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The reactivity of metal species towards thiuram sulfides: an alternative route to the syntheses of metal dithiocarbamates

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Contents

Abstract

The chemical properties of tetraalkylthiuram sulfides are reviewed from the perspective of their interaction with transition and main group metal species. From the available literature, few examples are found of metal ion interactions with the monosulfide. These examples almost invariably lead to metal adducts. The case for the disulfides is more involved and usually leads to dithiocarbamate metal complexes. A few examples of ligand oxidation are also found. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Thiuram sulfides; Ligand oxidation; Metal dithiocarbamates

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1. Introduction

Thiuram sulfides, otherwise known as bis(*N*,*N*-dialkylthiocarbamoyl)sulfides, $R_2NC(S)S_nC(S)NR_2$ are the thiocarbamoyl esters of dialkyldithiocarbamic acids. The disulfides ($n = 2$) R_4tds are known on account of their biological activity, which leads to applications as fungicides, rubber vulcanization accelerators, agents of alcoholism therapy [1–3], and quite recently, as arrestors of Human Immunodefficiency Virus infections such as AIDS [4]. This wide diversity of examples of biological activity has been attributed to a combination of at least two factors[5]: Namely the capability to fit into a receptor site and ability to undergo reversible redox reactions at suitable potentials. From this point of view, the equilibrium relating thiuram disulfides and dithiocarbamates is very relevant to the chemistry of the disulfides.

A peculiarity of metal dithiocarbamate chemistry is the recognized ability of the ligands to stabilize unusually high oxidation states in transition metals, a property which has been attributed to the ligand ability to delocalize positive charge from the metal towards the periphery of the complex [6]. Thiuram disulfides are unique among thiolato-type ligands, in that reductive scission of the S–S bond leads to chelating systems (dithiocarbamate anions), which are particularly well suited to stabilize high oxidation states under the premise outlined above.

The monosulfides ($n = 1$) R_4tms, perhaps because they lack the wide breadth of applications known for the disulfides in agriculture and experimental medicine, have been much less extensively studied and where such studies deal with the subject of interaction of monosulfides and metal species, the field remains virtually unexplored.

The present article intends to review the chemistry of thiuram sulfides and metal species. The number of papers appeared in the literature concerning this topic is probably close to one hundred. Yet the subject has not been reviewed previously, particularly from the point of view of different patterns of reactivity found in the systems described. Good compilations have appeared related to the general chemical properties of thiuram disulfides [1], and these reviews have covered the information then available on the interaction of such molecules with metal species. Also, the updates of Coucouvanis [7] and McCullough [8] on the chemistry of 1,1-dithiolate complexes constitute very informative first sources. More recently, Steggerda, Cras and Willemse have touched upon the subject [4]. Our own efforts have resulted in more recent updates [9–11].

Typical reactions of thiurams mono and disulfides with metal species fall under three distinct categories: (a) Adduct formation; (b) ligand reduction with concomitant degradation to dithiocarbamate and/or thiocarboxamide ligands; and (c) thiuram oxidation. We shall address each of these in the same order. Within each section, thiuram disulfides will be treated first, followed by the monosulfides.

2. Adduct formation

Metal species which display a closed shell configuration typically react with thiuram disulfides to yield adducts. Thus, a limited number of well defined thiuram complexes have been obtained from the reaction of Group 12 halides and the ligands. These adducts span the general formulation MLX_2 (M = Zn, Cd and Hg; L = Et_4tds, Et_4tms; X = Cl, Br, I, not all combinations) [12–14]. The ^{1}H-NMR of the complexes reveals a higher barrier to rotation about the C–N bond in the complexes than in the free ligands [12,13]. The crystal structure of $HgEt_4tdsI_2$ features a monomeric tetracoordinated species [15,16] with an approximately tetrahedral arrangement of two iodine and two sulfur atoms about mercury. The Hg–I and Hg–S distances are significantly longer than the corresponding ones in $(Et_2dtcHgI)_2$, an observation which is explained in terms of the tricoordination exhibited by the metal in the dtc complex. The Zn adduct reacts with one, two and three equivalents of triphenylphosphine to give $[I_2Zn(R_4tms)]$, $[Ph_3P(S)NMe_2]^+$ $[I_2Zn(Me_2dtc)]^-$ and $[Ph_3P(S)NMe_2]^+[I_3ZnPPh_3]^-$, respectively [14].

The crystal structure of $[\{(C_5H_{10})_2tmsCuI\}_2]$ reveals a centrosymmetric dimer in the solid state [17]. The copper atoms are approximately tetrahedrally coordinated by one iodine, two sulphur atoms from one thiuram monosulfide and by one bridging sulphur atom from another monosulfide unit. The Cu–I distance of 2.535(2) Å is slightly shorter than the corresponding distance in Cu–I.

Copper(II) halides and *N*,*N*,*N*′,*N*′-tetraalkylthiuram monosulfides yield trihalocuprate(I) of the bis-(dialkyliminium)trithiolane cation and stoichiometric amounts of copper(I) halides, which may be isolated from the reaction mixtures as adducts [18], the nature of which has been determined by single crystal X-ray diffraction [9]. Complexes $CuMe_4tmsX$ exist as chelated units formed by a molecule of the ligand and one of copper(I) halide. In all three cases, coordination about copper(I) is tetrahedral and is completed by sulfur and halogen. The chloro derivative is a centrosymmetric dimer, isostructural to the dipentamethylenethiuram monosulfide-copper iodide complex described above. All three copper–sulfur distances are slightly shorter in the chloro derivative. The molecular structure of the bromo derivative corresponds to a polymer. Association of basic chelated units generates long chains parallel to the x-axis of the unit cell. The copper coordination is completed by one bromine and three sulfur atoms. Unlike the pentamethylene complex described above, the iodo complex contains two μ-iodine bridged units of $CuMe_4tmsI$. As in the chloro and bromo derivatives, coordination about copper is tetrahedral and it is completed by two iodine and two sulfur atoms.

Other CuR_4tmsX complexes (R = Et, X = Cl and Br [11]; R = ^{n}Pr, ^{i}Pr, X = Br [19]) feature monomers containing tricoordinate copper(I). The Cu–S distances are about 2.24 Å in the ethyl complexes, values which are noticeably shorter than those found in the methyl derivatives. This is attributed to the non-bridging nature of the sulfur atoms in the heavier alkyl homologues.

Reaction of acetonitrile solutions of cuprous iodide and Et_4tms leads to a crystalline phase of composition $(CuI)_5(Et_4tms)_2$ [10,11]. The solid state structure of this aggregate (see Fig. 1) may be described as formed by a central $(CuI)_3$ distorted octahedral element, and two additional $CuEt_4tmsI$ units fused to the central $(CuI)_3$ cage by means of sulfur and iodine bridges. The molecule displays a twofold crystallographic axis through one copper and one iodine, coincident with the long axial position of the 'octahedron'.

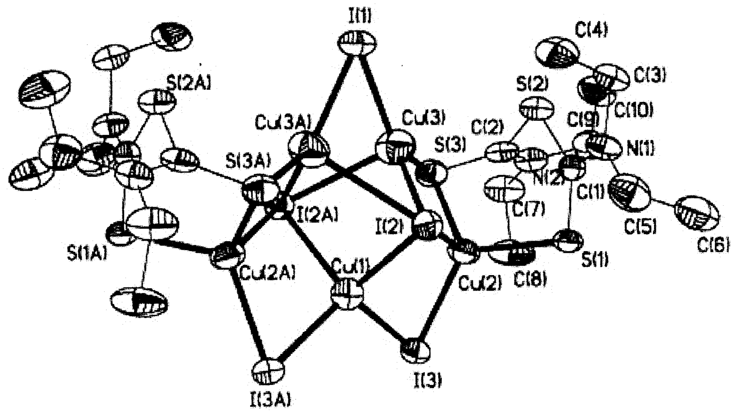


Fig. 1. The structure of (CuI)$_5$(Et$_4$tms)$_2$ [10,11].

The severely bent equatorial plane of the octahedron is defined by two additional copper and two iodine atoms. Each CuEt$_4$tmsI unit contains one tetrahedral copper, a bidentate sulfur ligand and one iodine atom. These units are fused to two faces of the octahedron by means of two iodine bridges and by one sulfur bridge.

Discrete pentanuclear copper(I) complexes have been so far reported for Cu$_5$(SPh)$_7^{2-}$ [20] and Cu$_5$X$_7^{2-}$ (X = Br, Y). The anion Cu$_5$I$_7^{2-}$ has been described as a pentagonal bipyramid of seven iodine atoms, where only slight deviations from C_{5h} symmetry occur [21]. In the bromo derivative, the pentagonal bipyramid of ligand atoms is more severely distorted [22]. With the hindsight afforded by the previous models, we may now view the structure of the tetraethylthiuram monosulfide complex as consisting of the same basic structural unit, viz. a pentagonal bipyramid conformed by the two apical iodine atoms and by a distorted basal plane conformed by two sulfurs and three iodines. All copper atoms display tetrahedral coordination and appear as three distinct sets. The shortest metal–metal distance found (2.533(8) Å) rules out any possible metal–metal bonding. The iodine atoms are either μ$_2$- or μ$_4$-bridged and the shortest I...I contact (4.261 Å) compares well with the one found in [Cu$_2$I$_4^{2-}$] [23] and other related systems [24].

The structure of the pentanuclear derivative is unique within a series of thiuram complexes known thus far. A variety of experimental conditions have failed to yield a mononuclear copper complex in combinations of copper(I) iodide and tetraethylthiuram monosulfide. Also, all efforts to isolate a species of higher nuclearity using combinations of different copper(I) halides and methyl, ^{n}Pr or ^{i}Pr substituents on the ligand have not met with any success. It is speculated that the kinetics of complexation might be slow in the case of CuI/Et$_4$tms, so that the available free CuI competes with the monomeric CuEt$_4$tmsI for extension of the association.

The tetrahedral and trigonal planar stereochemistries found in R_4tms complexes of copper(I) are not surprising. For d^{10} Cu(I), stereochemistry is dictated by charge and steric effects on the ligand, and tetrahedral and trigonal geometries are the norm [25].

Silver halide complexes with tetramethylthiuram monosulfide have been prepared and characterized by vibrational spectroscopy [26]. The data show that the complexes possess a halogen-bridged structure of D_{2h} symmetry. In addition the complex $[(PPh_3)_2Ag(Me_4tms)]NO_3$ has also been made.

The systems constituted by Ni(II), Co(II) and Cr(III) with R_4tms and R_4tds are also apparently uncomplicated by further reactivity and would seem to yield the corresponding straightforward cationic or neutral coordination compounds [27,28]. However, this proposal admittedly needs to be more carefully examined [29], especially in the light of earlier claims [30], which consider the formation of metal dithiocarbamates as the most important process under otherwise similar experimental conditions.

3. Ligand reduction and degradation

Other reactions of metal containing species with thiuram sulfides are characterized by the oxidizing properties of the thiuram. Reduction of the ligand and scission of the S–S bond results in incorporation of the dtc fragments into the metal coordination sphere. In many of the early studies the redox balance in the products isolated could not account for the observed reduction of the ligand. As exemplified in the modern literature, rarely are these systems fully described by redox and complexation schemes alone. Bond breaking and extensive redistribution of the ligand systems are common.

3.1. Main group elements

Studies involving reactions of non-transition elements and thiuram sulfides have been limited to a handful of reports. The stability of high oxidation states in dithiocarbamate complexes seems to be restricted to transition metals, where empty d orbitals can behave as Π acceptors [6].

Early experiments [31] indicated that reaction of thallous chloride with tetraalkylthiuram disulfides results in thallic dithiocarbamates. The crystal structure of $Tl(Me_2dtc)_3$, was determined at a later date and consists of a TlS_6 core of approximate D_3 symmetry [32].

The reaction of R_4tds with MI_3 ($M = As$ or Sb) affords $[M(R_2dtc)_2]^+ \; I_3^-$ [33]. The same products may be obtained by the alternative route involving iodine oxidation of the tris-dithiocarbamate complexes. The reaction products would be explained by a mechanism involving firstly oxidative addition of the homonuclear bond to the M(III) species to give $[M(dtc)_3I_2]$, followed by reductive elimination of iodine. In support of the mechanism proposed, the authors have isolated $Me_3Sb(dtc)_2$ from the reaction of Me_4tds with $SbMe_3$. This product fails to produce $Sb(dtc)_3$ [34].

Crystallographic and spectroscopic evidence indicate that asymmetric coordination of the dithiocarbamate ligands occurs in the $M(dtc)_2^+$ cations [35].

3.2. Titanium, zirconium and hafnium

A single report has been produced on this area of transition metal chemistry. Orange–red dithiocarbamates formulated as $[(C_5H_5)Ti(R2dtc)X_2]$ are produced upon oxidation of $(C_5H_5)TiX_2$ with thiuram disulfides ($R = Me$, Et, ^{n}Bu; $X = Cl$ or Br) [36].

3.3. Vanadium, niobium and tantalum

Brown $[V_2(\mu\text{-}S_2)_2(Et_2dtc)_4]$ was produced upon reaction of VS_4^{3-} with Et_4tds in toluene. The solvate $[V_2(\mu\text{-}S_2)_2(Et_2dtc)_4] \times 2CHBr_3$ displays a structure (Fig. 2) where the V(IV) atoms in the dimer are bridged by two S_2^{2-} ligands and a metal–metal single bond. Each vanadium atom is further coordinated by two bidentate dithiocarbamate ligands [37]. The same synthetic approach had previously afforded the ^{i}Bu$_2$dtc derivative [38].

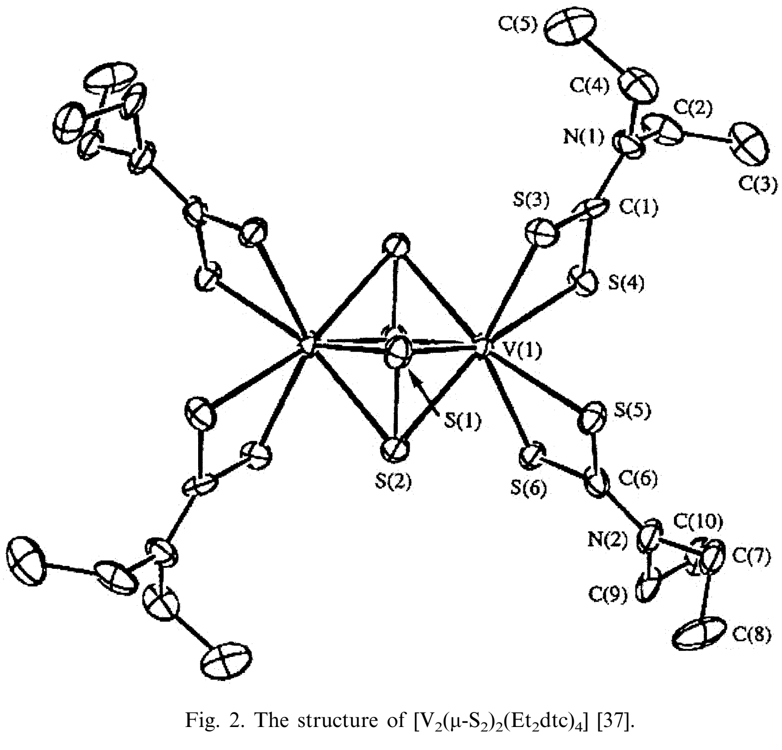


Fig. 2. The structure of $[V_2(\mu\text{-}S_2)_2(Et_2dtc)_4]$ [37].

3.4. Chromium, molybdenum and tungsten

The chemistry of chromium and thiuram disulfides has remained virtually unexplored. A single report claiming formation of the cationic complexes $[Cr(R_4tds)_2Cl_2]^+$ from $CrCl_3$ and the ligand in ethanol admittedly needs to be re-examined [29].

Molybdenum on the other hand has been subjected to extensive synthetic studies. Much of the interest stems from attempts to prepare complexes with sulfur ligands which may serve as models for biological systems or increase our understanding of industrial catalysts.

Oxidative decarbonylation of molybdenum hexacarbonyl with tetraalkylthiuram disulfides leads to the isolation of a series of neutral species formulated as $[Mo(R_2dtc)_4]$ (R = Me [39], Et [39,40] and Ph [41] or ^{i}Pr, Bz and Ph [41]). This reaction has also led to materials of composition $Mo(dtc)_5$ which, based on IR and conductivity experiments, has been formulated as $Mo(dtc)_4^+$ dtc^- [41].

Reaction of $(C_7H_8)Mo(CO)_3$ with Et_4tds was a controversial subject for several years. Brown et al. isolated a material of composition Mo_2dtc_6 from this system [42], while others only succeeded in obtaining $Mo(Et_4dtc)_4$ and $Mo(Ph_4dtc)_4$ from similar reaction media [41]. Publication of full experimental details settled the issue [43]. The dimer is obtained in the dark, while the tetrakis species requires sunlight irradiation. Thus, the series of dimers was expanded to include the Me, Et, ^{n}Pr and ^{n}Bu derivatives [44].

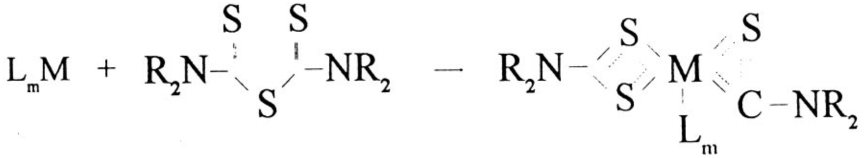
Oxidative decarbonylation of $[Mo(CO)_5I]^-$ with Et_4tds produces the cationic species $[Mo(Et_2dtc)_4]^+$ [45], while a similar reaction using Ph_4tds results in the neutral $[Mo(Ph_2dtc)_4]$. The latter may be oxidized to the cationic Mo(V) species with bromine or iodine [41].

When $Mo_2(Et_2dtc)_6$ is subjected to prolonged reflux in toluene, the species $Mo_4(\mu_3\text{-}S)_4(Et_2dtc)_6$ is obtained. The crystal structure of this interesting species (Fig. 3) features a cubane-like Mo_4S_4 cluster, where two of the dtc ligands each bridge between two of the metal atoms on opposite sides of the cube. The remaining four dtc ligands coordinate in a bidentate fashion to each of the molybdenum atoms. In addition, the four metal atoms are mutually bonded via Mo–Mo short bonds for the two atoms bridged by the same dtc, and by two longer bonds to the remaining metal atoms in the cage [46,47].

The oxidative decarbonylation approach has been used further to generate the species $[CpMo(CO)_2(Me_2dtc)]$ from $[CpMo(CO)_3]$ and the corresponding disulfide [48]. Partial decarbonylation–oxidation is surprising when compared to the results obtained with Et_4N $[\{HB(Me_2pz)_3\}Mo(CO)_3]$ and tetramethylthiuram disulfide, where the final product is $[\{HB(Me_2pz)_3\}Mo(\mu_2\text{-}Me_2dtc)(\mu_1\text{-}Me_2dtc)]$. This product exhibits a distorted octahedral *fac*-N_3-*fac*-S_3 coordination sphere (Fig. 4) composed of the tridentate $HB(Me_2pz)_3^-$ ligand a bidentate dithiocarbamate and an additional monodentate dithiocarbamate [49,50].

Oxidation of $(^nBu_4N)_2MoS_4$ with Et_4tds yields $[Mo(S_2)(dtc)_3]$. The crystal structure of this product reveals a monomer with octacoordinate Mo linked to three bidentate dithiocarbamates and to one $(\mu_2\text{-}S_2)$ ligand [51,52] (Fig. 5).

Tetramethylthiuram monosulfide reacts with the electron-rich species $Mo(CO)_3(MeCN)_3$ to produce a complex $[(CO)_2(Me_2NCS_2)Mo(Me_2NCS)]$ which contains bidentate dithiocarbamate and thiocarboxamide ligands [54].



Much less attention has been given to tungsten analogues despite the use of tungsten sulfide as a hydro-treating catalyst and the capability of tungsten to replace molybdenum in certain biological systems.

Another fundamental difference noted in the comparison of the two heavier elements in the triad is related to the oxidative decarbonylation reaction, which has played such an important part in the development of the chemistry of molybdenum systems. Thus, oxidation of $W(CO)_6$ with thiuram disulfides leads to analytically unsatisfactory material [54]. In a review paper, Dori [55] refers to unpublished work involving the preparation of $[W(Et_2dtc)_4]$ starting from $[W(CO)_3(MeCN)_3]$ and Et_4tds. There was no further confirmation of these results. Experiments carried out with $[W(CO)_5I]^-$ and Ph_4tds are more successful and yield $[W(Ph_2dtc)_4I]^-$ [41].

Brief mention was made of materials of composition $W_2(dtc)_6$ [42] although no experimental details were given at the time. Ten years after the original report, a full account was given [56], which has contributed much to our current understanding of the subject, as far as tungsten chemistry is concerned. Thus, in contrast to the

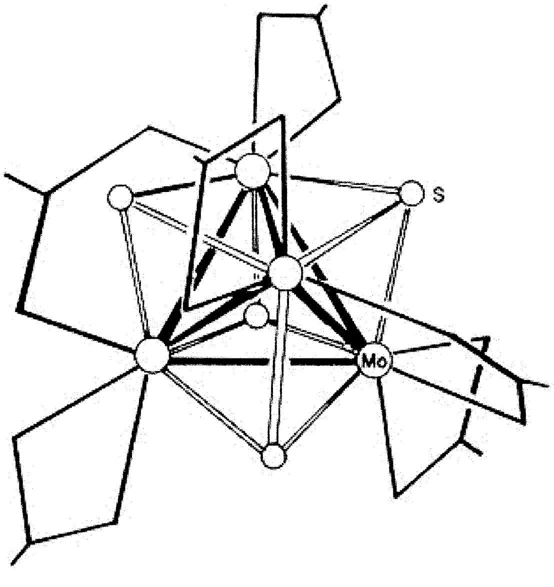


Fig. 3. The crystal structure of $Mo_4(\mu_3\text{-}S)_4(Et_2dtc)_6$ [46,47].

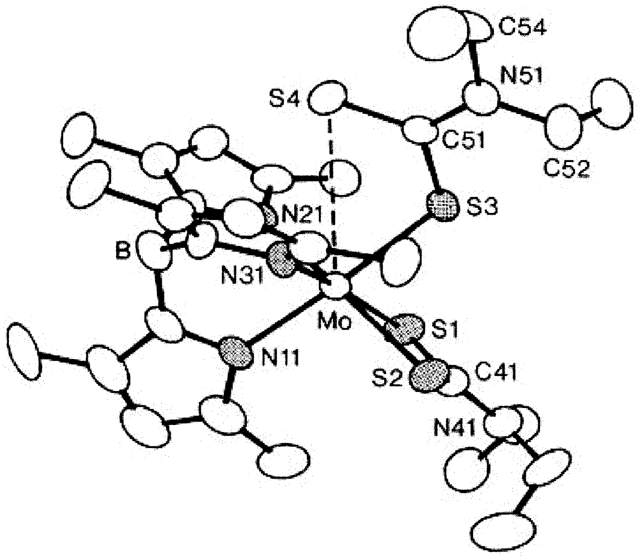


Fig. 4. A view of the structure of [{HB(Me_2pz)$_3$}Mo(μ_2-Me_2dtc)(μ_1-Me_2dtc)] [49,50].

molybdenum complexes (vide supra), both the tris and tetrakis tungsten series may be prepared by oxidative photochemical decarbonylation of [(η^6-C_7H_8)W(CO)$_3$] with R_4tds (R = Et, ^{n}Pr, ^{n}Bu; R_2 = pentamethylene) or by thermal oxidative decarbonylation with R_4tds (R = Et; R_2 = pentamethylene). In the photochemical experiments, the nature of the products depends only on the molar ratio of the reactants,

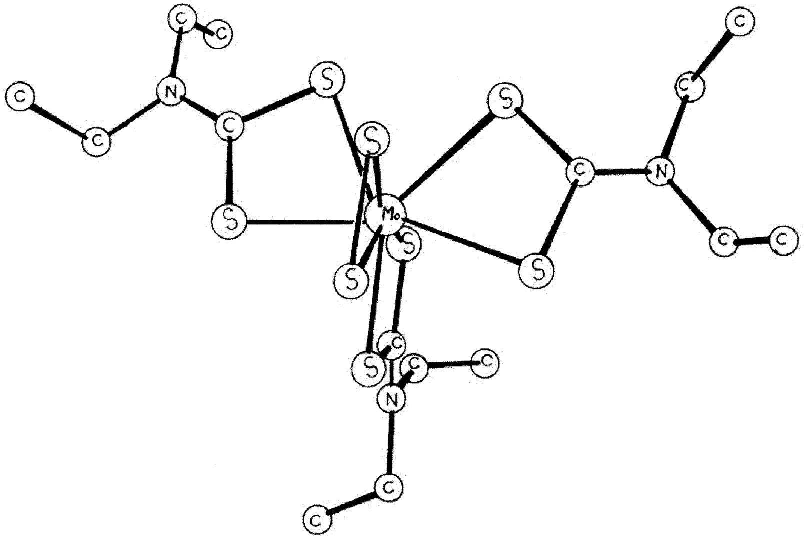


Fig. 5. The monomer [Mo(S_2)(dtc)$_3$] [51,52].

while in the thermal processes not only must the molar ratio be carefully adjusted but rigorous exclusion of light is also essential to obtain the tris complex.

Reaction of the anion WS_4^{2-} with R_4tds (R = Et, ^{i}Bu) produces $WS(S_2)(dtc)_2$ which displays a seven-coordinate tungsten atom, as revealed by the crystal structure determination (Fig. 6) [51,52].

Thiuram disulfides and $HB(Me_2pz)_3W(CO)_3$ have been reported [57] to afford $HB(Me_2pz)_3W(CO)_2R_2dtc$ and $[HB(Me_2pz)_3W^{II}(CO)_2(\mu\text{-}S)W^{IV}(R_2dtc)_2$(thiocarboxamido)] ($HB(Me_2pz)_3$ = 3,5-dimethylpyrazol-1-yl borate). Other products arising from this extremely complicated reaction are $W(R_2dtc)_4^+$ and $HB(Me_2pz)_3$-$W(S)R_2dtc$ [58].

3.5. Manganese, technetium and rhenium

No reports have appeared relating thiuram disulfides and manganese or technetium compounds, while only two papers refer to rhenium chemistry.

The oxidative decarbonylation of $Re(CO)_5Cl$ was attempted with Et_4tds. The main product was the diamagnetic monomer $Re(CO)_2(dtc)_3$ which contains chelated dithiocarbamate ligands. In addition $[Re(dtc)_4]^+[Re(CO)_3Cl(dtc)]^-$, characterized by polarography, was obtained [59]. Treating solutions of the ionic compound with $^n Bu_4NCl$ or $NaBF_4$ afforded, respectively, the salts $[Re(dtc)_4]^+BF_4^-$ and $^n Bu_4N^+$ $[Re(CO)_3Cl(dtc)]^-$. The same article describes the reaction of $ReCl_4(PPh_3)_2$ with Et_4tds in benzene which leads to $[Re(dtc)_4]^+Cl^-$ and to the red crystalline paramagnetic $ReCl_2dtc$.

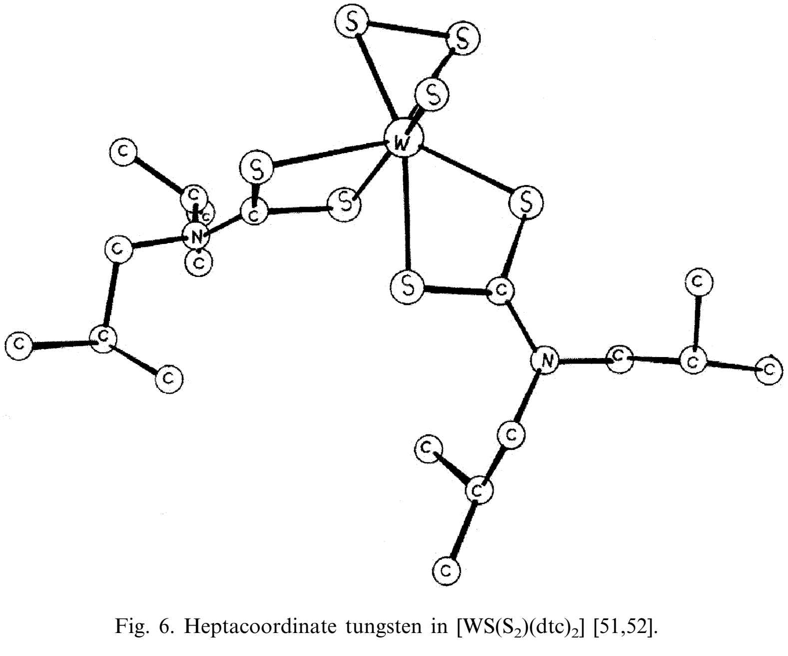


Fig. 6. Heptacoordinate tungsten in $[WS(S_2)(dtc)_2]$ [51,52].

$ReOX_3(PPh_3)_2$ reacts with R_4tds to give the series of complexes $ReOX(R_2dtc)_2$ (X = Cl, Br; R = Me, Et; R_2 = piperidyl) [60]. The same paper describes the reaction of $[Re(=NPh)Cl_3(PPh_3)_2]$ with Et_4tds in acetone to yield $[Re(=NPh)Cl(Et_2dtc)_2]$. The result is tantalizing since it involves *reduction* of the metal under *oxidizing* conditions.

3.6. Iron, ruthenium and osmium

Activity in this triad has been scant, with the appearance of only four reports published in fifty years. Iron(III) chloride and Et_4tds react in Et_2O to form preferentially $Fe(dtc)_2Cl$ and a product which was later shown to be a salt of the *bis-dialkyliminium-trithiolane* dication (see Section 4 on oxidation of the ligand for a discussion of this type of product) [61]. The same type of complex was isolated from the reaction of $FeCl_2$ or $FeCl_3$ with Me_4tms in refluxing ethanol [62].

Oxidative decarbonylation of iron carbonyls with bispentamethylenethiuram disulfide generated $(CO)_2Fe(dtc)_2$ [63]. Using a large excess of the disulfide resulted in the trisdithiocarbamate complex [64].

3.7. Cobalt, rhodium and iridium

The reaction of $CoCl_2$ with Me_4tms in boiling ethanol produces $Co(dtc)_3$ [62]. This is similar to the case of ferrous chloride in that it involves oxidation of the metal.

The complexes $(C_8H_{14})M(Et_2dtc)$ (M = Rh, Ir) undergo a two-electron oxidation with Et_4tds to give $Rh(dtc)_3$ and the interesting $(C_8H_{14})Ir(dtc)_3$. The latter contains both monodentate and bidentate dithiocarbamate ligands, and probably features hexacoordinate Ir. In the case of $(C_8H_{14})MCl$, oxidation leads to the dimer $[\{M(dtc)_2Cl\}_2]$ [65].

Formation of the thiocarboxamido ligand has been observed in reactions of thiuram monosulfides with the electron-rich system $RhCl(PPh_3)_3$ [66]. The result is similar to the one observed with low-valent Mo complexes (vide supra).

3.8. Nickel, palladium and platinum

Reaction of the complex $[Ni(^nBu_2dtc)_2X_2]$ with $^nBu_4$tds yields the octahedral $[Ni(dtc)_3]^+X^-$ species [13]. This is consistent with experiments of oxidation of $Ni(dtc)_3$ with Me_4tds in benzene which result in the dissappearance of the EPR signal due to the Ni(III) complex. Thus observation of a featureless spectrum is attributed to the formation of a Ni(IV) species [67].

The oxidizing ability of the disulfides is again shown in the reaction of $[Ni(EtXan)_2]$ with Et_4tds which gives a red–brown solution. The low temperature EPR spectrum of this solution consists of a single line, and is therefore attributed to the species $[Ni(EtXan)(Et_2dtc)_2]^+$ [68].

As with $FeCl_2$ and $CoCl_2$, Me_4tms reacts with $NiCl_2$ to give the Ni(II) dithiocarbamate [62]. In this case the metal ion is not oxidized.

The chemistry of the heavier members and thiuram sulfides has been the subject of two reports in this triad. The complexes $[MX_2(Bu_2dtc)_2]$ ($M = Pd$ or Pt; $X = Br$ or Cl) give $[MX(Bu_2dtc)_3]$ upon treatment with $^nBu_4tds$ [69].

$Pt(PPh_3)_3$ is said to insert into the C–S bond of Me_4tms, but no experimental details are available [6].

3.9. Copper, silver and gold

Oxidation of copper powder by carbon disulfide solutions of thiuram disulfides lead to dark solutions of $Cudtc_2$, which are reduced by excess metal to the cuprous Cudtc [70–72]. The crystal structure of the ethyl derivative features a tetrameric species $(CuEt_2dtc)_4$ where the copper atoms are arranged at the corners of a tetrahedron and all ligands are bidentate with singly bridging sulfur atoms [73]. While well defined bis adducts are formed with triphenylphosphine,other donors such as dimethylsulphoxide, triphenylarsine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine or tetramethylthiuram monosulfide have no effect on solutions of cuprous dithiocarbamates [72].

Addition of copper(II) halides CuX_2 to tetrahydrofuran solutions of thiuram disulfides generate dark purple–blue $R_2dtcCuBr_2$ or brown–red $R_2dtcCuCl_2$ ($R =$ Me, Et, ^iPr). The diamagnetic products are characterized by abnormally high C–N and Cu–S stretching frequencies in the IR spectra and by high values of the observed binding energies in the photoelectron spectra. All the data are consistent with a formulation incorporating copper(III). A single crystal structure determination shows planar $C_2NCS_2CuBr_2$ monomeric units featuring a distorted square planar environment about Cu, with Cu–S and Cu–Br distances, which are shorter than those found in related Cu(II) systems [74,75].

Dark green crystals of composition $[Cu_2Au(^nBu_2dtc)_6][HgBr_3]_2$ are isolated from the reaction of $[Cu(^nBu_2dtc)_2][HgBr_3]$ and $[Au(^nBu_2dtc)]_2$ in the presence of $^nBu_4tds$. The complex is isomorphous to $[Cu_2(^nBu_2dtc)_6][CdBr_3]_2$, of known structure. The structure of the new compound shows a set of M–S distances comparable to known Cu(III) and Au(III) dithiocarbamates [76].

Mixed valence dithiocarbamates of general formulation $Cu_2(R_2dtc)_3X_2$ ($X = Cl$ and Br, but not I;) have been isolated by admixing solutions of Cu(I) halides and thiuram disulfides in different organic solvents [53]. IR and PE spectra are indicative of Cu(II) and Cu(III) mixtures in 1:1 mole ratios. A tentative formulation $Cu^{III}dtc_2^+\ Cu^{II}dtcX_2^-$ is proposed [55]. Experiments performed with Me_4tds are more involved, since a variety of product compositions including CudtcCl, $Cu_4dtc_2Br_3$ and $Cu_3dtc_2Br_3$ are obtained. Based on magnetic data and spectral comparisons with known compounds, the following structures are respectively proposed. Dimeric, halogen bridged $Cu_2dtc_2Cl_2$, a polymeric network of $Cudtc_2$ and CuBr for $Cu_4dtc_2Br_3$ and ionic $Cudtc_2^+\ Cu_2Br_3^-$ [56].

Copper(I) bromide reacts with R_4tds ($R = Me$, Et, ^nPr and ^nBu) in the appropriate soichiometric ratios to yield the compounds $Cu_n(dtc)_2Br_n$ ($n = 2$, 4 and 6). From IR, ESCA and magnetic measurements, the presence of the Cu(III)-containing cation $[Cu(dtc)_2]^+$ is inferred. The complexes are formulated as $[Cu(dtc)_2]^+$-

$[Cu_{(n-1)}Br_n]^-$ [77,78]. Mixing equimolar ratios of the reactants leads to the series of complexes $Cu_2(dtc)_3X_2$ (R = Me, Et; X = Cl, Br, not all combinations) [78,79]. The crystal structure of $Cu_2(Et_2dtc)_3Br_2$ reveals chains of alternating $Cu(dtc)_2$ and $CuBr_2(dtc)$ units. The Cu–S bonds in the former are conspicuously shorter than those in the latter. Therefore the complexes seem to be better formulated as $[Cu(R_2dtc)]^+[CuX_2(R_2dtc)]^-$ [79].

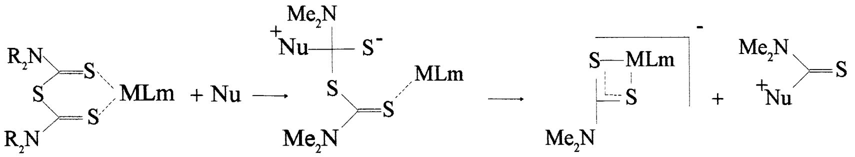
Reflux of copper(II) halides with Me_4tms in ethanol results in the formation of $Cu(dtc)_2$ [62]. However, at low temperatures these mixtures lead to the products $Cu(Me_4tms)X$ and trihalocuprate(I) of the bis-(dialkyliminium)trithiolane cation [9] (X = Cl, Br or I) (see previous section on adducts of Cu(I), and next one, on oxidation of the ligands). Solutions of complexes $Cu(Me_4tms)X$ indeed decompose to $Cu(Me_2dtc)_2$ upon standing [78], but $[Me_4bitt]^{2+}[CuBr_3]^{2-}$ has been shown [62] to degrade to $Cu(Me_2dtc)_2(CuBr)_3$.

Little work has been done on silver derivatives. The oxidation of $[Ag(^nBu_2dtc)]_6$ with $^nBu_4tds$ produces a dark red solution which is attributed to an Ag(III) complex. The color of the solution fades in minutes to blue, which is characteristic of Ag(II) dithiocarbamates [80].

Oxidation of $[Au(^nBu_2dtc)]$ with $^nBu_4tds$ leads to $Au(dtc)_3$. Alternatively, molecular bromine could be used as the oxidizing agent, in which case $[Au(dtc)_2]^+$ $[AuBr_2]^-$ is obtained. The latter reacts with $^nBu_4tds$ to give $[Au(dtc)_2Br]$, which could also be obtained from $AuBr_2^-$ and $^nBu_4tds$ [81].

3.10. Zinc, cadmium and mercury

As mentioned before, the Zn adduct $[I_2Zn(R_4tds)]$ reacts with one, two and three equivalents of triphenylphosphine to give $[I_2Zn(R_4tms)]$, $[Ph_3P(S)NMe_2]^+$ $[I_2Zn(Me_2dtc)]^-$ and $[Ph_3P(S)NMe_2]^+[I_3ZnPPh_3]^-$, respectively [14]. It is now clear, that rupture of the C–S bond is a consequence of the nucleophilic attack on the thiocarbamoyl carbon, by a suitable agent.

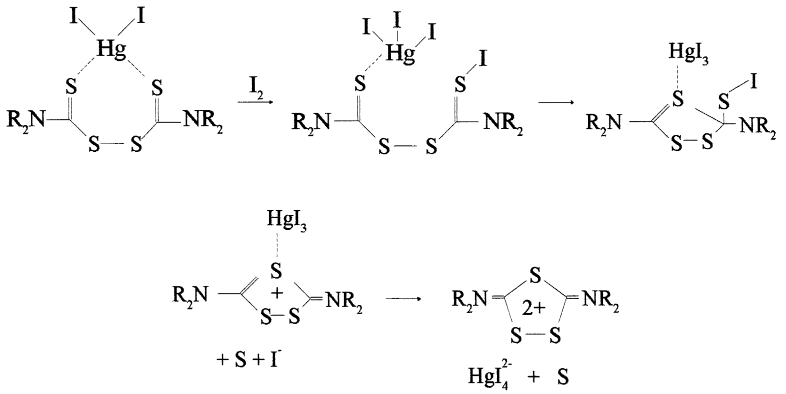


Reaction of Et_4tds with MeHgCl gives $Hg(dtc)_2$ and MeHg(dtc) [82]. The crystal structure of the latter reveals a two-coordinate mercury atom with a slightly bent C–Hg–S skeleton. In contrast, Et_4tds and HgI_2 give the dimer [IHg(dtc)], which contains four-coordinate mercury with two iodine bridges [83].

4. Ligand oxidation

Oxidation of metal dithiocarbamates may proceed further than the expected formation of thiuram disulfides, leading to the formation of cyclic five membered dications, usually stabilized by formation of anionic halogen complexes of the metal species. The mechanistic aspects of this oxidation are so far of a speculative nature and do not offer explanations as to the fate of the supernumerary sulfur atom (see scheme below). Reports dealing with this aspect of the chemistry of thiuram sulfides are as follows.

Iodine oxidation of $HgtdsI_2$ results in elimination of one sulfur atom and formation of the 3,5-bis(*N*,*N*-dialkyliminium)-1,2,4-trithiolane ($[R_4bitt\text{-}3]^{2+}$) dication refered to in the previous paragraph. This may come about through the ability of the thiocarbamoyl carbon to undergo nucleophilic attack by a suitable species. Sulfur elimination may then follow [84]. A single crystal structure determination has confirmed the nature of the resulting $[R_4bitt\text{-}3]^{2+}HgI_4^{2-}$ species [85].



Related systems are exemplified by the reaction of Et_4tds with $FeCl_3$ [61], which results in $[Et_4bitt\text{-}3]^{2+}2FeCl_4^-$, also accessible through halogen oxidation of $Fe(Et_2dtc)_3$ or $Fe(Et_2dtc)_2Cl$ [86]. A similar oxidation carried out on $Cu^I(Bu_2dtc)$ yields $[Bu_4bitt\text{-}3]^{2+}Cu_2X_6^{2-}$ ($X = Cl$, Br). In the absence of X-ray studies for these materials there seems to be a reasonable body of evidence based on IR spectroscopy, to support the structures proposed [86]. An interesting short lived species of formulation $[Et_4bitt\text{-}3]^{2+}2[Fe(Et_2dtc)_3]^-$ has been recently reported in a mass spectrometric study of oxidation products of $Fe(Et_2dtc)_3$ [87].

Formation of the $[R_4bitt\text{-}3]^{2+}$ cations is also apparent in reactions involving thiuram *mono*sulfides. Thus, oxidation of the ligand accounts for reduction of two equivalents of copper(II) during the reaction of copper(II) halides with R_4tms ($R = Me$, Et), where one of the products isolated corresponds to the trihalocuprate(I) dianion of the $[R_4bitt\text{-}3]^{2+}$ cation [9]. Other oxidizing agents used in the transformation of thiuram monosulfides to dialkyliminium trithiolanes have been $FeCl_3$ and solutions of halogens.

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