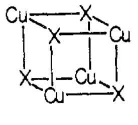
M-(P or As)R_3 species from a regular tetrahedral value is, of course, a well-known phenomenon.[27]

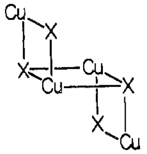
Finally we may note that the C(1)-C(2) distances are 1.545 (28) Å in $[AsEt_3CuI]_4$ and 1.510 (21) Å in $[PEt_3CuI]_4$.

A Survey of Species with a $P_4Cu_4X_4$ or $As_4Cu_4X_4$ Core

To date crystallographic studies on five of these species have been reported. $[PPh_3CuCl]_4$[1], $[PEt_3CuI]_4$, and $[AsEt_3CuI]_4$ each have the cubane skeleton (I), while $[PPh_3CuBr]_4$[2] and $(Ph_2PCH_2PPh_2)_2Cu_4I_4$[28] each possess a "step" skeleton (II).



I



II

The factors governing the stability of one skeletal form over another have been listed previously,[2] but it is still not possible to *predict* which structure will be of lowest energy, or to determine the difference in energy between the two forms, for a given molecular stoichiometry. Further studies are under way in an effort to resolve some of these problems.

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Registry No. $[AsEt_3CuI]_4$, 51364-97-7; $[PEt_3CuI]_4$, 51364-98-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1899.

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Synthesis and Crystal Structure of a Dimeric Cyclic Copper(I)-Aliphatic Disulfide Complex: *cyclo*-Di-μ-{bis[2-(*N,N*-dimethylamino)ethyl] disulfide}-dicopper(I) Tetrafluoroborate

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The compound *cyclo*-di-μ-{bis-[2-(*N,N*-dimethylamino)ethyl] disulfide}-dicopper(I) tetrafluoroborate, alternatively named *cyclo*-di-μ-{2,2'-dithiobis[*N,N*-dimethyl]ethylamino}-dicopper(I) tetrafluoroborate, $Cu_2((CH_3)_2NCH_2CH_2SSCH_2CH_2N(CH_3)_2)_2(BF_4)_2$, was synthesized by direct reaction between Cu(I) and the disulfide ligand and also by disulfide ligand reduction with Cu(II) and subsequent Cu(I) coordination with excess disulfide. Its crystal structure has been determined by single-crystal X-ray diffraction techniques. After nearly full-matrix least-squares refinement using anisotropic thermal parameters only for atoms heavier than carbon, the conventional *R* index converged at 0.063. The yellow crystals form in the noncentric orthorhombic space group $Pn2_1a$ with $a = 28.763$ (8), $b = 11.451$ (2), and $c = 9.293$ (4) Å. Two ligand molecules coordinate to each of two Cu(I) ions, forming a dipositive complex cation with a central six-membered CuSSCuSS ring in a twisted-boat conformation. A very approximate twofold axis is normal to the best plane through that ring. Four strained CuSCCN rings share an edge with the central ring; the coordination of Cu(I) is badly distorted tetrahedral with angles varying from 89.6 to 123.9°. The length of the disulfide bond and the CSSC dihedral angle are altered by complexation, as compared to the values observed in the structure of the relatively unconstrained hydrochloride salt, as are the CS and SS stretching frequencies, as determined by infrared and laser-Raman methods. The bond length has increased from 2.037 (1) to 2.075 (6) Å and the dihedral angle has increased from 82.4 (4) to 106.3 (9)°. The Cu(I)-S bond lengths are short, averaging 2.30 Å, and the average Cu(I)-N bond is 2.13 Å. The perchlorate salt of the same complexed cation is isostructural.

Introduction

A host of metalloproteins and metalloenzymes contain Cu(I) or Cu(II) ions which are necessary for their function.[1,2] These ions can also act as enzymatic inhibitors[2] and are useful as specific reagents in protein analysis.[3] The metalloproteins hemocyanin[4] and tyrosinase[1] (phenol oxidase) contain copper ions which undergo cyclic redox processes *in vivo*. Some proteins such as neonatal hepatic mitochondrocuprein have unusually high copper and cysteine contents,[2] which suggest important copper-sulfur interactions. Although Cu(II) is usually associated with oxygen and nitrogen, and occasionally sulfur ligands in protein structure, Cu(I) is more likely to coordinate to sulfur-containing groups. In response to the suggestion that ligands such as organic disulfides might behave "noninnocently"[5] in redox processes by direct participation involving delocalized orbitals, we have chosen to investigate aliphatic disulfide complexes of Cu(I).

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The crystal structure of chloro(diethyl disulfide)copper(I)[6] shows such complexation, where each Cu(I) is coordinated by a sulfur atom from two ligands, each sulfur atom coordinates to a Cu(I) ion, the Cu(I) ions are bridged by chloride ions to form chains, and a central $\overline{\mathrm{CuSSCuSS}}$ ring in the boat conformation is formed. The coordination of one sulfur atom of an aliphatic disulfide linkage to Ni(II) was observed in chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) perchlorate.[7] The second sulfur atom remained uncoordinated. In neither complex[6,7] was the S-S bond length nor the CSSC dihedral angle affected by coordination; the geometry of the disulfide linkage was near the mean encountered for a range of uncomplexed aliphatic disulfides.[8] Infrared and chemical evidence indicates that a dimeric Pd(II) diphenyl disulfide complex[9] has been isolated which has a central $\overline{\mathrm{PdSSPdSS}}$ ring. Additional chemical and crystallographic references[7] to disulfide coordination are available, as is a preliminary account of this work.[10]

Preparation and Characterization

Cupric tetrafluoroborate and cupric perchlorate, hydrated, were obtained from Research Organic/Inorganic Chemicals Corp. and G. Frederick Smith Chemical Co., respectively. Tetrafluoroboric acid was obtained from Alfa Inorganics, while 2-dimethylaminoethanethiol hydrochloride was obtained from Matheson Coleman and Bell. All other chemicals were of reagent grade quality.

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared, uv–visible, and Raman spectra were obtained using Perkin-Elmer IR-10, Cary 14, and Cary 82 laser-Raman instruments, respectively. Elemental analysis was performed by Galbraith Laboratories, Inc.

Tetrakis(acetonitrile)copper(I) Salts. The perchlorate and tetrafluoroborate salts of $Cu(CH_3CN)_4{}^+$ were prepared using 60% perchloric acid and 48% tetrafluoroboric acid, respectively, by following the method of Hemmerich and Sigwart.[11]

Preparation of the Ligand. The ligand salt, bis[2-(*N,N*-dimethylamino)ethyl]disulfide dihydrochloride or 2,2′-dithiobis[*N,N*-dimethyl]ethylamine dihydrochloride, was prepared by the oxidation of 2-dimethylaminoethanethiol hydrochloride with dimethyl sulfoxide.[12] The crude product was isolated by filtration and recrystallized from acidified aqueous ethanol to give colorless cyrstals. The purified product softens at 225° and melts completely at 248° (lit. mp 222[13] and 242°[14]). *Anal.* Calcd for $C_8H_{22}Cl_2N_2S_2$: C, 34.16; H, 7.88; Cl, 25.21; N, 9.96; S, 22.80. Found: C, 33.96; H, 7.76; Cl, 25.35; N, 9.88; S, 22.98.

The free ligand was obtained by dissolving the hydrochloride salt in enough 10% aqueous Na_2CO_3 to give a pH of 8–9 and extracting with chloroform. The chloroform solution was then reduced to an oil on a rotary evaporator. Any excess water was removed by repeated additions of absolute ethanol and evaporation on a rotary evaporator. The ligand was dissolved in the appropriate solvent, generally methanol, and filtered to remove any insoluble impurities before being used in the complexation reactions.

Preparation of Salts of *cyclo*-Di-μ-{bis[2-(*N,N*-dimethylamino)ethyl] disulfide}-dicopper(I), Alternatively Named *cyclo*-Di-μ-{2,2′-dithiobis[*N,N*-dimethyl]ethylamino}-dicopper(I), $Cu_2[(CH_3)_2NCH_2CH_2SSCH_2CH_2N(CH_3)_2]_2{}^{2+}$. (a) Tetrafluoroborate Salt. A 1.98-g sample (0.00546 mol) of $Cu(H_2O)_6(BF_4)_2$ was dissolved in methanol and filtered to remove insoluble impurities. To this solution was added 40 ml of methanol containing 0.0119 mol of free ligand. Immediately upon mixing of these solutions, gelatinous cupric hydroxide complexes formed. Upon standing overnight clusters of yellow, needlelike crystals formed. These clusters were isolated first by decanting the slurry of hydroxides and blue powder and then washing with methanol. Recrystallization from hot methanol gave yellow, platelike crystals in a yellow-green solution. Generally a very small amount of blue powder also formed, but it was separated from the desired product by decantation. The yellow, crystalline product was washed with methanol and ether and dried under vacuum at room temperature for 6 hr; yield 1.14 g, 58.5%. *Anal.* Calcd for $C_8H_{20}BCuF_4N_2S_2$: C, 26.78; H, 5.62; Cu, 17.71; F, 21.18; N, 7.81; S, 17.88. Found: C, 26.84; H, 5.77; Cu, 17.60; F, 20.92; N, 7.76; S, 17.67.

An identical tetrafluoroborate salt was prepared by adding 0.0021 mol of the free ligand in 20 ml of methanol to 0.64 g (0.002 mol) of $Cu(CH_3CN)_4(BF_4)$ suspended in 50 ml of methanol. The mixture was heated to boiling. Upon cooling the blue solution cleared to yellow-green and, after several hours, yellow crystals were deposited. They were isolated by filtration, washed with methanol and ether, and vacuum-dried for 6 hr.

(b) **Perchlorate Salt.** The perchlorate salt was prepared following the methods described above, except for the substitution of $Cu(H_2O)_6(ClO_4)_2$ and $Cu(CH_3CN)_4(ClO_4)$ for $Cu(H_2O)_6(BF_4)_2$ and $Cu(CH_3CN)_4(BF_4)$, respectively. *Anal.* Calcd for $C_8H_{20}ClCuN_2O_4S_2$: C, 25.87; H, 5.43; Cl, 9.55; Cu, 17.11; N, 7.54; S, 17.27. Found: C, 25.68; II, 5.41; Cl, 9.69; Cu, 17.06; N, 7.50; S, 17.33.

Characterization of Complexes. The infrared spectra of the tetrafluoroborate and perchlorate salts of the dimeric copper(I) disulfide complex, $[CuL]_2{}^{2+}$, are essentially identical except for the anion absorptions. The anion and other assigned vibrational modes are listed in Table I. While the infrared assignments for ν_{str}(–C–S–) and ν_{str}(–S–S–) are not unequivocal, they do lie within the ranges expected[15] for these stretches and agree with the more easily assigned corresponding Raman frequencies.[16] In both the $[CuL]_2{}^{2+}$ complex and the free ligand salt, the α carbons are approximately gauche to the distal sulfur atoms across the CS bond; yet these results are not consistent with the previously reported[16a] linear relationship between the Raman shifts for the SS stretch and the CSSC dihedral angle. In the case of $[CuL]_2{}^{2+}$ this departure is most likely due to the perturbations caused by disulfide complexation with Cu(I). The lowering of the CS and SS Raman stretch frequencies of the complex as compared to those of the free ligand salt (Table I) is consistent with the observed lengthening of the SS bond and with the incorporation of the SS and CS moieties into the strained-ring systems (see later discussion) of the complex.

The electronic absorption spectra of Nujol mulls of the colorless ligand dihydrochloride and yellow $[CuL]_2X_2$ salts exhibit intense bands at 248 and 293 mμ, respectively. Both bands appear as shoulders on more intense bands centered at higher frequencies. The ligand band is characteristic of the $n_a \rightarrow \sigma^*$ transition that occurs in aliphatic disulfides.[17]

Cu(I) complexes are colorless except where color results from anions, ligands, or charge transfer. The 293-mμ band of medium intensity accounts for the yellow color of $[CuL]_2{}^{2+}$ and must be due either to charge transfer between Cu(I) and the disulfide moiety or to a significantly red-shifted disulfide absorption. Orbital perturbations due to strong complexation[18] and/or deviations of the CSSC dihedral angle from 90°[17,19,20] can cause disulfide absorptions to be significantly red-shifted. Whether this 293-mμ band is due to charge transfer or to a disulfide transition lowered in energy due to strong complexation to Cu(I) and a dihedral angle of 106° (see Discussion) is unknown. However, an identical 293-mμ absorption is observed for the complex {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate[21] which exhibits a CSSC dihedral angle and an SS bond distance of 59.7 (1)° and 2.081 (1) Å, respectively, for the penicillin

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Table I. Infrared and Raman Data (cm^{-1})

	Infrared[a]				Raman[b]	
	T_d anion		Ligand		Ligand	
	ν_3	ν_4	ν_{str}(-C-S-)	ν_{str}(-S-S-)	Δ(-C-S-)	Δ(-S-S-)
$[CuL]_2(BF_4)_2$	1035 s, br		629 w, br	469 w, sh	633 m	463 s
$[CuL]_2(ClO_4)_2$	1070 s, br	613 m, sp	630 w, sh	450 w, br		
L·2HCl			639 w, br		651 m, sp	506 s, sp

[a] All infrared data taken on Nujol mulls. Band characteristics: str, stretch; s, strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder. [b] Raman spectra taken of solids. The rotating solid sample technique[16c] was used for colored samples.

analogs *cis*-dithiazabicyclooctanes,[22] which show a CSSC dihedral angle of 60.5°, and for *trans*-2,3-dithiadecalin whose CSSC dihedral angle is reported to be 56°.[16] This suggests that the 293-mμ-absorption band is a red-shifted $n_a \rightarrow \sigma^*$ disulfide transition.

The complexes $[CuL]_2X_2$ are relatively unstable. After several days the crystals begin to darken and a mercaptan odor becomes detectable. They are only slightly soluble in methanol but dissolve in nitromethane and pyridine to give yellow solutions which become turbid after several hours. Excessive heating of the methanol solutions results in extensive complex and disulfide ligand decomposition, as is evident from the intensely brown copper-containing residues and the mercaptan odors that are produced. Upon dissolution in acetonitrile, colorless solutions are formed. Tetrakis(acetonitrile)copper(I) salts[11] can be isolated from these solutions, indicating the disulfide ligand can be readily displaced by the more Cu(I) specific ligand acetonitrile.

Discussion. Copper(II) reacts with mercaptides in a reversible process to give a disulfide and copper(I)

$$2Cu^{2+} + 2RS^- \rightleftharpoons 2Cu^+ + RSSR \qquad (1)$$

The direction in which this reaction proceeds is dependent upon the valence specificity[23] of the coordination environment available to the copper. It will only proceed to the right if Cu(I) specific reagents are involved. When the source of the reagents on the right of eq 1 is tetrakis(acetonitrile)copper(I) perchlorate and bis[2-(*N,N*-dimethylamino)ethyl] disulfide, a cyclic, dimeric copper(I)–disulfide complex forms (eq 2) in a relatively clean straightforward reaction.

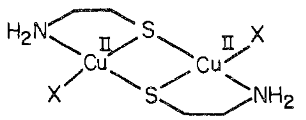
$$2Cu(I) + 2RSSR \xrightarrow{CH_3OH} [Cu(RSSR)]_2{}^{2+} \qquad (2)$$

Upon mixing Cu(II) salts with the disulfide ligand in methanol, green gelatinous hydroxide complexes were formed. After standing for 1 day, crystals of the Cu(I) complex $[CuL]_2X_2$ were formed. The initial formation and subsequent dissolution of copper hydroxide complexes to form a copper chelate is very similar to that observed in the reaction of Cu(II) salts with *N,N,N′,N′*-tetramethylethylenediamine to form mono- and bis(diamine)-copper(II) complexes;[24] however, in this latter case, no Cu(II) to Cu(I) reduction occurred. Presumably, in the former case the reducing agent was mercaptide ion, RS^-, formed in a hydroxide-induced cleavage of the disulfide.

Since no product other than the Cu(I) complex discussed herein was isolated, a judgment concerning the possible mechanism for the disulfide cleavage reaction cannot be made. However, of the four kinds that are known to occur (direct OH^- attack upon a sulfur atom,[25] α or β elimination[26-28] or concomitant electrophilic and nucleophilic catalysis[29]), the last is the most likely. Chelation of the disulfide ligand in solution or on the surface of the hydroxide gel would certainly enhance subsequent OH^- attack upon the disulfide moiety. Future investigation of this disulfide cleavage in the presence of Cu(II) and hydroxide is planned.

The Cu(I) specificity of the disulfide moiety accounts for the formation of the Cu(I) complex, even though the disulfide ligand contains both hard-base donors (amine nitrogens) and five-membered ring chelating ability, each of which is Cu(II) specific.[23] However, the relative instability of the complex may reflect, at least in part, the presence of these Cu(II)-specific characteristics.

The dinuclear copper(I) disulfide complex $[CuL]_2{}^{2+}$ is very different from that reported to form between an analogous ligand, cystamine ($H_2NCH_2CH_2SSCH_2CH_2NH_2$), and Cu(I). When an anaerobic titration of cystamine dihydrochloride is carried out in the presence of Cu(I), a violet copper complex is formed at pH >5.[30] The same deeply colored complex is obtained upon reaction of Cu^{2+} and cysteamine (2-aminoethanethiol). This complex has been isolated and assigned the dinuclear structure[30] I.



I, X = $ONO_2{}^-$

Similar red-violet complexes form upon mixing Cu^{2+} with *o*-aminothiophenols, thiomalic acid,[31] mercaptoacetic acid,[32] 1,1-dimethyl-2-aminoethanethiol,[33] and penicillamine (β,β-dimethylcysteine)[34] and have been reported to be "mixed-valence" complexes. An absolute prerequisite[30,33] for the formation of these red-violet copper–mercaptide complexes seems to be the presence of the SCCN moiety which can form a five-membered chelate ring upon coordination to the copper atom. In this regard it is interesting to note that while 2-(*N,N*-dimethylamino)ethanethiol (the parent thiol of the disulfide reported herein) has the prerequisite SCCN five-membered ring chelating ability, it does not form a red-violet copper complex. Instead, it presumably only participates in a redox reaction with Cu^{2+}.[33]

Diffraction Section

Preliminary oscillation and Weissenberg photographs of crystals of $CuC_8H_{20}N_2S_2BF_4$ and $CuC_8H_{20}N_2S_2ClO_4$ indicated that they are orthorhombic and isostructural. A single crystal of the former, for reasons of stability and a lesser tendency to twin (as noted on Weissenberg photographs of both materials), was mounted in a thin-walled glass capillary for future investigation. The cell constants of the latter are, approximately, $a = 28.9$, $b = 11.4$, and $c = 9.3$ Å.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation ($K\alpha_1$, λ 0.70926 Å; $K\alpha_2$, λ 0.71354 Å) and with a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants were determined by a least-squares procedure using the centered angular coordinates of 15 intense reflections with 2θ values up to 36.2°. They are, at 20°, $a = 28.763$ (8), $b = 11.451$ (2), and $c = 9.293$ (4) Å. Other crystal data are $V = 3060.7$ Å³, mol wt 358.7, $d_{flotation} = 1.55$ (5) g/cm³, $d_{X\text{-ray}} = 1.557$ g/cm³, $Z = 8$, and $F(000) = 1472$. The systematic absences $k + l$ odd for $(0kl)$ and h odd for $(hk0)$ are indicative of the space groups $Pn2_1a$ and $Pnma$.

Diffraction intensities were collected using a purposely misaligned crystal (to avoid Renninger reflections) by the θ–2θ scan technique at a scan rate, ω, variable between 1 and 24°/min (in 2θ). All 3119 unique reciprocal lattice points for which 2θ < 50° were

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examined. The scan range varied from 2.0° at low 2θ to 2.3° at $2\theta = 50°$. A time equal to half of the scan time for each reflection was spent counting background at each end of the scan range. Three check reflections which were measured periodically during data collection showed slow decay to 90% of the original values, followed by relatively rapid but still entirely isotropic decay to approximately 58% of the initial intensities. Correction for this effect was made, but the data were accepted in two stages; the latter fraction of the data set was added only after it was noted that it did not cause the near-final error indices to rise appreciably. The data were corrected for absorption[35,36] using a $6 \times 6 \times 6$ matrix for the crystal whose extreme dimensions were $0.025 \times 0.020 \times 0.010$ cm; $\mu = 17.7\ \mathrm{cm}^{-1}$ and the transmission factors ranged from 0.676 to 0.836.

Standard deviations were assigned according to eq 3, where CT is

$$\sigma(I) = (\omega^2\,[\mathrm{CT} + 0.25(t_c/t_b)^2(B_1 + B_2)] + (pI)^2)^{1/2} \qquad (3)$$

the total integrated count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = \omega[\mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02, found to be appropriate for the instrumentation used, was assigned to the empirical parameter p to account for instrumental inaccuracies. The net counts were then corrected for Lorentz and polarization effects. Each of the 1178 reflections for which the net count exceeded 3 times its standard deviation was used in the final refinement of the structure.

Structure Determination

An initial three-dimensional Patterson function prepared using the fast-Fourier algorithm[37] indicated that the noncentric space group $Pn2_1a$ was correct. Successive cycles of Fourier refinement beginning with one of the solutions suggested by the Patterson function for two Cu(I) ions led eventually to the correct solution as illustrated in Figure 1. Full-matrix least-squares refinement with anisotropic thermal parameters for all atoms heavier than carbon led to the final error indices $R_1 = \Sigma|F_o - |F_c||/\Sigma F_o = 0.063$ and $R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma w F_o)^2)^{1/2} = 0.067$. The "goodness-of-fit," $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 0.79. The number of observations used in least-squares is m (1178), and s (234) is the total number of parameters. The overdetermination ratio (5.0) was judged to be too small to allow for the anisotropic refinement of the carbon atoms. No hydrogen atoms were located. The largest peak on the final difference Fourier function, whose standard deviation was approximately 0.2 e Å^{-3}, was 0.5 e Å^{-3}.

The full-matrix least-squares program used[38] minimizes $\Sigma w \cdot (\Delta|F|)^2$, and the weights used were the reciprocal squares of σ, the standard deviation of each observation. The scattering factors used were those of Doyle and Turner[39] for Cu$^+$, S^0, N^0, F^0, C^0, and B^0. The first two of these were corrected for the real part of the anomalous dispersion correction.[40] In the final cycle of least-squares refinement, all shifts were less than 30% of their estimated standard deviations. All shifts in the complexed anion were less than 6% of their esd's.

A listing of observed and calculated structure factors is available.[41] The final positional and thermal parameters are listed in Table II.

Discussion

Two Cu(I) ions and two bis[2-(*N*,*N*-dimethylamino)ethyl] disulfide molecules have come together to form a dipositive complex cation (Figures 1 and 2) containing a nearly twofold molecular axis normal to a central $\overline{\mathrm{CuSSCuSS}}$ ring. Each ligand is tetradentate, and each sulfur atom per ligand coordinates a different Cu(I) ion. The six-membered ring has a twisted boat conformation; four strained five-membered rings share edges with this central ring. Badly distorted tetrahedral coordination of the Cu(I) ions is observed.

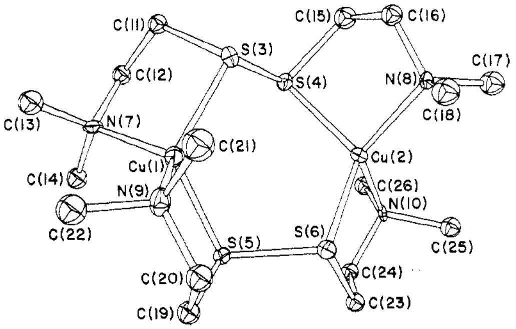

Figure 1. Molecular structure of the $[\mathrm{Cu_2(C_8H_{20}N_2S_2)_2}]^{2+}$ ion. Hydrogen atoms and $\mathrm{BF_4}^-$ groups are omitted. Ellipsoids of 15% probability are shown.

The four independent five-membered $\overline{\mathrm{CuSCCN}}$ rings in each molecule are found in two distinct conformations. In each, one carbon atom lies relatively close to the plane of the Cu, S, and N atoms, and the other deviates appreciably (Table III) from this plane. In each ligand, the atom deviating from the plane of the other four is the carbon atom bonded to nitrogen at one end (of the ligand) and the carbon bonded to sulfur at the other. This is apparently due to the reluctance of the obtuse CSSC torsion angles at the disulfide groups to become larger.

The largest deviations of the complexed cation from twofold symmetry are found in the differing conformations of the two pairs of five-membered rings (planes 2 and 4, and 3 and 5 of Table III) and are apparently due to packing effects.

The "tetrahedral" angles about the Cu(I) ions range widely from 89.6 to 123.9° (each value is the average of two, assuming the presence of a twofold axis), presumably indicative of the magnitude of the ring strain in the molecule. The average internal angle in a five-membered ring at Cu(I) is only 90.2°. Although tetrahedral Cu(I) complexes are apparently easily deformed, the range of S-Cu(I)-S angles in several other complexes is less (110-112,[42] 95-120,[43] 101-118,[44] and 104-112°[45]) than is observed in $[\mathrm{CuL}]_2{}^{2+}$.

The aliphatic disulfide bonds are 2.084 (9) and 2.068 (8) Å in length. The mean with its standard deviation[46] is 2.075 (6) Å, and the mean torsion angle (see Table IV) at the disulfide groups is 106.3 (9)°. This bond length is significantly longer, and the dihedral angle is larger, than the corresponding values of 2.037 (1) Å and 82.4 (4)° observed in the crystal structure of the dihydrochloride salt[10,47] of this same ligand, in which the ligand is relatively free to adopt its lowest energy conformation. Previous results on a host of disulfide compounds, as supported by qualitative and quantitative discussions of the orbitals involved in bonding,[8,9,17,20,48] are in close agreement with the results observed for the structure of the dihydrochloride salt, supporting the observation that the geometry about the disulfide linkage of this ligand has

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Table II. Fractional Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations[a]

	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	906 (1)	0	1883 (3)	13 (0.5)	65 (2)	104 (3)	−8 (2)	−14 (3)	1 (5)
Cu(2)	1804 (1)	2184 (3)	3789 (3)	11 (0.4)	52 (2)	108 (3)	14 (2)	−9 (2)	−28 (5)
S(3)	770 (2)	1968 (5)	1924 (7)	14 (0.9)	59 (4)	124 (7)	−5 (3)	−10 (5)	−40 (10)
S(4)	1420 (2)	2760 (5)	1759 (7)	10 (0.8)	63 (4)	112 (7)	−4 (3)	−18 (5)	−9 (10)
S(5)	1617 (2)	−713 (5)	2611 (6)	10 (0.9)	62 (4)	96 (6)	8 (3)	−11(4)	−12 (10)
S(6)	1777 (2)	225 (4)	4446 (6)	12 (1)	61 (4)	97 (6)	4 (4)	−2 (5)	−2 (9)
N(7)	788 (6)	−66 (16)	−392 (19)	10 (3)	53 (12)	118 (24)	17 (13)	−11 (14)	36 (36)
N(8)	1444 (6)	3446 (14)	5003 (19)	8 (3)	39 (13)	117 (26)	−10 (10)	−31 (15)	−54 (29)
N(9)	562 (8)	−1166 (17)	3408 (21)	18 (4)	87 (17)	94 (30)	−26 (14)	−12 (17)	16 (34)
N(10)	2528 (6)	2070 (14)	3640 (15)	10 (2)	42 (11)	41 (17)	−9 (11)	−2 (12)	−36 (28)
C(11)	585 (9)	2030 (21)	24 (24)	3.7 (5)					
C(12)	837 (8)	1201 (20)	−904 (26)	3.8 (4)					
C(13)	324 (12)	−518 (25)	−776 (33)	5.8 (7)					
C(14)	1148 (10)	−778 (23)	−1089 (30)	4.7 (5)					
C(15)	1288 (10)	4192 (26)	2564 (32)	5.1 (6)					
C(16)	1134 (10)	4098 (21)	4056 (27)	4.1 (5)					
C(17)	1778 (11)	4234 (25)	5745 (30)	5.6 (6)					
C(18)	1166 (12)	2818 (28)	6127 (38)	5.9 (6)					
C(19)	1355 (9)	−2030 (20)	3384 (27)	4.3 (5)					
C(20)	937 (12)	−1720 (23)	4216 (30)	5.2 (6)					
C(21)	239 (13)	−463 (28)	4353 (38)	6.9 (8)					
C(22)	274 (12)	−2035 (28)	2566 (39)	6.4 (7)					
C(23)	2395 (8)	64 (21)	4499 (24)	3.4 (4)					
C(24)	2650 (8)	811 (18)	3466 (22)	3.3 (5)					
C(25)	2757 (10)	2487 (20)	4958 (28)	4.5 (6)					
C(26)	2705 (10)	2749 (23)	2392 (29)	4.6 (5)					
F(27)	2167 (6)	776 (14)	9882 (16)	26 (3)	134 (17)	140 (21)	−30 (12)	6 (14)	51 (31)
F(28)	1995 (7)	1040 (21)	7548 (18)	27 (4)	236 (23)	121 (21)	7 (17)	−24 (15)	16 (43)
F(29)	2351 (13)	2421 (13)	8768 (24)	93 (10)	74 (15)	243 (31)	−81 (18)	81 (32)	−76 (36)
F(30)	2707 (8)	788 (24)	8144 (26)	27 (4)	293 (32)	270 (34)	64 (20)	68 (22)	133 (57)
F(31)	4301 (11)	−234 (16)	3682 (38)	56 (7)	100 (16)	573 (71)	34 (16)	−145 (39)	−113 (56)
F(32)	3914 (10)	1294 (23)	2748 (43)	33 (5)	184 (27)	677 (88)	29 (18)	−152 (39)	−117 (85)
F(33)	4243 (18)	1431 (22)	4839 (37)	92 (14)	167 (27)	352 (56)	41 (28)	−123 (52)	−193 (63)
F(34)	4643 (12)	1348 (38)	3188 (50)	32 (6)	413 (62)	551 (87)	3 (31)	−33 (40)	135 (129)
B(35)	2306 (12)	1290 (24)	8612 (37)	4.2 (6)					
B(36)	4210 (22)	944 (49)	3721 (64)	8.4 (12)					

[a] The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The above values are all given $\times 10^4$. The isotropic temperature factor has the units of Å^2. See Figure 1 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

Table III. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

	Plane 1		Plane 2		Plane 3		Plane 4		Plane 5	
	Cu(1)	84	Cu(1)	**1**	Cu(1)	**0**	Cu(2)	**1**	Cu(2)	**0**
	Cu(2)	**162**	S(3)	**−14**	S(5)	**−3**	S(6)	**−10**	S(4)	**1**
	S(3)	**527**	N(7)	**−101**	N(9)	**−59**	N(10)	**−65**	N(8)	**8**
	S(4)	**−636**	C(11)	**115**	C(19)	−652	C(23)	**74**	C(15)	−666
	S(5)	**−656**	C(12)	−594	C(20)	**61**	C(24)	−586	C(16)	**−9**
	S(6)	**520**								
q_a		5952		−9616		615		490		−7242
q_b		794		−1775		7257		2658		−6624
q_c		7997		2092		6853		9628		1918
D		−0.236		−2.141		1.359		4.308		−4.739
δ		486		77		42		50		6

[a] Boldface deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table II lies between that plane and the origin. The direction cosines ($\times 10^4$), q, are with respect to orthogonal axes. The rms boldface deviation (Å $\times 10^3$) of the atoms from the plane is δ. D is the distance (in Å) from the plane to the origin.

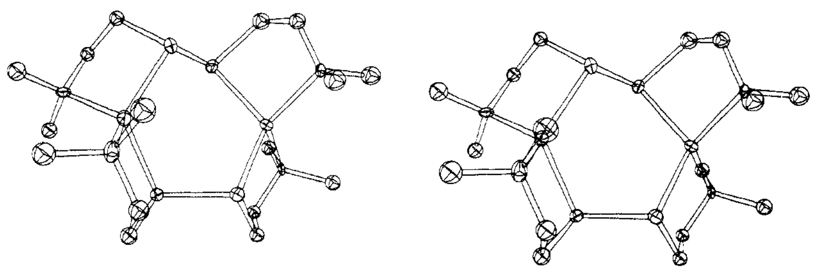

Figure 2. Stereoview of the $[Cu_2(C_8H_{20}N_2S_2)_2]^{2+}$ ion, as described in the caption to Figure 1.

been significantly altered by complexation with Cu(I).

The four Cu(I)-S bonds (Table IV) average 2.300 Å in length, much less than the average of 2.37 Å (from 2.34 (1) and 2.40 (1) Å) found in chloro(diethyl disulfide)copper-

Table IV. Molecular Dimensions[a]

	Bond Lengths, A		
Cu(1)-S(3)	2.288 (6)	C(12)-N(7)	1.53 (3)
Cu(1)-S(5)	2.302 (7)	C(16)-N(8)	1.46 (3)
Cu(2)-S(4)	2.283 (7)	C(20)-N(9)	1.46 (4)
Cu(2)-S(6)	2.326 (6)	C(24)-N(10)	1.49 (3)
Cu(1)-N(7)	2.143 (18)	N(7)-C(13)	1.47 (4)
Cu(1)-N(9)	2.184 (20)	N(7)-C(14)	1.47 (3)
Cu(2)-N(8)	2.105 (17)	N(8)-C(17)	1.49 (4)
Cu(2)-N(10)	2.089 (17)	N(8)-C(18)	1.50 (4)
S(3)-S(4)	2.084 (9)	N(9)-C(21)	1.51 (4)
S(5)-S(6)	2.068 (8)	N(9)-C(22)	1.51 (4)
		N(10)-C(25)	1.47 (3)
S(3)-C(11)	1.845 (23)	N(10)-C(26)	1.49 (3)
S(4)-C(15)	1.841 (30)	B(35)-F(27)	1.38 (4)
S(5)-C(19)	1.834 (25)	B(35)-F(28)	1.36 (4)
S(6)-C(23)	1.789 (24)	B(35)-F(29)	1.31 (3)
C(11)-C(12)	1.47 (3)	B(35)-F(30)	1.36 (4)
C(15)-C(16)	1.46 (4)	B(36)-F(31)	1.38 (6)
C(19)-C(20)	1.47 (4)	B(36)-F(32)	1.31 (7)
C(23)-C(24)	1.48 (3)	B(36)-F(33)	1.18 (7)
		B(36)-F(34)	1.42 (7)
	Bond Angles, Deg		
S(3)-Cu(1)-S(5)	119.8 (2)	Cu(1)-S(3)-S(4)	105.9 (3)
S(4)-Cu(2)-S(6)	118.7 (3)	Cu(1)-S(5)-S(6)	104.8 (3)
S(3)-Cu(1)-N(7)	91.4 (5)	Cu(2)-S(4)-S(3)	104.3 (3)
S(4)-Cu(2)-N(8)	90.4 (5)	Cu(2)-S(6)-S(5)	107.0 (3)
S(5)-Cu(1)-N(9)	89.7 (6)	Cu(1)-S(3)-C(11)	94.1 (8)
S(6)-Cu(2)-N(10)	89.5 (4)	Cu(1)-S(5)-C(19)	92.4 (9)
S(3)-Cu(1)-N(9)	120.9 (6)	Cu(2)-S(4)-C(15)	91.2 (10)
S(4)-Cu(2)-N(10)	116.4 (5)	Cu(2)-S(6)-C(23)	94.2 (8)
S(5)-Cu(1)-N(7)	114.7 (5)	S(3)-S(4)-C(15)	99.9 (10)
S(6)-Cu(2)-N(8)	120.3 (5)	S(4)-S(3)-C(11)	99.9 (8)
N(7)-Cu(1)-N(9)	123.1 (8)	S(5)-S(6)-C(23)	100.9 (8)
N(8)-Cu(2)-N(10)	124.6 (7)	S(6)-S(5)-C(19)	101.3 (9)
Cu(1)-N(7)-C(12)	105.0 (13)	C(12)-N(7)-C(13)	109.9 (19)
Cu(1)-N(9)-C(20)	105.4 (16)	C(12)-N(7)-C(14)	108.9 (18)
Cu(2)-N(8)-C(16)	109.2 (14)	C(16)-N(8)-C(17)	111.3 (18)
Cu(2)-N(10)-C(24)	107.6 (11)	C(16)-N(8)-C(18)	109.8 (20)
		C(20)-N(9)-C(21)	112.8 (21)
Cu(1)-N(7)-C(13)	113.2 (17)	S(3)-C(11)-C(12)	113.2 (17)
Cu(1)-N(7)-C(14)	110.0 (15)	S(4)-C(15)-C(16)	112.6 (21)
Cu(1)-N(9)-C(21)	109.3 (17)	S(5)-C(19)-C(20)	110.1 (19)
Cu(1)-N(9)-C(22)	108.3 (17)	S(6)-C(23)-C(24)	114.6 (16)
Cu(2)-N(8)-C(17)	110.4 (15)	C(20)-N(9)-C(22)	112.6 (22)
Cu(2)-N(8)-C(18)	107.9 (16)	C(24)-N(10)-C(25)	107.4 (18)
Cu(2)-N(10)-C(25)	111.8 (13)	C(24)-N(10)-C(26)	109.8 (17)
Cu(2)-N(10)-C(26)	111.1 (13)	F(27)-B(35)-F(28)	110 (2)
C(13)-N(7)-C(14)	109.7 (19)	F(27)-B(35)-F(29)	111 (3)
C(17)-N(8)-C(18)	108.2 (20)	F(27)-B(35)-F(30)	110 (3)
C(21)-N(9)-C(22)	108.3 (23)	F(28)-B(35)-F(29)	111 (3)
C(25)-N(10)-C(26)	109.0 (19)	F(28)-B(35)-F(30)	104 (3)
N(7)-C(12)-C(11)	112.5 (19)	F(29)-B(35)-F(30)	112 (3)
N(8)-C(16)-C(15)	115.1 (22)	F(31)-B(36)-F(32)	114 (5)
N(9)-C(20)-C(19)	116.0 (22)	F(31)-B(36)-F(33)	118 (5)
N(10)-C(24)-C(23)	111.7 (19)	F(31)-B(36)-F(34)	98 (4)
		F(32)-B(36)-F(33)	121 (6)
		F(32)-B(36)-F(34)	103 (4)
		F(33)-B(36)-F(34)	95 (4)
	Selected Dihedral Angles, Deg		
C(11)-S(3)-S(4)-C(15)	105.9 (13)	Cu(1)-S(3)-S(4)-Cu(2)	63.1 (4)
C(19)-S(5)-S(6)-C(23)	106.7 (13)	Cu(1)-S(5)-S(6)-Cu(2)	59.9 (4)
N(7)-Cu(1)-S(3)-C(11)	6.8 (9)	S(3)-S(4)-Cu(2)-S(6)	46.2 (4)
S(5)-Cu(1)-N(9)-C(20)	5.4 (17)	S(6)-S(5)-Cu(1)-S(3)	43.0 (4)
S(4)-Cu(2)-N(8)-C(16)	0.8 (15)	S(4)-Cu(2)-S(6)-S(5)	21.9 (4)
N(10)-Cu(2)-S(6)-C(23)	4.6 (9)	S(5)-Cu(1)-S(3)-S(4)	25.0 (4)

[a] The esd given is in the units of the least significant digit given for the corresponding value.

(I).[6] Shorter distances have been observed in the CuSCuSCuS ring in *cyclo*-tri-μ-(trimethylphosphine sulfide)-tris(chlorocopper(I))[42] (2.265 (1) Å), in the trigonal-planar bis(thiourea)copper(I) chloride (2.27 Å),[49a] and in tris(trimethylphosphine sulfide)copper(I) perchlorate (2.259 (4) Å).[50] A similar average distance, 2.315 Å, occurs in the

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CuSCuSCuS ring[49b] in decakis(thiourea)tetracopper(I) hexafluorosilicate monohydrate. Distances up to 0.1 Å longer are found elsewhere in the last mentioned compound and in tris(thiourea)copper(I) chloride.[44] In tetrakis(thioacetamide)copper(I) chloride,[45] the monomeric molecule has $\bar{4}$ symmetry and a Cu(I)-S bond of 2.343 (5) Å. It should be noted that the average Cu(I)-S (disulfide) bond length in $[CuL]_2^{2+}$ is much (0.17 Å) shorter than the corresponding Ni(II)-S distance (2.47 Å) in chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) perchlorate.[7]

Short metal-sulfur interactions, lengthened SS bonds, and altered CSSC dihedral angles have been observed in other transition metal-organic disulfide complexes,[21,51] but not in all.[6,7] These features appear to be interrelated. The opening of the CSSC dihedral angle upon complexation is certainly due, at least in part, to the steric requirements that are imposed upon the ligand in the complex. Similar proposals[20,52] have been made to explain the CSSC dihedral angle decrease upon organic disulfide complexation with halogens.

A series of disulfides discussed by Hordvik[53] indicates that the SS bond length for uncomplexed organic disulfides should be 2.04 Å for a CSSC dihedral angle of 106°, significantly less than the distance observed. This discrepancy might be explained in terms of SS bond stretching necessitated by the relatively high degree of strain associated with the CuNCCS five-membered chelate rings and the central CuSSCuSS ring.

Electronic factors may also be operating. Lone pair-lone pair repulsions within the disulfide moiety are at a minimum in free disulfides when the CSSC dihedral angle is 90°.[8b] Removal or polarization of the electron density associated with these pairs upon covalent bonding or complexation would reduce the repulsions[17,29,48] and allow the dihedral angle to deviate more from 90° with a diminished increase in the potential energy of the SS bond.

The shorter Cu(I)-S bond in $[CuL]_2^{2+}$, as compared with the corresponding bond in chloro(diethyl disulfide)copper(I), might be due to steric effects in the former complex where the sulfur atoms participate in several ring systems. Also, it could be associated with Cu(dπ) to S(dπ) back-bonding. The additional electron density in the π system of the S-S moiety could be antibonding[3,17] in nature and account, in part, for the SS bond lengthening. Similar shortening of CS bonds (and corresponding lengthening of SS bonds) due to C(pπ) to S(dπ) back-bonding in bis(aryl) disulfides has been proposed.[8a]

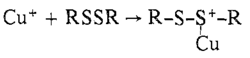
In support of this suggestion is the observation that changes in disulfide geometry do not occur in a related ligand upon coordination[7] with Ni(II) where, in a chelated N_4SCl coordination environment, back-bonding to the disulfide is not expected. In the complex *N,N'*-ethylenebis(monothioacetylacetoniminato)cobalt(II), where metal (3d) to S(3d) π bonding is not anticipated, such bonding has been suggested to explain certain chemical observations.[54] Also, it has been suggested[55] that metal-sulfur dπ-dπ bonding may be occurring in $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$,[55a] in a copper(I)-disulfide system with cytochrome oxidase,[55b] and in 1,2-dithiolene complexes.[55c]

In further support of the above suggestions concerning disulfide moiety alterations due to complexation are the observations that the CSSC dihedral angle, SS bond length, and lowest energy absorption in a related Cu(I) complex containing the ligand bis[2-(2-pyridyl)ethyl] disulfide are 59.7 (1)°, 2.081 (1) Å, and 293 mμ, respectively.[21]

The mean Cu(I)-N bond length (see Table IV) of 2.13 (1) Å can be compared to the corresponding distances, involving saturated nitrogen, in $CuCN\cdot NH_3$[56] (2.070 (1) Å) and in $CuCN\cdot N_2H_4$[57] (2.17 (1) Å). The triazeno function (-N=N-N-) coordinates Cu(I) in a bidentate manner with approach distances that average 1.87 Å (and range from 1.82 to 1.91 Å) in 1,3-dimethyltriazinocopper(I)[58] and 1.92 (2) Å in 1,3-diphenyltriazinocopper(I) (alternative name: diazoaminobenzenecopper(I)).[59] In azomethanecopper(I) chloride[60] the Cu(I)-N distance is 1.993 (16) Å. Nitriles coordinate Cu(I)[61-63] at similar distances: for example, 1.987 (5) Å in bis(succinonitrile)copper(I) perchlorate.[64] At 2.26 (3) Å, the Cu(I)-N distance in di-μ-iodo-bis[(*o*-dimethylaminophenyl)dimethylarsine-*As,N*]dicopper(I), $[CuI(nas)]_2$, is long,[65] possibly because of steric factors.

With unsaturated nitrogen-containing ligands, Cu(I) can back-bond into empty low-lying nitrogen 2pπ* orbitals. It is possible that in $[CuL]_2^{2+}$ coordination by a tertiary amine has been facilitated by the concurrent delocalization of electron density from Cu(I) to the disulfide groups. Since the saturated amine cannot have a π-back-bonding component in its coordination interaction, the Cu(I)-N bond is longer and more illustrative of simple σ coordination. Accordingly, the possible shift of π density from Cu(I) to S might serve to stablize further all of the coordinate covalent bonds about Cu(I).

The lengthening of the disulfide bond *via* coordination with a metal ion in a relatively unstable oxidation state may be important in biological processes involving disulfide-mercaptide couples and metal oxidation state changes. The lengthened disulfide bond may be weakened and become more susceptible to nucleophilic attack and participation in redox processes. Also, the complex may represent an example of an intermediate in concomitant electrophilic and nucleophilic (eq 4 and 5) catalysis of the scission of a sulfur-



$$\mathrm{Cu^+ + RSSR \rightarrow R\text{-}S\text{-}\underset{Cu}{\underset{|}{S^+}}\text{-}R} \qquad (4)$$

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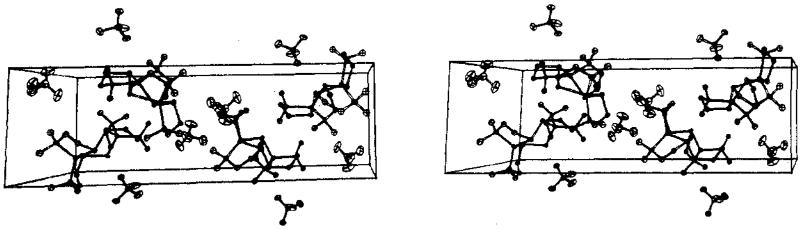
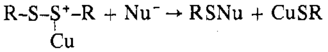


Figure 3. Stereoview of the structure, illustrating the packing of the ions within the unit cell. Ellipsoids of 15% probability are used.



$$\underset{\mathrm{Cu}}{\mathrm{R{-}S{-}S^{+}{-}R}} + Nu^- \rightarrow RSNu + CuSR \qquad (5)$$

sulfur bond.[29] Such a mechanism could explain the susceptibility of the $[CuL]_2^{2+}$ complex to decomposition in boiling methanol (see Characterization of Complexes). A similar intermediate disulfide complex has been isolated in the palladium chloride assisted scission of the disulfide bond in diphenyl disulfide.[9]

The mean sulfur-carbon bond length is 1.83 (2) Å. It has not been very precisely determined, but it appears to be normal.[8] Other features of the molecular geometry, as given in Table IV, are not unusual. The tetrafluoroborate groups are normal except for one B-F distance, which is quite short but insignificantly so. The large standard deviations in the bonds and angles involving boron, carbon, and nitrogen make a further detailed discussion of these values inappropriate. The arrangement of the ions in the crystal is indicated in Figure 3.[66]

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Registry No. $[CuL]_2(BF_4)_2$, 51065-42-0; $[CuL]_2(ClO_4)_2$, 51153-48-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1904.

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X-Ray Structural Characterization of an Outer-Sphere Copper(II) Dimer, $[Cu_2(tren)_2(CN)_2](BPh_4)_2$. Hydrogen Bonding between Two Trigonal-Bipyramidal Copper Cations

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The structure of $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, the tetraphenylborate salt of an outer-sphere dimer of cyano-2,2′,2″-triaminotriethylaminecopper(II) cation, where tren = 2,2′,2″-triaminotriethylamine, has been determined using heavy-atom least-squares X-ray methods to conventional observed–calculated agreement factors of $R_F = 0.067$ and $R_{wF} = 0.047$ for 2773 reflections measured on a four-circle diffractometer. The molecule crystallizes in the $P2_1/c$ space group with two formula weights in a cell measuring $a = 13.792$ (7) Å, $b = 10.338$ (6) Å, $c = 20.316$ (14) Å, and $\beta = 94.27°$ (4). The crystal densities are 1.26 (calculated) and 1.27 g/cm^3 (measured). Discrete cationic $[Cu_2(tren)_2(CN)_2]^{2+}$ and anionic BPh_4^- units are found. Each copper atom in the cation is trigonal bipyramidally coordinated with tren occupying four sites [Cu–N = 2.076 (5), 2.090 (5), 2.119 (5), and 2.083 (5) Å] and with an axial carbon-bonded cyanide [Cu–CN = 1.967 (7) Å and C–N = 1.127 (9) Å]. The trigonal bipyramids are distorted from perfect threefold symmetry with trigonal-plane angles of 122.6 (2), 120.4 (2), and 112.5 (2)°. The cation is dimeric by virtue of the fact that the coordinated cyanide on each copper atom is hydrogen bonding through its nitrogen atom to a primary amine of the tren ligand coordinated to the second copper atom, *i.e.*, Cu–CN···HN–Cu. The N–N distance across the hydrogen bond is 3.047 (7) Å. The dimeric cation is located on a center of inversion in the unit cell and the Cu–Cu distance is 6.090 (1) Å. The angle between the two copper pseudotrigonal axes (each defined as being collinear with the Cu–C bond) and the Cu–Cu vector is 44°. The conformation and inter-ring interactions of the BPh_4^- anion are discussed.

Introduction

Several reviews[3-7] have appeared in part or in total concerned with transition metal cyanide complexes. The bridging nature of the cyanide ion has been well documented and, in fact, this aspect of the interaction of cyanide with transition metals has been the focal point of two[5,6] of the above reviews. The best known systems with bridging cya-

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