2.9° between the mean plane through the six atoms of the pyrimidine ring and the mean plane through the five atoms of the imidazole moiety, respectively. This angle is less than 0.4° for ring 2. For both adenine molecules, the nitrogen atoms of the amino groups are pulled out of the planes of the purine rings by ~0.06 (1) Å. The copper atom is found at 0.072 (2) Å from that same plane for ring 2, but a much greater distance of 0.209 (2) Å is observed for ring 1. All these deviations are most likely due to the different hydrogen-bonding schemes in which the two independent ligands are involved.

Packing and Hydrogen Bonding. Figure 3 shows how the $[Cu_2(AdH)_4(H_2O)_2]^{4+}$ cations, the ClO_4^- anions, and the lattice water molecules are held together in an intricate network of hydrogen bonds.

From Figure 1, it is obvious that the oxygen atoms in the perchlorate groups have a large thermal motion (isotropic *B* ranging from 6 to 11 $Å^2$). However, all the bond lengths and angles (Table III) are quite reasonable and there is no evidence for disorder in these anions from the difference Fourier map.

Table IV lists a series of intermolecular contacts involving hydrogen, most of which undoubtedly correspond to hydrogen bonds. The hydrogen atom H2O10 of one of the water molecules was not located, but a search around O10 revealed no basic site close enough to imply appreciable hydrogen bonding through the missing hydrogen. The table shows that the atoms N7 and N1 of ring 1 are involved in rather strong hydrogen bonding and it is reasonable to believe that this can result in significant distortions in the ring. On the other hand, ring 2 forms strong hydrogen bonds only through the hydrogen atoms of the amino group. This group being removed from the ring itself, little distortion is expected in the ring, in agreement with the above observations.

Registry No. $[Cu_2(C_5H_5N_5)_4(H_2O)_2](ClO_4)_4 \cdot 2H_2O$, 38744-29-5.

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Crystal Structure of *cyclo*-Tri-μ-(trimethylphosphine sulfide)-tris(chlorocopper(I))

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The crystal structure of the copper(I) complex $[Cu((CH_3)_3PS)Cl]_3$ has been determined from three-dimensional X-ray data collected by counter methods. The material crystallized in space group C_s^3-*Im* of the monoclinic system,with two trimeric units in a cell of dimensions $a = 6.294$ (3), $b = 20.399$ (12), $c = 9.271$ (5) Å, and $\beta = 99.04$ (2)° (temperature 25°). The observed and calculated densities are 1.75 and 1.755 g cm^{-3}, respectively. The structure was solved by conventional heavy-atom methods and has been refined to a final *R* factor of 0.024 on *F*, using 2501 independent reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$. The molecular structure consists of a six-membered ring of alternating Cu atoms and bridging S atoms which is bisected by a crystallographic mirror plane. The ring is puckered into a chair conformation with equatorial $(CH_3)_3P$ groups, and the phosphine sulfide is symmetrically bridged. The copper atoms are three-coordinate, with approximately trigonal-planar coordination to two bridging S atoms of the phosphine sulfides and one terminal chlorine atom. The bond angles about the S and P atoms are nearly tetrahedral. Important bond distances follow: Cu–S, 2.265 (1) Å; Cu–Cl, 2.209 (2) and 2.220 (1) Å; S–P, 2.025 (1) Å.

Introduction

While investigating the coordination properties of phosphine sulfide ligands with copper(I), we found that the preferred coordination number is apparently 3 rather than 2 or 4.[2] In fact, the X-ray structure determination of $[Cu((CH_3)_3PS)_3]ClO_4$ showed that the cation contained a trigonal-planar arrangement of sulfur atoms around the copper atom.[3]

Another class of compounds, $[CuLX]_n$ (X = Cl, Br, I, SCN; L = tertiary phosphine sulfide), has recently been isolated.[4] On the basis of their relative insolubilities, we assumed that these compounds were polymeric. For the complexes $[Cu((CH_3)_3PS)X]_n$ (X = Cl, Br, I) the shift of the P–S stretching frequency upon coordination of $(CH_3)_3PS$ (as observed from their infrared spectra) was twice as large as the shift for $[Cu((CH_3)_3PS)_3]ClO_4$ (40–45 and 25 cm^{-1}, respectively). The larger shift of the P–S infrared absorption in the halide complexes was attributed to sulfur atom bridges,[4] even though few bridging phosphine sulfides have ever been proposed.[5]

The X-ray structural determination of $[Cu((CH_3)_3PS)Cl]_3$, which is reported herein, was undertaken to clarify (1) the nature of the polymer, (2) the bridging atom, and (3) the coordination number and geometry of copper(I) in this compound. To our knowledge this is the first X-ray determination of the structure of a complex involving a bridging phosphine sulfide ligand. A preliminary account of the structure has been reported.[6]

Experimental Section

Microcrystalline $[Cu((CH_3)_3PS)Cl]_3$ was readily prepared by

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(1) (a) Ohio State University Postdoctoral Fellow, Sept 1971–Sept 1972. (b) Postdoctoral Research Associate.

(2) J. A. Tiethof, A. T. Hetey, P. E. Nicpon, and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, 8, 841 (1972).

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stirring an acetonitrile solution of $[Cu((CH_3)_3PS)_3]BF_4$ with LiCl. The preparation and characterization is discussed in more detail elsewhere.[4] X-Ray quality crystals were obtained when this solid was dissolved in warm (50°) acetonitrile (with a slight excess of $(CH_3)_3PS$ present) and allowed to cool slowly to ambient temperature.

Unit Cell and Space Group. Preliminary Weissenberg and precession photographs of the $h0l$, $h1l$, $0kl$, and $1kl$ layers exhibited monoclinic symmetry. The systematic absences hkl ($h + k + l \neq 2n$), $h0l$ ($h + l \neq 2n$), and $0k0$ ($k \neq 2n$) were consistent with space groups $C_2{}^3$-$I2$, $C_s{}^3$-Im, and $C_{2h}{}^3$-$I2/m$.[7] The cell dimensions, obtained in the usual way[8] by least-squares refinement of the setting angles of 20 reflections that were carefully centered on a Picker FACS-III four-circle diffractometer using Mo Kα_1 radiation (λ 0.70926 Å), are a = 6.294 (3), b = 20.399 (12), c = 9.271 (5) Å, and β = 99.04 (2)° (temperature 25°). The observed density of 1.75 (1) g/cm^3, determined by flotation in a carbon tetrachloride-methyl iodide solution, agrees well with that of 1.755 g/cm^3 calculated for two $[Cu((CH_3)_3PS)Cl]_3$ units in the cell.

Collection and Reduction of Intensity Data. The intensity data were collected from a crystal with approximate dimensions 0.2 × 0.2 × 0.2 mm mounted nearly parallel to the large (010) and $(0\bar{1}0)$ faces. A Picker four-circle diffractometer, controlled by an EMR 6130 computer, was used for data collection. Integrated intensities were obtained by a θ–2θ scan technique, scanning the Kα_1 peaks symmetrically for 2° at a rate of 2°/min. Mo Kα radiation was used with a graphite monochromator and a takeoff angle of 2.3° (giving intensities 80% of their maximum value for the 101 and 507 reflections). Stationary-crystal, stationary-counter background counts of 10 sec were taken at the beginning and end of each scan. The diffracted beams were attenuated with successive layers of brass foil whenever necessary to prevent coincidence losses. The scintillation counter was placed 26 cm from the crystal and had an aperture of 6.5 × 6.5 mm.

Intensity data were collected in two quadrants to values of $\lambda^{-1} \sin\theta$ of 0.60 and in a third quadrant to $\lambda^{-1} \sin\theta = 0.75$. The intensities of 18 reflections were measured after each interval of 400 reflections, and these standard intensities showed no significant variation with time. The intensity data were corrected for background, and standard deviations were assigned as previously described[9a] using a value of 0.05 for p; Lorentz and polarization corrections were also applied.[9b] Averaging the data in two quadrants in which reflections were compared to their mirror equivalents (hkl and hkl) showed an average deviation from the mean of 1.5%, whereas averaging the two quadrants in which data were compared to their C_2 rotational equivalents (hkl and $\bar{h}kl$) showed a significantly larger deviation from the mean of 2.6%. This was consistent with the space group $C_s{}^3$-Im, and this assignment has been confirmed by the solution and refinement of the structure. The crystal was measured, and a gaussian absorption correction was applied. The 13 faces were identified by optical and X-ray means as six pairs of faces of the forms {010}, {011}, $\{01\bar{1}\}$, {110}, $\{\bar{1}10\}$, and $\{03\bar{1}\}$ and the face $(\bar{1}0\bar{1})$. The linear absorption coefficient used was 34.95 cm^{-1},[10] and corrections to F^2 varied from 1.61 to 1.79. The data were then averaged to give a final set of 3275 data, assuming the acentric space group Im. The 2501 data that obeyed the condition $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ were used in the subsequent solution and refinement of the structure.

Solution and Refinement of the Structure. The structure was solved by the usual combination of Patterson, Fourier, and least-squares methods.[11] In least-squares calculations, $w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weights, w, were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for Cu, Cl, S, P, and C were taken from the usual tabulation,[12] while those for H were taken from the calculations of Stewart, *et al.*[13] The values of the anomalous terms for Cu, Cl, S, and P, $\Delta f'$ and $\Delta f''$, were taken from the calculations of Cromer.[14]

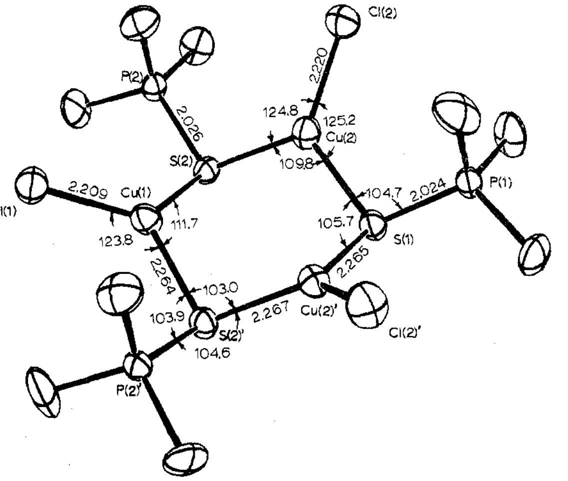

Figure 1. A perspective drawing of $[Cu((CH_3)_3PS)Cl]_3$. The primed atoms designate those related by the crystallographic mirror plane.

Positions of the two independent Cu and S atoms consistent with the space group Im were found from a Patterson function. Indications of the P and Cl atoms were also found. (The equivalent positions for space group Im are x, y, z; $x, \bar{y}, z$; $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; and $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.) Refinement of the trial structure containing only Cu and S atoms, followed by a difference Fourier map, led to the location of the P atoms. Four cycles of refinement with Cu and S atoms having anisotropic thermal parameters and P atoms having isotropic thermal parameters gave values of R_1 and R_2 of 0.217 and 0.296, respectively, where $R_1 = \|F_o| - |F_c\|/\Sigma F_o$ and $R_2 = (w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{1/2}$. After the first two cycles of refinement, the signs of all atomic coordinates were changed as a result of comparisons of intensities of Friedel pairs for several strong high-angle reflections which suggested that the polarity of the space group had been incorrectly assigned. Another difference Fourier was used to locate the Cl atoms. These were included in four cycles of refinement in which the Cu, S, Cl, and P atoms were allowed anisotropic thermal parameters, reducing R_1 and R_2 to 0.084 and 0.112, respectively. The five unique C atoms were located from another difference Fourier map and four cycles of refinement, the last two with all atoms having anisotropic thermal parameters, reduced R_1 and R_2 to 0.032 and 0.038. Before continuing with the solution, the assignment of the polarity of the crystal was confirmed by refining the present model with the signs of $\Delta f''$ reversed for Cu, S, Cl, and P.[15] The resulting refinement increased the values of R_1 and R_2 to 0.051 and 0.059. In the refinement where R_1 and R_2 were 0.032 and 0.038 several of the most intense reflections had $|F_c| > |F_o|$, which suggested that secondary extinction effects were important. Two cycles of refinement including a variable extinction coefficient[16] reduced the values of R_1 and R_2 significantly to 0.029 and 0.035, respectively. A subsequent difference Fourier map was used to locate the 14 unique H atoms. A structure factor calculation including the hydrogen atoms gave R_1 and R_2 values of 0.028 and 0.034. A final least-squares refinement was carried out in which the hydrogen atoms were refined with isotropic thermal parameters, and all other atoms were refined with anisotropic thermal parameters. After four full-matrix, least-squares cycles with 157 variables and 2501 observations the refinement had converged, and the values of R_1 and R_2 were significantly reduced to 0.024 and 0.028. This led to the final atomic parameters given in Tables I

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(7) The choice of the nonconventional I-centered space group rather than the conventional C-centered one allows a more convenient choice of axes.

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

(9) (a) P. W. R. Corfield and S. Shore, *J. Amer. Chem. Soc.*, 95, 1480 (1973). (b) The following programs by P. W. R. Corfield and G. J. Gainsford were used with the EMR computer: COZLS, for least-squares determination of cell parameters; ASSET, for automatic collection of intensity data; PLPIC, for Lorentz and polarization corrections; PICABS, for gaussian integration absorption corrections; MERGE, for data averaging; FOUR and FPRNT, for Patterson and Fourier syntheses.

(10) The linear absorption coefficient is actually 35.66 cm^{-1}; owing to a calculation error the 34.95-cm^{-1} value was used. Since the corrections to F^2 were limited to the range 1.61–1.79, the small error will not affect the results significantly.

(11) An IBM 370-165 computer was used for the structure solution and refinements. Local programs in addition to local variations of the following programs were used: Zalkin's FORDAP Fourier program, the Busing-Levy ORFFE error function and ORFLS least-squares programs, and Johnson's ORTEP plotting program.

(12) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

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Table I. Fractional Coordinates and Thermal Parameters for $[Cu((CH_3)_3PS)Cl]_3$

Atom	x	y	z	$\beta_{11}{}^a$	$\beta_{22}{}^a$	$\beta_{33}{}^a$	$\beta_{12}{}^a$	$\beta_{13}{}^a$	$\beta_{23}{}^a$
Cu(1)	0	0	0	252 (2)	14 (0)	80 (0)	0	40 (1)	0
Cu(2)	−0.2352 (1)	0.0885 (0)	0.2639 (1)	213 (1)	17 (0)	89 (0)	2 (0)	46 (1)	4 (0)
S(1)	−0.4354 (2)	0	0.3039 (1)	229 (3)	14 (0)	66 (1)	0	40 (2)	0
S(2)	−0.1925 (2)	0.0919 (0)	0.0257 (1)	196 (2)	13 (0)	85 (1)	−6 (0)	50 (1)	0 (0)
P(1)	−0.4371 (2)	0	0.5220 (1)	235 (3)	12 (0)	65 (1)	0	54 (2)	0
P(2)	0.0202 (2)	0.1656 (0)	0.0148 (1)	184 (2)	11 (0)	79 (1)	0 (0)	48 (1)	2 (0)
Cl(1)	0.3154 (2)	0	−0.0760 (2)	218 (3)	21 (0)	112 (1)	0	53 (2)	0
Cl(2)	−0.1222 (2)	0.1653 (0)	0.4277 (1)	309 (3)	21 (0)	107 (1)	−14 (1)	45 (1)	−7 (0)
C(1)	−0.1728 (13)	0	0.6248 (7)	410 (26)	33 (2)	73 (7)	0	−34 (10)	0
C(2)	−0.5709 (10)	0.0716 (2)	0.5742 (6)	443 (19)	18 (1)	143 (6)	22 (3)	150 (10)	−1 (2)
C(3)	0.2634 (7)	0.1577 (2)	0.1424 (6)	174 (10)	24 (1)	145 (6)	−4 (3)	3 (6)	−1 (2)
C(4)	0.0916 (11)	0.1688 (2)	−0.1641 (5)	478 (20)	24 (1)	106 (5)	−32 (4)	131 (9)	4 (2)
C(5)	−0.1003 (9)	0.2422 (2)	0.0503 (6)	327 (14)	11 (1)	190 (7)	14 (3)	98 (9)	5 (2)

[a] All $\times 10^4$. The anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Fractional Coordinates and Thermal Parameters for the Hydrogen Atoms

Atom	x	y	z	B, Å^2
C(1)H(1)	−0.186 (11)	0	0.705 (8)	5.4 (1.7)
C(1)H(2)	−0.097 (10)	0.045 (3)	0.598 (6)	8.5 (1.5)
C(2)H(1)	−0.707 (9)	0.072 (2)	0.513 (5)	4.9 (1.1)
C(2)H(2)	−0.604 (9)	0.065 (3)	0.682 (7)	7.6 (1.4)
C(2)H(3)	−0.479 (12)	0.111 (4)	0.528 (8)	9.8 (1.7)
C(3)H(1)	0.323 (10)	0.119 (3)	0.127 (6)	6.6 (1.2)
C(3)H(2)	0.364 (9)	0.190 (2)	0.142 (6)	6.6 (1.2)
C(3)H(3)	0.235 (10)	0.160 (2)	0.250 (7)	7.4 (1.3)
C(4)H(1)	0.166 (10)	0.123 (3)	−0.177 (7)	8.9 (1.7)
C(4)H(2)	−0.036 (15)	0.176 (3)	−0.241 (10)	10.3 (2.0)
C(4)H(3)	0.179 (10)	0.208 (3)	−0.167 (6)	8.3 (1.5)
C(5)H(1)	−0.229 (11)	0.249 (4)	−0.011 (7)	8.9 (1.8)
C(5)H(2)	−0.097 (10)	0.240 (3)	0.165 (7)	9.1 (1.6)
C(5)H(3)	−0.020 (8)	0.277 (3)	0.012 (6)	7.0 (1.3)

and II. The variable extinction parameter had a value of 5.4 (3) × 10^{-6}, and the maximum correction to F_o was 1.14. The maximum parameter shift for nonhydrogen atoms was $\leqslant 0.1\sigma$ except for β_{11} on C(2) which had a shift of 0.2σ. The maximum shift was 0.54σ, which was for the x coordinate of H(5). An analysis of $|F_o|$ and $|F_c|$ as a function of scattering angle, magnitude of $|F_o|$, and Miller indices revealed no unexpected trends, and the final value of the error in an observation of unit weight was 0.94. This suggests that the weighting scheme used was reasonable. A final difference Fourier map had no peaks greater than 0.26 e/Å^3, approximately 5% of the height of a carbon atom. The final values of $10|F_o|$ and $10|F_c|$ (for which $F_o{}^2 \geqslant 3\sigma F_o{}^2$) in electrons are available.[17] Using *all nonzero* data, R_1 and R_2 were 0.035 and 0.031, respectively.

Description of the Structure and Discussion

The crystal structure consists of discrete $[Cu((CH_3)_3PS)Cl]_3$ molecules, two in each *Im* unit cell. A view of one of these trimers (excluding hydrogen atoms) is shown in Figure 1, including the 50% probability thermal ellipsoids and some of the pertinent bond distances and angles. A full tabulation of bond distances and bond angles for nonhydrogen atoms and some selected intermolecular and intramolecular nonbonding distances are presented in Table III. The closest approach of adjacent molecules is between two hydrogen atoms (2.30 Å) and a hydrogen and a chlorine atom (2.72 Å), both of which are somewhat shorter than the sum of the van der Waals radii, 2.4 and 3.0 Å, respectively.

Each trimer forms a six-membered ring composed of three copper and three sulfur atoms. The crystallographic mirror imposes C_s symmetry on the trimeric unit, and the mirror bisects the ring. One copper and one sulfur atom lie on the mirror (Cu(1), S(1)) and the remaining pairs of these atoms (Cu(2), Cu(2)′ and S(2), S(2)′) lie off the mirror in symmetry-equivalent positions. The ring is puckered into a chair conformation. The degree of puckering can be described by the torsional angles about the Cu-S bonds. These angles are defined as the dihedral angles between the S-Cu-S and Cu-S-Cu planes of the ring. These values are presented in Table IV and range from 64.31 to 66.70°, suggesting a substantial but rather uniform degree of puckering. The ring substituents $P(CH_3)_3$ occupy positions equatorial to the ring while the chlorine substituents are intermediate between axial and equatorial. Aside from the crystallographic mirror passing through Cu(1), S(1), P(1), Cl(1), C(1), there are two symmetry-related least-squares planes passing through Cu(2), S(2)′, P(2)′, Cl(2), C(3)′ and Cu(2)′, S(2), P(2), Cl(2)′, C(3) (see Table IV). These planes are nearly mirror planes for the remaining pairs of atoms, giving the trimer approximate C_{3v} symmetry.

The copper atoms are three-coordinate, each being bonded to two bridging sulfur atoms and a terminal chlorine atom. The coordination geometry around each copper is a distorted trigonal plane. This geometry has been observed several times recently for three-coordinate copper(I).[18-23] The angles around the copper atoms vary substantially (109.8-125.2°), but their sums are close to 360° (359.4-359.8 (1)°). This places the copper only 0.059-0.108Å from the plane of the three donor atoms. The sulfur atoms are nearly tetrahedral. The two independent Cu-S-Cu angles are 102.98 and 105.69°, and the Cu-S-P angles have a range of 103.88-104.72°. From an examination of a molecular model, it appears that the ring puckering would have the effect of increasing H-Cl intramolecular nonbonding distances, which are relatively small even for the puckered form observed (see Table III). Thus, the intramolecular nonbonding interactions may influence the ring puckering and contribute to the small ring angles (average 107.1°)—particularly those around copper(I)—rather than the converse possibility.

The Cu-S distances are all equal within experimental error. The mean value of 2.265 (1) Å is within experimental error

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(17) A listing of observed and calculated structure factor amplitudes 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. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1170.

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Table III. Selected Distances (Å) and Angles (deg)

Bond distances		Selected nonbonding distances			
Atoms	Distance	Atoms	Distance	Atoms	Angle
Cu(1)-S(2)	2.264 (1)			S(2)-Cu(1)-S(2)′	111.70 (6)
Cu(2)-S(1)	2.265 (1)	Intramolecular		S(1)-Cu(2)-S(2)	109.75 (4)
Cu(2)-S(2)	2.267 (2)	Cu(1)-Cu(2)	3.546 (1)	S(2)-Cu(1)-Cl(1)	123.80 (3)
Cu(1)-Cl(1)	2.209 (2)	Cu(2)-Cu(2)′	3.610 (2)	S(1)-Cu(2)-Cl(2)	125.24 (6)
Cu(2)-Cl(2)	2.220 (1)	S(1)-C(2)H(3)	3.12 (7)	S(2)-Cu(2)-Cl(2)	124.80 (5)
		Cl(1)-C(4)H(1)	2.79 (7)	Cu(2)-S(1)-Cu(2)′	105.69 (7)
S(1)-P(1)	2.024 (2)	Cl(2)-C(2)H(3)	2.79 (7)	Cu(1)-S(2)-Cu(2)	102.98 (4)
S(2)-P(2)	2.026 (1)	Cl(2)-C(3)H(3)	2.99 (6)	Cu(2)-S(1)-P(1)	104.72 (5)
P(1)-C(1)	1.782 (8)	Cl(2)-C(5)H(2)	2.91 (7)	Cu(1)-S(2)-P(2)	103.88 (6)
P(1)-C(2)	1.790 (4)			Cu(2)-S(2)-P(2)	104.58 (4)
P(2)-C(3)	1.788 (5)	Intermolecular		S(1)-P(1)-C(1)	112.5 (3)
P(2)-C(4)	1.787 (4)	Cu(1)-C(1)H(1)	2.80 (8)	S(1)-P(1)-C(2)	110.3 (2)
P(2)-C(5)	1.791 (4)	Cu(2)-C(3)H(1)′	2.94 (6)	S(2)-P(2)-C(3)	113.8 (2)
		Cl(1)-C(2)H(2)	2.72 (6)	S(2)-P(2)-C(4)	109.8 (2)
		C(2)H(2)-C(4)H(1)	2.41 (9)	S(2)-P(2)-C(5)	109.6 (2)
		C(2)H(3)-C(5)H(3)	2.30 (10)	C(1)-P(1)-C(2)	107.1 (3)
				C(2)-P(1)-C(2)′	109.3 (3)
				C(3)-P(2)-C(4)	107.7 (3)
				C(3)-P(2)-C(5)	107.5 (2)
				C(4)-P(2)-C(5)	108.3 (2)

Table IV. Distances of Atoms from Various Least-Squares Planes and Dihedral Angles between Planes

	Distance, Å	Planes		Dihedral angle, deg
S(2)[a]		Cu(1)	Cu(1)	
S(2)′		S(2)	S(2)	66.70
Cl(1)		S(2)′	Cu(2)	
Cu(1)	0.108 (1)			
S(1)[a]		Cu(2)	Cu(2)	
S(2)		S(1)	S(1)	65.15
Cl(2)		S(2)	Cu(2)′	
Cu(2)	0.059 (1)			
Cu(2)′	0.003	Cu(2)	Cu(2)	
Cl(2)′	0.000	S(2)	S(2)	64.31
S(2)	−0.012	Cu(1)	S(1)	
P(2)	0.015			
C(3)	−0.006			
Cu(1)	0.007			
Cu(2)′	−0.007			
S(1)	0.007			
S(2)	−0.007			

[a] The first three atoms were used in determining the plane.

Table V.

Compd	P-S distance, Å	ν_{P-S}, cm^{-1}	Ref
$(CH_3)_3PS$	1.959 (2)	565	3
$[Cu((CH_3)_3PS)_3]ClO_4$	1.982-2.001 (4)	540	3
$[Cu((CH_3)_3PS)Cl]_3$	2.025 (2)	520	*a*
$[(CH_3)_3PS(CH_3)]I$	2.05 (1)[b]	502	*a*

[a] This work. [b] P. W. R. Corfield, personal communication, 1970.

of the range of Cu-S bond distances reported for $[Cu((CH_3)_3PS)_3]ClO_4$ (2.253-2.264 (5) Å).[3] The Cu-Cl distances, 2.209 (2) and 2.220 (1) Å, are nearly equal and significantly shorter than the Cu-Cl distances previously reported (2.25-2.36 Å) for three-coordinate copper(I) complexes. (All of the previously reported Cu-Cl distances have involved bridging chlorine atoms.[18,21-23]) The relatively long Cu-Cu distances of 3.54 and 3.61 Å preclude any metal-metal interactions.

The geometry of the coordinated trimethylphosphine sulfide is similar to that of the free sulfide and the coordinated sulfide in $[Cu((CH_3)_3PS)_3]ClO_4$.[3] The P-S distances in the trimer are equal within experimental error, averaging 2.025 (1) Å; these P-S distances are longer than for the free ligand and slightly longer than for $[Cu((CH_3)_3PS)_3]ClO_4$ where the ligand is nonbridging (see Table V). The average P-C distance of 1.788 (4) Å differs little from P-C distances reported for the free ligand (1.798 (2) Å) or for the tris sulfide-copper(I) complex (1.793 (8) Å). The C-H distances average 0.99 (10) Å. Phosphorus angles are typically tetrahedral, with S-P-C angles of 109.6-113.8 (2)° and C-P-C angles of 107.1-109.3 (3)°. Similarly, the angles about carbon are typically tetrahedral. The H-C-H angles (97-130 (5)°) average 111 (9)° while P-C-H angles (101-112 (4)°) average 108 (4)°.

It is surprising that trimethylphosphine sulfide is bridging the copper atoms since chloride ions are commonly bridging in copper(I) complexes.[18,19,21-23] Bridging phosphine sulfide ligands have rarely been postulated with any metal,[5] unlike other sulfur donors. To our knowledge this is the first X-ray structural determination of a complex involving a bridging phosphine sulfide. It would appear from the preceding discussion of bond distances and angles that the bridging Cu-S bond in $[Cu((CH_3)_3PS)Cl]_3$ is very similar to the terminal Cu-S bonds of $[Cu((CH_3)_3PS)_3]ClO_4$, consisting of the simple σ donation of filled sp^3 orbitals on a tetrahedral sulfur atom.[3] Copper(I) complexes of trimethylphosphine sulfide appear to differ from those of thiourea in this respect, since bridging and terminal Cu-S bond distances in the thiourea complexes have much different values, 2.23 and 2.26-2.47 Å, respectively, and angles around sulfur vary over a wide range, 60-138°.[20,24]

Table V presents a comparison of P-S bond distances *vs.* ν_{P-S} for various compounds of trimethylphosphine sulfide. A small change in the P-S bond length is observed as the sulfur lone pairs are involved in bonding, and this change increases as the degree of bonding is increased. Thus, the P-S bond length of the free sulfide is shorter than that of the nonbridging coordinated sulfide, which is shorter than that of the bridging sulfide, and all of these are shorter than the P-S distance of the sulfide bonded to CH_3^+. A parallel but more sensitive trend is seen in the change of the P-S infrared stretching frequency; it is this latter effect that made us suspect that the present structure involved a bridging sulfur linkage.

A final point that should be considered is the presence of the Cu-S six-membered ring, an unusual phenomenon for copper(I) chemistry. Polynuclear copper(I) compounds are sometimes bridged to form chains;[20] more commonly, four-membered rings composed of two copper atoms and two bridging atoms are found.[18,19,21-23,24] The latter form

(24) R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **88**, 4270 (1966).

requires the bridging atom to take a relatively small ring angle, *i.e.*, in the range 69–87°. From the two structures of copper(I) complexes of trimethylphosphine sulfide, it appears that the sulfur atom exhibits a definite tendency to be tetrahedral. Thus, it forms the less strained six-membered ring instead of the more common four-membered ring, which would be highly strained. Similar considerations were used to explain the formation of a trimeric palladium complex with a mercapto ligand,[25] although the analogous nickel complex was dimeric.[26]

Registry No. $\{Cu[(CH_3)_3PS]Cl\}_3$, 38656-77-8.

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Base Adducts of β-Ketoenolates. V.[1,2] Crystal and Molecular Structures of *cis*-Bis(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)bis(pyridine)zinc(II) and -copper(II)

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Single crystals of bis(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)bis(pyridine)zinc(II), $Zn(F_6acac)_2(py)_2$, have been prepared and doped to about 2% with $Cu(F_6acac)_2(py)_2$. Crystals of the pure copper(II) complex also have been prepared and studied. $Zn(F_6acac)_2(py)_2$ crystallizes in space group $C2/c$, $Z = 4$. The monoclinic cell dimensions are $a = 9.2027$ (5), $b = 17.512$ (1), $c = 16.518$ (1) Å, and $\beta = 105.78$ (1)°. Diffractometric data for 2500 symmetry-independent reflections were collected using Cu radiation. Full-matrix, least-squares refinement led to $R_1 = 7.8\%$ and $R_2 = 10.6\%$. The molecule, which is required to have C_2 symmetry, shows a cis octahedral ZnN_2O_4 geometry with alternating long and short bond lengths in the metal ketoenolate rings. The sense of distortions about the metal and in the chelate rings is opposite to that found in $Cu(F_6acac)_2(py)_2$. This copper complex, which crystallizes in space group $P2_1/c$, $Z = 4$, shows also a cis octahedral geometry. The monoclinic cell dimensions are $a = 15.7643$ (4), $b = 10.3651$ (3), $c = 16.8517$ (6) Å, and $\beta = 99.37$ (1)°. Diffractometric data for ~4000 symmetry-independent reflections were collected using Cu radiation. Full-matrix, least-squares refinement produced $R_1 = 6.9\%$ and $R_2 = 9.8\%$. Metal–oxygen distances trans to the metal–nitrogen bonds are for Cu–O 1.998 (4) Å and for Zn–O 2.159 (7) Å, while the axial metal–oxygen bond lengths are for Cu–O 2.283 (6) Å and for Zn–O 2.069 (8) Å. The Cu–N and Zn–N bond lengths are 2.012 (8) and 2.116 (7) Å, respectively. Correlation between the C–O distances and C–O stretching frequencies for some of the adducts of $Zn(F_6acac)_2$ and $Cu(F_6acac)_2$ show that these infrared bands are very sensitive to the extent that metal chelate interactions occur in these complexes.

Introduction

Adduct formation of metal β-ketoenolates with Lewis bases such as ammonia, pyridine, and aniline was reported as early as 1904.[3] Recent work on base adducts of divalent transition metal β-ketoenolate complexes has been reviewed by Graddon.[4] A variety of copper(II) β-ketoenolate base adducts have been isolated[2,5-12] since the first of these compounds was obtained by crystallization of bis(acetylacetonato)copper(II) from quinoline.[12] Comparatively little work has been done on zinc(II) β-ketoenolates and their base adducts. These complexes resemble the copper(II) β-ketoenolates in forming both five- and six-coordinate adducts. The six-coordinate complexes of Zn(II) appear to be rather more stable than those of Cu(II), but for adducts of zinc β-ketoenolates as well as those of Cu(II) the preferred coordination number is 5. Most of these adducts have small formation constants and are somewhat unstable when prepared as solids, decomposing on exposure to the atmosphere with loss of base, leaving a residue of the β-ketoenolate complex. Incorporation into the β-diketone of strongly electron-withdrawing groups increases the strength as a Lewis acid of the complex and gives more stable adducts.[7,8,13] Complexes such as bis(hexafluoroacetylacetonato)copper(II), $Cu(F_6acac)_2$ (the ligand $C_5HF_6O_2^-$ has been abbreviated F_6acac), form 1:1 and 2:1 base adducts in solution. The formation of adducts is essentially complete when stoichiometric molar ratios are attained.[10,14]

A wide variety of physical methods have been used for studying the interaction of bases with copper(II) diketonates. These interactions have been mainly established by their

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