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Supplementary Material Available: Listing of the structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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(18) This discussion about the various data sets is included to show the general degree of reliability of the intensity data.

The Novel Crystal and Molecular Structure of Bis[bis(2-pyridyl) disulfide]copper(I) Perchlorate

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Abstract: The structure of bis[bis(2-pyridyl) disulfide]copper(I) perchlorate, $[\mathrm{Cu(C_{10}H_8N_2S_2)_2}]\mathrm{ClO_4}$, has been determined by single-crystal x-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional R index of 0.051. The yellow crystals form as needles in the space group $P\bar{1}$ with a = 13.898, b = 21.867, c = 8.278 Å, α = 92.78, β = 100.79, γ = 84.37°, and Z = 4. The structure contains both isolated mononuclear complexed cations, $\mathrm{CuL_2}^+$, and polynuclear cationic polymers, $\mathrm{Cu}_n\mathrm{L}_{2n}{}^{n+}$. In each case, Cu(I) is tetrahedrally coordinated by two ligands. One ligand coordinates through its two pyridyl nitrogen atoms to form a seven-membered chelate ring ($\overline{\mathrm{SCNCuNCS}}$) in the mononuclear species and a bridge between two Cu(I) ions in $\mathrm{Cu}_n\mathrm{L}_{2n}{}^{n+}$. The disulfide groups of this kind of ligand do not participate in coordination. The second ligand at each Cu(I) coordinates through one pyridyl nitrogen and the more distant sulfur atom, forming a five-membered chelate ring ($\overline{\mathrm{CNCuSS}}$); the remaining pyridine ring of this kind of ligand does not coordinate. Two independent times, then, the coordination geometry $\mathrm{N_3S}$ has occurred, which might be similar to that of Cu(I) at the ESR-inactive Cu site in ceruloplasmin and in the fungal laccases. Three of the S–S bonds in the four nonequivalent ligand molecules are approximately equal, averaging to 2.028 Å, somewhat longer than the 2.016 Å found in the structure of the uncoordinated ligand. The fourth S–S bond is significantly longer, 2.047 Å, and has occurred because the seven-membered chelate ring, of which it is a part, requires that the C–C–S–S and N–C–S–S torsion angles deviate widely from near 0 or 180°. The C–S–S–C torsion angles range within 9° of 90° and neither these angles nor coordination of sulfur to Cu(I) appears to affect the observed S–S bond lengths. Cu(I)–S distances average 2.42 Å in length, and Cu(I)–N averages to 2.024 Å. Coordination angles at Cu(I) range from 88.1 to 137.8°. Several times, whenever coordination requirements permit, a close intraligand C–H . . . S approach occurs (C . . . S = 3.2 Å), which could have been readily avoided, without changing the pattern of π interactions in the ligand, by a ring rotation of 180° about the C–S bond. This supports the existence of an energetically favorable C–H . . . S interaction. One sulfur atom of each uncoordinated disulfide group participates in a close charge-transfer interaction with the plane of a pyridine ring at distances of 3.31 and 3.37 Å, respectively. One or two water molecules are present per unit cell.

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 more detailed introduction can be found in the reports of previous structures determined in this laboratory, particularly 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, $[\mathrm{Cu(RSSR)}]_2(\mathrm{BF_4})_2$. More recently, the crystal structure of another Cu(I) disulfide complex, {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate,[3] was determined. In both Cu(I) complexes, the Cu(I)–S coordination bonds are particularly short, 2.30 and 2.32 Å, respectively, and the corresponding S–S distances are long, approximately 2.08 Å in both structures; this is consistent with a π back-bonding scheme from Cu(I) to the disulfide group.[3]

A π interaction occurring between a metal ion and the disulfide group might be modified if the sulfur atoms participated in additional π interactions with the R groups in the R–S–S–R ligand itself. In the previous disulfide transition metal complexes which have been studied crystallographically, those of Ni(II),[1,4,5] Fe(III),[6] Cu(II) (the Cu–S distance is very long),[7] and Cu(I),[2,3,8] the carbon atoms bonded to sulfur are saturated in all cases except one. In that structure, that of chloro(bis{2-[(2-pyridylmethyl)imino]phenyl} disulfide)nickel(II) perchlorate,[4] the S–S bond was particularly long, 2.089 (8) Å, for reasons which did not appear to involve back-bonding from the metal ion. To further investigate the effect of unsaturation of the R group (at the carbon atom bound to the disulfide group) upon the coordination bond between sulfur and a metal ion (one with which a back-bonding interaction is possible), complexes of the ligand bis(2-pyridyl) disulfide were prepared with Cu(I), and, in addition, with Hg(II)[9] and Co(II).[10] The crystal structures were determined to learn which groups participate in coordination and the effect of coordination on the geometry of the ligand. In this case, the S-S bond length and the C-S-S-C torsion angle, where each sulfur atom is bonded directly to an unsaturated carbon atom, were of interest. The structure of the ligand itself has been determined[11] for comparison. A preliminary report of the structure of the Cu(I) complex was made.[12]

It has recently been reported that the oxidized form of the two-electron copper oxidase ceruloplasmin, present in the α_2-globulin fraction of mammalian blood serum, has Cu(I)-complexed RSSR at its two-copper site.[13] 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. It is plausible to believe that only one disulfide group coordinates to Cu(I) in the protein so that the ion is strongly held by three other ligand atoms, which can serve to maintain the integrity of the Cu(I) site through successive cycles of disulfide reduction and oxidation. The previously reported Cu(I) complexes of organic disulfides[2,3,8] all have two disulfide groups coordinated to each Cu(I). The stoichiometry of the bis(2-pyridyl) disulfide complex, CuL_2ClO_4, provides the usually four-coordinate tetrahedral Cu(I) ion with four nitrogen and four sulfur atoms as potential donors and could allow other coordination compositions to occur. The hope that a coordination stoichiometry like that of Cu(I) in ceruloplasmin would occur in this complex contributed to the decision to determine its structure.

Experimental Section

Preparation. Cupric perchlorate and cupric tetrafluoroborate, hydrated, were obtained from G. Frederick Smith Chemical Co. and Research Organic/Inorganic Chemical Corp., respectively, and bis(2-pyridyl) disulfide was purchased from Aldrich Chemical Co. All other chemicals were of reagent grade quality. The laser Raman (excitation at 5145 Å), ultraviolet, and infrared spectra were obtained using Cary 82, Cary 14, and Beckman IR-10 spectrometers, respectively. Elemental analyses were performed by Galbraith Laboratories.

Preparation of Salts of Bis[bis(2-pyridyl) disulfide]copper(I). a. Perchlorate Salt. A 1.56-g (0.0045 mol) sample of cupric perchlorate, hydrated, was dissolved in 90 ml of methanol. The solution was filtered. To the filtrate was added 110 ml of a methanol solution containing 0.0135 mol of free ligand, bis(2-pyridyl) disulfide. The initially blue solution gradually became yellow as it was allowed to stand open to the atmosphere. Overnight, clusters of yellow needles formed which were isolated by filtration, washed with methanol and ether, and vacuum dried at room temperature.

Anal. Calcd for $CuC_{20}H_{16}N_4S_4ClO_4$: Cu, 10.53; C, 39.80; H, 2.67; S, 21.25; Cl, 5.87. Found: Cu, 10.60; C, 39.80; H, 2.50; S, 21.38; Cl, 6.08.

b. Tetrafluoroborate Salt. The tetrafluoroborate salt was similarly prepared, following the procedures described above. Cupric tetrafluoroborate, hydrated (0.52 g, 0.0015 mol), was reacted with bis(2-pyridyl) disulfide (0.99 g, 0.0045 mol) in 70 ml of methanol. The yellow-green solution stood at room temperature for 3 days without precipitating the salt. The volume of the solution was subsequently reduced to approximately 25 ml and the resulting solution was allowed to stand at room temperature for 12-18 h. The solution became bright yellow; however, it failed to precipitate the tetrafluoroborate salt. By diluting the solution with methanol, adding ether until the cloud point, and allowing the resulting solution to stand in the refrigerator for 9 h, the salt was finally crystallized as yellow plates. The crystals, which were filtered, washed with ethanol and ether, and dried under vacuum at room temperature, decompose upon exposure to the atmosphere.

Anal. Calcd for $CuC_{20}H_{16}N_4S_4BF_4$: Cu, 10.75; C, 40.64; H, 2.73; S, 21.70; F, 12.86. Found: Cu, 10.98; C, 40.12; H, 2.49; S, 21.68; F, 12.54.

Spectroscopic Data. The shift of the infrared ν(C=C) and ν(C=N) stretches to higher frequency in pyridine complexes has been extensively used as an indicator of pyridine coordination.[2,3,9,10,14] In the infrared spectrum of bis[bis(2-pyridyl) disulfide]copper(I) perchlorate (in a Nujol mull), such shifts are observed. Four ν(C=C) and ν(C=N) bands at 1563, 1552, 1440, and 1412 cm^{-1} in the uncomplexed ligand are shifted to 1578, 1550, 1440-1453, and 1410 cm^{-1}, respectively, in the Cu(I) complex. These stretches appear as strong bands with unresolved shoulders. Three ring breathing modes which occur at 1005, 997, and 978 cm^{-1} suggest the presence of both coordinated and uncoordinated pyridine groups in the complex;[14] the lowest frequency band is almost identical with that of the free ligand (980 cm^{-1}).

An intense band is observed at 536 cm^{-1} with a shoulder of medium intensity at 530 cm^{-1} in the Raman spectrum. While the specific assignments of these bands are not unequivocal, they do fall within the ν(S-S) region (520-540 cm^{-1}) of diaryl disulfides[15,16] and represent a shift of 17-22 cm^{-1} to lower energy relative to that of the free ligand. These shifts are believed to be due in part to the shifts in electron density associated with coordination and incorporation into chelate rings.

The electronic absorption spectrum of a Nujol mull of this Cu(I) salt exhibits intense bands at 238 and 282 mμ with a shoulder centered at 335 mμ. The first two bands are due to the pyridine chromophore and are substantially shifted to longer wavelength relative to the corresponding bands of the free ligand (λ_{max} 228 and 272 mμ), thus supporting the infrared data for pyridine coordination. The 335-mμ absorption accounts for the yellow color of the complex and could be due either to charge transfer between Cu(I) and the disulfide moiety or to a significantly red-shifted disulfide absorption.[2,3] A disulfide group could be perturbed directly by coordination[17,18] to Cu(I) or indirectly by σ inductive effects, or by changes in its geometry required by complexation,[19,20] causing a significant bathochromic effect to be observed in the disulfide absorption.

It is not clear to which (one or more) of the four nonequivalent ligands observed crystallographically in the Cu(I) complex, or to which structural feature involving the ligand(s), the 335-mμ absorption band should be assigned. However, the similarity of this band to the 330-340-mμ band associated with a Cu(I) disulfide site in the oxidized form of ceruloplasmin[13] and some laccases[21] suggests a structural similarity between this complex and the Cu(I) disulfide chromophore. Unassigned red-shifts were also observed for the complexes {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate (λ_{max} 290 mμ)[3] and *cyclo*-di-μ-{bis[2-(*N*,*N*-dimethylamino)ethyl] disulfide}dicopper(I) tetrafluoroborate (λ_{max} 293 mμ),[2] in which the Cu(I) environment is N_2S_2.

Similar shoulders appear in the uv spectra of the Hg(II) and Co(II) complexes of the same ligand at 305 and 325 mμ, respectively. These red-shifted bands must result from indirect orbital perturbation because the disulfide group does not coordinate to either Hg(II) or Co(II).

The infrared, Raman, and electronic absorption spectra of the tetrafluoroborate salt of the Cu(I) complex are essentially identical with those of the perchlorate salt, except for the anion absorptions.

Diffraction Data. A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($K\alpha_1$, λ 0.70930; $K\alpha_2$, λ 0.71359 Å) and with a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 16° using $\bar{\lambda}$ (0.71073 Å). They are a = 13.898 (12), b = 21.867 (16), c = 8.278 (4) Å, α = 92.78 (5), β = 100.79 (6), and γ = 84.37 (6)°. Other crystal data are V = 2458 (3) Å^3, mol wt 603.6, d_{obsd} (flotation) = 1.666 (10) g cm^{-3}, d_{calcd} = 1.643 (2) g cm^{-3}, Z = 4, and $F(000)$ = 1224, assuming one water molecule per unit cell, as is indicated crystallographically. The figures in parentheses are estimated standard deviations in units of the least significant digit given for the corresponding parameter.

A single crystal of $Cu(C_{10}H_8N_2S_2)_2ClO_4$ of extreme dimensions 0.11 × 0.15 × 0.44 mm was used to collect diffraction intensities by the θ-2θ scan technique with a scan rate (ω) in 2θ of 1° min^{-1}. The

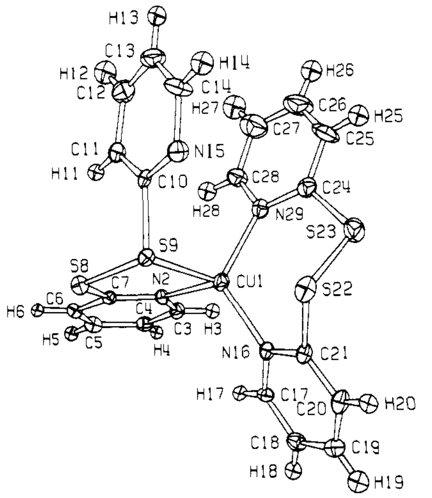

Figure 1. The molecular structure of the $[Cu(C_{10}H_8N_2S_2)_2]^+$ ion. The perchlorate group has been omitted. Ellipsoids of 15% probability are shown.[32]

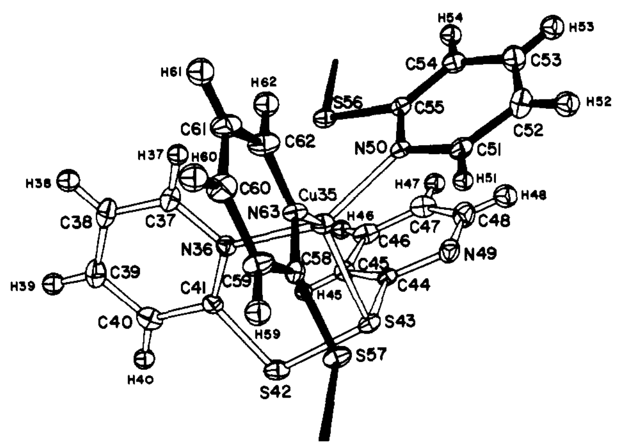

Figure 3. Partial structure of the polymeric complex, $[Cu_n(C_{10}H_8N_2S_2)_{2n}]^{n+}$ with two half bridging ligand molecules, which are blackened in this figure. The perchlorate group has been omitted. Ellipsoids of 15% probability are used.[32]

scan range varied from 2.0° at low 2θ to 2.3° at 45°. The total background counting time, equal to the scan time, was equally spent at each end of the scan. The temperature was maintained between 22 and 23° throughout. The intensities of three check reflections, which were remeasured after every 100 reflections, showed a small average decrease in intensity of 1%, for which the appropriate "decay" correction was applied. An absorption correction was applied[22] which approximated the crystal shape by a 6 × 6 × 6 grid;[23] μ = 13.9 cm^{-1} and the calculated transmission factors ranged from 0.895 to 0.942.

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

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

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 $I = \omega(CT - B_1 - B_2)$. 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 6550 symmetry-independent reflections measured, those for which $2\theta < 45°$, 3079 had intensities larger than three times their corresponding standard deviations. These were regarded as observed reflections and only these were used in further calculations. The intensities were corrected for Lorentz and polarization effects.[24] The monochromator crystal was assumed to be half perfect and half mosaic in character in the polarization correction.

Structure Determination. The cuprous ion positions were learned from an initial three-dimensional Patterson function. With the exception of two oxygen atoms, O(66) and O(68) of a perchlorate group, the positions of all other nonhydrogen atoms were found by successive cycles of Fourier refinement using the fast-Fourier algorithm.[25] The two perchlorate oxygen positions were subsequently calculated assuming that the anion was tetrahedral. Hydrogen atom positions were calculated[26] assuming C–H distances[27] of 0.95 Å. Full-matrix least-squares refinement[28] with anisotropic thermal parameters for nonhydrogen atoms led to the error indices $R_1 = \Sigma|F_o - F_c||/\Sigma F_o = 0.057$ and $R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.052$. The hydrogen atoms were not refined. At this stage, an oxygen atom of a water molecule was discovered on a difference Fourier function. The atom was isotropically refined to the final error indices, $R_1 = 0.051$ and $R_2 = 0.042$ as its occupancy factor refined to 0.57.

The "goodness-of-fit", $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 1.46. The number of observations (3079) is m, and s, the number of parameters (746), is rather large. The overdetermination ratio (m/s) is 4.1. in the final cycles of least-squares refinement, all shifts in atomic parameters for nonhydrogen atoms, excluding atoms of the perchlorate ions, were less than 19% of their esd's and the largest shift in a thermal parameter was 37% its esd. The largest peak on the final difference Fourier function, whose esd was calculated to be 0.1 eÅ^{-3}, was 0.6 eÅ^{-3} in height and was located very close to a perchlorate group.

The atomic scattering factors of Doyle and Turner[29] were used for Cu^+, Cl^0, S^0, O^0, N^0, and C^0. The first three were modified to include the anomalous dispersion correction.[30] The atomic scattering factors of Stewart et al.[31] were used for hydrogen.

The positional and thermal parameters of the nonhydrogen atoms are presented in Table I and those assigned to hydrogen are in Table II.

Discussion

The structure is surprisingly varied. It contains both mononuclear complexed CuL_2^+ cations, as shown in Figures 1 and 2, where L is bis(2-pyridyl) disulfide; and polynuclear polymeric $Cu_nL_{2n}^{n+}$ complexed cations which are shown in Fig-

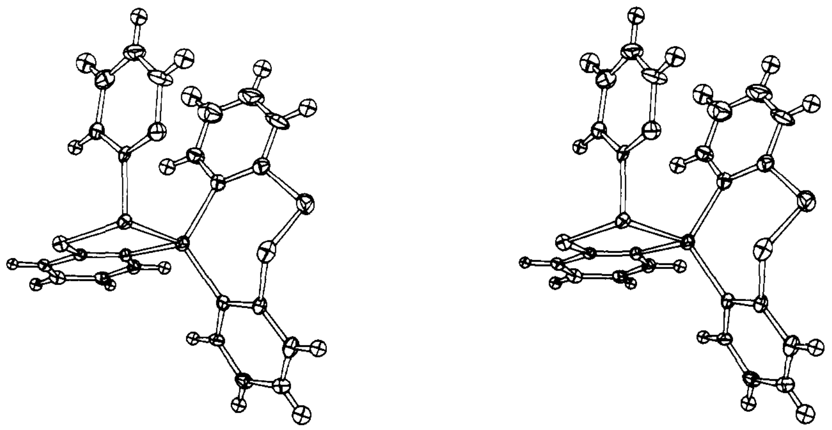

Figure 2. A stereoview of the $[Cu(C_{10}H_8N_2S_2)_2]^+$ ion showing ellipsoids of 15% probability.[32]

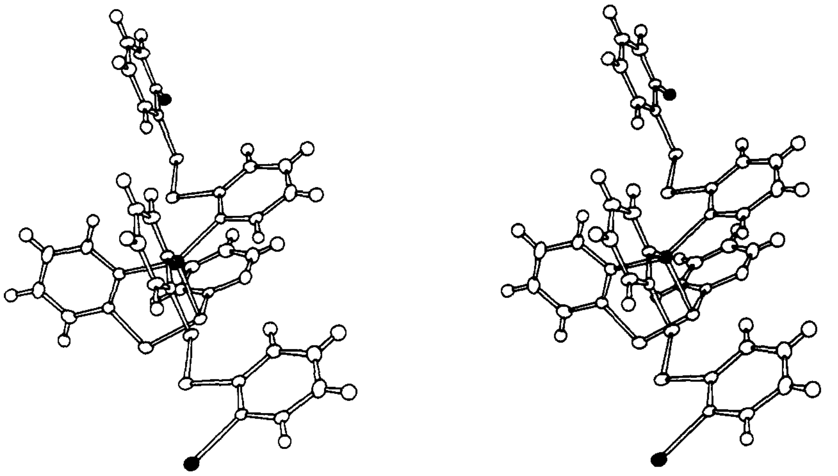

Figure 4. A stereoview of a section of the polymeric chain showing two complete bridging ligands. The Cu(l) ions are blacken probability are shown.[32]

ures 3 and 4. In both cases, Cu(I) is coordinated tetrahedrally by three nitrogen atoms and one sulfur atom.

One of the ligands on each cation coordinates through one pyridyl nitrogen atom and the more distant sulfur atom to form a five-membered $\overline{\text{CNCuSS}}$ ring; the remaining pyridyl group in each of these two ligands does not coordinate. In $CuL_2{}^+$, the second ligand coordinates through its two pyridyl nitrogen atoms to form a seven-membered $\overline{\text{SCNCuNCS}}$ ring, and neither sulfur atom coordinates. However, in $Cu_nL_{2n}{}^{n+}$, the Cu(I) ions are bridged by ligands which coordinate through their pyridyl nitrogens; each Cu(I) is coordinated by one-half of each of two bridging ligand molecules. The sulfur atoms in this bridging ligand do not coordinate.

Each of the four nonequivalent ligands coordinates through only two of its potential donor atoms. The chemical considerations which govern the selection of coordinating atoms are not clear. It appears that N_3S coordination is preferred by Cu(I) with bis(2-pyridyl) disulfide for intramolecular thermodynamic reasons, not involving crystal packing considerations, because this unusual selection is made two independent times involving relatively different intracrystalline environments in this structure. In the mononuclear cation, both ligands might have coordinated through two nitrogen atoms to give an N_4 coordination sphere, or both through one nitrogen and one sulfur atom to give N_2S_2 coordination, depending upon which coordination mode for a single ligand is of lower energy. For chemical or steric reasons, neither of these coordination situations has occurred. An analogous discussion could be made for the polynuclear complexed cation.

It has been reported that a Cu(I) complex of an organic disulfide group exists at the ESR-inactive copper site of ceruloplasmin[13] in its oxidized (resting) state. If that site is to survive alternate cycles of oxidation and reduction, it is reasonable to expect that each Cu(I) is bound to only one disulfide group. Accordingly, the N_3S coordination geometry which has occurred in this crystal may be similar to that in ceruloplasmin and may have occurred in both places because of its thermodynamic stability.

It is surprising to note that the S–S bond lengths in this complex (see Table III) as well as in others (presented in Table IV) do not depend upon whether coordination to a metal ion has occurred. The Cu(I)–S distances (Table III) averaging 2.42 Å in length are appreciably longer than those averaging 2.32 Å in {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate[3] and 2.30 Å in *cyclo*-di-*μ*-{bis[2-(*N*,*N*-dimethylamino)ethyl] disulfide}dicopper(I) tetrafluoroborate,[2] where S–S bond lengthenings of approximately 0.04 Å were observed upon complexation. Table V indicates that the values of the Cu–S–S–C torsion angles correlate with the Cu(I)–S bond length. The C–S–S–C torsion angle, on the other hand, is rather constant in all four ligand molecules, remaining within 9° of 90° (Table III), and does not correlate (see Table IV) with the observed S–S bond lengths.

The S–S bond length does increase by a small amount upon complexation, whether or not sulfur participates in coordination, from 2.016 Å, the value in the free ligand,[11] to 2.030 (2), 2.026 (4), 2.032 (4), and 2.025 (4) Å, averaging 2.028 (3) Å, in those ligands of Table IV which do not form a seven-membered chelate ring. When such a ring does occur, once in the structure of the Co(II)[10] complex of this ligand and again in one ligand molecule of this work, longer S–S distances averaging 2.043 (3) Å are found. This is apparently related to the large deviations of the C–C–S–S and N–C–S–S angles from 0 to 180°, as required by the seven-membered ring (see Table IV). A similar seven-membered ring is found in diiodo-(*N*,*N*,*N*′,*N*′-tetramethylthiuram disulfide)mercury(II),[34] but its longer bond lengths do not require its S–C–S–S torsion angles to be far from 0°—they are 5.2 and 3.5°—and the S–S bond length, 2.03 (1) Å, is close to the corresponding average value of 2.028 (3) Å discussed earlier in this paragraph.

As can be seen in Table VI, the eight independent pyridine rings are each nearly planar and a Cu(I) cation lies within a few tenths of an ångstrom of each of the six coordinating pyridyl planes. The bond lengths and angles in the rings are presented in Table III and are in agreement with previous results.[9-11]

The Cu(I)–N distances (Table III) average 2.024 Å in length, in agreement with the corresponding value, also involving pyridyl nitrogen atoms, observed in {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate.[3]

The angles at Cu(I) range widely (Table III) from 89.6 to 118.5° about Cu(1) and from 88.1 to 137.8° at Cu(35). Ranges of 15[3] and 34°[2] had been found in other Cu(I) complexes in this laboratory. The smallest angles for each Cu(I) are the internal angles of the five-membered chelate ring.

In this structure, disulfide coordination to Cu(I) is observed two independent times, in contrast to the results observed with the same ligand and Hg(II)[9] or Co(II),[10] where the disulfide group does not coordinate at all. The complex between this ligand and Cu(I) is stable enough to allow it to be readily isolated from solution with the counterions $ClO_4{}^-$ or $BF_4{}^-$ Hg(II) and Co(II) complexes could not be isolated at all under similar conditions; in both cases, the addition of chloride, which coordinates to the cation, was required as a last step in their preparation. It appears, then, that the ability of the disulfide group to coordinate to Cu(I) in the five-membered chelate ring

Table I. Fractional Atomic Coordinates (× 10^4) and Thermal Parameters (× 10^4) for Nonhydrogen Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A. Mononuclear Cation, CuL_2^+									
Cu(1)	1668 (1)	1507 (1)	6975 (2)	43 (1)	25 (0)	180 (3)	−8 (1)	19 (1)	−6 (1)
N(2)	496 (9)	1132 (5)	5525 (15)	37 (9)	17 (4)	112 (27)	−9 (4)	12 (12)	3 (8)
C(3)	500 (11)	1000 (7)	3905 (22)	42 (12)	23 (5)	158 (38)	−7 (6)	7 (17)	−1 (11)
C(4)	−211 (13)	708 (7)	2882 (19)	69 (15)	19 (5)	130 (34)	2 (7)	34 (19)	9 (10)
C(5)	−991 (13)	535 (7)	3524 (21)	67 (14)	22 (5)	119 (35)	−8 (7)	−14 (18)	−2 (10)
C(6)	−1024 (11)	666 (7)	5144 (20)	52 (12)	16 (4)	129 (34)	−8 (6)	16 (16)	9 (10)
C(7)	−262 (11)	962 (7)	6094 (18)	34 (11)	15 (4)	126 (31)	−1 (6)	−3 (16)	7 (9)
S(8)	−302 (2)	1039 (1)	8256 (4)	63 (2)	25 (1)	137 (6)	−15 (1)	33 (1)	−5 (2)
S(9)	832 (2)	1538 (1)	9264 (4)	42 (2)	21 (1)	118 (6)	−3 (1)	9 (3)	0 (2)
C(10)	300 (11)	2320 (7)	9226 (18)	27 (11)	27 (5)	78 (3)	−6 (6)	6 (14)	−8 (10)
C(11)	−564 (13)	2522 (9)	8285 (21)	44 (13)	27 (6)	195 (39)	−10 (7)	−8 (18)	3 (12)
C(12)	−808 (16)	3156 (13)	8465 (30)	72 (18)	37 (8)	318 (60)	15 (10)	16 (25)	45 (18)
C(13)	−293 (19)	3537 (10)	9416 (33)	88 (21)	25 (7)	365 (66)	19 (10)	21 (29)	−4 (17)
C(14)	508 (20)	3290 (10)	10273 (28)	135 (23)	16 (6)	350 (60)	−8 (9)	13 (30)	−22 (15)
N(15)	859 (10)	2669 (8)	10226 (18)	63 (12)	29 (5)	219 (35)	−6 (6)	−5 (16)	−11 (11)
N(16)	2886 (9)	942 (6)	7040 (16)	41 (10)	22 (4)	122 (26)	−10 (5)	10 (13)	−2 (8)
C(17)	2976 (13)	446 (8)	6065 (20)	59 (14)	14 (5)	183 (37)	−2 (6)	35 (18)	−5 (11)
C(18)	3823 (16)	62 (8)	6169 (22)	79 (16)	21 (5)	181 (39)	−15 (8)	8 (21)	−12 (11)
C(19)	4622 (14)	183 (9)	7339 (28)	73 (17)	24 (6)	310 (54)	1 (8)	37 (25)	11 (15)
C(20)	4556 (13)	698 (10)	8387 (20)	49 (14)	40 (7)	141 (37)	−9 (8)	−5 (18)	13 (13)
C(21)	3671 (14)	1062 (8)	8157 (20)	45 (13)	29 (5)	145 (36)	−8 (7)	57 (18)	5 (11)
S(22)	3519 (3)	1714 (2)	9527 (4)	66 (3)	46 (1)	140 (7)	−15 (2)	15 (3)	−33 (2)
S(23)	3669 (3)	2443 (2)	8163 (5)	87 (3)	38 (1)	322 (10)	−35 (2)	74 (5)	−53 (3)
C(24)	2478 (14)	2760 (10)	7100 (21)	72 (15)	31 (7)	186 (39)	−8 (8)	86 (20)	−22 (13)
C(25)	2362 (23)	3391 (11)	6823 (35)	183 (30)	16 (7)	459 (76)	−40 (11)	163 (38)	34 (17)
C(26)	1544 (27)	3638 (12)	5860 (41)	190 (37)	25 (9)	523 (92)	13 (14)	127 (47)	68 (22)
C(27)	827 (22)	3292 (14)	5295 (34)	184 (31)	40 (11)	425 (74)	15 (14)	138 (39)	32 (23)
C(28)	967 (17)	2680 (10)	5594 (26)	95 (19)	24 (6)	263 (50)	−10 (9)	48 (25)	21 (14)
N(29)	1741 (12)	2397 (7)	6478 (18)	57 (12)	29 (5)	169 (32)	−13 (7)	38 (16)	−5 (10)
B. Polynuclear Cation, $Cu_nL_{2n}^{n+}$									
Cu(35)	5897 (1)	3110 (1)	4990 (2)	60 (1)	18 (0)	114 (3)	−4 (1)	18 (1)	−2 (1)
N(36)	4755 (7)	2599 (5)	4237 (12)	50 (8)	16 (3)	133 (21)	−10 (4)	28 (10)	−1 (6)
C(37)	3877 (11)	2872 (6)	3408 (17)	43 (11)	27 (4)	201 (32)	0 (6)	5 (15)	−6 (9)
C(38)	3061 (11)	2572 (9)	2990 (18)	43 (11)	41 (6)	227 (35)	5 (7)	30 (15)	−16 (12)
C(39)	3086 (11)	1968 (9)	3358 (19)	52 (12)	38 (6)	189 (33)	−18 (7)	34 (16)	−32 (11)
C(40)	3947 (12)	1686 (6)	4159 (16)	90 (13)	22 (4)	142 (28)	−20 (7)	64 (16)	−14 (9)
C(41)	4758 (9)	2025 (6)	4617 (13)	56 (10)	22 (4)	81 (22)	−17 (5)	21 (12)	−5 (7)
S(42)	5823 (3)	1625 (1)	5809 (4)	82 (3)	16 (1)	163 (7)	−5 (1)	36 (4)	11 (2)
S(43)	6923 (2)	2160 (1)	5738 (4)	55 (2)	19 (1)	106 (6)	3 (1)	7 (3)	2 (2)
C(44)	7298 (10)	1970 (6)	3789 (15)	44 (10)	12 (3)	138 (26)	15 (5)	19 (13)	5 (8)
C(45)	6811 (9)	1602 (6)	2570 (17)	59 (10)	17 (4)	154 (28)	−5 (5)	25 (14)	−9 (8)
C(46)	7180 (13)	1550 (6)	1114 (17)	102 (14)	22 (4)	134 (31)	5 (6)	20 (17)	−15 (9)
C(47)	7961 (14)	1848 (8)	955 (20)	99 (15)	27 (5)	189 (35)	4 (7)	66 (19)	−4 (10)
C(48)	8411 (11)	2184 (7)	2229 (26)	54 (12)	32 (5)	346 (47)	11 (6)	69 (20)	17 (13)
N(49)	8096 (8)	2268 (5)	3726 (15)	47 (9)	25 (3)	230 (28)	7 (4)	29 (13)	3 (8)
N(50)	6766 (7)	3594 (4)	3966 (12)	42 (7)	13 (3)	95 (20)	4 (3)	6 (10)	3 (6)
C(51)	7406 (10)	3931 (6)	4955 (15)	61 (11)	26 (4)	99 (25)	−5 (6)	−11 (13)	10 (8)
C(52)	8095 (10)	4236 (7)	4414 (20)	55 (11)	36 (5)	206 (36)	−13 (6)	4 (16)	−17 (11)
C(53)	8107 (10)	4209 (7)	2743 (21)	63 (12)	30 (5)	242 (37)	−13 (6)	46 (17)	8 (11)
C(54)	7463 (11)	3870 (6)	1723 (15)	66 (11)	24 (4)	127 (27)	−3 (6)	25 (15)	5 (9)
C(55)	6809 (9)	3571 (5)	2374 (15)	46 (9)	19 (4)	114 (26)	7 (4)	30 (13)	12 (8)
S(56)	5914 (2)	3101 (1)	1279 (4)	68 (2)	21 (1)	90 (6)	−6 (1)	17 (3)	2 (2)
S(57)	6092 (2)	3108 (1)	8907 (3)	68 (2)	21 (1)	85 (6)	10 (1)	18 (3)	1 (2)
C(58)	5336 (8)	3738 (5)	8089 (15)	37 (8)	16 (3)	110 (25)	−6 (4)	16 (11)	−9 (7)
C(59)	4774 (10)	4156 (6)	8922 (14)	76 (11)	23 (4)	95 (25)	10 (6)	32 (14)	5 (8)
C(60)	4188 (10)	4622 (6)	8125 (19)	71 (12)	20 (4)	204 (33)	4 (5)	46 (16)	−9 (9)
C(61)	4168 (10)	4654 (6)	6434 (19)	82 (12)	15 (4)	199 (34)	3 (5)	17 (16)	16 (9)
C(62)	4740 (11)	4229 (7)	5666 (15)	94 (13)	23 (4)	92 (25)	0 (6)	27 (14)	3 (9)
N(63)	5299 (7)	3772 (4)	6454 (12)	57 (8)	16 (3)	98 (20)	1 (4)	9 (10)	15 (6)
C. Perchlorate Anions, ClO_4^-									
Cl(30)	2526 (2)	47 (1)	1229 (4)	43 (2)	21 (1)	157 (6)	−3 (1)	9 (3)	2 (2)
O(31)	1543 (8)	131 (5)	639 (18)	59 (9)	54 (4)	886 (52)	5 (5)	−27 (17)	34 (12)
O(32)	2999 (9)	−99 (5)	−126 (13)	234 (14)	45 (4)	326 (28)	−22 (6)	158 (17)	−9 (8)
O(33)	2771 (7)	−406 (4)	2269 (11)	152 (10)	29 (3)	214 (20)	−10 (4)	−23 (11)	36 (6)
O(34)	2883 (8)	580 (4)	1945 (12)	192 (12)	23 (3)	336 (25)	−24 (5)	−71 (14)	−36 (7)
Cl(64)	2456 (4)	4691 (2)	1531 (5)	95 (4)	32 (1)	182 (8)	−6 (2)	34 (5)	−3 (3)
O(65)	3339 (13)	4750 (16)	1916 (20)	133 (15)	303 (24)	398 (44)	−24 (16)	24 (22)	60 (25)
O(66)	2246 (15)	4433 (8)	64 (19)	415 (28)	119 (8)	504 (43)	−152 (13)	279 (29)	−183 (17)
O(67)	2120 (13)	4463 (7)	2772 (16)	375 (24)	94 (7)	374 (34)	−101 (10)	208 (24)	9 (12)
O(68)	2143 (19)	5245 (10)	1392 (22)	553 (41)	77 (8)	543 (52)	102 (14)	117 (34)	84 (17)

D. Oxygen Atom of the Water Molecule

Atom	x	y	z	B, Å^2	Occupancy
O(69)	93 (15)	4962 (9)	7508 (25)	15.3 (6)	0.57 (2)

[a] See Figures 1 and 3 for the identities of the atoms. The estimated standard deviation is in the units of the least significant figure given for the corresponding parameter. The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Calculated Fractional Atomic Coordinates ($\times 10^3$) and Assigned Thermal Parameters ($Å^2$)[a] for Hydrogen Atoms[b]

	Mononuclear cation, CuL_2^+					Polynuclear cation, $Cu_nL_{2n}^{n+}$			
	x	y	z	B		x	y	z	B
H(3)	103	112	346	3.5	H(37)	385	329	312	3.5
H(4)	−17	62	176	2.9	H(38)	247	278	244	4.5
H(5)	−150	33	285	3.5	H(39)	252	175	306	4.3
H(6)	−156	56	561	2.5	H(40)	399	126	440	4.0
H(11)	−97	226	757	3.8	H(45)	626	140	271	3.3
H(12)	−141	332	783	7.2	H(46)	688	130	22	4.2
H(13)	−49	396	948	4.6	H(47)	819	182	−6	5.0
H(14)	90	355	1101	6.2	H(48)	898	237	210	5.7
H(17)	242	35	526	3.2	H(51)	738	396	610	3.1
H(18)	386	−28	544	4.3	H(52)	855	446	516	4.7
H(19)	521	−8	744	6.0	H(53)	856	442	231	4.8
H(20)	509	80	922	4.3	H(54)	747	384	58	4.2
H(25)	286	364	732	5.8	H(59)	480	412	1007	3.8
H(26)	148	406	559	6.5	H(60)	381	491	869	4.4
H(27)	22	346	469	8.2	H(61)	376	497	582	4.5
H(28)	45	244	511	5.4	H(62)	473	427	452	4.5

[a] The temperature factors assigned to hydrogen atoms are equal to those of the carbon atoms, after isotropic refinement, to which they are bonded. [b] See Figures 1 and 3 for the identities of the atoms.

has contributed to the stability of this complex. Previous work has also indicated a particular ease in the isolation of Cu(I) complexes of organic disulfides.[2,3]

The pattern of variations and constancies in the seven molecular structures of bis(2-pyridyl) disulfide presented in Table IV can be interpreted in terms of π interactions involving all of the nonhydrogen atoms in the molecule. A very simplified model using only elementary atomic and molecular orbitals can qualitatively support the preferred torsion angles at C–S–S–C (90°) and C–C–S–S or N–C–S–S (0 or 180°), as well as the dependence of the S–S bond length on these latter torsion angles. Sulfur d orbitals are not used in this discussion because their contribution to C–S bonding has recently been shown to be quite unimportant.[35]

The disulfide bond tends to lie in the plane of each pyridine ring, so that each sulfur 3p lone pair can delocalize into the π^* orbitals of the nearest ring. This requires that the C–C–S–S and N–C–S–S torsion angles be near 0 or 180°. The p lone pairs on the two sulfur atoms are staggered, minimizing their unfavorable interaction and causing the C–S–S–C torsion angle to be near 90°.[19] Finally, the increase in the S–S bond length as each ring rotates away from coplanarity with the S–S bond is due to added repulsion between the sulfur lone pairs, whose ability to delocalize density into ring π^* is diminished. The C–S bonds should also lengthen under these conditions, perhaps by a smaller amount; no regular trend is observed (Table IV).

When the lowest energy conformation exists, each sulfur lone pair has a directional character which extends toward the nearest hydrogen atom of the more distant ring, as though to complete a SSCCH ring, in a 1,4 interaction.[36]

Of the eight independent pyridine rings, two do not coordinate to Cu(I) and their orientations are governed by other considerations. All eight rings participate in C–C–S–S torsion angles within 20° of 0 or 180°, with N–C–S–S angles approximately supplementary to these in each case. Within this constraint, the torsion angle near 0° (the cis arrangement about the C–S bond) could be C–C–S–S or N–C–S–S for the uncoordinated rings. In both cases, it is the C–C–S–S angle which is near 0°, even though this requires close C–H . . . S contacts (C . . . S = 3.23 and H . . . S = 2.8 Å in each case), which could have been readily avoided by a rotation of 180° about the C–S bond so that the 1,4 atoms would be S and N. In either case, the near coplanarity of the disulfide group and the ring is preserved. The same orientation is selected by the ordered ring in the structure of the free ligand,[11] the only other uncoordinated (ordered) ring in the structures presented in Table IV. These results support the suggestion by Scheraga et al.[36] that C–H . . . S interactions are energetically favorable.

In all three cases, the deviation of the C–C–S–S angles (17.8 and 8.3° in this work; 10.2° in the free ligand[11]) from 0° is in the same sense away from the lone pair of the more distant sulfur and toward the more distant ring. Even when coordination occurs, the C–C–S–S angles remain near 0° in the bridging ligands between Cu(I) ions (0.3 and 2.7°, this work) and in the ligand which bridges between Hg(II) ions[9] (12.7 and 16.9°). These deviations from 0° are all in the same sense as those observed in the uncoordinated rings. Apparently this occurs in order to lessen the C–H to sulfur-lone pair contact distances, which are approximately the same as those presented in the previous paragraph. For example, for the ligand which bridges between two Cu(I) ions, C(54) . . . S(57) = 3.23 and C(59) . . . S(56) = 3.19 Å; the corresponding H . . . S distances are 2.7 Å. For comparison, some relatively short van der Waals radii[36] are S = C = 1.7 and H = 1.2 Å.

The above argument would actually be somewhat stronger if sp^3-hybridized sulfur atoms were used and two lone pairs of electrons with directional character[37] were considered. This would be more consistent with the S–S–C angles, which average to 105.4°, closer to the tetrahedral angle than to 90°, in the Cu(I) complex. Presumably there is some s character and some directional character in the two lone pairs on sulfur, so that the angle between these symmetrically placed lone pairs is somewhere between the tetrahedral angle and 180°.[19] In that case, the observed deviations of the S–S–C–C angles from 0° are all in the only sense which decreases the 1,4 C–H to sulfur-lone pair interaction.

In the seven-membered chelate rings, the C–C–S–S torsion angles and their approximately supplementary N–C–S–S angles are far from equal (see the bottom of Table IV). The deviations of the carbon and sulfur atoms from plane 6 in Table VI also illustrate the asymmetry. The discrepancy is of the same order of magnitude in this Cu(I) complex (46°) as in the Co(II) complex[10] of this ligand (35°). Models indicate that a conformational energy maximum exists for the ligand coordinated through both pyridyl nitrogens so as to maintain its twofold axis, and that the observed deviations from such symmetry are reasonable. Packing effects may also be important.

At least one atom of each noncoordinating disulfide group participates in an unusually close contact with the plane of a pyridine ring. It can be noted in Figure 5 that one sulfur atom, S(22), of the uncoordinated disulfide group of the mononuclear

Table III. Molecular Dimensions and Esd's[a]

A. Bond Lengths, Å

Mononuclear cation, CuL_2^+				Polynuclear cation, $Cu_nL_{2n}^{n+}$			
Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
Cu(1)–S(9)	2.396 (3)	C(3)–C(4)	1.36 (2)	C(37)–C(38)	2.439 (3)	Cu(35)–S(43)	1.35 (2)
Cu(1)–N(2)	2.049 (12)	C(4)–C(5)	1.38 (2)	C(38)–C(39)	2.017 (10)	Cu(35)–N(36)	1.37 (3)
Cu(1)–N(16)	1.989 (13)	C(5)–C(6)	1.37 (2)	C(39)–C(40)	2.005 (9)	Cu(35)–N(50)	1.36 (2)
Cu(1)–N(29)	2.025 (15)	C(6)–C(7)	1.39 (2)	C(40)–C(41)	2.057 (10)	Cu(35)–N(63)	1.39 (2)
S(8)–S(9)	2.032 (4)	C(10)–C(11)	1.35 (2)	C(44)–C(45)	2.025 (4)	S(42)–S(43)	1.38 (2)
S(22)–S(23)	2.047 (5)	C(11)–C(12)	1.40 (3)	C(45)–C(46)	2.026 (4)	S(56)–S(57)	1.39 (2)
		C(12)–C(13)	1.29 (4)	C(46)–C(47)			1.35 (2)
S(8)–C(7)	1.800 (15)	C(13)–C(14)	1.29 (4)	C(47)–C(48)	1.793 (13)	S(42)–C(41)	1.35 (2)
S(9)–C(10)	1.795 (16)				1.804 (12)	S(43)–C(44)	
S(22)–C(21)	1.798 (17)	C(17)–C(18)	1.37 (3)	C(51)–C(52)	1.779 (12)	S(56)–C(55)	1.37 (2)
S(23)–C(24)	1.812 (19)	C(18)–C(19)	1.37 (3)	C(52)–C(53)	1.733 (11)	S(57)–C(58)	1.38 (2)
		C(19)–C(20)	1.39 (3)	C(53)–C(54)			1.36 (2)
N(2)–C(3)	1.36 (2)	C(20)–C(21)	1.38 (3)	C(54)–C(55)	1.38 (2)	N(36)–C(37)	1.37 (2)
N(2)–C(7)	1.32 (2)				1.31 (2)	N(36)–C(41)	
N(15)–C(10)	1.30 (2)	C(24)–C(25)	1.40 (3)	C(58)–C(59)	1.35 (2)	N(49)–C(44)	1.38 (2)
N(15)–C(14)	1.40 (3)	C(25)–C(26)	1.34 (4)	C(59)–C(60)	1.39 (2)	N(49)–C(48)	1.36 (2)
		C(26)–C(27)	1.31 (4)	C(60)–C(61)			1.40 (2)
N(16)–C(17)	1.33 (2)	C(27)–C(28)	1.36 (4)	C(61)–C(62)	1.34 (2)	N(50)–C(51)	1.37 (2)
N(16)–C(21)	1.33 (2)				1.33 (2)	N(50)–C(55)	
N(29)–C(24)	1.37 (2)	Cl(30)–O(31)[b]	1.36 (1)	Cl(64)–O(65)[b]	1.35 (2)	N(63)–C(58)	1.23 (2)
N(29)–C(28)	1.30 (3)	Cl(30)–O(32)	1.41 (1)	Cl(64)–O(66)	1.32 (2)	N(63)–C(62)	1.31 (2)
		Cl(30)–O(33)	1.41 (1)	Cl(64)–O(67)			1.34 (2)
		Cl(30)–O(34)	1.38 (1)	Cl(64)–O(68)			1.25 (2)

B. Bond Angles, deg

Mononuclear cation, CuL_2^+				Polynuclear cation, $Cu_nL_{2n}^{n+}$			
Atoms	Angle	Atoms	Angle	Atoms	Angle	Atoms	Angle
S(9)–Cu(1)–N(2)	89.6 (3)	C(4)–C(5)–C(6)	119.1 (15)	S(43)–Cu(35)–N(36)	88.1 (3)	C(38)–C(39)–C(40)	118.2 (14)
S(9)–Cu(1)–N(16)	118.5 (4)	C(5)–C(6)–C(7)	118.5 (15)	S(43)–Cu(35)–N(50)	103.4 (3)	C(39)–C(40)–C(41)	119.2 (13)
S(9)–Cu(1)–N(29)	105.4 (5)	C(6)–C(7)–N(2)	124.1 (14)	S(43)–Cu(35)–N(63)	130.0 (3)	C(40)–C(41)–N(36)	123.3 (12)
N(2)–Cu(1)–N(16)	110.5 (5)	C(7)–N(2)–C(3)	115.8 (12)	N(36)–Cu(35)–N(50)	137.8 (4)	C(41)–N(36)–C(37)	116.3 (11)
N(2)–Cu(1)–N(29)	112.5 (6)			N(36)–Cu(35)–N(63)	101.3 (4)		
N(16)–Cu(1)–N(29)	117.2 (6)	N(15)–C(10)–C(11)	124.2 (16)	N(50)–Cu(35)–N(63)	101.5 (4)	N(49)–C(44)–C(45)	127.1 (12)
		C(10)–C(11)–C(12)	113.7 (17)			C(44)–C(45)–C(46)	115.4 (12)
Cu(1)–S(9)–S(8)	99.1 (2)	C(11)–C(12)–C(13)	126.2 (21)	Cu(35)–S(43)–S(42)	97.4 (2)	C(45)–C(46)–C(47)	120.6 (14)
Cu(1)–S(9)–C(10)	100.9 (5)	C(12)–C(13)–C(14)	114.5 (23)	Cu(35)–S(43)–C(44)	98.7 (4)	C(46)–C(47)–C(48)	120.0 (16)
Cu(1)–N(2)–C(3)	120.3 (10)	C(13)–C(14)–N(15)	126.2 (22)	Cu(35)–N(36)–C(37)	119.6 (8)	C(47)–C(48)–N(49)	123.6 (14)
Cu(1)–N(2)–C(7)	123.7 (10)	C(14)–N(15)–C(10)	115.2 (16)	Cu(35)–N(36)–C(41)	123.8 (9)	C(48)–N(49)–C(44)	113.2 (11)
Cu(1)–N(16)–C(17)	125.1 (11)			Cu(35)–N(50)–C(51)	118.5 (8)		
Cu(1)–N(16)–C(21)	117.8 (11)	N(16)–C(17)–C(18)	123.3 (16)	Cu(35)–N(50)–C(55)	124.5 (8)	N(50)–C(51)–C(52)	123.7 (12)
Cu(1)–N(29)–C(28)	117.4 (14)	C(17)–C(18)–C(19)	119.2 (17)	Cu(35)–N(63)–C(62)	115.5 (9)	C(51)–C(52)–C(53)	117.7 (13)
Cu(1)–N(29)–C(24)	127.3 (12)	C(18)–C(19)–C(20)	119.2 (18)	Cu(35)–N(63)–C(58)	125.5 (8)	C(52)–C(53)–C(54)	119.3 (13)
		C(19)–C(20)–C(21)	116.9 (17)			C(53)–C(54)–C(55)	119.1 (13)
S(8)–S(9)–C(10)	104.6 (5)	C(20)–C(21)–N(16)	124.3 (16)	S(42)–S(43)–C(44)	105.3 (4)	C(54)–C(55)–N(50)	123.4 (11)
S(9)–S(8)–C(7)	105.7 (5)	C(21)–N(16)–C(17)	117.1 (14)	S(43)–S(42)–C(41)	104.3 (5)	C(55)–N(50)–C(51)	116.8 (10)
S(8)–C(7)–N(2)	120.6 (11)			S(42)–C(41)–N(36)	121.3 (8)		
S(8)–C(7)–C(6)	115.1 (11)	N(29)–C(24)–C(25)	120.6 (18)	S(42)–C(41)–C(40)	115.4 (10)	N(63)–C(58)–C(59)	121.3 (11)
S(9)–C(10)–N(15)	111.0 (12)	C(24)–C(25)–C(26)	119.9 (27)	S(43)–C(44)–N(49)	108.3 (9)	C(58)–C(59)–C(60)	120.9 (12)
S(9)–C(10)–C(11)	124.8 (12)	C(25)–C(26)–C(27)	119.2 (30)	S(43)–C(44)–C(45)	124.5 (10)	C(59)–C(60)–C(61)	117.0 (12)
		C(26)–C(27)–C(28)	118.9 (28)			C(60)–C(61)–C(62)	119.9 (13)
S(22)–S(23)–C(24)	110.9 (7)	C(27)–C(28)–N(29)	126.2 (23)	S(56)–S(57) –C(58)	104.8 (4)	C(61)–C(62)–N(63)	122.4 (12)
S(23)–S(22)–C(21)	103.3 (6)	C(28)–N(29)–C(24)	115.0 (17)	S(57)'–S(56)–C(55)	104.7 (4)	C(62)–N(63)–C(58)	118.5 (11)
S(22)–C(21)–N(16)	116.4 (12)			S(56)–C(55)–N(50)	110.0 (8)		
S(22)–C(21)–C(20)	119.1 (13)	O(31)–Cl(30)–O(32)[b]	107.6 (7)	S(56)–C(55)–C(54)	126.6 (10)	O(65)–Cl(64)–O(66)[b]	111.1 (18)
S(23)–C(24)–N(29)	122.0 (15)	O(31)–Cl(30)–O(33)	111.9 (6)	S(57)–C(58)–N(63)	112.0 (8)	O(65)–Cl(64)–O(67)	111.8 (17)
S(23)–C(24)–C(25)	117.2 (16)	O(31)–Cl(30)–O(34)	111.4 (7)	S(57)–C(58)–C(59)	126.7 (9)	O(65)–Cl(64)–O(68)	99.0 (18)
		O(32)–Cl(30)–O(33)	106.1 (6)			O(66)–Cl(64)–O(67)	118.6 (11)
N(2)–C(3)–C(4)	124.2 (15)	O(32)–Cl(30)–O(34)	106.4 (6)	N(36)–C(37)–C(38)	122.8 (14)	O(66)–Cl(64)–O(68)	106.5 (15)
C(3)–C(4)–C(5)	118.3 (15)	O(33)–Cl(30)–O(34)	113.1 (6)	C(37)–C(38)–C(39)	120.1 (14)	O(67)–Cl(64)–O(68)	108.9 (14)

C. Selected Torsion Angles, deg

Mononuclear cation, CuL_2^+				Polynuclear cation, $Cu_nL_{2n}^{n+}$			
Atoms	Angle	Atoms	Angle	Atoms	Angle	Atoms	Angle
C(7)–S(8)–S(9)–C(10)	92.4	N(15)–C(10)–S(9)–S(8)	162.3	C(41)–S(42)–S(43)–C(44)	81.1	N(49)–C(44)–S(43)–S(42)	174.2
C(21)–S(22)–S(23)–C(24)	93.3	N(16)–C(21)–S(22)–S(23)	81.2	C(55)–S(56)–S(57)–C(58)'	88.7	N(50)–C(55)–S(56)–S(57)'	179.3
C(6)–C(7)–S(8)–S(9)	175.9	N(29)–C(24)–S(23)–S(22)	36.1	C(40)–C(41)–S(42)–S(43)	165.9	N(63)–C(58)–S(57)–S(56)'	173.9
C(11)–C(10)–S(9)–S(8)	17.8	Cu(1)–S(9)–S(8)–C(7)	11.4	C(45)–C(44)–S(43)–S(42)	8.3	Cu(35)–S(43)–S(42)–C(41)	20.1
C(20)–C(21)–S(22)–S(23)	103.0	Cu(1)–N(2)–C(7)–S(8)	1.1	C(54)–C(55)–S(56)–S(57)'	0.3	Cu(35)–N(36)–C(41)–S(42)	2.4
C(25)–C(24)–S(23)–S(22)	148.7	Cu(1)–N(16)–C(21)–S(22)	1.9	C(59)–C(58)–S(57)–S(56)'	-2,7	Cu(35)–N(50)–C(55)–S(56)	4.8
N(2)–C(7)–S(8)–S(9)	9.7	Cu(1)–N(29)–C(24)–S(23)	14.1	N(36)–C(41)–S(42)–S(43)	15.0	Cu(35)–N(63)–C(58)–S(57)	7.9

[a] The esd is in the units of the least significant figure given for the corresponding parameter. The coordinates of the primed atoms related to those given in Table I by *x*, *y*, ±*z*. [b] The perchlorate anions are not associated with CuL_2^+ or $Cu_nL_{2n}^{n+}$ as their placement in this table suggests.

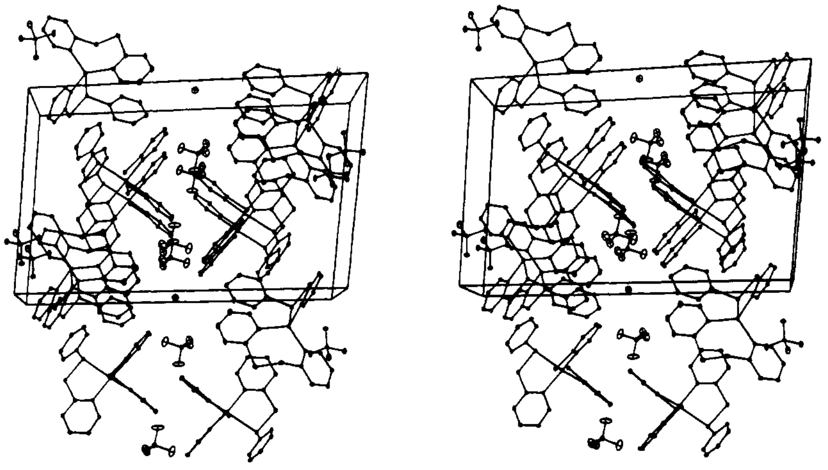

Figure 5. A stereoview of the packing of the complexed cations, perchlorate ions, and the oxygen atoms of H_2O molecules. Ellipsoids of 5% probability are used.[32] The view is approximately along the $+c$ direction, with $+a$ extending upward in the plane of the page and $+b$ horizontal toward the right.

Table IV. A Compilation of Selected Features of the Molecular Structure of Bis(2-pyridyl) Disulfide, L, from Seven Chemically Nonequivalent Crystallographic Determinations[a]

	L[b]	$CoLCl_2$[c]	$HgLCl_2$[d]	CuL_2^+, NN[e]	$Cu_nL_{2n}^{n+}$, NN[f]	CuL_2^+, NS[g]	$Cu_nL_{2n}^{n+}$, NS[h]
S–S	2.016 (2)	2.040 (2)	2.030 (2)	2.047 (5)	2.026 (4)	2.032 (4)	2.025 (4)
S–C, mean	1.785	1.774	1.778	1.805	1.756	1.798	1.799
C–N, mean	1.328	1.348	1.336	1.33	1.34	1.36	1.36
C–C, mean	1.368	1.373	1.381	1.36	1.38	1.35	1.37
SSC, mean	105.7	105.4	105.0	106.9	104.8	105.2	104.8
SCN, mean	110.5	119.2	111.7	119.2	111.0	115.8	114.8
SCC, mean	125.6	118.8	125.3	118.2	126.6	120.0	120.0
CSSC	87.1 (1)	102.2 (3)	93.7 (3)	93.3 (8)	88.7 (6)	92.4 (7)	81.1 (6)
CCSS, mean[i]	10	125	15	126	2	*j*	*j*
NCSS, mean[i]	172	59	166	59	177	*j*	*j*
S–C	1.785 (2)	1.773 (6)	1.774 (6)	1.798 (17)	1.779 (12)	1.800 (15)	1.793 (13)
	1.785 (2)	1.776 (6)	1.783 (7)	1.812 (19)	1.733 (11)	1.795 (16)	1.804 (12)
C–N(inside)[k]	1.329 (4)	1.358 (7)	1.339 (7)	1.33 (2)	1.33 (2)	1.36 (2)	1.31 (2)
		1.345 (7)	1.336 (7)	1.37 (2)	1.35 (2)	1.30 (2)	1.35 (2)
C–N(outside)[l]	1.327 (4)	1.334 (7)	1.333 (9)	1.33 (2)	1.34 (2)	1.36 (2)	1.38 (2)
		1.353 (7)	1.339 (9)	1.30 (3)	1.32 (2)	1.40 (3)	1.39 (2)
SSC	105.8 (1)	103.9 (2)	104.6 (2)	103.3 (6)	104.7 (4)	105.7 (5)	104.3 (5)
	105.6 (1)	106.8 (2)	105.3 (2)	110.5 (6)	104.8 (4)	104.6 (5)	105.3 (4)
SCN	110.5 (2)	117.1 (4)	111.6 (4)	116.4 (12)	110.0 (8)	120.6 (11)	121.3 (8)
		121.2 (4)	111.8 (4)	122.0 (15)	112.0 (8)	111.0 (12)	108.4 (9)
SCC	125.6 (2)	121.4 (4)	125.5 (5)	119.1 (13)	126.6 (10)	115.1 (11)	115.4 (10)
		116.1 (4)	125.1 (5)	117.2 (16)	126.7 (9)	124.8 (12)	124.5 (10)
CCSS	10.2	107.2	12.7	102.9	0.3	175.9	165.9
		142.3	16.9	148.7	2.7	17.8	8.3
NCSS	171.7	77.4	168.6	81.2	179.3	9.7	15.0
		40.4	164.2	36.1	173.9	162.3	174.2

[a] Bond lengths are in angstroms, angles and torsion angles in degrees. Most of the individual values of the bonds and angles which are averaged are presented with their esd's in the second part of the table. [b] Values given are those not suffering from disorder in the structure of the free ligand.[11] [c] The ligand coordinates to Co(II) through both pyridyl nitrogen atoms, forming a seven-membered chelate ring.[10] [d] The ligand bridges between two Hg(II) ions by coordinating to each through a pyridyl nitrogen atom.[9] [e] The ligand coordinates to Cu(I) as described in footnote *c*. See Figure 1. [f] The ligand coordinates to Cu(I) as described in footnote *d*. See Figure 3. [g] The ligand coordinates to Cu(I) through one pyridyl nitrogen and the further sulfur atom, forming a five-membered chelate ring. See Figure 1. [h] The ligand coordinates to nonequivalent Cu(I) ions as described in footnote *g*. See Figure 3. [i] The absolute values of the torsion angles are given. [j] The two angles are qualitatively different. Averaging them would be inappropriate. [k] The carbon atoms in these C–N bonds are bonded to sulfur. [l] The carbon atoms in these C–N bonds are not bonded to sulfur.

cation (Figures 1 and 2) approaches a pyridine plane, that of N(36)-C(41) (Figures 3 and 4), quite closely, at 3.31 Å. The shortest interatomic distances involved are S(22)-C(39), 3.35 Å, and S(22)-C(38), 3.48 Å. The other sulfur atom of this group is 3.57 Å from the plane of an equivalent ring related to the first by a translation of one unit cell along *c*. By further translation along *c*, an infinite stack is generated. The second close contact of this sort, also notable in Figure 5, but most easily seen in Figure 4 with the aid of Figure 3, is between S(56) of the uncoordinated disulfide group of the polynuclear cation and the uncoordinated pyridine plane, C(44)-N(49), at a distance of 3.37 Å. The shortest interatomic distances involved are S(56)-C(44), 3.49 Å, and S(56)-C(45), 3.53 Å. The other sulfur atom of this group is no closer to a member of a pyridine ring than 3.82 Å (to the same ring), which is greater than the van der Waals distance, approximately 1.85

Table V. A Compilation of Selected Features of the Structures of Cu(I) Complexes of Organic Disulfides[a]

	$[Cu(Et_2S_2)Cl]_n$[b]	$[Cu(py_2Et_2S_2)]_n^{n+}$[c]	$[Cu((Me_2N)_2Et_2S_2)]_2^{2+}$[d]		$[Cu(py_2S_2)_2]^+$[e]		$[Cu_n(py_2S_2)_{2n}]^{n+}$[e]
Cu(I) coord. environment	Cl_2S_2	N_2S_2	N_2S_2		N_3S		N_3S
SS	2.04 (2)	2.0807 (9)	2.084 (9) 2.068 (8)	[2.037 (1)][f]	2.032 (4)	[2.016 (2)][g]	2.025 (4)
CSSC	97.7 (30)	59.73 (13)	105.9 (13) 106.7 (13)	[82.4 (2)]	92.4 (7)	[87.1 (1)]	81.1 (6)
CCSS	72.5 71.5	161.2 72.0	72.6 61.1 61.2 76.8	[55.1] [66.5]	175.9 17.8	[10.2]	165.9 8.3
NCSS					9.7 162.3	[171.7]	15.0 174.2
CuS	2.34 (1) 2.40 (1)	2.318 (1) 2.325 (1)	2.288 (6) 2.302 (7) 2.283 (7) 2.326 (6)		2.396 (1)		2.439 (3)
CuSS	102.0 (6) 97.4 (6)	100.61 (3) 111.06 (4)	105.9 (3) 104.8 (3) 104.3 (3) 107.0 (3)		99.1 (2)		97.4 (2)
CuSC	115.6 (20) 117.9 (15)	101.15 (10) 98.62 (11)	94.1 (8) 92.4 (9) 91.2 (10) 94.2 (8)		100.9 (5)		98.7 (4)
CuSSC	158.6 (20) 157.1 (20)	163.4 (1) 163.5 (1)	157.0 (10) 157.8 (8) 160.3 (8) 155.4 (9)		11.4 (5)		20.1 (5)

[a] Bond lengths are in angstroms, angles and torsion angles in degrees. Esd's in the units of the least significant figure given follow that parameter in parentheses. Complexes in which the disulfide group, while present in the ligand molecule, does not coordinate, are omitted from this table; the only examples are reported in this paper. [b] Reference 8. [c] Reference 3. [d] Reference 2. [e] This work. [f] Numbers in brackets are the corresponding parameters in the structure of the free ligand, bis[2-(*N*,*N*-dimethylamino)ethyl] disulfide dihydrochloride. [g] Numbers in brackets are the corresponding parameters in the structure of the free ligand, bis(2-pyridyl) disulfide, not involving the disordered ring.

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

Mononuclear Cation, CuL_2^+

Plane 1		Plane 2		Plane 3		Plane 4		Plane 5		Plane 6	
N(2)	1	C(10)	−4	N(16)	3	C(24)	−7	N(2)	0	N(16)	0
C(3)	−3	C(11)	4	C(17)	2	C(25)	19	Cu(1)	0	Cu(1)	0
C(4)	0	C(12)	0	C(18)	−6	C(26)	−25	S(9)	0	N(29)	0
C(5)	4	C(13)	−8	C(19)	2	C(27)	16	C(7)	124	C(21)	1034
C(6)	−4	C(14)	7	C(20)	7	C(28)	−6	S(8)	337	S(22)	2342
C(7)	1	N(15)	1	C(21)	−9	N(29)	3			S(23)	1617
Cu(1)	158	Cu(1)	−2371	Cu(1)	51	Cu(1)	227			C(24)	746
$q_{b\times(a\times b)}$	4704		−6287		−4425		−5591		3817		918
q_b	−8499		−2536		6153		1049		−8919		1917
$q_{a\times b}$	2376		7351		6523		8224		2426		9771
D	−0.979		4.932		1.099		4.077		−1.039		6.276
δ	3		5		6		15		0		0

Polynuclear Cation, $Cu_nL_{2n}^{n+}$

Plane 7		Plane 8		Plane 9		Plane 10		Plane 11	
N(36)	−7	C(44)	−9	N(50)	0	C(58)	9	N(36)	0
C(37)	−4	C(45)	7	C(51)	−7	C(59)	−5	Cu(35)	0
C(38)	12	C(46)	4	C(52)	12	C(60)	−2	S(43)	0
C(39)	0	C(47)	−15	C(53)	−7	C(61)	−4	C(41)	281
C(40)	−18	C(48)	10	C(54)	−1	C(62)	12	S(42)	640
C(41)	17	N(49)	4	C(55)	3	N(63)	−9		
Cu(35)	141	Cu(35)	−2554	Cu(35)	157	Cu(35)	−313		
$q_{b\times(a\times b)}$	−4424		5495		6442		7352		−3986
q_b	2118		−7613		−7526		6512		186
$q_{a\times b}$	8714		3442		1363		1882		9170
D	1.688		2.380		−0.411		11.337		0.908
δ	12		9		6		8		0

[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 I lies between that plane and the origin. The direction cosines (× 10^4), *q*, are with respect to orthogonalized axes. The root mean square deviation (Å × 10^3) of the boldface atoms from the plane is δ. *D* is the distance (in Å) from the plane to the origin.

+ 1.85 = 3.70 Å.[38] These short S-to-ring interactions can be considered charge-transfer in nature, involving a delocalization of electron density from sulfur into π orbitals in pyridine.

The density of this material was measured by flotation in a mixture of bromoform and chloroform and is somewhat larger (1.666 (10) g cm^{-3}) than that calculated (1.643 (2) g

cm^{-3}) assuming one water molecule per unit cell. It may be that the water position is filled in fresh crystals, but only half-filled in the crystal which was exposed to an atmosphere of 50% humidity during x-ray exposure. The zeolitic channels through which these water molecules may move are apparent in Figure 5, parallel to *c*, the line of view. This is plausible and, if it is correct, the calculated density would be 1.655 (2) g cm^{-3}, somewhat closer to the value observed by flotation.

The water oxygen atom is 3.18 Å from O(67), the oxygen atom with the smallest thermal parameter in its perchlorate group, which otherwise has large thermal parameters (Table I) and Cl-O distances which are severely foreshortened (Table III). Together, these observations indicate the presence of a hydrogen bond between O(67) and O(69). This contact can be seen in Figure 5, the stereoview of the crystal structure. The contact distance O(69)-C(53) is also short, 3.27 Å, and O(69)-H(53) is calculated to be 2.4 Å.

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Supplementary Material Available: observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Valence Level Photoelectron Spectra of Some Heavy Group 4-6 Diatomic Molecules

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Abstract: The He I photoelectron spectra of GeS, GeSe, SnS, SnTe, and PbTe in the gas phase have been obtained by the photoionization of the vapors above appropriate solids at temperatures ranging from 700 to 1000 K. Spectra are assigned using observed relative band areas, vibrational fine structure, and spin-orbit splitting along with electron impact ionization potentials and parallel mass spectrometric studies. It is demonstrated that there is significant mixing of the $\Sigma_{1/2}$ and $\Pi_{1/2}$ states in the heavier species. Distinct differences between the Π states of light and heavy diatomics are observed. Similarities and differences between the valence regions of group 4-6 diatomics and diatomics of group 5-5 and group 3-7 are also reported.

Molecular photoelectron spectroscopy reveals the electronic structure of ions. It also provides an approximate, but valuable, representation of the filled molecular orbital structure of molecules.[1] As such it provides a really useful test of molecular orbital calculations.[2] The technique is most informative when applied to small molecules and small stable molecules have received much attention in the past.[1] Recently, the technique has been applied to less stable species, thereby greatly increasing the number of small systems able to be studied.[3]

Our major objective in this work was to study the photoelectron spectra of the heavier congeners of CO in order to explore the electronic structure of diatomics in a region of the periodic table not readily accessible via calculation. Such species have been the subject of numerous studies utilizing mass spectrometry,[4] microwave spectroscopy,[5] and other