

Registry No. $[\text{Co}(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2]_4 \cdot 2\text{C}_6\text{H}_6$, 71370-71-3; $\text{Co}(\text{O}_2\text{C}_{14}\text{H}_8)_2$, 41173-19-7; $\text{Ni}(\text{O}_2\text{C}_{14}\text{H}_8)_2$, 41173-20-0.

Supplementary Material Available: Listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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A Centric Organic Disulfide ($\text{C-S-S-C} = 180^\circ$): Crystal and Molecular Structures of Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate and of Bis(2-pyrimidyl) Disulfide¹

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The crystal and molecular structures of chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate, $\text{Cu}(\text{C}_4\text{H}_6\text{N}_2\text{S}_2)\text{Cl} \cdot \text{H}_2\text{O}$, and of bis(2-pyrimidyl) disulfide, $\text{C}_8\text{H}_6\text{N}_4\text{S}_2$, have been determined by single-crystal X-ray diffraction techniques using 2401 and 1873 unique reflections, respectively. These structures were refined by full-matrix least-squares procedures to final conventional R indices of 0.039 and 0.036, respectively. Counter methods and monochromatized $\text{Mo K}\alpha$ radiation were employed. The complex crystallizes in the monoclinic space group $C2/m$ with $a = 11.916$ (3) Å, $b = 17.405$ (4) Å, $c = 6.642$ (2) Å, and $\beta = 116.58$ (2)° and with 4 formula units per unit cell. The ligand crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.673$ (5) Å, $b = 15.033$ (6) Å, $c = 7.045$ (3) Å, $\alpha = 98.73$ (3)°, $\beta = 100.02$ (4)°, and $\gamma = 86.45$ (4)° and with 4 molecules per unit cell. In the complex, ligand molecules bridge between Cu(I) ions to form polymeric sheets. Each Cu(I) ion is coordinated by two chloride ions and by two nitrogen atoms from two bis(2-pyrimidyl) disulfide ligand molecules, forming a distorted tetrahedron with coordination angles ranging from 95.7 to 142.2°. The chloride ions bridge between pairs of Cu(I) ions to form rhombic CuClCuCl rings. The relatively short Cu^I-N bond distance, 1.966 (3) Å, indicates strong $d \rightarrow \pi^*$ back-bonding from the Cu(I) d orbitals into the lowest lying π^* molecular orbital of each pyrimidine ring. The most unusual structural feature of the complex is the C-S-S-C torsion angle of 180° (by symmetry), a value not heretofore reported for an organic disulfide. This unusual torsion angle is stabilized by a π system which extends over the entire planar ligand, although the π component of the S-S bond is small. In this conformation, the repulsive forces between the sulfur 3p_z lone-pair electrons and those of the nitrogens on adjacent rings are largely eliminated. Repulsions between the sulfur atoms are at a maximum, however, accounting for the long S-S bond distance of 2.113 (1) Å. The two independent molecules in the structure of the free ligand have normal C-S-S-C torsion angles (83.9 and 85.4°) and normal S-S bond lengths (2.017 (2) and 2.020 (2) Å) for aromatic disulfides in the equatorial conformation (N-C-S-S torsion angle near 0°).

Introduction

The first crystal structure determination of a metal ion complexed to an organic disulfide, that of chloro(diethyl disulfide)copper(I),^{2a} showed the presence of tetrahedral copper(I) ions each bonded to two chloride ions in continuous -Cu-Cl- chains and to two sulfur atoms, one from each of two disulfide groups. This indicated that a sulfur atom of a disulfide group could act as a ligand. Other copper(I)-disulfide complexes whose crystal structures have been determined^{2b-d} also show direct coordination of sulfur to tetrahedral

Cu(I). To investigate this effect further, we prepared the complex reported herein and determined its crystal structure. Although sulfur does not coordinate to copper(I), the disulfide ligand is found in a conformation not heretofore reported.

Experimental Section

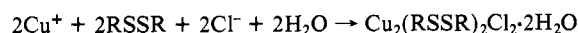
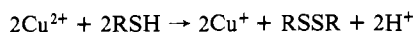
Syntheses. Cupric chloride dihydrate, cupric perchlorate hexahydrate (99.9%), and 2-pyrimidinethiol (alternative name: 2-mercaptopyrimidine) were obtained from Mallinckrodt Chemical Works, Gallard-Schlessinger Chemical Manufacturing Corp., and Aldrich Chemical Co., respectively. All other chemicals were of

reagent grade quality. Elemental analyses were performed by the University of California Chemical Analytical Services.

A 1-mmol sample of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ was reacted with a 2-mmol sample of 2-pyrimidinethiol in methanol. An orange powder which, according to its chemical analysis, contained the unreacted thiol as an impurity was isolated by suction filtration. Reddish orange single crystals were isolated from a latter batch. The weight of the asymmetric unit was established from the unit cell volume and the density. It is consistent with the formula $\text{Cu}(\text{R}_2\text{S}_2)\text{Cl}\cdot\text{H}_2\text{O}$, which was determined crystallographically.

This reaction was also tried with $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ in a dilute aqueous ammonia solution with a 4:1 molar ratio of 2-pyrimidinethiol to cupric ion. However, the major product was yellow crystals of bis(2-pyrimidyl) disulfide dihydrate, according to its density³ and chemical analysis. A few large yellow single crystals with a different density were also isolated. A crystal structure determination established the identity of this product as the anhydrous disulfide.

The formation of disulfides by the reaction of cupric salts with thiols is well established.⁴ In general, the cuprous ion thus formed complexes with the disulfide, as shown by the crystal structure determinations of the products.² Thus the chloro[bis(2-pyrimidyl) disulfide]copper(I) complex is formed by the reactions



Because the reaction was carried out in an oxygen atmosphere, it is expected that the Cu(I) ions produced by the first reaction, in excess of those needed by the second, were reoxidized to the 2+ state, thus driving the reaction toward the products.

Diffraction Section. Single crystals of the complex, $\text{Cu}(\text{C}_8\text{H}_6\text{N}_4\text{S}_2)\text{Cl}\cdot\text{H}_2\text{O}$, and of the ligand, $\text{C}_8\text{H}_6\text{N}_4\text{S}_2$, were selected for X-ray diffraction study and were mounted about axes approximately parallel to their longest dimensions. The ligand crystal was a parallelepiped with extreme dimensions $0.42 \times 0.15 \times 0.13$ mm; for the complex, an approximate hexagonal prism with extreme dimensions $0.41 \times 0.25 \times 0.13$ mm was chosen.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\text{K}\alpha_1$, λ 0.709 30 Å; $\text{K}\alpha_2$, λ 0.713 59 Å) was used for preliminary experiments and for the measurement of the diffraction intensities of both crystals. The cell constants and their standard deviations (see Crystal Data) were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 19.9° for the ligand and 23.6° for the complex. The temperature was maintained at $26(1)^\circ\text{C}$ throughout. The θ - 2θ scanning mode was used with a constant scan rate (ω , in degrees of 2θ) of 4°min^{-1} for the ligand and 1°min^{-1} for the complex. The background time to scan time ratio used was 1.0. The scan range varied from 2.03° at low 2θ to 2.29° at $2\theta = 45^\circ$ and to 2.49° at $2\theta = 70^\circ$. The intensities of three standard reflections, measured after every 100 reflections, showed a small decrease of about 1% for the complex, and the appropriate correction was applied; no discernible intensity decrease was observed for the ligand reflections.

Standard deviations were assigned according to the formula

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

where 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 $\sigma(F_o)$. For the ligand, of the 2625 unique reflections measured (those for which $4^\circ < 2\theta < 45^\circ$), 1873 had intensities such that $I > 3\sigma(I)$. For the complex, of the 2808 unique reflections measured (those for which $4^\circ < 2\theta < 70^\circ$), 2401 had intensities such that $I > 2\sigma(I)$. All intensities were corrected for Lorentz and polarization effects.⁵ The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction. An absorption correction ($\mu = 23.1 \text{ cm}^{-1}$) was applied⁶ which approximated the crystal shape of the complex by a $4 \times 10 \times 10$ grid; the calculated transmission coefficients ranged from 0.709 to 0.820. An absorption correction was not applied to the ligand intensities ($\mu = 4.8 \text{ cm}^{-1}$). The atomic scattering factors for Cu^+ , Cl^- , S^0 , O^0 , N^0 , C^0 ,^{7a} and H (bonded)^{7b} were used; the first three were modified to include the real parts of the anomalous dispersion correction.^{7c}

Crystal Data. a. Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate. $\text{Cu}(\text{C}_8\text{H}_6\text{N}_4\text{S}_2)\text{Cl}\cdot\text{H}_2\text{O}$: monoclinic, $C2/m$, $a = 11.916(3)$ Å, $b = 17.405(4)$ Å, $c = 6.642(2)$ Å, $\beta = 116.58(2)^\circ$, $V = 1232.1(4)$ Å³, f_w 339.3, d_{obsd} (flotation) = $1.82(1)$ g cm^{-3} , $d_{\text{calcd}} = 1.829$ g cm^{-3} , and $Z = 4$. The only condition for systematic absences, $h + k = 2n + 1$, was consistent with the following space groups: $C2$, Cm , or $C2/m$. The structure was solved by using $C2/m$.

b. Bis(2-pyrimidyl) Disulfide. $\text{C}_8\text{H}_6\text{N}_4\text{S}_2$: triclinic, $P\bar{1}$, $a = 9.673(5)$ Å, $b = 15.033(6)$ Å, $c = 7.045(3)$ Å, $\alpha = 98.73(3)^\circ$, $\beta = 100.02(4)^\circ$, $\gamma = 86.45(4)^\circ$, $V = 996.5(8)$ Å³, mol wt 222.3, $d_{\text{calcd}} = 1.482$ g cm^{-3} , and $Z = 4$. Wilson intensity statistics⁸ indicated centricity, and the structure was subsequently solved in the space group $P\bar{1}$.

Figures in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Structure Determination. a. Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate. The positions of the Cu(I) and Cl^- ions were learned from a three-dimensional Patterson function prepared by using the fast-Fourier algorithm.⁹ A Fourier function whose phases were based on the Cu(I) and Cl^- positions in the $C2$ space group revealed the bis(2-pyrimidyl) disulfide ligands and water molecules. It soon became evident that a mirror plane of symmetry was present in the structure, and reexamination of the Patterson function revealed the Harker elements characteristic of $C2/m$. After several cycles of isotropic full-matrix least-squares refinement,¹⁰ all hydrogen atoms, except the water hydrogens, were located on a Fourier difference synthesis. Finally, several cycles of least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms led to the final error indices $R_1 = \sum |F_o - |F_c|| / \sum F_o = 0.039$ and $R_2 = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.043$. The "goodness-of-fit", $[\sum w(F_o - |F_c|)^2 / (m - s)]^{1/2}$, is 2.52. The number of observations used in least-squares refinement (2401) is m , and s (93) is the total number of parameters. The overdetermination ratio (m/s) is therefore 25.8. In the final cycle of least-squares refinement, the largest shift in a nonhydrogen positional or thermal parameter was 5% of its corresponding esd and for a hydrogen parameter 2%. The largest peak on the final difference function, whose esd is $0.18 \text{ e } \text{Å}^{-3}$, was $1.0 \text{ e } \text{Å}^{-3}$ in height and was located very near the Cu(I) ion at a chemically implausible position. The positional and thermal parameters of the atoms are listed in Table I.

b. Bis(2-pyrimidyl) Disulfide. The positions of the sulfur atoms could not be readily determined from a three-dimensional Patterson function. An overall isotropic thermal parameter ($B_{\text{iso}} = 4.2 \text{ Å}^2$) was estimated from a Wilson plot,¹¹ and normalized structure factor amplitudes for the 300 reflections with $|E| \geq 1.56$ were used in the computer program MULTAN.¹² A three-dimensional E function, phased as indicated by the solution with the largest combined figure of merit, 2.84, revealed the positions of all nonhydrogen atoms. After several cycles of isotropic and then anisotropic full-matrix least-squares refinement of the 28 nonhydrogen atoms, all 12 hydrogen atoms were located on a Fourier difference synthesis. Finally, three cycles of least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms led to the final error indices $R_1 = R_2 = 0.036$. The goodness-of-fit is 1.72. The number of observations used in least squares to refine the 301 parameters was 1873, so the overdetermination ratio is 6.2. In the final cycle of least-squares refinement, the largest shift in a nonhydrogen positional or thermal parameter was 1% of its corresponding esd, and for a hydrogen parameter, 4%. The largest peaks on the final difference function, whose esd is $0.08 \text{ e } \text{Å}^{-3}$, were $0.2 \text{ e } \text{Å}^{-3}$ in height and were located at chemically implausible positions. The positional and thermal parameters of the atoms are given in Table I.

Discussion of the Structures

Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate.

The crystal and molecular structure of chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate is presented in Figures 1 and 2. Ligand molecules bridge between Cu_2Cl_2 groups to form polymeric sheets which stack along c (see Figure 2). Each Cu(I) ion coordinates to two nitrogen atoms from two different ligands and to two chloride ions which bridge to another Cu(I) to complete a planar four-membered Cu_2Cl_2 ring. A water molecule approaches each chloride ion at an $\text{O}\cdots\text{Cl}$ distance

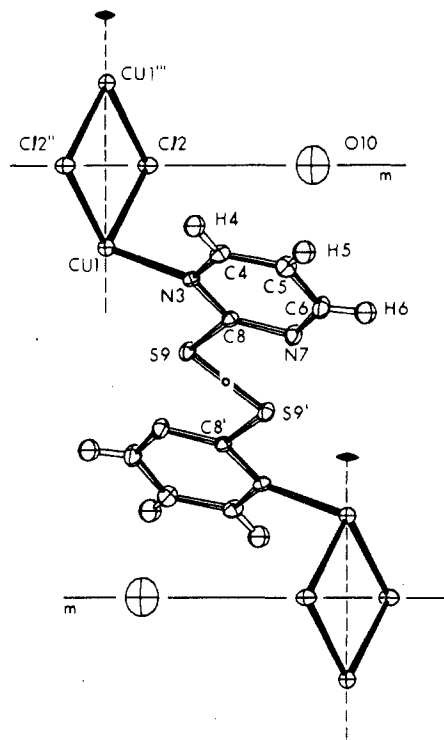


Figure 1. Portion of the polymeric sheet of chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate showing ellipsoids of 20% probability.¹³ Mirror planes, twofold axes, and an inversion center are indicated. The coordinates of the singly, doubly, and triply primed atoms are related to those in Table I by $1/2 - x, 1/2 - y, -z; -x, y, -z$; and $x, -y, z$, respectively.

of 3.30 Å. A portion of this structure, with its associated symmetry, is shown in Figure 1.

The coordination geometry about copper(I) is distorted tetrahedral with bond angles ranging from 95.7 to 142.2° (see Table II). The N(3)-Cu(1)-N(3)'' angle, 142.2°, is nearly 33° greater than an ideal tetrahedral angle. The two nitrogen atoms and the two chloride ions act as σ donors, and there is cooperative $d \rightarrow \pi^*$ back-donation of electron density from the filled Cu(I) d orbitals into the lowest lying π^* molecular orbital of each pyrimidine ring (vide infra).

The Cu_2Cl_2 rhombic ring of the complex is planar by symmetry. The Cu-Cl bond distance is 2.464 (1) Å, and the diagonal distances across the ring are $\text{Cu}\cdots\text{Cu} = 3.306$ Å and $\text{Cl}\cdots\text{Cl} = 3.655$ Å. The angle at copper is therefore obtuse ($\text{Cl}(2)-\text{Cu}(1)-\text{Cl}(2)'' = 95.7^\circ$), and that at chloride is its supplement. The following geometries have been reported for

other planar Cu_2Cl_2 rings: dimeric (tricyclohexylphosphine)-copper(I) chloride,^{14a} $\text{Cu}-\text{Cl} = 2.285$ and 2.322 Å, $\text{Cu}\cdots\text{Cu} = 3.066$ Å, $\text{Cl}\cdots\text{Cl} = 3.439$ Å, $\text{Cl}-\text{Cu}-\text{Cl} = 96.6^\circ$; cuprous chloride-1,5-cyclooctadiene dimer,^{14b} $\text{Cu}-\text{Cl} = 2.288$ and 2.299 Å, $\text{Cu}\cdots\text{Cu} = 2.944$ Å, $\text{Cl}\cdots\text{Cl} = 3.518$ Å, $\text{Cl}-\text{Cu}-\text{Cl} = 100.1^\circ$; (1-allyl-3,5-dimethylpyrazole)copper(I) chloride,^{14c} $\text{Cu}-\text{Cl} = 2.252$ and 2.525 Å, $\text{Cu}\cdots\text{Cu} = 3.172$ Å, $\text{Cl}\cdots\text{Cl} = 3.583$ Å, $\text{Cl}-\text{Cu}-\text{Cl} = 97.0^\circ$. The geometry of the Cu_2Cl_2 ring varies widely in these four structures; it is largest in chloro[bis(2-pyrimidyl) disulfide]copper(I).

The copper-nitrogen bond distance, 1.966 (3) Å, is one of the shortest distances yet reported for a Cu(I) ion bonded to an unsaturated nitrogen atom in a cyclic ligand. (The mean $\text{Cu}^{\text{I}}-\text{N}$ bond distance determined for such compounds is 2.04 Å.^{2b,2d,14c,15}) The relatively short $\text{Cu}^{\text{I}}-\text{N}$ bond argues for appreciable copper-to-nitrogen π back-bonding. For example, the following copper(I)-pyridyl disulfide complexes have longer $\text{Cu}^{\text{I}}-\text{N}$ bonds, even though 2-pyridinethiol is a stronger base than 2-pyrimidinethiol:¹⁶ [bis[2-(2-pyridyl)ethyl] disulfide]copper(I) perchlorate^{2b} (mean 2.029 Å; range from 2.022 to 2.036 Å) and bis[bis(2-pyridyl) disulfide]copper(I) perchlorate^{2d} (mean 2.024 Å; range from 1.989 to 2.057 Å). With aza substitution into the aromatic ring, the π and π^* molecular orbital levels are reduced in energy as a result of the lower energy of an electron in a nitrogen orbital, as compared to carbon. It has been observed¹⁷ that, relative to those of pyridine, the $n \rightarrow \pi^*$ transitions of the polyazines are bathochromic. The lone-pair orbitals of the azines all have approximately the same energy, and thus the shift in the $n \rightarrow \pi^*$ transitions can be accounted for by the relative energies of the lowest lying π^* orbitals of pyridine and the other azines.¹⁷ (The relative ease of reduction of azines, as shown by the polarographic half-wave potentials for one-electron reduction, also correlates with the energy of the lowest unoccupied π molecular orbitals of the aromatic nitrogen heterocycles, according to Wiberg and Lewis;^{18a} see also ref 18b.) It may be concluded that the pyrimidine ring with its low-lying π^* orbitals (relative to those of pyridine) allows more π density to be transferred from Cu(I) to the ring. As this occurs, σ donation to Cu(I) is enhanced and the $\text{Cu}^{\text{I}}-\text{N}$ bond is shortened.

The pyrimidine rings in the complex are quite planar (see plane I, Table III); the maximum deviation from the least-squares plane is 0.014 Å. Most of the bond distances and bond angles in the pyrimidine rings are close to the corresponding values both in the free ligand (see Table IV) and in crystalline pyrimidine.²⁰ However, the N(3)-C(4), N(3)-C(8), and C(4)-C(5) bonds in the ring, those which involve or are near the coordinated nitrogen atom, are slightly greater (from 2σ

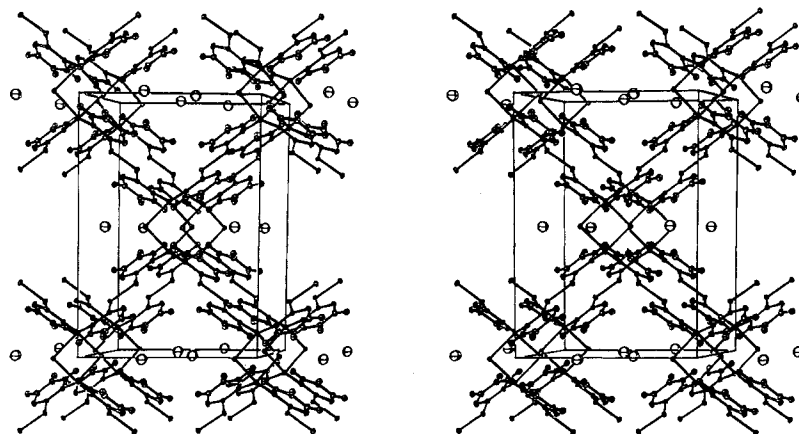


Figure 2. Stereoview of the crystal structure of chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate showing ellipsoids of 15% probability.¹³ The view is approximately into the $+c$ direction, with $+a$ extending horizontally to the right and $+b$ extending upward in the plane of the page.

Table I. Fractional Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations (All $\times 10^4$)^a

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A. Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate									
Cu(1)	0.0	949.9 (4)	0.0	286 (3)	293 (3)	304 (3)	0.0	117 (2)	0.0
Cl(2)	1015 (1)	0.0	-1402 (2)	392 (6)	263 (5)	387 (6)	0.0	265 (5)	0.0
N(3)	1468 (3)	1316 (2)	2693 (5)	287 (13)	235 (12)	286 (13)	-36 (10)	147 (11)	2 (10)
C(4)	1831 (4)	1028 (2)	4772 (6)	413 (19)	330 (17)	325 (16)	-55 (15)	200 (15)	27 (14)
C(5)	3003 (4)	1177 (3)	6498 (7)	448 (21)	437 (20)	286 (17)	-19 (17)	136 (16)	71 (15)
C(6)	3778 (4)	1647 (3)	6022 (7)	331 (18)	502 (23)	348 (18)	-53 (17)	80 (15)	36 (17)
N(7)	3434 (3)	1962 (2)	3991 (6)	297 (14)	426 (17)	353 (15)	-70 (13)	112 (13)	53 (13)
C(8)	2300 (3)	1779 (2)	2439 (6)	276 (14)	241 (13)	298 (14)	-11 (11)	143 (12)	25 (12)
S(9)	1716.7 (8)	2148.5 (5)	-310 (1)	291 (4)	358 (4)	296 (4)	-78 (3)	111 (3)	63 (3)
O(10)	4025 (11)	0.0	2173 (23)	1162 (90)	1490 (95)	2078 (134)	0.0	193 (86)	0.0
H(4)	1274 (51)	706 (29)	5020 (85)	$U = 460 (135)$					
H(5)	3222 (53)	1009 (29)	7822 (103)	$U = 515 (149)$					
H(6)	4584 (47)	1709 (29)	7006 (83)	$U = 455 (134)$					
B. Bis(2-pyrimidyl) Disulfide									
N(1)	3040 (3)	6386 (2)	4814 (4)	533 (23)	570 (23)	607 (22)	-91 (19)	11 (17)	126 (17)
C(2)	3763 (5)	7123 (3)	5652 (6)	543 (30)	769 (37)	588 (28)	-139 (28)	-18 (24)	174 (24)
C(3)	3164 (5)	7976 (3)	5778 (6)	765 (35)	560 (32)	545 (27)	-222 (30)	125 (25)	21 (24)
C(4)	1777 (5)	8043 (3)	5038 (6)	853 (38)	510 (31)	606 (29)	29 (30)	230 (27)	32 (24)
N(5)	1008 (3)	7343 (2)	4218 (4)	587 (22)	590 (24)	591 (22)	23 (20)	147 (18)	23 (18)
C(6)	1705 (4)	6553 (3)	4158 (5)	514 (26)	561 (27)	410 (23)	-127 (21)	135 (20)	43 (19)
S(7)	569 (1)	5676 (1)	2961 (2)	596 (7)	778 (8)	735 (8)	-250 (6)	156 (6)	-67 (6)
S(8)	1765 (1)	4530 (1)	3052 (2)	1252 (11)	543 (7)	610 (7)	-286 (7)	92 (7)	129 (6)
C(9)	2668 (4)	4445 (3)	1022 (5)	637 (26)	400 (24)	550 (26)	-50 (21)	-114 (20)	-8 (20)
N(10)	2465 (3)	5071 (2)	-132 (5)	508 (20)	487 (21)	549 (21)	-3 (16)	19 (17)	101 (17)
C(11)	3191 (5)	4924 (3)	-1609 (6)	645 (30)	784 (34)	599 (29)	-111 (26)	26 (25)	28 (25)
C(12)	4084 (5)	4207 (4)	-1881 (8)	638 (33)	956 (43)	943 (42)	32 (31)	85 (29)	-318 (34)
C(13)	4224 (6)	3612 (4)	-580 (11)	813 (40)	761 (43)	1319 (58)	319 (32)	-275 (39)	-398 (40)
N(14)	3494 (5)	3713 (2)	909 (6)	1049 (33)	475 (26)	947 (34)	215 (23)	-235 (26)	2 (22)
N(15)	8638 (3)	10902 (2)	9792 (4)	443 (19)	431 (19)	575 (20)	38 (17)	11 (16)	64 (15)
C(16)	9833 (4)	11315 (3)	10626 (6)	469 (25)	502 (27)	677 (27)	94 (21)	-25 (20)	144 (21)
C(17)	9940 (4)	12223 (3)	10982 (5)	589 (27)	542 (28)	565 (26)	-48 (22)	-7 (20)	119 (21)
C(18)	8750 (5)	12731 (2)	10438 (5)	847 (32)	396 (23)	496 (25)	-51 (24)	149 (23)	56 (19)
N(19)	7531 (3)	12363 (2)	9611 (4)	645 (23)	444 (21)	511 (20)	104 (18)	136 (17)	106 (16)
C(20)	7566 (4)	11464 (3)	9336 (5)	475 (24)	527 (26)	356 (21)	49 (20)	116 (17)	69 (18)
S(21)	5907 (1)	11040 (1)	8184 (1)	401 (6)	700 (7)	635 (7)	56 (5)	64 (5)	123 (5)
S(22)	6123 (1)	9700 (1)	8257 (1)	532 (7)	713 (7)	553 (6)	-158 (5)	87 (5)	169 (5)
C(23)	6873 (3)	9244 (3)	6163 (5)	342 (21)	536 (27)	505 (24)	-69 (18)	-55 (17)	110 (20)
N(24)	7245 (3)	9775 (2)	5027 (5)	592 (21)	580 (21)	526 (21)	-29 (17)	111 (17)	113 (18)
C(25)	7780 (4)	9341 (3)	3500 (6)	717 (30)	698 (34)	684 (31)	-23 (25)	173 (25)	165 (25)
C(26)	7957 (5)	8434 (4)	3174 (7)	734 (32)	825 (38)	723 (33)	93 (28)	143 (25)	-19 (28)
C(27)	7564 (5)	7957 (3)	4483 (8)	718 (32)	516 (29)	970 (39)	18 (24)	-101 (29)	40 (28)
N(28)	6990 (3)	8356 (2)	6006 (5)	594 (22)	549 (24)	686 (25)	-50 (18)	-53 (19)	132 (19)
C. Bis(2-pyrimidyl) Disulfide Hydrogen Atoms									
atom	x	y	z	U	atom	x	y	z	U
H(2)	4685 (39)	7000 (23)	6142 (51)	622 (124)	H(16)	10570 (25)	10941 (16)	10930 (34)	386 (72)
H(3)	3742 (38)	8471 (25)	6411 (49)	696 (123)	H(17)	10787 (28)	12478 (19)	11505 (39)	634 (90)
H(4)	1274 (35)	8607 (23)	5073 (46)	535 (111)	H(18)	8751 (28)	13340 (18)	10635 (38)	557 (84)
H(11)	3026 (32)	5345 (20)	-2505 (43)	834 (107)	H(25)	8065 (31)	9721 (20)	2704 (42)	758 (100)
H(12)	4577 (41)	4102 (26)	-2954 (55)	1313 (149)	H(26)	8298 (31)	8128 (20)	2125 (42)	766 (101)
H(13)	4735 (40)	3133 (25)	-579 (54)	1261 (145)	H(27)	7581 (30)	7363 (19)	4337 (41)	704 (96)

^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 for the corresponding parameter. The anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The thermal parameters have the units of Å^2 .

to 4σ) than the corresponding bonds in the free ligand (see Table IV, rows 1-3, and Figure 1). This may be the result of the donation of electron density from both Cu(I) and sulfur into the empty π^* orbitals of the pyrimidine rings (vide infra). Also, a σ polarization of the ring by Cu(I) via the coordinated nitrogen is likely to have contributed to these small bond lengthenings.

The most surprising structural feature of the chloro[bis(2-pyrimidyl) disulfide] copper(I) complex is the conformation of the coordinated ligand. Bis(2-pyrimidyl) disulfide has a C-S-S-C torsion angle of exactly 180° by symmetry, a value not heretofore reported for an organic disulfide.²¹ The long S-S bond length, 2.113 (1) Å , is a consequence of this torsion angle; it is consistent with a plausible extension of the relationship between S-S bond lengths and C-S-S-C torsion angles in acyclic and saturated cyclic disulfides observed by

Hordvik.^{23,24} He noted that the shortest S-S bonds occur when the R-S-S-R torsion angle is near 90° , as is usually the case in unconstrained disulfides, and that longer bonds are found for smaller (or somewhat larger) torsion angles.²⁹ The longest S-S bonds are found when C-S-S-C = 0 or 180° , i.e., when the lone-pair-lone-pair repulsion between the sulfurs is a maximum. (The longest S-S bond distance observed crystallographically is that in $\text{Na}_2\text{S}_2\text{O}_4$, 2.389 (8) Å ,³¹ and the longest S-S distance reported for a symmetric aromatic disulfide (complexed or uncomplexed) is that observed in $[\text{Re}_2\text{Br}_2(\text{C}-\text{O})_6]\text{S}_2(\text{C}_6\text{H}_5)_2$, 2.140 (9) Å .³² The latter is partly attributable to the back-bonding by two Re(I) ions of electron density into the σ^* system of the S-S group.³³)

The unusual 180° C-S-S-C torsion angle in the complex is stabilized by (1) a π system which extends over the entire planar disulfide ligand (vide infra) and (2) the near absence

Table II. Molecular Dimensions and Esd's^a

A. Bond Lengths, Å					
chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate		bis(2-pyrimidyl) disulfide			
Cu(1)-Cl(2)	2.464 (1)	N(1)-C(2)	1.348 (6)	N(15)-C(16)	1.345 (5)
Cu(1)-N(3)	1.966 (3)	N(1)-C(6)	1.317 (5)	N(15)-C(20)	1.322 (5)
Cl(2)-O(10)	3.298 (12)	C(2)-C(3)	1.371 (7)	C(16)-C(17)	1.357 (6)
N(3)-C(4)	1.346 (5)	C(3)-C(4)	1.355 (7)	C(17)-C(18)	1.371 (6)
N(3)-C(8)	1.347 (4)	C(4)-N(5)	1.326 (6)	C(18)-N(19)	1.335 (5)
C(4)-C(5)	1.378 (6)	N(5)-C(6)	1.327 (5)	N(19)-C(20)	1.335 (5)
C(5)-C(6)	1.373 (6)	C(6)-S(7)	1.782 (4)	C(20)-S(21)	1.777 (4)
C(6)-N(7)	1.340 (5)	S(8)-C(9)	1.786 (4)	S(22)-C(23)	1.782 (4)
N(7)-C(8)	1.320 (5)	S(7)-S(8)	2.017 (2)	S(21)-S(22)	2.020 (2)
C(8)-S(9)	1.759 (3)	C(9)-N(10)	1.319 (5)	C(23)-N(24)	1.318 (5)
S(9)-S(9)' ^b	2.113 (1)	C(9)-N(14)	1.320 (6)	C(23)-N(28)	1.322 (5)
C(4)-H(4)	0.94 (5)	N(10)-C(11)	1.338 (5)	N(24)-C(25)	1.337 (5)
C(5)-H(5)	0.85 (6)	C(11)-C(12)	1.351 (7)	C(25)-C(26)	1.353 (7)
C(6)-H(6)	0.89 (5)	C(12)-C(13)	1.360 (9)	C(26)-C(27)	1.366 (7)
		C(13)-N(14)	1.349 (8)	C(27)-N(28)	1.338 (6)
		C(2)-H(2)	0.92 (4)	C(16)-H(16)	0.90 (2)
		C(3)-H(3)	0.96 (4)	C(17)-H(17)	0.92 (3)
		C(4)-H(4)	0.95 (3)	C(18)-H(18)	0.90 (3)
		C(11)-H(11)	0.95 (3)	C(25)-H(25)	0.94 (3)
		C(12)-H(12)	0.95 (4)	C(26)-H(26)	0.91 (3)
		C(13)-H(13)	0.85 (4)	C(27)-H(27)	0.88 (3)

B. Bond Angles, Deg					
chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate		bis(2-pyrimidyl) disulfide			
Cl(2)-Cu(1)-Cl(2)'' ^b	95.74 (4)	C(2)-N(1)-C(6)	114.3 (4)	C(16)-N(15)-C(20)	113.8 (3)
Cl(2)-Cu(1)-N(3)	100.00 (9)	N(1)-C(2)-C(3)	122.9 (4)	N(15)-C(16)-C(17)	123.5 (3)
N(3)-Cu(1)-N(3)''	142.2 (1)	C(2)-C(3)-C(4)	116.1 (4)	C(16)-C(17)-C(18)	116.9 (4)
N(3)-Cu(1)-Cl(2)''	105.11 (9)	C(3)-C(4)-N(5)	123.8 (4)	C(17)-C(18)-N(19)	122.5 (3)
Cu(1)-Cl(2)-Cu(1)'''	84.26 (4)	C(4)-N(5)-C(6)	114.7 (4)	C(18)-N(19)-C(20)	114.7 (3)
Cu(1)-N(3)-C(4)	124.0 (2)	N(1)-C(6)-N(5)	128.2 (3)	N(15)-C(20)-N(19)	128.5 (3)
Cu(1)-N(3)-C(8)	119.0 (2)	C(9)-N(10)-C(11)	114.4 (3)	C(23)-N(24)-C(25)	114.4 (3)
C(4)-N(3)-C(8)	115.8 (3)	N(10)-C(11)-C(12)	123.1 (4)	N(24)-C(25)-C(26)	122.9 (4)
N(3)-C(4)-C(5)	121.6 (4)	C(11)-C(12)-C(13)	117.2 (5)	C(25)-C(26)-C(27)	117.3 (4)
C(4)-C(5)-C(6)	117.1 (4)	C(12)-C(13)-N(14)	122.3 (5)	C(26)-C(27)-N(28)	122.2 (4)
C(5)-C(6)-N(7)	122.8 (4)	C(9)-N(14)-C(13)	114.4 (4)	C(23)-N(28)-C(27)	114.7 (4)
C(6)-N(7)-C(8)	115.7 (3)	N(10)-C(9)-N(14)	128.5 (4)	N(24)-C(23)-N(28)	128.5 (4)
N(3)-C(8)-N(7)	126.9 (3)	N(1)-C(6)-S(7)	121.5 (3)	N(15)-C(20)-S(21)	120.2 (3)
N(3)-C(8)-S(9)	112.2 (2)	N(5)-C(6)-S(7)	110.2 (3)	N(19)-C(20)-S(21)	111.3 (3)
N(7)-C(8)-S(9)	120.9 (3)	S(8)-C(9)-N(14)	111.3 (3)	S(22)-C(23)-N(28)	110.6 (3)
C(8)-S(9)-S(9)'	96.0 (1)	S(8)-C(9)-N(10)	120.2 (3)	S(22)-C(23)-N(24)	120.9 (3)
N(3)-C(4)-H(4)	118 (3)	C(6)-S(7)-S(8)	105.2 (1)	C(20)-S(21)-S(22)	104.5 (1)
C(5)-C(4)-H(4)	120 (3)	C(9)-S(8)-S(7)	105.2 (1)	C(23)-S(22)-S(21)	105.4 (1)
C(4)-C(5)-H(5)	122 (4)	N(1)-C(2)-H(2)	114 (2)	N(15)-C(16)-H(16)	115 (2)
C(6)-C(5)-H(5)	121 (4)	C(3)-C(2)-H(2)	123 (2)	C(17)-C(16)-H(16)	122 (2)
C(5)-C(6)-H(6)	121 (3)	C(2)-C(3)-H(3)	118 (2)	C(16)-C(17)-H(17)	121 (2)
N(7)-C(6)-H(6)	116 (3)	C(4)-C(3)-H(3)	125 (2)	C(18)-C(17)-H(17)	122 (2)
		C(3)-C(4)-H(4)	122 (2)	C(17)-C(18)-H(18)	121 (2)
		N(5)-C(4)-H(4)	114 (2)	N(19)-C(18)-H(18)	116 (2)
		N(10)-C(11)-H(11)	116 (2)	N(24)-C(25)-H(25)	114 (2)
		C(12)-C(11)-H(11)	121 (2)	C(26)-C(25)-H(25)	123 (2)
		C(11)-C(12)-H(12)	122 (2)	C(25)-C(26)-H(26)	124 (2)
		C(13)-C(12)-H(12)	120 (2)	C(27)-C(26)-H(26)	119 (2)
		C(12)-C(13)-H(13)	127 (3)	C(26)-C(27)-H(27)	123 (2)
		N(14)-C(13)-H(13)	110 (3)	N(28)-C(27)-H(27)	114 (2)

C. Selected Torsion Angles, Deg					
chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate		bis(2-pyrimidyl) disulfide			
N(3)-C(8)-S(9)-S(9)' ^b	3.37	N(1)-C(6)-S(7)-S(8)	2.53	N(15)-C(20)-S(21)-S(22)	8.11
N(7)-C(8)-S(9)-S(9)'	3.31	N(5)-C(6)-S(7)-S(8)	1.36	N(19)-C(20)-S(21)-S(22)	7.62
C(8)-S(9)-S(9)'-C(8)'	180.0	C(6)-S(7)-S(8)-C(9)	83.9	C(20)-S(21)-S(22)-C(23)	85.4
		N(10)-C(9)-S(8)-S(7)	0.29	N(24)-C(23)-S(22)-S(21)	4.34
		N(14)-C(9)-S(8)-S(7)	0.21	N(28)-C(23)-S(22)-S(21)	3.47

^a The esd is in the units of the least significant figure given for the corresponding parameter. ^b The symmetry operations used to generate the positions of the variously primed atoms are given in the caption to Figure 1.

Table III. Coefficients of Least-Squares Planes $Ax + By + Cz = D$

plane	atoms in plane	A	B	C	D	dist from plane, Å
A. Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate						
I	N(3), C(4), C(5), C(6), N(7), C(8)	-0.5510	0.7936	0.2580	1.7161	Cu(1), ^a -0.404; N(3), -0.009; C(4), 0.014; C(5), -0.002; C(6), -0.012; N(7), 0.005; C(8), 0.005; S(9), ^a 0.026
II	N(3), C(4), C(5), C(6), N(7), C(8), S(9), N(3)', C(4)', C(5)', C(6)', N(7)', C(8)', S(9)'	-0.5919	0.7644	0.2555	1.563	N(3), 0.035; C(4), 0.077; C(5), 0.014; C(6), -0.062; N(7), -0.067; C(8), -0.018; S(9), -0.017; N(3)', ^b -0.035; C(4)', -0.077; C(5)', -0.014; C(6)', 0.062; N(7)', 0.067; C(8)', 0.018; S(9)', 0.017
B. Bis(2-pyrimidyl) Disulfide						
III	N(1), C(2), C(3), C(4), N(5), C(6)	-0.3815	-0.2559	0.8882	-0.3394	N(1), -0.002; C(2), 0.008; C(3), -0.005; C(4), -0.003; N(5), 0.003; C(6), -0.002; S(7), ^a -0.044
IV	C(9), N(10), C(11), C(12), C(13), N(14)	0.6637	0.4781	0.5753	5.256	S(8), ^a -0.004; C(9), -0.002; N(10), 0.004; C(11), -0.010; C(12), 0.001; C(13), 0.013; N(14), -0.006
V	N(15), C(16), C(17), C(18), N(19), C(20)	-0.4066	-0.1454	0.9020	0.8288	N(15), 0.001; C(16), 0.000; C(17), 0.001; C(18), -0.003; N(19), 0.003; C(20), -0.002; S(21), ^a -0.030
VI	C(23), N(24), C(25), C(26), C(27), N(28)	0.8334	0.0362	0.5514	7.7657	S(22), ^a -0.004; C(23), -0.006; N(24), 0.008; C(25), -0.009; C(26), -0.006; C(27), 0.015; N(28), -0.003

^a Note that this atom was not included in the calculation of the least-squares plane. ^b The symmetry operation used to generate the positions of the primed atoms is given in the caption to Figure 1.

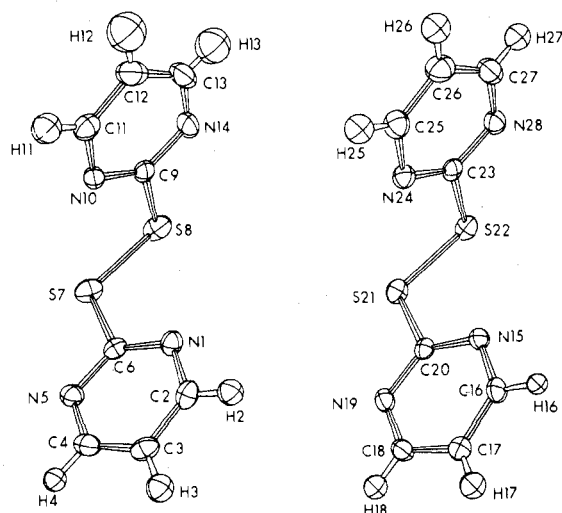
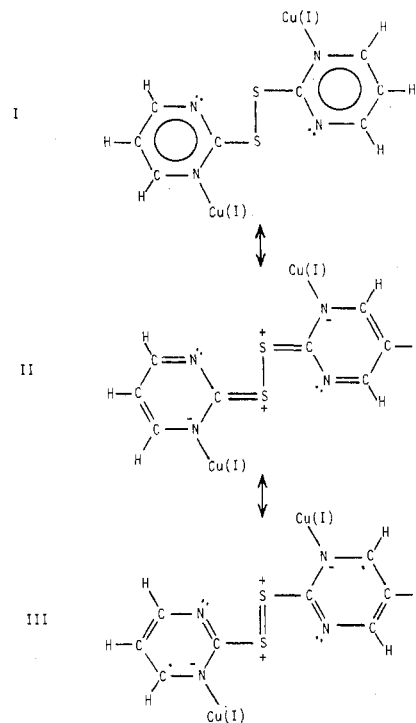


Figure 3. The two crystallographically nonequivalent bis(2-pyrimidyl) disulfide molecules with ellipsoids of 20% probability.¹³ Their orientations have been chosen to facilitate comparison.

of electron repulsion, which is large in the free ligand, between each S $3p_\pi$ lone pair and the adjacent-ring nitrogen lone pair (e.g., between the S(8) lone pair and the N(1) lone pair; see Figure 3). Crystal packing forces may also be important in stabilizing the C-S-S-C = 180° conformation.

A consequence of the near elimination of the lone-pair electron repulsion between the S $3p_\pi$ lone pairs and the adjacent-ring nitrogen lone pairs, brought about by the adoption of the 180° C-S-S-C torsion angle, is that the C-S-S angle in the complex, 96.0 (1)°, is much smaller than that in the ligand, 105.1 (1)°. This can also be seen in the greater mean 1,4 intramolecular N...S contact distance in the ligand, 3.09 Å, as compared to that in the complex, 2.83 Å. Because the latter distance is less than the sum of the van der Waals radii (about 3.4 Å³⁶), there still exists a N...S steric repulsion which compresses the N(3)-C(8)-S(9) angle from a normal value of about 116° ((360° - 128°)/2; the N-C-N angle in pyrimidine is 128.2°²⁰) to 112.2°. The corresponding angle in the ligand (mean 110.9°) indicates a similar but somewhat greater steric strain for the same reason.

Possible resonance structures for the ligand in the complex are given as I-III.



Resonance structures II and III are not very favorable because they place a positive charge on each of two adjacent atoms.³⁷ Resonance structure III is particularly unfavorable because of its diradical character. Also, because the S-S bond length in the complex, 2.113 (1) Å, is approximately that of a single bond, resonance structures II and III are relatively unimportant. (According to Hordvik,²³ the minimum length of a single bond between two divalent sulfur atoms when C-S-S-C = 0° is 2.10 Å; Bonds and Ibers³⁸ prefer to use 2.13 Å as found in Na₂S₂.³⁹)

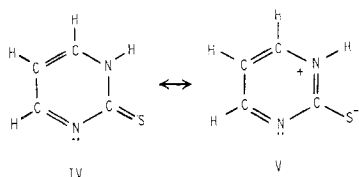
Nevertheless, the relatively long bonds between the ring atoms near the coordinated nitrogen atom (see Table IV) support resonance structures II and III. The C-S bond distance in the complex, 1.759 (3) Å, indicates that the bond has

Table IV. Comparison of Selected Features of the Molecular Structures of Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate and of Bis(2-pyrimidyl) Disulfide^a

	L^b	L(1), L(2) ^c	CuLCl·(H ₂ O) ^{c,d}
A. Bond Lengths, Å			
N(1)-C(2)	1.337 (2) ^e	1.335 (3) ^g	1.346 (5) ^f
N(1)-C(6)	1.332 (1)	1.326 (3)	1.347 (4)
C(2)-C(3)	1.365 (2)	1.364 (3)	1.378 (6)
C(3)-C(4)	1.370 (2)	1.359 (3)	1.373 (6)
C(4)-N(5)	1.342 (1)	1.342 (3)	1.340 (5)
N(5)-C(6)	1.318 (1)	1.319 (2)	1.320 (5)
C(6)-S(7)	1.781 (1)	1.782 (2)	1.759 (3)
S(7)-S(7')	2.016 (1) ^f	2.019 (1) ^e	2.113 (1)
B. Bond Angles, Deg			
C(2)-N(1)-C(6)	115.4 (1) ^e	114.6 (2) ^g	115.8 (3) ^f
N(1)-C(2)-C(3)	122.1 (1)	122.8 (2)	121.6 (4)
C(2)-C(3)-C(4)	117.2 (1)	116.8 (2)	117.1 (4)
C(3)-C(4)-N(5)	122.8 (1)	123.1 (2)	122.8 (4)
C(4)-N(5)-C(6)	114.5 (1)	114.2 (2)	115.7 (3)
N(1)-C(6)-N(5)	128.1 (1)	128.4 (2)	126.9 (3)
N(1)-C(6)-S(7)	110.6 (1)	110.9 (1)	112.2 (2)
N(5)-C(6)-S(7)	121.4 (1)	120.7 (1)	120.9 (3)
C(6)-S(7)-S(7')	104.8 (1)	105.1 (1)	96.0 (1)
C. Torsion Angles, Deg			
C(6)-S(7)-S(7')-C(6)'	82.5 ^f	84.6 ⁱ	180.0 ^f
(N(1), N(5))-C(6)-S(7)-S(7')	3.9 ^h	3.5 ^j	3.3 ⁱ

^a The atoms are numbered according to the purposes of this table; they differ from those used consistently elsewhere. Bonds and angles between primed atoms and corresponding unprimed atoms are nearly chemically equivalent and have been used in the computation of weighted mean values in this table. ^b Reference 3. ^c This work. ^d CuLCl(H₂O) represents chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate. ^e The weighted mean of two values is given. The weighted mean values, \bar{x} , and their esd's, $\sigma(\bar{x})$, were estimated according to $\bar{x} = \sum_i(x_i/\sigma_i^2)/\sum_i(1/\sigma_i^2)$ and $\sigma(\bar{x}) = [1/\sum_i(1/\sigma_i^2)]^{1/2}$, where x_i and σ_i are individual values.¹⁹ ^f Only a single value exists for this entry (in this column). ^g The weighted mean of four values is given in this column. ^h The mean of four values is given for this entry. ⁱ The mean of two values is given for this entry. ^j The mean of eight values is given for this entry.

about 25% π character, compared to about 15% in the free ligand;⁴⁰ this supports hybrid II which has reduced ring aromaticity and enhanced thione character. (The thione resonance hybrid (IV) of 2-pyrimidinethiol, the precursor of bis(2-pyrimidyl) disulfide, is more important than the zwitterionic hybrid (V) in aqueous solution.¹⁶) Also, resonance forms II



and III reduce the repulsion between the lone-pair electrons on the sulfur atoms. (The closest Cu^I-S approach is long, 3.0 Å, and sulfur lone pairs are not directed toward Cu(I), so a similar reduction of lone-pair repulsion via a copper-sulfur interaction is unimportant.) Taken together, resonance forms I, II, and III describe a planar disulfide molecule (plane II in Table III) which has an extended π system with little conjugation across the central CSSC group.

A necessary result of the extended π system is a net partial positive charge on each sulfur atom. This is strongly supported by an ESR investigation of γ -irradiated CH₃SSCH₃ single

crystals by Gillbro,^{41a} who reported that the cation radicals formed are planar. Furthermore, recent CNDO/2 calculations by Gillbro^{41b} of the total energy of the HSSH⁺ and CH₃SSCH₃⁺ cation radicals as a function of torsion angle show a maximum at 90° and two minima, one at 0° and the other at 180°, the latter conformation being more stable.⁴² According to these calculations, the spin density (ρ) of the unpaired electron in HSSH⁺ and CH₃SSCH₃⁺ is localized mainly in the 3p _{π} orbital of each sulfur atom with $\rho = 0.53$ and 0.52, respectively.

The unusual conformation of the Co-O-O-Co group in the [(NH₃)₅CoO₂Co(NH₃)₅]⁵⁺ cation, as indicated by the crystal structures of its monosulfate tris(bisulfate) and pentanitrate salts, was interpreted in the same way.^{44a-c} The O-O bond of the superoxide anion radical is described as having a single σ bond and a three-electron π bond. The Co-O-O-Co group is nearly planar, with a torsion angle of 175.3°, in close agreement with the trans planar conformations of HSSH⁺ and CH₃SSCH₃⁺. The reduced form of the complex is, however, far from planar (Co-O-O-Co = 145.8°, relatively large for steric reasons); the bridging O₂ group, a peroxide ion, has a longer O-O bond (1.47 vs. 1.31 Å).^{44d}

The contribution of resonance structure II is also consistent with a recent empirical study²⁶ of the relationships between S-S bond lengths, (N or C)-C-S-S torsion angles, and substituents in uncomplexed symmetric aromatic disulfides.²⁷ According to this study, the equatorial conformation (X-C-S-S torsion angle near 0 or 180°) is adopted if there are no ring substituents⁴⁵ or if there is an electron-withdrawing group in only one β position (as used in ref 26, β and ortho are synonymous) of each R group. The withdrawal of electron density from the π system facilitates the donation of sulfur 3p _{π} lone-pair electron density to the π^* system of the unsaturated R group. Therefore, because this complex adopts the equatorial conformation, it is expected that the sulfur 3p _{π} orbitals interact with the π^* MO's in the pyrimidine rings, as indicated by hybrid II.⁴⁷

Lee⁵³ and Shefter²⁸ have noted that an inverse relationship exists between the lengths of the S-S and C-S bonds in disulfides. The mean C-S and S-S bond lengths for uncomplexed symmetric aromatic disulfides, as determined from the data compiled in ref 26, are as follows: equatorial conformers, C-S = 1.78 Å and S-S = 2.03 Å; axial conformers,⁵⁴ C-S = 1.76 Å and S-S = 2.08 Å. (Figure 9B of ref 36 shows that axial conformers generally have shorter C-S bond lengths than equatorial conformers.) The mean C-S and S-S bond lengths in the equatorial free ligand molecule reported herein, 1.782 and 2.019 Å, respectively, are in accordance with this relationship.

Although the adoption of the equatorial conformation by both the coordinated and the uncoordinated ligand allows the sulfur atoms to form partial π bonds with the ring carbon atoms, it appears, however, that the C-S bonds are shorter in the complex because of the extended π system (resonance hybrid II) and because of the absence, due to the 180° C-S-S-C torsion angle, of any back-donation or hyperconjugation effects.⁵⁵

A class of organic disulfides which are also planar, but have C-S-S-C torsion angles of 0°, are the following unsaturated five-membered cyclic molecules or cations: (1) xanthan hydride,⁵⁹ (2) rhodan hydrate,⁶⁰ (3) 4-methyl-1,2-dithia-4-cyclopentene-3-thione,⁶¹ (4) 3,5-diamino-1,2,4-dithiazolium ion (DADT⁺, also known as the thiuret ion),⁶² (5) 1,2-dithiolium ion (1,2-DT⁺),^{61b} (6) 3- and 4-phenyl-1,2-dithiolium ions (3- and 4-Ph-1,2-DT⁺),⁶³ (7) 3,5-diamino-1,2-dithiolium ion (3,5-DA-1,2-DT⁺),⁶⁴ and (8) 3,5-diacetamido-1,2-dithiolium ion (3,5-DAC-1,2-DT⁺).⁶⁵ Despite the unfavorable C-S-S-C torsion angle, these disulfides are stable and have considerable

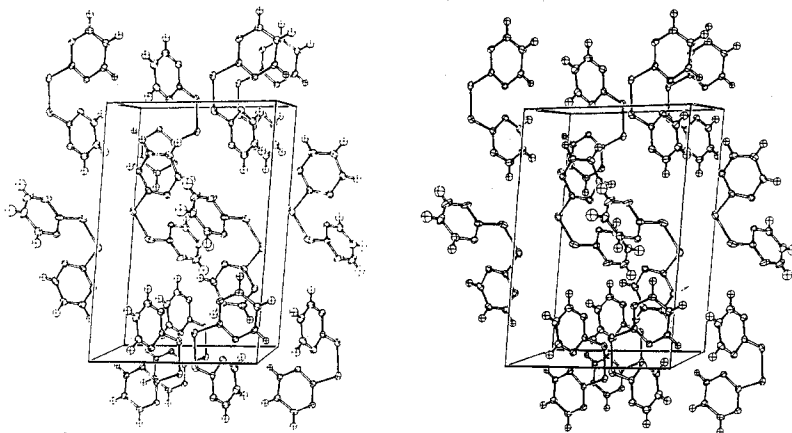


Figure 4. Stereoview of the crystal structure of bis(2-pyrimidyl) disulfide showing ellipsoids of 15% probability.¹³ The view is approximately into the $+c$ direction, with $+a$ extending horizontally to the right and $+b$ extending upward in the plane of the page.

"pseudoaromatic" character, in contrast to the relatively weak conjugation which exists in the CSSC group of the 180° disulfide molecule. For example, the π -bond orders calculated by Bergson^{61b} for the S-S and C-S bonds in 1,2-DT⁺ (0.42 and 0.69, respectively; nonoverlap case) indicate considerable participation of the S-S lone-pair electrons in the mesomeric π -electron ring system. Similarly, the π -bond orders for the S-S and C-S bonds in 3- and 4-Ph-1,2-DT⁺ range from 0.41 to 0.43 and from 0.66 to 0.71, respectively.^{63f} Crystal structure determinations^{63a-c} of the various 3- and 4-Ph-1,2-DT⁺X⁻ salts (X⁻ = SCN⁻, I⁻, Br⁻, and Cl⁻) indicate relatively short S-S and C-S bonds (means 2.01 and 1.68 Å, respectively), which agree with the strong ring conjugation predicted by the MO calculations.

Another planar organic disulfide molecule which has recently been studied is naphthalene 1,8-disulfide. Sandman et al.^{66a} have interpreted its ultraviolet photoelectron spectrum by PMO and CNDO/S2 calculations assuming the sulfur lone pairs to be orthogonal to the naphthalene plane (i.e., C-S-S-C = 0°). It was found that the HOMO is the result of a π interaction between the sulfur lone pairs and naphthalene π orbitals and that the C-S π interaction is substantial (PMO $\beta_{CS} \approx -1.8$ eV). (Their results agree with the ab initio STO-3G calculations by Riga et al.^{66b}). The calculated sulfur spin density (ρ_S^π) in the naphthalene 1,8-disulfide cation radical is 0.23,^{66c} this also indicates considerable π -electron delocalization throughout the molecule.

Bis(2-pyrimidyl) Disulfide. The crystal and molecular structure of bis(2-pyrimidyl) disulfide is presented in Figures 3 and 4. The two crystallographically nonequivalent ligand molecules have similar bond distances and angles (see Table II), which agree closely with the values reported by Furberg and Solbakk³ for bis(2-pyrimidyl) disulfide dihydrate (see Table IV).

Bis(2-pyrimidyl) disulfide adopts the equatorial conformation with a mean N-C-S-S torsion angle of 3.5° . The equatorial conformational geometry allows the sulfur atoms to donate $3p_\pi$ lone-pair electron density to the relatively low-lying π^* MO's in each pyrimidine ring. The $S_1 3p_\pi - S_2 3d_\pi$ overlap component is nearly at a maximum, according to an extended Hückel calculation,³⁰ due to the near 90° C-S-S-C torsion angle (mean 84.6°). The S-S bond length (mean 2.019 Å) is among the shortest for equatorial aromatic disulfides. The C-S bond distance (mean 1.782 Å), which is 0.023 Å longer than that in the complex, is normal for equatorial aromatic disulfides with near 90° C-S-S-C torsion angles.

The four pyrimidine rings of the two ligand molecules are nearly identical. The N-C-N angle is large (mean 128.4°) and agrees with the corresponding angle in pyrimidine (128.2°).²⁰ Although each pyrimidine ring could be expected

to have mirror symmetry perpendicular to its ring through C(3) and C(6), C(17) and C(20), etc. (see Figure 3), an examination of the data given in Tables II and IV indicates significant departures from this ideal. The largest occurs in the C-N bonds of the N-C-N part of the ring (see N(1)-C(6) and N(5)-C(6) of Table IV). This effect is probably related to the N(1)···S(8), N(10)···S(7), etc. (see Figure 3) interactions (vide supra).³

All four pyrimidine rings are quite planar; the maximum deviation from a least-squares plane is 0.015 Å (see Table III). There are several contacts between ring-nitrogen lone pairs and ring hydrogens: H(13)···N(19), 2.86 Å; H(11)···N(1), 2.63 Å; H(12)···N(1), 2.85 Å; H(2)···N(14), 2.78 Å; H(12)···N(2), 2.75 Å.

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Registry No. Chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate, 70615-14-4; bis(2-pyrimidyl) disulfide, 15718-46-4.

Supplementary Material Available: Listings of observed and calculated structure factors for chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate and bis(2-pyrimidyl) disulfide (23 pages). Ordering information is given on any current masthead page.

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