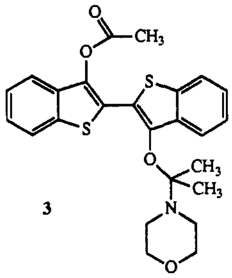
products, as yet unidentified, are produced in the much more complex reactions occurring under comparable photolysis in the absence of water or in more polar solvents; these products could result from "radical-like" reactivity of the partners such as has been observed in photoinduced electron transfer reactions of cyanoaromatics with donors such as triethylamine in studies by Ohashi,[9] Arnold,[10] and others.[11]

Related reactions have been observed with other donor-acceptor combinations, suggesting that this reaction path may be fairly general for photogenerated contact ion pairs in nonpolar solvents. Irradiation of thioindigo in the presence of **1** in degassed benzene solution leads cleanly to a metastable adduct whose NMR and visible spectra are consistent with the structure **3**, which could by formed by a comparable aar-induced cleavage of $\mathbf{1}^{\bullet+}$. Irradiation of DCA in the presence of amino ketones **4** and **5** also leads to amide and carbonyl products; in both cases, the corresponding 4-benzoylmorpholine, benzaldehyde, benzoin, and deoxybenzoin products are formed.



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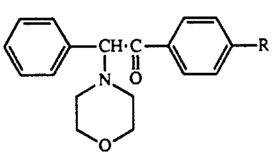

4 R=H
5 R=CH$_3$

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Interception of Copper Polysulfide Clusters in the Reaction of Copper and Sulfur in Donor Solvents: Polysulfide Complexes as the Link between Molecular and Nonmolecular Metal Sulfides

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We report a simple and potentially powerful entry into metal sulfide chemistry which involves donor solvent-assisted synthesis from the elements. The new methodology has synthetic and mechanistic implications bearing on the relationship of metal polysulfides[1] to solid-state materials.

With an interest in layered, mixed valent copper chalcogenides, we sought to develop a low-temperature synthesis of CuS (covellite).[2] We prepared covellite by the reaction of 200-mesh copper powder (928 mg, 14.6 mmol) and sulfur (458 mg, 14.3 mmol) in refluxing pyridine (py, 30 mL). After 12 h, the colorless supernatant was removed, leaving a 95% yield of covellite, pure by powder X-ray diffraction. If the same reaction is conducted at room temperature, the formation of CuS is accompanied by the appearance of an orange soluble species. After 12 h, the solution was filtered and diluted with hexanes, to give a 10-15% yield of orange crystalline $[CuS_{2.5}(py)]_n$ (**1**).[3] Compound **1** was identified as $Cu_4(S_5)_2(py)_4$ by a single-crystal X-ray diffraction study[4] of its pyridine solvate (Figure 1). This cluster consists of a compressed tetrahedral array of four copper atoms bound together by two pentasulfido chains.[5,6] The cluster has ap-

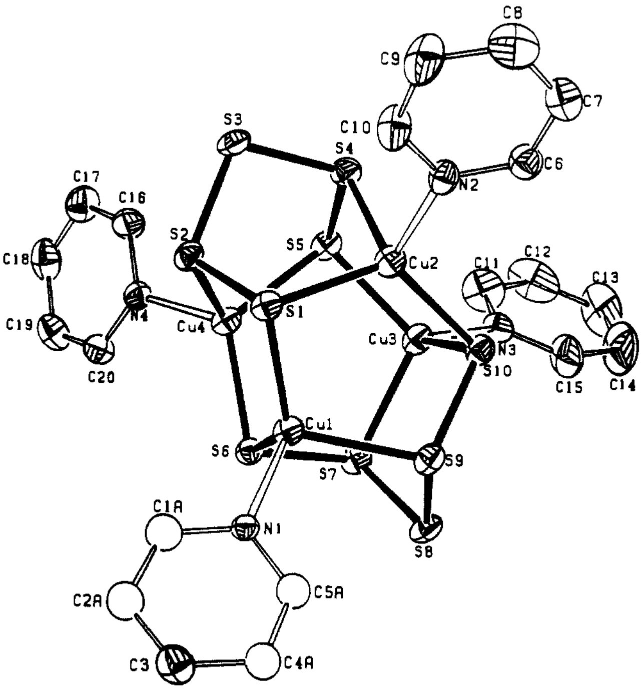
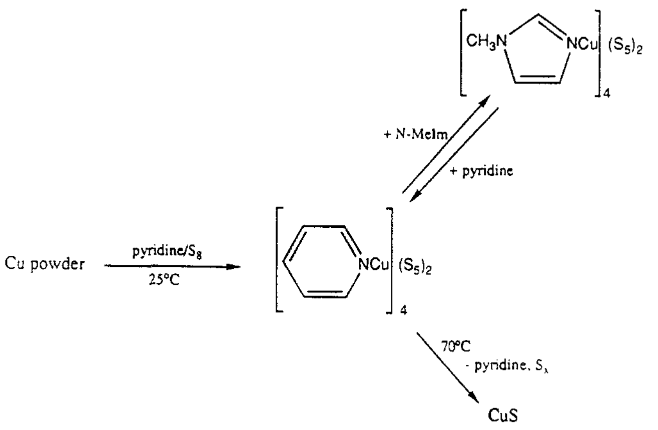


Figure 1. The structure of the $Cu_4(S_5)_2(NC_5H_5)_4$ molecule with thermal ellipsoids drawn at the 35% probability level. Representative distances (Å): Cu(1)S(1) = 2.286 (2), Cu(1)-S(6) = 2.304 (2); Cu···Cu distances fall into two categories, four distances at 3.206 (1)-3.309 (1), the two others at 3.881 (2) and 3.917 (1); Cu(1)-S(9) = 2.361 (2), Cu-N(1) = 2.074 (6); S-S distances range from 2.055 (3) to 2.081 (3). L-Cu-L angles range from 101.45 (8) to 120.85 (8)°.

Scheme I



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(3) Anal. Found (Calcd): C, 27.37 (26.95); H, 2.49 (2.27); N, 6.44 (6.29); Cu, 28.05 (28.52); S, 34.65 (35.97).

(4) $[Cu_4(S_5)_2py_4]\cdot 1.5py$ crystallizes from pyridine/hexane in the monoclinic space group $P2_1/n$ with $\alpha = 90°$, $\beta = 93.35$ (2)°, $a = 9.200$ (2) Å, $b = 21.839$ (4) Å, $c = 18.754$ (2) Å, $Z = 4$, and $\rho_{calcd} = 1.783$ g/cm^3. Using Mo Kα radiation, 5890 reflections were collected (-70 °C), of which 3418 were observed ($I > 2.58\sigma(I)$). The structure was solved by SHELX-86 and refined to a final $R = 0.040$, $R_w = 0.046$. Further details are provided in the supplementary material.

(5) For a recent discussion of copper polysulfide anions, see: Kanatzidis, M. G.; Park, P. *J. Am. Chem. Soc.* **1989**, *111*, 3767.

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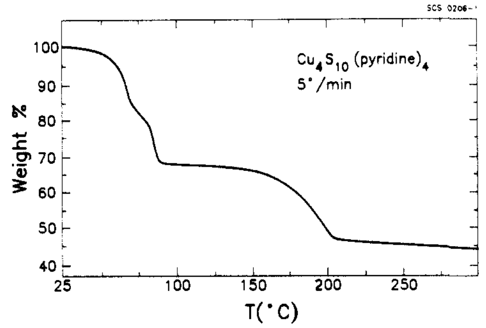

Figure 2. Thermal gravimetric analysis trace for $Cu_4(S_5)_2(py)_4$ (**1**) under an argon atmosphere. The heating rate was 5 °C/min. The theoretical values for weight changes are 82% for **1** – 2py, 64.5% for **1** – 4py. The theoretical residual weight fraction (CuS/**1**) is 43%.

proximate S_4 symmetry and can be viewed as the union of two norbornane-like Cu_2S_5 cages. The Cu–S distances indicate that each S_5 ligand is hexadentate. The copper centers achieve the inert gas configuration through bonding to three sulfur atoms as well as a nitrogen donor.

Compound **1** is an unusual example of a charge-neutral metal polysulfide and is the only polysulfide complex shown to undergo ligand substitution reactions. For example, dissolution of **1** in *N*-methylimidazole (*N*-MeIm) followed by diethyl ether precipitation gives $Cu_4S_{10}(N\text{-MeIm})_4$. This process is reversible, and the following experiment suggests that substitution occurs dissociatively (Scheme I). When suspended in toluene for 6 h at room temperature, **1** is transformed into a brown solid of the composition $Cu_4S_{10}(py)$.[7] This solid redissolves in pyridine (seconds, room temperature), and addition of hexane crystallizes **1** in 80% isolated yield.

Studies on the relationship of **1** to covellite were guided by thermogravimetric analysis (TGA).[8] The first two TGA events correspond reasonably well to the loss of 2py/**1**, and the final weight loss involves evaporation of sulfur, leaving a residue of covellite (Figure 2). Heating samples of **1** in vacuo at 70 °C cleanly gave microcrystalline covellite admixed with elemental (orthorhombic) sulfur. After a few hours at 70 °C, pyridine solutions of **1** deposited a microcrystalline powder of covellite, which was pure by powder X-ray diffraction. Given the stoichiometric simplicity of metal polysulfides, their conversion to technologically significant inorganic phases is an obvious area of application.[9,10]

The 4-Mepy and 4-*t*-Bupy analogues of **1** were prepared from suspensions of copper and sulfur in the substituted pyridines.[11] Our search for alternate solvents for this dissolving-metal synthesis uncovered the remarkable activity of *N*-methylimidazole. *A solution of sulfur in N-methylimidazole dissolves copper metal in seconds at room temperature, to give $Cu_4(S_5)_2(N\text{-MeIm})_4$ in 50% yield after diethyl ether precipitation.* Preliminary experiments show that this method works with several other metals.[12]

To summarize, we have isolated an intermediate in the reaction $M + S_8 \rightarrow MS$. Donor solvents promote this reaction, possibly by stripping polysulfide intermediates from the surface of the metal particles via complexation. Metal polysulfides have been shown to be the structural and mechanistic link between the sulfur homocycles, c-S_x,[13] and the binary metal sulfides, MS_n.

Acknowledgment. This research is supported by the National Science Foundation through Grants NSF CHE-87-11460 and NSF DMR-86-12860. We thank Professor John C. Bailar, Jr., for interesting discussions.

Supplementary Material Available: Powder X-ray diffraction patterns of covellite samples prepared under differing conditions and tables of selected bond distances and angles, positional parameters, and thermal parameters (7 pages); table of structure factors (15 pages). Ordering information is given on any current masthead page.

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(6) Other, *anionic* copper polysulfide clusters are known. $(Et_4N)_3[Cu_3(S_6)_3]$: Müller, A.; Schimanki, U. *Inorg. Chim. Acta* **1983**, *77*, L187. $(PPh_4)_2[Cu_4(S_5)_{3-x}(S_4)_x]$: Müller, A.; Römer, M.; Bögge, H.; Krickenmeyer, E.; Schmitz, K. *Inorg. Chim. Acta* **1984**, *85*, L39. $(PPh_4)_2\{[Cu(S_6)]_2(\mu\text{-}S_8)\}$ and $(PPh_4)_2(NH_4)[Cu_4(S_4)_3\}$: Müller, A.; Baumann, F.-W.; Bögge, H.; Römer, M.; Krickemeyer, E.; Schmitz, K. *Angew. Chem., Int. Ed. Engl.* **1984**, *13*, 632; *Angew. Chem.* **1984**, *96*, 607. $(PPh_4)_2[Cu_6(S_4)_3(S_5)]$: Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Bergmann, D. *J. Chem. Soc., Chem. Commun.* **1984**, 384. Related copper 1,1-dithiolate clusters: Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233.

(7) Anal. Calcd for $C_5H_5Cu_4NS_{10}$ (found, two samples for C, H, N): C, 9.18 (9.90, 8.51); H, 0.77 (0.81, 0.74); N, 2.14 (2.38, 2.05); S, 49.02 (47.63, –).

(8) Thermal gravimetric data were collected by using a Perkin Elmer TGA Series TAS instrument. X-ray powder diffraction data were collected on a Rigaku D/Max-B diffractometer using graphite-filtered Cu Kα radiation with a scan speed of 5 deg/min. The diffraction patterns were matched with CuS and orthorhombic S_8 ($I/I_0 = 100$ at $d = 3.85$ Å) in the JCPDS—International Centre for Diffraction Data 1989 powder diffraction files no. 6-464 (covellite) and 8-247 (orthorhombic S_8).

(9) A Chemical Abstracts Service search for "CuS" retrieved 24 patents for the three-year period 1987–1989. Subjects include secondary nonaqueous batteries, electrophotographic toners, fabrics, varistor materials, electrically conductive polymer composites, electrically conductive pastes, and synthesis gas catalysts.

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(11) Analytical data for $Cu_4(S_5)_2(4\text{-}t\text{-Bupy})_4$: C, 39.13 (38.75); H, 4.83 (4.71); N, 4.92 (5.02); S, 28.92 (28.74). For $Cu_4(S_5)_2(4\text{-Mepy})_4$: C, 29.36 (30.43); H, 3.22 (2.99); N, 5.90 (5.92); S, 33.61 (33.84). For $Cu_4(S_5)_2(N\text{-MeIm})_4$: C, 21.52 (21.27); H, 2.80 (2.68); N, 12.60 (12.41); S, 35.24 (35.49).

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^{17}O Isotopic Tracer Evidence for the Formation of a Sulfurane Intermediate during Sulfide Photooxidation

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In 1983 Foote and co-workers[1] reported a detailed kinetic study of diethyl sulfide photooxidation which requires that sulfide photooxidation is more complicated than previously assumed.[2] Trapping experiments with diphenyl sulfide and sulfoxide in aprotic solvents demonstrated the need for at least two intermediates on the reaction surface. In contrast, in protic solvents only one intermediate was necessary to accommodate the kinetic results.

A variety of structures for these intermediates have been suggested and include a persulfoxide,[3] a thiadioxirane,[4] an ion pair,[5] a sulfurane,[6] and a hydrogen-bonded persulfoxide.[3] Direct experimental evidence, however, for the structures of these intermediates is limited. The scarce experimental evidence supporting one or more of these intermediates includes (1) Ando's report[7] that the intermediate is electrophilic in methanol, consistent with either a thiadioxirane or sulfurane; (2) Sawaki and Ogata's report[8] that the intermediate is nucleophilic in benzene, consistent

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(2) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.

(3) For a diradical formulation of the persulfoxide, see: Takata, T.; Ando, W. In *Singlet Oxygen. Reaction Modes and Products. Part 2*; CRC Press, Inc.: Boca Raton, FL, 1985; Vol. III, p 1. For a zwitterionic formulation, see: Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

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