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Synthesis and Characterization of Some Halocopper(I)–Alkyl Sulfide Complexes Including the Crystal Structure of μ-(Diethyl sulfide)-bis(diethyl sulfide)tetra-μ-iodo-tetracopper(I), $[(C_2H_5)_2S]_3[CuI]_4$[1]

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Dimethyl sulfide reacts with copper(I) iodide, bromide, and chloride to yield a series of 1:1 complexes. Similar reaction with diethyl sulfide produces a homologous series of complexes with a ligand to copper ratio of 3:4. Treatment of copper(I) iodide and bromide with *n*-butyl sulfide results in a complex which is operationally characterized as halo[bis(di-*n*-butyl sulfide)]copper(I). The unusual stoichiometry of the diethyl sulfide complexes was definitively established by a X-ray diffraction determination of the crystal and molecular structure of $[(CH_3CH_2)_2S]_3[CuI]_4$. Refinement using full-matrix least-squares techniques revealed a structure consisting of infinite chains of sulfide-bridged Cu_4I_4 cores, each of which resembles a distorted cube with alternating vertices of copper and iodine. Individual copper–sulfur distances clearly reflect the presence of both bridging (Cu–S distances 2.331 (8) and 2.337 (6) Å) and terminal (Cu–S distances 2.297 (10) and 2.298 (9) Å) ligands. Each copper atom exists in a distorted tetrahedral environment provided by three bridging iodine atoms and a diethyl sulfide ligand. The intramolecular copper···copper distances range from 2.741 (6) to 2.901 (5) Å. The average copper–iodine distance is 2.692 Å. Crystallographic data are as follows: space group $P2_1/a$; unit cell $a = 13.201$ (4) Å, $b = 11.573$ (3) Å, $c = 18.466$ (5) Å, $\beta = 104.21$ (2)°; $V = 2735$ Å^3; d_{calcd} for $Z = 4$ is 2.508 g/cm^3. A total of 2018 independent reflections with $F^2 \geq 3\sigma$ were used to refine the structure to final values of $R_F = 0.058$ and $R_{wF} = 0.075$.

The coordination chemistry of copper(I) has been studied extensively in recent years and a multiplicity of stoichiometries has been observed. Complexes with ligand to copper ratios of 1:1, 2:1, 3:1, 4:1, and 3:2 are known for a variety of monodentate ligands.[2] Much of this work and particularly the structural studies have focused on complexes of the copper(I) halides with tertiary phosphine and arsine ligands.[2b,3–5] A number of sulfur-coordinated copper(I) complexes are known and several have been structurally characterized.[6,7] The ligands in these instances, however, have involved either bidentate disulfides or ligand systems such as thioureas, phosphine sulfides, or related compounds, in which the sulfur center participates in extensive π bonding. Complexes of copper(I) halides with simple alkyl sulfides are not well-known.[8] Here we report the preparation and characterization of several halocopper(I)–alkyl sulfide complexes including the single-crystal X-ray structure determination of one such complex, μ-(diethyl sulfide)-bis(diethyl sulfide)tetra-μ-iodo-tetracopper(I)], $[(C_2H_5)_2S]_3[CuI]_4$.

Experimental Section

General Data. Copper(I) halides were purchased from Alfa Inorganics, Inc., and used as received. Alkyl sulfides were obtained from either Aldrich Chemical Co. or Fairfield Chemical Co. and were employed without additional purification. Elemental analyses and molecular weights were determined at Galbraith Laboratories, Knoxville, Tenn.

Spectra. Raman spectra were obtained on a Cary Model 82 laser Raman spectrometer equipped with rotating sample cells. Unless otherwise noted, a slit width of 3 cm^{-1} and a scanning rate equal to the ratio of the slit width to time constant were employed. Red (6471 Å) or green (5145 Å) excitation was provided by Coherent Radiation Laboratory Model 52 krypton and argon ion lasers, respectively. Reported frequencies are precise to ±1 cm^{-1}. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer employing Nujol mulls supported on polyethylene plates or as potassium bromide disks. Frequencies are precise to ±1 cm^{-1}.

$[(C_2H_5)_3PCuI]_4$ was prepared as described by Wells.[3]

Preparation of $(CH_3)_2SCuI$. Copper(I) iodide (47.5 g, 0.250 mol) was placed in a 250-ml flask equipped with a Teflon-coated stirrer bar and a condenser. In a well-ventilated hood, dimethyl sulfide (100 ml) was added gradually over a 5-min period through the top of the condenser. A mildly exothermic reaction occurred upon mixing. The resulting mixture was stirred for 2 hr at room temperature, refluxed for 1 additional hr, and then gravity filtered. The filtrate was treated with 250 ml of petroleum ether (bp 30°–60°) and chilled to –20° for 3 hr. The crystalline precipitate that formed was collected by suction filtration, washed with 100 ml of petroleum ether, and air-dried.

Table I. Analytical Data for Some Alkyl Sulfide–Copper(I) Halide Complexes

		% C		% H		% Hal	
Complex	Formula	Calcd	Found	Calcd	Found	Calcd	Found
$[(CH_3)_2SCuI]$	C_2H_6CuIS	9.50	9.00	2.38	2.29	50.30	49.66
$[(CH_3)_2SCuBr]$	C_2H_6BrCuS	11.68	11.81	2.92	3.22	38.89	38.66
$[(CH_3)_2SCuCl]$	C_2H_6ClCuS	14.90	15.10	3.72	3.50	22.05	22.14
$[(C_2H_5)_2S]_3[CuI]_4$	$C_{12}H_{30}Cu_4I_4S_3$	13.95	14.06	2.91	3.00	49.22	49.71
$[(C_2H_5)_2S]_3[CuBr]_4$	$C_{12}H_{30}Br_4Cu_4S_3$	16.99	16.62	3.54	3.42	37.71	36.78
$[(C_2H_5)_2S]_3[CuCl]_4$	$C_{12}H_{30}Cl_4Cu_4S_3$	20.34	20.79	4.24	4.40	20.06	20.48
$[(n\text{-}C_4H_9)_2S]_2CuI$	$C_{16}H_{36}CuIS_2$	40.52	41.25	7.66	7.76	26.80	25.65
$[(n\text{-}C_4H_9)_2S]_2CuBr$	$C_{16}H_{36}BrCuS_2$	44.08	45.09	8.44	8.15	18.37	18.97

Recrystallization from a minimal amount of warm acetonitrile containing ~5% methyl sulfide yielded 58 g (93%) of off-white crystals, whose elemental analysis (Table I) is consistent with the empirical formulation $(CH_3)_2SCuI$. The insolubility of this substance in most organic solvents prevented a molecular weight determination.

Preparation of $(CH_3)_2SCuBr$ and $(CH_3)_2SCuCl$. These compounds were prepared from copper(I) bromide (38 g, 0.25 mol) and copper(I) chloride (25 g, 0.25 mol), respectively, by procedures analogous to that described for the preparation of $(CH_3)_2SCuI$. The bromo complex was recrystallized from a minimal amount of warm acetonitrile–dimethyl sulfide (20:1). A second crop was obtained by flooding the mother liquor with diethyl ether. The isolated yield was 90%. A similar procedure yielded the chloro complex in 83% yield. Analytical data are given in Table I.

Preparation of $[(C_2H_5)_2S]_3[CuI]_4$. Crystals of $[(C_2H_5)_2S]_3[CuI]_4$ were prepared by warming copper(I) iodide (47.5 g, 0.250 mol) and diethyl sulfide (100 ml) together at 80° for 30 min and treating the filtered solution with hexane (500 ml) before chilling to −20° for 12 hr. The crude product was collected by suction filtration and recrystallized from warm acetonitrile containing ~5% diethyl sulfide, and the crystals were allowed to air-dry. The isolated yield was 88%. The general insolubility of this complex in all but strongly coordinating solvents such as pyridine and acetonitrile precluded a determination of its molecular weight in solution. Analytical data are given in Table I.

Preparation of $[(C_2H_5)_2S]_3[CuBr]_4$ and $[(C_2H_5)_2S]_3[CuCl]_4$. These complexes were prepared from copper(I) bromide (38 g, 0.25 mol) and copper(I) chloride (25 g, 0.25 mol), respectively, by procedures analogous to that described above for the preparation of $[(C_2H_5)_2S]_3[CuI]_4$. The crude bromo complex was recrystallized from a minimal amount of warm acetonitrile–dimethyl sulfide (20:1). Addition of diethyl ether to the mother liquor provided a substantial second crop. The total yield was 89%. A similar recrystallization procedure provided analytically pure chloro complex in 80% yield. The analytical data are given in Table I.

Reaction of Copper(I) Iodide with Di-*n*-butyl Sulfide. This was carried out according to the procedure indicated by Whitesides and coworkers.[8] Copper(I) iodide (195 g, 1.05 mol) was stirred with di-*n*-butyl sulfide (290 g, 2.00 mol) in a 500-ml beaker. Following an initial, mildly exothermic reaction, the resulting mixture was warmed on a steam bath for 10 min. The small amount of residual solid that remained was removed by suction filtration. The resulting complex, a yellow-orange liquid, is stable indefinitely in air. It is soluble in a broad spectrum of organic solvents including pentane, benzene, and chloroform. Analytical data (Table I) are consistent with its formulation as iodo[bis(di-*n*-butyl sulfide)]copper(I). Molecular weight: calcd for $[(C_4H_9)_2S]_2CuI$, 477; Found (osmometric in benzene), 485.

Reaction of Copper(I) Bromide with Di-*n*-butyl Sulfide. The above procedure was repeated using copper(I) bromide (77.5 g, 0.505 mmol) and di-*n*-butyl sulfide (145 g, 1.00 mol). Analysis (Table I) of the resulting orange-brown liquid indicated a ligand to copper ratio consistent with its formulation as bromo[bis(di-*n*-butyl sulfide)]-copper(I), $[(n\text{-}C_4H_9)_2S]_2CuBr$. It, too, is soluble in a variety of organic solvents.

The ligand to copper ratio of the product produced in the reaction of copper(I) bromide with di-*n*-butyl sulfide was observed to vary with reaction conditions. Repetition of the above reaction using, for example, 107 g (0.75 mol) of copper(I) bromide and an extended reaction time of 12 hr at 100° yielded an orange-brown liquid having a ligand to copper ratio of ~1.5. Anal. Found: C, 36.09; H, 6.79; Br, 24.73.

Reactions of Copper(I) Chloride with Di-*n*-butyl Sulfide. Copper(I) chloride (50.0 g, 0.505 mol) was placed in an erlenmeyer flask along with di-*n*-butyl sulfide (146 g, 1.00 mol), stirred for 30 min at room temperature, and then warmed briefly on a steam bath. Considerable residual solid remained and was removed by suction filtration. Elemental analysis of the filtrate, a dark, somewhat viscous liquid, revealed a ligand to copper ratio of ~2.0. Anal. Calcd for $C_{16}H_{36}ClCuS_2$ (i.e., $[(C_4H_9)_2S]_2CuCl$): C, 49.10; H, 9.21; Cl, 9.07. Found: C, 52.10; H, 10.21; Cl, 6.41.

The composition of product from the reaction of copper(I) chloride with di-*n*-butyl sulfide varied with reaction conditions. Thus, in a similar experiment in which 75 g (0.75 mol) of copper(I) chloride was heated with 146 g (1.00 mol) of di-*n*-butyl sulfide for 12 hr at 100°, the isolated product (a dark, viscous liquid) had a ligand to copper ratio of ~1.0. Anal. Found: C, 36.23; H, 6.93; Cl, 15.36.

Reaction of Di-*sec*-butyl Sulfide with Copper(I) Iodide. Copper(I) iodide (9.60 g, 0.051 mol) was stirred with di-*sec*-butyl sulfide (14.5 g, 0.010 mol) in a 100-ml erlenmeyer flask for 2 hr at 100°. The residual solid was removed by suction filtration. Analysis of the resulting clear yellow liquid indicated only limited incorporation of copper(I) iodide. Anal. Calcd for $C_{16}H_{36}CuIS_2$ (i.e., $[(sec\text{-}C_4H_9)_2S]_2CuI$): C, 40.52; H, 7.66; I, 26.80. Found: C, 57.80; H, 10.91; I, 8.10.

Reaction of Di-*tert*-butyl Sulfide with Copper(I) Iodide. Copper(I) iodide does not coordinate to an appreciable extent with di-*tert*-butyl sulfide. Elemental analysis of the product mixture produced by refluxing a 1:2 mixture of copper(I) iodide in *tert*-butyl sulfide for 12 hr revealed that essentially no copper(I) iodide had been incorporated into the liquid. The ir spectrum of the residual solid indicated the absence of coordinated di-*tert*-butyl sulfide.

Reaction of Copper(I) Iodide with Di-*n*-propyl Sulfide. Copper(I) iodide (45 g, 0.23 mol) was placed in a 250-ml beaker along with 88 g (0.46 mol) of di-*n*-propyl sulfide and the mixture was stirred for 1 hr. The residual solid was removed by suction filtration and the yellow-orange liquid analyzed. Anal. Calcd for $[C_3H_{18}S]_2CuI$: C, 33.76; H, 6.56; I, 29.78. Found: C, 27.66; H, 5.44; I, 22.48.

X-Ray Diffraction Procedures. A crystal of $[(C_2H_5)_2S]_3[CuI]_4$ was cut to an approximate cube of edge 0.2 mm and placed in a quartz capillary, and a small amount of crushed crystals was added to hinder the decomposition of the diffraction crystal. The two regions were separated by a small glass wool plug and the capillary was sealed. In the absence of this procedure, the crystal deteriorated rapidly and accurate diffraction data could not be obtained.

The crystal was mounted on a Syntex $P2_1$ four-circle, computer-controlled automated diffractometer. Unit cell parameters $a = 13.201$ (4) Å, $b = 11.573$ (3) Å, $c = 18.466$ (5) Å, and $\beta = 104.21$ (2)° were obtained at 23° by least-squares refinement of the cell and orientation parameters using the centered angular coordinates of 15 intense reflections with 2θ values less than 30.11°. These values were subsequently confirmed using 15 intense, high-angle reflections ($25° > \theta > 15°$) obtained from the complete data set. For all diffraction measurements, graphite-monochromated Mo Kα radiation (Kα_1, λ 0.70926 Å; Kα_2, λ 0.71354 Å) was detected with a scintillation counter and a pulse height analyzer set to admit approximately 90% of the Kα peak. The unit cell volume V, based on the above dimensions, is 2735 Å^3 while the calculated density for mol wt 1032.3 and $Z = 4$ is 2.508 g/cm^3. Attempts to determine the density of this material by flotation were repeatedly unsuccessful due to crystal decomposition under a variety of experimental conditions. Weissenberg photographs of a different crystal from the same batch indicated a monoclinic space group with systematic absences of $h0l$ when h is odd and of $0k0$ when k is odd; these conditions, which were verified by the diffraction data, define the space group as $P2_1/a$.

Diffraction data were collected at room temperature (23 ± 1°)

Table II. Fractional Atomic Coordinates[a] and Thermal Parameters[b] with Standard Deviations

Atom[c]	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
I(1)	1133 (1)	4809 (2)	−2870 (1)	54 (1)	83 (2)	49 (1)	14 (1)	9 (1)	4 (1)
I(2)	4434 (1)	4881 (2)	−3089 (1)	63 (1)	95 (2)	42 (1)	−7 (1)	16 (1)	14 (1)
I(3)	3114 (1)	1558 (1)	−2684 (1)	63 (1)	61 (1)	41 (1)	2 (1)	8 (1)	−2 (1)
I(4)	3626 (1)	4207 (2)	−898 (1)	48 (1)	96 (2)	35 (1)	−2 (1)	10 (1)	−9 (1)
Cu(1)	4297 (2)	3298 (3)	−2070 (2)	49 (2)	91 (3)	43 (1)	4 (2)	6 (1)	5 (1)
Cu(2)	2205 (2)	3134 (3)	−2007 (2)	56 (2)	85 (3)	43 (1)	−1 (2)	16 (1)	1 (2)
Cu(3)	3110 (3)	5355 (3)	−2219 (2)	79 (2)	84 (3)	55 (2)	0 (2)	13 (2)	1 (2)
Cu(4)	2663 (2)	3671 (3)	−3336 (2)	71 (2)	97 (3)	44 (1)	2 (2)	7 (2)	3 (2)
S(1)	1032 (4)	2147 (6)	−1470 (4)	41 (4)	91 (6)	41 (3)	−4 (4)	9 (3)	4 (4)
S(3)	3231 (7)	7268 (7)	−1861 (5)	120 (7)	92 (8)	75 (4)	−21 (7)	26 (5)	−18 (5)
S(4)	1944 (6)	3177 (7)	−4561 (4)	78 (5)	142 (9)	47 (3)	18 (6)	0 (4)	−4 (5)

Atom[c]	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(11)	1001 (20)	2870 (26)	−572 (15)	6.6 (7)	C(34)	2293 (37)	8078 (42)	−3300 (27)	13.3 (1.5)
C(12)	603 (22)	3976 (28)	−732 (17)	7.4 (8)	C(41)	726 (29)	2365 (34)	−4396 (20)	10.9 (1.1)
C(13)	1509 (21)	665 (25)	−1192 (15)	6.6 (7)	C(42)	81 (31)	1909 (36)	−5156 (21)	12.2 (1.2)
C(14)	2661 (22)	678 (26)	−678 (16)	7.2 (8)	C(43)	1239 (33)	4443 (38)	−5061 (23)	13.0 (1.3)
C(31)	4465 (33)	7895 (38)	−1846 (23)	13.2 (1.3)	C(44)	2114 (28)	5308 (32)	−5092 (20)	10.4 (1.1)
C(32)	5283 (29)	7535 (35)	−1236 (20)	11.0 (1.1)					
C(33)	2189 (38)	8154 (45)	−2594 (31)	8.9 (1.4)					

[a] All coordinates are ×10^4. [b] Anisotropic thermal parameters are ×10^4 and are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Sulfur and carbon atoms are numbered according to the copper atom to which they are bonded.

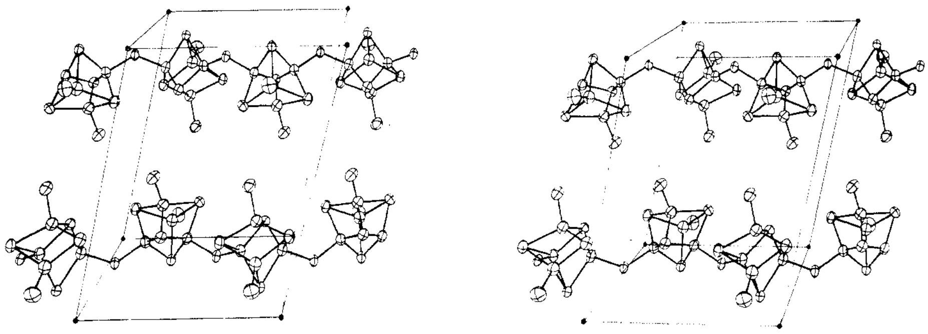

Figure 1. Stereoscopic view of the structure of $[(C_2H_5)_2S]_3[CuI]_4$ showing the polymeric nature imposed by the bridging sulfide ligands. Ellipsoids of 50% probability are shown.

to a maximum of 2θ = 50°. Reflections with $2\theta < 2°$ were shielded by the beam stop and were not recorded. The scan speed used varied between 2 and 29°/min (in 2θ) depending on the intensity of the reflection while the scan range varied from 1.63° at low 2θ to 1.93° at 2θ = 50°. Background measurements were made at the beginning and end of each scan with the counter stationary; the total time for background counts was equal to the scan time. The intensities of four standard reflections, measured at 50 reflection intervals, were consistent to ±6% over the period of data collection and showed no significant trends.

A total of 5135 unique diffraction maxima were collected and corrected for Lorentz and polarization effects. Absorption corrections were not applied: for a cylindrical crystal (μ = 79.66 cm^{-1} for Mo Kα radiation), the average effect of absorption was calculated to be less than 10%.[9] Standard deviations were assigned to F^2 values according to the equation

$$\sigma(F^2) = \frac{1}{Lp}[N_t + (0.03N_n)^2]^{1/2}$$

where N_t is the total count (background plus scan) and N_n is the net count (scan minus background). An estimate of the overall scale factor was obtained using Wilson's method and subsequently refined. Each of the 2018 reflections for which $F^2 \geq 3\sigma(F^2)$ was used in the structure solution and refinement.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and refined using full-matrix least-squares techniques. All iodine and copper atoms were determined unambiguously from a normally sharpened three-dimensional Patterson map.[10] The remaining nonhydrogen atoms were located via a series of ten three-dimensional difference Fourier maps, each successive map being phased by an increasing number of atoms. This large number was required because the carbon atoms were difficult to locate in the presence of so many heavy atoms.

Iodine, copper, and sulfur parameters were refined anisotropically while all carbon parameters were refined isotropically. No attempt was made to locate hydrogen atoms. Scattering factors for neutral iodine, copper, sulfur, and carbon were taken from the compilations of Cromer and Waber.[11] Both the real and imaginary components of the anomalous dispersion[12] for copper, iodine, and sulfur were included in the structure factor calculations. Refinement was based on F and the function minimized was $\sum w(|F_o| - |F_c|)^2$. Weights, set according to $w = 1/\sigma^2$, were chosen by an analysis of variance[13] to make $|\Delta F|/\sigma$ independent of F_o. This procedure led to a straight-line dependence of $\sigma(F_o)$ with a slope of 0.01356 and an intercept of 0.9394 over a maximum region of F_o = 166.73. Several anisotropic refinement cycles led to final error indices of $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.058 and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.075 while a final difference Fourier map showed no significant features. A listing of observed and calculated structure factors is available.[14] Final atomic parameters are listed in Table II, while Figure 1 shows the unit cell contents.

Results

The analytical data summarized in Table I indicate that alkyl sulfides react with copper(I) chloride, bromide, and iodide to produce complexes of at least three different stoichiometries. Treatment of copper(I) halides with dimethyl sulfide yields complexes of the general formulation LCuX. Halocopper(I) complexes of equivalent stoichiometry exist for a variety of monodentate ligands and their production in this instance is unexceptional.

Copper(I) iodide and bromide dissolve readily in di-*n*-butyl sulfide. Complete dissolution requires 2 mol of di-*n*-butyl sulfide/mol of copper(I) halide. The resulting material is an air-stable, yellow-orange liquid whose nature remains unclear. A molecular weight determination for the copper(I) iodide complex yielded a value consistent with its formulation *in*

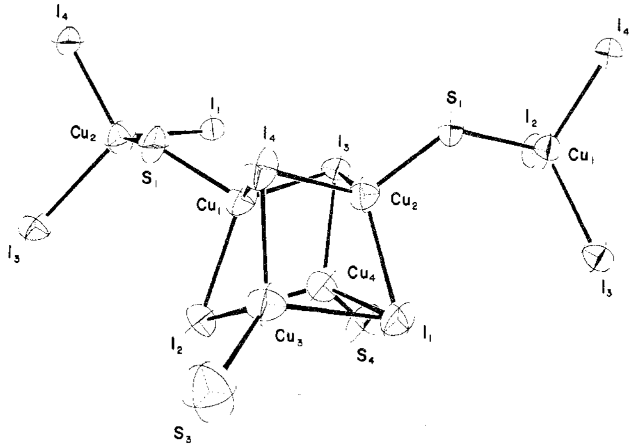

Figure 2. Core structure of the $[(C_2H_5)_2S]_3[CuI]_4$ molecule (ORTEP[17] diagram, 50% probability ellipsoids) illustrating the role of the bridging sulfide ligand. Ethyl groups are omitted for clarity.

solution as $[(n\text{-}C_4H_9)_2S]_2CuI$. However, the fact that the solution behavior of several halocopper(I)–tertiary phosphine complexes has been found to be quite complicated[15] suggests that this molecular weight value and its accompanying implications ought to be viewed with caution. Nonetheless, it is noteworthy that the 2:1 complexes $[(C_6H_{11})_3P]_2CuX$ (X = Cl, Br) also appear, based on molecular weight determination, to be monomeric in solution.[3] Regardless of the exact nature of these substances, their operational description as halo[bis(di-*n*-butyl sulfide)]copper(I) is a useful one.

Products similar to but less well-defined than iodo[bis(di-*n*-butyl sulfide)]copper(I) are obtained from the reaction of di-*n*-butyl sulfide with copper(I) chloride. The product ligand to copper ratios could be made to vary substantially for this material depending on reaction conditions. The product from the reaction of di-*sec*-butyl and di-*tert*-butyl sulfide with copper(I) iodide exhibited only very limited incorporation of copper iodide.

The compound $[(C_2H_5)_2S]_3[CuX]_4$ represents a previously unknown stoichiometry for complexes of copper(I) halides. The unusual stoichiometry of this material prompted its further structural characterization by X-ray crystallography.

Diffraction Section. A consideration of the bond angles and the interatomic distances shown in Table III leads to the following conclusions. First, the gross molecular geometry of $[(C_2H_5)_2S]_3[CuI]_4$ can be described as an infinite chain of sulfide-bridged Cu_4I_4 cores, whose geometry resembles a distorted cube with alternating vertices of copper and iodine atoms. Each copper atom resides in a distorted tetrahedral environment provided by three bridging iodine atoms and a diethyl sulfide ligand (Figures 1 and 2).

Second, individual copper–sulfur distances reflect the presence of both terminal and bridging sulfide groups. Distances involving the bridging ligand [Cu(1)–S(1) = 2.337 Å, Cu(2)–S(1) = 2.331 Å] are significantly shorter than the corresponding distances for the terminal ligands [Cu(3)–S(3) = 2.297 Å, Cu(4)–S(4) = 2.298 Å]. However, these differences are not extremely large and the average Cu–S distance compares favorably with those reported.[6,7]

Third, copper···copper distances, which have been noted to vary appreciably in other copper(I) complexes,[5] range irregularly with a mean value of 2.811 Å. By comparison, the average copper···copper distances in iodotetrakis(triethylphosphine)copper(I), $[(C_2H_5)_3PCuI]_4$, and iodotetrakis(triethylarsine)copper(I), $[(C_2H_5)_3AsCuI]_4$, are 2.9272 (20) and 2.7826 (24) Å, respectively.[5c] The average copper–iodine bond distance of 2.692 Å is nearly identical with the mean copper–iodine value of 2.683 Å observed for $[(C_2H_5)_3PCuI]_4$.[5c]

Table III. Molecular Dimensions

Distances, Å

I(1)–I(2)	4.473 (2)	Cu(3)–I(4)	2.717 (4)
I(1)–I(3)	4.549 (3)	Cu(4)–I(1)	2.721 (4)
I(1)–I(4)	4.324 (2)	Cu(4)–I(2)	2.664 (4)
I(2)–I(3)	4.364 (3)	Cu(4)–I(3)	2.732 (4)
I(2)–I(4)	4.498 (3)	Cu(1)–S(1)	2.337 (6)
I(3)–I(4)	4.430 (2)	Cu(2)–S(1)	2.331 (8)
Cu(1)–Cu(2)	2.801 (4)	Cu(3)–S(3)	2.297 (10)
Cu(1)–Cu(3)	2.828 (5)	Cu(4)–S(4)	2.298 (9)
Cu(1)–Cu(4)	2.803 (4)	S(1)–C(11)	1.83 (4)
Cu(2)–Cu(3)	2.901 (5)	S(1)–C(13)	1.85 (3)
Cu(2)–Cu(4)	2.741 (6)	S(3)–C(31)	1.78 (6)
Cu(3)–Cu(4)	2.794 (5)	S(3)–C(33)	1.89 (6)
Cu(1)–I(2)	2.664 (4)	S(4)–C(41)	1.96 (5)
Cu(1)–I(3)	2.634 (4)	S(4)–C(43)	1.82 (5)
Cu(1)–I(4)	2.747 (4)	C(11)–C(12)	1.42 (5)
Cu(2)–I(1)	2.680 (4)	C(13)–C(14)	1.56 (4)
Cu(2)–I(3)	2.660 (4)	C(31)–C(32)	1.43 (6)
Cu(2)–I(4)	2.714 (3)	C(33)–C(34)	1.37 (7)
Cu(3)–I(1)	2.664 (4)	C(41)–C(42)	1.52 (6)
Cu(3)–I(2)	2.706 (5)	C(43)–C(44)	1.51 (7)

Angles, Deg

I(1)–Cu(4)–I(2)	112.3 (1)	Cu(1)–I(4)–Cu(2)	61.8 (1)
I(1)–Cu(3)–I(2)	112.8 (1)	Cu(1)–I(3)–Cu(2)	63.88 (1)
I(1)–Cu(4)–I(3)	113.0 (2)	Cu(1)–I(2)–Cu(3)	63.6 (1)
I(1)–Cu(2)–I(3)	116.8 (1)	Cu(1)–I(4)–Cu(4)	62.5 (1)
I(1)–Cu(2)–I(4)	106.6 (1)	Cu(1)–I(2)–Cu(4)	63.5 (1)
I(1)–Cu(3)–I(4)	106.9 (1)	Cu(1)–I(3)–Cu(4)	62.9 (1)
I(2)–Cu(4)–I(3)	107.9 (1)	Cu(2)–I(1)–Cu(3)	65.7 (1)
I(2)–Cu(1)–I(3)	110.9 (1)	Cu(2)–I(4)–Cu(3)	64.6 (1)
I(2)–Cu(1)–I(4)	112.8 (1)	Cu(2)–I(1)–Cu(4)	61.0 (1)
I(2)–Cu(3)–I(4)	112.1 (1)	Cu(2)–I(3)–Cu(4)	61.1 (1)
I(3)–Cu(2)–I(4)	111.0 (1)	Cu(3)–I(2)–Cu(4)	62.7 (1)
I(3)–Cu(1)–I(4)	111.1 (1)	Cu(3)–I(1)–Cu(4)	62.48 (1)
Cu(2)–S(1)–C(11)	108.9 (1.2)	Cu(4)–S(4)–C(43)	108.6 (1.6)
Cu(2)–S(1)–C(13)	110.7 (1.1)	Cu(4)–S(4)–C(41)	97.4 (1.3)
C(11)–S(1)–C(13)	102.6 (1.5)	C(43)–S(4)–C(41)	97.4 (2.2)
Cu(3)–S(3)–C(31)	112.6 (2.0)	Cu(1)–S(1)–Cu(2)	118.6
Cu(3)–S(3)–C(33)	109.3 (1.9)		
C(31)–S(3)–C(33)	106.5 (2.7)		

Vibrational Spectral Data. The far-infrared and Raman spectra for the 1:1 and 3:4 alkyl sulfide–copper(I) halides were examined. Despite the presence of both bridging and terminal sulfide ligands and environmentally dissimilar halo centers in $[(C_2H_5)_2]_3[CuI]_4$ and quite possibly other 3:4 complexes in this series, the vibrational spectra of these compounds reveal no readily apparent features that would suggest such differences exist. The only band to which an unambiguous assignment is made is that of the copper–iodine stretching mode which occurs as a somewhat broadened band at 129 cm^{-1} in the Raman spectrum of $[(CH_3)_2S]CuI$ and at 121 cm^{-1} in the Raman spectrum of $[(C_2H_5)_2S]_3[CuI]$. Bands of similar intensity and position were also observed in the Raman spectra of $[(C_2H_5)_3PCuI]_4$ and $[(n\text{-}C_4H_9)_2S]_2CuI$ (118 and 122 cm^{-1}, respectively). The strong intensity of these bands reflects the high polarizability associated with bonds that involve covalently bonded iodine while their position is consistent with the stretching frequency values reported for other metal iodides.[16]

Discussion

The data presented in this paper establish that copper(I) halides are capable of combining with alkyl sulfides to form a variety of complexes. Dimethyl sulfide forms 1:1 complexes. Diethyl sulfide reacts with copper(I) iodide, bromide, and chloride to produce a homologous series of 3:4 complexes, $[(C_2H_5)_2S]_3[CuX]_4$. Finally, the higher molecular weight normal alkyl sulfides such as di-*n*-propyl and di-*n*-butyl sulfides dissolve copper(I) halides readily. The resulting complexes display compositions that in some instances depend on reaction conditions. A 2:1 limiting stoichiometry of ligand to copper appears to prevail for di-*n*-butyl sulfide complexes of copper(I) iodide.

The results serve to illustrate and reemphasize[5b] the delicate balance of factors which control the structure of copper(I) complexes. Thus, for example, dimethyl and diethyl sulfides are quite similar and a change from one to the other would not, a priori, be expected to result in a substantially different complex; yet, it is clear from the present work that the subtle changes associated with such remote homologous variations are sufficient to effect substantial changes in the stoichiometry of halocopper(I) complexes.

Both the structure and stoichiometry of μ-(diethyl sulfide)-bis(diethyl sulfide)tetra-μ-iodo-tetracopper(I) are unique in the family of copper(I) halide complexes. Moreover, such a structure provides a relatively rare example of an instance in which an alkyl sulfide serves as a bidentate bridging ligand between two first-row transition metal centers and suggests that similar bonding may provide a pathway for the intermolecular ligand exchange between halocopper(I)–alkyl sulfide clusters in solution.

It is tempting to extrapolate this structural result and suggest that the other complexes in this series, i.e., $[(C_2H_5)_2S]_3[CuBr]_4$ and $[(C_2H_5)_2S]_3[CuCl]_4$, are isostructural with $[(C_2H_5)_2S]_3[CuI]_4$. Likewise, it would seem reasonable to propose that the complexes of dimethyl sulfide with copper(I) halide form complexes that are isostructural with other 1:1 copper(I) halide complexes, e.g., $[(C_2H_3)_3PCuI]_4$,[5c] $[(C_2H_5)_3AsCuI]_4$,[5c] and $[(C_6H_5)_3PCuCl]_4$.[5c] However, in view of the structural rearrangements that have been shown to result from slight variations in the steric and electronic properties of ligand molecules and halide centers (cf. $[(C_6H_5)_3PCuCl]_4$ and $[(C_6H_5)_3PCuBr]_4$) such an extrapolation is premature in the absence of additional structural information for these complexes.

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Registry No. $[(CH_3)_2SCuI]$, 54678-24-9; $[(CH_3)_2SCuBr]$, 54678-23-8; $[(CH_3)_2SCuCl]$, 54678-22-7; $[(C_2H_5)_2S]_3[CuI]_4$, 54751-67-6; $[(C_2H_5)_2S]_3[CuBr]_4$, 54822-97-8; $[(C_2H_5)_2S]_3[CuCl]_4$, 54822-96-7; $[(n\text{-}C_4H_9)_2S]_2CuI$, 35907-81-4; $[(n\text{-}C_4H_9)_2S]_2CuBr$, 54751-68-7; CuCl, 7758-89-6; CuI, 7681-65-4; di-*n*-butyl sulfide, 544-40-1; di-*sec*-butyl sulfide, 626-26-6; di-*n*-propyl sulfide, 111-47-7.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC408291.

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