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THE REACTION OF COPPER(II) HALIDES AND TETRAALKYLTHIURAM MONOSULPHIDES

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Abstract—Tetraalkylthiuram monosulphides reacted with copper(II) chloride and bromide to yield 3,5-bis(*N*,*N*-dialkylimonium)-1,2,4-trithiolane trihalocuprate(I) and a neutral halogenobis-(*N*,*N*-dialkylthiocarbamoyl)sulphidocopper(I). The products were characterized by elemental analyses, IR spectroscopy and magnetic susceptibility measurements.

Bis(*N*,*N*-dialkylthiocarbamoyl)sulphides, also known as tetraalkylthiuram sulphides, R_4tms,† are potential bidentate ligands to metal ions, and although they have been less extensively used than the related disulphides in rubber vulcanization, agriculture and medicine, there is still an advantage in comparing the chemistry of both classes of compounds.

Both ligands form simple coordination compounds. Examples of these in the case of the monosulphide are the cationic $[CrR_4tmsX_2]^{+}$[1] and the neutral MR_4tmsX_2 (M = Zn,[2] Hg,[3] Ni and Co[4]) and MR_4tmsX (M = Cu and Ag[5]).

Metal-containing fragments also insert oxidatively into the C—S linkage of a monosulphide to yield mixed dithiocarbamato–thiocarboxamido complexes. Examples of metal moieties that undergo such transformation are $MCl(PPh_3)_3$ (M = Rh and Pt[6]) and $Mo(CO)_3(CH_3CN)_3$.[7]

An ubiquitous reaction of thiuram disulphides and metal ions involves scission of the S—S bond and formation of metal dithiocarbamates. This transformation has become a standard preparative route to metal dithiocarbamates. We have recently reviewed this topic.[8] In contrast, monosulphides offer only one example of dithiocarbamate formation. Reaction of Me_4tms and $CuCl_2$ in boiling ethanol yields $Cu(Me_2dtc)_2$.[9]

Novel rection products have now been isolated from reactions similar to the one just described. These products are formed through the two-electron oxidation of the ligand, with reduction of the Cu^{II} salt and stabilization of the Cu^{I} species as trihalocuprate(I) anion. This behaviour parallels the chemistry described for the disulphides.[8]

EXPERIMENTAL

General

Et_4tms and iPr_4tms were prepared by standard literature procedures.[10] Carrying out the desul-

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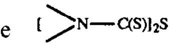
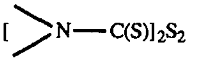
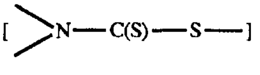
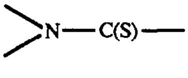
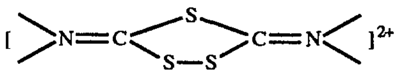
†Except where relevant to the chemistry under discussion, tetraalkylthiuram monosulphides and dithiocarbamates are abbreviated as tms or dtc, with no specification of the alkyl substituents. Abbreviations used:

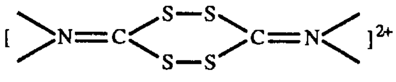
tms, thiuram monosulphide


tds, thiuram disulphide


dtc, dithiocarbamate


tca, thiocarboxamide


$[bitt\text{-}3]^{2+}$, bis-(dialkylimonium)-trithiolane


$[bitt\text{-}4]^{2+}$, bis-(dialkylimonium)tetrathiolane.


phurization of the corresponding disulphide with alcoholic KCN (**CAUTION**: acid hydrolysis of potassium cyanide generates HCN, an exceedingly poisonous gas). The methyl derivative (Fluka) was recrystallized from EtOH. $CuCl_2 \cdot 2H_2O$ (Merck) was oven dehydrated at 115°C and kept under nitrogen. Solvents (THF, acetone, CH_3CN, EtOH) were dried with $CaCl_2$ which had been activated at 350°C and then filtered and distilled under nitrogen. All synthetic manipulations involving the copper complex were carried out under dry nitrogen, using Schlenk or cannulation techniques.[11] Anhydrous $CuBr_2$ was prepared from CuBr and an excess of bromine under nitrogen. The excess Br_2 was allowed to evolve and the resulting microcrystalline solid was pumped dry to give $CuBr_2$ in theoretical yield.

Spectroscopy

IR spectra were obtained as KBr pellets in the range 4000–500 cm^{-1} using a Nicolet Magna 550 spectrometer and as Nujol mulls over polyethylene film below 500 cm^{-1}, using a Perkin–Elmer FTIR 2000 spectrometer.

Analyses

Carbon and hydrogen analyses were performed by standard combustion techniques. Other elements were determined titrimetrically, by iodometry (copper) or Volhard (chlorine) methods.

Preparation of the complexes

3,5 - *Bis*(N,N - *dialkylimonium*) - 1,2,4 - *trithiolane tribromocuprate*(I), $[R_4bitt\text{-}3]^{2+}$ $CuBr_3^{2-}$ (R = Me, Et, iPr). A solution of 0.67 g (3 mmol) of $CuBr_2$ in 60 cm^3 EtOH was cooled to −10°C (ice-salt bath) and a solution of the monosulphide (5 mmol) in EtOH (500 cm^3 for the Me, 100 for Et, 60 for iPr) was added dropwise with stirring. The material precipitated (red-orange for Me, orange for Et, brown for iPr) was filtered, washed with 20 cm^3 fresh EtOH, pumped dry and ground to a fine powder, which was extracted with three portions of CH_3CN (50 cm^3 each for Me, 20 cm^3 each for Et) or acetone (five portions of 20 cm^3 for iPr). The solutions contain the thiuram–copper(I) complex (Me, Et) or its decomposition products (iPr). The residual solid was filtered and pumped dry. Attempts to purify the more soluble (Et, iPr) derivatives by crystallization resulted in decomposition. Experiments performed with Me_4tms and $CuCl_2$ resulted in a green solid residue, not further investigated. Yields varied from near-quantitative (Me) to 0.08 g (iPr).

$[Me_4bitt\text{-}3]^{2+}CuBr_3^{2-}$. Orange amorphous powder, m.p. 192°C (d). Found: Cu, 12.4; Br, 46.5; C, 14.1; H, 2.3. Calc. for $C_6H_{12}N_2S_3Br_3Cu$: Cu, 12.4; Br, 46.8; C, 14.1; H, 2.4%. IR (KBr) cm^{-1}: 3030w, 1587s, 1408s, 1266s, 1070s, 1036s, 885m, 870m, 570s, 510m.

$[Et_4bitt\text{-}3]^{2+}CuBr_3^{2-}$. Orange amorphous powder, m.p. 181° (d). Found: Cu, 11.3; Br, 42.5; C, 21.1; H, 3.5. Calc. for $C_{10}H_{20}N_2S_3Br_3Cu$: Cu, 11.2; Br, 42.2; C, 21.1; H, 3.6%. IR (KBr) cm^{-1}: 2973m, 2875m, 1552s, 1479s, 1446s, 1387m, 1341m, 1275m, 1203s, 1078m, 841m, 775m, 565m, 507m.

$[iPr_4bitt\text{-}3]^{2+}CuBr_3^{2-}$. Light brown, café-au-lait powder, m.p. 155°C (d). Found: Cu, 10.3; Br, 38.5; C, 26.9; H, 4.4. Calc. for $C_{14}H_{28}N_2S_3Br_3Cu$: Cu, 10.2; Br, 38.43; C, 26.9; H, 4.5%. IR (KBr) cm^{-1}: 2968w, 2926m, 2849w, 1621s, 1460m, 1383m, 1320m, 1185w, 1137s, 1046w, 625w, 561w.

Halogeno - bis(N,N - *dialkylthiocarbomoyl*)*sulphido copper*(I), CuR_4tms X (X = Br, R = Me, Et; also X = Cl, R = Me). The acetonitrile extracts from the previous experiment 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 filtered and recrystallized in the same fashion.

$CuMe_4tmsBr$. Bright red needles, m.p. 174–176°C (d). Found: Cu, 18.1; Br, 22.6; C, 20.4; H, 3.4. Calc. for $C_6H_{12}N_2S_3BrCu$: Cu, 18.1; Br, 22.7; C, 20.5; H, 3.4%. IR (KBr) cm^{-1}: 2941w, 1524s, 1383s, 1250s, 1230s, 1143s, 1050m, 987s, 943s, 867m, 570m, 445m.

$CuEt_4tms$ Br. Orange plates, m.p. 115–117°C (d). Found: Cu, 15.7; Br, 19.2; C, 29.3; H, 4.9. Calc. for $C_{10}H_{20}N_2S_3BrCu$: Cu, 15.6; Br, 19.6; C, 29.4; H, 4.9. IR (KBr) cm^{-1}: 2980m, 2921m, 2862w, 1499s, 1440s, 1348s, 1267s, 1190s, 1143m, 1071s, 982m, 959m, 900s, 833s, 781w, 568w, 550w.

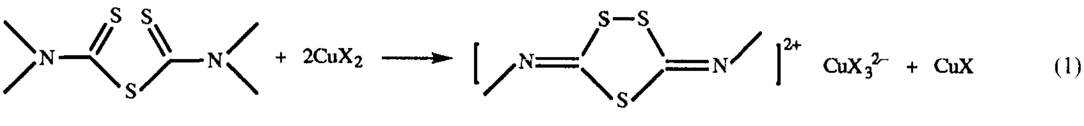
$CuMe_4tmsCl$. Red orange plates, m.p. 135–137°C (d). Found: Cu, 20.7; Cl, 11.5; C, 23.3; H, 4.0. Calc. for $C_6H_{12}N_2S_3ClCu$: Cu, 20.7; Cl, 11.5; C, 23.4; H, 3.9%. IR (KBr) cm^{-1}: 2941w, 1531s, 1389s, 1245s, 1227s, 1143s, 1049m, 985s, 943s, 867m, 527m.

$CuiPr_4tmsBr$. The preparative method outlined above failed to yield the iPr derivative. However, this was obtained from CuBr (from aqueous $CuSO_4$, 2 N H_2SO_4 and Na_2SO_3 in the presence of KBr) and iPr_4tms, by the method of Willemse and co-workers.[5a] Orange-brown needles, m.p. 148°C (d). Found: Cu, 13.6; Br, 17.3; C, 36.2; H, 6.1. Calc. for $C_{14}H_{28}N_2S_3BrCu$: Cu, 13.7; Br, 17.2; C, 36.2; H, 6.1%. IR (KBr) cm^{-1}: 3011w, 2968m, 2926m, 2858w, 1495s, 1430s, 1371m, 1329s, 1310s, 1187m, 1144s, 1011m, 935w, 890w, 850w, 771w, 583m.

RESULTS AND DISCUSSION

Reaction between copper(II) *halides* CuX_2 *and tetraalkylthiuram monosulphides*

The reaction generates 3,5-bis(*N*,*N*-dialkylimonium)-1,2,4-trithiolane which, for the case X = Br, can be isolated as the corresponding tribromocuprate(I):



The Cu^{I} halide is stabilized as a thiuram–copper(I) complex, CuR$_4$tmsX. All three alkyl derivatives of the organic cation, Me, Et and iPr, can be prepared in this manner. As the alkyl substituent size increases, so does the solubility of the tribromocuprate(I) in the reaction solvent. The solution stability of the newly formed species is limited, which results in lower yields of isolable tribromocuprate(I).

In some cases the complexes CuR$_4$tmsX can be isolated from the reaction mixture. The procedure is tedious and these compounds are more easily accessible through the direct preparative route of Willemse and co-workers.[5a] When $CuCl_2$ is used as the oxidizing agent, no tetraalkylimonium trithiolane is isolated. The course of the reaction is therefore inferred from the isolation of the CuR$_4$tmsX species. The rapid decomposition of the (presumed) Cu(iPr)tmsBr derivative prevents its isolation, and its formation is inferred from the isolation of [iPr$_4$bitt-3]$^{2+}$CuBr$_3^{2-}$.

All compounds in the [R$_4$bitt-3]$^{2+}$ series are orange, diamagnetic non-crystalline solids. This is consistent with their formulation as Cu^{I} species. Limited solubility of the Me derivative and lack of solution stability of the Et and iPr derivatives in acetone or acetonitrile have so far prevented NMR characterization and conductivity measurements, while at the same time frustrating attempts at crystal growth.

IR spectroscopy

Table 1 summarizes the characteristic IR bands of the compounds prepared. In general, the analysis of these features follows trends similar to those noted for the disulphides.[8]

Thiuram sulphides display a strong IR absorption at *ca* 1500 cm^{-1}. This band corresponds to a stretching of the R$_2$N—C bond and its abnormally high position is related to an important contribution of the polar $^{-}S_2C{=}N^{+}$ form to the overall structure of the ligand.[12] Complexation of thiuram sulphides to metal ions shifts electron density away from the sulphur atoms and enhances the importance of the polar form to the total resonance hybrid, thus shifting the corresponding absorption to higher wavenumbers.[1–5] This effect is noted in the values reported in Table 1. Complexation of thiuram sulphides to Cu^{I} produces a shift of some 5–25 cm^{-1} in the position of the band. The C—N stretch is also sensitive to the oxidation state of the attached metal. In a series of copper dithiocarbamates,[12] Cu^{III} compounds show the IR band some 50–80 cm^{-1} higher than the corresponding Cu^{II} compounds. Thus, the high C—N stretching frequencies observed in the series of R$_4$bitt^{2+} compounds reported in Table 1 would also be consistent with structures containing Cu^{III}–dithiocarbamate units.

The latter alternative is ruled out on inspection of the 900–1000 cm^{-1} region of the spectra. Thiuram sulphides display two bands in this region, assigned to C=S stretching modes. The intensity of these bands is greatly enhanced in dithiocarbamate compounds.[13] The corresponding stretches for the C—S bands are located near 850 cm^{-1}. Both spectral features are apparent in the IR of the CuR$_4$tmsX complexes. However, in those compounds formulated as R$_4$bitt^{2+}, the C=S stretch is conspicuously absent. This is in full agreement with the structure proposed.

As noted elsewhere,[8] the five-membered cyclic organic cation 3,5-bis(*N*,*N*-dialkylimonium)-1,2,4-trithiolane [R$_4$bitt-3]$^{2+}$ has been reported in oxidation reactions of metal dithiocarbamates. Thus, the reaction of Fe(Et$_2$dtc)$_3$ or Fe(Et$_2$dtc)$_2$Cl with halogens yields [R$_4$bitt-3]$^{2+}$2FeCl$_4^-$, also accessible through oxidation–desulphurization of Et$_4$tds with anhydrous $FeCl_3$.[14] The same report gives details on the preparation of [nBu$_4$bitt-3]$^{2+}$Cu$_2$X$_6^{2-}$ (X = Cl, Br) from halogens and the cuprous dithiocarbamate. An oxidation–desulphurization reac-

Table 1. Selected IR frequencies for the compounds synthesized

	ν(C—N)	ν(C—S)	ν(C—S)
Me_4tms	1523	961	863
Et_4tms	1500	1000, 970	919
iPr_4tms	1479, 1446	959	890, 850
$CuMe_4tms$ Br	1524	987, 943	867
$CuEt_4tms$ Br	1508	990, 970	900, 830
$CuiPr_4tms$ Br	1495, 1430	1011, 935	890, 850
$CuMe_4tms$ Cl	1531	985, 943	867
$[Me_4bitt]^{2+}CuBr_3^{2-}$	1587		877, 866
$[Et_4bitt]^{2+}CuBr_3^{2-}$	1552		841
$[iPrbitt]^{2+}CuBr_3^{2-}$	1621		850

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

tion also yields $[Et_4bitt\text{-}3]^{2+}Hg_2I_6^{2-}$ from $HgEt_4tdsI_2$ and iodine. This affords the only known crystal structure of R_4bitt-3 compounds.[15] Very relevant to this series of reports is the recent observation[16] in the mass spectrum of solutions of $(Et_2dtc)_3Fe$ oxidized with NO^+, where the highest mass is assigned to the molecular ion of $(Fedtc_3)_2[Et_4bitt\text{-}3]^{2+}$, of unknown structure.

Far-IR characterization

Table 2 shows the low frequency region of the IR spectrum for the compounds reported here. Copper dithiocarbamates and thiurams are characterized by medium intensity bands in the 300–400 cm^{-1} region ascribed to Cu—S stretching. 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} [12] and Cu^{I}—S vibrations span the region 310–365 cm^{-1},[5b] while Cu^{II}—S stretches have been assigned at *ca* 350 cm^{-1} in a series of Cu^{II}–dithiocarbamates.[9] The series of $CuMe_4tmsX$ compounds prepared in the course of this work show bands consistent with their formulation as Cu^{I}–tms compounds. The spectral features in this series are explained on the basis of a dimeric, halogen-bridged structure of D_{2h} symmetry, in which two Cu—S and two Cu—X IR-active modes are apparent. The low frequencies found for the Cu—X vibrations denote the bridging nature of the halogens.[17] Dramatic changes in coordination must occur in the Et derivative, since a third feature appears in the Cu—S region. More importantly, the absorptions which could be assigned as Cu—Br stretches have moved considerably, indicating a higher bond order. Thus, the site symmetry in the solid must be much lower than D_{2h}, and perhaps involves a loose polymer. In the absence of additional data, no more speculation is warranted.

The solid state structure of these compounds formulated as $[R_4bitt]^{2+}CuBr_3^{2-}$ is more complicated than such simple formulation would imply. The featureless spectra between 300 and 400 cm^{-1} negate coordinative interactions between the metal and the ligand, and supports the correctness of the structural assignment as ionic. However, the nature of the anion is unclear. The far-IR is inconsistent with $CuBr_3^{2-}$, for which a strong 185 cm^{-1} absorp-

Table 2. IR frequencies below 500 cm^{-1} for the compounds synthesized

	Cu—S	Cu—X
$CuMe_4tms$ Br	345w, 300s	193s, 161sh
$CuMe_4$ tms Cl	347s, 310m	284w, 224m
$CuEt_4tms$ Br	343s, 329s, 311s	255s, 232s, 219s
$[Me_4bitt]^{2+}CuBr_3^{2-}$		211m, 179m, 158w, 103vs
$[Et_4bitt]^{2+}CuBr_3^{2-}$		203m, 174m, 151w, 100vs
$[iPr_4bitt]^{2+}CuBr_3^{2-}$		202m, 170m, 161w, 100vs

All figures in cm^{-1}.

tion would be expected.[18] The possibility of $CuBr_2^-$ plus Br^- must also be considered and then rejected on the basis of the absence of a feature at 313 cm^{-1}, as present in the spectra of $[Ph_3MeP][CuBr_2]Br$.[18] Other structural possibilities of overall stoichiometry $Cu^IBr_3^{2-}$ involve a polymeric chain of tetrahedra sharing one corner,[19] as found in the structures of materials of composition M_2CuX_3 (M = alkali metal). A polymeric ionic form would be consistent with the lack of solubility of the materials.

The behaviour of monosulphides and disulphides towards copper(II) *halides*

Monosulphides react with copper(II) halides according to reaction (1). This behaviour is similar to that described recently[8] for the disulphides. Both mono- and disulphides undergo a two-electron oxidation of the ligand to form large organic cations which act as counterions of cuprous haloanions. Some differences must be noted.

(a) The oxidation of the disulphides by Cu^{II} salts is the result of an equilibrium which may be displaced by adequate manipulation of the solubilities of the species involved; oxidation of the monosulphides proceeds irreversibly in THF. Spectroscopy and reaction chemistry fail to give any evidence for the presence of unreacted species in mixtures of CuX_2 (X = Cl, Br) and R_4tms (R = Me, Et, iPr). It seems that subtle changes in the packing of the solid lattice on going from a five-membered to a six-membered ring in the cation are enough to influence the solubility and therefore the position of the oxidation–reduction equilibrium.

(b) All Cu^I compounds reported here undergo eventual decomposition to dithiocarbamate-containing compounds when kept at room temperature. This decomposition is essentially instantaneous in boiling EtOH and the rate of decomposition is more pronounced for $CuCl_2$ than it is for $CuBr_2$. Thus, previous results[9] and the present ones are in agreement.

In the $[R_4\text{bitt-4}]^{2+}$ series,[8] all compounds isolated contained chlorine. No Br^--containing haloanions were isolated from R_4tds and $CuBr_2$. We are unable to explain this difference at the present time.

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