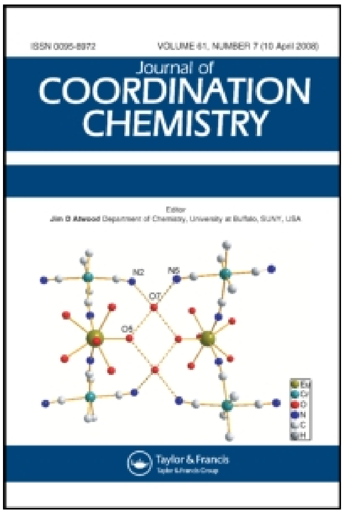

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Luis I. Victoriano[a]; Ximena A. Wolf[a]
[a] Departamento de Química Analítica e Inorgánica, Facultad de Ciencias Químicas, Universidad de, Concepción, Chile

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THE REACTION OF COPPER (II) CHLORIDE AND TETRAALKYLTHIURAM DISULFIDES

LUIS I. VICTORIANO* and XIMENA A. WOLF

Departamento de Química Analítica e Inorgánica, Facultad de Ciencias Químicas, Universidad de Concepción, Chile

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Reaction of copper(II) chloride and tetraalkylthiuram disulfides, R_4tds (R = Me, Et, i-Pr), affords the title compounds, $(R_4\text{bitt-4})^{2+}2CuCl_2^-$. The products are characterized by elemental analyses spectroscopy infrared, nuclear magnetic resonance spectroscopy solution conductivity, magnetic susceptibility measurements and reaction chemistry.

KEYWORDS: Copper(II) chlorides, tetraalkylthiuram disulfides, tetrathiolanes, and dithiocarbamates

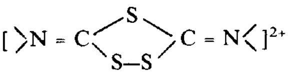
ABBREVIATIONS: tms: thiuram monosulfide $[{>}N{-}CS)]_2S$

tds: thiuram disulfide $[{>}N{-}C(S)]_2S_2$

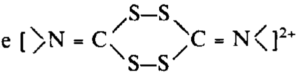
dtc: dithiocarbamate $[{>}N{-}C(S){-}S{-}]$

tca: thiocarboxamide ${>}N{-}C(S){-}$

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

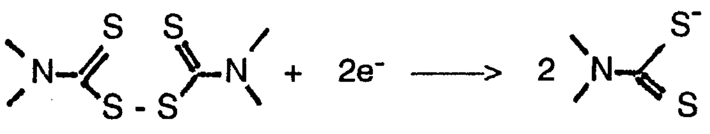


$[\text{bitt-4}]^{2+}$: bis-(dialkylimonium)tetrathiolane



INTRODUCTION

Thiuram disulfides(**) and their allied compounds, dithiocarbamates are related by the two-electron redox process



and the biological activity of both types of compounds has been attributed to the ease of interconversion of the species, as well as the coordination properties of the dithiocarbamate ligands[1]. This activity is reflected in the many applications which

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*Author for correspondence

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

include: acceleration of vulcanization, fungicides, pesticides and many others. However, the reactions involving thiuram disulfides and dithiocarbamates are often complex and rarely amenable to description by redox and complexation schemes alone.

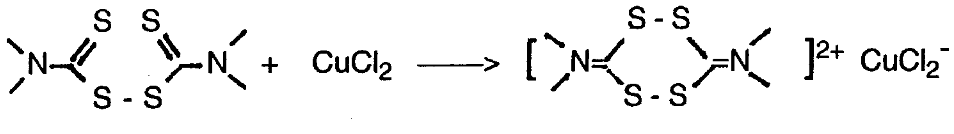
Dithiocarbamates and their metal derivatives have been the subject of extensive research and their chemistry is now reasonably well understood[2]. On the basis of the available reports, reactions of the much less studied thiuram disulfides may be broadly classified in two groups: (1) Systems where the thiuram disulfide forms simple coordination compounds, either neutral (Hg(II)[3] or Co(II)[4]) or cationic (Cr(III)[5]) and (2) Reactions characterized by the oxidizing properties of the thiuram, which lead to dithiocarbamate complexes of the oxidized metal species. Recent examples are the oxidation of $M(CO)_4$ to $Mdtc_3$[6] and $M(CO)_6$ to $Mdtc_4$[7] (M = Mo and W). Also, $Re(CO)_5Cl$ and thiuram disulfides give $Redtc_4^+$ $Re(CO)_3Cl^-$[8] and $MdtcR_n$ affords $Mdtc_3$ or $Mdtc_3R_n$($M = Rh$, $R_n = (C_8H_{12})$ and $(C_8H_{12})_2$; $M = Ir$, $R_n = (C_8H_{12})$)[9].

Further breakdown of the ligand may also occur, with attendant stabilization of the fragments by coordination to the metal. In this manner, the reaction of R_4tds with $Mo(CO)_6$ has been reported to yield $Mo_4(\mu\text{-}S)_4dtc_6$.[10] Also $W(CO)_3(CH_3CN)_3$ and Et_4tds have produced $W_4(\mu\text{-}S)_2dtc_4$,[11] while the products of the reaction of $HB(Me_2pz)_3W(CO)_3$ with tds are $HB(Me_2pz)_3W(CO)_2dtc$ and $HB(Me_2pz)_3$ W^{II} $(CO)_2(\mu\text{-}S)W^{IV}dtc_2tca$ ($HB(Me_2pz)_3$ = hydridotris (3,5-dimethyl-1-pyrazolyl) borate; tca = thiocarboxamido).[12] A related system includes the synthesis of $V_2(\mu\text{-}S_2)_2dtc_4 \cdot 2CHBr_3$ from VS_4^{3-} and the corresponding thiuram disulfide.[13]

Reductive fragmentation of the thiuram disulfide with no apparent oxidation of the metala is puzzling and yet common feature in the chemistry of these ligands. Thus R_4tds and mercury halides yield $Hgdtc_2$[14] or IHgdtc.[15] Similar reactions include the preparation of $Mdtc_3$ X^- from Mx_2dtc_2 (M = Pd, Pt; X = Br, I)[16] and of $Nidtc_2$ from $NiCl_2$.[14]

Copper(II) dithiocarbamates have been widely studied, and the preparative chemistry is well founded.[2] Copper(II) and thiuram disulfides on the other hand, have been reported to yield $Cudtc_2$.[17]

Novel reaction products have now been isolated, 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. The resulting species are isolated as derivatives of the large cations 3,6-bis(N,N-dialkylimonium)-1,2,4,5-tetrathiolane $(R_4bitt\text{-}4)^{2+}$ (R = Me,Et,iPr).



EXPERIMENTAL

General

Me_4tds and i-Pr_4tds were prepared by standard literature procedures.[18] The Et derivative (Aldrich) was recrystallized from EtOH. $CuCl_2 \times 2H_2O$ (Merck) and

Me_4NCl (Fluka) were oven dehydrated at 115°C and kept under nitrogen. Solvents were distilled from $CaCl_2$ which had been activated at 350°C (THF, EtOH and CH_3CN), or from sodium ribbon (hexanes). All synthetic manipulations involving the copper complexes were carried out under an atmosphere of dry nitrogen using Schlenk or cannulation techniques.[19]

Spectroscopy

Infrared 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. ^1H-NMR spectra were obtained using a Brücker AC250P spectrometer.

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; $[Me_4bitt\text{-}4]^{2+}2CuCl_2^-$. Anhydrous $CuCl_2$ (1.34 g, 10 mmol) was dissolved in THF (80 mL). 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 pumped dry. The solution changed to a brown color within 15 min., and eventually deposited black, highly crystalline $Cu(Me_2dtc)_2$. 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 pumped dry. Yield: 0.45 g. $(C_6H_{12}N_2S_4)^{2+}(CuCl_2)_2$: Dark red solid, m.p. 127° (d). *Anal.* Calcd. for $C_6H_{12}N_2S_4Cl_4Cu_2$(%): Cu, 24.95; Cl, 27.85; C, 14.15; H, 2.36. Found: Cu, 24.58; Cl, 27.73; C, 14.19; H, 2.41. I.R. (KBr): 2920 vw, 1618 vs, 1414 m, 1249 m, 1170 m, 1058 wm, 960 w, 865 w. ^1H-NMR ($CDCl_3$):3.26 (s, br).

$[Et_4bitt\text{-}4]^{2+}(CuCl_2^-)_2$

The Et derivative was prepared as described above. Yields were lower due to better solubility. 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): 2999 m, 2934 m, 2875 w, 1604 s, 1460 s, 1289 m, 1190 m, 1160 w, 1090 w; 1070 w, 1040 w, 847 m. ^1H-NMR ($CDCl_3$): 4.16 (s, br, 2), 1.45 (s, br, 3).

$[i\text{-}Pr_4bitt\text{-}4]^{2+}(CuCl_2^-)_2$

This compound was made by mixing THF solutions of $CuCl_2$ and a hexane (80 mL) solution of the ligand (5 mmol). 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. IR(KBr): 316 w, 2967 m, 2901 m, 1585 vs, 1453 m, 1400 w, 1380 m, 1361 s, 1175 w, 1144 s, 1032 w, 830 w. ^{1}H-NMR($CDCl_3$): 4.28(s,br,1), 1.32(s,br,6).

Reaction of $[Et_4bitt\text{-}4]^{2+}(CuCl_2^-)_2$ *and* Me_4NCl

The red copper compound (0.566 g, 1 mmol) was dissolved in 80 mL THF and a solution of Me_4NCl (0.22 g, 2 mmol) in EtOH (50 mL) was added dropwise with stirring to the cooled (0°) wine-red solution of bitt-4. The bright yellow precipitate was filtered and washed with 10 mL of 1:1 THF-EtOH and finally dried by pumping. $(Me_4N)_2CuCl_4$: Bright yellow microcrystalline solid. *Anal.* Calcd. for $C_8H_{24}N_2Cl_4Cu$(%): Cu, 17.96; Cl, 40.10. Found: Cu, 17.58; Cl, 40.15. I.R.(KBr): 3026 m, 2954 w, 1486 s, 1420 sh, 1289 w, 966 s. FIR (Nujol-polyethylene): 282 s, br, 237 sh, 146 m, 126 m. The mother solution of THF and EtOH was concentrated to *ca.* 30 mL and poured over 100 mL H_2O. The oil was extracted with Et_2O (20 mL) and the extract was evaporated to dryness. The syrup was taken up in EtOH (50 mL) and upon standing. off-white Et_4tds crystallized. This was filtered and dried. Et_4tds, off-white solid, m.p. 70°. The $[i\text{-}Pr_4\ bitt\text{-}4]^{2+}$ $(CuCl_2^-)$ reacted in a similar fashion to give $(Me_4N)_2CuCl_4^-$. No attempt was made in this case to isolate the i-Pr_4tds.

RESULTS AND DISCUSSION

Attempts to prepare coordination complexes of thiuram disulfides and copper(II) yield 3,6-bis(N,N-dialkylimonium)-1,2,4,5-tetrathiolane dichlorocuprate(I) as the only products. These arise through two-electron oxidation of the ligand by the copper salt.

The products are, in all the examples studied, soluble diamagnetic red solids, with analyses which are consistent with the formulation $(R_2NCS_2)_2Cu_2Cl_4$. In light of the chemistry discussed in the Introduction, these formulations may result from copper(III) dithiocarbamates or copper(II) thiuram complexes. The infrared spectra of the solids, summarized in Table 1, rule out either formulation. Three regions are of importance. (1) The free ligands show strong absorptions at *ca.* 1500 cm^{-1}. This so called "thiureide" band results from the stretching of a C = N linkage with a strong double bond character.[20] The position of this band is sensitive to shifts of electron density on the sulfur atoms and as such it has been used as a probe for complexation

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

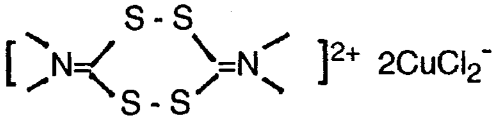
	C–N	C = S	C–S
Me_4tds(KBr)	1500	988	860
$[Me_4bitt\text{-}4]2CuCl_2$(KBr)	1618		875
Et_4tds(KBr)	1500	971	823
$[Et_4bitt\text{-}4]2CuCl_2$(KBr)	1604		847
$[Et_4bitt\text{-}4]2CuCl_2(CHCl_3)$	1606, 1503	973	850, 825
iPr_4tds(KBr)	1481	947	850
$[iPr_4bitt\text{-}4]2CuCl_2$(KBr)	1585		830
$[iPr_4bitt\text{-}4]2CuCl_2(CHCl_3)$	1590, 1485	950	850, 830

All frequencies in cm^{-1}

in dithiocarbamate and thiuram compounds, as well as an indication of the oxidation state of the metal center. For example, dithiocarbamates of copper(III) show the thiureide band some 50 to 80 cm^{-1} higher than the corresponding copper(II) complexes,[21] while thiuram monosulfide complexes of copper(I) show this band 5 to 25 cm^{-1} higher than the free ligands.[22] 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 300–400 cm^{-1} region, due to Cu-S stretching vibrations. The position of these bands depends on the oxidation state of the metal, Cu(III)-S vibrations spanning the region 345–410 cm^{-1},[21a] with Cu(I)-S stretches being found between 310 to 365 cm^{-1}.[23] The corresponding Cu(II)-S stretching modes have been assigned at *ca.* 350 cm^{-1} in a series of copper(II) bis(dithiocarbamates).[24] The spectra of the materials $(R_2NCS_2)_2Cu_2Cl_4$ reported here show no features 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.[26] The symmetry is preserved in the solid.[26] Thus, the lack of features in the far infrared spectra of the materials reported here point at a linear centrosymmetric anion in the solid.

The materials are diamagnetic and thus inconsistent with their formulation as copper(II) compounds. On the basis of the foregoing evidence, the solid state structures are assigned as ionic:



The situation in solution is more involved and calls for consideration of the equilibrium

$$R_4tds + CuCl_2 \rightleftharpoons R_4bitt\text{-}4^{2+} + 2\ CuCl_2^-$$

The infrared spectra of chloroform solutions of the isolated products show bands characteristic of both thiuram disulfide and R_4bitt-4^{2+}, as shown in Table 1. No solution data are available for the Me compound, due to limited solubility.

The ^{1}H-NMR spectra of $CDCl_3$ solutions of the products (Table 2) show the resonances characteristic of the ligands, along with those of the R_4bitt-4^{2+} products. The temperature dependence of the ^{1}H-NMR of R_4tds has been interpreted in terms of free rotation about the C-N bond, which causes inequivalence of the alkyl groups and broadening of the signals at near-to-room-temperature.[27] In the spectra of solutions of the R_4bitt-4^{2+} compounds, two sets of alkyl resonances are apparent. One set matches the resonances of the free ligands, while the remaining set, located at lower field is assigned to the organic cation. The position of the signals relative

Table 2 The room temperature ^{1}H-NMR spectra ($CDCl_3$) of 3,6-bis(N,N-dialkylimonium)-1,2,4,5-tetrathiolanes and parent thiuram disulfides.

Et_4tds	4.36	1.75
$[Et_4bitt\text{-}4]^{2+}$	4.36, 4.16	1.75, 1.45
iPr_4tds	4.62	1.45
$[iPr_4bitt\text{-}4]^{2+}$	4.62, 4.28	1.45, 1.32

All resonances in ppm downfield from tetramethylsilane.

to the free ligand is in accordance with deshielding of the alkyl protons due to the removal of electron density from the N atom. Almost simultaneous with attainment of the equilibrium observed, there is the onset of decomposition ending in dithiocarbamate fragments. This is evident from the appearance of an additional set of alkyl resonances at 1.60 and 4.08 ppm for the i-Pr derivative, which closely match the absorptions present in an authentic sample of $Cu(i\text{-}Pr_2dtc)_2$. This observation, and isolation of the corresponding dithiocarbamates (see Experimental) show that a close agreement exists between the present work and previously reported results.[17]

The molar conductivities of solutions of the $(R_4bitt\text{-}4)^{2+}$ compounds are not particularly informative, but lend support to the equilibrium proposed. Freshly made solutions display molar conductivities in the borderline between 1:1 and 1:2 electrolytes, and the values drop rapidly with time. Simultaneously, changes of color and eventual deposit of highly crystalline $Cu(i\text{-}Pr_2\text{-}dtc)_2$ are observed.

The proposed equilibrium may be shifted by precipitation of the copper(I) compound, but also by formation of an insoluble Cu(II) species. Thus, the addition of tetramethylammonium chloride causes the immediate formation of yellow $(Me_4N)_2CuCl_4$, which can be isolated in almost quantitative yield. The solution contains the corresponding amount of R_4tds. The $CuCl_4^{2-}$ species has been fully characterized and its far infrared spectrum compared to that published.[25a]

Crystal growth for X-ray diffraction studies is prevented by the lack of stability of the solutions. In the absence of these structural studies, there is a reasonable body of evidence in support of the structure proposed and of the reversibility of the reaction. The reported series of compounds offers the first example of molecules containing the 3,6-bis(N,N-dialkylimonium)-1,2,4,5-tetrathiolane cation. However, this is not the first example of thiuram oxidation by copper(II) halides. In a series of papers[28] we reported the preparation of 3,5-bis(N,N-dialkylimonium)-1,2,4-trithiolanes by reaction of thiuram monosulfides and copper(II) halides (Cl, Br).

$$2Me_4tms + 2CuX_2 \longrightarrow XCuMe_4tms + Me_4bitt\text{-}3\ CuX_3^2$$

Others have not had success in this transformation,[29] no doubt because of scant experimental data available. We plan to give full details of these experiments in due course.

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 $Fe(Et_2dtc)_2Cl$ with halogens yields $(R_4bitt\text{-}3)^{2+}2FeCl_4^-$, also accessible through oxidation-desulfurization of Et_4tds with anhydrous $FeCl_3$.[30] 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 (R_4bitt-3) compounds.[31] Very relevant to this series of reports is the recent observation[32] 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.

In contrast to the examples described in the previous paragraph, there is no evidence of sulfur abstraction in the course of the reactions described here. The mechanism responsible for desulfurization in I_2HgEt_4tds most probably involves nucleophilic attack on one of the thiocarbamoyl carbons by sulfur.[33] It is reasonable to assume that the nucleophilicity of any sulfur atom in $R_4bitt\text{-}4^{2+}$ must be very low compared to R_4tds and so sulfur abstraction does not take place.

In conclusion, copper(II) salts react with thiuram disulfides by oxidation of the ligand and formation of copper(I) haloanions. Work is proceeding on other aspects of the chemistry of thiuram sulfides.

Acknowledgements

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