412	4805	4149	C(23)H(53)	7288	0385	5136
C(14)H(26)	6424	3703	3902	C(24)H(54)	7186	−0747	5876
C(15)H(27)	7137	7762	4958	C(24)H(55)	8323	−0034	5766
C(15)H(28)	6876	7200	5375	C(24)H(56)	7614	0195	6167

[a] Based on C–H = 0.98 Å. [b] C(*m*)H(*n*) corresponds to hydrogen *n* of carbon *m*.

This same map, however, revealed plausible locations of nearly all the 56 independent hydrogen atoms, as determined by calculation of the hydrogen atom positions based on those found in the molecule $[(i\text{-}C_3H_7O)_2PS_2]_2$.[15] These hydrogen atoms were subsequently included in the remaining cycles of refinement as fixed atoms[16] with an isotropic thermal parameter of 7.0 Å^2.

Convergence was reached with $R_1 = 0.072$ and $R_2 = 0.069$ for the 1904 observed reflections. The corresponding values for all 2093 reflections were $R_1 = 0.082$ and $R_2 = 0.076$. The final standard deviation for an observation of unit weight was 1.09. On the final cycle the shift in each positional and thermal parameter averaged 0.008 times its own σ. A statistical analysis of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) *vs.* $|F_o|$ as well as $(\sin \theta)/\lambda$ showed no unusual trends. A final difference synthesis showed no peaks greater than 0.2 e/Å^3 or at most 5.6% of a terminal carbon atom. Comparison of the final values of F_o and F_c indicated that a correction for secondary extinction was not necessary.

The final positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Tables I and II, along with the associated standard deviations in these parameters as estimated from the inverse matrix.[17] The final hydrogen positional parameters are given in Table III. Principal root-mean-square amplitudes of vibration of Cu, S, and P are given in Table IV.

Description of the Structure

$Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$ exists in the crystalline form as a discrete tetramer, the nucleus of which is a copper tetrahedron. Surrounding this tetrahedron are four effectively tridentate $S_2P(OC_3H_7)_2$ ligands, coordinated to copper through the sulfur atoms. One sulfur atom in each ligand is coordinated to two copper atoms while the other is coordinated to only one. Each phosphorus is thus centered more or less above a face of the copper tetrahedron, as shown in Figure 1. Of the six Cu–Cu bonds comprising the edges of the tetrahedron, two are not bridged by sulfur. Accordingly, each copper atom interacts with six neighboring atoms, three of which are copper and three are sulfur. By virtue of

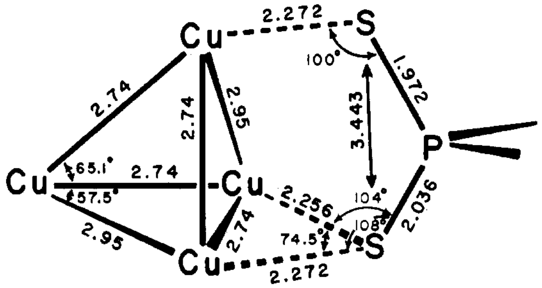

Figure 1.—Molecular configuration of the copper tetrahedron and one of the four bidentate ligands in $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$, summarizing the average bond lengths and angles.

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(15) S. L. Lawton, *Inorg. Chem.*, **9**, 2269 (1970).

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

(17) Observed and calculated structure amplitudes utilized in the least-squares refinement 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 author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche. Included in the listing (F_c only) are four strong low-order reflections excluded from the refinement, *viz.*, 002, 011, 012, and 101 with $2\theta < 4.1°$.

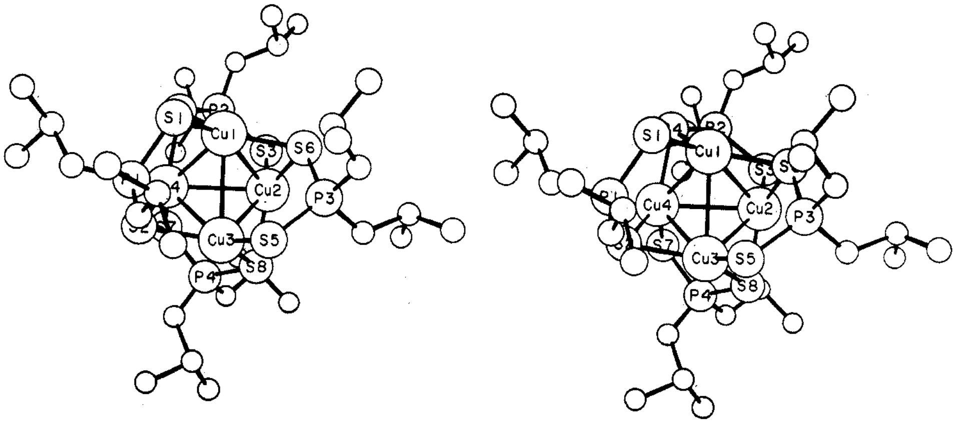

Figure 2.—Stereographic view of the $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$ molecule parallel with the S_4-symmetry axis.

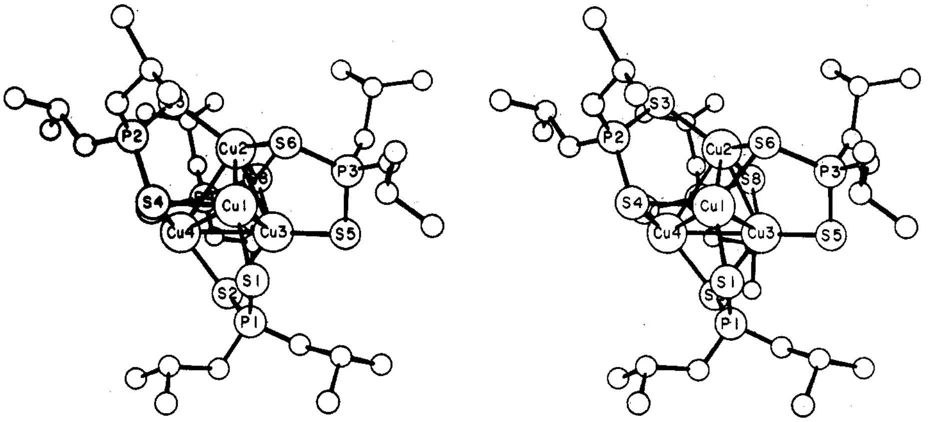

Figure 3.—Stereographic view of the $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$ molecule normal to a Cu_3 face of the copper tetrahedron.

the nominal S_4 symmetry and the small bite of the PS_2 group, these six bonded neighbors are constrained to occupy space within a hemisphere. The complete arrangement of all four ligands about the copper cluster is depicted in Figures 2 and 3. The rms thermal displacements of atoms in the inner coordination sphere are shown in Figure 4. Tables V and VI summarize the final interatomic distances and angles; corresponding standard deviations were computed from the final variance–covariance matrix. Owing to the complexity of thermal motion within the molecule, no corrections in the bond lengths were made.

The copper–copper distances fall into two categories. Those (four out of six) bridged by sulfur average 2.74 (3) Å and those not bridged average 2.950 (6) Å. Other copper clusters and their average copper–copper

TABLE IV

FINAL ROOT-MEAN-SQUARE THERMAL AMPLITUDES OF VIBRATION (Å) IN $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$[a]

Atom	Min	Med	Max
Cu(1)	0.210 (6)	0.231 (6)	0.249 (6)
Cu(2)	0.211 (5)	0.236 (6)	0.257 (5)
Cu(3)	0.207 (6)	0.220 (5)	0.250 (6)
Cu(4)	0.213 (6)	0.221 (6)	0.249 (6)
S(1)	0.198 (13)	0.242 (14)	0.293 (13)
S(2)	0.191 (12)	0.224 (12)	0.240 (12)
S(3)	0.178 (15)	0.236 (12)	0.285 (13)
S(4)	0.206 (12)	0.228 (13)	0.258 (12)
S(5)	0.189 (13)	0.222 (13)	0.297 (12)
S(6)	0.175 (13)	0.211 (13)	0.303 (12)
S(7)	0.207 (13)	0.221 (13)	0.270 (13)
S(8)	0.194 (12)	0.210 (12)	0.258 (12)
P(1)	0.168 (15)	0.232 (12)	0.250 (13)
P(2)	0.190 (14)	0.211 (13)	0.228 (13)
P(3)	0.174 (14)	0.207 (13)	0.250 (13)
P(4)	0.198 (12)	0.219 (13)	0.248 (13)

[a] An indication of the directions of these principal axes of vibration is given in Figure 4.

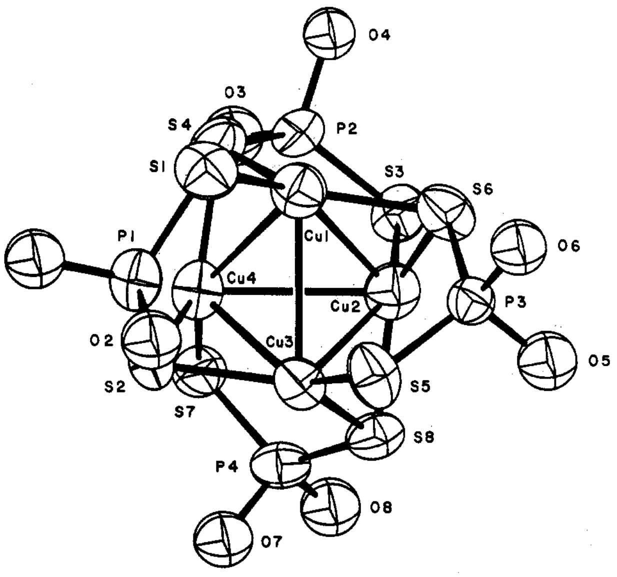

Figure 4.—A parallel projection of the $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$ molecule, showing the principal rms thermal displacements of the atoms in the inner coordination sphere.

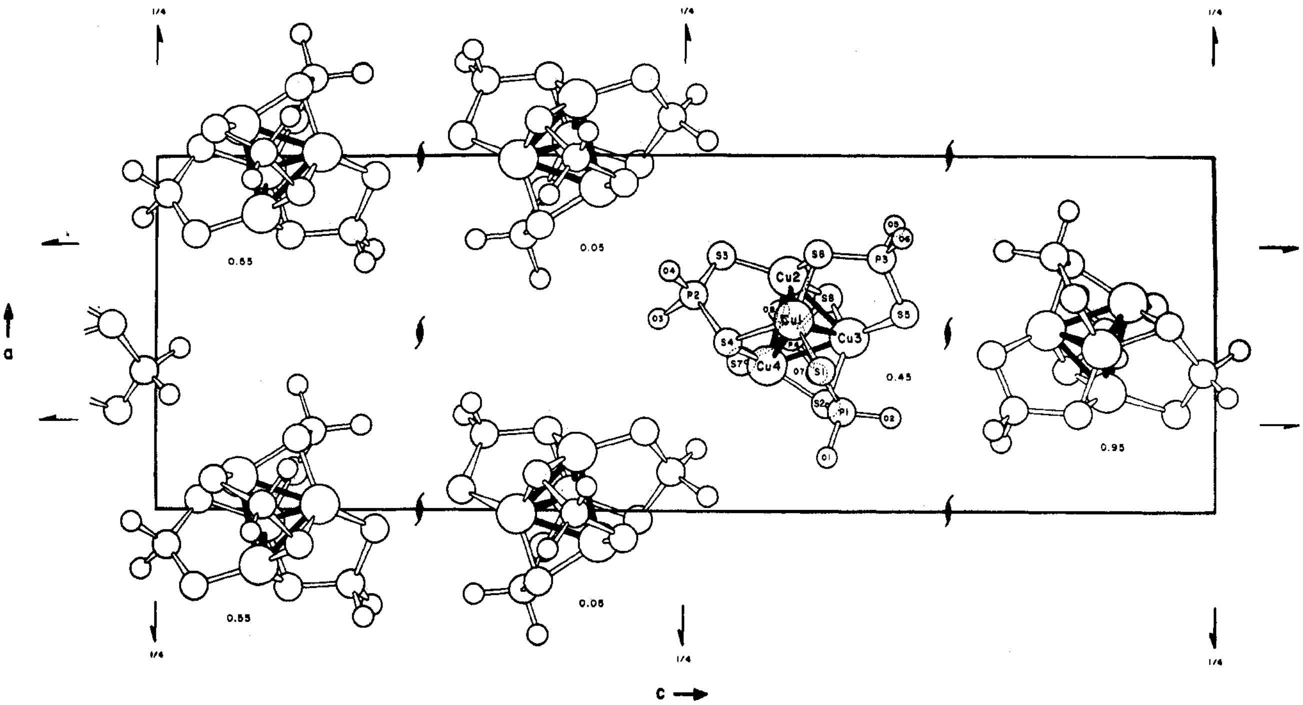

Figure 5.—[010] projection of the primitive unit cell of $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$. The numbered atoms define the asymmetric unit (Table I). Numbers adjacent to the molecules represent the fractional unit cell y coordinates (elevation) of the Cu_4 centroids, where the plane of the paper is $y = 0.0$. For clarity the isopropyl groups are not shown.

TABLE V

INTERATOMIC DISTANCES (Å) IN $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$

Atoms	Type	Dist	Atoms	Type	Dist
Cu(1)–Cu(2)	a	2.706 (5)	P(1)–O(2)	i	1.55 (2)
Cu(1)–Cu(3)	b	2.954 (5)	P(2)–O(3)	i	1.53 (2)
Cu(1)–Cu(4)	a	2.730 (5)	P(2)–O(4)	i	1.57 (2)
Cu(2)–Cu(3)	a	2.752 (5)	P(3)–O(5)	i	1.53 (2)
Cu(2)–Cu(4)	b	2.945 (5)	P(3)–O(6)	i	1.59 (2)
Cu(3)–Cu(4)	a	2.775 (5)	P(4)–O(7)	i	1.57 (2)
Cu(1)–S(1)	c	2.277 (9)	P(4)–O(8)	i	1.54 (2)
Cu(1)–S(4)	d	2.283 (9)	O(1)–C(1)	j	1.50 (3)
Cu(1)–S(6)	e	2.256 (10)	O(2)–C(2)	j	1.47 (4)
Cu(2)–S(3)	c	2.266 (8)	O(3)–C(3)	j	1.50 (3)
Cu(2)–S(6)	d	2.289 (9)	O(4)–C(4)	j	1.42 (4)
Cu(2)-S(8)	e	2.252 (9)	O(5)–C(5)	j	1.52 (4)
Cu(3)–S(2)	e	2.268 (8)	O(6)–C(6)	j	1.43 (4)
Cu(3)–S(5)	c	2.265 (9)	O(7)–C(7)	j	1.51 (3)
Cu(3)–S(8)	d	2.256 (9)	O(8)–C(8)	j	1.49 (4)
Cu(4)–S(2)	d	2.263 (8)	C(1)–C(9)	k	1.55 (5)
Cu(4)–S(4)	e	2.247 (9)	C(1)–C(10)	k	1.42 (5)
Cu(4)–S(7)	c	2.283 (9)	C(2)–C(11)	k	1.43 (4)
S(1)···S(2)	f	3.452 (11)	C(2)–C(12)	k	1.46 (5)
S(3)···S(4)	f	3.450 (11)	C(3)–C(13)	k	1.41 (5)
S(5)···S(6)	f	3.432 (11)	C(3)–C(14)	k	1.46 (5)
S(7)···S(8)	f	3.440 (11)	C(4)–C(15)	k	1.44 (5)
P(1)–S(1)	g	1.971 (12)	C(4)–C(16)	k	1.50 (5)
P(1)–S(2)	h	2.041 (12)	C(5)–C(17)	k	1.52 (5)
P(2)–S(3)	g	1.982 (11)	C(5)–C(18)	k	1.40 (5)
P(2)–S(4)	h	2.020 (11)	C(6)–C(19)	k	1.48 (5)
P(3)–S(5)	g	1.962 (12)	C(6)–C(20)	k	1.47 (5)
P(3)–S(6)	h	2.045 (10)	C(7)–C(21)	k	1.51 (5)
P(4)–S(7)	g	1.973 (12)	C(7)–C(22)	k	1.38 (5)
P(4)–S(8)	h	2.038 (12)	C(8)–C(23)	k	1.42 (5)
P(1)–O(1)	i	1.57 (2)	C(8)–C(24)	k	1.50 (6)

Averages of Chemically Equivalent Bond Lengths (Å)

Bond	Type	Av (rms dev)	Bond	Type	Av (rms dev)
Cu–Cu	a	2.74 (3)	P–S	g	1.972 (8)
Cu–Cu	b	2.950 (6)	P–S	h	2.036 (11)
Cu–S	c	2.272 (9)	P–O	i	1.56 (2)
Cu–S	d	2.272 (16)	O–C	j	1.48 (4)
Cu–S	e	2.256 (9)	C–C	k	1.46 (5)
S···S	f	3.443 (9)			

distances which may be compared with this tetrahedron are as follows: $Cu_4[S_2CN(C_2H_5)_2]_4$, 2.658 (5) Å, bridged, and 2.757 (5) Å, nonbridged;[2] $Cu_6[SOCN(C_3H_7)_2]_6$, 2.97 (7) Å, bridged, and 2.79 (8) Å, nonbridged;[3] $Cu_8[S_2CC(CN)_2]_6{}^{4-}$, 2.83 (3) Å, all bridged.[4] The distance in copper metal is 2.556 Å.[18]

A qualitative assessment of the extent of metal–metal bonding in the copper cluster may be obtained by using the Pauling expression[19] $D(n) = D(1) - 0.60 \log n$, where $D(n)$ is the length of a bond having a bond order n and $D(1)$ is the length of a single bond (2.70 Å for copper[20]). For the four bridged Cu–Cu bonds averaging 2.74 Å in length and the two nonbridged bonds averaging 2.950 Å, fractional bond orders of 0.86 and 0.38, respectively, are obtained. It follows from this that three copper atoms collectively contribute two electrons to the valence shell of the fourth copper atom. These two electrons, together with six electrons from the negatively charged $[(i\text{-}C_3H_7O)_2PS_2]^-$ anion and ten valence electrons from Cu^+, result in a closed-shell configuration for each copper atom.

The average copper–sulfur distances are summarized in Figure 1. Variations among the 12 individual distances are small, amounting to no more than 0.04 Å. The range, 2.247 (9)–2.289 (9) Å, is similar to that, 2.246 (7)–2.290 (6) Å, in the related tetrameric molecule $Cu_4[S_2CN(C_2H_5)_2]_4$ but slightly longer than those in the hexamer $Cu_6[SOCN(C_3H_7)_2]_6$, with a range of 2.20 (1)–2.25 (1) Å, and the octamer $Cu_8[S_2CC(CN)_2]_6{}^{4-}$, with a range of 2.237 (5)–2.266 (5) Å. All tend to be shorter than those in tetrahedral copper(I) complexes

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(18) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11**, S5 (1958).

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 255.

(20) Reference 19, p 246.

TABLE VI

INTERATOMIC ANGLES (DEG) IN $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$

Atoms	Type	Angle
Copper Coordination		
Cu(2)–Cu(1)–Cu(3)	a	58.0 (1)
Cu(2)–Cu(1)–Cu(4)	b	65.6 (1)
Cu(3)–Cu(1)–Cu(4)	a	58.3 (1)
Cu(1)–Cu(2)–Cu(3)	b	65.5 (1)
Cu(1)–Cu(2)–Cu(4)	a	57.6 (1)
Cu(3)–Cu(2)–Cu(4)	a	58.2 (1)
Cu(1)–Cu(3)–Cu(2)	a	56.5 (1)
Cu(1)–Cu(3)–Cu(4)	a	56.8 (1)
Cu(2)–Cu(3)–Cu(4)	b	64.4 (1)
Cu(1)–Cu(4)–Cu(2)	a	56.8 (1)
Cu(1)–Cu(4)–Cu(3)	b	64.9 (1)
Cu(2)–Cu(4)–Cu(3)	a	57.4 (1)
Cu(2)–Cu(1)–S(1)	c	153.1 (3)
Cu(2)–Cu(1)–S(4)	d	86.6 (2)
Cu(2)–Cu(1)–S(6)	e	54.0 (2)
Cu(3)–Cu(1)–S(1)	f	95.1 (3)
Cu(3)–Cu(1)–S(4)	g	110.2 (3)
Cu(3)–Cu(1)–S(6)	h	81.9 (2)
Cu(4)–Cu(1)–S(1)	i	101.6 (3)
Cu(4)–Cu(1)–S(4)	j	52.3 (2)
Cu(4)–Cu(1)–S(6)	k	119.0 (3)
Cu(1)–Cu(2)–S(3)	i	105.7 (3)
Cu(1)–Cu(2)–S(6)	j	52.9 (3)
Cu(1)–Cu(2)–S(8)	k	117.7 (3)
Cu(3)–Cu(2)–S(3)	c	151.4 (3)
Cu(3)–Cu(2)–S(6)	d	86.1 (2)
Cu(3)–Cu(2)–S(8)	e	52.5 (2)
Cu(4)–Cu(2)–S(3)	f	93.7 (3)
Cu(4)–Cu(2)–S(6)	g	110.0 (3)
Cu(4)–Cu(2)–S(8)	h	83.2 (3)
Cu(1)–Cu(3)–S(2)	h	82.2 (2)
Cu(1)–Cu(3)–S(5)	f	89.0 (3)
Cu(1)–Cu(3)–S(8)	g	108.5 (2)
Cu(2)–Cu(3)–S(2)	k	116.2 (2)
Cu(2)–Cu(3)–S(5)	i	107.7 (3)
Cu(2)–Cu(3)–S(8)	j	52.3 (2)

Atoms	Type	Angle
Copper Coordination		
Cu(4)–Cu(3)–S(2)	e	52.1 (2)
Cu(4)–Cu(3)–S(5)	c	144.2 (3)
Cu(4)–Cu(3)–S(8)	d	87.1 (2)
Cu(1)–Cu(4)–S(2)	d	87.6 (2)
Cu(1)–Cu(4)–S(4)	e	53.5 (2)
Cu(1)–Cu(4)–S(7)	c	144.1 (3)
Cu(2)–Cu(4)–S(2)	g	109.4 (2)
Cu(2)–Cu(4)–S(4)	h	81.6 (3)
Cu(2)–Cu(4)–S(7)	f	88.2 (3)
Cu(3)–Cu(4)–S(2)	j	52.3 (2)
Cu(3)–Cu(4)–S(4)	k	117.9 (3)
Cu(3)–Cu(4)–S(7)	i	105.1 (3)
S(1)–Cu(1)–S(4)	l	104.5 (3)
S(1)–Cu(1)–S(6)	m	128.2 (3)
S(4)–Cu(1)–S(6)	n	125.2 (3)
S(3)–Cu(2)–S(6)	l	111.0 (3)
S(3)–Cu(2)–S(8)	m	124.8 (3)
S(6)–Cu(2)–S(8)	n	121.9 (3)
S(2)–Cu(3)–S(5)	m	118.8 (3)
S(2)–Cu(3)–S(8)	n	123.7 (3)
S(5)–Cu(3)–S(8)	l	116.5 (3)
S(2)–Cu(4)–S(4)	n	125.8 (4)
S(2)–Cu(4)–S(7)	l	114.2 (3)
S(4)–Cu(4)–S(7)	m	119.2 (3)
Sulfur Coordination		
Cu(3)–S(2)–Cu(4)	o	75.5 (3)
Cu(1)–S(4)–Cu(4)	o	74.1 (3)
Cu(1)–S(6)–Cu(2)	o	73.1 (3)
Cu(2)–S(8)–Cu(3)	o	75.2 (3)
Cu(1)–S(1)–P(1)	p	102.2 (4)
Cu(3)–S(2)–P(1)	q	101.0 (4)
Cu(4)–S(2)–P(1)	r	110.6 (4)
Cu(2)–S(3)–P(2)	p	101.1 (4)
Cu(1)–S(4)–P(2)	r	110.7 (4)

Atoms	Type	Angle
Sulfur Coordination		
Cu(4)–S(4)–P(2)	q	103.6 (4)
Cu(3)–S(5)–P(3)	p	98.5 (4)
Cu(1)–S(6)–P(3)	q	106.5 (4)
Cu(2)–S(6)–P(3)	r	105.8 (4)
Cu(4)–S(7)–P(4)	p	99.2 (4)
Cu(2)–S(8)–P(4)	q	105.6 (4)
Cu(3)–S(8)–P(4)	r	104.7 (4)
Phosphorus Coordination		
S(1)–P(1)–S(2)	s	118.7 (5)
S(3)–P(2)–S(4)	s	119.1 (5)
S(5)–P(3)–S(6)	s	117.9 (5)
S(7)–P(4)–S(8)	s	118.1 (5)
S(1)–P(1)–O(1)	t	111.0 (9)
S(1)–P(1)–O(2)	t	113.3 (9)
S(2)–P(1)–O(1)	u	107.1 (9)
S(2)–P(1)–O(2)	u	105.0 (9)
S(3)–P(2)–O(3)	t	112.9 (9)
S(3)–P(2)–O(4)	t	110.7 (8)
S(4)–P(2)–O(3)	u	101.9 (9)
S(4)–P(2)–O(4)	u	108.5 (8)
S(5)–P(3)–O(5)	t	107.9 (8)
S(5)–P(3)–O(6)	t	113.9 (9)
S(6)–P(3)–O(5)	u	108.2 (8)
S(6)–P(3)–O(6)	u	106.3 (8)
S(7)–P(4)–O(7)	t	106.6 (9)
S(7)–P(4)–O(8)	t	112.1 (9)
S(8)–P(4)–O(7)	u	109.9 (8)
S(8)–P(4)–O(8)	u	106.3 (9)
O(1)–P(1)–O(2)	v	100.0 (11)
O(3)–P(2)–O(4)	v	102.1 (10)
O(5)–P(3)–O(6)	v	101.3 (10)
O(7)–P(4)–O(8)	v	102.7 (10)

Atoms	Type	Angle
Oxygen Coordination		
P(1)–O(1)–C(1)	w	121 (2)
P(1)–O(2)–C(2)	w	125 (2)
P(2)–O(3)–C(3)	w	122 (2)
P(2)–O(4)–C(4)	w	125 (2)
P(3)–O(5)–C(5)	w	122 (2)
P(3)–O(6)–C(6)	w	118 (2)
P(4)–O(7)–C(7)	w	123 (2)
P(4)–O(8)–C(8)	w	119 (2)
Carbon Coordination		
O(1)–C(1)–C(9)	x	104 (3)
O(1)–C(1)–C(10)	x	109 (3)
O(2)–C(2)–C(11)	x	107 (3)
O(2)–C(2)–C(12)	x	109 (3)
O(3)–C(3)–C(13)	x	109 (3)
O(3)–C(3)–C(14)	x	105 (3)
O(4)–C(4)–C(15)	x	111 (3)
O(4)–C(4)–C(16)	x	110 (3)
O(5)–C(5)–C(17)	x	102 (3)
O(5)–C(5)–C(18)	x	108 (3)
O(6)–C(6)–C(19)	x	110 (3)
O(6)–C(6)–C(20)	x	105 (3)
O(7)–C(7)–C(21)	x	101 (3)
O(7)–C(7)–C(22)	x	112 (3)
O(8)–C(8)–C(23)	x	108 (3)
O(8)–C(8)–C(24)	x	101 (3)
C(9)–C(1)–C(10)	y	112 (3)
C(11)–C(2)–C(12)	y	111 (3)
C(13)–C(3)–C(14)	y	117 (4)
C(15)–C(4)–C(16)	y	116 (4)
C(17)–C(5)–C(18)	y	115 (4)
C(19)–C(6)–C(20)	y	106 (3)
C(21)–C(7)–C(22)	y	109 (4)
C(23)–C(8)–C(24)	y	109 (4)

Averages of Chemically Equivalent Bond Angles (deg)

Angle	Type	Av (rms dev)	Angle	Type	Av (rms dev)	Angle	Type	Av (rms dev)	Angle	Type	Av (rms dev)
Cu–Cu–Cu	a	57.5 (7)	Cu–Cu–S	h	82.2 (7)	Cu–S–Cu	o	74.5 (11)	O–P–O	v	101.6 (12)
Cu–Cu–Cu	b	65.1 (6)	Cu–Cu–S	i	105 (3)	Cu–S–P	p	100 (2)	P–O–C	w	122 (3)
Cu–Cu–S	c	148 (5)	Cu–Cu–S	j	52.4 (3)	Cu–S–P	q	104 (2)	O–C–C	x	107 (4)
Cu–Cu–S	d	86.9 (7)	Cu–Cu–S	k	117.6 (12)	Cu–S–P	r	108 (3)	C–C–C	y	112 (4)
Cu–Cu–S	e	53.0 (9)	S–Cu–S	l	112 (5)	S–P–S	s	118.5 (6)			
Cu–Cu–S	f	92 (3)	S-Cu–S	m	123 (5)	S–P–O	t	111 (3)			
Cu–Cu–S	g	109.5 (8)	S–Cu–S	n	124 (2)	S–P–O	u	107 (2)			

(range 2.23–2.47 Å).[21] The distances are also shorter than the 2.39-Å sum of the covalent radii of copper (1.35 Å) and sulfur (1.04 Å).[20]

The two P–S bonds within each ligand are unequal in length. Sulfur donating only one electron pair to the copper tetrahedron is more tightly bonded to phosphorus than is the sulfur donating two electron pairs to the tetrahedron. The P–S bond lengths associated with these sulfur atoms average 1.972 (8) and 2.036 (11) Å, respectively. The eight P–O bonds average 1.56 (2) Å, a value entirely comparable to those in other *0,0'*-dialkylphosphorodithioates.

A selected list of weighted least-squares planes[22] through sets of atoms in the molecule and distances of these atoms from their respective planes are presented in Table VII. The results may be summarized as follows. (1) Each ligand is attached to two sites in the copper tetrahedron, one of which may be considered a vertex atom and the other an edge of the corresponding base plane. The sulfur straddling the edge lies in an extension of the base plane. (2) The three sulfur atoms bonded to a given copper atom are approximately coplanar with that atom. (3) The atoms in the linkage Cu–S–P–S< do not deviate greatly from a common plane.

Within each $S_2P(OC_3H_7)_2$ group, each pair of C–O bonds assumes both a trans and a gauche conformation with respect to the associated P–O bonds. The rotational isomers may be defined by (O'S'S)P–O(CEE'), where S' denotes the nonbridging sulfur atom (*i.e.*, that which is singly bonded to copper), E and E' denote the unshared pairs of electrons associated with the unprimed oxygen atom, O, and P–O denotes the reference bond about which the rotations may occur. The more energetically favored trans conformation corresponds to the planar array of atoms C,O,P,O' with C being "trans" to O'. The gauche conformation corresponds to the planar array of atoms C,O,P,S' with C being "trans" to S'.

Figure 5 shows the [010] view of the noncentrosymmetric primitive unit cell containing the four discrete tetrameric molecules. These molecules are separated by normal van der Waals distances. The closest intermolecular H···S, H···O, and H···H approaches are

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TABLE VII

WEIGHTED LEAST-SQUARES PLANES AND DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE PLANES IN $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$[a]

Plane no.	Equation of best plane: $Ax + By + Cz - D = 0$ *A*	*B*	*C*	*D*	Defining atoms and distances (Å) from plane
1	7.504	4.050	22.708	20.159	Cu(1), −0.026 (3); Cu(2), 0.031 (3); Cu(3), 0.022 (3); S(8), −0.145 (7)
2	3.010	2.820	−31.676	−15.930	Cu(1), 0.039 (3); Cu(2), 0.039 (3); Cu(4), −0.031 (3); S(6), −0.193 (6)
3	9.491	−5.641	−9.853	−4.100	Cu(1), −0.029 (3); Cu(3), 0.026 (3); Cu(4), −0.036 (3); S(4), 0.187 (7)
4	0.842	12.336	1.290	6.177	Cu(2), 0.031 (4); Cu(3), −0.030 (3); Cu(4), −0.032 (4); S(2), 0.144 (7)
5	4.201	10.487	−12.826	0.691	Cu(1), −0.076 (3); S(1), 0.119 (7); S(4), 0.094 (7); S(6), 0.124 (7)
6	10.358	−4.041	7.616	9.903	Cu(2), −0.073 (3); S(3), 0.106 (7); S(6), 0.139 (8); S(8), 0.142 (7)
7	4.474	7.668	−22.920	−9.877	Cu(3), 0.046 (3); S(2), −0.075 (7); S(5), −0.096 (7); S(8), −0.080 (7)
8	9.678	−0.992	17.176	13.456	Cu(4), 0.046 (3); S(2), −0.059 (6); S(4), −0.088 (7); S(7), −0.076 (7)
9	4.998	−1.457	30.062	20.016	Cu(1), 0.009 (3); S(1), −0.080 (8); S(2), −0.038 (7); P(1), 0.058 (7)
10	6.660	9.842	4.738	11.139	Cu(2), 0.003 (4); S(3), −0.035 (8); S(4), −0.021 (7); P(2), 0.033 (7)
11	6.446	−9.987	5.111	2.522	Cu(3), 0.024 (3); S(5), −0.242 (8); S(6), −0.182 (8); P(3), 0.240 (7)
12	8.702	2.060	−20.783	−7.614	Cu(4), −0.021 (3); S(7), 0.228 (8); S(8), 0.126 (7); P(4), −0.263 (8)

[a] Equations of the best planes are expressed in terms of the orthorhombic unit cell axes.

2.90, 2.47, and 2.35 Å, respectively,[23] compared with the respective van der Waals radius sums of 3.0, 2.6, and 2.4 Å, indicating that there are no unusual intermolecular interactions. The closest Cu···H approach occurs at 3.9 Å, well beyond the distance for any significant interaction.

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[23] Based on the final hydrogen coordinates adjusted to give C–H bond lengths of 1.11 Å.

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The Crystal Structure of Triethylammonium Phenylthioarsenate

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The crystal and molecular structure of triethylammonium phenylthioarsenate, $(C_2H_5)_3NH^+(C_6H_5)AsSO(OH)^-$, was determined from three-dimensional X-ray data collected with a manual diffractometer using Mo Kα (λ 0.71069 Å) radiation. The compound crystallizes in the triclinic space group $P\bar{1}$, with a = 11.807 (1) Å, b = 10.558 (1) Å, c = 8.788 (1) Å, α = 116.21 (2)°, β = 98.95 (1)°, γ = 117.91 (1)°, Z = 2, d_{measd} = 1.40 (1) g cm^{-3}, and d_{calcd} = 1.373 (3) g cm^{-3}, at 23°. The structure was determined by Patterson and Fourier methods and refined with 362 observed reflections by full-matrix least squares to an R of 0.051. In the final refinement the phenyl ring was constrained as a rigid group, and the As and S atoms were refined with anisotropic thermal parameters. The anion of the structure consists of an arsenic atom tetrahedrally bonded to a phenyl group, two oxygen atoms, and a sulfur atom at distances of 1.90 (2), 1.65 (2), 1.75 (3), and 2.08 (2) Å, respectively. Hydrogen bonding holds pairs of anions together and one cation to each anion. This is the first monothioarsenate structure to be reported, and the As–S bond length is one of the shortest values reported for that bond.

Introduction

Several structures of cyclic arsenic–sulfur molecules are under investigation in our laboratory, with an interest in the structural evidence for possible p → d or d → d π bonding in the As–S linkages. There is a paucity, however, of As–S bond distances in the structural literature: less than a dozen molecular structures with As–S bonds have been reported. The As–S distances reported range from 2.075 (7) in $(Me_2AsS)_2$[1] to 2.21 to 2.25 Å for several arsenic sulfides (As_4S_3,[2] As_4S_4,[3] and As_4S_6[4]) and the tetrathioarsenate ion,[5] to 2.32–2.35 Å for As(III)–S bonds.[6,7]

We wish to report here the structure of the phenylthioarsenate ion, $(C_6H_5)AsSO(OH)^-$, which has an As–S distance (2.08 (2) Å) that is equal in length to the shortest As–S bond distance previously reported.

Data Collection and Reduction

Triethylammonium phenylthioarsenate, $(C_2H_5)_3NH^+(C_6H_5)AsSO(OH)^-$, was obtained from the reaction of $As_2S_3(C_6H_5)_2$ with an excess of moist triethylamine. The reaction was carried out over a period of 48 hr in benzene under reflux. *Anal.* Calcd for $(C_2H_5)_3NH^+(C_6H_5)AsSO(OH)^-$: As, 23.46; S, 10.04; N, 4.39; C, 45.13; H, 6.96. Found: As, 24.55; S, 10.52; N, 4.42; C, 45.34; H, 7.27; mp 114–115°. Crystals were obtained from dioxane solutions by slow cooling. Since the compound

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