rangement of the rings N(1)–C(1)–C(2)–S(1)–C(3) (see Figure 11).

It seems that these interactions may be more effective in the A form. Moreover, the chains of close contacts between the sulfur atoms are apparent. The corresponding intermolecular distances are S(1)–S(5) = 3.35 Å for A and S(2)–S(4) = 3.61 Å, S(1)–S(6) = 3.42 Å, and S(3)–S(5) = 3.42 Å for the B form. It would appear that the structure of polymorph A allows for more effective intermolecular interactions (despite the lower density) than the structure of polymorph B does. The difference between both structures is not very dramatic, however.

Conclusions

This is, to our knowledge, the first case of two polymorphs of an iron(II) compound in which the "spin-crossover" behavior is seen in only one modification. The complex bis(thiocyanato)-bis(2,2'-bipyridyl)iron(II) forms three polymorphs. All three exhibit the "spin crossover" at similar temperatures, however.[31] The triclinic modification of bis(3-chloropyridine)(octaethyl-porphinato)iron(III) perchlorate exhibited a $S = \frac{1}{2} \leftrightarrow S = \frac{5}{2}$ spin transition,[32,33] while the monoclinic form had the iron in a mixed $\frac{3}{2}$–$\frac{5}{2}$ spin state. In this case there were distinct differences in the orientation of the 3-Cl-py ligand that readily explained the difference in behavior. In the system studied here, the two structures are very similar and it was difficult to pin down any differences that could be called key factors.

The EPR parameters observed for the low- and high-spin phases indicate that the change in crystal geometry must be very minor during the phase transition. EPR line widths of the low-spin resonance observed during the spin transition in large crystals have shown that the transition involves rather larger domains than have been proposed in studies on powders. The dependence of the rate of the high- to low-spin transition on crystal size suggests that the domains start at a few centers and that there are fewer such centers in the larger single crystals.

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Transition-Metal-Promoted Oxidation of Organic Sulfides. Synthesis, Characterization, and Structure of (μ4-Oxo)hexakis(μ2-chloro)tetrakis(dialkyl sulfoxide)tetracopper(II)

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The transition-metal-promoted dioxygen oxidation of thioethers was examined under ambient reaction conditions. Direct reactions of CuCl$_2$·2H$_2$O with alkyl thioethers is shown to yield the unique copper tetramer Cu$_4$Cl$_6$O(OSR$_2$)$_4$ (R = ethyl (1), n-butyl (2)) upon oxidation. These complexes were examined by IR, UV–vis, and X-ray diffraction techniques. The species Cu$_4$Cl$_6$O(OS-(CH$_2$CH$_3$)$_2$)$_4$ was determined by X-ray crystallography to contain a central μ$_4$-oxide surrounded pseudotetrahedrally by four trigonal-bipyramidal Cu(II) atoms. The five-coordinate copper atoms have bridging chlorides in the equatorial position with the μ$_4$-oxygen and a sulfoxide oxygen in the axial positions. The complex crystallizes in the orthorhombic noncentrosymmetric space group $P2_12_12_1$ with a = 10.436 (2) Å, b = 11.092 (2) Å, and c = 29.679 (7) Å. Final discrepancy values of R = 0.049 (R_w = 0.059) were obtained from 2378 unique, observed reflections. Distortions from ideal symmetry are observed in the {Cu$_4$O} core, in which the Cu–O$_{cen}$ bond distances range from 1.883 (7) to 1.911 (7) Å. The equatorial planes of the five-coordinate coppers are also distorted from true trigonal-bipyramidal geometry with Cu–Cl bond distances ranging from 2.360 (3) to 2.451 (3) Å and Cl–Cu–Cl bond angles ranging from 109.4 (1) to 129.4 (1)°. The IR spectra of the complexes show $\nu_{S=O}$ stretches of 956 and 930 cm^{-1} and $\nu_{Cu—O}$ of 585 and 583 cm^{-1} for 1 and 2, respectively. The formation mechanism is proposed to involve a Cu^I–SR^2 intermediate followed by air oxidation to the Cu^{II} tetramer with coordinated sulfoxide ligands.

Introduction

The chemistry of Cu^{II} with sulfur donor ligands has important implications in a variety of diverse areas. These include the naturally occurring blue copper proteins[1] and the copper-promoted oxidation of thioethers to sulfoxides.[2] Copper complexes of chelating, multidentate ligands with cyclic thioethers have been studied extensively in the past due to the enhanced stability of the Cu–S bond in such complexes.[3] In contrast, relatively little is known about Cu^{II} reactions with less complex thioethers. Simple alkyl thioethers tend to form more ephemeral copper compounds due to their weak coordination to the metal center and can readily

reduce the Cu^{II} to Cu^I.[4] In light of this, we have undertaken a study of the reactivity of Cu^{II} with simple thioethers and have successfully characterized the reaction product of CuCl$_2$ with the alkyl thioethers (C$_2$H$_5$)$_2$S, (CH$_3$(CH$_2$)$_3$)$_2$S, and ((CH$_3$)$_3$C)$_2$S by IR and UV–visible spectra, elemental analysis, and X-ray dif-

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Table I. Summary of X-ray Diffraction Data for 1

formula	$C_{16}H_{40}Cl_6Cu_4O_5S_4$
fw	907.63
space group	$P2_12_12_1$
a, Å	10.436 (2)
b, Å	11.092 (2)
c, Å	29.679 (7)
V, Å^3	3435.20 (14)
Z	4
ρ_{calcd}, g/cm^3	1.75
cryst dimens, mm	0.38 × 0.40 × 0.22
temp, K	230
instrument	Nicolet R3MV
radiation (λ = 0.710 69 Å)	Mo Kα, graphite monochromator
μ, mm^{-1}	3.18
2θ max, deg	45
scan type, rate	$\theta/2\theta$, variable 10–60°/min
scan width, deg	$2\theta(K\alpha_1)$ − 0.9 to $2\theta(K\alpha_2)$ + 0.9
no. of unique observns	2594
check reflcns	3 std/100 new
check reflcn variations	3.5% random
no. of data, $F_o > 3\sigma(F_o)$	2378
$R(R_w)$	0.049 (0.059)
goodness of fit	1.37
max shift/esd	0.01
diff Fourier excursions, e/Å^3	0.594, −0.661

fraction. Under extreme conditions (120 °C, 50 atm of O_2) $CuCl_2$ is known to catalyze the oxidation of sulfides to sulfoxides and sulfones.[5] Under milder reaction conditions, cyclic thioethers and dithioethers have been shown to yield either a mixed-valent complex such as $\{Cu^I_3Cu^{II}Cl_5(SC_4H_8)_3\}_n$ or Cu^I complexes such as [CuLCl].[2] Simpler thioethers were previously thought to react with $CuCl_2$ to generate impure complexes, which were formulated as $CuCl_2(OSR_2)$ complexes.[2] Our exploration of this system has shown that the direct reaction of $CuCl_2\cdot 2H_2O$ with alkyl thioethers yields the air oxidation product $Cu_4Cl_6O(OSR_2)_4$, when R = CH_2CH_3 (**1**) or $(CH_2)_3CH_3$ (**2**). Conversely, a more sterically hindered sulfide, such as $((CH_3)_3C)_2S$, reduces Cu^{II} to Cu^I to generate a species that is formulated as $Cu_2Cl_2S(C(CH_3)_3)_2$ (**3**).

Experimental Section

Sulfides were purchased from Aldrich Chemical Co. and used without further purification. $CuCl_2\cdot H_2O$ was purchased from Sigma Chemical Co. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1710 FTIR or on a Perkin-Elmer 1430 dispersion IR instrument. Electronic spectra were collected in acetonitrile solution on a Cary 2390 spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc.

Preparation of $Cu_4Cl_6O(OSR_2)_4$, R = CH_2CH_3 (1), $(CH_2)_3CH_3$ (2). $CuCl_2\cdot 2H_2O$ (3.7 g, 22 mmol) was suspended in 200 mL of acetone, the appropriate sulfide (4 mL, 23 mmol) was added, and then the mixture was stirred in air for 24 h. The product that formed was collected by filtration, yielding orange crystals, which were washed with copious amounts of diethyl ether (yields 40–50%).

Anal. Calcd for $C_{16}H_{40}Cl_6Cu_4O_5S_4$ (**1**): C, 21.17; H, 4.44; Cl, 23.44; S, 14.13; Cu, 28.00. Found: C, 21.08; H, 4.41; Cl, 23.49; S, 14.36; Cu, 28.13. IR (KBr): 2983, 2968, 2939, 2924, 2880, 1456, 1409, 1381, 1374, 1267, 956 (b, S=O), 783 (b, S—C), 774 (sh, S—C), 585 (b, Cu—O), 509, 445 cm^{-1}. UV–vis (CH_3CN), λ_{max}, nm (ϵ L·mol^{-1}·cm^{-1}): 221 (2259), 277 (4259), 403 (482), 914 (296).

Anal. Calcd for $C_{32}H_{72}Cl_6Cu_4O_5S_4$ (**2**): C, 33.95; H, 6.41; Cl, 18.79; S, 11.33; Cu, 22.45. Found: C, 33.70; H, 6.41; Cl, 19.10; S, 11.38; Cu, 22.63. IR (KBr): 2956, 2936, 2904, 2870, 1469, 1451 (sh), 1414, 1400 (sh), 1377 (w), 1367 (w), 930 (b, S=O), 739 (s, S—C), 583 (s, Cu—O), 575 (sh), 479 cm^{-1}. UV–vis (CH_3CN), λ_{max}, nm (ϵ, L·mol^{-1}·cm^{-1}): 222 (2369), 278 (4253), 372 (599), 408 (447), 915 (351).

Preparation of $Cu_2Cl_2S(C(CH_3)_3)_2$ (3). $CuCl_2\cdot H_2O$ (3.6 g, 21 mmol) was suspended in 200 mL of acetone. $((CH_3)_3C)_2S$ was then added (4 mL, 22 mmol), and the reaction mixture was stirred in air for 24 h. A precipitate of white needles was collected and washed with diethyl ether

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Table II. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **1**

	x	y	z	$U(eq)^a$
Cu(1)	4023 (1)	4432 (1)	911 (1)	21 (1)
Cu(2)	2974 (1)	6254 (1)	1612 (1)	22 (1)
Cu(3)	1336 (1)	5585 (1)	782 (1)	24 (1)
Cu(4)	1754 (1)	3711 (1)	1528 (1)	29 (1)
Cl(12)	5160 (2)	5795 (3)	1400 (1)	39 (1)
Cl(13)	2984 (3)	5069 (3)	241 (1)	44 (1)
Cl(14)	3494 (3)	2467 (3)	1240 (1)	45 (1)
Cl(23)	1451 (3)	7410 (3)	1214 (1)	46 (1)
Cl(24)	2269 (3)	4838 (3)	2194 (1)	46 (1)
Cl(34)	1 (3)	3959 (3)	1015 (1)	53 (1)
S(1)	5420 (3)	2837 (3)	274 (1)	47 (1)
S(2)	4579 (3)	7571 (3)	2296 (1)	52 (1)
S(3)	−1123 (3)	5791 (3)	225 (1)	48 (1)
S(4)	1579 (3)	1540 (3)	2124 (1)	53 (1)
O(1)	5555 (7)	3916 (8)	612 (3)	44 (3)
O(2)	3370 (8)	7586 (8)	2010 (3)	49 (3)
O(3)	190 (8)	6285 (9)	345 (3)	58 (3)
O(4)	863 (9)	2469 (9)	1844 (4)	72 (4)
O(5)	2540 (6)	4984 (7)	1212 (2)	27 (2)
C(1)	6198 (14)	1578 (14)	559 (6)	69 (6)
C(2)	7442 (14)	1790 (18)	748 (5)	83 (7)
C(3)	6563 (13)	3170 (13)	−155 (4)	52 (5)
C(4)	6040 (15)	4221 (16)	−458 (5)	77 (7)
C(5)	5705 (16)	8521 (15)	1991 (6)	77 (7)
C(6)	5185 (23)	9641 (17)	1845 (6)	112 (10)
C(7)	4207 (16)	8539 (16)	2752 (5)	74 (6)
C(8)	3145 (17)	7945 (16)	3050 (6)	89 (8)
C(9)	−1536 (13)	6707 (14)	−246 (4)	57 (5)
C(10)	−745 (16)	6265 (18)	−661 (5)	86 (7)
C(11)	−2252 (15)	6286 (18)	643 (6)	80 (7)
C(12)	−2058 (16)	7638 (20)	752 (5)	87 (8)
C(13)	692 (15)	1544 (19)	2636 (5)	83 (7)
C(14)	1204 (20)	967 (29)	3005 (6)	160 (15)
C(15)	1185 (16)	116 (16)	1864 (7)	82 (7)
C(16)	−256 (15)	64 (15)	1739 (5)	73 (6)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(30% yield). This compound is thought to be similar to the Cu^I species reported previously.[2]

Anal. Calcd for $C_8H_{18}Cl_2Cu_2S$: C, 27.91; H, 5.27; Cl, 20.59; S, 9.31; Cu, 36.91. Found: C 27.71; H, 5.14; Cl 20.60; S, 9.65; Cu, 36.60. IR (KBr): 3001, 2989, 2969, 2948 (sh), 2925 (sh), 2904, 2869 (b), 1482 (sh), 1470, 1457 (sh), 1442, 1398 (sh), 1391, 1367 (s), 1169 (sh), 1150, 1037 (w), 1029 (w), 1021 (w), 800, 669 (s), 573, 557 (sh), 475 cm^{-1}.

X-ray Data and Structure Determination

Pertinent collection parameters are contained in Table I. Due to crystal decomposition the crystal was covered with stopcock grease and a rapid minimum scan rate was used for data collection. The structure was solved by a combination of direct methods that located the Cu, Cl, S, and O atoms and difference Fourier methods to locate the C atoms. Refinement was by full-matrix least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2|F_o| + g(F_o)^2]$, $g = 0.001$. Positions and anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogens were included by using a riding model in which the coordinate shifts of the covalently bonded atoms were also applied to the hydrogens (C–H distances held at 0.96 Å), and they were given an overall isotropic parameter of $U = 0.08$ Å^2. All programs used were part of the Microvax versions of the SHELXTL system of programs.[6]

X-ray Structure Results

Figure 1 illustrates the results of the X-ray study on **1**. It has been drawn by using the experimental atomic coordinates given in Table II. The bond lengths and angles are included in Tables III and IV, respectively.

The copper atoms are located in a distorted tetrahedron around the central oxygen (O(5)) with Cu–O(5) distances of 1.888 (7), 1.898 (7), 1.911 (7), and 1.883 (7) Å for Cu(1)–Cu(4), respectively. The maximum difference in the Cu–O(5) distance is approximately 4 times the standard deviation for the Cu–O(5)

(6) Sheldrick, G. "SHELXTL80. Minicomputer Programs for X-ray Structure Determination"; University of Göttingen, 1980.

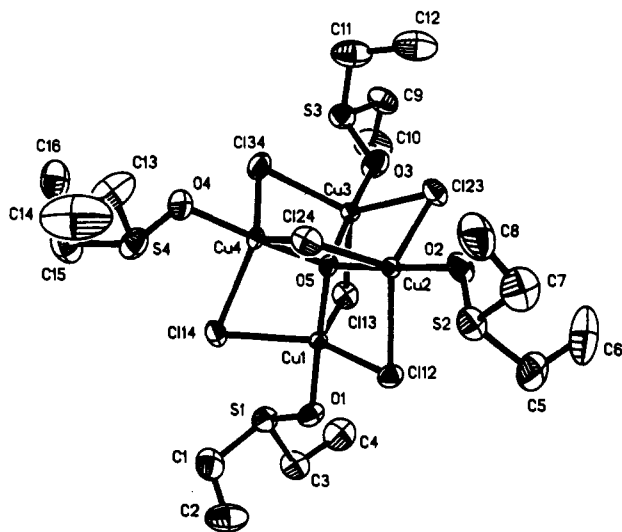**Figure 1.** Molecular geometry and atomic numbering scheme for **1**.

Table III. Bond Lengths (Å) for **1**

Cu(1)–Cl(12)	2.409 (3)	Cu(1)–Cl(13)	2.374 (3)
Cu(1)–Cl(14)	2.451 (3)	Cu(1)–O(1)	1.917 (7)
Cu(1)–O(5)	1.888 (7)	Cu(2)–Cl(12)	2.421 (3)
Cu(2)–Cl(23)	2.360 (3)	Cu(2)–Cl(24)	2.447 (3)
Cu(2)–O(2)	1.935 (8)	Cu(2)–O(5)	1.898 (7)
Cu(3)–Cl(13)	2.422 (3)	Cu(3)–Cl(23)	2.398 (3)
Cu(3)–Cl(34)	2.383 (3)	Cu(3)–O(3)	1.928 (8)
Cu(3)–O(5)	1.911 (7)	Cu(4)–Cl(14)	2.436 (3)
Cu(4)–Cl(24)	2.399 (4)	Cu(4)–Cl(34)	2.396 (3)
Cu(4)–O(4)	1.909 (10)	Cu(4)–O(5)	1.883 (7)
S(1)–O(1)	1.566 (8)	S(1)–C(1)	1.823 (16)
S(1)–C(3)	1.785 (12)	S(2)–O(2)	1.522 (8)
S(2)–C(5)	1.820 (17)	S(2)–C(7)	1.770 (15)
S(3)–O(3)	1.518 (9)	S(3)–C(9)	1.782 (13)
S(3)–C(11)	1.795 (15)	S(4)–O(4)	1.520 (10)
S(4)–C(13)	1.779 (14)	S(4)–C(15)	1.806 (17)
C(1)–C(2)	1.434 (20)	C(3)–C(4)	1.569 (21)
C(5)–C(6)	1.423 (24)	C(7)–C(8)	1.563 (21)
C(9)–C(10)	1.562 (19)	C(11)–C(12)	1.547 (25)
C(13)–C(14)	1.376 (24)	C(15)–C(16)	1.550 (20)

bond lengths and therefore represents a true deviation from perfect tetrahedral symmetry. A slight distortion around the central oxygen is also observed in the Cu–O(5)–Cu bond angles, which vary from 107.9 (3)° for Cu(4)–O(5)–Cu(3) to 110.5 (4)° for Cu(4)–O(5)–Cu(1). Similar distortions in the {Cu₄O} framework are observed in analogous complexes such as Cu₄Cl₆O(OPEt₃)₄,[7] Cu₄Cl₆O(NC₇H₇)₄,[8] and Cu₄Cl₆O(C₆H₁₂N₄)₄.[9] The distortion from tetrahedral geometry appears to be a predominant character for complexes of the type Cu₄Cl₆OL₄,[7-10,11] with some distortion observed in all of the reported examples that do not have crystallographically imposed symmetry.

The halide bridges also exhibit a large degree of asymmetry. The Cu–Cl bond distances range from 2.360 (3) to 2.447 (3) Å

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Table IV. Bond Angles (deg) for **1**

Cl(13)–Cu(1)–Cl(12)	122.9 (1)	Cl(14)–Cu(1)–Cl(12)	115.5 (1)
Cl(14)–Cu(1)–Cl(13)	119.7 (1)	O(1)–Cu(1)–Cl(12)	93.2 (2)
O(1)–Cu(1)–Cl(13)	94.6 (3)	O(1)–Cu(1)–Cl(14)	96.1 (3)
O(5)–Cu(1)–Cl(12)	85.2 (2)	O(5)–Cu(1)–Cl(13)	85.7 (2)
O(5)–Cu(1)–Cl(14)	85.2 (2)	O(5)–Cu(1)–O(1)	178.3 (3)
Cl(23)–Cu(2)–Cl(12)	128.2 (1)	Cl(24)–Cu(2)–Cl(12)	109.4 (1)
Cl(24)–Cu(2)–Cl(23)	120.0 (1)	O(2)–Cu(2)–Cl(12)	96.7 (3)
O(2)–Cu(2)–Cl(23)	92.0 (3)	O(2)–Cu(2)–Cl(24)	97.1 (3)
O(5)–Cu(2)–Cl(12)	84.6 (2)	O(5)–Cu(2)–Cl(23)	85.9 (2)
O(5)–Cu(2)–Cl(24)	83.9 (2)	O(5)–Cu(2)–O(2)	177.9 (3)
Cl(23)–Cu(3)–Cl(13)	121.2 (1)	Cl(34)–Cu(3)–Cl(13)	115.4 (1)
Cl(34)–Cu(3)–Cl(23)	120.9 (1)	O(3)–Cu(3)–Cl(13)	95.1 (3)
O(3)–Cu(3)–Cl(23)	92.9 (3)	O(3)–Cu(3)–Cl(34)	97.9 (3)
O(5)–Cu(3)–Cl(13)	83.9 (2)	O(5)–Cu(3)–Cl(23)	84.6 (2)
O(5)–Cu(3)–Cl(34)	85.8 (2)	O(5)–Cu(3)–O(3)	176.2 (4)
Cl(24)–Cu(4)–Cl(14)	114.7 (1)	Cl(34)–Cu(4)–Cl(14)	114.3 (1)
Cl(34)–Cu(4)–Cl(24)	129.4 (1)	O(4)–Cu(4)–Cl(14)	97.3 (3)
O(4)–Cu(4)–Cl(24)	94.6 (4)	O(4)–Cu(4)–Cl(34)	91.3 (3)
O(5)–Cu(4)–Cl(14)	85.7 (2)	O(5)–Cu(4)–Cl(24)	85.6 (2)
O(5)–Cu(4)–O(4)	86.0 (2)	O(5)–Cu(4)–O(4)	176.6 (4)
Cu(2)–Cl(12)–Cu(1)	79.8 (1)	Cu(3)–Cl(13)–Cu(1)	80.7 (1)
Cu(4)–Cl(14)–Cu(1)	78.7 (1)	Cu(3)–Cl(23)–Cu(2)	81.0 (1)
Cu(4)–Cl(24)–Cu(2)	79.7 (1)	Cu(4)–Cl(34)–Cu(3)	79.9 (1)
C(1)–S(1)–O(1)	104.4 (6)	C(3)–S(1)–O(1)	103.8 (6)
C(3)–S(1)–C(1)	101.1 (7)	C(5)–S(2)–O(2)	104.5 (7)
C(7)–S(2)–O(2)	103.8 (6)	C(7)–S(2)–C(5)	99.8 (8)
C(9)–S(3)–O(3)	101.3 (6)	C(11)–S(3)–O(3)	108.7 (7)
C(11)–S(3)–C(9)	102.0 (8)	C(13)–S(4)–O(4)	102.1 (8)
C(15)–S(4)–O(4)	104.3 (7)	C(15)–S(4)–C(13)	104.4 (9)
S(1)–O(1)–Cu(1)	116.7 (4)	S(2)–O(2)–Cu(2)	120.6 (5)
S(3)–O(3)–Cu(3)	124.8 (6)	S(4)–O(4)–Cu(4)	121.2 (6)
Cu(2)–O(5)–Cu(1)	109.9 (3)	Cu(3)–O(5)–Cu(1)	109.7 (4)
Cu(3)–O(5)–Cu(2)	108.4 (4)	Cu(4)–O(5)–Cu(1)	110.5 (4)
Cu(4)–O(5)–Cu(2)	110.4 (4)	Cu(4)–O(5)–Cu(3)	107.9 (3)
C(2)–C(1)–S(1)	117.3 (13)	C(4)–C(3)–S(1)	109.2 (9)
C(6)–C(5)–S(2)	114.2 (13)	C(8)–C(7)–S(2)	109.4 (12)
C(10)–C(9)–S(3)	108.2 (10)	C(12)–C(11)–S(3)	110.8 (13)
C(14)–C(13)–S(4)	118.5 (14)	C(16)–C(15)–S(4)	110.8 (12)

for the Cu(2)–Cl(23) and Cu(2)–Cl(24) bond lengths, respectively. It is interesting to note that the longest and shortest Cu–Cl bond distances emanate from the same copper atom. The remaining Cu–Cl bonds show a large range of Cu–Cl bond distances. This is surprising in light of the expected chemical equivalence of the chlorides. Asymmetry in the chloride bridges is also in accord with the other structures reported from this series.[10]

The copper atoms reside in a pseudo-trigonal-bipyramidal geometry. The axial distortion is due in part to the differences in the donor ability of the ligating oxygens. Equatorial distortions are also observed that are due to the previously mentioned asymmetry in the {Cu–O(5)} framework. The Cu–Oₛ bond lengths range from 1.909 (10) Å for Cu(4)–O(4) to 1.935 (8) Å for Cu(2)–O(2). These are all shorter than the Cu–Oₛ bond length in the similar compounds CuCl₂(C₄H₈SO), CuCl(DMSO),[12] and Cu₂Br₄(OSC₄H₈)₄.[13] The average bond length between the copper and the sulfoxide oxygen (Cu–Oₛ) is slightly larger than the average Cu–O5 bond length and the O(5)–Cu–Oₛ bond angles deviate by 2–4° from the expected 180° for a perfect trigonal bipyramidal structure.

Distortion from trigonal-bipyramidal geometry is also observed in the equatorial plane of the copper atoms, as seen in the variability of the Cl–Cu–Cl bond angles, which range from 109.4 (1)° for Cl(24)–Cu(2)–Cl(12) to 129.4 (1)° for Cl(34)–Cu(4)–Cl(24). The Oₛ–Cu–Cl bond angles also show some distortions from 90° with angles ranging from 91.3 (3) to 97.9 (3)°.

The S=O bond length is approximately 1.52 Å for three of the terminal sulfoxide ligands and 1.566 (8) Å for the remaining ligand. These compare to S=O bond lengths of 1.557 (10) and 1.543 (4) Å in CuCl₂(TMSO) and CuCl₂(DMSO), respectively.[12] The Cu–O–S bond angles and organic fragments are as expected with the exception of the deviations in the C(13)–C(14) bond length and the large thermal displacement parameters of C(14).

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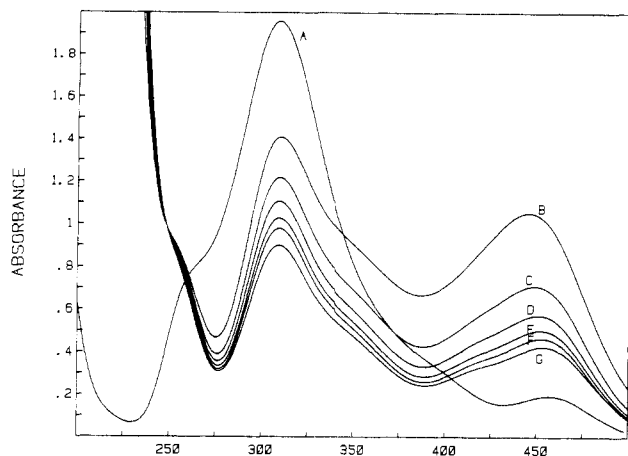
Figure 2. Time-dependent UV–visible spectrum of the reaction of $CuCl_2$ with Et_2S: A, prior to sulfide addition; B, after 5 min; C, after 25 min; D, after 45 min; E, after 70 min; F, after 90 min; G, after 205 min.

These anomalies are most likely due to a slight disorder of the terminal methyl groups.

Spectroscopic Results

Both of the copper tetramers examined exhibit strong IR absorptions at 585 and 583 cm^{-1} for **1** and **2**, respectively, characteristic of the T_2 vibrational mode of the $\{Cu_4O\}$ core.[14] The Cu–Cl vibrations are generally lower in energy and relatively weak, thereby making assignment of this mode difficult.

Sulfoxides are known to coordinate to metal centers through either the oxygen or the sulfur. Ligation of sulfoxide through the oxygen tends to weaken the S=O bond strength, resulting in a decrease in the S=O stretching frequency. A case in point is the oxygen-bound sulfoxide in complexes such as Ru(NO)Br$_3$((C-H$_3$CH$_2$)$_2$S)(CH$_3$CH$_2$)$_2$SO, which exhibit a $\nu_{S=O}$ stretching frequency at 925 cm^{-1}.[15] Conversely, sulfur-bound sulfoxides in the similar Ru^{II} complexes[16] normally show an increase in the S=O stretching frequencies (1020–1080 cm^{-1}). The IR absorptions at 956 cm^{-1} for **1** and 934 cm^{-1} for **2** indicate that the sulfoxide is bound via the oxygen. The corresponding copper complexes with a sulfur-bound sulfoxide are not known, making direct comparisons between the two ligation types difficult.

The reaction mechanism for the formation of the title compound most likely proceeds via a [Cu^{I}SR^2] intermediate. This is evident from the UV–visible spectrum of the reaction mixture versus time, as shown in Figure 2. Prior to the addition of ethyl sulfide, the Cu^{II} exhibits a strong electronic transition at 309 nm and a weaker transition at 457 nm. Immediately after addition of the sulfide, the 309-nm transition decreases in intensity with a concomitant

introduction of a new peak at 445 nm. On the basis of the relatively high intensity of the 445-nm peak,[17] it is assigned to a LMCT band from the σ lone pair of the sulfide to the σ orbital of the copper. Similar assignments have been made in Cu^{II} complexes of proteins,[18] dithioalkanes,[19] and others.[20] With time, both peaks decrease in intensity owing to the disappearance of Cu^{II} via the expected sulfide-promoted reduction to Cu^I. The reappearance of Cu^{II} and the title complex is not observed in CH$_3$CN. Attempts to duplicate the spectroscopic results in acetone were limited by overlapping solvent absorptions. Further evidence for a Cu^I intermediate is suggested by the reactions of CuCl$_2$·2H$_2$O with the sulfides ((CH$_3$)$_3$C)$_2$S, C$_5$H$_{10}$S, and C$_4$H$_8$S.[2] These sulfides form the insoluble Cu^I complexes Cu$_2$Cl$_2$S(C(CH$_3$)$_3$)$_2$, CuClSC$_5$H$_{10}$, and Cu$_4$Cl$_5$(SC$_4$H$_8$)$_3$, respectively, in acetone. The insolubility of these Cu^I complexes results in precipitation prior to subsequent air oxidation to Cu^{II} and possible tetramer formation. The Cu^{II} complexes **1** and **2** do not form when oxygen is rigorously excluded from the reaction. The oxidation of Cu^I and Cu^0 with dioxygen[11,21] has been demonstrated to yield Cu^{II} tetramers of the general formula Cu$_4$Cl$_6$OL$_4$, which further supports a Cu^I intermediate in the reaction above.

Conclusions

The reaction of CuCl$_2$·H$_2$O with simple alkyl thioethers yields the unique copper tetramer Cu$_4$Cl$_6$O(OSR$_2$)$_4$ (R = ethyl, butyl) or Cu$_2$Cl$_2$SR$_2$, when R is the more sterically hindered *tert*-butyl group. Geometric distortions in Cu$_4$Cl$_6$O(OS(CH$_2$CH$_3$)$_2$)$_4$ are evident both in the $\{Cu–O\}$ core and in the Cu–Cl bond lengths and angles. The reasons for this distortion are unclear, yet it is consistent with other complexes of the general formula Cu$_4$Cl$_6$-OL$_4$.[10] Continuing experimental and theoretical work on this unique cage will focus on understanding the reasons for these distortions.

The IR frequency for the Cu–O stretch of $\sim$584 cm^{-1} is consistent with spectral assignments made on similar complexes.[14] The S=O stretching frequencies of 956 and 930 cm^{-1} for **1** and **2**, respectively, suggest oxygen-bound sulfoxide, an assignment that is supported by the X-ray crystallographic studies.

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