Synthesis, Structure, and Characterization of Cu_4S_{10}(4-methylpyridine)$_4$

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The title compound, Cu_4S_{10}(4-methylpyridine)$_4 \cdot$ 4-methylpyridine was prepared by three different reactions: the oxidation of copper power by sulfur and the reaction of copper (I) sulfide (or $CuBr \cdot SMe_2$) with excess sulfur, both in the coordinating solvent, 4-methylpyridine. Red crystals of the compound obtained by layering with hexanes were subjected to single crystal X-ray diffraction. The structure was refined to $R = 0.026$ and $R_w = 0.036$ in a space group $P1$bar (No. 2), with $Z = 2$, $a = 13.983$ (2) Å, $b = 15.384$ (2) Å, $c = 9.660$ (1) Å, $\alpha = 93.87$ (1)°, $\beta = 93.38$ (1)°, $\gamma = 99.78$ (1)°, $V = 2037.9$ (9) Å^3. The commpound has approximate S_4 symmetry and consists of two pentasulfide chains linking four Cu(1) ions, each with a coordinating 2-methylpyridine. The infrared spectrum was dominated by absorption due to coodinated 4-methylpyridine with several low-energy peaks attributable to S–S stretches, which were also observed by Raman spectroscopy. A featureless electronic absorption spectrum yielded a single peak in the near ultraviolet upon computer enhancement ($\lambda = 334$ nm, $\varepsilon = 10,000$), most likely an intraligand transition. Cyclic voltammetry indicates that the polysulfide complex undergoes irreversible oxidation and reduction at $+0.04$ and -0.34 V vs. SCE, respectively, at 298 K in 4-methylpyridine when swept at 20 mV/sec. The electrochemical behavior was unvaried even at sweep rates as high as 100 V/sec.

KEY WORDS: Copper; polysulfide; X-ray crystal structure; infrared spectroscopy; UV/visible spectroscopy.

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INTRODUCTION

Metal sulfide chemistry is rich in its diverse structural motifs [1], particularly cluster [2], and polysulfide complexes [3, 4]. These molecules have some utility related to both hydrodesulfurization catalysis [5, 6] and materials science [7 9]. Interesting developments in the use of these complexes for materials science include insights into the structure and formation of solid-state sulfides [2, 7] and also their use as precursor compounds for low-temperature production of metal sulfides [8, 9].

Work reported by Rauchfuss *et al.* [10] is an excellent example of an interesting structure, solid-state insight, and precursor utility of a cluster polysulfide. Using a number of aromatic nitrogen base compounds such as 1-methylimidizole and pyridine, a four-copper polysulfide cluster was produced with pendant nitrogen base ligands, $Cu_4S_{10}(pyridine)_4 \cdot 1.5$ pyridine (1), being one example [10]. These complexes could then be converted to covellite, CuS, at modest tempertures ($<200°C$). A very similar structure, $Cu_4S_{10}(pyridine)_4 \cdot S_x$ (1'), was also produced by Wu and co-workers by the reaction of Cu powder with a $K_2S_x S_x$ solution in pyridine [11].

In the course of our investigations of the reactions of low-valent metal complexes, metal chalcogenides, and metal powders with molecules containing O O or S S bonds [12–14], we synthesized the 4-methyl-pyridine (2) analog of the parent pyridine complex. The crystal and molecular structures are virtually identical to those of (1) [10] and (1') [11]. To gain an understanding of bonding and structural parameters of molecule (2), we subjected it to several spectroscopic and analytical techniques including infrared and electronic absorption spectroscopies, and electrochemical studies. We note that there is a relative absence of physical studies of polysulfide complexes [3, 4]. We report on the structural parameters, spectroscopic and analytical data, and discuss these as they relate to the reactivity, stability, and bonding of polysulfides.

EXPERIMENTAL

Materials and Synthetic Procedure

All operations of moisture- and air-sensitive materials were performed under an inert atmosphere using standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. drybox equipped with an HE-493 dri-train. Solvents were freshly distilled from sodium benzophenone ketyl prior to use. Solutions

were transferred via stainless steel cannulae and/or syringes. Copper powder and sulfur (Aldrich) and copper (I) sulfide (Alfa) were used without additional purification. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Inc. (Knowville, TN).

Preparation of Cu₄S₁₀(4-methylpyridine)₄

Compound 2 was prepared by reaction of sulfur with either Cu or Cu_2S. Under argon, copper powder (1 g, 15.7 mmol) and sulfur, S_8, (1.26 g, 39.3 mmol) were stirred together in 75 mL of 4-methylpyridine for 24 hr at 25°C. Alternatively, Cu_2S powder (0.478 g, 3 mmol) and sulfur, S_8, (0.384 g, 12 mmol) were stirred together in 75 mL of 4-methylpyridine for 24 hr at 25°C. The resulting red solution was filtered and mixed with 125 mL of hexane. The yield, 9% (for Cu) and 27% (for Cu_2S) is low due most likely to the decomposition of 2 to black microcrystalline CuS [10]. Elemental analysis demonstrates that at least one coordinated 4-methylpyridine ligand is labile [15]; the same observation was made by Rauchfuss [10].

X-Ray Crystallography

Red single crystals, suitable for X-ray diffraction studies, were grown by slow interdiffusion of hexane into a 4-methylpyridine solution of $Cu_4S_{10}(4\text{-}CH_3C_5H_4N)_4$. Pertinent crystallographic data are summarized in Table I. A crystal of dimensions $0.45 \times 0.35 \times 0.28$ mm was mounted on a glass fiber and quickly transferred to the cold stream ($-120°C$) of a Rigaku AFC6S diffractometer. Unit cell parameters were determined from least-squares refinement using the setting angles of 25 high-angle reflections in the range $34.7° < \theta < 35.0°$. Intensities of three standard reflections were monitored showing no significant variation. Empirical absorption corrections were applied following standard ψ scanning of several reflections. Transmission factors were in the range of 0.76–1.00. All calculations were performed on a VAXstation 3250 computer using the TEXSAN 5.0 crystallographic software package [16]. The structure was solved by direct methods in SIR88 [17]. Full-matrix least-squares refinement with anisotropic thermal displacement parameters for all non-hydrogen atoms yielded the final R of 0.026 ($R_w = 0.036$). The hydrogen atoms were located from difference Fourier maps and included in calculations without further refinement. The difference map was featureless with the highest peak being $0.37 \, e/\text{Å}^3$.

Table I. Crystallographic Data

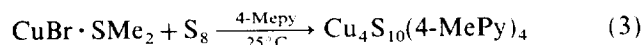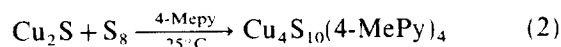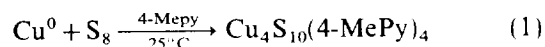|	
Empirical formula	$C_{10}H_{15}N_5S_{10}Cu_4$
Formula weight	1042.42
Crystal color and habit	red prism
Crystal dimensions	$0.45 \times 0.35 \times 0.28$ mm
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Lattice parameters	$a = 13.983(2)$ Å
	$b = 15.384(2)$ Å
	$c = 9.660(1)$ Å
	$\alpha = 93.87(1)°$
	$\beta = 93.38(1)°$
	$\gamma = 99.78(1)°$
	$V = 2037.9(9)$ Å³
Z	2
D_{calc}	1.695 gcm⁻³
Radiation, wavelength	MoK, $(\lambda = 0.71069$ Å)
$\mu(MoK_\alpha)$	25.89 cm⁻¹
No. of reflections measured	Total: 7473
	Unique: 7151 ($R_{int} = 0.023$)
No. of reflections ($I > 3\sigma(I)$)	5317
No. of variables	442
Residuals R; R_w	0.026; 0.036
Goodness-of-fit	1.08

Spectroscopy and Electrochemistry

Infrared spectra were obtained from KBr pellets, using a Mattson 4020 Galaxy series FT-IR spectrophotometer. UV/visible spectra of picoline solutions of the compound were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Computer enhancement of the UV/visible spectrum using resolution enhancement protocol was performed using SPECTRUM 1.1 (© Univ. of Maryland, 1991) on a Apple Macintosh IICX. Raman spectra were obtained by Prof. Raj Khanna at the University of Maryland, College Park, MD, using a krypton laser with an excitation energy of 6471 Å at a power of 100 milliwatts. Cyclic voltammetry was performd on an EG&G Model 250 electrochemical analysis system, with a glassy carbon working electrode, a silver wire reference and a platinum counter-electrode; the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. Potentials were corrected by running ferrocene in the same solvent reference system.

RESULTS AND DISCUSSION

Reaction Chemistry

In 1990, Rauchfuss *et al.* reported that the reaction of Cu with S_8 in pyridine (C_5H_5N, Py), reaction (1), produces the cluster $Cu_4S_{10}(Py)_4 \cdot$ 1.5 Py, where Py is a solvent of crystallization in the solid-state structure [10]. Recently, Wu *et al.* reported that the reaction of Cu with a K_2S_x/S_8 solution in pyridine produces $Cu_4S_{10}(Py)_4 \cdot S_8$ [11]. We report here that carrying out the reaction in 4-methylpyridine produces the cluster Cu_4S_{10}(4-methylpyridine)$_4 \cdot$ 4-methylpyridine (4-MePy) (**2**) whose Cu_4S_{10} cluster unit is the same as that of the Rauchfuss compound. The 4-methylpyridine cluster (**2**) can also be prepared by other routes. In fact, compound (**2**) was first produced by the reaction of Cu_2S with excess sulfur in 4-methylpyridine as shown in Eq. (2). We have also prepared (**2**) according to Eq. (3) in which $CuBr \cdot SMe_2$ reacts with S_8.

$$Cu^0 + S_8 \xrightarrow[25^\circ C]{\text{4-Mepy}} Cu_4S_{10}(\text{4-MePy})_4 \qquad (1)$$

$$Cu_2S + S_8 \xrightarrow[25^\circ C]{\text{4-Mepy}} Cu_4S_{10}(\text{4-MePy})_4 \qquad (2)$$

$$CuBr \cdot SMe_2 + S_8 \xrightarrow[25^\circ C]{\text{4-Mepy}} Cu_4S_{10}(\text{4-MePy})_4 \qquad (3)$$

The structure of compound (**2**) was determined by X-ray crystallography. The structure determination shows that this compound consists of two pentasulfide chains linking four Cu(1) ions each with a coordinating 4-methylpyridine and has approximate S_4 symmetry. The structure of (**2**) is shown in Fig. 1. Selected structural parameters are given in Table I.

The compound seems to form quite readily in systems of Cu(I)-polysulfide chemistry. Similar reaction conditions with other metals did not produce analogs of (**1**) and (**2**), but instead produced $[M(\text{N-MeIm})_6]S_8$ for $M =$ Mg, Mn, Fe, and Ni, ((N-MeIm) = N-methylimidazole $(N(CH_3)NC_3H_3)$) [18]. However, Cu_2S also served as a starting material for the production of the N-MeIm analog of (**1**) and (**2**) [18]. Compound (**1**) was found to produce CuS quite readily at $200^\circ C$ by Rauchfuss *et al.* [10]. Its facile formation but ease of decomposition seems to be a result of the metastability of Cu(1); even moderate temperatures, by solid-state processing standards, drives the redox chemistry of Cu^+ and S_n^{2-} to form CuS.
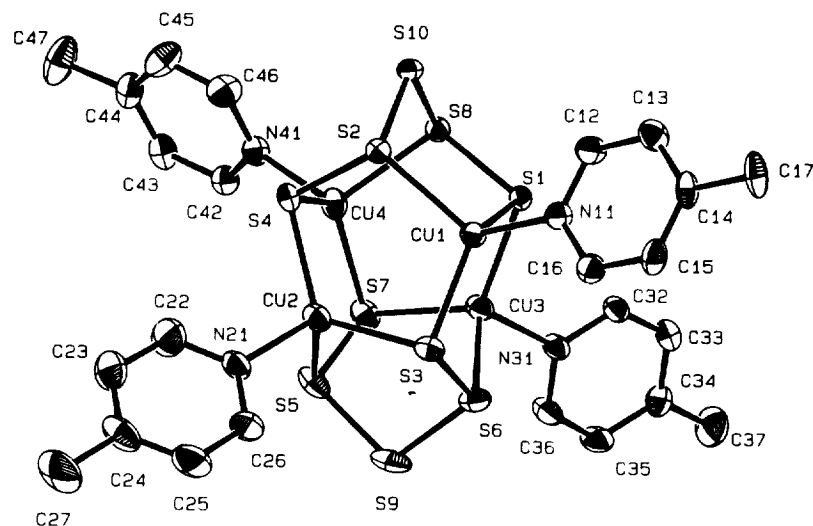
Fig. 1. ORTEP drawing of compound (2). The thermal ellipsoids enclose 50% of electron density.

Structure

The title compound (2), was characterized by single crystal X-ray diffraction. The ORTEP drawing with its labeling scheme is given in Fig. 1. This study shows that (2) is very similar to (1) and (1'), as described by Rauchfuss [10] and Wu [11], respectively. This hexadentate coordination of S_5^2 to a Cu(1) cluster was first obtained for $[Cu_6S_{17}]^2$ by Müller and co-workers [19]. The molecular structure of (2) consists of a tetrahedral arrangement of four copper (I) centers held together by two pentasulfide ligands. The shape of the cluster, which approximates S_4 symmetry, may be viewed as a distorted pentagonal prism capped by atoms S5. S6, and S9 on one end and bridged by atom S10 on the other. The most important distances are Cu1 S1 = 2.23222(9) A, Cu1-S3 = 2.296(1) A. Cu1 S2 = 2.332(1) A, and Cu1 N11 = 2.062(3) A. The S1 S8 and S2 S10 distances are 2.075(1) A and 2.059(1) A, respectively. The S1 Cu1 S2 bond angle is 100.97(3)°, the S1 Cu S1 angle is 124.39(4)°, and the S1 Cu1 N11 angle is 103.24(8)° (see Table II for relevant data).

Spectroscopy and Electrochemistry

The infrared spectrum of (2) superficially resembles that of free 4-methyl-pyridine; the results are displayed in Fig. 2 [19]. Careful comparison

Table II. Bond Distances (Å) and Angles (°)

Cu(1)	S(1)	2.3222(9)	Cu(1)	S(2)	2.332(1)
Cu(1)	S(3)	2.296(1)	Cu(1)	N(11)	2.062(3)
Cu(2)	S(3)	2.293(1)	Cu(2)	S(4)	2.275(1)
Cu(2)	S(5)	2.345(1)	Cu(2)	N(1)	2.083(3)
Cu(3)	S(1)	2.2847(9)	Cu(3)	S(6)	2.366(1)
Cu(3)	S(7)	2.298(1)	Cu(3)	N(1)	2.082(3)
Cu(4)	S(4)	2.324(1)	Cu(4)	S(7)	2.292(1)
Cu(4)	S(8)	2.340(1)	Cu(4)	N(41)	2.063(3)
S(1)	S(8)	2.075(1)	S(2)	S(4)	2.080(1)
S(2)	S(10)	2.059(1)	S(3)	S(6)	2.072(1)
S(5)	S(7)	2.083(1)	S(5)	S(9)	2.076(1)
S(6)	S(9)	2.063(1)	S(8)	S(10)	2.077(1)

S(1)	Cu(1)	S(2)	100.97(3)	Cu(1)	S(3)	S(6)	97.29(4)
S(1)	Cu(1)	S(3)	124.39(4)	Cu(1)	S(2)	S(4)	104.78(4)
S(1)	Cu(1)	N(11)	103.24(8)	Cu(1)	S(2)	S(10)	101.39(4)
S(2)	Cu(1)	S(3)	108.67(4)	Cu(1)	S(1)	Cu(3)	85.78(3)
S(2)	Cu(1)	N(11)	112.38(8)	Cu(1)	S(3)	Cu(2)	90.63(3)
S(3)	Cu(1)	N(11)	107.08(8)	Cu(1)	S(1)	S(8)	100.40(4)
S(3)	Cu(2)	S(4)	119.24(4)	Cu(2)	S(3)	S(6)	100.33(5)
S(3)	Cu(2)	S(5)	102.26(4)	Cu(2)	S(4)	Cu(4)	89.22(4)
S(3)	Cu(2)	N(21)	108.28(9)	Cu(2)	S(4)	S(2)	99.80(4)
S(4)	Cu(2)	S(5)	112.87(4)	Cu(4)	S(4)	S(2)	99.81(4)
S(4)	Cu(2)	N(21)	108.58(9)	Cu(2)	S(5)	S(7)	103.40(5)
S(5)	Cu(2)	N(21)	104.54(9)	Cu(2)	S(5)	S(9)	99.52(5)
S(1)	Cu(3)	S(6)	114.48(4)	Cu(3)	S(1)	S(8)	101.22(4)
S(1)	Cu(3)	S(7)	118.74(4)	Cu(3)	S(6)	S(3)	103.28(4)
S(1)	Cu(3)	N(31)	108.09(8)	Cu(3)	S(6)	S(9)	99.44(5)
S(6)	Cu(3)	S(7)	102.29(4)	Cu(3)	S(7)	S(5)	99.97(5)
S(6)	Cu(3)	N(31)	103.31(8)	Cu(3)	S(7)	Cu(4)	90.83(3)
S(7)	Cu(3)	N(31)	108.77(8)	Cu(4)	S(8)	S(10)	99.75(4)
S(4)	Cu(4)	S(7)	120.33(4)	Cu(4)	S(7)	S(5)	99.59(5)
S(4)	Cu(4)	S(8)	101.39(3)	Cu(4)	S(8)	S(1)	104.48(4)
S(4)	Cu(4)	N(41)	103.99(8)	S(3)	S(6)	S(9)	104.96(6)
S(7)	Cu(4)	S(8)	110.24(4)	S(1)	S(8)	S(10)	104.35(5)
S(7)	Cu(4)	N(41)	111.49(8)	S(5)	S(9)	S(6)	101.26(5)
S(8)	Cu(4)	N(41)	108.49(8)	S(2)	S(10)	S(8)	100.83(5)
S(4)	S(2)	S(10)	103.68(5)	S(7)	S(5)	S(9)	105.09(6)

the polysulfide ligands, leading eventually to production of smaller S_n^{2-} units and decomposition.

Structure and Bonding

The stability of this structure can be explained by the preferred near-tetrahedral geometry about Cu(I) and the multiple chelate effect of the S_5^{2-} ligands, forming eight pentacyclic rings. In addition, we would suggest that, in a solution that contains an equilibrium mixture of a series of polysulfide anions, Cu(I) would prefer S_5^{2-} because the delocalization of the negative charge makes it a softer ligand [22]. By contrast, S_2^{2-} tends to form complexes with harder metals having higher oxidation states and/or empty d orbitals, such as Fe(III), Co(III), Mo(IV), and Mo(V) [3]. The availability of sigma and/or pi pathways for charge delocalization onto the metal is much more important for S_2^{2-} than for S_5^{2-}, whose negative charge is less concentrated.

The lack of empty d orbitals on d^{10} Cu(I) to drain electron density from S_n^{2-} π^* orbitals explains the low observed sulfur–sulfur stretching frequencies, which are typically observed in the 480–600 cm^{-1} range [3]. A similar argument using sigma obitals leads to the same predicted result. We consider in Fig. 5 the molecular orbitals formed by combining sigma symmetry p obitals on S2 and S4 with a sigma symmetry d obital on Cu 1. In (2), all three obitals would be occupied, whereas in a metal polysulfide with fewer than 10 electrons on the metal, the highest energy orbital would be unoccupied. This orbital is antibonding with respect to the two sulfur atoms, so its occupation is expected to increase the sulfur–sulfur bond distance and reduce the sulfur–sulfur streching frequency, compared with compounds of other metals.
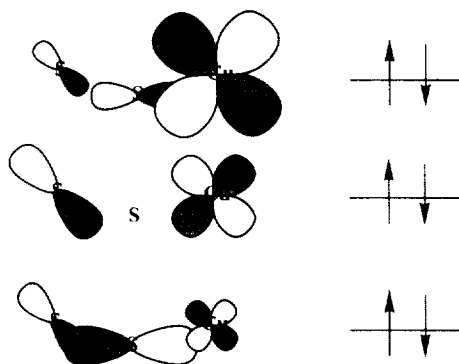

Fig. 5. Molecular obital diagram Cu and S atoms of compound (2) depicting bonding, nonbonding, and anti-bonding orbitals.

SUMMARY AND CONCLUSIONS

The compound seems to form quite readily in systems of Cu(I)-polysulfide chemistry through multiple pathways. The structure of (2) is very similar to the pyridine analogs [10, 11]. Tentative assignments of S–S stretches can be made by analogy to the literature. Computer enhancement of the UV/visible spectrum shows a near-UV band consistant with polysulfide intraligand transition. Cyclic voltammetry shows no stable oxidation or reduction. A molecular orbital analysis explains sulfur sulfur stretching frequencies at the low end of normal range.

SUPPLEMENTARY MATERIALS AVAILABLE

All atomic coordinates for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom.

ACKNOWLEDGMENTS

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