

the CN stretches. Discrepancies in isotope shifts for MC stretching modes have been observed previously though to a lesser extent. In this case the deviations are well outside experimental error and must arise from some perturbation we do not yet understand. The observed shifts in the solid state for the Pt compound are in much better agreement. This suggests that there may be some distortion caused by interaction with the solvent for the Pt and Pd species. Nevertheless, as mentioned above, the force field is well fixed by the CN stretches so that the results on the stretching constants are definitely significant. The use of solid-state frequencies has little effect on the calculated force constants.

In Table VI we present the internal coordinate stretching force constants for comparison among the $M(CN)_4^{2-}$ complexes and with $Co(CN)_6^{3-}$. It is apparent that both the CN and MC bond strengths are greater for $Pt(CN)_4^{2-}$ than for $Ni(CN)_4^{2-}$. This indicates greater σ -bond strength for Pt-C than for Ni-C.¹³ Note also that $F_{MC,CN}$ and $F_{MC,MC}^t$ are greater for the Pt complex, as can be expected for stronger M-C bonding. The Pd complex falls in between with Pd-C more like Ni-C but $F_{CN}(Pd)$ more like $F_{CN}(Pt)$. The picture is no doubt complicated by some differences in π bond-

ing. Intensity studies¹⁴ indicate that M-CN "back" π bonding is greater for $Pt(CN)_4^{2-}$ than for the other two. A comparison of intensities and force constants suggests that Pd-C has slightly greater σ -bond strength than Ni-C while Pt-C has greater σ -bond strength and greater π -bond strength than either of the other two species.

A comparison with $Co(CN)_6^{3-}$ indicates that the M-C bond is weaker for the hexacyanide even though intensity studies¹⁴ indicate that the Co-C π bonding is stronger than that for Pt-C. The comparison suggests that the M-C σ bond is inherently weaker for hexacyanides though its effect on strengthening the CN bond is greater. Similar studies of other metal cyanide complexes should throw further light into these interesting bonding systems.

Registry No. $Ni(^{12}C^{14}N)_4^{2-}$, 48042-08-6; $Ni(^{12}C^{15}N)_4^{2-}$, 52540-55-3; $Ni(^{13}C^{14}N)_4^{2-}$, 52540-56-4; $Pd(^{12}C^{14}N)_4^{2-}$, 15004-87-2; $Pd(^{12}C^{15}N)_4^{2-}$, 52540-57-5; $Pd(^{13}C^{14}N)_4^{2-}$, 52540-58-6; $Pt(^{12}C^{14}N)_4^{2-}$, 15004-88-3; $Pt(^{12}C^{15}N)_4^{2-}$, 52540-59-7; $Pt(^{13}C^{14}N)_4^{2-}$, 52540-60-0; $K_2Ni(^{12}C^{14}N)_4$, 14220-17-8; $K_2Ni(^{12}C^{15}N)_4$, 52540-61-1; $K_2Ni(^{13}C^{14}N)_4$, 52540-62-2; $K_2Pd(^{12}C^{14}N)_4 \cdot H_2O$, 16457-34-4; $K_2Pd(^{12}C^{15}N)_4 \cdot H_2O$, 52540-63-3; $K_2Pd(^{13}C^{14}N)_4 \cdot H_2O$, 52540-64-4; $K_2Pt(^{12}C^{14}N)_4 \cdot 3H_2O$, 14323-36-5; $K_2Pt(^{12}C^{15}N)_4 \cdot 3H_2O$, 52540-65-5; $K_2Pt(^{13}C^{14}N)_4 \cdot 3H_2O$, 52540-66-6.

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Synthesis and Crystal Structure of a Polymeric Copper(I) Aliphatic Disulfide Complex. {Bis[2-(2-pyridyl)ethyl] disulfide}copper(I) Perchlorate

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{Bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate, alternatively named [2,2'-(dithiodiethylene)dipyridine]copper(I) perchlorate, $Cu(C_5H_4NCH_2CH_2SSCH_2CH_2C_5H_4N)ClO_4$, has been synthesized by disulfide ligand reaction 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 large-block-diagonal least-squares refinement using anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogens, the conventional R index converged at 0.043. The yellow crystals form in the monoclinic space group $P2_1/c$ with $a = 10.408$ (3) Å, $b = 8.249$ (2) Å, $c = 20.662$ (7) Å, $\beta = 108.99$ (3)°, and $Z = 4$. Half $(C_5H_4NCH_2CH_2S^-)$ of two different ligands is coordinated to each Cu(I) ion. This results in two six-membered chelate rings and a somewhat distorted tetrahedral coordination environment of two sulfur and two nitrogen atoms about each Cu(I). The remaining halves of each disulfide ligand associate with different Cu(I) ions, forming a cationic polymeric chain. The average Cu(I) bond distances to the sulfur and nitrogen donor atoms are 2.322 (1) and 2.029 (1) Å, respectively. The Raman shift of the S-S stretch is 484 cm^{-1} , significantly less than the expected value for the uncoordinated disulfide ligand. This correlates qualitatively with the observed coordination of the disulfide moiety, the closing of the CSSC dihedral angle to 59.7 (1)°, and the lengthening of the S-S bond to 2.081 (1) Å. A uv band associated with the complexed disulfide appears at $293\text{ m}\mu$, as compared to $248\text{ m}\mu$ in the uncoordinated ligand. A similar band at approximately $330\text{ m}\mu$ is observed in the oxidized form of ceruloplasmin, in which the complexation of Cu(I) by disulfide has been reported.

Introduction

In order to elucidate the role of transition metal ions in the structure and function of some metalloenzymes and metalloproteins, attempts have been made to synthesize aliphatic disulfide complexes of transition metal ions and to determine their molecular structures. A detailed introduction can be found in the reports of the first two structures determined in this laboratory: those of a Ni(II) complex,¹ chloro[bis-[2-[(2-pyridylmethyl)amino]ethyl] disulfide]nickel(II) perchlorate, and of a Cu(I) complex,² *cyclo*-di- μ -[bis[2-(*N,N*-

dimethylamino)ethyl] disulfide]dicopper(I) tetrafluoroborate, $[Cu(RSSR)]_2(BF_4)_2$.

It has recently been reported that the oxidized form of the two-electron copper oxidase ceruloplasmin, present in the β -globulin fraction of mammalian blood serum, has Cu(I)-complexed RSSR at its two-copper site.³ Perhaps the readily prepared copper(I) organic disulfide small-molecule complexes can act as models for the corresponding active site in the large metalloprotein ceruloplasmin and in other copper oxidases as well.

Unfortunately, $[Cu(RSSR)]_2(BF_4)_2$ is unstable, both in

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the atmosphere and in an X-ray beam, so that the diffraction data were less than optimal. Small and possibly important alterations in the geometry of the disulfide ligand were indicated upon complexation, but the high associated standard deviations made these results only marginally significant. By replacing the dimethylamino groups at each end of the symmetric ligand with α -pyridyl groups, a complex was formed with CuClO_4 which was stable. In order to verify that another disulfide complex had been prepared and to establish (with greater precision) the small structural alteration in the disulfide portion of the ligand upon complexation, the molecular structure was determined crystallographically.

Preparation Section

Cupric perchlorate, hydrated, and 2-mercaptoethylpyridine were obtained from the G. Frederick Smith Chemical Co. and Chemicals Procurement Laboratories, Inc., respectively. All other chemicals were of reagent grade quality. The laser Raman (excitation at 5145 Å), infrared, and ultraviolet spectra were obtained using Cary 82, Perkin-Elmer IR-10, and Cary 14 spectrometers, respectively. The elemental analyses were performed by Galbraith Laboratories.

Preparation of Bis[2-(2-pyridyl)ethyl] Disulfide (Alternately Named 2,2'-(Dithiodiethylene)dipyridine), $\text{pyCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{py}$. This ligand was prepared following the method of Bauer and Gardella.⁴ Solid disulfide could not be isolated from this extract; therefore the solution was reduced to an oil using a rotary evaporator and dissolved in methanol. This methanol solution was used in the complexation reactions.

Preparation of {Bis[2-(2-pyridyl)ethyl] disulfide}copper(I) Perchlorate, $[\text{Cu}(\text{pyCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{py})](\text{ClO}_4)$. A 0.93-g (0.0025-mol) sample of cupric perchlorate, hydrated, was dissolved in 50 ml of methanol and filtered. The methanolic ligand solution (0.0075 mol) was added to the Cu(II) salt solution. Initially the solution was deep green, but it gradually turned yellow as a small amount of tan precipitate formed. The tan precipitate was removed by filtration. Clusters of yellow, lath-shaped crystals formed from the filtrate by slow evaporation over a period of 10 hr. These crystals were isolated by filtration, washed with methanol and ether, and vacuum-dried at room temperature. *Anal.* Calcd for $\text{CuC}_{14}\text{H}_{16}\text{N}_2\text{S}_2\text{ClO}_4$: Cu, 14.46; C, 38.27; H, 3.67; S, 14.59; Cl, 8.07. Found: Cu, 14.33; C, 38.29; H, 3.60; S, 14.53; Cl, 8.24.

Attempts to recrystallize this yellow copper(I) disulfide complex, $[\text{CuL}]_n(\text{ClO}_4)_n$, from hot methanol led only to decomposition. Also, attempts to isolate this complex *via* direct combination of $\text{Cu}(\text{CH}_3\text{-CN})_2\text{ClO}_4$ and the disulfide ligand were unsuccessful.

Discussion. It is well known that mercaptides react reversibly with Cu(II) to produce Cu(I) and disulfides



The direction in which this equilibrium lies is dependent upon the valence specificity⁵ of the coordination environment available to copper. With regard to the formation of the Cu(I) complex discussed herein, the mercaptide apparently was produced *via* a base⁶ and/or metal ion^{2b,7} induced cleavage of the disulfide bond. In the presence of excess disulfide, the copper(I) disulfide complex forms and is stabilized by the Cu(I) specificity of the disulfide moiety.

The enhanced stability of this complex, $[\text{CuL}]_n(\text{ClO}_4)_n$, relative to *cyclo-di- μ -{bis[2-(*N,N*-dimethylamino)ethyl] disulfide}copper(I), $[\text{Cu}(\text{RSSR})_2]_2^{2+}$, may be accounted for in part by the coordination of the trigonal pyridine nitrogen in the former, in place of the pyramidal amine nitrogen of the latter. The greater s character of the bonding orbital of the pyridine in $[\text{CuL}]_n^{n+}$ is expected to cause a greater Cu(I) affinity. Also, the six-membered chelate ring in $[\text{CuL}]_n^{n+}$ is much less Cu(II) specific than is the five-membered chelate ring in $[\text{Cu}(\text{RSSR})_2]_2^{2+}$.*

The instability of $[\text{CuL}]_n^{n+}$ in hot methanol is analogous to that observed for an intermediate disulfide complex isolated in the pal-

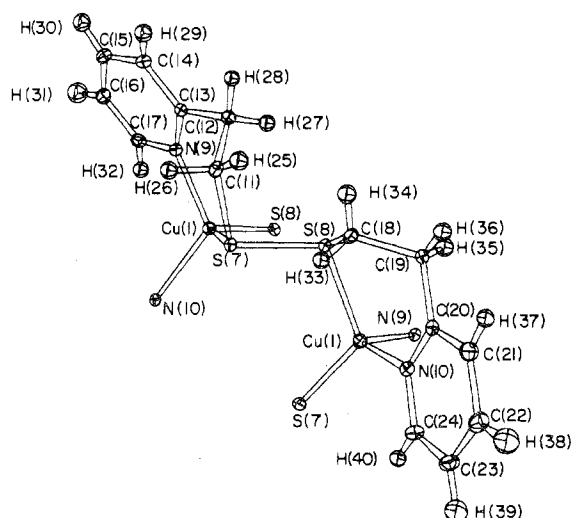


Figure 1. The bis[2-(2-pyridyl)ethyl] disulfide tetradentate ligand coordinated to two symmetry-equivalent Cu(I) ions, whose coordination spheres are further completed with the coordinating atoms of two other disulfide molecules. Ellipsoids of 15% probability are used. [C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.]

adium chloride assisted scission of the disulfide bond in diphenyl disulfide.⁷ These complexes as well as $[\text{Cu}(\text{RSSR})_2]_2^{2+}$ may be examples of intermediates in the concomitant electrophilic and nucleophilic catalysis of the scission of a sulfur-sulfur bond.^{6a}

Characterization and Spectra

Extensive infrared correlations pertaining to the coordination and equivalence of pyridyl groups have been made for ligands containing the 2-substituted pyridine moiety.^{8,9} The infrared spectrum (of a Nujol mull) of the complex $[\text{CuL}]_n(\text{ClO}_4)_n$ falls into series "A."⁸ Four $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$ bands occur at 1604, 1580, 1481, and 1443 cm^{-1} as compared to bands at 1592, 1570, 1472, and 1434 cm^{-1} in the uncoordinated ligand L. The presence of only four bands and the shifts to higher energy have been taken as indicators of the approximate equivalence⁸ and of the coordination⁸⁻¹⁰ of the 2-pyridyl groups, respectively. The disappearance of the ring-breathing mode at 991 cm^{-1} in the ligand and its replacement by a 1019-1003- cm^{-1} band in the complex also indicate pyridine moiety coordination.^{8,11}

Two bands of medium intensity occur at 760 and 744 cm^{-1} in the uncoordinated ligand and are tentatively assigned^{8,12} to $\gamma(\text{C}-\text{H})$ and $\phi(\text{C}-\text{C})$. In the complex, the first of these bands occurs at 763 cm^{-1} , while the second splits into a sharp band at 747 cm^{-1} and a shoulder at 720 cm^{-1} . This splitting also is believed to be an indicator of pyridine coordination.^{8,11,13}

As the crystal structure shows (see Discussion of the Structure) the 2-pyridyl groups are coordinated but are not equivalent. It seems apparent that the previously described infrared correlations are valid and useful. However, given the crystallographic nonequivalence of the pyridyl groups in the complex $[\text{CuL}]_n^{n+}$ and the observed multiplicity in the form of unresolved shoulders of each band in the 1450-1610- cm^{-1} region for both the "free" ligand and the complex, the num-

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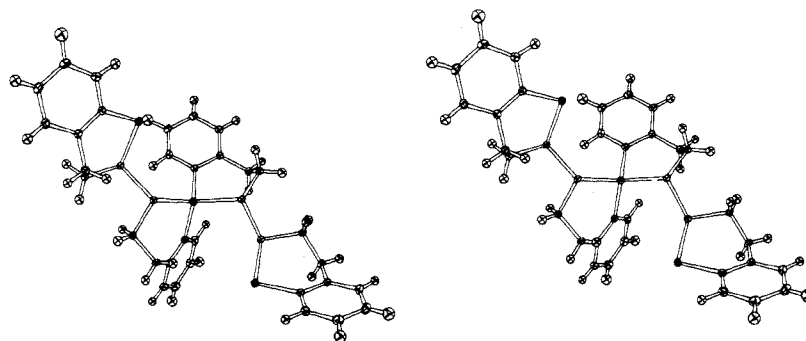


Figure 2. A stereoview (ORTEP) of a section of the polymeric chain showing two complete disulfide ligands. Ellipsoids of 15% probability are used. Cu(I) ions are blackened.

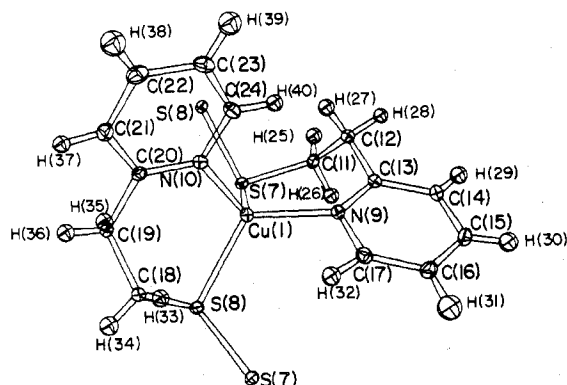


Figure 3. The near-tetrahedral coordination about a single Cu(I) ion illustrated (ORTEP) with two half ligand molecules. The coordinates in Table I are plotted directly to give this figure. Ellipsoids of 15% probability are used.

ber of $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$ bands should be used with caution in deciding the relative equivalence of 2-pyridyl groups.

Although considerable difficulty was encountered in obtaining the Raman spectra of these compounds (that of the "free" ligand was not obtained) due to fluorescence and extensive localized heating by the laser beam, a strong band at 484 cm^{-1} was observed for the complex using a rapidly rotating sample holder.¹⁴ This band is assigned to $\nu(\text{S}-\text{S})$ and represents a significant shift (of about 25 cm^{-1}) to lower energy relative to that expected for the uncomplexed ligand. Linear aliphatic disulfides ($\text{R}-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{R}$) generally prefer the gauche, gauche, gauche conformation¹⁵⁻¹⁷ about the CSSC moiety, which is present (see Figures 1-3) in the complex, and exhibit a $\nu(\text{S}-\text{S})$ Raman band in the $506-512\text{-cm}^{-1}$ region.^{2b, 15, 18-21} The $\nu(\text{S}-\text{S})$ Raman band in $[\text{Cu}(\text{RSSR})_2(\text{BF}_4)_2]^{2+}$ occurs at 463 cm^{-1} , 43 cm^{-1} lower than its position in the uncomplexed ligand salt¹⁶ $\text{RSSR}\cdot 2\text{HCl}$. These shifts in $\nu(\text{S}-\text{S})$ are believed to be due to shifts in electron density associated with disulfide coordination and incorporation into chelate rings and are expected to correlate with the lengthening of the S-S bond and the alteration of the CSSC dihedral angle (See Discussion of the Structure).

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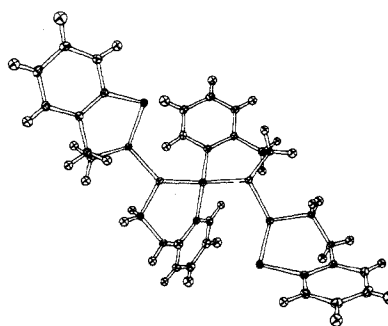
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The gauche, gauche, gauche conformation about the CSSC moiety occurs in both complexes $[\text{CuL}]_n(\text{ClO}_4)_n$ and $[\text{Cu}(\text{RSSR})_2(\text{BF}_4)_2]$ and the S-S bond lengths do not differ significantly in these determinations; however the magnitude of the $\nu(\text{S}-\text{S})$ shifts (relative to those of the uncomplexed ligands) are significantly different (25 cm^{-1} vs. 43 cm^{-1} , respectively). The direction (increased shift) and perhaps the magnitude of this difference appears to be consistent with the enhanced Cu-S interaction, the smaller chelate rings, and the increased strain throughout the cyclic dimeric complex² $[\text{Cu}(\text{RSSR})_2]^{2+}$ as compared to $[\text{CuL}]_n^{n+}$. It also may be related to the very different CSSC dihedral angles observed: $106.3(9)^\circ$ in the dimer and $59.7(1)^\circ$ in $[\text{CuL}]_n^{n+}$. Apparently $\nu(\text{S}-\text{S})$ is a function of some if not all these parameters, and it appears likely that $\nu(\text{S}-\text{S})$ of complexed organic disulfide ligands and its shift relative to that of the uncomplexed ligand might be a useful indicator of the stereochemistry and of the degree of coordination of the S-S group.

The uv spectrum of $[\text{CuL}]_n(\text{ClO}_4)_n$, whether taken of a Nujol mull, a DMSO solution, or a methanol solution, exhibits a broad shoulder at about $290\text{ m}\mu$ ($\epsilon \sim 10^3\text{ M}^{-1}\text{ cm}^{-1}$) and a multiplet absorption at $261\text{ m}\mu$ ($\epsilon \sim 10^4\text{ M}^{-1}\text{ cm}^{-1}$) due to the pyridine chromophore. The relatively intense $290\text{-m}\mu$ absorption accounts for the yellow color of this complex and is nearly identical with the lowest energy uv absorption observed^{2b} for $[\text{Cu}(\text{RSSR})_2]^{2+}$. This band is expected to be due to a charge transfer between Cu(I) and the disulfide moiety² or to a disulfide absorption that has been significantly red-shifted due to complexation^{22, 23} and/or CSSC dihedral angle alteration from 90° .²⁴⁻²⁶ The similarity of this $290\text{-m}\mu$ band to the $293\text{-m}\mu$ band observed for the penicillin analogs *cis*-dithiazabicyclooctanes,²⁷ which have CSSC dihedral angles of 60.5° , suggests that they are due to red-shifted $n_a \rightarrow \sigma^*$ disulfide transitions. However, its similarity to the $290\text{-m}\mu$ band in $[\text{Cu}(\text{RSSR})_2]^{2+}$ where the CSSC dihedral angle is 106.3° and the $330\text{-m}\mu$ band associated with a copper(I) disulfide site in the oxidized form of ceruloplasmin³ suggests that these bands are due to charge transfer between Cu(I) ions and disulfide sulfur atoms. The specific assignment of these uv bands remains unresolved. The intense uv bands which occur at approximately $293\text{ m}\mu$ in both $[\text{Cu}(\text{RSSR})_2]^{2+}$ and $[\text{CuL}]_n^{n+}$ and at approximately $330\text{ m}\mu$ in ceruloplasmin³ may indicate a structural similarity between

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these complexes and the copper(I) disulfide protein chromophore.

The complex bis(2,2'-dithiodipyridine)copper(I) perchlorate recently has been prepared.²⁸ Its color and uv-visible and infrared spectra, as well as its overall stability, are comparable to those of the complex $[\text{CuL}]_n(\text{ClO}_4)_n$, described herein. The Raman shift values for the uncomplexed ligand 2,2'-dithiodipyridine and its Cu(I) complex are 548 and 536 cm^{-1} , respectively. This shift of 12 cm^{-1} to lower energy coupled with the other data strongly imply the formation of another organic disulfide complex containing pyridyl and/or disulfide moieties coordinated to Cu(I) ions.

Diffraction Section

Preliminary oscillation and Weissenberg photographs indicated monoclinic symmetry; all reflections ($h0l$) with l odd and ($0k0$) with k odd were systematically absent, uniquely defining the space group as $P2_1/c$.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ 0.70926 Å; $K\alpha_2$, λ 0.71354 Å) and a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell parameters and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 23.5°. The program used was written by Robert A. Sparks and is part of the diffractometer program library. The temperature was maintained between 19 and 20°.

A crystal of dimensions 0.45 × 0.28 × 0.08 mm was used for data collection. The θ - 2θ scanning mode was used with a scan speed (ω) variable from 1 to 24° min^{-1} , depending on the peak intensity of the reflection. Background counting time at each end of the scan range was equal to half of the scan time, and the scan range varied from 2.0° at low 2θ to 2.3° at 55°. The variations in the intensities of three check reflections, which were remeasured after every 100 reflections during data collection, were not significant, so no decay correction was applied.

Standard deviations were assigned to the individual reflections according to the formula

$$\sigma(I) = [\omega^2(\text{CT} + B_1 + B_2) + (pI)^2]^{1/2}$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\text{CT} - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrumental inaccuracies. The weights (w) used in least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 3872 unique reflections measured, those for which $2\theta < 52^\circ$, 3109 had intensities larger than 3 times their standard deviations. These were regarded as the observed reflections, and only these were used in further calculations. The intensities were corrected for Lorentz and polarization effects,²⁹ and for the absorption of X-rays ($\mu = 17.7 \text{ cm}^{-1}$);³⁰ transmission coefficients³¹ ranged from 0.80 to 0.99. The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction.

The atomic scattering factors of Doyle and Turner³² were used for Cu^+ , Cl^+ , S^+ , O^+ , N^+ , and C^+ . The first three were modified to account for the real part of the anomalous dispersion correction.³³ The atomic scattering factors used for hydrogen were those of Stewart, *et al.*³⁴

Crystal Data

{Bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate, alternatively named [2,2'-(dithiodiethylene)dipyridine]copper(I) per-

chlorate, $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4\text{ClS}_2\text{Cu}$, $[\text{CuL}]_n(\text{ClO}_4)_n$, is monoclinic, with space group $P2_1/c$: $a = 10.408$ (3) Å, $b = 8.249$ (2) Å, $c = 20.662$ (7) Å, $\beta = 108.99$ (3)°, $V = 1677$ Å³, mol wt 439.4 amu, $d_{\text{obsd}}(\text{floatation}) = 1.76$ (2) g/cm^3 , $d_{\text{calcd}} = 1.739$ g/cm^3 , $Z = 4$, $F(000) = 904$. Figures in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Structure Determination

The position of the cuprous ion was indicated on a three-dimensional Patterson function. Positions for all other nonhydrogen atoms were found by successive cycles of Fourier refinement using the fast-Fourier algorithm.³⁵ This model was refined to $R_1 = 0.083$. ($R_1 = (\sum |F_o| - |F_c|) / \sum F_o$ and $R_2 = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2}$.) After least-squares refinement to convergence using anisotropic thermal parameters, R_1 became 0.053. The positions of 12 of the 16 hydrogen atoms were determined from a difference Fourier function; the remaining four atomic positions were calculated.³⁶ All hydrogen atom positions and their isotropic thermal parameters were then refined, together with all other parameters, by large-block-diagonal least-squares (approximately half of the structure at a time by full-matrix methods) to the final error indices, $R_1 = 0.043$ and $R_2 = 0.046$. The program used, UCLALS4,³⁷ minimizes $\sum w(\Delta F)^2$.

The "goodness of fit," $\{\sum w(F_o - |F_c|)^2 / (m - s)\}^{1/2}$, is 1.76. The number of observations is m , and s , the number of parameters, is 281. The overdetermination ratio (m/s) is 11.1. In the final cycles of refinement, the parametric shifts involving hydrogen positional parameters were all less than 10% of their corresponding esd's, and those involving hydrogen thermal parameters were less than 25% of their esd's. For all nonhydrogen parameters, the final shifts were less than 1% of their corresponding esd's. The largest peak on the final difference Fourier function, whose esd is 0.12 $\text{e} \text{ \AA}^{-3}$, was 0.5 $\text{e} \text{ \AA}^{-3}$ in height and was located very near the Cu(I) ion at a chemically implausible position. The positional and thermal parameters of the nonhydrogen atoms are presented in Table I, and those of the hydrogen atoms are in Table II.

Discussion of the Structure

Cu(I) ions and bis[2-(2-pyridyl)ethyl] disulfide molecules have come together to form polymeric chains, portions of which are illustrated in Figures 1 and 2. The 2-pyridyl groups and the sulfur atoms all function as ligands, forming six-membered CuSCC^-N chelate rings, two of which are associated with each metal ion to give nearly regular tetrahedral Cu(I), as Figure 3 illustrates. The packing of these chains is indicated in Figure 4.

This complex has a morphology entirely different from that of {bis[2-(*N,N*-dimethylamino)ethyl] disulfide}copper(I),² $[\text{Cu}(\text{RSSR})_2]^{2+}$, in which discrete binuclear complexed cations with central CuSSCuSS rings and ancillary CuSCCN rings were found. The aliphatic disulfide bond length is, within experimental error, the same: 2.081 (1) Å as compared to 2.075 (6) Å in $[\text{Cu}(\text{RSSR})_2]^{2+}$. (Molecular dimensions are listed in Table III.) These disulfide bond lengths are approximately 0.04 Å longer than the value of 2.04 Å which is normally observed^{38,39} in aliphatic disulfides whose CSSC dihedral angles are close to 90°.

In contrast to $[\text{Cu}(\text{RSSR})_2]^{2+}$ whose CSSC dihedral angle is 106.3 (9)°, the comparable angle in the polymeric complex described herein, $[\text{CuL}]_n^{n+}$, is 59.7 (1)°. We suggest that these dihedral angles differ from the normal value^{24,38} of about 90° because of the steric requirements imposed by the polydentate coordination of the disulfide ligand and the strained nature of the chelate ring systems within each complex.

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Table I. Fractional Atomic Coordinates ($\times 10^5$) and Thermal Parameters ($\times 10^5$) for Nonhydrogen Atoms^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	10,786 (4)	38,480 (4)	26,353 (2)	717 (4)	899 (5)	145 (1)	12 (7)	128 (3)	-65 (3)
Cl(2)	68,001 (7)	9,543 (10)	41,843 (4)	657 (7)	1295 (11)	182 (2)	-3 (14)	79 (5)	27 (7)
O(3)	54,981 (30)	16,498 (48)	41,103 (17)	775 (27)	2516 (64)	313 (9)	608 (68)	212 (24)	-176 (37)
O(4)	78,562 (30)	21,198 (39)	44,771 (16)	972 (29)	1634 (46)	316 (8)	-717 (61)	64 (25)	117 (32)
O(5)	68,371 (37)	4,820 (66)	35,235 (17)	1218 (38)	3741 (100)	259 (8)	689 (101)	222 (28)	-598 (48)
O(6)	70,415 (41)	-4,153 (46)	46,268 (22)	1507 (45)	1718 (53)	429 (12)	-573 (81)	-65 (36)	739 (42)
S(7)	-203 (7)	25,980 (8)	33,124 (3)	604 (6)	685 (8)	172 (2)	34 (12)	168 (5)	31 (6)
S(8)	5,368 (7)	1,955 (8)	32,499 (3)	589 (6)	667 (8)	173 (2)	-59 (11)	155 (5)	-57 (6)
N(9)	25,565 (24)	51,860 (30)	33,137 (12)	555 (21)	923 (32)	171 (6)	-47 (44)	112 (17)	-56 (22)
N(10)	-19,713 (25)	-26,648 (30)	28,603 (12)	653 (23)	833 (31)	171 (6)	-123 (44)	161 (18)	-49 (21)
C(11)	10,912 (33)	31,402 (34)	41,672 (14)	928 (32)	770 (35)	149 (6)	-219 (54)	238 (23)	-64 (23)
C(12)	25,963 (33)	33,362 (36)	42,522 (15)	778 (30)	892 (37)	166 (7)	40 (54)	41 (22)	65 (25)
C(13)	29,475 (28)	49,253 (34)	39,959 (14)	556 (24)	856 (35)	170 (6)	111 (50)	89 (19)	-12 (25)
C(14)	36,546 (32)	61,104 (41)	44,561 (16)	691 (28)	1155 (43)	180 (7)	-134 (60)	40 (22)	-95 (29)
C(15)	40,018 (35)	75,603 (42)	42,185 (19)	782 (31)	1062 (45)	273 (9)	-449 (64)	154 (27)	-228 (33)
C(16)	36,485 (35)	77,941 (41)	35,193 (20)	778 (32)	996 (42)	295 (10)	-296 (61)	285 (28)	85 (33)
C(17)	29,308 (32)	65,915 (40)	30,880 (17)	663 (28)	1160 (43)	202 (7)	-91 (55)	186 (23)	153 (28)
C(18)	1,336 (32)	-6,979 (33)	39,727 (14)	813 (29)	743 (34)	156 (6)	-231 (51)	79 (21)	7 (23)
C(19)	74 (29)	-25,472 (33)	38,968 (15)	645 (26)	695 (34)	188 (7)	32 (50)	15 (21)	110 (25)
C(20)	-14,017 (28)	-31,408 (32)	35,139 (14)	598 (26)	691 (32)	179 (7)	58 (47)	172 (21)	-33 (24)
C(21)	-20,902 (35)	-41,585 (41)	38,250 (17)	842 (32)	1181 (45)	202 (8)	-131 (61)	250 (25)	175 (29)
C(22)	-33,869 (39)	-46,939 (47)	34,667 (21)	898 (35)	1311 (51)	324 (11)	-533 (72)	514 (32)	92 (39)
C(23)	-39,776 (34)	-41,855 (47)	27,998 (20)	650 (30)	1423 (53)	282 (10)	-452 (64)	239 (27)	-184 (35)
C(24)	-32,450 (32)	-31,750 (43)	25,161 (16)	639 (29)	1350 (47)	186 (7)	-325 (60)	92 (23)	-105 (29)

^a See Figure 1 for the identities of the atoms. The estimated standard deviation is in the units of the least significant digit given for the corresponding parameter. The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

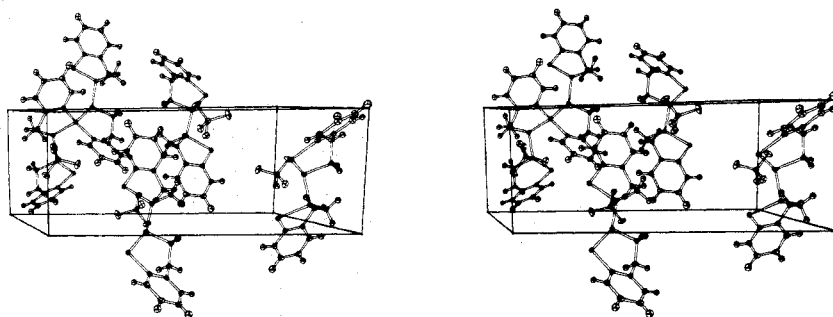


Figure 4. A stereoview (ORTEP) of the packing of the complexed cations and perchlorate ions. Ellipsoids of 15% probability are used. Cu(I) ions are blackened.

Table II. Fractional Atomic Coordinates ($\times 10^3$) and Thermal Parameters ($\text{\AA}^2 \times 10$) for Hydrogen Atoms

	x	y	z	B
H(25)	101 (5)	238 (6)	452 (3)	37 (9)
H(26)	68 (5)	421 (6)	427 (2)	34 (8)
H(27)	290 (5)	243 (6)	406 (2)	33 (8)
H(28)	314 (4)	330 (5)	473 (2)	28 (8)
H(29)	386 (5)	598 (6)	492 (3)	38 (9)
H(30)	453 (5)	830 (6)	454 (3)	41 (10)
H(31)	392 (7)	887 (8)	331 (4)	62 (14)
H(32)	259 (5)	660 (6)	260 (2)	37 (8)
H(33)	-68 (5)	-18 (6)	398 (2)	29 (8)
H(34)	81 (5)	-44 (6)	436 (3)	38 (9)
H(35)	29 (5)	-296 (6)	432 (2)	33 (8)
H(36)	61 (5)	-299 (6)	369 (2)	36 (9)
H(37)	-164 (4)	-440 (5)	426 (2)	28 (7)
H(38)	-382 (6)	-538 (8)	367 (3)	55 (12)
H(39)	-484 (6)	-457 (7)	250 (3)	50 (10)
H(40)	-364 (4)	-284 (6)	205 (2)	30 (8)

This conclusion is supported by the "normal" unaltered CSSC dihedral angle ($97.7 (8)^\circ$) and S-S bond length (2.04 (2) \AA) that have been observed crystallographically (see Table IV) for chloro(diethyl disulfide)copper(I),⁴⁰ $[\text{Cu}(\text{Et}_2\text{S}_2)\text{Cl}]_n$. This complex has six-membered CuSSCuSS rings but lacks the accompanying chelate rings or the bridging lig-

ands that would impose additional stereochemical influences upon the disulfide moiety.

According to Hordvik,^{25,38} a relationship exists between the CSSC dihedral angle and the S-S bond length in uncomplexed disulfides. At dihedral angles of approximately 106 or 60° , as are observed in $[\text{Cu}(\text{RSSR})_2]^{2+}$ and $[\text{CuL}]_n^{n+}$, respectively, the S-S bond length is expected to be between 2.05 and 2.06 \AA because of increased lone pair-lone pair repulsions and diminished π overlap between disulfide sulfur atoms. The additional 0.02-0.03 \AA lengthening (to 2.08 \AA) observed in $[\text{Cu}(\text{RSSR})_2]^{2+}$ and $[\text{CuL}]_n^{n+}$ is believed to be primarily electronic in origin, involving the Cu(I) cation.

An increase of about 0.02 \AA in the Cu-S bond distance and a corresponding decrease of 0.09 \AA in the Cu-N bond distance is observed in $[\text{CuL}]_n^{n+}$ as compared to $[\text{Cu}(\text{RSSR})_2]^{2+}$ (see Table IV). The decrease in the Cu-N distance is consistent with possible metal to nitrogen π back-bonding;^{41,42} this is possible only in $[\text{CuL}]_n^{n+}$ where the ligand contains a 2-pyridyl group. The 2-pyridyl group, with the greater s character of its nitrogen σ -bonding orbital and its relatively low-lying nitrogen $2p\pi^*$ orbitals, leads to a greater stability of the Cu(I) oxidation state. The pyridyl $2p\pi^*$ orbitals may compete with the sulfur $3d\pi$ orbitals for electron density

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Table III. Molecular Dimensions^a

Bond Lengths, Å			
Cu(1)-S(7)	2.318 (1)	Cl(2)-O(3)	1.433 (3)
Cu(1)-S(8)'	2.325 (1)	Cl(2)-O(4)	1.437 (3)
Cu(1)-N(9)	2.036 (2)	Cl(2)-O(5)	1.432 (4)
Cu(1)-N(10)'	2.022 (3)	Cl(2)-O(6)	1.423 (4)
S(7)-S(8)	2.0807 (9)		
S(7)-C(11)	1.824 (3)	C(11)-H(25)	0.98 (5)
S(8)-C(18)	1.832 (3)	C(11)-H(26)	1.04 (5)
C(11)-C(12)	1.527 (5)	C(12)-H(27)	0.95 (5)
C(18)-C(19)	1.535 (4)	C(12)-H(28)	0.97 (4)
C(12)-C(13)	1.503 (4)	C(14)-H(29)	0.92 (5)
C(19)-C(20)	1.504 (4)	C(15)-H(30)	0.94 (5)
N(9)-C(13)	1.351 (4)	C(16)-H(31)	1.06 (5)
N(10)-C(20)	1.345 (4)	C(17)-H(32)	0.95 (5)
N(9)-C(17)	1.353 (4)	C(18)-H(33)	0.95 (5)
N(10)-C(24)	1.351 (4)	C(18)-H(34)	0.90 (5)
C(13)-C(14)	1.395 (4)	C(19)-H(35)	0.89 (5)
C(14)-C(15)	1.385 (5)	C(19)-H(36)	0.93 (5)
C(15)-C(16)	1.383 (5)	C(21)-H(37)	0.89 (4)
C(16)-C(17)	1.379 (5)	C(22)-H(38)	0.90 (6)
C(20)-C(21)	1.390 (4)	C(23)-H(39)	0.96 (6)
C(21)-C(22)	1.384 (5)	C(24)-H(40)	0.96 (4)
C(22)-C(23)	1.375 (6)		
C(23)-C(24)	1.382 (5)		
Bond Angles, Deg			
S(7)-Cu(1)-S(8)'	108.36 (3)	O(3)-Cl(2)-O(4)	110.1 (2)
S(7)-Cu(1)-N(9)	103.67 (7)	O(3)-Cl(2)-O(5)	109.0 (2)
S(7)-Cu(1)-N(10)'	115.44 (7)	O(3)-Cl(2)-O(6)	110.4 (2)
S(8)'-Cu(1)-N(9)	118.24 (7)	O(4)-Cl(2)-O(5)	109.2 (2)
S(8)'-Cu(1)-N(10)'	108.33 (10)	O(4)-Cl(2)-O(6)	108.0 (2)
N(9)-Cu(1)-N(10)'	103.33 (7)	O(5)-Cl(2)-O(6)	110.0 (2)
Cu(1)-S(7)-S(8)	100.61 (3)	H(25)-C(11)-S(7)	112 (3)
Cu(1)' ^a -S(8)-S(7)	111.06 (4)	H(25)-C(11)-C(12)	109 (3)
Cu(1)-S(7)-C(11)	101.15 (10)	H(25)-C(11)-H(26)	104 (4)
Cu(1)' ^a -S(8)-C(18)	98.62 (11)	H(26)-C(11)-S(7)	104 (3)
Cu(1)-N(9)-C(13)	122.4 (2)	H(26)-C(11)-C(12)	111 (3)
Cu(1)-N(9)-C(17)	117.7 (2)	H(27)-C(12)-C(11)	110 (3)
Cu(1)' ^a -N(10)-C(20)	124.3 (2)	H(27)-C(12)-C(13)	113 (3)
Cu(1)' ^a -N(10)-C(24)	117.4 (2)	H(27)-C(12)-H(28)	104 (4)
S(7)-S(8)-C(18)	100.96 (9)	H(28)-C(12)-C(11)	111 (3)
S(8)-S(7)-C(11)	101.06 (9)	H(28)-C(12)-C(13)	105 (3)
S(7)-C(11)-C(12)	116.2 (2)	H(29)-C(14)-C(13)	122 (3)
S(8)-C(18)-C(19)	110.6 (2)	H(29)-C(14)-C(15)	118 (3)
C(11)-C(12)-C(13)	114.2 (2)	H(30)-C(15)-C(14)	118 (3)
C(18)-C(19)-C(20)	114.4 (2)	H(30)-C(15)-C(16)	123 (3)
C(12)-C(13)-C(14)	120.4 (3)	H(31)-C(16)-C(15)	122 (4)
C(19)-C(20)-C(21)	121.0 (3)	H(31)-C(16)-C(17)	120 (4)
C(12)-C(13)-N(9)	118.8 (2)	H(32)-C(17)-C(16)	128 (3)
C(19)-C(20)-N(10)	118.0 (2)	H(32)-C(17)-N(9)	109 (3)
N(9)-C(13)-C(14)	120.8 (3)	H(33)-C(18)-S(8)	106 (3)
C(13)-C(14)-C(15)	120.3 (3)	H(33)-C(18)-C(19)	114 (3)
C(14)-C(15)-C(16)	118.6 (3)	H(33)-C(18)-H(34)	109 (4)
C(15)-C(16)-C(17)	118.6 (3)	H(34)-C(18)-S(8)	108 (3)
C(16)-C(17)-N(9)	123.3 (3)	H(34)-C(18)-C(19)	110 (3)
C(17)-N(9)-C(13)	118.2 (2)	H(35)-C(19)-C(18)	107 (3)
N(10)-C(20)-C(21)	121.1 (3)	H(35)-C(19)-C(20)	110 (3)
C(20)-C(21)-C(22)	120.2 (3)	H(35)-C(19)-H(36)	104 (4)
C(21)-C(22)-C(23)	118.7 (4)	H(36)-C(19)-C(18)	113 (3)
C(22)-C(23)-C(24)	118.6 (4)	H(36)-C(19)-C(20)	108 (3)
C(23)-C(24)-N(10)	123.1 (3)	H(37)-C(21)-C(20)	114 (3)
C(24)-N(10)-C(20)	118.3 (3)	H(37)-C(21)-C(22)	125 (3)
		H(38)-C(22)-C(21)	120 (4)
		H(38)-C(22)-C(23)	122 (4)
		H(39)-C(23)-C(22)	124 (4)
		H(39)-C(23)-C(24)	117 (4)
		H(40)-C(24)-C(23)	118 (3)
		H(40)-C(24)-N(10)	119 (3)
Some Dihedral Angles, Deg			
C(11)-S(7)-S(8)-C(18)	59.73 (13)	Cu(1)' ^a -N(10)-C(20)-C(19)	1.7 (3)
Cu(1)-S(7)-S(8)-Cu(1)'	92.77 (5)	N(9)-Cu(1)-S(7)-C(11)	8.0 (2)
S(7)-S(8)-Cu(1)' ^a -S(7)'	128.42 (5)	N(10)-Cu(1)' ^a -S(8)-C(18)	3.3 (2)
S(8)' ^a -Cu(1)-S(7)-S(8)	121.93 (5)	S(7)-S(8)-Cu(1)' ^a -N(9)'	11.0 (1)
Cu(1)-S(7)-S(8)-C(18)	163.4 (1)	S(8)-S(7)-Cu(1)-N(10)'	6.7 (1)
Cu(1)' ^a -S(8)-S(7)-C(11)	163.5 (1)	S(7)-Cu(1)-N(9)-C(13)	16.5 (2)
Cu(1)-N(9)-C(13)-C(12)	18.0 (3)	S(8)-Cu(1)' ^a -N(10)-C(20)	21.1 (2)

^a The esd given is in the units of the least significant digit given for the corresponding value. The coordinates of the primed atoms are related to those given in Table I by $-x, 1/2 + y, 1/2 - z$.

Table IV. Comparisons of Crystallographic Information Concerning Copper(I) Disulfide Complexes^a

	CSSC dihedral angle, deg	Bond lengths, Å			
		S-S	Cu-S	Cu-N	C-S
[Cu(RSSR)] ₂ ²⁺	106.3 (8)	2.075 (6)	2.300 (8)	2.13 (2)	1.83 (2)
[CuL] _n ⁿ⁺	59.7 (1)	2.081 (1)	2.321 (1)	2.029 (2)	1.828 (3)
[Cu(Et ₂ S ₂)Cl] _n	97.7 (8)	2.04 (2)	2.37 (3)		1.85 (6)

^a [Cu(RSSR)]₂²⁺ is *cyclo-di-μ*-[bis-[2-(*N,N*-dimethylamino)ethyl] disulfide]dicopper(I).² [CuL]_nⁿ⁺ is {bis[2-(2-pyridyl)ethyl] disulfide}-copper(I) (this work). [Cu(Et₂S₂)Cl]_n is chloro(diethyl disulfide)copper(I) [C.-I. Branden, *Acta Chem. Scand.*, 21, 1000 (1967)].

delocalization from the Cu(I). The corresponding increase in the Cu-S bond distance is consistent with a reduction in Cu(I) *dπ* to S *dπ* back-bonding² that is required by the occurrence of Cu to N *π* bonding. The increased electron density that Cu to S *π* bonding would delocalize into the *π* system of each disulfide sulfur atom could be antibonding³⁹ in nature and account, at least in part, for the observed additional lengthening of the S-S bond.

The relatively short Cu^I-N bond length in [CuL]_nⁿ⁺, averaging 2.03 Å, is consistent with the presence of an appreciable covalent interaction and supports our interpretation of the bonding in these copper(I) organic disulfide complexes. Not only is the Cu-N bond distance in [CuL]_nⁿ⁺ significantly shorter than the corresponding distance of 2.13 Å in [Cu(RSSR)]₂²⁺, which possesses tertiary amine nitrogen donor atoms, it also is shorter than the Cu(I) to unsaturated nitrogen distance (2.12 Å) in Cu(I) complexes containing pyridazine and 4-cyanopyridine as ligands.⁴³ In contrast, shorter distances (1.82–1.99 Å; see ref 2b for further references) are observed for unsaturated acyclic nitrogen atoms in a series of cyanide, nitrile, triazine, and azo complexes.

The identical nature of the C-S bond lengths precludes the possibility of the participation of this bond³⁹ in the significant delocalization of electron density into the disulfide moiety, consistent with the metal-donor atom bonding proposed for these Cu(I) complexes.

The Cu *dπ* to S *dπ* back-bonding proposal requires that relatively little such bonding occurs in chloro(diethyl disulfide)copper(I) because its Cu-S bond length is longest (see Table IV) by approximately 0.05 Å, and the S-S bond length is "normal" or unaltered due to complexation. Such metal to sulfur *π* bonding coupled with the information in Table IV suggests that the two chloride ion donors of [Cu(Et₂S₂)Cl]_n are better stabilizers of Cu(I) electron density than are the two pyridyl nitrogen donor atoms of [CuL]_nⁿ⁺, which in turn are better stabilizers than are the two amine nitrogen donor atoms of [Cu(RSSR)]₂²⁺.

The tetrahedral angles about Cu(I) range from 103.3 to 118.2° (see Table III). This range is appreciably less than that found earlier in [Cu(RSSR)]₂²⁺, 89.6–123.9°. The "bite" angles at the Cu(I) ion, which are associated with the six-membered chelate rings in [CuL]_nⁿ⁺, and the five-membered chelate rings in [Cu(RSSR)]₂²⁺ range from 103.67 (7) to 108.33 (10)° and from 89.5 (4) to 91.4 (5)°, respectively. The smaller range of the tetrahedral angles about Cu(I) and the closer approximation of the chelate "bite" angles to the regular tetrahedral value imply a lesser degree of strain within the chelate rings and coordination environment of Cu(I) in [CuL]_nⁿ⁺. Not only is this consistent with the proposal that the small degree of S-S bond lengthening due to complexation is a result, at least primarily, of electronic factors rather than of chelate ring strain but it is also consistent with the greater overall stability of [CuL]_nⁿ⁺ in comparison to [Cu(RSSR)]₂²⁺.

Table V. Deviations of Atoms from Least-Squares Planes (Å × 10³)^a

	Plane 1	Plane 2	Plane 3	Plane 4			
N(9)	14	N(10)	-6	Cu(1)	0	Cu(1)'	0
C(13)	-15	C(20)	5	S(7)	0	S(8)	0
C(14)	4	C(21)	0	N(9)	0	N(10)	0
C(15)	16	C(22)	-8	C(11)	249	C(18)	-104
C(16)	-11	C(23)	3	C(12)	1078	C(19)	916
C(17)	-8	C(24)	6	C(13)	323	C(20)	399
Cu(1)	537	Cu(1)'	39				
S(7)	1584	S(8)	917				
C(11)	1251	C(18)	1238				
C(12)	-58	C(19)	14				
<i>q_b × c</i>	-9120		-5119		6166		7070
<i>q_b</i>	4101		7989		-7745		-7071
<i>q_c</i>	87		3157		1415		104
<i>D</i>	1.402		2.050		2.130		1.198
<i>δ</i>	12		5		0		0

^a Italic 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 I lies between that plane and the origin. The coordinates of the primed atoms are related to those given in Table I by $-x, 1/2 + y, 1/2 - z$. The direction cosines ($\times 10^4$), *q*, are with respect to orthogonal axes. *D* is the distance (in Å) from the plane to the origin. The rms of the italic deviations ($\text{Å} \times 10^3$) from the plane is *δ*.

The two nonequivalent six-membered $\overline{\text{CuSCCC-N}}$ rings have dissimilar conformations, as can best be seen by examining the displacements of the atoms not used to define the planes described in Table V. Specifically, the Cu(I) ion lies 0.04 Å from the plane of one coordinating pyridyl ring and 0.54 Å from the plane of the other, as can easily be seen in the figures. The Cu(1)-N(10) distance, corresponding to the near-planar contact in plane 2 of Table V, is slightly shorter (by 0.014 Å) than the Cu(1)-N(9) distance, perhaps because the planar conformation is more suitable for *π* back-bonding. The atoms of the pyridine rings are nearly planar, exhibiting rms deviations of 0.012 and 0.005 Å from the best least-squares plane. The C-S bond lengths are also normal,³⁹ averaging 1.828 Å. The perchlorate group is very regular with bond lengths averaging 1.431 Å (see Table III), in excellent agreement with the value (1.43 Å) reported in bis(*m*-xylene)silver perchlorate.⁴⁴ The O-Cl-O angles are all quite close to the regular tetrahedral value, ranging from 108.0 to 110.4°.

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Supplementary Material Available. A listing of structure factor amplitudes for [CuL]_n(ClO₄)_n 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, 20X 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.,

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Cyclomer Complexes. II. Crystal Structure of a 2:1 Octahydrate Complex of 1,4,7,10-Tetraoxacyclododecane with Sodium Hydroxide

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The crystal structure of the complex $\text{NaOH} \cdot 2\text{C}_8\text{H}_{16}\text{O}_4 \cdot 8\text{H}_2\text{O}$, where $\text{C}_8\text{H}_{16}\text{O}_4$ is 1,4,7,10-tetraoxacyclododecane, has been determined by a single-crystal three-dimensional X-ray diffraction study. This substance crystallizes in space group *Pbcn*, with lattice constants $a = 14.794 \pm 0.004$, $b = 15.845 \pm 0.004$, and $c = 23.960 \pm 0.006$ Å ($Z = 8$). The intensities of 4781 unique reflections were measured on a Picker four-circle diffractometer (θ - 2θ scan, Cu K α radiation) and the structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement of the coordinates and anisotropic temperature factors of the Na, O, and C atoms converged at a final $R_1 = 6.6\%$ for 2926 reflections above background. The methylene hydrogens were located but their positions were not refined. The sodium ion forms an eight-coordinated sandwich complex of approximate D_4 symmetry with two polyether rings, each of which manifests approximate C_4 symmetry. The oxygen atoms are arranged at the corners of a square antiprism at an average Na-O distance of 2.485 Å. The hydroxide ion is associated with the water molecules to form infinite sheets of linked four- and five-membered rings extending in planes perpendicular to the c axis.

Introduction

Crystallographic investigations of 1,4,7,10-tetraoxacyclododecane complexes with alkali halide salts have revealed some novel structural properties.² In these compounds, species of D_4 symmetry are formed, where the oxygen atoms of two cyclomer molecules occupy the vertices of a square antiprism centered on the cation. These units form organic layers through the crystal, while the halide ions are associated with water molecules in infinite two-dimensional hydrogen-bonded networks. These aqueous layers have an interesting structure based on six-membered rings. As a result of this organization of the crystal lattice the positive and negative ions are completely separated.

The discovery of these structures raised the question of whether the basic D_4 unit and the presence of discrete, alternating aqueous and organic strata might be unique to the alkali halide complexes $\text{MX} \cdot 2\text{C}_8\text{H}_{16}\text{O}_4 \cdot 5\text{H}_2\text{O}$ or occur generally in a broader class of compounds. The preparation of a crystalline complex of 1,4,7,10-tetraoxacyclododecane with NaOH afforded an opportunity to explore this question further and to extend our knowledge of the structural systematics of cyclomer chelates with alkali ions as applied to a chemical of major industrial significance. We report here a three-dimensional X-ray diffraction study of $\text{NaOH} \cdot 2\text{C}_8\text{H}_{16}\text{O}_4 \cdot 8\text{H}_2\text{O}$ which establishes that the structural principles of the alkali halide series are effectively retained in the caustic complex. However, as might be expected from the differences in stoichiometry, the detailed arrangement of atoms within the hydrogen-bonded aqueous layer is fundamentally dissimilar in the caustic structure and is in fact based on five-membered rings.

Experimental Section

Crystals of $\text{NaOH} \cdot 2\text{C}_8\text{H}_{16}\text{O}_4 \cdot 8\text{H}_2\text{O}$ are readily obtained by cool-

(1) The crystallographic work was carried out by F. P. Boer, M. A. Neuman, and F. P. van Remoortere; E. C. Steiner synthesized the complex.

(2) (a) F. P. van Remoortere and F. P. Boer, *Inorg. Chem.*, **13**, 2071 (1974); (b) H. W. Rinn, E. C. Steiner, and F. P. Boer, unpublished results.

ing slightly a saturated aqueous solution of NaOH, to which 2 equiv of cyclomer had been added. The crystals are colorless rectangular prisms, elongated markedly along the b axis and flattened along a .

A crystal of dimensions $0.12 \times 0.50 \times 0.20$ mm (along a , b , and c , respectively) was selected and mounted in a 0.3-mm diameter thin-walled glass capillary with the b axis of the crystal approximately parallel to the capillary axis. The crystal was then aligned and examined by photographic methods on a Weissenberg goniometer to determine the space group and preliminary lattice constants. The reciprocal lattice symmetry D_{2h} and the reflection conditions $0kl$ ($k = 2n$), $h0l$ ($l = 2n$), and $hk0$ ($h + k = 2n$) recorded on the $h0l$ and $h1l$ Weissenberg levels establish the space group uniquely as *Pbcn* (No. 60, D_{2h}^{14}). The crystal was then carefully centered on a Picker four-circle goniostat, and the dimensions of the orthorhombic cell were calculated by least-squares refinement of the setting angles of 11 reflections with Cu K α radiation (λ 1.5418 Å). The lattice parameters $a = 14.794 \pm 0.004$, $b = 15.845 \pm 0.004$, and $c = 23.960 \pm 0.006$ Å (at 25°) are consistent with a calculated density of 1.232 g cm^{-3} for mol wt 536.55 and $Z = 8$. The estimated standard deviations of the lattice constants, as computed in the least-squares analysis, were a factor of 10 better than the errors assigned above, which reflect our experience with systematic errors and reproducibility of results under different experimental conditions. The presence of 8 formula units/unit cell does not impose any requirements on the symmetry of the complex.

Intensity data were gathered using the θ - 2θ scan mode of the diffractometer with Ni-filtered Cu K α radiation. The takeoff angle of the tube was 3° , and a counter aperture 6.0×6.0 mm was placed 30 cm from the crystal; 1.5 mm diameter incident- and exit-beam collimators were used to restrict stray radiation. The scan speed was $2^\circ/\text{min}$ over 2θ angles of $2^\circ + \Delta$, where Δ is the separation of the K α doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Two stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. Attenuators were used to prevent the count rate from exceeding 12,000/sec. The reciprocal lattice was recorded to near the instrumental limit ($\sin \theta = 0.906$) and a total of 4781 independent reflections was measured. A test reflection (614) monitored after every 50 measurements showed fair stability; the root-mean-square deviation in intensity was 1.5% and some measurements deviated by as much as 4%. An error $\sigma(I) = [(0.02I)^2 + N_o + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Here N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities corrected for Lorentz and polarization effects. The 1852 reflections for which