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Reaction of Bis(*N*,*N*-dimethylthiocarbamoyl) Sulfide with Copper(II) Halides and the Crystal and Molecular Structures of Halogeno(bis(*N*,*N*-dimethylthiocarbamoyl) sulfido)copper(I) Complexes

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Bis(*N*,*N*-dimethylthiocarbamoyl) sulfide (Tetramethylthiuram monosulfide) reacts with copper(II) halides (halide = Cl and Br) to yield 3,5-bis(*N*,*N*-dialkyliminio)-1,2,4-trithiolane trihalocuprate(I) and the neutral halogeno(bis(*N*,*N*-dimethylthiocarbamoyl) sulfido)copper(I) complex. The proposed structure for the trihalocuprate(I) compounds is supported mostly by infrared studies. The copper(I) adducts may also be prepared by straightforward reaction of copper(I) halides and the ligand, and single-crystal x-ray studies show a wide diversity of structural variations. All molecules consist of basic S_2CuX units. The Cl derivative **(1)** is an S-bridged dimer ($C_6H_{14}ClCuN_2OS_3$, monoclinic, $P2_1/c$ (No. 14), $Z = 4$, $a = 9.525(8)$ Å, $b = 13.022(10)$ Å, $c = 10.835(7)$ Å), while the Br analogue **(2)** features a polymeric network of S_2CuBr units, also bridged by S atoms ($C_6H_{12}BrCuN_2S_3$, orthorhombic, $P2_12_12_1$ (No.19), $Z = 4$, $a = 7.043(2)$ Å, $b = 9.442(3)$ Å, $c = 17.889(4)$ Å). The iodo compound **(3)** exists as a halogen-bridged dimer ($C_6H_{12}CuIN_2S_3$, monoclinic, $P2_1/m$ (No. 11), $Z = 4$, $a = 9.570(1)$ Å, $b = 10.578(1)$ Å, $c = 12.422(1)$ Å). The molecular structures found support the assignment of the IR and Raman spectral data in all three cases. The diversity of structural variations is attributed to the relative basicity of the S and halogen potential bridging atoms. Molecular weight studies in acetonitrile are consistent with a monomer for **2**, while the temperature dependence of the ^{1}H-NMR for **1** is interpreted in terms of a monomer−dimer equilibrium.

Introduction

Thiuram sulfides, otherwise known as bis(*N*,*N*-dialkylthiocarbamoyl) sulfides, $R_2NC(S)S_nC(S)NR_2$ are the thiocarbamoyl esters of dialkyldithiocarbamic acids. The disulfides ($n = 2$) R_4tds are known on account of their biological activity, which leads to applications as fungicides, rubber vulcanization accelerators, and agents of alcoholism therapy[1] and, quite recently, as arrestors of human immunodefficiency virus infections such as AIDS.[2] This wide diversity of examples of biological activity has been attributed to a combination of at least two factors:[3] capability to fit into a receptor site and ability to undergo reversible redox reactions at suitable potentials. From this point of view, the equilibrium relating thiuram disulfides and dithiocarbamates is very relevant to the chemistry of the disulfides.

Coordination compounds containing ligands with sulfur atoms as donors have received much attention, due to their role as analogues of proteins containing metal−sulfur bonds.[4] Among these ligands, dithiocarbamates have been used to synthesize model compounds for enzyme activity.[5,6] Also, polynuclear metal dithiocarbamates may act as mineral analogues and thus as models of sulfide mineral degradation by microorganisms,[7] a topic which has a strong relevance in connection with biolixiviation.[8] It must also be stated that one successful approach to the development of new metal sulfide catalysts involves thermolysis of discrete metal thio complexes containing coligands rich in sulfur, such as dithiocarbamates.[9,10]

The monosulfides ($n = 1$) R_4tms, perhaps because they lack the wide breadth of applications known for the disulfides in agriculture and experimental medicine, have been much less extensively studied, and where such studies deal with the subject of interaction of monosulfides and metal species, the field remains virtually unexplored. Exceptions have been reports dealing with the preparation and properties of the neutral complexes MR_4tmsX_2 (M = Zn,[11] Hg,[12] Ni, and Co;[13] X = halogen) or $M'R_4tmsX$ (M′ = Ag[14]) and of the cationic [CrR$_4$-

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tmsX_2]$^+$.[15] The spectroscopic properties of the latter complexes are inconsistent with a possible oxidative addition of the ligand to the metal center and it has been suggested that their electrochemistry be examined.[16] Thiuram monosulfides may also undergo C−S bond scission to give dithiocarbamate−metal−thiocarboxamido complexes or straightforward dithiocarbamates. Examples of the former are the reaction of monosulfides with tris(triphenylphosphine)−metal halides (metal = Rh and Pt)[17] or zerovalent molybdenum complexes,[18] while the interaction of a series of metal halides with thiuram monosulfides has afforded metal dithiocarbamates (metal = Ni^{2+}, Pt^{2+}, Cu^{2+}, Co^{3+}, and Fe^{3+}).[19]

Thiuram monosulfides may also undergo a two-electron oxidation and generate cyclic 5-membered cations upon interaction with a suitable agent. Thus, tetramethylthiuram monosulfide and $FeCl_3$ afford 3,5-bis(*N*,*N*-dimethyliminio)-1,2,4-trithiolane pentachloroferrate(III).[**20**] The studies of this unusual pattern of reactivity are now extended to the reaction of thiuram monosulfides and copper(II) halides.

Experimental Section

General Preparative Methods, Spectroscopy, and Analyses. Synthetic manipulations were carried out in air. No special precautions to exclude water and/or air were taken. This was an important modification to previous experimental procedures,[20] which made extensive use of Schlenk or cannulation techniques.[21] $CuBr_2$ was prepared from CuBr and an excess of Br_2.[22] Me_4tms (Fluka) was recrystallyzed from hot EtOH. $CuCl_2·2H_2O$ (Merck) was used with no further purification. CuBr was made from aqueous copper(II) sulfate, potassium bromide, and sodium sulfite. CuI was obtained by reaction of potassium iodide with copper(II) sulfate and further reduction of the iodine produced with sodium thiosulfate. Instrumentation and analyses have been described in previous publications.[**20**]

Preparation of the Complexes. The complexes CuMe_4tmsX (X=Cl (**1**) and Br (**2**)) were prepared by a general procedure described here in full for the bromo derivative.

$CuBr_2$ (0.67 g, 3.0 mmol) dissolved in EtOH (60 mL) was cooled to −10 °C (ice-salt bath) and a solution of the monosulfide (0.63 g, 3.0 mmol) in EtOH (250 mL) was added dropwise while stirring. The red-orange solid was filtered, washed with 20 mL of fresh EtOH, pumped dry and ground to a fine powder, which was extracted with three 50-mL portions of CH_3CN. The orange insoluble solid was characterised as 3,5-bis(*N*,*N*-dimethyliminio)-1,2,4-trithiolane tribromocuprate(I). The acetonitrile extracts were concentrated in a rotary evaporator, keeping the temperature below 35 °C. The resulting solution was cooled to −10 °C and the red crystalline material given off was filtered and recrystallized in the same fashion. Experiments performed with copper(II) chloride dihydrate resulted in an acetonitrile-insoluble greenish solid residue, which was not further investigated. From the acetonitrile solution the corresponding monosulfide−copper(I) chloride complex (**1**) could be isolated in the manner just described.

[Me_4bitt-3]$^{2+}$CuBr_3^{2-}: orange amorphous powder; mp 192 °C dec. Anal. Calcd for $C_6H_{12}N_2S_3Br_3Cu$: Cu, 12.4; Br, 46.8; C, 14.1; H, 2.4. Found: Cu, 12.4; Br, 46.5; C, 14.1; H, 2.3. IR: 3030 w, 1587 s, 1408 s,1266 s, 1070 s, 1036 s, 885 m, 870 m, 570 s, 510 m, 211 m, 179 m, 158 w, 103 vs. μ_{EFF}: 0.00 μ_B. Low solubility and general lack of stability prevented further characterization in solution.

CuMe_4tmsCl (**1**): red microcrystalline solid; mp blackens from 80 to 127 °C and melts at 136 °C dec. Anal. Calcd for $C_6H_{12}N_2S_3ClCu$: Cu, 20.7; Cl, 11.5; Cl, 23.3; H, 4.0. Found: Cu, 20.7; Cl, 11.5; C, 23.4; H, 3.9. IR: 2941 w, 1531 s, 1389 s, 1245 s, 1227 s, 1143 s, 1049 m, 985 s, 943 s, 867 m, 527 m, 347 s, 310 m, 280 w, 247 m. δ_H($CDCl_3$): 3.57 (s, 4.5), 3.51 (s, 1.5), 3.48 (s, 1.5), 3.43 (s, 4.5). μ_{EFF}: 0.02 μ_B. Λ_M: 30−35 Ω^{-1} cm^2 mol^{-1} (10^{-3}−10^{-4} M).

CuMe_4tmsBr (**2**): bright red, needle-shaped microcrystalline solid, mp 174−176 °C dec. Anal. Calcd for $C_6H_{12}N_2S_3BrCu$: Cu, 18.1; Br, 22.7, C, 20.5; H, 3.4. Found: Cu, 18.1; Br, 22.6; C, 20.4; H, 3.4. IR: 2941 w, 1524 s, 1383 s, 1250 s, 1230 s, 1143 s, 1050 m, 987 s, 943 s, 867 m, 570 m, 445 m, 345 m, 324 m, 193 s, 162 sh. δ_H($CDCl_3$): 3.59 (s, 6), 3.41 (s, 6). μ_{EFF}: 0.00 μ_B. Λ_M : 28−37 Ω^{-1} cm^2 mol^{-1} (10^{-3}−10^{-4} M). Mol wt (osmometry): 318−320 (assoc in CH_3CN: 0.91 at 10^{-3}−10^{-4} m).

The iodo derivative was prepared as follows. CuI (0.57 g, 3.0 mmol) was dissolved in CH_3CN (15 mL) and added to a cooled (ice-salt bath) solution of Me_4tms (0.62 g, 3.0 mmol) in the same solvent (10 mL). The solid formed was filtered, washed with Et_2O and dried.

CuMe_4tmsI (**3**): orange-red powder; mp blackens progressively up to 189 °C, melts at 192 °C dec. Anal. Calcd for $C_6H_{12}N_2S_3ICu$: Cu, 15.4; I, 31.8; C, 18.1; H, 3.0. Found: Cu, 15.4; I, 31.7; C, 18.0; H, 3.0. IR: 2929 w, 1507 s, 1370 s, 1229 m, 1145 w, 1045 w, 989 m, 945 m, 860 w, 365 s, 325 s. μ_{EFF}: 0.0 μ_B. Limited solubility prevented further characterization in solution.

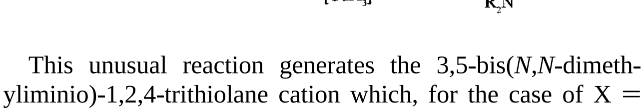
Crystal Growth for X-ray Diffraction. Approximately 0.1 g of crude **1** or **2** was dissolved in 2−3 mL of CH_3CN, and the supernatant was filtered into a test tube which was taken to a freezer at −15 °C. Approximately 1−2 mL of diethyl ether was layered on top of the CH_3CN solution, and the tube was capped and left until crystals were apparent (2−10 h). The excess solvent was decanted, and the crystals were washed with fresh ether and dried. The red-orange plates obtained for the chloro derivative had the composition CuMe_4tmsClXH_2O, which was not specroscopically characterized. The iodo derivative was obtained from the mother solutions of the reaction mixture, using the same layering technique.

Crystal Structure Determinations. Diffraction intensities were collected on a Siemens P3 diffractometer, which included a beam monochromator. Two standard reflections checked every 98 reflections showed no significant crystal decay. Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the program package SHELXTL PLUS[23] (personal computer version), and refined by full-matrix least-squares methods on F^2 using the SHELDRICK93 program.[24] H atoms were included in their idealized position with the isotropic thermal parameter fixed at 0.08 Å^2, except for the water molecules, which were found from the difference Fourier map.

Additional material comprises H-atoms coordinates and thermal parameters.

Results and Discussion

Reaction of Copper(II) Halides and Tetramethylthiuram Monosulfide. The interaction of thiuram monosulfides and copper(II) halides is described by the following scheme



This unusual reaction generates the 3,5-bis(*N*,*N*-dimethyliminio)-1,2,4-trithiolane cation which, for the case of X = Br, can be isolated as the salt of the corresponding tribromocu-

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Table 1. Crystallographic Data and Refinement Details for **1**−**3**

	1	**2**	**3**
chem formula	$C_6H_{14}ClCuN_2OS_3$	$C_6H_{12}BrCuN_2S_3$	$C_6H_{12}CuIN_2S_3$
a/Å	9.525(8)	7.043(2)	9.570(1)
b/Å	13.022(10)	9.442(3)	10.578(1)
c/Å	10.835(7)	17.889(4)	12.422(1)
α/deg	90	90	90
β/deg	110.78(1)	90	104.42(1)
γ//deg	90	90	90
V/Å^3	1256.5(16)	1189.6(6)	1217.9(2)
Z	4	4	4
cryst dimens/mm	0.75 × 0.45 × 0.20	0.13 × 0.16 × 0.12	0.12 × 0.09 × 0.09
fw	325.36	351.81	398.80
space group (No.)	$P2_1/c$ (14)	$P2_12_12_1$ (19)	$P2_1/n$ (14)
D_c/g cm^{-3}	1.72	1.96	2.17
μ/cm^{-1}	24.2	56.8	48.0
R^a	0.049	0.046	0.037
$R_w{}^b$	0.151	0.085	0.052

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**−**3**

	x	*y*	*z*	U(eq)^a
		(Me$_4$tmsCuCl)$_2$ (**1**)		
Cu	0.5420(1)	0.9637(1)	0.1389(1)	0.0433(4)
S(1)	0.4436(1)	1.1243(1)	0.0623(1)	0.0344(5)
S(3)	0.3436(2)	0.8886(1)	0.1878(2)	0.0407(5)
Cl	0.7605(2)	0.9308(1)	0.3071(2)	0.0444(5)
S(2)	0.7617(2)	1.1739(1)	0.1013(1)	0.0403(5)
C(1)	0.5674(6)	1.2058(4)	0.0349(5)	0.0307(13)
N(1)	0.5293(5)	1.2946(3)	−0.0273(5)	0.0373(11)
C(3)	0.3685(8)	1.3215(5)	−0.0847(8)	0.059(2)
C(2)	0.6339(8)	1.3693(5)	−0.0452(7)	0.052(2)
N(2)	0.9391(5)	1.1397(4)	−0.0318(5)	0.0407(12)
C(2)	0.7970(6)	1.1415(4)	−0.0449(6)	0.0331(13)
C(4)	1.0590(6)	1.1740(6)	0.0939(7)	0.056(2)
C(5)	0.9902(7)	1.1131(5)	−0.1400(7)	0.053(2)
O(1w)	1.0226(8)	1.1047(6)	0.3866(6)	0.112(3)
		(Me$_4$tmsCuBr)$_n$ (**2**)		
Cu	0.0101(3)	−0.5976(1)	−1.0034(1)	0.0571(5)
Br	−0.0359(2)	−0.4391(1)	−0.9029(1)	0.0497(4)
S(1)	0.0284(6)	−0.4953(3)	−1.1221(2)	0.0569(11)
S(3)	−0.1392(5)	−0.8115(3)	−1.0059(2)	0.0368(8)
S(2)	−0.0276(9)	−0.7940(3)	−1.1689(2)	0.075(2)
C(2)	−0.0754(16)	−0.8898(10)	−1.0873(6)	0.029(3)
C(1)	−0.1235(31)	−0.6212(12)	−1.1506(7)	0.041(4)
N(2)	−0.0455(15)	−1.0254(8)	−1.0938(5)	0.034(2)
C(5)	−0.0141(21)	−1.0947(10)	−1.1665(6)	0.052(4)
C(6)	−0.0519(20)	−1.1211(11)	−1.0307(6)	0.048(4)
C(4)	−0.4402(26)	−0.7062(17)	−1.1936(8)	0.096(6)
N(1)	−0.3037(18)	−0.5996(12)	−1.1703(6)	0.054(3)
C(3)	−0.3762(21)	−0.4569(14)	−1.1666(8)	0.079(5)
		(Me$_4$tmsCuI)$_2$ (**3**)		
Cu(1)	0.0268(1)	0.5208(1)	−0.1120(1)	0.0474(3)
I(1)	0.1011(1)	0.3142(1)	0.0080(1)	0.0410(2)
S(1)	0.2328(2)	0.6158(2)	−0.1438(2)	0.0383(5)
S(3)	−0.1377(2)	0.4576(2)	−0.02846(2)	0.0462(6)
S(2)	0.1301(2)	0.4750(2)	−0.3600(2)	0.0448(6)
C(1)	0.2694(7)	0.5475(7)	−0.2558(5)	0.028(2)
N(2)	−0.0540(6)	0.6667(6)	−0.3706(4)	0.035(2)
N(1)	0.3977(6)	0.5380(6)	−0.2728(5)	0.036(2)
C(2)	−0.0292(7)	0.5480(8)	−0.3363(5)	0.030(2)
C(4)	0.4250(8)	0.4733(7)	−0.3714(6)	0.047(2)
C(6)	−0.1844(8)	0.7300(8)	−0.3559(6)	0.052(2)
C(3)	0.5221(7)	0.5922(8)	−0.1927(6)	0.052(2)
C(5)	0.0452(8)	0.7469(8)	−0.4140(6)	0.055(2)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

prate(I) anion, while the excess of cuprous ion generated by the reaction is stabilized as the thiuram−copper(I)−halide complex. When $CuCl_2$ is used as the oxidizing agent, no tetramethylimonium trithiolane is isolated. Its formation is therefore inferred from the isolation of the CuMe$_4$tmsCl species **(1)**. The latter and its analogue **(2)** are isolated from the reaction mixture by a tedious extraction procedure. A convenient alternative is the direct synthesis of the complexes from cuprous halides and the ligand. This is a trivial transformation which merits no further comment.

Solid State Structure of CuMe$_4$tmsX Complexes. Because assignment of the infrared spectral features for **1**−**3** has been done on the basis of the results of the X-ray crystallographic work, the latter will be presented first. The solubility properties and low melting point of the complexes hint at a discrete non ionic structure in the solid. This expectation is for the most part confirmed from the single-crystal X-ray structure determinations. Crystal data for complexes **1**−**3** are given in Table 1. Additional experimental details are found in the Supporting Information section. Final fractional atomic coordinates are reported in Table 2. Figures 1−3 show the structural diagrams and the atomic numbering scheme. Packing diagrams for the chloro and bromo derivatives are found with the Supporting Information. Selected bond distances and angles for all three complexes are given in Table 3.

Complexes CuMe$_4$tmsX exist as fundamental chelated units formed by a molecule of the ligand and one of copper(I) halide, degrees of association being different for each compound. In all three cases, coordination about copper(I) is tetrahedral and is completed by sulfur and halogen atoms. Complex **1** is a dimer, which contains two ligand molecules forming bridges between two copper atoms through one of the sulfurs from the ligands. The other terminal sulfur atom of the organic ligand completes copper coordination. The copper−copper distance of 2.981(2) Å is indicative of no metal−metal interactions. The angles around the copper atoms indicate slight distortion from the tetrahedral geometry. Atoms Cu−S(1)−Cu(a)−S(1a) form a plane, a consequence of the center of symmetry. The dihedral angle between this plane and the one defined by Cu(1), C(l), and S(3) has a value of 82.4°, which deviates from the expected value of 90°, probably due to ligand form requirements in order to complete coordination. The packing structure of **1** is stabilized by CH---Cl contacts. The smallest hydrogen chlorine distances are 2.934 and 3.000 Å. Complex **1** incorporates water in its crystalline structure. Water does not coordinate directly to the copper atom, the smallest Cu−O distance being 4.776 Å. The packing structure shows hydrogen bonds between the water hydrogens and chlorine atoms. The smallest H---Cl distance has a value of 2.501 Å.

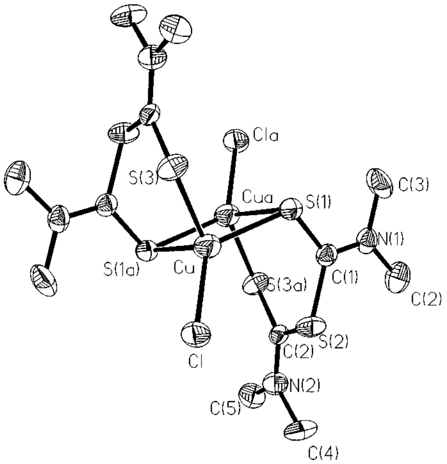

Figure 1. Structure of (CuMe$_4$tmsCl)$_2$ (**1**) and numbering scheme with 50% displacement ellipsoids for non-hydrogen atoms.

The molecular structure of **2** corresponds to a polymer. Association of basic chelated units generates long chains parallel

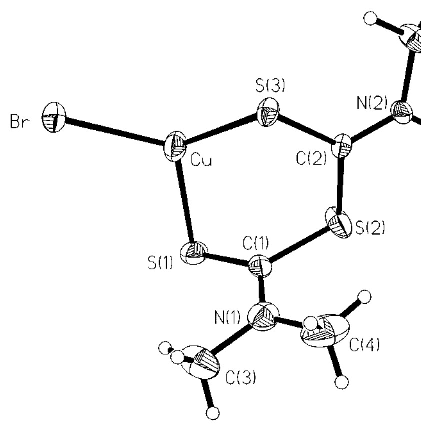

Figure 2. Structure of $(CuMe_4tmsBr)_n$ (**2**) and numbering scheme with 50% displacement ellipsoids for non-hydrogen atoms.

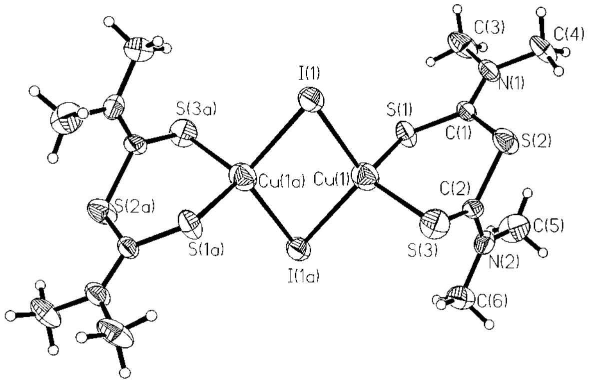

Figure 3. Structure of $(CuMe_4tmsI)_2$ (**3**) and numbering scheme with 50% displacement ellipsoids for non-hydrogen atoms.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**−**3**[a]

	$(Me_4tmsCuCl)_2$ (**1**)		
Cu−Cl	2.268(2)	Cu−S(1)	2.322(2)
Cu−S(3)	2.349(2)	Cu−S(1)#1	2.509(2)
Cu−Cu#1	2.981(2)	S(1)−C(1)	1.689(5)
S(3)−C(2)#1	1.695(6)	S(2)−C(1)	1.781(5)
S(2)−C(2)			
C1−Cu−S(1)	126.60(6)	Cl−Cu−S(3)	108.82(8)
S(1)−Cu−S(3)	101.56(7)	Cl−Cu−S(1)#1	107.14(7)
S(1)−Cu−S(2)#1	103.89(6)	S(3)−Cu−S(1)#1	107.60(6)
	$(Me_4tmsCuBr)_n$ (**2**)		
Cu−S(3)	2.278(3)	Cu−S(1)	2.336(3)
Cu−Br	2.362(2)	Cu−S(3)#1	2.620(4)
S(1)−C(1)	1.678(13)	S(3)−C(2)	1.694(10)
S(2)−C(2)	1.751(10)	S(2)−C(1)	1.796(12)
S(3)−Cu−S(1)	111.98(13)	S(3)−Cu−Br	120.90(11)
S(1)−Cu−Br	115.97(10)	S(3)−Cu−S(3)#1	98.39(7)
S(1)−Cu−S(3)#1	98.10(14)	Br−Cu−S(3)#1	106.76(10)
Cu−S(3)−Cu#2			
	$(Me_4tmsCuI)_2$ (**3**)		
Cu(1)−S(1)	2.332(2)	Cu(1)−S(3)	2.417(2)
Cu(1)−I(1)	2.6411(12)	Cu(1)−I(1)#1	2.6453(11)
Cu(1)−Cu(1)#1	2.985(2)	S(1)−C(1)	1.680(6)
S(3)−C(2)	1.653(7)	S(2)−C(1)	1.784(7)
S(2)−C(2)	1.798(7)		
S(1)−Cu(1)−S(3)	111.11(8)	S(1)−Cu(1)−I(1)	109.38(7)
S(3)−Cu(1)−I(1)	107.22(7)	S(1)−Cu(1)−I(1)#1	108.18(7)
S(3)−Cu(1)−I(1)#1	109.72(7)	S(1)−Cu(1)−I(1)#1	108.18(7)
Cu(1)−I91)−Cu(1)#1	68.75(4)	I(1)−Cu(1)−I(1)#1	111.25(4)

[a] Symmetry transformations used to generate equivalent atoms: $(Me_4tmsCuCl)_2$ (**1**), #1, $-x + 1, -y + 2, -z$; $(Me_4tmsCuBr)_n$ (**2**), #1, $-x + 1, -y - {}^3/_2, -z - 2$, #2, $x - {}^1/_2, -y - {}^3/_2, -z - 2$; $(Me_4tmsCuI)_2$ (**3**), #1, $-x, -y + 1, -z$.

to the *x* axis of the unit cell. The copper coordination is completed by one bromine and three sulfur atoms; two of these belong to the same chelated unit as the copper atom, and the third one belongs to the closest chelated ring. This is reflected in the copper−sulfur distances, two of which are shorter than the other (Cu(1)−S(1) = 2.336(3) Å, Cu(1)−S(3) = 2.278(3) Å and Cu−S(1a) = 2.620(4) Å). The situation is similar to the case of complex **1**, except that in the latter only two chelated units conform the association.

Complex **3** contains two *μ*-iodine bridged units of $CuMe_4$-tmsI (see Figure 3). As in **1** and **2**, coordination about copper is tetrahedral, and it is completed by two iodine and two sulfur atoms. The dihedral angles formed by the planes defined by Cu, Cu(a), I, and I(a) on one hand, and Cu, S(1), and S(3) on the other, has a value of 91.3°. The crystal structure is stabilized by van der Waals interactions between independent dimeric units.

The structural trends in the crystals are explained on the basis of the relative donor strengths of the potential bridging halogen and sulfur atoms in a hypothetic monomer. Thus the lower electron density available on the halogen atom of a monomeric chloro complex prevents intermolecular donation towards copper, and 4-coordination on the latter is achieved by bridging to one of the sulfur atoms of the chelate ring from another monomeric unit. A similar type of bridge is observed in the Br derivative, except that copper now binds to a singly bridging sulfur atom, leading to a polymeric network. For the iodo derivative, the better base I from the monomer competes successfully with S for coordination positions on Cu(I). The results are in good agreement with the trends noted in the literature, as far as a comparison can be established. Thus the $ClSCuS_2CuSCl$ chromophore found in **1** is similar to the one reported for $[Cu(1\text{-methylimidazoline-2-thione})_2Cl]_2$,[25] [CuCl(2,4-dithiobiuret)]$_2$,[26] or [CuCl{bis((diphenylphosphino)thioyl)methane]$_2$.[27] In complexes containing both chlorine and sulfur as potential donor atoms, the trend is for chlorine to form the bridge.[28] The most relevant comparison for the $S_2CuI_2CuS_2$ skeleton found in **3** involves the isostructural iodo(dipentamethylenethiuram monosulfide)copper(I),[29] the crystal structure of which was brought to our attention only during revision of the present text. As expected, both structures present similar bonding distances and geometries. The polymeric chains of −Cu--S--Cu--S− associations featured in the structure of **2** admit many precedents,[30] although none of these are based on $BrCuS_2$ monomeric units.

Further crystallographic work on ethyl and isopropyl derivatives of thiuram monosulfides and copper(I) halides is in progress and will be reported shortly.

Spectroscopic Characterization of the Reaction Products. $[Me_4bitt\text{-}3]^{2+}$ $CuBr_3^{2-}$ is an orange, diamagnetic, noncrystalline solid, properties which are in accord with its formulation as a Cu(I) species. Its limited solubility and general lack of stability have so far prevented further characterization in solution, while at the same time frustrating attempts at crystal growth. The $CuMe_4tmsX$ adducts **1**−**3** are red, highly crystalline, diamagnetic, low melting point solids which dissolve well in organic-

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(27) Ainscough, E. W.; Brodie, A. M.; Brown, K. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1042.

(28) We thank a reviewer for bringing this point to our attention.

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Table 4. Infrared and Raman Spectral Data for **1**−**3**[a]

	ν_{C-N}	$\nu_{C=S}$	ν_{C-S}	ν_{Cu-S} IR	ν_{Cu-S} Ra	ν_{Cu-X} IR	ν_{Cu-X} Ra
Me_4tms	1507	961	863				
1	1531	985, 943	867	347, 310	339, 332	247	264
2	1524	987, 943	867	345, 314	340, 328	193	184
3	1507	989, 945	860	365, 325	344, 331		120, 115
$Me_4bitt^{2+}CuBr_3^{2-}$	1587		877, 866			*b*	*b*

[a] All frequencies in cm^{-1}. See Experimental Section for band intensities. [b] See Experimental Section.

like solvents to yield nonconducting solutions, although the stability of such solutions is in most cases low. We shall return to this point later.

Table 4 summarizes the characteristic IR bands of the compounds prepared. Thiuram sulfides display a strong IR absorption at *ca.* 1500 cm^{-1}. This band corresponds to a stretching of the R_2N-C bond, and the unusually high position of the absorption has been attributed to the contribution of a polar canonical form $^-S_2C{=}N^+$ to the total resonance hybrid of the ligand.[31] The drain of electron density about the sulfur atoms upon complexation to metal ions shifts the absorption of this band to higher wavenumbers, and is a good indicative of complexation.[32] This effect is noted upon inspection of the values from Table 4. Complexation of the monosulfide to Cu(I) produces a shift of 5−10 cm^{-1} in the position of the absorption.

The C−N stretch is also sensitive to the oxidation state of the metal attached. In a series of copper dithiocarbamates**,** the IR band of copper(III) compounds has been reported some 50−80 cm^{-1} higher than the corresponding copper(II) compounds.[33] Thus the high C-N stretching frequency observed in the $[Me_4bitt\text{-}3]^{2+}$ compound reported in Table 4, which is presently attributed to the iminium-type linkage, would also be consistent with structures incorporating Cu(III)−dithiocarbamate units. This alternative is ruled out upon inspection of the 900−1000 cm^{-1} region of the IR spectra. Thiuram sulfides display two bands in this region, assigned to C═S stretching modes. The intensity of these bands is greatly enhanced in dithiocarbamate complexes.[34] The corresponding stretches for the C−S bands are located near 850 cm^{-1}. Both spectral features are apparent in the IR of the $CuMe_4$tmsX complexes. However, in the compound formulated as $[Me_4bitt\text{-}3]$, the C═S stretch is conspicuously absent. This agrees with the proposed structure.

The 5-membered cyclic organic cations $[R_4bitt\text{-}3]^{2+}$ have been reported in oxidation reactions of metal dithiocarbamates. For example, chlorine oxidation of iron(III) dithiocarbamates yields $[Et_4bitt\text{-}3]^{2+}2FeCl_4^-$, which can also be prepared from Et_4tds and anhydrous $FeCl_3$.[35] Similarly, $[^nBu_4Bitt\text{-}3]^{2+}Cu_2X_6^{2-}$ is accessible through halogen oxidation of cuprous dithiocarbamates (X = Cl and Br). An oxidation-desulfurization reaction is also responsible for the formation of $[Et_4bitt\text{-}3]^{2+}Hg_2I_6^{2-}$, which affords the only known crystal structure of tetraalkyliminio trithiolane cations.[36] Recent reports dealing with this sort of complexes are the observation[37] of the molecular ion of $(Fedtc_3)_2[Et_4bitt\text{-}3]^{2+}$ in the mass spectra of solutions of $Fe(Et_2dtc)_3$ oxidized with NO^+ and our synthesis of $[Me_4bitt\text{-}3]^{2+}$ $FeCl_5^{2-}$ from the reaction of $FeCl_3$ and Me_4tms**[20]**.

The low frequency region of the IR spectra, also reported in Table 4, supplies additional support for the structures assigned. Copper dithiocarbamates and thiuram sulfide complexes are characterized by medium intensity bands in the 300−400 cm^{-1} region, which are assigned to Cu−S stretching modes. The position of these bands is sensitive to the oxidation state of the metal. Thus Cu(III)−S stretches are found between 345 and 410 cm^{-1} **[33]** and Cu(I)−S vibrations span the region 310 to 365 cm^{-1},**[14a]** while Cu(II)−S stretchings have been assigned at *ca.* 350 cm^{-1} in a series of dithiocarbamate complexes.**[19]** For $[Me_4bitt\text{-}3]^{2+}$ $CuBr_3^{2-}$, the featureless spectra between 300 and 400 cm^{-1} rule out interactions between the metal and the sulfur ligand, and support the structural assignment as ionic. The nature of the anion is unclear. The far-IR is inconsistent with trigonal planar $CuBr_3^{2-}$, for which a strong 185 cm^{-1} absorption would be expected.[38] The ionic alternative consisting of a linear $CuBr_2^- + Br^-$ is also rejected on the basis of the absence of a 313 cm^{-1} feature, as present in the spectra of $(Ph_3MeP)_2$ $CuBr_2^-Br^-$.**[38]** A third possibility of overall stoichiometry $CuBr_3^{2-}$ involves polymeric infinite chains of vertex-linked tetrahedra.[39] A polymeric ionic form would explain the lack of solubility of the compound.

The series of $CuMe_4$tmsX compounds show bands which are consistent with formulations involving Cu(I)−S bonds. Assignment of the features in this region has been possible only with the hindsight afforded by the crystal structure determinations, reported above. Thus, the abnormally low Cu(I)−I frequencies at 120 and 115 cm^{-1} in $CuMe_4$tmsI (*cf.* 170 and 161 cm^{-1} in $Cu_2I_3^{-}$ [40] and comparable values for $Cu_2I_4^{2-}$ [41]) may now be understood on the basis of halogen bridges in a centrosymmetric four-coordinate structure of D_{2h} symmetry. Group theory predicts four Cu−S stretching modes, two IR active ($B_{2u} + B_{3u}$) and two Raman active ($A_{1g} + B_{1g}$), and four Cu−X stretchings, of symmetries $A_g + B_{2g}$ (Raman) and $B_{1u} + B_{3u}$ (IR). The data agrees reasonably well with this model, although attempts to obtain reliable IR data in this region have proved unsuccessful for the I derivative. The low intensities of the IR and Raman bands for the chloro and bromo derivatives make the assignment of the spectral features less certain. Still, for the chloro complex, compliance with the rule of mutual exclusion is observed. No coincidences of IR and Raman lines are apparent, in agreement with the presence of a centrosymmetric $S_4Cu_2X_2$ *kernel*.

The $CuMe_4$tmsX complexes show conductivities which are typical of nonelectrolites in acetonitrile or chloroform. Molecular weight determinations could only be performed in a reliable manner for the $CuMe_4$tmsBr derivative. A monomer

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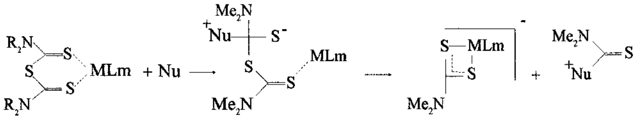
formulation in acetonitrile is not surprising, considering the strong coordination properties of the solvent. The halogen bridges present in the solid are broken and acetonitrile occupies the fourth coordination position on copper.

The ^{1}H-NMR spectra of the complexes **1** and **2** are reported under the protocol for each compound. The temperature dependence of the ^{1}H-NMR spectra of thiuram sulfides has been interpreted in terms of restricted rotation about the C−N bond which causes inequivalence of the alkyl groups and broadening of the signals at temperatures close to ambient.[31] This is apparent in the spectra of the complexed CuR_4tmsX and parent ligand. Two sets of CH_3 resonances are present in all the cases studied.

The spectra of $CuMe_4tmsCl$ calls for additional comments. At room temperature the spectrum consists of four singlets of approximately equal height. The outer components are much broader and altogether account for three quarters of the overall integrated intensity (see Experimental Section). In a range of temperature between ambient and 55 °C, pronounced broadening and shifting of the position of the outer components to higher field is observed. These changes, which are accompanied by darkening of the originally red solutions, are irreversible and therefore attributed to degradation of the materials, the nature of which is addressed further on. Below room temperature, and down to −10 °C, the outer signals decrease in intensity (63% of the total), and the center of the system shifts slightly upfield (0.01 ppm). These changes are reversible and are attributed to the onset of a monomer−dimer equilibrium in solution. If the bond-making process of dimer formation from monomers were the only thermodynamically relevant event, one would expect the monomer−dimer equilibrium (exothermic) to shift to monomer at room temperature, and to dimer at lower temperatures. This allows one to assign the room temperature most intense signals as monomer, and in turn allows evaluation of the related equilibrium constant. The values thus obtained are 0.22 and 0.47 L mol^{-1} at +27 and −10 °C respectively. The limited temperature range available does not warrant further speculation as to the significance of the enthalpy value thus obtained for the dimerization process.

Solutions of $CuMe_4tmsX$ complexes are not stable. Upon standing or heating, decomposition is observed. One of the decomposition products is the corresponding $Cu(Me_2dtc)_2$ compound, which has been isolated and characterized by melting point, IR and elemental analyses. The ability of tetraalkylthiuram monosulfides to generate metal dithiocarbamates has been used as a synthetic alternative to the preparation of the latter compounds[19]. It is now clear, after the work of McCleverty and Morrison, that rupture of the C−S bond is a consequence of the nucleophilic attack on the thiocarbamoyl carbon, by a suitable agent.[42] Our work with tetramethylthiuram monosulfide and iron(III) chloride has given indirect evidence on the course of the degradation of the monosulfide,[20] which may be written as:



Possible nucleophiles in our case are the solvent or the halide ions, but efforts to determine the fate of the missing dimethylthiocarboxamido residue have been unsuccessful.

Further crystallographic work is in progress for analogues of the series CuR_4tmsX with different alkyl substituents. Preliminary results indicate striking changes in the degrees of association in the solid and in the stereochemistry of the metal center.

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Supporting Information Available: Listings of full crystallographic data with refinement details, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacements **1**−**3** and packing diagrams for **1** and **2** (9 pages). Ordering information is given on any current masthead page.

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