Institute of General Medical Sciences.

Registry No. $Ni(C_{18}H_{14}N_4)$, 22462-42-6; $Co(C_{18}H_{14}N_4)$, 22462-43-7; $Ni(C_{22}H_{22}N_4)$, 51223-51-9.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Bis(2-pyridine sulfinato)copper(II)

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The crystal and molecular structure of bis(2-pyridine sulfinato)copper(II), $CuC_{10}H_8N_2S_2O_4$, 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 0.028. The green monoclinic crystals form in the space group $P2_1/c$ with $a = 7.587$ (2) Å, $b = 10.106$ (3) Å, $c = 8.373$ (2) Å, $\beta = 114.08$ (2)°, and two molecules per unit cell. The tetragonally distorted octahedral Cu(II) ion lies at an inversion center where it is equatorially coordinated by two chelating 2-pyridine sulfinato ligands with Cu–N = 1.972 (2) Å and Cu–O = 1.957 (1) Å. The five-membered $\overline{\mathrm{CNCuOS}}$ chelate rings which form are nearly coplanar, with N–Cu–O = 85.20 (6)°. The remaining oxygen atoms of the ligands participate in axial approaches of 2.580 (2) Å to other Cu(II) ions; sulfinato is a bridging ligand. This compound is another product of the reaction of Cu(II) with organic disulfides to give copper(I) disulfide complexes and indicates that disulfides can be oxidized by Cu(II) in the presence of water, independent of the presence of O_2.

Introduction

Several copper(I) complexes of organic disulfides have been prepared and studied spectroscopically and crystallographically.[1-3] The reaction of bis(2-pyridyl) disulfide with $Cu(ClO_4)_2$ yielded a yellow precipitate (whose structure was subsequently determined by x-ray diffraction techniques to be a copper(I)–disulfide complex[3]) and a green product whose chemical analysis indicated that it could be a copper(II)–disulfide complex. This work was undertaken to learn its structure, to better understand the reaction of Cu(II) with organic disulfides.

Preparation Section

Cupric perchlorate hexahydrate, 99.9%, was obtained from Gallard-Schlessinger Chemical Manufacturing Corp. Bis(2-pyridyl) disulfide, trade name Aldrithiol-2, 98%, was obtained from Aldrich Chemical Co. and was recrystallized from ethanol–water as yellow needles (mp 57–58 °C). All other chemicals were of reagent grade quality. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were obtained using a Beckman IR-10 spectrometer.

Crystals were isolated by slow evaporation of a mixture of methanol solutions of cupric perchlorate hexahydrate and bis(2-pyridyl) disulfide in 1:1 and 1:2 ratios of the metal to the ligand. In the second preparation, the pH of the solution was checked periodically. Yellow and green crystals formed over a period of 2 weeks. The preparation was repeated successfully in a nitrogen atmosphere.

Anal. Calcd for the green product, $C_{10}H_8CuN_2O_4S_2$: C, 34.53; H, 2.32; Cu, 18.27; N, 8.05; O, 18.40; S, 18.43. Found: C, 34.60; H, 2.58; Cu, 17.77; N, 8.08; O (by difference), 18.30; S, 18.68.

Infrared Spectra

Infrared spectra of complexes containing the 2-pyridyl group have been studied.[4,5] The infrared spectrum of bis(2-pyridine sulfinato)copper(II), taken as a Nujol mull, has four ν(C=N), ν(C=C) bands at 1590, 1550, 1440, and 1418 cm^{-1}. The presence of only four bands indicates the approximate equivalence of the two pyridine rings.[5] The corresponding bands of bis(2-pyridyl) disulfide occur at 1568, 1552, 1440, and 1407 cm^{-1}, respectively. The shift of the 1568-cm^{-1} band to higher energy indicates coordination to the metal atom through the pyridine nitrogen. The ring-breathing mode, which appears in the disulfide at 980 cm^{-1}, is shifted to 1000 cm^{-1} in the complex and also indicates pyridine coordination.

The strong bands at 748 and 710 cm^{-1} in the disulfide are assigned to γ(C–H) and ϕ(C–C), respectively.[5] The γ(C–H) band occurs at 765 cm^{-1} in the complex, while the ϕ(C–C) band is split into two components at 712 and 700 cm^{-1}. A similar splitting has been observed in 2,2′-azopyridine complexes.[5]

The C–C out-of-plane deformation occurs at 460 cm^{-1} in the disulfide and is increased in frequency to 480 cm^{-1} in the complex, again indicating pyridine coordination. The presence of one band is indicative of a trans configuration of the pyridine rings.[5]

Sulfur–oxygen stretching vibrations have been studied.[6] Free gaseous sulfur dioxide has an antisymmetric stretch at 1362 cm^{-1} and a symmetric stretch at 1151 cm^{-1}.[7] These frequencies are shifted

Table I. Fractional Atomic Coordinates (×10^4), Thermal Parameters (×10^4), and Their Standard Deviations[a, b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0	0	0	83.6 (7)	42.7 (3)	83.3 (6)	4.8 (4)	17.4 (5)	−19.3 (4)
N(2)	2619 (2)	405 (2)	1753 (2)	95 (3)	34 (1)	71 (3)	−1 (2)	28 (2)	−2 (2)
C(3)	4243 (3)	−90 (2)	1701 (3)	107 (4)	46 (2)	92 (3)	5 (2)	42 (3)	0 (2)
C(4)	6054 (3)	292 (2)	2868 (3)	95 (4)	60 (2)	124 (4)	−2 (2)	45 (3)	8 (2)
C(5)	6214 (3)	1221 (2)	4133 (2)	102 (4)	61 (2)	109 (4)	−27 (3)	12 (3)	0 (2)
C(6)	4555 (3)	1722 (2)	4204 (3)	142 (4)	45 (2)	84 (3)	−19 (2)	24 (3)	−9 (2)
C(7)	2780 (3)	1298 (2)	2990 (2)	107 (4)	31 (2)	73 (3)	−2 (2)	30 (3)	3 (2)
S(8)	507.4 (7)	1855.4 (5)	3021.0 (6)	119 (1)	41.8 (4)	80.0 (8)	1.6 (5)	45.6 (7)	−6.4 (5)
O(9)	669 (2)	3326 (1)	2988 (2)	171 (4)	40 (1)	147 (3)	−2 (2)	62 (3)	−29 (2)
O(10)	−854 (2)	1341 (1)	1215 (2)	97 (3)	47 (1)	112 (3)	4 (2)	30 (2)	−28 (2)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	4088 (34)	−691 (22)	786 (31)	2.1 (5)	H(5)	7243 (41)	1444 (27)	4823 (36)	3.2 (6)
H(4)	6936 (53)	−100 (29)	2705 (47)	5.0 (8)	H(6)	4547 (39)	2322 (28)	5031 (34)	3.0 (6)

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

downward in complexes containing the SO_2 group. Crystal structures have been determined for two sulfinato complexes bonded through one of the oxygens.[8,9] The antisymmetric and symmetric S–O stretching frequencies for these complexes are as follows: $[Cu(p\text{-}MeC_6H_4SO_2)_2(H_2O)_4]$, 998, 938 cm^{-1};[10] $[C_5H_5Fe(CO_2)_2]Sn(SO_2Ph)_2$, 1103–1088, 869–853 cm^{-1}.[11] In the present study the sulfinato group is also bonded through an oxygen atom to Cu(II) and these S–O (coordinated) bands occur as strong absorptions at 1040 and 930 cm^{-1}. The absorptions at 1070 and 1020 cm^{-1} are assigned to the "free" S–O stretch.[6] By correlating the infrared data with crystal structure information, we can assign the S–O stretching vibration to the ranges ν_{as} 1100–ca. 1000 and ν_{sym} 1000–800 cm^{-1} in sulfinato-*O* complexes.

Some sulfinato complexes of transition metals are thought to contain a metal–sulfur bond (see, for example, ref 12). The sulfur–oxygen stretching vibrations occur at higher frequencies in organic sulfones $RS(O_2)R'$ than in corresponding sulfinate esters $RS(O)OR'$.[13,14] On the basis it has been suggested that sulfinato-*S* complexes will absorb at a higher frequency than sulfinato-*O* complexes and this has been confirmed crystallographically[15] in the case of several compounds. The crystal structure of μ-(sulfur dioxide)-bis(π-cyclopentadienyldicarbonyliron) shows that the sulfur atom bridges between two iron atoms.[16] In this compound ν_{as} occurs at 1135 cm^{-1}, and ν_{sym}, at 993 cm^{-1}.[16] These frequencies are higher than the ranges assigned to sulfinato-*O* complexes and fall in the general range expected for other sulfinato-*S* complexes.[6,15] Thus ν_{as} 1250–1100 and ν_{sym} 1100–ca. 1000 cm^{-1} indicate metal–sulfur bonding in sulfinato complexes, as has been suggested.[6] Sulfinic acids and sulfinates have wide industrial applications,[6] and a reliable infrared diagnostic for the mode of bonding in their complexes would be useful.

Diffraction Section

A single crystal of $CuC_{10}H_8N_2S_2O_4$, a rectangular prism with extreme dimensions 0.14 × 0.20 × 0.24 mm, was selected for x-ray diffraction study and was mounted approximately along its longest dimension.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ 0.709 30; Kα_2, λ 0.713 59 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 27°. The temperature was maintained at 22 (1) °C throughout. The θ–2θ scan mode was used with a scan rate (ω) in 2θ of 1° min^{-1}. The total background counting time, equal to the scan time, was spent equally at each end of the scan range, which varied from 2.0° at low 2θ to 2.4° at 60°. The data were corrected for minor fluctuations in the check reflections, which were measured after every 100 reflections during the data collection process.

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

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

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 $I = \omega(\mathrm{CT} - B_1 - B_2)$. 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 1986 symmetry-independent reflections measured, those for which $2\theta < 60°$, 1444 had intensities larger than 3 times their standard deviations, and all but two of these were used in subsequent calculations. The intensities were corrected[17] for Lorentz and polarization effects; the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character.

The atomic scattering factors for Cu^+, S^0, O^0, N^0, C^0,[18] and H (bonded)[19] were used. The first two were modified to include the anomalous dispersion correction.[20]

Crystal Data

Bis(2-pyridine sulfinato)copper(II), $CuC_{10}H_8N_2S_2O_4$, crystallizes in the monoclinic space group $P2_1/c$: $a = 7.587$ (2) Å, $b = 10.106$ (3) Å, $c = 8.373$ (2) Å, $\beta = 114.08$ (2)°, $V = 586.12$ (2) Å^3, mol wt 347.8, d_{obsd} (flotation) = 1.98 (1) g cm^{-3}, d_{calcd} = 1.9704 g cm^{-3}, $Z = 4$, and $F(000) = 346$. The space group $P2_1/c$ was assigned on the basis of the systematic absences, l odd for $(h0l)$ and k odd for $(0k0)$. Figures in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Structure Determination

The positions of Cu(II) and S were indicated on a three-dimensional Patterson function which was prepared using the fast-Fourier algorithm.[21] By successive cycles of Fourier refinement, the positions of all other nonhydrogen atoms were found. The hydrogen atom positions were revealed by a difference function. Full-matrix least-squares refinement[22] with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms led to final error indices $R_1 = \sum|F_o - |F_c||/\sum F_o = 0.028$ and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.032$. The "goodness of fit", $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 1.96. The number of observations used in least-squares is m (1442), and s (104) is the total number of parameters. The overdetermination ratio (m/s) is, therefore, 13.9. In the final cycle of full-matrix least squares, the largest shift in a nonhydrogen parameter was less than 2% of its corresponding esd; for the hydrogen atoms, this value was 12%. The only significant peak on the final difference Fourier function, whose esd is 0.06 e Å^{-3}, was 0.40 e Å^{-3} in height and was located very near the Cu(II) ion at a chemically implausible position. The positional and thermal parameters of the atoms are given in Table I.

Discussion of the Structure

The structure consists of neutral planar molecules of composition $CuC_{10}H_8N_2S_2O_4$ (see Figures 1 and 2). The tetragonally elongated octahedral Cu(II) ion lies at an inversion center where it is coordinated to two pyridyl nitrogen atoms and to two oxygen atoms of the sulfinate groups of the two ligands, to give two five-membered $\overline{\mathrm{CNCuOS}}$ chelate rings. Two other oxygens from neighboring molecules occupy the apical sites at 2.580 (2) Å, indicating an appreciably weaker axial interaction. Such axial Cu–O bond lengths are typically 0.3–0.5 Å longer than the corresponding equatorial

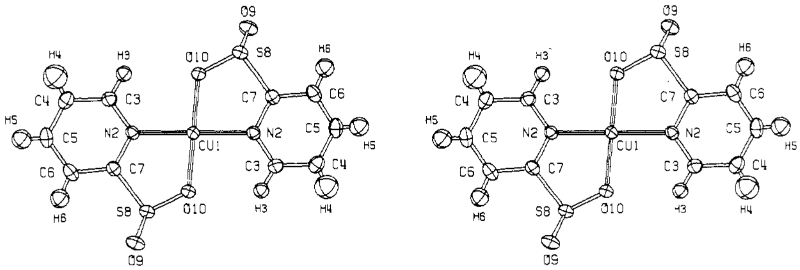


Figure 1. Stereoview of bis(2-pyridine sulfinato)copper(II) showing ellipsoids of 50% probability.[23]

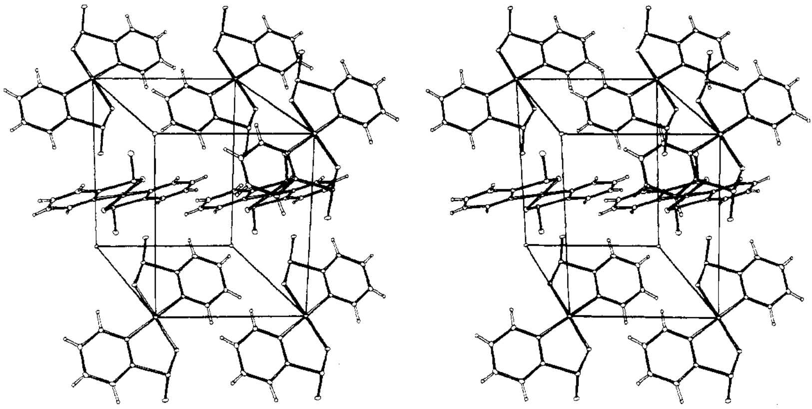


Figure 2. Stereoview of the crystal structure of bis(2-pyridine sulfinato)copper(II) in the unit cell, showing ellipsoids of 10% probability.[23] The view is approximately along *c*, with *a* horizontal and *b* vertical in the plane of the page.

distances.[24] The sulfur atoms do not coordinate. The angles at Cu(II) range from 85.2 to 93.3°, as is shown in Table II.

The Cu^{II}–N coordination distance is 1.972 (2) Å, in general agreement with the corresponding distances found in four imidazole complexes of Cu(II).[24] The Cu–N distances are 1.98 (1) Å in elongated distorted octahedral glycyl-L-histidinatocopper(II) sesquihydrate, 2.010 (12) Å in square-pyramidal β-alanyl-L-histidinatocopper(II) dihydrate, 1.99 (1) and 2.00 (1) Å in square-planar bis(imidazolato)copper(II), and 1.96 (1) and 1.97 (1) Å in flattened tetrahedral bis(imidazolato)copper(II).[24]

The equatorial Cu–O coordination distance is 1.957 (1) Å. This compares favorably with the average equatorial Cu–O distance of 1.96 ± 0.02 Å found in bis(copper(II) D-penicillamine disulfide) nonahydrate,[25] and 1.973 (4) Å in bis(toluene-*p*-sulfinato)copper(II) tetrahydrate.[8]

The angles around the trigonal-pyramidal sulfur atom, C(7)–S(8)–O(10) = 98.13 (8)°, C(7)–S(8)–O(9) = 102.85 (9)°, and O(9)–S(8)–O(10) = 110.29 (9)°, differ only marginally from those of 100.4 (5), 101.2 (5), and 108.7 (5)° in sodium hydroxymethanesulfinate dihydrate.[26] The corresponding angles in methanesulfinic acid are 95 (1), 104 (1), and 107.5 (7)°;[28] the first and third angles again differ only marginally from those found in this work. In 2-guanidoethanesulfinic acid dihydrate, these angles were found to be 100, 103.5, and 108°;[27] in bis(toluene-*p*-sulfinato)copper(II) tetrahydrate, they are 98.7 (2), 102.3 (2), and 109.1 (2)°, respectively.[8] Presumably the larger O(9)–S(8)–O(10) bond angle of 110.29 (9)° reported herein is a consequence of the steric requirements of the five-membered chelate ring.

The S–O bond distances of 1.492 (2) and 1.533 (2) Å are in agreement with those of 1.513 (9) and 1.513 (8) Å observed in sodium hydroxymethanesulfinate dihydrate[26] and 1.50 and 1.54 Å observed in 2-guanidoethanesulfinic acid dihydrate.[27] In bis(toluene-*p*-sulfinato)copper(II) tetrahydrate, these were found to be 1.511 (4) Å, which differs marginally from that reported here, and 1.541 (4) Å.[8] In methanesulfinic acid, the distances are 1.502 (9) and 1.604 (9) Å, the latter being unusually long, presumably because it is protonated.[28]

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

A. Bond Lengths, Å

Cu(1)–N(2)	1.972 (2)	S(8)–C(7)	1.825 (2)
Cu(1)–O(10)	1.957 (1)	S(8)–O(9)	1.492 (2)
Cu(1)–O(9′)	2.580 (2)	S(8)–O(10)	1.533 (2)
C(3)–C(4)	1.377 (3)	C(3)–H(3)	0.95 (2)
C(4)–C(5)	1.383 (3)	C(4)–H(4)	0.84 (4)
C(5)–C(6)	1.381 (3)	C(5)–H(5)	0.79 (3)
C(6)–C(7)	1.383 (3)	C(6)–H(6)	0.92 (3)
N(2)–C(3)	1.347 (3)		
N(2)–C(7)	1.341 (2)		

B. Bond Angles, Deg

O(10)–Cu(1)–N(2)	85.20 (6)	O(10)–S(8)–O(9)	110.29 (9)
O(9′)–Cu(1)–O(10)	85.39 (6)	O(9)–S(8)–C(7)	102.85 (9)
O(9′)–Cu(1)–N(2)	93.25 (6)	S(8)–C(7)–C(6)	122.4 (2)
Cu(1)–O(10)–S(8)	120.99 (9)	Cu(1)–N(2)–C(3)	123.8 (1)
O(10)–S(8)–C(7)	98.13 (8)	H(6)–C(6)–C(7)	117 (2)
S(8)–C(7)–N(2)	115.5 (1)	H(6)–C(6)–C(5)	124 (2)
C(7)–N(2)–Cu(1)	117.5 (1)	H(5)–C(5)–C(6)	121 (2)
C(7)–C(6)–C(5)	119.1 (2)	H(5)–C(5)–C(4)	120 (2)
C(6)–C(5)–C(4)	119.0 (2)	H(4)–C(4)–C(5)	128 (2)
C(5)–C(4)–C(3)	119.0 (2)	H(4)–C(4)–C(3)	113 (2)
C(4)–C(3)–N(2)	122.3 (2)	H(3)–C(3)–C(4)	121 (1)
C(3)–N(2)–C(7)	118.6 (2)	H(3)–C(3)–N(2)	117 (1)
C(6)–C(7)–N(2)	122.1 (2)		

C. Selected Torsion Angles, Deg

Cu(1)–N(2)–C(7)–S(8)	7.4	C(7)–S(8)–O(10)–Cu(1)	10.4
N(2)–C(7)–S(8)–O(10)	15.0	C(3)–N(2)–C(7)–C(6)	0.0

[a] The esd is in the units of the least significant digit given for the corresponding parameter. The coordinates of the primed atoms are related to those given in Table I by inversion at the origin.

The C–S bond length of 1.825 (2) Å is in agreement with all of the previously mentioned structures, the largest marginal difference being at the 3.5σ level observed in the bond length of 1.786 (11) Å in methanesulfinic acid.[28]

The molecular packing is shown in Figure 2. The shortest intermolecular distances not involving hydrogen are O(10)–C(5) = 3.30 Å, O(10)–C(4) = 3.35 Å, O(9)–O(10) = 3.11 Å, N(2)–O(9) = 3.16 Å, C(4)–C(6) = 3.36 Å, and

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

	Plane 1	Plane 2		Plane 1	Plane 2
Cu(1)	*0*	−151	S(8)	309	72
N(2)	*0*	*−1*	O(9)	−805	−1075
C(3)	−139	*1*	O(10)	*0*	−285
C(4)	−238	*3*	H(3)	−204	−37
C(5)	−202	*−6*	H(4)	−304	20
C(6)	−48	*4*	H(5)	−248	5
C(7)	44	*0*	H(6)	13	27
q_a	−3735	−2726	D	0.000	0.151
q_b	−7057	−7369	δ	0	3
q_c*	6021	6186			

[a] Italic deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with 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 rms 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. See Figure 1 to identify the planes.

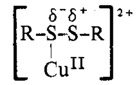
C(5)–C(7) = 3.37 Å. A short intramolecular O(10)–H(3) distance of 2.4 Å is found.

The angle between planes 1 and 2 of Table III, representing the equatorial coordination plane of Cu(II) and the pyridine plane, is 6.1°. Apart from the two O(9) oxygen atoms, each molecule is close to being planar.

Discussion

The thiol–disulfide system is biologically important.[29] The main reactions of this system with transition metal ions are (1) cleavage of the disulfide bond by metal ions, particularly by those in the second and third rows, such as mercury and silver, and (2) oxidation of thiol to disulfide with reduction of the metal ion, particularly Cu(II) to Cu(I).[30,31]

Both of these reactions occur in the present system, as indicated by the nature of the products isolated. Disulfide bond cleavage is often facilitated by concomitant electrophilic and nucleophilic attack.[32] A kinetic study of the reaction of silver nitrate with several organic disulfides indicates that the reaction proceeds with an initial attack on the S–S bond by the silver ion.[33] Cu(II), having a higher positive charge and smaller ionic radius, is more electrophilic than silver ion and polarizes the disulfide bond as shown in



$$\left[\begin{array}{c}\overset{\delta^-\delta^+}{\text{R-S-S-R}}\\ |\\ \text{Cu}^{II}\end{array}\right]^{2+}$$

Subsequent nucleophilic attack by water cleaves the disulfide bond heterolytically into RSH and RSOH. Cu(II) is reduced to Cu(I) by the thiol formed, re-forming some disulfide, and the cuprous ion is stabilized by complexation with that and excess disulfide. The sulfinato complex of copper probably forms by disproportionation of the unstable RSOH.[29,31] The total reaction is

$$7\text{Cu}^{2+} + 13\text{RSSR} + 4\text{H}_2\text{O} + 6\text{ClO}_4^- \rightarrow \text{Cu}^{\text{II}}(\text{RSO}_2)_2 + 6\text{Cu}^{\text{I}}(\text{RSSR})_2(\text{ClO}_4) + 8\text{H}^+$$

The pH of the solution is observed to decrease as the reaction progresses, as the net reaction indicates. Also supportive of this net reaction is the observation that much more disulfide complex (yellow) than sulfinato complex (green) is produced. The yield of $\text{Cu(RSSR)}_2(\text{ClO}_4)$ is improved if the initial solution contains an excess of disulfide. The green sulfinatocopper complex forms in the presence of water under a nitrogen atmosphere as well, indicating the oxidation of the disulfide to sulfinic acid can occur without oxygen.

We have previously prepared {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate[1] from the reaction of cupric ion with the corresponding disulfide, and *cyclo*-di-μ-{bis[2-(*N*,*N*-dimethylamino)ethyl] disulfide}-dicopper(I) tetrafluoroborate[2] from either the cupric ion or the cuprous ion reaction with the corresponding disulfide. The mechanism proposed here applies to those previous reactions as well.

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Registry No. Bis(2-pyridinesulfinato)copper(II), 60840-48-4.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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