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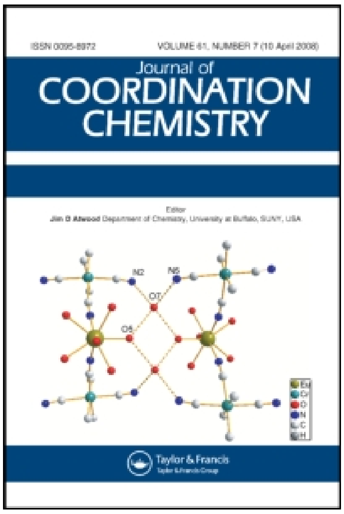

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COPPER(III) DITHIOCARBAMATE COMPLEXES FROM THIURAM DISULFIDES AND COPPER(I) HALIDES

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COPPER(III) DITHIOCARBAMATE COMPLEXES FROM THIURAM DISULFIDES AND COPPER(I) HALIDES

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Tetraalkylthiuram disulfides react with Cu(I) halides to give materials of composition $Cu_2(dtc)_3X_2$, which are presumed to be the ionic species $Cu\,(dtc)_2^+Cu\,(dtc)X_2^-$ containing Cu(II) and Cu(III), on the basis of magnetic susceptibilities, IR and ESCA spectroscopies. In the presence of triphenylphosphine, sulfur abstraction from the monosulfides leads to known monosulfide complexes of Cu(I). Some of the dithiocarbamate complexes are also accessible through degradation of alkylimonium trithiolane and tetrathiolane halocuprate(I) compounds.

Keywords: dithiocarbamates; thiuram disulfides; copper(III)

INTRODUCTION

Interaction of thiuram disulfides, $R_2NC(S)S\text{-}SC(S)NR_2$ (R4tds), with metal species has long been recognized as a convenient route to metal dithiocarbamates, R_2NCS_2M (dtcM),[1] although the formal oxidation state in the final metal species does not always follow from the electron count of the system under study. Thus Et_4(tds) and Cu(II) halides have been reported to yield $Cu(II)(dtc)_2$ where the oxidation state of the metal is maintained, despite the obvious reduction of the ligand.[2] In a recent paper[3] we reported a novel pattern of reactivity for this system, which involves oxidation of the ligand at some point.

Copper(I) halides CuX (X=Cl, Br) react with thiuram disulfides R_4tds (R=Me, Et) to yield compounds of stoichiometry $Cu_2(dtc)_3X_2$. Infrared, magnetic

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susceptibility and ESCA analysis of these materials point to an ionic formulation Cu(III)(dtc)$_2^+$ Cu(II)(dtc)X_2^- in the solid. In the presence of triphenylphosphine, sulfur abstraction from the ligand leads to formation of a monosulfide-copper(I) complex. The latter desulfurization and complexation to yield Cu(I) halide compounds is similar to the work of McCleverty *et al.* with Zn halides.[4]

EXPERIMENTAL

General

Me$_4$tds was prepared by a literature procedure.[5] CuCl (Merck) was washed with aqueous sodium sulfite and the white solid thus obtained was filtered, washed with water, then acetone and finally pumped dry. CuBr was made by reduction of aqueous copper(II) sulfate with sodium sulfite in solution containing suitable amounts of potassium bromide. The isolation of the white solid product was similar to the method described for the chloro derivative.

3, 5-bis(N, N-dialkylimonium)-1, 2, 4-trithiolane tribromocuprate(I) was made by an established procedure.[6] All preparations were carried out in air and solvents were of technical grade, used with no further purification.

Instrumentation and Analyses

Infrared spectra were obtained as KBr pellets in the range 4000 to 500 cm^{-1} using a Nicolet Magna 550 spectrometer and as Nujol mulls over polyethylene film below 500 cm^{-1}, using a Perkin Elmer 2000 spectrometer. ^{1}H-NMR were obtained using a Brucker AC 250 P spectrometer. Resonances are reported in ppm downfield from TMS. Integrated intensities are normalized to the total number of protons per formula unit. Conductivities were measured at room temperature with a Wiss-Techn-Werkstanten 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°C.

ESCA spectra were run on a Fissons Instruments Escalab 220 iXL spectrometer with a monochromatic X-ray source. Charge compensation was achieved using a coaxial electron source. Spectra were calibrated using the carbon 1s line at Binding Energy (BE) 284.8 eV. Samples were mounted on double-sided adhesive tape.

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

Bis-(N, N-dimethyldithiocarbamato)copper(III) dichloro (N, N-dimethyldithiocarbamato)cuprate(II) $[Me_2dtc)_2Cu]^+$ $[(Me_2dtc)_2Cu]^+$ $[(Me_2dtc)CuCl_2]^-$

A solution of 0.297 g (3.0 mmol) of CuCl, dissolved in acetonitrile (15 mL) was added at room temperature to a stirred solution of Me4tds (0.74 g, 3.0 mL) in the same solvent (35 mL). The fine dark brown powder was gravity filtered, washed with 10 mL of fresh acetonitrile then by 5 mL of diethylether and dried. Yield 0.6445 g. Lack of solubility in most organic solvents prevented further purification. $C_9H_{18}N_3S_6Cu_2Cl_2$; Brown microcrystalline solid, m.p. 197° (d). Anal. calcd.(%): Cu, 22.75; Cl, 12.69; C, 19.35; H, 3.25. Found: Cu, 22.69; Cl, 12.63; C, 19.29;, 3.31. IR (KBr) 2923 vw, 1571 vs, 1550 sh, 1403 s, 1241 m, 1150 s, 975 m. (Nujol) 444 m, 398 m, 376 m, 355 w. μ_{EFF} = 1.83 M.B.

Upon standing, the mother solution produced deposit of bis(N,N-dimethyldithiocarbamato)copper(II), as black amorphous powder, m.p. above 300°, IR (KBr) 1520 vs. Anal. calcd.(%): Cu, 20.90; Found: Cu, 20.83. When the experiment was repeated, inverting the order of addition, or refluxing CuCl and Me_4tds in acetonitrile in a 2:1 molar ratio, materials of the following characteristics were obtained: Anal. calcd.(%): Cu, 25.4 to 28.1; Cl, 14.4 to 15.6; m.p. 218 to 225°; IR (KBr) 1553 vs (Nujol) 444 m, 365 m. Analytically pure samples of this compound were obtained by the method described in the following paragraph.

Bis(N, N-dimethyldithiocarbamato)(μ-dichloro)dicopper(II). $Cu_2(Me_2dtc)_2Cl_2$.

3, 6-Bis(N,N-dimethylimonium)-1, 2, 4, 5-tetrathiolane bis(dichlorocuprate(I))[3] (1.75 g, 3.4 mmol) was suspended in 96% ethanol (150 mL), refluxed for 4 and filtered hot to obtain 1.25 g of dark powder. $C_3H_6NS_2CuCl$: shiny black microcrystalline solid, m.p. 228° (d). Anal. calcd.(%): Cu, 28.99; Cl, 16.17; C, 16.44; H, 2.76. Found: Cu, 28.55; Cl, 16.08; C, 16.35; H, 2.71. IR (KBr) 2927 vw, 1553 vs, 1407 s, 1253 m, 1165 s, 983 m. (Nujol) 365 m. μ_{EFF} = 1.81 M.B.

Air evaporation of the EtOH mother solution generated light yellow plates of tetramethylthiuram disulfide, m.p. 148°.

Bis(dimethyldithiocarbamato)copper(III) dibromo(dimethyldithiocarbamatocuprato(II). $[(Me_2dtc)_2Cu]^+$ $[(Me_2dtc)CuBr_2]^-$

The compound was made in the manner described for the chloro derivative from 3 mmol each of CuBr and Me_4tds. Yield 0.82 g. $C_9H_{18}N_3$Cu2Br_2: Brown powder, m.p. 205–207° (d). Anal. calcd.(%): Cu, 19.62; Br, 24.68; C, 16.69; H, 2.81. Found: Cu, 19.35; Br, 24.83; C, 16.35; H, 2.71. IR (KBr) 2930 w, 1567 vs, 1543 sh, 1386 s, 1234m, 1155 s, 959 m. (Nujol) 390 s, 350 m. $\mu_{EFF} = 1.80$ M.B. When the material thus obtained was suspended in fresh acetonitrile, rapid darkening of the solid was observed.

Bis(dimethyldithiocarbamato)copper(III) tribromodicuprate (I). $[Me_2dtc)_2Cu]^+ [Cu_2Br_3]^-$

Me_2tds (0.48 g, 2 mmol) was dissolved in CH_2Cl_2 (50 mL) and CuBr (0.86 g, 6.0 mmol) was added. The dark precipitate was stirred for one, filtered, washed with fresh solvent and air dried to yield 1.22 g of solid. $C_6H_{12}N_2S_4Cu_3Br_3$: Black microcrystalline solid, m.p. 140°, crystalline transition, 208° melts with decomposition. Anal. calcd.(%): Cu, 28.42; Br, 35.74; C, 10.74; H, 1.81. Found: Cu, 28.30; Br, 35.55; C, 10.35; H, 1.75. IR (KBr) 2925 w, 1574 vs, 1414 s, 1246 m, 1162 s, 973 m. (Nujol) 404 sh, 395 s, 385 sh, 360 w. $\mu_{EFF} = 0.00$ M.B.

$Cu(Me_2dtc)_2(CuBr)_3$

Method a) Me_4tds (0.6011 g, 2.5 mmol) in tetrahydrofuran (50 mL) was added at room temperature to a stirred solution of CuBr (1.1168 g, 5 mmol) in the same solvent (50 mL). The dark suspension was heated and 80 mL of the solvent was removed by distillation. 100 mL of 96% EtOH was added to the cold dark mass and the mixture was refluxed for 3 h. The suspension was cooled, then filtered and washed with fresh EtOH and Et_2O and air dried to yield 0.57 g of black solid.

Method b) [Me_4bitt-3][$CuBr_3$] (1.1719 g, 2.3 mmol) was suspended in 100 mL of 96% EtOH and refluxed for 5 h. The suspension was cooled and filtered to afford 0.33 g of material. $C_6H_{12}N_2S_4Cu_4Br_3$: Black shiny microcrystalline solid, m.p. 275° (d). Anal. calcd.(%): Cu, 34.61; Br, 32.65; C, 9.81; H, 1.65. Found: Cu, 34.56; Br, 32.40; C, 9.60; H, 1.60. IR (KBr) 2920 w, 1546 s, 1393 s, 1225 m, 1141 m, 952 s. (Nujol) 365 sh, 350 m$_{\mu EFF} = 1.80$ M.B.

Bis-(N, N-diethyldithiocarbamato)copper(III) dichloro(N, N-diethyldithiocarbamato)cuprate(II), $[Et_2dtc)_2Cu]^+ [(Et_2dtc)CuCl_2]^-$

The procedure employed for the Me derivative was repeated using 4 mmol CuCl in 15 mL CH_3CN and 3 mmol Et_4tds in 10 mL of the same solvent. The ligand was added to the stirred solution of the metal cooled in an ice-salt bath. 25 mL of Et_2O was added and the dark solution was left in the cooling bath for two.

The solid produced was gravity filtered, washed with ether and dried in air. $C_{15}H_{30}N_3S_6Cu_2Cl_2$: lustrous black microcrystalline solid, mp: at 135° forms large crystals which in turn melt at 160°. Anal. calcd.(%): Cu, 19.77; Cl, 11.03; C, 28.02; H, 4.71. Found: Cu, 20.02; Cl, 11.09; C, 27.96; H, 4.46. IR(KBr): 2979w, 2930w, 2870w, 1546vs, 1518s, 1442s, 1295s, 1210m, 1130m, 1080m, 981w, 854m. (Nujol): 395s, 360s. μ_{EFF}: 1.83 MB. Attempts at recrystallization of the material from CH_3CN and Et_2O produced highly crystalline Cu(Et_2dtc), characterized by melting point and IR spectra.

Bis-(N, N-diethyldithiocarbamato)copper(III) dibromo(N, N-diethyldithiocarbamato)cuprate(II), $(Et_2dtc)_2Cu^+(Et_2dtc)CuBr_2^-$

0.89 g (3.0 mmol) Et4tds in 10 mL acetonitrile was cooled in an ice-salt bath. 0.57 g (4.0 mmol) CuBr in 20 mL of the same solvent was added rapidly, followed by 50 mL ether. After 30 min the solid mass was gravity filtered, washed with fresh ether and air dried. $C_{15}H_{20}N_3S_6Cu_2Cl_2$: Brown-red microcrystalline solid, mp: 112°. Anal. calcd.(%): Cu. 17.37; Br, 21.84; C, 24.62; H, 4.14. Found: Cu, 17.55, Br, 21.99; C, 24.82; H, 4.38. IR(KBr): 2986w, 2930w, 2870w, 1537vs, 1516s, 1449s, 1288s, 1155m, 1073m, 980w, 861m, (Nujol): 390s, 355s. μ_{EFF}: 1.80 MB.

Chlorobis(N, N-dimethylthiocarbamoyl)sulfidocopper(I). [$(Me_4tms)CuCl$]

Ph3P (0.79 g, 3.0 mmol) in CH_3CN (40 mL) was added to a solution of Me_4tds (0.72 g, 3.0 mmol) in the same solvent (40 mL). The slightly off-white solution thus obtained was cooled in ice and CuCl (0.297 g, 3.0 mL) in 15 mL CH_3CN was added dropwise with stirring. After the addition was completed, the red solution was allowed to stand for 30 min in ice and then filtered to separate a black noncrystalline solid which was thoroughly washed with CH_3CN. Yield: 0.40 g, m.p. 198–205°, IR (KBr) 2934 w, 1550 s, 1520 sh, 1525 m, 1400 s, 1242 m, 1144 s, 980 s. (Nujol) 365 m, 355 sh. The red solution was left in a freezer overnight to yield large yellow needles which were separated by decanting the solvent and washing with ether. These needles were identified as Ph_3PS. Yield 0.35 g. *Triphenylphosphine sulfide*, m.p. 162–165°, IR (Nujol) 3059 vw, 1477 m, 1433 s, 1388 w, 1309 w, 1102 s, 991 w, 710 vs.

After separating triphenylphosphine sulfide, the mother solution was treated with 20 mL Et_2O and returned to the freezer. After 12 h, there was a crop of red highly crystalline needles. Yield: 0.38 g. $C_6H_{12}N_2S_3CuCl$: Red microcrystalline solid, m.p.: blackens to 123°, melts at 135°. 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): 2930 w, 1522 s, 1380 s, 1230 m, 1150 m, 1050 w, 980 m, 945 m, 865 w. (Nujol) 344 s, 310 m, 280 w, 247 m. 1H-NMR ($CDCl_3$): 3.57 (s, 4.5), 3.51 (s, 1.5), 3.48 (s, 1.5), 3.43 (s, 4.5). μ_{EFF} = 0.02 M.B. Molar conductivity 30–35 Ohm^{-1} cm^2 mol^{-1} (10^{-3}–10^{-4} M).

***Bromobis(N, N-dimethylthiocarbamoyl)sulfido copper (I).** [(Me_4tms)CuBr]*

The preparative procedure was similar to the one described for [(Me_4tms)CuCl], using PPh3 (1.31 g, 5 mmol), Me4tms (1.20 g, 5 mmol) and CuBr (0.717 g, 5.00 mmol). After allowing the reaction mixture to stand in ice for 30 min the dark precipitate was filtered, washed with CH_3CN and dried to yield 0.50 g of black-brown non crystalline powder. IR (KBr) 2920 w, 1574 s, 1525 s, 1386 s, 1243 m, 1155 s, 980 m. (Nujol) 390 m, 350 m. The nature of this material is addressed in the Results and Discussion section.

The mother solution was left in a freezer. After 10 h, needles of (Me_4tms)CuBr were obtained. The solvent was decanted and the crystalline material was washed with ether, which was added to the mother solvent. Further cooling raised the total yield to 0.58 g. No attempt was made to isolate Ph_3PS in this experiment. $C_6H_{12}N_2S_3CuBr$: Red, needle-shaped microcrystalline solid, m.p. 174–176° (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) 2924 w, 1513 s, 1378 s, 1225 w, 1139 m, 1046 w, 984 w, 940 m, 864 w. (Nujol): 345 m, 324 m, 193 s, 161 sh. ^{1}H-NMR ($CDCl_3$): 3.59 (s, 6), 3.41 (s, 6). μ_{EFF} = 0.00 M.B. Molar conductivity: 28–37 Ohm^{-1} cm^2 mol^{-1} (10^{-3}–10^{-4} M). Mol. wt: 318–320. (Association: 0.91, 10^{-3}–10^{-4} m).

***Iodobis(N, N-dimethylthiocarbamoyl)sulfidocopper(I).** [(Me_4tms)CuI].*

In a manner similar to the one just described, Ph_1P (1.30 g, 5 mmol) Me_4tms (1.20 g, 5 mmol) and CuI (0.45 g, 5 mmol) were reacted in a total of 100 mL CH_3CN. The dark brown solid precipitated after 0.5 h was filtered, washed with CH_3CN (20 mL) and air dried. Yield 0.38 g. IR (KBr): 1571 sh, 1521 vs. (Nujol) 400 m, 355 m.

RESULTS AND DISCUSSION

Thiuram Disulfides and Cuprous Halides

A characteristic reaction of tetraalkylthiuram disulfides is the formation of metal dithiocarbamates, upon interaction with a metal-bearing species. Examples are abundant in the literature[1–7] and we have recently reviewed the topic.[3–6] The transformation of thiuram disulfide to dithiocarbamate is unarguably a reduction process. However, examination of the final product does not always reveal attendant oxidation of the metal. Again, the literature offers many examples of this.[1–7]

In the present examples, reaction of cuprous halides CuX (X=Cl, Br) with tetraalkylthiuram disulfides R_4tds (R=Me, Et) leads to products of composition $Cu_2(dtc)_3X_2$, which display magnetic susceptibilities corresponding to one unpaired electron (Table I). This observation is consistent with the existence of a single d^9 Cu(II) unit. Therefore the stoichiometry found must include either a d^{10} Cu(I) or a spin-paired d^8 Cu(III). The IR and ESCA data (discussed later) support the formulation of these species as $[Cu(III)(dtc)_2][Cu(II)(dtc)X_2]$. The overall stoichiometry of the reaction is postulated as:

$$4CuX + 3(R_2dtc)_2 \rightarrow 2[Cu(R_2dtc)_2]^+ [Cu(R_2dtc)x2]^-$$

Infrared and ESCA Results

The compounds described so far are either insoluble solids, or else they do not present enough solution stability to attempt purification or further characterization in solution. Therefore all measurements available have been made on the raw solids, straight from the reaction mixtures.

Table I shows relevant infrared bands for the compounds synthesized. Analysis of the features shows a pattern already established in previous publications.[3–6]

The values of frequency for the thiureide band at *ca.* 1570 cm^{-1} in the Me series, and close to 1540 cm^{-1} for the Et compounds, are attributed to formulations where the CS_2 group donates electron density to metals in high oxidation states. For instance, oxidation of $Cu(Et_2dtc)_2$ to the cation $Cu(Et_2dtc)_2^+$ causes a shift from 1490 to approximately 1540 cm^{-1}. A similar effect is noted in the Me series. From the values in Table 1, a shift of the M-S stretch from *ca.* 350 cm^{-1} in Cu(II) dithiocarbamates to values close to 400 cm^{-1} in the $Cudtc_2^+$ cations is apparent. This is consistent with strengthening of the bond due to removal of electron density from an antibonding orbital composed mainly of metal and sulfur character.[8]

In the species formulated as $[CuX_2(Me_2dtc)]^-$ (X=Cl, Br), bonding of Cu(II) to electronegative halogens shifts electron density away from the metal and produces stronger Cu—S bonding than in $Cu(Me_2dtc)_2$, for example. This results in ν_{C-N} and ν_{M-S} values which are larger than those found in $Cu(Me_2dtc)_2$, but smaller than in $[Cu(Me_2dtc_2)]^+$. The effect is also apparent from the values in Table I.

Table II collects all the information related to ESCA spectroscopy. Cu(II) states are generally recognized by a main peak at binding energy (BE) of 933–934 eV, in

TABLE I Characteristic IR absorptions and magnetic properties of some mixed valence copper-dithiocarbamato compounds

	$\nu C{=}N^{\dagger}$		$\nu M{-}S^{\dagger}$		$\mu_{EFF}{}^{*}$, *M.B.*
$Cu(Me_2dtc)_2$		1550	350		1.80
$Cu_2(Me_2dtc)_3Cl_2$	1571	1550	398	376	1.83
$Cu(Me_2dtc)Cl$		1551		365	1.81
$Cu_2(Me_2dtc)_3Br_2$	1567	1545	390	350	1.80
$Cu(Me_2dtc)_2(CuBr)_3$		1546		350	1.80
$Cu(Me_2dtc)_2{}^{+}Cu_2Br_3{}^{-}$	1574		395		0.00
$Cu(Et_2dtc)_2$		1501		355	1.82
$Cu_2(Et_2dtc)_3Cl_2$	1546	1518	395	360	1.83
$Cu_2(Et_2dtc)_3Br_2$	1537	1516	390	355	1.80

*Per formula unit.

†All frequencies in cm^{-1}. See Experimental section for band intensities.

TABLE II Characteristic binding energies for representative mixed valence copperdimethyldithiocarbamato complexes

Assignment	*Cu(I)*	*Cu(II)*	*Cu(III)*
$Cudtc_2{}^{+}CudtcCl_2{}^{-}$		933.4	
		942–945	935.2
$Cudtc_2{}^{+}Cu_2Br_3{}^{-}$	931.5		934.4
$(Cudtc)_2(CuBr)_3$		933	
CudtcCl		932.7	
		942–945	

addition to significantly intense shake-up satellites at 8–10 eV higher than the main peak.[9] Cu(I) and Cu(O) states have BE values around 932.5 eV, while Cu(III) states are not common, but are expected to have higher BE values than Cu(II). The values available for $Cu_2(R_2dtc)_3X_2$ samples (X = Cl, Br; R = Me, Et) show features which are fully consistent with their formulation as Cu(II)-Cu(III) species, and strongly support our interpretation of the synthetic experiments.

Decomposition Chemistry, Alternative Syntheses of some Species

Preparative conditions which include long reaction times or reflux of the mixtures result in reduction of the Cu(III) fragment and isolation of the species Cu(dtc)Cl or $Cu(dtc)_2(CuBr)_3$ in the Me series. The complex $Cu(Me_2dtc)Cl$ displays magnetic susceptibility and ESCA features which support its formulation as a Cu(II) complex. The position of the thiureide band at 1551 cm^{-1} is coincident with the position assigned to the absorption of the $Cu(dtc)_2Cl_2^-$ anion and supports the assignment of the structure as a bridged dimer $(dtc)CuCl_2Cu(dtc)$. This is indeed the structure revealed by X-ray analysis of the Et derivative, made from $Cu(dtc)_2$ and CuC_{12}.[10] In our hands, this method failed to give an analytically pure sample of the Me derivative. A balance of solvation and lattice effects must be involved.

Isolation of Me_4tds from decomposition experiments of $Cu_2(Me_2dtc)_3Cl_2$ in EtOH (see Experimental) lends credibility to the following scheme for reduction.

$$[Cu(Me_2dtc)_2]^+ [CuCl_2(Me_2dtc)]^- \rightarrow Cu_2(Me_2dtc)_2Cl_2 + 1/2(Me_2dtc)_2$$

A similar reduction must be responsible for the formulation of $Cu(Me_2dtc)_2(CuBr)_3$ Well characterized materials of overall stoichiometry $Cu(R_2dtc)_2(CuBr)n$ (n = 4, 6; R = piperidyl) have been prepared from $Cu(dtc)_2$ and copper(II) bromide. The X-ray analysis of the solids reveals individual $Cu(dtc)_2$ molecules linked *via* bridging sulfur atoms to polymeric CuBr chains.[11] The bridging nature of the S atoms is consistent with the shift of the C—N stretch from 1500 cm^{-1} in $Cu(dtc)_2$, to 1520 cm^{-1} in the polymer, indicating delocalization of electron density from nitrogen to sulfur. The same effect is noted in the values reported in Table I. As pointed out earlier, further characterization is hindered by lack of solubility of the materials.

A different solid phase ($Cu_3(dtc)2Br_3$) was isolated from the system $Me_4tds/CuBr/CH_2Cl_2$. The stoichiometry has not been reported previously. The diamagnetic nature of the sample and the presence of IR bands at 1570 and 395 cm^{-1} suggest the presence of the Cu(III) cation $Cu(dtc)_2^+$. The identity of the anion is unclear. The $Cu2Br_3-$ stoichiometry has no precedent in halocuprate(I) chemistry,[12] but the dimeric cluster $Cu_4Br_6^{2-}$ has been synthesized, featuring four copper(l) halide triangles linked through common vertices.[13] Although vibrational spectroscopic studies have been published for the iodo derivative,[14] no comparative data exist for the analog of the Br compound reported here.

In summary, the reactions of thiuram disulfides and Cu(l) halides are characterized by oxidizing properties of the disulfide and subsequent redistribution of the dithiocarbamate and halide ligands. Dramatic deviations from this pattern occur when a putative sulfur scavenger is present, as is clear from the following discussion.

Sulfur Abstraction by Triphenylphosphine

Sulfur abstraction by aqueous KCN is an established method for the preparation of monosulfides from the corresponding disulfides.[7a] Triphenylphosphine has been claimed[15] to effect the same transformation. In our experience the latter procedure fails to yield the monosulfide. Other authors have made similar observations.[16] Addition of cuprous halides to solutions containing the disulfide and triphenylphosphine generate deep red colors. From these solutions, the copper-monosulfide-halide complex may be isolated in good yield.

The position of the equilibrium above must lie well to the left in the presence of triphenylphosphine, but it is shifted by formation of an adduct with copper(I)

halide. These complexes were first reported in connection with the reduction of copper(II) halides with thiuram monosulfides.[6]

The physical and spectroscopic properties of all compounds reported in this section, have been published previously.[6] From the available evidence, there is no doubt that the materials isolated from the reaction of thiuram disulfides and copper(I) halides in the presence of triphenylphosphine (this work) are identical to the compounds obtained from thiuram monosulfides and copper(I) or copper(II) halides.

Now the nature of the dark solid products obtained from the reaction of Cu(I) halides/triphenylphosphine/disulfide may be addressed. When Ph_3P is added to solutions of Me_4tds, the system consists of equilibrium mixtures of monosulfide and disulfide. Addition of cuprous halides causes complexation of the monosulfide to give the red compounds described, which may then degrade to $Cu(Me_2dtc)_2$. Simultaneously the cuprous halide may insert oxidatively into the S—S bond of the disulfide present to yield the mixed valence compounds. The product distribution is governed by the relative rates at which both processes occur, as much as by the position of the equilibrium above.

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