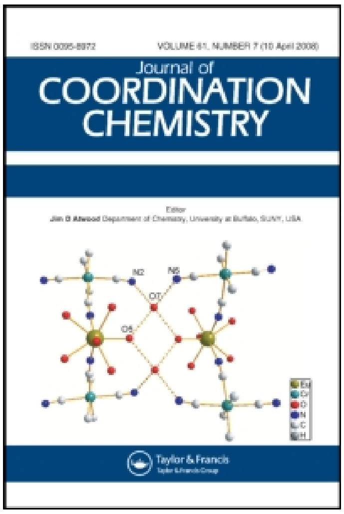

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3,6-BIS (N,N-DIALKYLIMONIUM)-1,2,4,5-TETRATHIOLANES. COPPER(I) COMPOUNDS WITH AN UNUSUAL ORGANIC CATION

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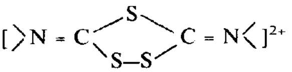
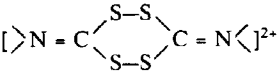
The first example of a compound containing the 3,6-bis(N,N-dialkylimonium)-1,2,4,5-tetrathiolane cations, $(R_4\text{bitt-4})^{2+}$ is reported. In contrast to previous examples, no desulfurization is apparent, perhaps due to the mild reaction conditions. Other structures may be ruled out on the basis of the lack of features in the far infrared spectra and also considering that the ^{1}H-NMR spectra of the Et and iPr derivatives show only one alkyl set of resonances.

KEYWORDS: tetrathiolanes, copper (I), tetroalkylthiurom, disulfides

ABBREVIATIONS: tms: thiuram monosulfide [>N-CS)]$_2$S
tds: thiuram disulfide [>N-C(S)]$_2$S$_2$
dtc: dithiocarbamate [>N-C(S)-S-]
tca: thiocarboxamide >N-C(S)-
[bitt-3]$^{2+}$: bis-(dialkylimonium)-trithiolane 
[bitt-4]$^{2+}$: bis-(dialkylimonium)-tetrathiolane 

INTRODUCTION

Bis-(N,N-dialkylthiocarbamoyl) disulfides, commonly known as tetraalkylthiuram disulfides, R$_4$tds(**) have been employed as vulcanization accelerators and fungicides for over a century.[1] The reactivities of these molecules toward transition and main group metals have been explored to some extent, and a pattern has emerged which can be summarized as follows: (1) The ligand may preserve its molecular integrity and form simple neutral (Hg(II)[2] and Co(II)[3]) or cationic (Cr(III)[4]) coordination compounds. (2) The ligand may oxidatively add on the metal-bearing residue, and form metal dithiocarbamates:

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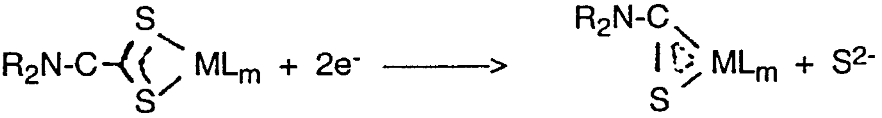
(**) Except where relevant to the chemistry under discussion, tetraalkylthiuram disulfides and dithiocarbamates are abbreviated tds or dtc, with no specification of the alkyl substituents.

Scheme 1

Several cases may be noted: (1) Electron count and stoichiometry in the final product fit exactly the scheme above. Thus, thiuram disulfides react with Tldtc,[5] copper metal,[6] monovalent coinage metal dithiocarbamates,[7] M(O) (M = Mo and W)[8], Irdtc $(C_8H_{12})_n$ (n = 1,2)[9] and $Re(CO)_5Cl$[10] to give metal species where the number of dithiocarbamate ligands has been increased by an even number, with simultaneous two-electron oxidation of the metal species. (2) Extensive redistribution may occur. Examples include the reactions of thiuram disulfides with $Re(CO)_5Cl$ to yield $[Redtc_4]^+[Re(CO)_3dtcCl]^-$,[10] with $CpTiX_2$ to afford $CpTidtcX_2$ (X = Cl, Br),[11] with $AuBr_2$- to give $Audtc_2Br$,[7b] and with copper bronze to produce Cudtc.[6] (3) Further breakdown of the ligand may also occur, with attendant stabilization of the fragments by coordination to the metal:



Scheme 2

In this manner, the reaction of R_4tds with $Mo(CO)_6$ has been reported[12] to yield $Mo_4(\mu\text{-}S)_4dtc_6$. Also, $W(CO)_3(CH_3CN)_3$ and Et_4tds have produced $W_4(\mu\text{-}S)_2dtc_4$,[13] while the products of the reaction of $HB(Me_2pz)_3W(CO)_3$ with tds are $HB(Me_2pz)_3W(CO)_2dtc$ and $HB(Me_2pz)_3W^{II}(CO)_2(\mu\text{-}S)W^{IV}dtc_2tca$.[14]

Many of the reactions of thiuram disulfides and metal derivatives do not seem to conform to any of the schemes described above. Some typical examples are as follows:

R_4tds and mercury halides yield $Hgdtc_2$(6a) or IHgdtc.[15] Similar reactions include the preparation of $Mdtc_3^+X^-$ from MX_2dtc_2 (M = Pd, Pt; X = Br, I)(16) and that of $Nidtc_2$ from $NiCl_2$(6a).

A standard feature of these reactions is reductive fragmentation of the disulfide with no apparent oxidation of the metal center. Judging from early experiments,[7a] it would seem that reactions of copper(II) salts and Et_4tds follow the pattern described, that is, reduction of the ligand and preservation of the oxidation number of the metal center.

Novel reaction products which correspond to a two-electron *oxidation* of the ligand, with simultaneous reduction of the copper salt and stabilization of the copper(I) species as a dichlorocuprate(I) anion, have now been isolated. Reactions with ligands bearing different alkyl groups show that this is general behaviour in the systems under study.

EXPERIMENTAL

General

Me_4tds and i-Pr_4tds were prepared by standard literature procedures.[17] The Et derivative (Aldrich) was recrystallyzed from EtOH. $CuCl_2 \times 2H_2O$ (Merck) was oven-dehydrated at 115°C and kept under nitrogen. Solvents were distilled from activated (380°C) $CaCl_2$ (THF, CH_3CN) or from sodium ribbon (hexane). All synthetic manipulations involving the copper complexes were carried out under an atmosphere of dry nitrogen using Schlenck or cannular techniques.[18]

Spectroscopy

Infrared spectra were obtained as KBr pellets in the range 4000–500cm^{-1} using a Nicolet Magna 550 spectrometer and as Nujol mulls over polyethylene film below 500cm^{-1}, using a Perkin Elmer FTIR 2000 spectrometer. ^{1}H-NMR spectra were obtained using a Brücker AC250P spectrometer.

Other measurements

Conductivities at room temperature were measured in acetonitrile, using a Wiss-Techn-Werkstaten bridge and a platinum electrode. Magnetic susceptibilities were measured at room temperature, using a Faraday-type system, with a permanent field and electrobalance.

Analyses

C and H analyses were performed by standard combustion techniques. Other elements were determined titrimetrically, by iodometry (Cu) or Volhard (Cl) methods.

Preparation of the complexes

A standard procedure was followed, exemplified here for the Me derivative: Anhydrous $CuCl_2$ (1.34 g, 10 mmol) was dissolved in THF (80mL). The solution was cooled to ice-salt bath temperature (−10°C) and a solution of Me_4tds (1.20 g, 5 mmol) in hexane (80 mL) was added dropwise with stirring. The brick-red solid produced was filtered immediately from the wine-red solution and dried by vaccum. The solution changed to a brown color within 15 min., and eventually, deposited black, highly crystalline $Cu(Me_2dtc)_2$, characterized by infrared spectroscopy and analyses. The red solid was dissolved in 250 mL of fresh THF, filtered and precipitated immediately by addition of hexanes (100 mL). The purified solid was filtered and dried by vacuum. Yield: 0.45 g. $(C_6H_{12}N_2S_4)^{2+}(CuCl_2)_2$: Dark red solid, m.p. 127°(d). *Anal.* calcd. for $C_6H_{12}N_2S_3Cl_4Cu_2$(%): Cu, 24.58; Cl, 27.73; C,14.19; H, 2.41. Found: Cu, 24.95; Cl, 27.85; C, 14.15; H, 2.36. I.R. (KBr): 2920vw, 1618vs, 1414m, 1249m, 1170m, 1058wm, 960w, 865w. ^{1}H-NMR($CDCl_3$): 3.26 (s,br). μ_{EFF} = 0.00 B.M.

The ethyl derivative was obtained by the method just described. The i-Pr compound was made by mixing THF solutions of $CuCl_2$ and hexane solutions of the ligand.

$(C_{10}H_{20}N_2S_3)^{12+}$ $(CuCl_2^-)_2$

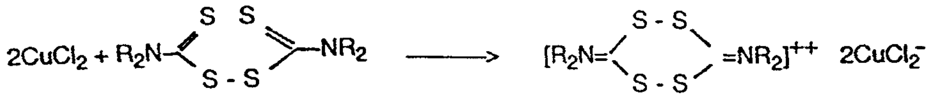
Red microcrystalline solid, m.p. 138°(d). *Anal.* Calcd. for $C_{10}H_{20}N_2S_4Cl_4Cu_2$(%): Cu, 22.47; Cl, 25.08; C, 21.24; H, 3.57. Found: Cu, 22.22, Cl, 24.98; C, 21.20; H, 3.63. I.R. (KBr): 2999m, 2934m, 2875w, 1604s, 1460s, 1289m, 1190m, 1160w, 1090w, 1070w, 1040w, 847m. ^{1}H-NMR($CDCl_3$): 4.16(s,br,2), 1.45(s,br,3). μ_{EFF} = 0.00B.M.

$(C_{14}H_{28}N_2S_3)^{2+}(CuCl_2^-)_2$

Red-orange solid, m.p.: 153° (d): *Anal.* Calcd. for $C_{14}H_{28}N_2S_4Cl_4Cu_2$(%): Cu, 20.45; Cl, 22.81; C, 27.05; H, 4.55. Found: Cu, 20.32; Cl, 22.86; C, 26.98; H, 4.53. I.R. (KBr): 3164w, 2967m, 2901m, 1585vs, 1453m, 1400w, 1380m, 1361s, 1175w, 1144s, 1032w, 830w. ^{1}H-NMR($CDCl_3$): 4.28(s,br,1), 1.32(s,br,6). μ_{EFF} = 0.00 B.M.

RESULTS AND DISCUSSION

Reactions of copper(II) chloride and thiuram disulfides lead to a two-electron oxidation of the ligand, reduction of the metal to copper(I) and stabilization of the latter as a chlorocuprate(I) anion.



Scheme 3

Analyses agree well with the formulation $(R_2NCS_2)_2Cu_2Cl_4$. The materials are diamagnetic red solids. Both observations are consistent with copper(I).

Table 1 lists the characteristic infrared frequencies found in the products, along with those of the starting materials. It is immediately apparent that the spectra of

Table 1 Characteristic infrared frequencies of 3,6-bis(N,N-Dialkylimonium)-1,2,4,5-tetrathiolanes and parent thiuram disulfides.

	C-N	C = S	C-S
[Me_4tds	1500	988	860
[Me_4bitt-4]$_2CuCl_2$	1618		875
Me_4tms$CuBr^{20}$	1517	987,943	867
Et_4tds	1500	971	823
[Et_4bitt-4]2$CuCl_2$	1604		847
iPr_4tds	1481	947	850
[iPr_4bitt-4]2$CuCl_2$	1585		830

All frequencies in cm^{-1}.

the products are distinctly different from those of the parent ligands, either free or coordinated. Three regions of the spectra must be examined: (1) The free ligands are characterized by a strong band at *ca.* 1500 cm^{-1}. This absorption is associated with the stretching of a C-N bond which has a partial double bond character, thus shifting the absorption from the 'normal' C-N region (1250–1350 cm^{-1}) towards the C = N zone (1620–1680 cm^{-1}).[19] Complexation to copper(I) further shifts this band to higher wavenumbers due to electron donation of the C = S bond to the metal, which causes more double bond character for the carbon-nitrogen bond. Typical shifts are 5 to 25 cm^{-1}.[20] The displacement observed in the products reported herein, being far larger than that expected from coordination alone, must be related to the presence of a formal C = N bond, in agreement with the structure proposed. (2) Thiuram sulfides, as examples of 'asymmetric' dithiocarbamates display two bands between 950 and 1000 cm^{-1}. These absorptions are associated with C = S stretching modes. The corresponding stretching frequencies for the C-S bonds are located near 850 cm^{-1}. Only the latter are observed in the spectra of the reaction products reported here. (3) Copper complexes of dithiocarbamates and thiuram sulfides show medium to strong intensity bands in the 400–300 cm^{-1} region, due to Cu-S stretching vibrations.[21] The position of these bands depends somewhat on the oxidation state of the metal, Cu(III)-S stretchings being found at higher wavenumbers than Cu(II)-S, which in turm are higher than Cu(I)-S.[22] No significant absorptions are found for the materials synthesized. In fact, the spectra are featureless between 500 and 150 cm^{-1}. Linear $CuCl_2^-$ anions in solution are characterized by a Raman line at 296 cm^{-1}, with no infrared counterpart, as expected for a centrosymmetric structure.[23] The symmetry is preserved in the solid.[24] Thus, the lack of features in the far infrared spectra of the materials reported here point at a linear centrosymmetric anion in the solid. Poor crystallinity and deep colors of the samples have so far prevented Raman studies.

Acetonitrile solutions of the products show molar condutivities typical of 1:2 electrolytes. The conductivity of a fresh solution of the i-Pr derivative drops rapidly with time, and this is in agreement with the isolation of $Cu(R_2dtc)_2$ from the solutions.

Oxidation of thiuram sulfides by copper(II) halides is a distinct feature in the chemistry of these ligands. In a brief note[25] we reported the preparation of $(Me_4bitt\text{-}3)^{2-}CuX_3^{2-}$ (X = Cl, Br) through the sequence.

$$2Me_4tms + 2CuX_2 \longrightarrow CuMe_4tmsX + (Me_4bitt\text{-}3)^{2+}CuX_3^{2-}$$

This finding was challenged,[26] but we have absolutely confirmed all experimental details and expect to give a full account shortly.

The five membered cyclic organic cation 3,5-bis(N,N-dialkylimonium-1,2,4-trithiolane $(R_4bitt\text{-}3)^{2+}$ has been reported in oxidation reactions of metal dithiocarbamates. Thus, the reaction of Fe $(Et_2dtc)_3$ or Fe $(Et_2dtc)_2$ Cl with halogens yields $(Et_4bitt\text{-}3)^{2-}(FeCl_4^-)_2$ also accessible through oxidation-desulfurization of, Et_4tds with anhydrous $FeCl_3$.[27] The same report gives details on the preparation of $(nBu_4bitt\text{-}3)^{2+}$ $Cu_2X_6^{2-}$ (X = Cl, Br) from halogens and the cuprous dithiocarbamate. An oxidation-desulfurization reaction 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 an $(R_4bitt\text{-}3)$ compound.[28] Very relevant to this series of reports is the recent observation.[29] of the mass spectrum of solutions of $(Et_2dtc)_3$ Fe oxidized with NO^+, where the highest mass is assigned to the molecular ion, $(Fedtc_3)_2(Et_4bitt\text{-}3)^{2+}$, of unknown structure.

This report offers the first example of a compound containing the 3,6-bis(N,N-dialkylimonium)-1,2,4,5-tetrathiolane cations, $(R_4bitt\text{-}4)^{2+}$. In contrast to previous examples, no desulfurization is apparent, perhaps due to the mild reaction conditions. Other formulations such as those shown in Scheme 2 may by ruled out, on the basis of the lack of features in the far infrared region, and also considering that the ^{1}H-NMR of the Et and iPr derivatives shows only one alkyl set of resonances.

Work is proceeding on further characterization of these interesting materials.

Acknowledgements

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