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### THE SYNTHESSES AND CHARACTERIZATION OF HALOGENOBIS(N,N-DIALKYLTHIO-CARBAMOYL)SULFIDOCOPPER(I)

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## THE SYNTHESSES AND CHARACTERIZATION OF HALOGENOBIS(N,N-DIALKYLTHIO- CARBAMOYL)SULFIDOCOPPER(I)

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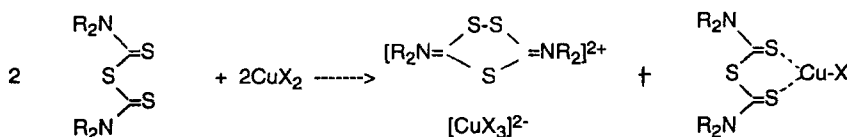
Tetraalkylthiuram monosulfides react with Cu(I) halides to form 1:1 adducts, which are characterized by IR, Raman and <sup>1</sup>H-NMR spectroscopy, as well as magnetic susceptibility, molecular weight and conductivity measurements. The compounds are monomers or dimers, according to the nature of the alkyl substituent. The molecules in solution exist as equilibrium mixtures of monomers and dimers.

KEYWORDS: tetraalkylthiuram, sulfur ligands, copper(I)

### INTRODUCTION

Bis(N,N-dialkylthiocarbamoyl)sulfides, also known as tetraalkylthiuram monosulfides, R<sub>4</sub>tms(\*\*), are potential bidentate sulfur ligands. Perhaps because they have been less extensively used than the related disulfides (R<sub>4</sub>tds) in rubber vulcanization, agriculture and medicine, their chemistry has remained largely unexplored. Modest advances in this field have been realized through preparation of cationic [CrR<sub>4</sub>tmsX<sub>2</sub>]<sup>+</sup> and neutral MR<sub>4</sub>tmsX<sub>2</sub> (M = Zn<sup>2+</sup>, Hg<sup>3+</sup>, Ni and Co<sup>4+</sup>) or M'R<sub>4</sub>tmsX (M' = Ag and Cu<sup>5+</sup>). Also, there have been cases where a metal moiety inserts oxidatively into the C-S bond of a monosulfide to give dithiocarbamato-metalthiocarboxamido complexes. Some examples include monovalent rhodium and platinum tris(triphenylphosphine) halides<sup>6</sup> and zerovalent molybdenum compounds.<sup>7</sup>

The reaction of tetraalkylthiuram monosulfides and copper(II) halides was demonstrated to produce 3,5-bis(N,N-dialkylimonium)-1,2,4-trithiolane trihalocuprate(I) (R<sub>4</sub>bitt-3)<sup>2+</sup> and halogenobis(N,N-dialkylthiocarbamoyl)-sulfidocopper(I).<sup>8</sup>



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The vibrational spectra of the thiuram-Cu(I)-halide complexes could be assigned in terms of a planar, halogen-bridged dimeric structure of  $D_{2h}$  symmetry for the methyl-substituted compounds. The spectra of the ethyl derivatives however, are different than one would expect from a  $D_{2h}$  structure. Moreover, from a synthetic point of view, the tedious extraction procedure necessary to separate the two components of the reaction mixture was ill suited to scaleup. Also, and for reasons trivial to state, no iodo derivatives were available through this route.

Therefore, a complete synthetic and structural study of tetraalkylthiuram-monosulfide-Cu(I) complexes was undertaken. The results reveal that the entire series of  $CuR_4tmsX$  compounds, with the exception of  $CuEt_4tmsl$ , is accessible through the reaction of Cu(I) halides and tetraalkylthiuram monosulfides,  $R_4tms$  ( $R = Me, Et; X = Cl, Br, I$ ). Striking changes in the coordination environment of the Cu(I) center are also apparent.

## EXPERIMENTAL

### *General Preparative*

Cu(I) chloride (Merck) was finely ground and washed with aqueous sodium sulfite. Cu(I) bromide was made from aqueous Cu(II) sulfate, potassium bromide and sodium sulfite. Cu(I) iodide was obtained by reaction of potassium iodide and Cu(II) sulfate and further reduction of the iodine produced with sodium thiosulfate.

Tetramethylthiuram monosulfide (Fluka) was recrystallized from EtOH. The ethyl derivative was prepared from the corresponding disulfide<sup>9</sup> and potassium cyanide in boiling aqueous EtOH (CAUTION: ACID HYDROLYSIS OF POTASSIUM CYANIDE GENERATES HYDROGEN CYANIDE, AN EXCEEDINGLY POISONOUS GAS). The cool solution was diluted with water and extracted with  $Et_2O$ . The organic extract was dried with  $CaCl_2$  and evaporated to give a red syrup. Attempts to crystallize this material were unsuccessful. Satisfactory elemental analyses,  $^1H$ -NMR and IR prompted the use of this material with no further purification.

### *Instrumentation and Analyses*

Infrared spectra were obtained as KBr pellets in the range  $4000$  to  $500\text{ cm}^{-1}$  using a Nicolet Magna 550 spectrometer and as Nujol mulls over polyethylene film below  $500\text{ cm}^{-1}$ , using a Perkin Elmer FTIR 2000 spectrometer.  $^1H$ -NMR were obtained using a Brücker AC 250 P spectrometer. Resonances are reported in ppm downfield from TMS. The standard abbreviations *s*: singlet, *t*: triplet and *q*: quartet are used. Integrated intensities are normalized to the total number of protons per formula unit. Raman spectra were run in crystalline solids enclosed in a glass capillary, using a Spex Compact 1301 spectrometer with a He-Ne laser. Conductivities were measured at room temperature with a Wiss-Techn-Werkstatten bridge. Magnetic susceptibilities were determined by means of a Faraday system and electrobalance. Molecular weights were measured with a Knauer vapor pressure osmometer at  $37^\circ C$ .

Standard combustion techniques were used in the determination of carbon and hydrogen. Copper was determined by iodometry and halides by the Volhard method.

### *Preparation of the Complexes*

A standard procedure was followed for the preparation of the complexes. Full details are given for  $\text{CuMe}_4\text{tmsCl}$ . Other compounds were prepared through slight modifications of this procedure. Such modifications are noted in the text.

#### *Chlorobis(N,N-dimethylthiocarbamoyl)sulfidocopper(I)*

$\text{CuMe}_4\text{tmsCl}$ : 0.297 g (3.0 mmol)  $\text{CuCl}$  was dissolved in  $\text{CH}_3\text{CN}$  (15 mL) and added to a cooled (ice-salt bath) solution of 0.625 g (3.0 mmol)  $\text{Me}_4\text{tms}$  in  $\text{CH}_3\text{CN}$  (10 mL).  $\text{Et}_2\text{O}$  was layered on top of the dark red solution obtained. Red microcrystalline solid was given off within 2 h. The product was filtered by suction, washed with fresh  $\text{Et}_2\text{O}$  and air dried. Yield: 0.84 g.  $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3\text{CuCl}$ ; Red microcrystalline solid, m.p: blackens from 80 to 127°C, melts at 136°C (d). *Anal.* Calcd (%): Cu, 20.67; Cl, 11.53; C, 23.44; H, 3.94. Found: Cu, 20.58; Cl, 11.36; C, 23.38; H, 3.90. IR (KBr): 2929w, 1520s, 1381s, 1231m, 1147m, 1049w, 981m, 945m, 865w. (Nujol): 347s, 310m, 280w, 247m.  $^1\text{H-NMR}(\text{CDCl}_3)$ : 3.57(s, 4.5), 3.51 (s, 1.5), 3.48(s, 1.5), 3.43(s, 4.5).  $\mu_{\text{EFF}} = 0.02$  MB. Molar conductivity: 30–35  $\text{Ohm}^{-1}\text{-cm}^2\text{-mol}^{-1}$  ( $10^{-3}$ – $10^{-4}\text{M}$ ).

#### *Bromobis(N,N-dimethylthiocarbamoyl)sulfidocopper(I), CuMe<sub>4</sub>tmsBr*

Addition of  $\text{Et}_2\text{O}$  to the reaction mixture of  $\text{CuBr}$  and  $\text{Me}_4\text{tms}$  in acetonitrile produced immediate precipitation of the red product. The solid was filtered and dried. Yield: 0.92 g.  $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3\text{CuBr}$ ; red, needle-shaped microcrystalline solid, m.p: 174–176°C (d). *Anal.* Calcd: (%) Cu, 18.06; Br, 22.71; C, 20.48; H, 3.44. Found: Cu, 18.18; Br, 22.65; C, 20.40; H, 3.40. IR (KBr): 2924w, 1513s, 1378s, 1225w, 1139m, 1046w, 984w, 940m, 864w. (Nujol): 345m, 324m, 193s, 161sh.  $^1\text{H-NMR}(\text{CDCl}_3)$ : 3.59(s,6), 3.41(s,6).  $\mu_{\text{EFF}} = 0.00$  MB. Molar conductivity: 28–37  $\text{Ohm}^{-1}\text{-cm}^2\text{-mol}^{-1}$  ( $10^{-3}$ – $10^{-4}\text{M}$ ). Mol. wt.: 318–320. (Association: 0.91,  $10^{-3}$ – $10^{-4}\text{m}$ ).

#### *Iodobis(N,N-dimethylthiocarbamoyl)sulfidocopper(I), CuMe<sub>4</sub>tmsI*

The product precipitated immediately upon mixing of acetonitrile solutions of the reagents. The solid was filtered, washed with  $\text{Et}_2\text{O}$  and dried. Yield: 1.18 g,  $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3\text{CuI}$ : Orange-red powder, m.p: blackens progressively up to 189°C, melts at 192°C (d). *Anal.* Calcd. (%): Cu, 15.93; I, 31.82; C, 18.07; H, 3.04. Found: Cu, 15.38; I, 31.71; C, 18.00; H, 3.04. IR(KBr): 2929w, 1507s, 1370s, 1229m, 1145w, 1045w, 989m, 945m, 860w. (Nujol): 365s, 325s. Limited solubility prevented observation of NMR spectra.  $\mu_{\text{EFF}} = 0.00$  MB.

#### *Chlorobis(N,N-diethylthiocarbamoly)sulfidocopper(I), CuEt<sub>4</sub>tmsCl*

The acetonitrile reaction mixture was treated with 15 mL  $\text{Et}_2\text{O}$ , layered over the dark red-brown solution. Standing in a freezer for several hours gave a small

amount of black needles, m.p: 198°. The solution was treated with additional (5 mL) Et<sub>2</sub>O and returned to the freezer overnight, large orange-red plates separated. The solvent was decanted, the product was washed with Et<sub>2</sub>O and air dried. Yield: 0.39g. C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>S<sub>3</sub>CuCl: Orange-red prisma, m.p: 118–120°C (d). *Anal.* Calcd (%): Cu, 17.48; Cl, 9.75; C, 33.04; H, 5.56. Found: Cu, 17.40; Cl, 9.70; C, 33.17; H, 5.43. IR(KBr): 2980m, 2936m, 2861w 1500s, 1428s, 1376w, 1349m, 1267s, 1193s, 1145m, 1069m, 987w, 960w, 904m, 831m, 775w. (Nujol): 364w, 329sh, 307s. <sup>1</sup>H-NMR(CDCl<sub>3</sub>): 4.02(q,7Hz,4), 3.73(q,7Hz,4), 1.39(t,7Hz,6), 1.32(t,7Hz,6). μ<sub>EFF</sub> = 0.00 MB. Molar conductivity: 25–30 Ohm<sup>-1</sup>·cm<sup>2</sup>·mol<sup>-1</sup> (10<sup>-3</sup>–10<sup>-4</sup> M).

*Bromobis(N,N-diethylthiocarbamoyl)sulfidocopper(I), CuEt<sub>4</sub>tmsBr*

The isolation procedure was similar to the one described for the chloro derivative, except that no dark needle-shaped crystals were given off. Yield 0.45g. C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>S<sub>3</sub>CuBr: Orange-red prisma, m.p.: 115–117°C (d). *Anal.* Calcd (%): Cu, 15.58; Br, 19.59; C, 29.44; H, 4.95. Found: Cu, 15.66; Br, 19.21; C, 29.35; H, 4.86. IR(KBr): 2980s, 2962s, 2927m, 2868w, 1504s, 1495s, 1430s, 1373w, 1347m, 1295w, 1269s, 1197s, 1143m, 1088w, 1069m, 984w, 960w, 905m, 829m, 777w. (Nujol): 349w, 326m, 250s. <sup>1</sup>H-NMR: 4.02(q,7Hz,4), 3.66(q,7Hz,4), 1.44(t,7Hz,6), 1.34(t,7Hz,6). μ<sub>EFF</sub> = 0.00 MB. Molar conductivity: 28–38 Ohm<sup>-1</sup>·cm<sup>2</sup>·mol<sup>-1</sup> (10<sup>-3</sup>–10<sup>-4</sup>M).

## RESULTS AND DISCUSSION

### *The Reaction of Cu(I) Halides and Tetraalkylthiuram Monosulfides*

Cu(I) halides form well defined adducts with thiuram monosulfides. The stoichiometry of the complexes is 1:1 in most cases, regardless of the ratio of mixing. Cu(I) iodide and tetraethylthiuram monosulfide are an exception to the general pattern, and the exact nature of the product in this case is still under investigation. In our hands, previous synthetic procedures based on the interaction of acetone solutions of Me<sub>4</sub>tms and solid cuprous halides<sup>5b</sup> did not yield analytically pure samples. The insoluble halide becomes heavily crusted with the product. Longer reaction times result in decomposition of the samples. A modification of an earlier method<sup>5a</sup> worked well and produced acceptable yields of high quality materials.

The compounds are red diamagnetic solids. Considering the spectra data, especially the IR spectra (see below), they must be regarded as authentic Cu(I)-thiuram complexes, and not as the analytically indistinguishable Cu(III)-thiocarboxamido-dithiocarbamate formulation. The latter would arise as a consequence of the (apparent) oxidative insertion of the Cu(I) halide into the thiocarbamoyl carbon of the monosulfide. All physical and chemical properties of the materials are identical to those found in the complexes isolated from the reaction of Cu(II) halides and thiuram monosulfides,<sup>8</sup> as far as this comparison can be established.

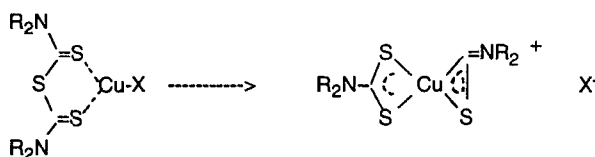
### *The Structure and Properties of Solid CuR<sub>4</sub>tmsX Complexes*

The solubility properties and low melting point of the sample hint at a discrete non-ionic structure in the solid. The rest of the characterization is done mostly by

IR and Raman spectroscopy. Table 1 summarizes the most prominent features found in the IR spectra of the complexes and the parent ligands, and Table 2 contains the frequencies associated to the vibrations in the metal-ligand region of the spectra.

The general appearance of the spectra above  $500\text{ cm}^{-1}$  (Table 1) confirms the complexes as authentic thiuram monosulfide complexes. The band at *ca.*  $1500\text{ cm}^{-1}$  ("thiureide band") corresponds to a stretching of the  $\text{R}_2\text{N-C}$  bond and its abnormally high position is related to an important contribution of the polar  $^-\text{S}_2\text{C}=\text{NR}_2$  form to the overall structure of the ligand.<sup>10</sup> Complexation of thiuram sulfides to metal ions shifts electron density away from the sulfur atoms and enhances the importance of the polar form to the total resonance hybrid, thus shifting the corresponding absorption to higher wavenumbers.<sup>1-5</sup> This effect is noted in the values reported in Table 1.

As pointed out above, a structural alternative to the compounds under discussion involves a Cu(III)-dithiocarbamate-thiocarboxamide (Cu(III)-dtc-tca) formulation. This would come about through the (formal) oxidative insertion of the cuprous halide into the C-S bond of the monosulfide.



This possibility must be ruled out, based on the presence of a single "thiureide" band. Dialkylthiocarboxamido ( $\text{R}_2\text{tca}$ ) metal complexes display a  $\text{C}=\text{N}$  stretch at *ca.*  $1600\text{ cm}^{-1}$ ,<sup>12</sup> which is absent in the spectra of the present compounds.

Assignments for the Cu-S and Cu-X stretches were made by comparison with previous work.<sup>10,11</sup> Complexes spanning the  $\text{CuMe}_4\text{tmsX}$  series display Cu-X stretching modes in an abnormally low region and thus the spectra are consistent with bridging halogen atoms. Consequently a planar four-coordinate structure of  $\text{D}_{2h}$  symmetry involving halogen bridges is postulated for these compounds. Group theory predicts four Cu-S stretching modes, two IR active ( $\text{B}_{2u} + \text{B}_{3u}$ ) and two

**Table 1** Selected IR frequencies for the complexes synthesized and parent ligands.

|                             | $\nu_{\text{C-N}}$ | $\nu_{\text{C-S}}$ | $\nu_{\text{C-S}}$ |
|-----------------------------|--------------------|--------------------|--------------------|
| $\text{Me}_4\text{tms}$     | 1507               | 995, 961           | 863                |
| $\text{Et}_4\text{tms}$     | 1500               | 1000, 970          | 819                |
| $\text{CuMe}_4\text{tmsCl}$ | 1520               | 981, 945           | 865                |
| $\text{CuMe}_4\text{tmsBr}$ | 1513               | 984, 940           | 864                |
| $\text{CuMe}_4\text{tmsI}$  | 1507               | 989, 945           | 860                |
| $\text{CuEt}_4\text{tmsCl}$ | 1500               | 987, 960           | 831                |
| $\text{CuEt}_4\text{tmsBr}$ | 1504               | 984, 960           | 830                |

All figures in  $\text{cm}^{-1}$ . See Experimental Section for band intensities.

**Table 2** Raman and IR bands of the complexes in the metal-ligand stretching region of the spectra.

|                         | Cu-S        |            | Cu-X        |            |
|-------------------------|-------------|------------|-------------|------------|
|                         | IR          | Raman      | IR          | Raman      |
| CuMe <sub>4</sub> tmsCl | 347s, 310m  | 339s, 332w | 280w, 247w  | 284w, 224w |
| CuMe <sub>4</sub> tmsBr | 345s, 314w  | 340s, 328w | 193m, 161sh | 184m, 157m |
| CuMe <sub>4</sub> tmsI  | 365s, 325s  | 344s, 331w |             | 120s, 115s |
| CuEt <sub>4</sub> tmsCl | 364w, 329sh |            | 307s        |            |
| CuEt <sub>4</sub> tmsBr | 349w, 326m  |            | 250s        |            |

All frequencies in cm<sup>-1</sup>.

Raman active ( $A_{1g} + B_{1g}$ ), and four Cu-X stretches, of symmetries  $A_g + B_{2g}$  (Raman) and  $B_{1u} + B_{3u}$  (IR). The data agree reasonably well with this model. So far, attempts to obtain reliable IR data in this region has proved unsuccessful for the iodide derivative.

The vibrational spectra of the compounds in the CuEt<sub>4</sub>tms series cannot be fitted into the scheme above. The IR spectra of the Cl and Br compounds reveal two features each, attributable to Cu-S stretchings. However, a single strong mode at 307 cm<sup>-1</sup> for the Cl derivative, and at 250 cm<sup>-1</sup> for the Br compound, is hardly consistent with a dimeric bridge structure. Considering these results, and the solution results, discussed below, these structures are tentatively assigned as monomeric S<sub>2</sub>CuX skeletons of C<sub>2v</sub> symmetry. Packing effects must be responsible for this difference in behavior with respect to the methyl series, since molecular models reveal no steric crowding at the copper environment in the methyl and ethyl derivatives. Indeed the final word on this matter must rest with suitable crystal studies, and work on this is being actively pursued.

#### *The Solution Structure and Properties of the CuR<sub>4</sub>tmsX Complexes*

The CuR<sub>4</sub>tmsX complexes show conductivities which are typical of non-electrolytes in acetonitrile or chloroform.<sup>12</sup> Contrary to earlier claims,<sup>5b</sup> no evidence was found of ionic dissociation in analytically pure samples of CuMe<sub>4</sub>tmsCl or CuMe<sub>4</sub>tmsBr. Molecular weight determinations could only be performed in a reliable manner for the CuMe<sub>4</sub>tmsBr derivative. A monomer formulation in acetonitrile is not surprising, considering the strong coordination properties of CH<sub>3</sub>CN. The halogen bridges present in the solid are broken and acetonitrile occupies the fourth coordination position on copper.

The <sup>1</sup>H-NMR spectra of the complexes is reported in Table 3. The temperature dependence of the <sup>1</sup>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.<sup>12</sup> This is apparent in the spectra of the complexed CuR<sub>4</sub>tmsX and parent ligand. Two sets of CH<sub>2</sub> and CH<sub>3</sub> resonances are present in all cases studied. In the ethyl series the chemical shifts of both inequivalent alkyl groups are close enough that a complicated signal is observed near 1.3 ppm, caused by overlap of two triplets.

The spectra of CuMe<sub>4</sub>tmsCl call 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). In a range of temperature between

**Table 3**  $^1\text{H-NMR}$  spectra of thiuram monosulfide complexes of Cu(I) halides and parent ligands in  $\text{CDCl}_3$ .

|                             | $\text{CH}_2$ |      | $\text{CH}_3$ |      |
|-----------------------------|---------------|------|---------------|------|
|                             |               |      |               |      |
| $\text{Me}_4\text{tms}$     |               | 3.44 | 3.36          |      |
| $\text{CuMe}_4\text{tmsCl}$ |               |      | 3.57          | 3.43 |
|                             |               |      | 3.51          | 3.48 |
| $\text{CuMe}_4\text{tmsBr}$ |               |      | 3.59          | 3.41 |
| $\text{Et}_4\text{tms}$     | 4.01          | 3.74 | 1.32          |      |
| $\text{CuEt}_4\text{tmsCl}$ | 4.02          | 3.73 | 1.39          | 1.32 |
| $\text{CuEt}_4\text{tmsBr}$ | 4.02          | 3.66 | 1.44          | 1.34 |

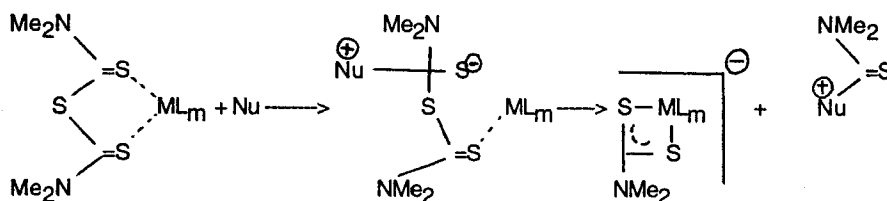
All resonances in ppm downfield from TMS. See Experimental Section for multiplicity and intensity of the signals.

ambient and  $55^\circ\text{C}$ , 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 original red solutions, are irreversible and therefore attributed to degradation of the materials, the nature of which is addressed in the following section. Below room temperature, and down to  $-10^\circ\text{C}$ , 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  $0.47 \text{ l}\cdot\text{mol}^{-1}$  at 27 and  $-10^\circ\text{C}$  respectively. The limited temperature range available does not warrant further speculation.

### Decomposition of the Thiuram Monosulfide Complexes

Solutions of  $\text{CuR}_4\text{tmsX}$  complexes are not stable. Upon standing or heating, decomposition is observed. One of the decomposition products is the corresponding  $\text{Cu}(\text{R}_2\text{dtc})_2$  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.<sup>11</sup> It is now clear that rupture of the C-S bond is a consequence of nucleophilic attack on the thiocarbamoyl carbon, by a suitable agent.<sup>20</sup>





Possible nucleophilic agents are the solvent or the halide ion, but efforts to determine the fate of the dialkylthiocarboxamido residue have been unsuccessful.

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(\*\*) Except where relevant to the chemistry under discussion, tetraalkylthiuram monosulfides and dithiocarbamates are abbreviated tms or dtc, with no specification of the alkyl substituents.

#### Abbreviations used

|                        |                                   |                                |
|------------------------|-----------------------------------|--------------------------------|
| tms                    | : thiuram monosulfide             | $[\text{>N-C(S)}]_2\text{S}$   |
| tds                    | : thiuram disulfide               | $[\text{>N-C(S)}]_2\text{S}_2$ |
| dtc                    | : dithiocarbamate                 | $[\text{>N-C(S)-S-}]$          |
| tca                    | : thiocarboxamide                 | $[\text{>N-C(S)-}]$            |
| [bitt-3] <sup>2+</sup> | : bis(dialkylimonium)-trithiolane | $[\text{>N=C-S-S-C=N<}]^{2+}$  |

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