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1,1-DITHIOLATO COMPLEXES OF THE TRANSITION ELEMENTS

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I. Introduction

We have recently published an article[1] on 1,2-dithio ligands, and have stressed the versatility of these ligands and the academic and industrial importance of their metal complexes.

Dithio acids and dithiols are formed by reaction of carbon disulfide with various nucleophiles (Z^- or Z^{2-}), as follows.

Dithio acid

(I)

Dithiol

(II)

Metal ions react readily with (I) and (II) to yield complexes in which the two sulfur atoms are bound to the same metal, thus forming a four-

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[1] Burns, R. P., and McAuliffe, C. A., *Adv. Inorg. Chem. Radiochem.* **22**, (1979).

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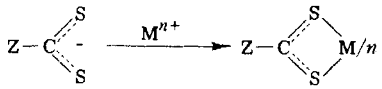
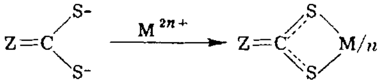
membered, chelate ring. A wide variety of ligands is thus available by





merely varying Z as shown in Table I.

Metal complexes of 1,1-dithiolates have been reviewed by Coucouvanis (*1*); Eisenberg (*2*) presented a systematic, structural review of dithiolato chelates, and Stokolosa *et al.* (*3*) reviewed dithiophosphate complexes in detail. Earlier reviews (*4–8*) covered less recent work in greater detail. Following initial work by Delepine (*9*), 1,1-dithiolato complexes were more intensively studied between 1930 and 1941 (*10–16*). There is, however, continuous interest in the synthesis, characterization, electronic structures, and bonding of these complexes.

II. The Ligands

Table I outlines the major types of 1,1-dithiolato ligands. Table IA shows the related dithio acid complexes derived from dithiophosphinic, dithiocacodylic (dithioarsinic), dithioarsenate, and dithiophosphoric acids. The complexes most intensively studied to date are those of the dithiocarbamates and dithiophosphates.

(a) N,N'-Disubstituted Dithiocarbamates

When carbon disulfide reacts with either aliphatic or aromatic, primary or secondary amines, dithiocarbamate salts are formed (*8, 9*). The following is an example.

$$2\ R_2NH + CS_2 \rightarrow [R_2NH_2]^+[R_2NCSS]^-$$

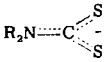
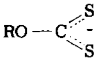
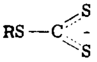
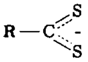
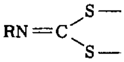
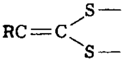
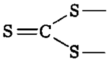
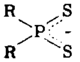
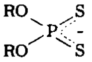
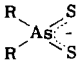
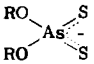
By using an alkali-metal hydroxide *in situ* as a proton acceptor, the alkali-metal dithiocarbamate salts, having various degrees of hydration, may be obtained (*17*).

$$R_2NH + CS_2 + MOH \xrightarrow{H_2O} R_2NCS_2^-M^+ + H_2O$$

Due to instability in air, very few free dithiocarbamic acids have been isolated (*18*). Dithiocarbamates derived from primary amines are

TABLE I

MAJOR TYPES OF 1,1-DITHIOLATO LIGANDS

Ligand	Name	Abbreviation
	Dithiocarbamate	R_2dtc
	Xanthates	RXant
	Thioxanthate	RSxant
	Dithiocarboxylate	
	Dithiocarbimate	
	1,1-Ethenedithiolate	
	Trithiocarbonate	
	Dithiophosphinate	dtp
	Dithiophosphate	
	Dithioarsinate	
	Dithioarsenate	

unstable, and, in the presence of base, are converted into the isothiocyanates (*19*). Disubstituted dithiocarbamates are more stable, but they decompose under acidic conditions (*20*). Thioformamides and quaternary ammonium dithiocarbamates have been obtained by heating a mixture of sulfur and formaldehyde in ethanol–water at 80° (*21*).

(b) O-Alkyldithiocarbonates (Xanthates)

The name xanthate, derived from the Greek "xanthos" (meaning blond), was coined by Zeiss in 1815, because the copper complexes that he isolated had a characteristic yellow color (*22*). Xanthates are formed by nucleophilic addition of an alkoxide ion to carbon disulfide.

$$M^+RO^- + CS_2 \longrightarrow RO{-}CS_2^- \; M^+$$

(M = an alkali metal)

Many alkali-metal xanthates are formed by direct xanthation of alcohols (*23*), but their chemistry is still vague. Acidification of the alkali-metal salts produces the unstable xanthic acids (*24*).

(c) Alkyltrithiocarbonates (Thioxanthates)

The alkali-metal salts of the thioxanthates are formed by a method analogous to that used for xanthates. Alkali-metal mercaptides react with carbon disulfide to form thioxanthate salts (*25*)

$$M^+RS^- + CS_2 \xrightarrow{THF} M^+RSCS_2^-$$

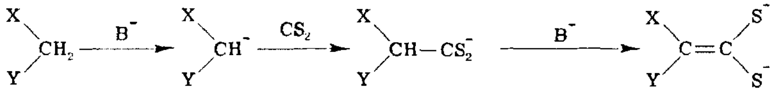
where THF = tetrahydrofuran. Air oxidizes these salts to disulfides (*26*). Unstable thioxanthic acids are formed upon acidification.

(d) Dithiocarboxylic Acids

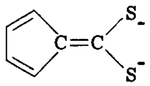
These are strong, unstable acids. Oxidation to disulfides takes place readily. Several methods have been used to prepare the dithio acids (*1*), the most useful of which is the reaction of CS_2 with a Grignard reagent (*27*).

(e) 1,1-Ethenedithiolates

In the presence of base, bifunctional CH acids, CH_2XY, react with CS_2 to form a dithio acid or a 1,1-ethenedithiolate. The formation of the latter depends on the electron-withdrawing nature of X and Y, and the base used. The proposed mechanism is as follows.



Examples of X and Y include CO_2Me, CO_2Et, CN, H, NO_2, Ph, COMe, and ROC (*1*). A novel 1,1-dithiolate has been synthesized.



Such weakly basic nucleophiles as $(CN)_3C^-$ or $(NO_2)_3C^-$ will not react with CS_2 (*28*). Jensen and Hendriksen reported syntheses, reactions, and IR, NMR, and electronic spectra of 1,1-ethendithiols and their derivatives (*29*).

(*f*) *Trithiocarbonates*

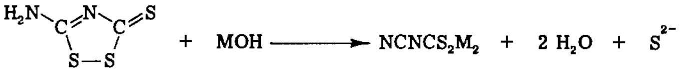
Trithiocarbonates were reviewed by Reid (*18*) and Drager and Gattow (*30*). Reaction of S^{2-} and S_2^{2-} with CS_2 produces CS_3^{2-} and CS_4^{2-}, respectively. Air-sensitive Na_2CS_3 has been obtained by reaction of CS_2 with aqueous sodium hydroxide.

$$CS_2 + 2\ NaOH \rightarrow Na_2CS_2O + H_2O$$

$$3\ Na_2CS_2O \rightarrow 2\ Na_2CS_3 + Na_2CO_3$$

(*g*) *Dithiocarbimates*

Little is known about the chemistry of dithiocarbimates. The cyanodithiocarbimate salts $(NCNCS_2)^{2-}$ are the most extensively studied to date (*31*–*34*). They are obtained by the reaction of xanthine hydrase with a base (*35*).



where M = a Group I metal. The calcium salt, $NCNCS_2Ca$, has been prepared by the action of calcium cyanamide on CS_2 in water (*36*).

III. Transition-Metal Complexes

The literature concerning the chemistry of transition-metal complexes containing 1,1-dithiolato ligands was extensively reviewed, up to 1968, by Coucouvanis (*1*). We attempt here to update that excellent account.

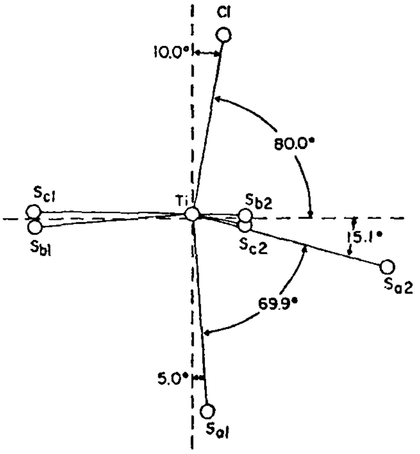
A. TITANIUM, ZIRCONIUM, AND HAFNIUM

Relatively few complexes of the early transition metals with 1,1-dithiolato ligands have been prepared and characterized. This is consistent with their classification as "hard" or "class a" acceptors. Thus, there is little tendency to form complexes with "soft" sulfur-donor ligands. There has been a limited number of complexes synthesized either by modifying the nature of the metal ion or by using novel, preparative methods (*37*).

To date, the only bidentate 1,1-dithiolato ligands present in complexes of titanium, zirconium, and hafnium have been the *N,N′*-dialkyldithiocarbamates and the 2-alkylxanthates. As early as 1934, Dermer and Fernelius (*38*) reacted dibenzylamine and dibutylamine with carbon disulfide and $TiCl_3$ *in situ,* to produce yellow solids, $[Ti(R_2CNS_2)_4]$ ($R = C_4H_9$ and Bz). The formulas of the products suggested that the dithiocarbamate ion forms in solution. However, as successful reactions of dithiocarbamate salts with simple titanium salts do not appear to have been reported, an alternative explanation may be hypothesized, namely, the formation of $Ti(R_2N)_4$ *in situ,* followed by CS_2 insertion. This may be a more feasible explanation, as Bradley and co-workers (*37, 39, 40*) produced a series of tetrakis(dithiocarbamates) of Ti(IV), Zr(IV), and Hf(IV) by an insertion reaction of CS_2 with the $M(NR_2)_4$ complexes. Crystal-structure (*41*) and spectroscopic studies (*42*) indicated an 8-coordinate, dodecahedral structure for $[Ti(Et_2dtc)_4]$. Kirnickev (*43*) reported the formation of brown $[Ti(Me_2NCS_2)_2(Me_2N)]$ and $[Ti(Me_2NCS_2)(Me_sN)Cl_2]$ by a similar reaction. The carbon disulfide insertion-reaction has also been used to prepare a whole series of first-row transition-metal complexes of morpholine-4-carbodithioate (*44*).

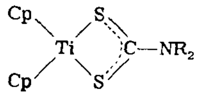
Straightforward addition of anhydrous sodium dithiocarbamate to titanium(IV) chloride in refluxing dichloromethane produces a series of complexes $[Ti(S_2CNR_2)_nCl_{4-n}]$ (n = 2, 3, or 4; R = Me, *i*-Pr, *i*-Bu, or, when n = 3, Et) (*45, 46*). Molecular weight, conductance, and infrared-spectral data indicated that the complexes are monomeric nonelectrolytes containing bidentate dithiocarbamate ligands. The titanium atom has been assigned the coordination numbers of 6, 7, and 8 when n = 2, 3, and 4, respectively. Previously, the existence of 7-coordinate titanium(IV) had been postulated for only a few complexes (*47*). An X-ray diffraction study of $[Ti(S_2CNMe_2)_3Cl]$ revealed that the titanium has, indeed, a 7-coordinate, pentagonal, bipyramidal structure (*48*) (**III**). Dipole-moment measurements indicated that the 6-coordinate $[Ti(S_2CNR_2)_2Cl_2]$ complexes have cis configurations. The small "bites" and low charge of the dithiocarbamate ligands are especially suited for stabilization of higher coordination numbers in complexes with first-row transition-metals.

Modification of the acceptor properties of the metal atom may be achieved by using complexes containing π-cyclopentadienyl ligands.

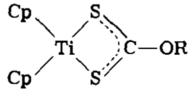


Thus, a series of bis-cyclopentadienetitanium(III) dithiocarbamate and xanthate complexes have been prepared by Coutts *et al.* (*49–51*) by reaction of the sodium salts of the ligands with [Cp_2Ti]Cl (Cp = π-cyclopentadiene) in air-free water under an inert atmosphere; the dithiocarbamate complexes are bright-green, and the xanthates are blue.

Both types of complex are extremely air-sensitive and are paramagnetic, with one unpaired electron per titanium atom. Their formulation as monomeric, symmetrical, bidentate, chelate complexes, (**IV**) and (**V**), has been established from spectral, magnetic, and molecular-weight data.



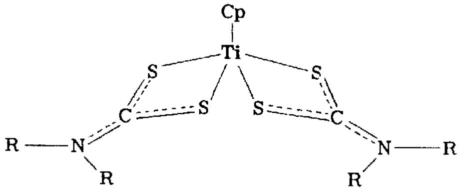
(IV)



(V)

Coutts and Wailes (*52, 53*) synthesized a series of 5-coordinate, monocyclopentadiene dithiocarbamate complexes of titanium(III) and titanium(IV), [$CpTi(S_2CNR_2)_2$] (R = Me, Et, or Pr), prepared by ligand-exchange reactions between $CpTiCl_2$ and $Na(S_2CNR_2)$. Infrared spectra and molecular-weight data suggested (*52*) structure (**VI**). $CpTiX_2$

(X =Cl or Br) are oxidized by thiuram disulfides, $R_2NC(S)S\text{-}SC(S)NR_2$



(VI)

(R =Me, Et, *n*-Bu), to monomeric, orange-red dithiocarbamates, $[CpTi(S_2CNR_2)X_2]$, which contain 5-coordinate titanium. It should be noted that several isomeric structures are possible for these compounds.

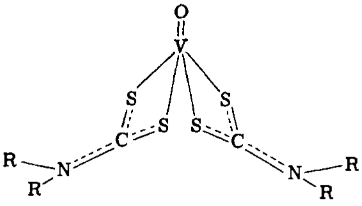
B. VANADIUM, NIOBIUM, AND TANTALUM

Until recently, there was little published material dealing with the chemistry of the Group V triad. This agrees with their classification as "class a" metal ions. Using new synthetic routes similar to those for the preparation of the titanium complexes, however, a number of V(III), V(IV), V(VI), Nb(IV), Nb(V), Ta(IV), and Ta(V) complexes have been prepared (*54*).

The first report of a group V metal complex containing 1,1-dithiolato ligands was (*55*) of the unstable $[V(Et_2dtc)_2(NO)]$, and following this, the majority of work was centered on the VO_2^{2+}–*N*,*N*′-dialkyldithiocarbamate systems. The monomeric $[VO(R^1R^2dtc)_2]$ ($R^1 = R^2$ =Me, Et, Pr^i, or pyrrolidine) complexes were prepared by McCormick (*56*, *57*). Similar complexes (R =piperidine, R^1 =Me, R^2 =cyclohexyl, $R^1 = R^2$ =cyclohexyl) were prepared by Vigee and Selbin (*58*). Following an epr study on the oxovanadium(IV) dithiocarbamate complexes, however, McCormick *et al.* (*59*), after rigorously excluding oxygen during spectral measurement, found poor agreement with the previous spectral results, but reasonable agreement with those of Garif'yanov and Kozyrev (*60*), who reported epr spectra of the diethyl complex in solution without isolation of the solid. Thus, the results of Vigee and Selbin (*58*) probably reflect air oxidation of the VO^{2+} species.

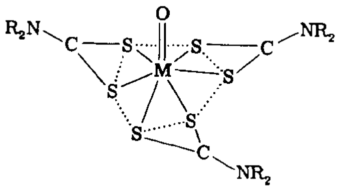
Of the 24 lines expected for coupling between ^{51}V (I =7/2) and two equivalent ^{13}C (I = ½) nuclei, 18 were resolved in the epr spectrum of $VO(S_2^{13}\ CNEt_2)_2$, showing that the C(2s) orbital can also participate in transannular interactions (*61*). $[Cp_2V(S_2CNEt_2)BF_4]$ and dithiophosphate have been used in an extension of studies on the C_{4v} oxovanadium(IV) chelates to yield C_{2v} bis(cyclopentadienyl) complexes.

Transannular interaction via the electron-delocalization mechanism was found, but lessened by ~10–15% for the ligand superhyperfine splitting and 30–35% for the ^{51}V hyperfine splitting (*62*) in the epr spectrum. The crystal structure of $[VOS_2CNEt_2)_2]$ shows that the molecular core has the expected C_{2v} symmetry [V–O = 159.1(4), V–S = 138.7(2)–241.0(2) pm] (*63*). Magnetic and spectral data provided evidence for a tetragonal, pyramidal structure (**VII**) for these complexes. Like many other coordinatively unsaturated, metal



(VII)

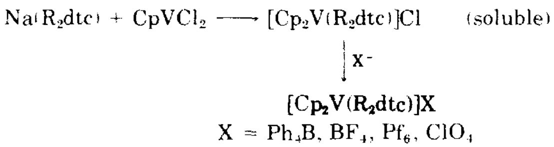
dithio complexes, $[VO(R_2dtc)_2]$ can undergo reaction with a Lewis base, and thus expand its coordination number. There is usually a correlation between the electronic properties of the ligands, and the ability to undergo Lewis base addition. Pyridine and 4-methylpyridine adducts of $[VO(R_2dtc)_2]$ have been isolated and characterized as solids (*64*). Attempts to isolate dimethylsulfoxide adducts failed, although spectral evidence suggests adduct formation in solution. Hoyer *et al.* (*65*) have synthesized $(Bu_4N)[VO\{S_2C{=}C(CN)_2\}_2]$ by reaction of $VOSO{\cdot}4H_2O$ and the ligand in methanol/water. This was the first report of a 1,1-ethendithiolato complex of vanadium. Vanadium oxo-complexes containing vanadium(III), (IV), (V) have been reported (*42*, 66, 67); $[V(III)OL{\cdot}H_2O]$, $[V(IV)OL_2]$, and $[V(V)O_2L]$ (HL = 3- and 5-phenyl and 3,5-diphenyl-pyrazolinedithiocarbamic acid were separated chromatographically (*66*), and $[VC(R_2dtc)_3]$ and $[NbO(R_2dtc)_3]$ have been prepared by reaction of sodium *N,N′*-dialkyldithiocarbamates with a metal oxo-salt (*57, 67*). X-Ray diffraction studies on the last two compounds showed (*68*) the environments of the metals to be 7-coordinate, pentagonal bipyramids (**VIII**). The



(VIII)

ability of VO^{2+} to form complexes with the sulfur ligands suggests that the double-bonded oxygen atom lessens the effective "hardness" of the V(IV) species. This modification has also been achieved by using π-bonded cyclopentadiene ligands in a manner analogous to that used for titanium. Thus, a series of green *N,N'*-dialkyldithiocarbamate complexes were prepared (*69*) by using the following routes.

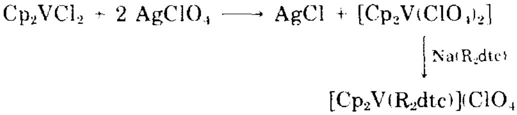
(1)



$$\begin{tikzcd} \text{Na(R}_2\text{dtc)} + \text{CpVCl}_2 \arrow[r] & {[\text{Cp}_2\text{V(R}_2\text{dtc)]Cl}} \arrow[d, "X^-"] & \text{(soluble)} \\ & {[\text{Cp}_2\text{V(R}_2\text{dtc)]X}} & \end{tikzcd}$$

$X = Ph_4B, BF_4, Pf_6, ClO_4$

(2)



$$\begin{tikzcd} \text{Cp}_2\text{VCl}_2 + 2\ \text{AgClO}_4 \arrow[r] & \text{AgCl} + {[\text{Cp}_2\text{V(ClO}_4)_2]} \arrow[d, "\text{Na(R}_2\text{dtc)}"] \\ & {[\text{Cp}_2\text{V(R}_2\text{dtc)](ClO}_4)} \end{tikzcd}$$

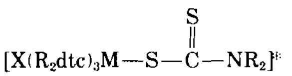
The first xanthates of V(IV), $[Cp_2V(Rxanth)]$ (R = Me, Et, Pr^i, or Bu), isolated as purple solids were prepared by the same method (*71*). Kwoka *et al.* (*70*) were able to obtain an alkylenebis(dithiocarbamate) vanadyl complex, $VO[S_2CNH(CH_2)_nNHCS_2]$ for $n = 2$, but not for $n = 6$.

In the Me_2dtc complex, a unique, 15-line, epr spectrum was reported (*69*) that was peculiar only to the tetraphenylborate salt. This suggests a V–V interaction in the lattice. Electrochemical studies on these $[Cp_2VL]^+$ complexes (L = dithiocarboxylato ligand) shows two well defined, polarographic, reduction waves, and, for the process at most positive potential, the reversible formation of a V(III) species was postulated (*72–74*).

The pure vanadium(IV) dialkyldithiocarbamates, $[V(R_2dtc)_4]$, have been prepared (*75*) by using a method analogous to that used for the titanium analogs, i.e., CS_2 insertion into the V–N bonds in $[V(NR_2)_4]$. Physical studies indicated a dodecahedral, 8-coordinate, vanadium system (*76–78*). Infrared spectra of freshly prepared, and aged, compounds suggested a tetrachelated species with bidentate dithiocarbamates, and a species having unidentate ligands, respectively (*79*). Isomerism of this type had not previously been reported.

Recently, several papers have appeared that report the isolation of stable complexes of vanadium(IV) with dithiocarboxylato ligands (*77, 80*). Dithiocarboxylato salts ($PhCS_2^-$, $p\text{-}CH_3C_6H_4CS_2^-$, $CH_3CS_2^-$, $PhCH_2CS_2^-$) react with both VO^{2+} and V(III) species, to give stable VL_4 species. Magnetic, molecular-weight, and electronic, infrared- and epr-spectral data are consistent with 8-coordinate vanadium(IV) and a VS_8 chromophore. X-Ray crystallographic studies (*78,* *81, 82*) confirmed this, and the structures approximate to dodecahedra with D_{2d} geometry. In the case of $V(MeCS_2)_4$, however, two different stereoisomers belonging to the dodecahedral subclasses 1d (symmetry D_{2d} and Vd (symmetry C_2) have been recognized (*82*).

Few complexes of niobium and tantalum with bidentate sulfur ligands have been reported, even though dithiocarbamates have been used for the determination of these metals (*83, 84*), [Nb(pyrroldtc)$_3$] was reported by Malissa and Kolbe-Rhode (*85*), and CS_2-insertion reactions with [Nb(NR$_2$)$_5$] and [Ta(NR$_2$)$_5$] result (*86*) in the reduction of Nb(V) to [Nb(R$_2$dtc)$_4$], and formation of [Ta(R$_2$dtc)$_5$]. Reaction of niobium tetrahalides with dithiocarbamato salts in a suitable solvent, such as acetonitrile, usually result in the formation of the 8-coordinate [Nb(R$_2$dtc)$_4$] complexes (*54, 87–89*). Using $TaCl_5$, the same reaction produced [Ta(R$_2$dtc)$_5$]; infrared spectra indicated the presence of one or more unidentate dithiocarbamate ligands in the complex (*54, 89*). From the reaction of niobium(V) and tantalum(V) halides and thiocyanates with sodium *N,N'*-dialkyldithiocarbamates in methanol, air-stable yellow, or white, crystals of [MX(OMe)$_2$(R$_2$dtc)$_2$] (X = Cl, Br, or NCS; R = Me, Et, or Bz) were isolated (*90*). X-Ray crystallographic studies on the niobium compounds showed that they are pentagonal bipyramids (*91*). Uvatova *et al.* (*92*) isolated two cationic complexes of niobium, [Nb(CH$_2$)$_4$NCS$_2$]$_4$ClO$_4$, and the corresponding pyrrolidine dithiocarbamate derivative, by reaction in the presence of ClO_4^- in acidic media. Holah *et al.* (*93, 94*) found that reaction of the metal pentahalides with Na(R$_2$dtc) in benzene and dichloromethane produced a new series of air-sensitive, substituted complexes of the type M(R$_2$dtc)$_3$X$_2$, M(R$_2$dtc)$_3$S, M(R$_2$dtc)$_2$X$_3$, and M(R$_2$dtc)$_2$X$_3$·nC$_6$H$_6$ (n = 0.7–1.0). The reaction scheme is depicted in Scheme 1.
It was proposed that the formation of the sulfur-rich species M(R$_2$dtc)$_3$S takes place via the activated complex

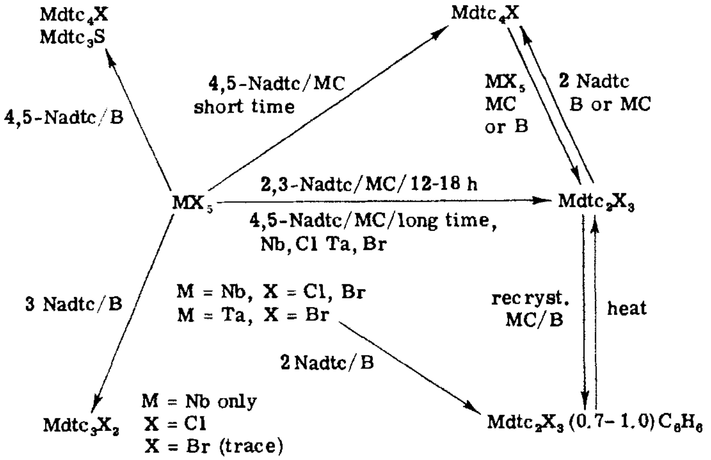


$$[X(R_2dtc)_3M{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NR_2]^{\ddagger}$$

and it was suggested that the structure is [(R$_2$dtc)$_3$M=S]. It may, however, be possible that the product is similar to the sulfur-rich, perthio complexes previously isolated in complexes of other metals (*356–362, 439*).

C. Chromium, Molybdenum, and Tungsten

Many complexes containing the octahedral CrS_6 chromophore are known (*95*). The early preparative work was performed by Delepine (*96*) and Malatesta (*97*), who synthesized various chromium(III) dial-



SCHEME 1. Summary of reactions between $NbCl_5$, $NbBr_5$, and $TaBr_5$ and Nadtc, B = benzene, MC = dichloromethane; all NbX_5/Nadtc B reactions also produce $Nbdtc_4$ (not shown), all MX_5/Nadtc/MC reactions also produce dtc_2CH_2 (not shown).

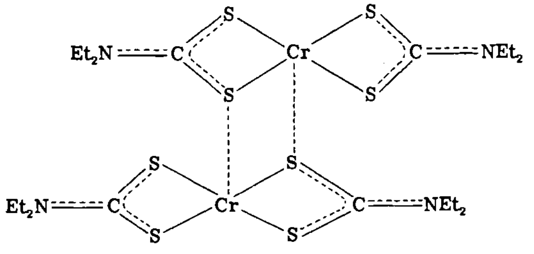
kyldithiocarbamates by using the straightforward reaction of an anhydrous chromium(III) salt with the ligand in a dry, organic solvent under acidic conditions (optimum pH, 5–6). Only $[Cr(Et_2dtc)_3]$ (*1, 85, 98, 99*) and $[Cr(piperydyldtc)_3]$ (*100*) have been systematically characterized. The $[Cr(R_2dtc)_3]$ complexes are violet in color, and contain three unpaired electrons; the general properties are consistent with an octahedral CrS_6 chromphore (*100*). The infrared characteristics of uni- and bidentate dtc have been discussed (*101*) on the basis of a normal coordinate analysis of $[Cr(Et_2dtc)_3]$.

From the reaction of the tetraalkylthiuram disulfides with $CrCl_3$ in absolute ethanol $[Cr(R_4tds)_2Cl_2]Cl$ were (*102, 103*) isolated (R = Me, or Et; tds = tetraalkylthiuram disulfide). Bradley *et al.* (*104*) showed that CS_2 insertion into metal dialkyl amides produces $[Cr(Et_2dtc)_3]$ in solution, but the complex was not isolated as a solid. The stereochemical rigidity of *N,N*-disubstituted dithiocarbamate complexes $[Cr(R^1R^2dtc)_3]$ has been established by ^{1}H-NMR in $CHCl_3$ solution at temperatures up to 357 K. The relative rates of rearrangement by a trigonal, twist mechanism (resulting in optical inversion) have been established for a series of tervalent metal ions, and the order is (*105*) Ga, In, V > Mn > Cr.

Blue $[Cr(Rxant)_3]$ (R = Me, Et, or L-menthyl) complexes have been prepared and characterized (*103, 106, 107*), and these complexes, together with some of the dialkyldithiocarbamate complexes, show spin-forbidden transitions, $^2E \leftarrow {}^4A_2$, $^2T_1 \leftarrow {}^4A_2$, and $^4T_2 \leftarrow {}^4A_2$, the last two respectively giving rise to phosphorescence and fluorescence (*108*). The [Cr(RSxanth)$_3$] (R = Et, Pr, or Bu) thioxanthate complexes, Cr(III) complexes of dithiocarboxylic acids [Cr(PhCS$_2$)$_3$], and [Cr(PhCH$_2$CS$_2$)$_3$], have been synthesized and characterized (*109–111*).

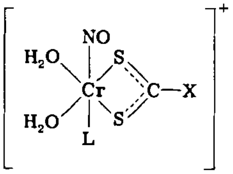
Only a few 1,1-dithiolate complexes of chromium(III) are known: [Pr$_4$N]$_3$[Cr(S$_2$C=C(CN)$_2$]$_3$ is formed as a green-brown solid by reaction of the ligand with a Cr(III) salt (*112*). The [Bu$_4$N]$_3$[Cr(S$_2$C=CHNO$_2$)$_3$] complex is similarly prepared, and both complexes have been shown to be effective insecticides (*113*). Recently, in a general study of trithiocarbonato complexes, [Cr(CS$_3$)$_3$]$^{3-}$ was isolated as its Ph$_4$P$^+$ and Ph$_4$As$^+$ salts (*114*).

Reaction of CrCl$_2$·2H$_2$O and anhydrous sodium diethyldithiocarbamate in water produces a bright-yellow-green solid, [Cr(Et$_2$dtc)$_2$], that is pyrophoric in air (*115*). X-Ray data show the complex to be isomorphous with Mn(II), Fe(II), and Zn(II) diethyldithiocarbamates. Solutions of [Cr(Et$_2$dtc)$_2$] can be oxidized to Cr(III) in air. These results, together with magnetic (the complex shows antiferromagnetic behavior) (*116*) and reflectance spectral data, indicated a CrS$_5$ donor grouping, i.e., square-pyramidal coordination of 5 sulfur atoms about each chromium atom in a dimeric unit (**IX**).



(IX)

A number of cationic Cr(I) species of the type depicted have been



[X = OEt, or NEt$_2$;
L = AsR$_2$Ph, or PR$_3$ (R = Me, Et, Pr, or Bu), (EtO)$_2$PPh, EtOPPh$_2$, Et$_2$POEt, EtP(SEt)$_2$, P(SEt)$_3$, Et$_2$P(SPh), EtP(SPh)Ph, py, NH$_3$, hydroxylamine or ethylenediamine]

formed in solution by reaction of $[Cr(NO)(H_2O)_3(S_2CX)]$ with the particular Lewis base, and studied by epr spectroscopy (*117–121*).

The dinitrosyl $[Cr(NO)_2(Et_2dtc)_2]$ was isolated as an air-stable solid by Malatesta (*15, 16*), and by Connelly and Dahl (*122*), from the following reaction.

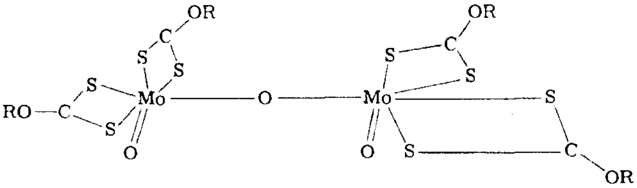
$$[Cr(NO)_2(MeCN)_4](PF_6)_2 \xrightarrow{As(Et_2dtc)_3} cis\text{-}[Cr(NO)_2(Et_2dtc)_2]$$

IR-spectral data indicated that the dinitrosyl has a cis conformation (*123*).

The complexes $[Cr_2(S_2CNH(C_2H_4)CNHCS_2)]$ and $[Cr_2(S_2CNH(C_6H_{12})CNHCS_2)]$ have been synthesized by the action of solutions of the appropriate ligand in aqueous ethanol on aqueous ethanol solutions of Cr(III). The magnetic susceptibilities of these purple, amorphous compounds fit the Curie–Weiss law with very small, negative values of θ, implying the presence of weak, antiferromagnetic interactions between the metal centers (*70*). Chromium(III) complexes $[Cr(R_2dtc)_3]$ have been isolated that contain the appropriate ligand and chromium acetate, and their temperature-dependent, ^{1}H-NMR spectra have been examined (*124*).

Complexes of molybdenum and tungsten with bidentate sulfur ligands have been investigated extensively. In recent years, the work in this field has been escalated by the impetus of designing models of such bioinorganic enzymes as nitrogenase and xanthine oxidase (*125*). The early work reviewed by Coucouvanis (*1*) dealt exclusively with the isolation of oxomolybdenum(V) and -(VI) species.

The dithiocarbamates form a series of oxomolybdenum complexes $[MoO_2(R_2dtc)_2]$ and $[Mo_2O_3(R_2dtc)_4]$. The xanthates, however, only form $[Mo_2O_3(Rxanth)_4]$. The structure of the latter complexes (*126*) is shown in (**X**).



(**X**)

The two Mo=O bonds are disposed in a mutually cis orientation, and it is now considered that this is the only stable orientation for this type of species.

Synthesis of $[Mo_2O_3(Rxanth)_4]$ and $[Mo_2O_3(R_2dtc)_4]$ was achieved by reduction of MoO_4^{2-} with SO_2 or sodium dithionite in the presence of

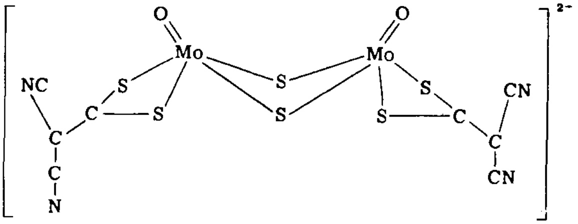
NaR_2dtc (*97*), and the synthesis, and electronic, IR-, and proton-NMR spectra of the compounds $[MoO(RXant)_2](R{=}Pr^i,Bu^t)$ have been reported. The crystal structures of $[MoO(Pr^iXant)_2]$ shows the molecule to be a pseudo-square-pyramidal monomer, with one thioxanthate group exhibiting the usual bidentate geometry, whereas the second thioxanthate group displays unusual, nonclassic coordination, with the Mo significantly displaced from the S_2CS plane (*127*). An interesting reaction takes place between $Mo_2O_3(Rxant)_4$ and H_2S, or thiols, in benzene. The products are $[MoS_2(Rxant)]$ and $[MoS(R'S)(Rxant)]$, respectively, and it was suggested that they consist of molecular associations; $[MoOS(Bu_2dtc)]_2$ was prepared by treating $[MoO_2(Bu^n_2dtc)_2]$ in the same way (*128*). Compounds of this type, and other oxomolybdenum dithiocarbamates, have been used as effective, extreme-pressure agents, antioxidants, and wear-inhibitors for lubricants (*129, 130*).

None of the earlier methods for the syntheses of $[Mo_2O_3(R_2dtc)_4]$ were wholly satisfactory, as they tended to produce mixtures. An epr study of $[Mo_2O_3(R_2dtc)_4]$ indicated the existence of two (presumably, sterically different) complexes in $CHCl_3$ solution, and this has been interpreted in terms of complicated redox mechanisms in solution (*131*). A recent innovation (*132*) produces pure $[Mo_2O_3(R_2dtc)_4]$ by reaction of an aqueous solution of molybdenum(V) with NaR_2dtc (greater than 4 molar excess) at 0°. If the reaction is conducted under reflux, however, a new complex, $[Mo_2O_4(R_2dtc)_2]$, can be isolated; it may be converted into the former complex by further reaction with $Na(R_2dtc)$. The interrelationship and chemistry of these two complexes, and of the reactions of $[Mo_2O_3(R_2dtc)_4]$ with carboxylic acids and pyridine (*1, 132*), suggest a possible model for the interaction of two molybdenum atoms at an active enzymic site. A similar, revised route was to produce pure μ-oxo-bis[bis(alkylxanthate)oxomolybdenum(V)], $[Mo_2O_3(ROCS_2)_4]$, complexes (*133*) that react with alcohols, or H_2S, with loss of a xanthate ligand to produce a new series of di-μ-sulfido-bis(alkylxanthate)oxomolybdenum(V), $[Mo_2O_2S_2(ROCS_2)_2]$. Casey et al. (*67*) reported the formation of $[Mo_2O_3(R_2dtc)_4]$ and $[MoO_2(R_2dtc)_2]$ from NaR_2dtc and Mo(V) salts. Both hydrogen chloride and hydrogen bromide react (*134*) with $[MoO(R_2dtc)_2]$ to produce 6-coordinate Mo^{IV} species $[MoX_2(R_2dtc)_2]$. Reactions of $[MoO(Et_2dtc)_2]$, including abstraction of an oxygen atom from various substrates to form $[MoO_2(Et_2dtc)_2]$ and $[Mo_2O_3(Et_2dtc)_4]$, have been studied in detail by Mitchell and Searle (*135*), and some of these compounds, $[MoO_2(R^1_2dtc)_2]$ (R^1 = Me, Et, or Ph), react (*136*) with phenyl-, methyl-, and benzoylhydrazine, to form $[R^2N{=}N{-}Mo(R^1_2dtc)_3]$. However, the analogous reactions with Me_2NNH_2 do not result in reduction giving the Mo^{VI} compounds, [MoO(N=NMe$_2$)(R$_2$dtc)$_2$]. The ubiquitous [MoO$_2$(R$_3$dtc)$_2$] reacts with concentrated hydrohalogenic acids, to yield novel compounds [MoOX$_2$(R$_2$dtc)] (X = F, Cl, Br; R = Me, Et, Pr^n), and the crystal structure of [MoOCl$_2$(Et$_2$dtc)$_2$] confirmed 7-coordination (*137*).

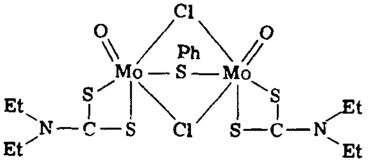
A series of oxomolybdenumdipropyldithiocarbamates has been structurally characterized by X-ray studies (*138*); [MoO$_2$(Pr$_2$dtc)$_2$] has a distorted, octahedral structure with cis-oxo groups, whereas [MoO(Pr$_2$dtc)$_2$]O has a similar structure, with a single, bridging oxygen atom linking the two units; and [MoO(Pr$_2$dtc)$_2$] is square-pyramidal, with oxygen at the apex. The crystal structure of [MoO(Et$_2$dtc)$_3$]Mo$_2$O$_4$F$_6$ shows that the [MoO(Et$_2$dtc)$_3$]$^+$ cation has a distorted, pentagonal, bipyramidal geometry about the molybdenum (*436*).

The similarly structured 5-phenyl-1-pyrazoline dithiocarbamate complexes were prepared, separated chromatographically, and characterized by epr and IR spectroscopy (*139*). Workers in the USSR found that reaction of MoO^{3+} with NaR$_2$dtc (NaL) in concentrated hydrohalic acids results in the formation of the halo-substituted complexes *cis*-MoOXL$_2$, MoOL$_3$, MoOBr$_2$L(LNa), and MoOCl$_2$L, the structures of which were established from epr data (*140*). The oxomolybdenum(IV) complexes [MoO(Et$_2$dtc)$_2$] have been prepared by reduction of [Mo$_2$O$_3$(Et$_2$dtc)$_4$] with benzenethiol, sodium dithionite, or Zn dust (*131*). Physical measurements indicated that the complex has square-pyramidal geometry, similar to that of the analogous, vanadyl complex (**VII**). It appears that oxomolybdenum(IV) is preferentially stabilized by sulfur donors.

The crystal structure of di-μ-oxodioxobis(diethyldithiocarbamate)dimolybdenum(V) has been determined, and the Mo–Mo distance is (*141*) 258.0(1) pm. The related sulfur compound, di-μ-sulfidodithiobis(dibutyldithiocarbamato)dimolybdenum(V), [Mo$_2$S$_4$(Bu$_2^n$dtc)], has a similar structure (*142*) with the Mo atoms separated by 280.1(2) pm. This is one of the few examples where Mo is bonded to terminal sulfur. The compounds tetrabutylammonium di-μ-sulfidobis(oxo-1,1-dicyanoethylene-2,2-dithiolato)molybdenum(V) (*143*) (**Xa**) and μ-oxo-μ-sulfidobis[oxodipropylthiocarbamatomolybdenum(V)] (*144*) represent examples of the ability of sulfur to occupy bridging positions having the "cis-bent" geometry, the dihedral angle between the two basal planes of the pseudo-square-pyramidal molybdenum atoms being ~150°. Treatment of [MoO$_2$(μ-O$_2$(Et$_2$dtc)$_2$] with benzenethiol leads to the formation of the salt [Mo$_2$O$_2$(μ-SPh)$_2$—(μ-Cl)—(Et$_2$dtc)$_2$] [MoOCl$_4$-(H$_2$O)], which has been shown by X-ray diffraction to have a triply bridged, dinuclear cation (**Xb**) and a mononuclear anion (*145*).

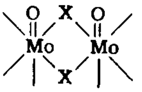


(Xa)



(Xb)

Sulfur ligands appear to be particularly adept at replacing oxygen ligands. Treatment of $[MoO_2(Pr^n_2dtc)_2]$ with H_2S produces the disulfur complex $[MoO(S_2)(Pr^n_2dtc)_2]$ in low yields, with other products of the reactions being compounds of the type shown in **Xc**, where X = S (*146*). In seeking an alternative route to



(Xc)

this disulfur complex, $[(Mo(CO)_2(Et_2dtc)_2]$ was treated with S_8, followed by oxidation with air, which produced small yields of the desired product, the main product being $[Mo(S_2O)(Et_2dtc)_2]_2$, in which S_2O ligands bridge the two metals (*146*). Treatment of $[Mo_2O_2(\mu\text{-}O)_2\text{-}(Pr^n_2dtc)_2]$ with H_2S in chloroform also gives $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)\text{-}(Pr^n_2dtc)_2]$, whereas in 1,2-dichloroethane at 80°C or by using P_4S_{10} in boiling xyline, all the oxide groups of the starting complex are replaced by sulfur, yielding $[Mo_2S_2(\mu\text{-}S)_2(Pr^n_2dtc)_2]$. Three-atom-bridged complexes similar to **Xb** result if 2-mercaptoethanol, *o*-mercaptobenzoic acid, *o*-mercaptophenol (1 mol), or *N*-methylaminobenzenethiol are used as reactants, and when *o*-mercaptophenol (2 mol) is used, complete cleavage of the di-μ-oxo-bridge occurs, giving $[MoO(o\text{-}C_6H_4OS)\text{-}(Pr^n_2dtc)_2]$. An excess of *o*-mercaptobenzene removes the oxide ligand completely to give $[Mo(o\text{-}C_6H_4XS)_2(Pr^n_2dtc)_2]$ (X = S, NH, or NMe) (*147*). Tertiary phosphines react with *cis*-$[MoO_2L_2]$(L = R_2dtc or R_2dtp) to give the complexes $[MoOL_2]$ (*148*). Thiophenol in the presence of [MoO-

$(R_2dtc)_2]$ reacts with diethyl azodicarboxylate, azobenzene, or dimethyl acetylenedicarboxylate to give the appropriate hydrazine and disulfide (*149*).

An exciting discovery of recent years has been the liquid-phase activation of molecular oxygen by $MoOCl_4$ and $[MoO_2(R_2dtc)_2]$ (R = Et, Pr^n, Bu^i) (*150–152*). These complexes catalyze selective oxidation of PBu_3 to $P(OBu)_3$. McDonald and Shulman (*153*) reported that the reduction of a large excess of $[MoO_2(Et_2dtc)_2]$ by PPh_3 in benzene solution provided a sensitive and accurate method for the determination of small quantities of PPh_3 by spectrophotometric assessment of $[Mo_2O_3(Et_2dtc)_4]$ produced in the reaction sequence as follows.

$$[MoO_2(R_2dtc) + PR'_3 \rightarrow [MoO(R_2dtc)_2] + PR'_3O \quad (1)$$

$$[MoO(R_2dtc)_2] + [MoO_2(R_2dtc)] \rightarrow [Mo_2O_3(R_2dtc)_4] \quad (2)$$

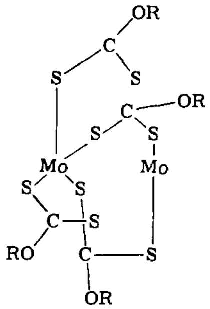
The kinetics of the oxygen-transfer reaction from $[MoO_2(Et_2dtc)_2]$ to PPh_3 in MeCN solution have been monitored (*154*) by using stop-flow techniques at temperatures lying between 15 and 45°. The reactivity of coordinatively unsaturated oxo-Mo(IV) species towards a variety of multiple bonds has recently been recognized (*155*), and 1:1 adducts with several organic molecules and $[MoO(R_2dtc)_2]$ have been isolated. Thus, tetracyanoethylene (TCNE) oxidatively adds to $[MoO(Pr^n_2dtc)_2]$ to form a deformed, pentagonal, bipyramidal complex (*156*), $[MoO(Pr^n_2dtc)_2(TCNE)]$, in which TCNE is considered to act as a bidentate ligand with considerable π-back donation from the metal, as reflected by the C═C and Mo—C distance of 228.5 and 147.3 pm, respectively (*156*).

The unsubstituted complexes $[Mo(R_2dtc)_4]$ and $[W(R_2dtc)_4]$ have been prepared by methods described earlier for synthesis of the vanadium-group complexes. They are 8-coordinate, with four bidentate dithiocarbamate ligands (*157*).

The 8-coordinate species $[Mo(Et_2dtc)_4]$ can be obtained by reaction of $Mo(CO)_6$ with tetraethylthiuram disulfide (1:2) in acetone under N_2. The X-ray structure revealed square-antiprismatic coordination, with a crystallographic, twofold axis coinciding with the molecular pseudo $\bar{4}$ axis (*158*). The magnetism and spectra of $[M(dtc)_4]^{n+}$ (M = Mo or W; $n = 0$ or 1) have been interpreted in terms of dodecahedral symmetry (*159*).

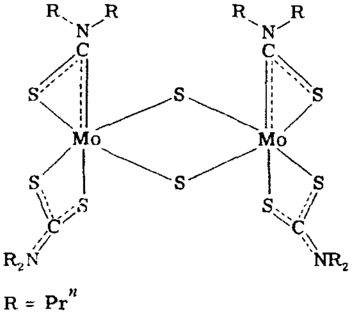
The complex $[Mo(Et_2dtc)_3]$ has been prepared (*160*) by reacting $Na(Et_2dtc)$ with $[Mo_2O_2Cl_2(H_2O)_6]$, having been previously prepared by reacting $Mo(CO)_4$ with tetraethylthiuram disulfide (*161*). The ionic halide complexes $[Mo(Me_2dtc)_4]X$ (X = Br, Br_3, I, I_3, or I_7) are produced by oxidation of $[Mo(R_2dtc)_4]$ with the appropriate halogen (*162*). The analogous series of Et_2dtc complexes, [Mo(Et_2dtc)$_4$]X (X = Cl, Br, I, or I_3) and [Mo(Et_2dtc)$_4$]X$CHCl_3$ (X = B, or I) have also been prepared (*163*). One of the syntheses provides the 7-coordinate complex [MoO(Et_2dtc)$_2Br_2$] [Et_2NH_2]. [Et_2dtc] in MeCN cleaves the Mo═O bond in $MoOCl_3$, to form the 8-coordinate complex [Mo(Et_2dtc)$_4$]Cl, which was converted into the BPh_4^- salt by treatment with $NaBPh_4$ (*164*). The electrochemistry of several of these Mo^V, as well as Mo^{IV} and Mo^{VI}, complexes of Et_2dtc has been studied in DMSO, DMF, and MeCN (*165*). A tungsten(V) analog [W(Et_2dtc)$_4$]Br has been shown by X-ray crystallography to involve an 8-coordinate, trigonal, dodecahedral WS_8 moiety (*166*). Very recently, several 8-coordinate, dodecahedrally structured complexes of molybdenum(IV) were synthesized (*167*); this was the first report of dithioaromatic or dithioaliphatic complexes of molybdenum. Electronic spectra revealed a higher degree of covalency in the metal-ligand bond than is found in any other 8-coordinate molybdenum(IV) species. The 6-coordinate [Et_4N]$_2$[Mo(CPDT)$_2$] (CPDT = cyclopentadienedithiocarboxylate) was obtained by reaction of the sodium dithiocarboxylate with $MoCl_4$ and Et_4NBr in MeCN (*168*).

Complexes of molybdenum in the lower valence-states of + 2 and + 3 have been produced only in the past two years. For the Mo(II) species, the usual starting-material is Mo_2(acetate)$_4$. Reaction of this with KS_2COEt in THF gives two products, a green complex tentatively assigned as [Mo_2(Etxant)$_4$], which solvates to form the red complex [Mo_2(Etxant)$_4$(THF)$_2$]. The structure of the latter complex was elucidated by X-ray analysis (*169*). Steele and Stephenson (*170*) were also able to synthesize a red, crystalline solid (methanol solution), which they formulated as [Mo(Etxant)$_2$]$_2$ (**XI**), and reacted this with Lewis bases, e.g., pyridine, to form [Mo(Etxant)$_2$L]$_2$. Thus, there appears to be a difference between the two compounds formulated as [Mo_2(Etxant)$_2$]$_2$ that



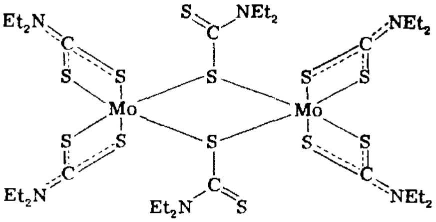
(XI)

may be due to two structurally different species. Molybdenum(II) dithiocarbamates have also been isolated (*171, 176*). The $[Mo(R_2dtc_2)_2]_n$ complex is formed as a green precipitate by using the reaction described previously with an excess of NaR_2dtc. In ethanol solution, or on standing in very dilute methanol, green solids, also of formula $[Mo(R_2dtc)_2]_n$, are obtained that have more-complicated NMR spectra than the previous complex; $[Mo(Pr^n_2dtc)_2]_2$ has been shown by X-ray structure determinations (*171*) to have the structure shown in **XII**.



(XII)

This structure contains a very short Mo–C bond (206.9 pm) that has been attributed to a carbene type of bond. A report of a Mo(III) species with dithiocarbamate ligands used $[Mo_2O_2Cl_2(H_2O)_6]$ as the starting material, and the product was $[Mo(Et_2dtc)_3]_2$ (*172*). This complex had previously been reported by Brown et al. (*173*). The structure was formulated as in **XIII**, with two bridging dithiocarbamate ligands (*172*). Butcher et al. (*174*) have shown that the electrochemical reduction of $[MoO(R_2dtc)]$ occurs in two steps via a Mo^{IV} intermediate, while treatment of this complex with Cl_2 or Br_2 affords the 7-coordinate species $[MoOX_2(R_2dtc)]$. Willemse et al. (*175*) recently tried to prepare these compounds by using the procedure reported by Brown *et al.* (*173*), but were only able to isolate $[Mo(R_2dtc)_4]$ despite exertion of considerable care and effort.



(XIII)

There has been great interest in molybdenum and tungsten nitrosyl and carbonyl dithiolate complexes; this has resulted mainly from interest in bioinorganic analogs and in organometallic derivatives. Thus, $Mo(CO)_3(Et_2dtc)_2$ and $Mo(CO)_2(Et_2dtc)_2$ constitute facile CO-carrying systems (*176*). When $[Mo(CO)_3)PPh_3)Cl_2]$ reacted with NaR_2dtc, it produced $[Mo(CO)_2(PPh_3)(R_2dtc)_2]$, oxidation of which gives molybdenum(VI) derivatives of empirical formula $[MoO_2(R_2dtc)_2]$, the properties of which differ from those reported earlier for compounds of the same formula (*177*).

Very few tungsten complexes with dithiolato ligands are known, although $[\pi\text{-}CpW(CO)_2(R_2dtc)]$ (R = Me, Et, or pip) have been prepared from $[\pi\text{-}CpW(CO)_3Cl]$ with NaR_2dtc (*178*) and $[Sn(Me)_3(R_2dtc)]$ (*179*). The 7-coordinate complex $[W(CO)_3(PPh_3)Et_2dtc)_2]$ reacts with $[Mo_2O_3\{S_2P(OEt)_2\}_4]$ to yield the 5-coordinate species $[WO(Et_2dtc)_2]$ (*180*). The complexes $[M(CO)_2(PPh_3)L_2]$ [M = Mo, W; L = R_2dtc, MeXant, $(EtO)_2PS_2$] have been prepared by a halide replacement-reaction of $[M(CO)_3(PPh_3)_2Cl_2]$ with the appropriate ligand. The routine synthesis of the tungsten complex was made possible by the development of an improved method of preparation of $[W(CO)_3(PPh_3)_2Cl_2]$ (*181*). Tungsten and molybdenum mono- and dinitrosyl complexes with dithiocarbamate (*182–188*) and 1,1-dicyano-2,2-dithiolate (*186, 188*) have been studied extensively in recent years. The cyclopentadiene rings in $[Mo(C_5H_5)_2(NO)(Me_2dtc)]$ and $[Ph_4P][Mo(C_5H_5)_2(NO)(i\text{-}mnt)]$ show fluxional behavior at various temperatures as detected by NMR (*186*).

Several fluxional allylnitrosyl complexes of Mo, including $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(C_3H_5)(S_2CNMe_2)]$ and $[(\eta^5\text{-}C_5H_5)Mo(NO)(C_3H_5)(S_2CNMe_2)]$ have been studied, and crystal structures obtained (*188*). $[Mo(Bu^n_2dtc)_3(NO)]$ contains 7-coordinate molybdenum and has a pentagonal, bipyramidal structure (*189*).

The cationic nitrosyl complexes $[M(NO)(CO)_3diphos)]PF_6$ (M = Mo, or W) react with NaX salts (X = halide, S_2CNMe_2, or S_2CNEt_2) to form the corresponding $[M(NO)(CO)_2(diphos)X]$ derivative (*183*). With phosphine ligands (L) in $CHCl_3$, $[M(NO)(CO)L(diphos)Cl]$ is obtained, but, in acetone, $[M(NO)(CO)_2L_2(diphos)](PF_6)(acetone)$ and $[M(NO)(CO)(diphos)_2]PF_6$ are formed (*183*). The synthesis and ^1H- and ^{13}C-NMR-spectral behavior, over a temperature range, of $[Mo(\eta^5\text{-}C_5H_5)(6\text{-}C_5H_5)(NO)(R_2dtc)]$(R = Me or Bu^n) have very recently been reported (*190*). An unusual μ-nitrido complex has been reported, $[Mo_3(N)_2(Etdtc)_9]^+$, which may be formulated as $[(dtc)_2Mo^{VI}{\equiv}NMo^{VI}(dtc)_3 \leftarrow N{\equiv}Mo^{VI}(dtc)_3]^{3+}$ because of the asymmetric Mo–N distances (*191*). An intermediate complex containing a nitrene is formed when dry HCl is reacted with $[Mo(Etdtc)_2(N_3)(Me_2SO)(NO)]$ to yield ammonia (*160*).

D. MANGANESE, TECHNETIUM, AND RHENIUM

The ease of oxidation of manganese(II) to manganese(III) in the dithiocarbamate complexes prevented early workers from isolating a pure $[Mn(R_2dtc)_2]$ complex. Using rigorous deoxygenation techniques and an inert atmosphere, Fackler and Holah (*115*) isolated the yellow $[Mn(Et_2dtc)_2]$ by reaction of $NaEt_2dtc$ with $MnCl_2$ in water. The complex is isomorphous with the divalent Cu, Zn, Fe, and Cr analogs, and probably has the dimeric 5-coordinate, square-pyramidal structure (**VII**) described earlier. X-Ray powder photography of $[Mn(Et_2dtc)_2]$, prepared in an alcoholic medium, shows the compound to be isostructural with the square-planar nickel analog (*192*). Epr spectroscopy and low-temperature magnetic susceptibility indicate that the compound has a pure spin quartet ground-state. The synthesis and properties of some ethylxanthate complexes, $[Mn(Etxant)_2]$ and $[Mn(Etxant)_3]^-$, have been reported (*193*), and reaction of these with such Lewis bases as phenanthroline and 2,2′-bipyridine results in the formation of $Mn(base)_3(Etxant)_3$, which is similar to the nickel system (*194*). The inability to obtain epr spectra for the complexes $[Mn(Et_2dtc)_2]$ and $[Mn(Buxant)_2]$ is puzzling, and the stereochemistry is thus put in doubt (*195*). It is possible that oxidation had taken place in solution before, or during, the recording of the spectrum.

Manganese(III) complexes with dithiocarbamate ligands have been known, and studied frequently, since the early part of this century (*1*), and there is still interest in their physical properties. Deviations from octahedral symmetry in $[Mn(Et_2dtc)_3]$ are reflected in the electronic spectrum (*196*). This was confirmed by an X-ray structural study that showed that the $[MnS_6]$ chromophore exhibits a large distortion from D_3 point symmetry, and this was attributed to the ^5E electronic ground-state of the molecule, which would be expected to show a large Jahn–Teller distortion. Golding and Lehonen (*197*) showed that there is a simple relationship between the $-NCH_2-$ proton hyperfine interaction observed in the NMR spectra of ferric and manganic tris(dithiocarbamates) and the half-wave polarographic potential ($E_{1/2}$) of these complexes. From this, it was inferred that the redox processes for these compounds take place through the nitrogen atom. Electrochemical studies (*198, 199*) of the reaction of Mn^{n+} and R_2dtc in aprotic solvents established that the dithiocarbamate ligand forms tris-chelated complexes of manganese in three oxidation states, namely, II, III, and IV. Thus, $[Mn(R_2dtc)_3]$ undergoes single, one-electron, oxidation and reduction steps at a platinum electrode.

$$[Mn^{IV}(R_2dtc)_3]^+ + e^- \rightleftharpoons [Mn^{III}(R_2dtc)_3] \rightleftharpoons [Mn^{II}(R_2dtc)_3]^- - e^-$$

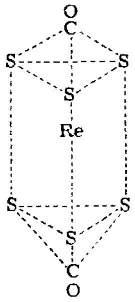
Titration of Mn^{2+} with pyrolidzyldithiocarbamate (R_2dtc) has been monitored by electrochemical means, and this showed (*200*) the existence of [Mn(R_2dtc)] and $[Mn(R_2dtc)]^-$.

Only a few cationic complexes of Mn(IV) are known (*201*). Saleh and Straub (*202*) bubbled BF_3 through a solution of $[Mn(R_2dtc)_3]$ in dichloromethane for five minutes, to produce $[Mn(R_2dtc)_3]BF_4$ complexes. Golding et al. (*203*) were able to isolate four explosive, air-sensitive $[Mn(R_2dtc)_3]ClO_4$ complexes (R_2 = Me_2, Et_2, pyridyl, or piperidyl) by reacting $[Mn(H_2O)_6](ClO_4)_2$ in acetone with $Mn(R_2dtc)_3$ in benzene. They also prepared the tetrafluoroborates in an analogous manner. Although the complexes were found to be difficult to study, the crystal and molecular structure of $[Mn(pipdtc)_3]ClO_4$ was determined. The manganese atom is surrounded (*203*) by three dithiocarbamate ligands in approximately D_3 symmetry.

Complexes of manganese with the 1,1-dithiolates have been restricted to the $(Pr^n_4N)_3[Mn(i\text{-mnt})_3]$ complex (*112*) and nitrosyl or carbonyl derivatives, e.g., $[\pi\text{-CpMn(NO)}(S_2C{=}X)]^-$ (X = C(CN)CO_2Et, C(CN)$CONH_2$, NCN, $C(CN)_2$, or (HNO_2) (*110, 204, 205*). These complexes undergo electrochemical, one-electron oxidations and reductions to afford the neutral or dianionic species.

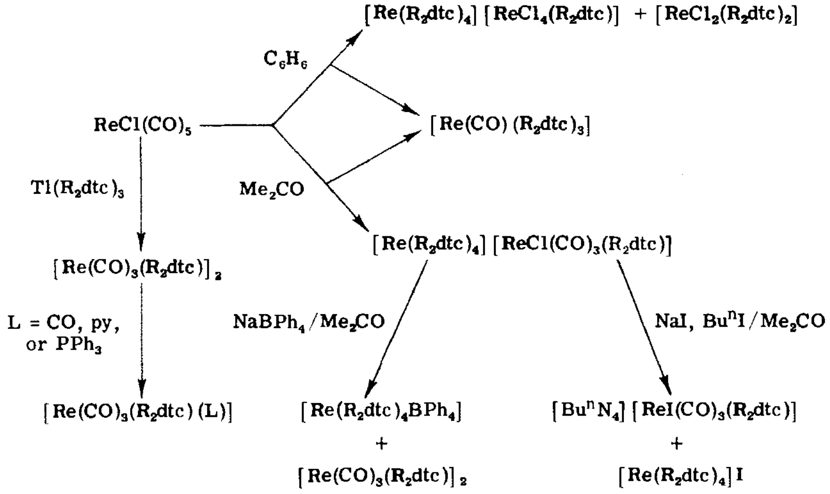
Manganese carbonyl complexes containing dithiocarbamate ligands have been synthesized by the method that Abel and Dunster (*179*) described earlier for tungsten complexes. A general method of preparing dithiocarboxylate complexes of the Group VII elements utilizes CS_2 insertion into M—R or M—H σ-bonds. Thus, the following complexes have been prepared by this method: $[M(CO)_4(RCS_2)]$ (M = Mn; R = Me, Ph, $p\text{-MeC}_6H_4$; M = Re; R = Me, Ph, $p\text{-MeC}_6H_4$, $p\text{-ClC}_6H_4$, Bz, or Ph_3C) (*206–208*) and $[Re(HCS_2)(CO)_2(phosphine)_{1,2}]$ (phosphine = PPh_3, diphos, dpm) (*209–211*). In the latter complexes, with bidentate phosphines, CS_2 insertion causes the phosphine to become monodentate. Treatment of $[Mn(CO)_5Br]$ with Me_2dtc^- produces $[Mn(CO)_4(Me_2dtc)]$, which can undergo (*200*) thermally induced dimerization to afford $[Mn(CO)_3Me_2dtc)_2]_2$.

Interest in the chemistry of rhenium with sulfur-containing ligands has increased in the past few years. In 1969, Hieber and Rohm (*213*) reacted $[Re(CO)_5Cl]$ with thiols, and thiocarboxylic and mercaptocarboxylic acids, and, among the products, they identified $[Re(CO)_3RS_2]_2$ complexes. Using the same starting material, Rowbottom and Wilkinson (*214*) isolated five dithiocarbamato derivatives from the reaction with tetraethylthiuram disulfide. The main product was the monomeric, diamagnetic $[Re(CO)_2(R_2dtc)_3]$, and its IR spectrum contained a single, carbonyl stretching-frequency at 1870 cm^{-1}, as well as the characteristic bands of chelated dithiocarbamate groups. The complex is very inert, and it was suggested that the molecular structure is that of rhenium(III) with a bicapped, trigonal, prismatic geometry (**XIV**).



(XIV)

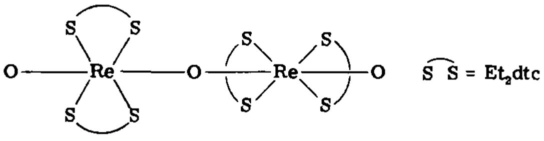
$[Re(Et_2dtc)_4]^+[Re(CO)_3Cl(R_2dtc)]^-$ was characterized, from the same reaction, by polarography. Subsequent work led to the isolation of numerous, interrelated rhenium dithiocarbamates (*215*) (see Scheme 2).



SCHEME 2

The structure of $[Re(Et_2)dtc_3(CO)]$ consists of monomeric Re with a distorted, pentagonal, bipyramidal geometry, having an axial CO group. This is the first, clear-cut example of monomeric 7-coordinate rhenium(III), as other examples usually involve Re–Re bonds (*216*).

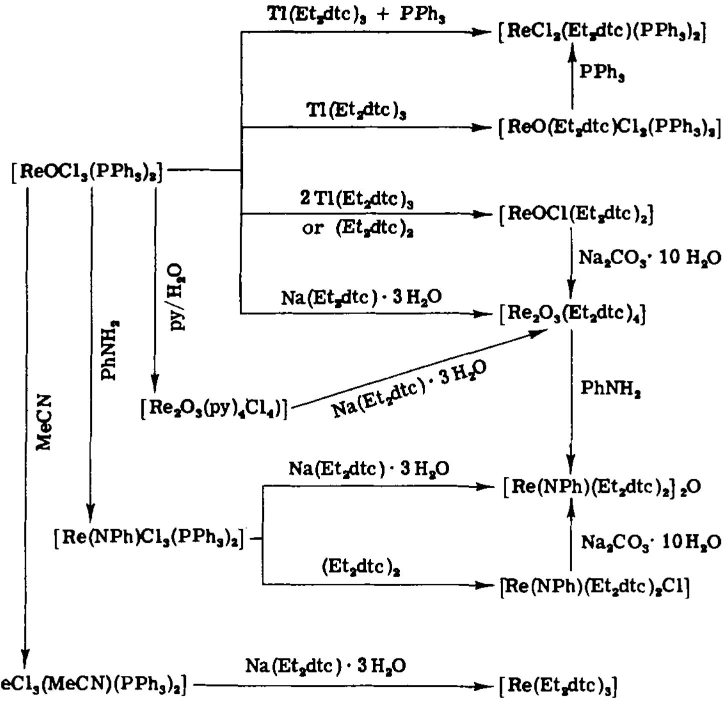
Oxorhenium complexes have appeared in a number of reports. Tisley et al. (*217*) produced orange-brown $[Re_2O_3(Et_2dtc)_4]$ from $[ReCl(PPh_3)_2]$, $[Re_2O_3py_4Cl_4]$, or $[Re_2O_2(CH_3)_4Cl_2]$ with $NaEt_2dtc$ in acetone. The almost linear O=Re–O–Re=O system has been identified by X-ray crystallography (*217, 218*) (**XV**).



(XV)

Rowbottom and Wilkinson (*219*) synthesized a series of new, and known, oxo-, chloro-, unsubstituted dithiocarbamates of Re(V) and Re(III) (see Scheme 3).

The only nitrido complex known is the square pyramidal $[ReN(Et_2dtc)_2]$, synthesized (*220*) from $[ReNCl_2(PPh_3)_2]$. The same structural type is suggested by epr for $[Mn(S_2CX)_2(NO)]$ (X = OEt, or NEt_2) and $[ReO(Et_2dtc)_2]$ (*221, 222*). An interesting series of novel dinitrogen complexes, $[Me_2PhP)_3(N_2)$-$(R_2dtc)Re]$, and their reactions with



SCHEME 3

hydrogen halides, have recently been studied as part of the design of models for nitrogenase (*223*).

The reaction of $[Re(CO)_5]^-$ with CS_2 and methyl iodide proceeds to give the trithiocarbonate derivatives $[Re(CO)_4S_2C(SMe)]$. When $[ReBr(CO)_5]$ is used instead of MeI, the dinuclear complex $[Re(CO)_4S_2CSRe(CO)_5]$ is isolated (*224*). The product of the reaction of $[CF_3Re(CO)_5]$ with CS_2 has been identified by X-ray crystallography (*225*) as the trithiocarbamato complex $[(OC)_4ReS_2CSRe(CO)_{4}{}_2SCS_2Re(CO)_4]$. The crystal structure of $[Re(PhCS_2)(CO)_4]$ confirmed the bidentate nature of the dithiocarboxylate group (*212*).

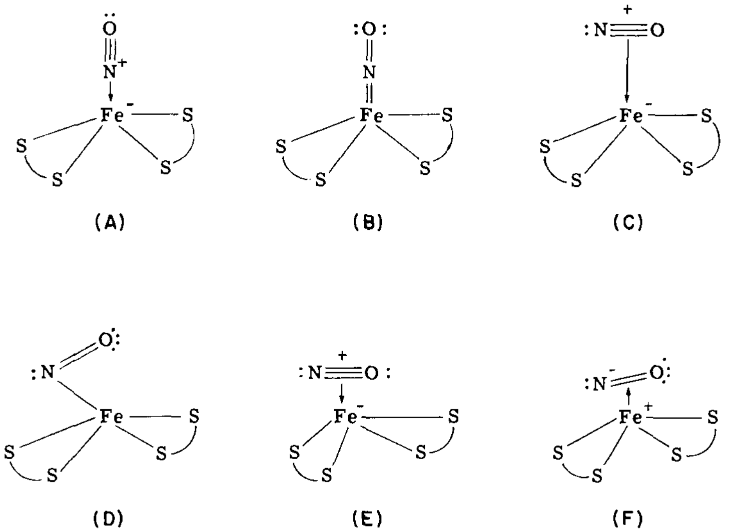
The only technetium complex has been reported (*226*) is $[Tc(CO)_4(R_2dtc)]$. There appear to be few reports of rhenium or technetium complexes with 1,1-dithiolato ligands.

E. IRON, RUTHENIUM, AND OSMIUM

The earlier literature containing work on 1,1-dithio complexes of iron has been covered in depth by Coucouvanis (*1*), and, since 1968, interest in these iron complexes has increased.

Ferrous complexes with the dithio ligands are difficult to isolate, as they are unstable to air oxidation (*227*). Magnetic susceptibility and Mössbauer spectral data (*227, 228*) show $[Fe(R_2NCS_2)]$ to be of two structural types: (*a*) intramolecular, antiferromagnetic dimers, e.g., $[Fe(Et_2dtc)_2]_2$ having each iron atom surrounded by five sulfur atoms, with square pyramidal geometry as in (**IX**); and (*b*) antiferromagnetic polymers, e.g., $[Fe(Me_2dtc)_2]_n$, believed to involve octahedral coordination about the metal (*227*). The crystal structures of a number of ferrous dithio complexes have been determined. These include (*229*) $[Fe(Et_2dtc)_2]$.

Although the bis(dithiocarbamate) complexes of Fe(II) are relatively unstable to air oxidation, early studies (*12, 15*) produced stable adducts of NO and CO. Both 5-coordinate $[Fe(NO)(R_2dtc)_2]$ and 6-coordinate $[Fe(NO)_2(R_2dtc)_2]$ complexes are known. There has been considerable interest in the mode of attachment of the NO molecule, as there are six possibilities (see Scheme 4). (**A**) and (**B**) represent valence-bond structures of the linear Fe–NO bond. Structure (**C**) involves a symmetric Fe–NO π-bond. Structure **D** illustrates the bent mode of attachment, in which nitrosyl is coordinated to the metal through the nitrogen atom, but the Fe–NO bond-angle differs greatly from 180°. Structures (**E**) and (**F**) are valence-bond formalisms of an unsymmetrical, metal–NO π-bond. The structure of $[Fe(NO)(R_2dtc)_2]$ (R = Me or Et) has been shown (*230, 231*) to be square pyramidal, with four sulfur atoms in



SCHEME 4

the basal plane. The nitrosyl is bonded through the nitrogen atom, and the length of the Fe–N bond in both compounds is ~170 pm, which indicates some multiple bonding. There is some controversy as to whether the Fe–NO group is linear, or bent. Infrared and ESCA studies have been reported (*232, 233*) for $[Fe(NO)(Me_2dtc)_2]$.

Buttner and Feltham (*234*) synthesized several new nitrosyl and carbonyl complexes of iron. These include *cis*-$[Fe(Et_2dtc)_2(I)(NO)]$, *cis*-$[Fe(Et_2dtc)_2(CO)_2]$, and the dimeric S-bridged species $[Fe(Et_2dtc)(CO)_2SCH_3]_2$. They also found that the compound previously identified as a dinitrosyl iron complex contains one NO group and one nitro group, $[Fe(Et_2dtc)_2(NO_2)(NO)]$. Cotton and McCleverty (*235*) prepared $[Fe(CO)_2(R_2dtc)_2]$ (R = Me, or Et) and $[(\pi\text{-}Cp)Fe(CO)(Me_2dtc)]$ by reacting NaR_2dtc with metal carbonyl halides, or by oxidation of metal carbonyls with tetraalkylthiocarbamoyl disulfides. The latter method was also used by Brennan and Bernal (*189*) and Bernal and co-workers (*236*) for the preparation of bis(cyclopentamethylenedithiocarbamate) Fe^{II} dicarbonyl. New dimeric carbonyls of iron dithiocarbamates were produced by Abel and Dunster (*179*).

Trivalent iron dithiocarbamate complexes have been extensively studied, because of the existence of "spin equilibria" in these complexes. Table II outlines the tris(1,1-dithiocarbamate) iron(III) complexes and, some of their physical properties.

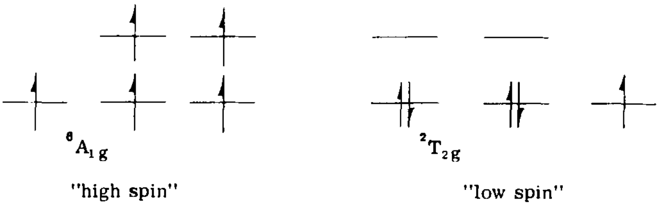
TABLE II

TRIS(N,N-DISUBSTITUTED DIALKYLDITHIOCARBAMATO)IRON(III) COMPLEXES

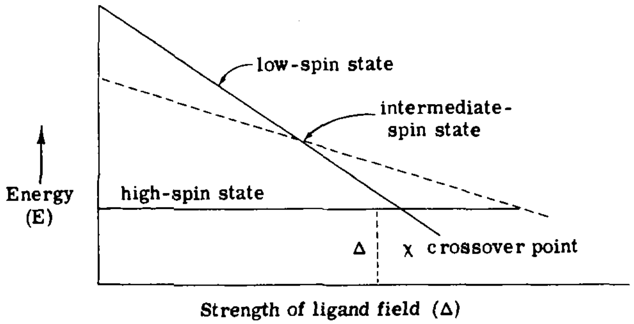
			μ_B →	
R^1	R^2	MP (°C)	Solid	Solution[a]
H	H			
Me	H			
Et	H			
Pr^n	H			
Bz	H			
Me	Me	300	4.17	4.20c
Et	Et	252–255	4.24	4.41c
Pr^n	Pr^n	167–168	4.48	4.24b
Pr^i	Pr^i	285–288	2.62	2.34b
Bu^n	Bu^n	146–151	5.32	4.34b
Bu^i	Bu^i	167–168	3.02	2.88cb
sec-Bu	*sec*-Bu	132		2.20cb
Amyl^n	Amyl^n	146–148		4.32cb
Amyl^i	Amyl^i	199–200	4.30	4.37b
Hexyl^n	Hexyl^n	164–166	3.52	4.42b
Heptyl^n	Heptyl^n			4.32b
Octyl^n	Octyl^n			
n-C$_{12}$H$_{25}$	n-C$_{12}$H$_{25}$			
n-C$_{16}$H$_{33}$	n-C$_{16}$H$_{33}$			
Bz	Bz	214–222	4.02	3.60b
Me	Ph	237–247	2.99	3.33c
Et	Ph	238–244	4.70	3.63c
Pr^n	Ph	212–214	4.68	3.55b
Pr^i	Ph			
Amyl^i	Ph	208–210	3.36	3.43b
Me	Bz			4.06cb
Et	Bz			4.22cb
Me	Bu^n			4.26cb
Et	Bu^n			4.40cb
Cyclopentyl	Cyclopentyl			
Cyclohexyl	Cyclohexyl	285–287	2.75	4.16c
Allyl	Allyl	106–107	4.40	4.34b
Piperidyl		284–293	4.01	4.16c
2-Me-Piperidyl				3.73cb
Piperazyl				
Phenylpiperazyl				4.06cb
Pyrrole		280	5.83	5.82b
Morpholinyl				4.02cb
Thiomorpholinyl		350	4.03	

[a] Solvent: b, benzene, c, chloroform.

The majority of octahedral ferric complexes exhibit simple Curie or Curie–Weiss magnetic behavior (i.e., magnetic susceptibility $\propto 1/T$). They can be classified as either "high spin" or "low spin." In high-spin complexes, the lowest term (ground state) is ${}^6A_{1g}$, which corresponds to the $t_{2g}{}^3e_g2$ configuration. The low-spin complexes have the ${}^2T_{2g}$ term as

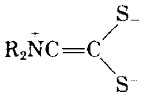


the lowest, and this corresponds to the t_{2g}^5 configuration. Whether the ${}^6A_2$ or the ${}^2T_2$ term is the ground state depends on the magnitude of the ligand field, Δ. There is a balance of the energy terms Δ and π, the "mean pairing energy," which determines whether the complex is high-spin or low-spin. For $\Delta > \pi$, a high-spin ground-state results, and, for $\Delta < \pi$, a low-spin ground-state results. The transition from high to low spin on increasing Δ can be shown diagrammatically.

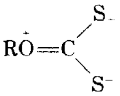


There will exist an equilibrium between the two states. If the energy between the two states, E, is of the order of kT, then the relative populations of the two states will vary with the temperature of the sample. In the Fe(III) dithiocarbamate series of complexes, $[Fe(R_1R_2dtc)_3]$, ΔE can be varied by suitable choice of substituents R_1 and R_2. Although these are well removed from the FeS_6 molecular core, they can appreciably affect the electronic parameters of the central iron atom and of the surrounding crystal field of the sulfur atom by way of the conjugated system of the ligand (*237*). The results of the spin crossover are reflected in magnetic susceptibility data.

Martin and co-workers (*238*) were the first to recognize the possibility of polar resonance forms of the type



and they suggested that they were predominant in high-spin complexes; this agrees with the fact that IR and X-ray studies have shown that



is unimportant in describing the structure of the low-spin xanthate complexes. Reaction of py with [FeL_3] (L = MeXant, EtXant, S_2PPh_2, or $S_2Pcyclohexyl_2$) gives bright-yellow compounds with magnetic moments (μ_{eff} = 4.9–5.0 μ_B) and Mössbauer spectra that strongly indicate iron(II). It is most likely (*239*) that they are of the type [$Fe(L)_2(py)_2$]. Ewald et al. (*240*) proposed that the principal trend influencing the magnetic behavior of the iron(III) dithiocarbamates is an increasing R–N–R bond-angle resulting from steric interactions between the nitrogen substituents. Eley *et al.* (*241*), however, conducted a study the results of which indicated that the primary function of the substituent, R, is as an electron-releasing group. They found that steric interactions appear to be relatively unimportant, except when a secondary carbon atom is the substituent. These workers and others (*242*) prepared a series of iron(III) dialkyldithiocarbamates in which the amino nitrogen atom is a member of a ring group, e.g., morpholine, 2-methylpyridine, or 3-methylpiperidine. On the basis of the evidence obtained from magnetic measurements, they concluded that a $^6A_1$–$^2T_2$ crossover situation exists, similar to that for the *N,N'*-dialkyl substituted dithiocarbamates. More recently, however, correlations between molecular geometry and temperature-dependent magnetic behavior of [$Fe(R_2dtc)_3$] complexes have been found (*243*).

When the Fe–S distances in all of the known Fe(III) dithiocarbamates are plotted against their magnetic moments, a smooth curve is obtained (see Fig. 1). Mössbauer spectral studies (*244, 245*) on [$Fe(R_2dtc)_3$] (R_2 = Bu^i_2, Pr^i_2, Me_2, piperidyl, or Bz_2) showed that the isomer shift is nearly identical in all of the complexes, and the temperature-dependence was explained through the existence of the almost equienergetic $^6A_1$ and $^2T_2$ ground-states in thermal equilibrium. The Fe–S bond contraction, on going from high to low spin, was originally attributed to a distortion from D_3 to C_3 symmetry, and spin–orbit

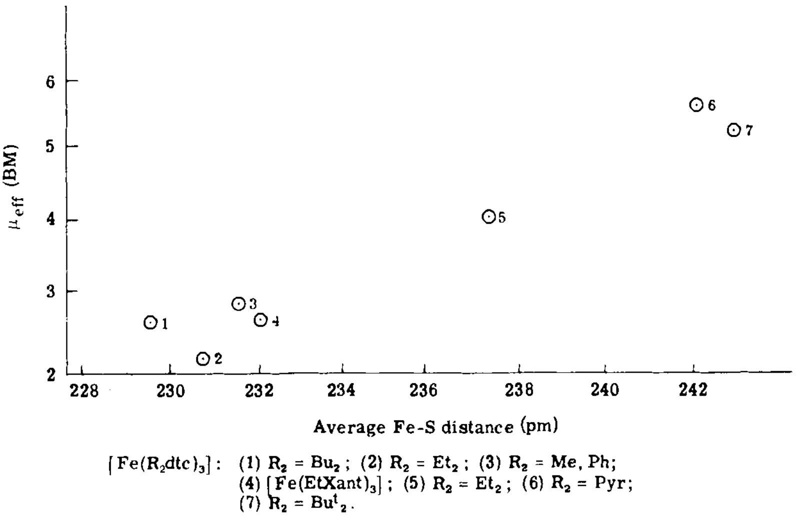


FIG. 1. Plot of effective magnetic moment vs. iron–sulfur bond length in [Fe(R_2dtc)$_3$] complexes.

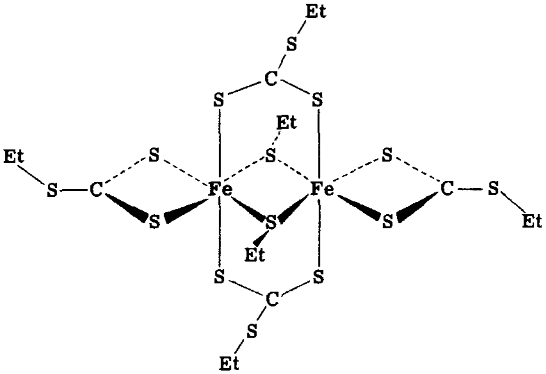
interactions inducing Jahn–Teller splitting in the ground state (*237, 246*), but this has since been discounted (*243*). In the epr spectra of some iron(III) dithiocarbamate complexes exhibiting spin equilibria, separate signals were observed from high- and low-spin forms (*247, 248*). The tris(dtc)iron(III) spin equilibrium has been reinvestigated (*249*) by variable-temperature determination of magnetic susceptibility (4.2–296 K), infrared spectra (30–300 K) and epr (4.2–85 K).

It is likely that these compounds will receive increasing attention as inorganic chemists, biochemists, and crystallographers (*437*) wrestle with the problems associated with spin changes in biological systems containing iron. Additional examples of $\overline{CH_2CH_2XCH_2CH_2C}S_2^-$ (X = S, or NMe) have (*250*) magnetic moments of 4.01 and 4.03μ_B. Paramagnetic anisotropy measurements on the single crystals of a series of halobis(diethyldithiocarbamate)iron(III) in which the ferric ion is an intermediate-spin state have been made (*251*).

A number of iron(III) xanthates and thioxanthates have been prepared (*1*). The structure of the predominantly low-spin [Fe(Rxant)$_3$] (R = Et, or SBu) complexes show features (*246, 252*) of coordination about the iron atom that are significantly different from those of [Fe(Bu_2dtc)$_3$], and it is estimated that there is 10–30% of double-bond character in coordinated S_2CX (X = OR, or SR), which is appreciably less than that of the dithiocarbamates (40–50%). Reactions of NaR_2dtc and KS_2OEt with Fe(II) halides in the presence of 2,2'-bipyridyl (bipyr) and 1,10-phenanthroline (phen) produce products similar to those found (*194*) for Mn(II). The magnetic properties of the thioxanthate complexes of Fe(III) indicate that a spin-equilibrium exists, with the low-spin form preponderating, as for the xanthates (*253*). The alkylthioxanthate complexes are thermally unstable, and, at room temperature, readily eliminate CS_2 to afford dimeric, diamagnetic compounds.

$$2\ Fe(RSXant)_3 \xrightarrow{THF} [Fe(SR)(S_2CSR)_2]_2 + 2\ CS_2$$

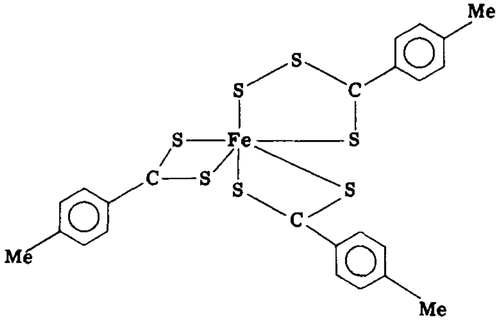
The crystal structure of one of the foregoing complexes (R = Et) was determined by Coucouvanis et al. (*253*) in a study of inorganic analogs of nonheme proteins; it is dimeric with bridging mercaptide and thioxanthate groups (**XVI**). The short Fe–Fe distance (261 pm) and the diamagnetism suggest a Fe–Fe single bond in the complex. The same workers (*254*) prepared a series of S-bridged, dimeric complexes of Fe(III), $[Fe(RSXant)_2(SR)]_2$ (R = Et, Pr^n, Bu^n, Bu^t, or Bz), and found that the *tert*-butyl thioxanthate is thermally more stable, due to steric factors, and a dimer of this complex was not isolated. The crystal structure of the *tert*-butyl thioxanthate (*255*) shows approximately octahedral configuration around Fe, but with distortion due to the small "bite" of the dithio ligands. $[Fe(S_2CSR)_3]$ compounds (R = Et, Pr^n, or Bu^n) have been synthesized as 6-coordinate, octahedral complexes (*256*). The ethyl derivative is diamagnetic, which contradicts earlier work (*252*), and this is ascribed to spin-pairing via Fe–Fe of Fe–S–S–Fe interactions between molecules, or to a change in symmetry due to packing. Lippard et al. (*255*), however, suggested that the material



(XVI)

that Pelezzi (*256*) had used had probably dimerized. A number of tris(dtc)iron(III) and -cobalt(III) complexes have been examined, and it was found that the inclusion of polar solvents appears to be a common phenomenon in crystals of these compounds; however, the iron complexes tend to lose solvent on standing. The structures of the tris(4-morphdtc) complexes of both metals were determined, and, although the [CoS_6] geometry is identical with that of previously reported complexes, the dimensions of the Fe complex (Fe–S = 44 pm, S–Fe–S = 72.5°) are atypical (*257*).

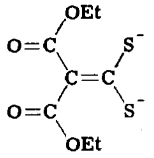
There have been but few reports of iron complexes with dithiocarboxylate ligands. Ferrous complexes are not very stable, and have only been reported qualitatively (*258*). The most stable dithiocarboxylate complexes of iron(III) are [$Fe(C_6H_5CS_2)_3$], the dithiobenzoate, and [$Fe(p\text{-}MeC_6H_4CS_2)_3$], the dithiotoluate; these were prepared by Coucouvanis and Lippard (*259, 260*), who, in the course of their study, also prepared "sulfur-rich" [$Fe(PhCS_3)_2(PhCS_2)$] and [$Fe(p\text{-}tolCS_3)(p\text{-}tolCS_2)$] complexes. The crystal structure of the latter shows iron in a distorted, octahedral environment of six sulfur atoms. It also appeared that one of the chelate rings had undergone expansion, to form a five-membered, chelate ring containing three sulfur atoms, a perthiotoluate complex (**XVII**).



(XVII)

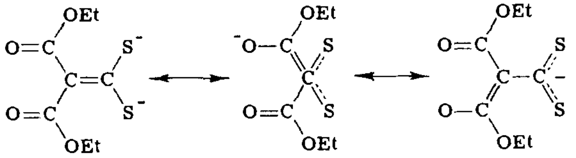
The preparation and characterization, and Mössbauer and epr spectra of Fe(II) and Fe(III) complexes of cyclopentadienyldithiocarboxylate have been reported recently (*261*).

Several complexes of iron with the 1,1-ethenedithiolates have been isolated. These are mainly tris-Fe(III) complexes with the 1,1-dicyano-2,2-ethylenedithiolate ligand (*1*). Recently, however, Coucouvanis et al. (*262*) synthesized a new 1,1-dithiolate ligand (**XVIII**) from the reaction of CS_2 with malonic ester in the presence of a base. The new lig-



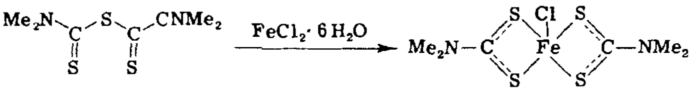
(XVIII)

and, 1,1-dicarboethoxyethylene-2,2-dithiolate dianion (DED^{2-}) can be represented by extensively delocalized structures. By reaction of the



potassium salt of DED with $Fe(ClO_3)_3 \cdot H_2O$ in the presence of $BzPh_3PCl$ in dichloromethane, a brown solution forms, from which an oil, and then a solid complex (*262*), $[BzPh_3P]_2[Fe(DED)_3]$, may be pentane-extracted. The complex has been characterized by Mössbauer and IR-spectral, polarographic and X-ray methods, and is octahedral, iron(IV) having a $^3T_1$ ground-state. The geometry of the MS_6 moiety in the structure can be described as originating from a trigonal prism that suffers individual rotations of the chelating ligands around the C_2 axes. One of the rotations is more severe than the other two, causing (*263*) a lowering of the overall symmetry to C_2.

Compounds of the type $[FeX(R_2dtc)_2]$ have been obtained by treating $[Fe(R_2dtc)_3]$ complexes with concentrated hydrohalic acids. $[FeCl(Et_2dtc)_3]$ has been studied by Hoskins and White (*264*); it has a square pyramidal structure, with the chlorine atom at the apex, and with the Fe atom situated 62 pm above the basal plane of the four sulfur atoms. A similar structure is found (*265*) for the monoiodo derivative $[FeI(Et_2dtc)_2]$. The chloro complex has been synthesized (*266*) by the following reaction.

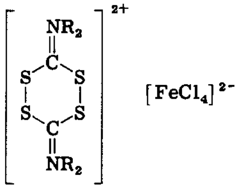


Reactions of $[Fe(Et_2dtc)_3]^n$ ($n = +1$, or 0), $[FeI(Et_2dtc)_2]$, and $[Fe(Et_2dtc)_2]$ with dppe, CNR, and PPh_3 have recently been described (*267*). Treatment of $[Fe(Et_2dtc)_3]^+$ with PPh_3 afforded (*267*)

$[Fe(Et_2dtc)_3]$, PPh_3S, and $[PPh_3\{C(NEt_2)S\}]^+$. The He(I) photoelectron spectra of $[Fe(Et_2dtc)_3]$ has been reported. (*268*).

Iron(IV) complexes are very rare. During the course of investigations into the synthesis and properties of iron dithiocarbamate complexes as model compounds for such naturally occurring, iron–sulfur proteins as ferredoxin, Pasek and Straub (*269*) isolated several cationic tris(dithiocarbamate) complexes of Fe(IV). The species $[Fe(R_2dtc)_3]BF_4$ (R = Et, Pr^i, pyrollidine, or cyclohexyl) and $[Fe(Et_2dtc)_3]PF_6$ are readily prepared by bubbling gaseous BF_3 for 30 sec through a benzene solution of $[Fe(R_2dtc)_3]$ in the presence of air, or by reaction of KPF_6 with an acidic solution of $[Fe(R_2dtc)_3]$ in acetone, followed by prolonged bubbling (5 h) of dry air through the mixture. Golding and co-workers (*270*) also produced cationic tris(dithiocarbamate) complexes of iron(IV), namely, $[Fe(R_2dtc)_3]X$ (X = ClO_4 and $FeCl_4$), by reaction of $Fe(ClO_4)_3$ or $FeCl_3$ with $[Fe(R_2dtc)_3]$. The structure of the iron(IV) complex $[Fe(pyrroldtc)_3](ClO_4)$ has been reported, and the $[FeS_6]$ core was shown to be intermediate between octahedral and trigonal prismatic (*271*).

Previous reactions of $FeCl_3$ and tetramethylthiuram disulfide and $[Fe(R_2dtc)_3]$ or $[Fe(R_2dtc)_2Cl]$ with Cl_2 or Br_2 resulted in the formation of complexes of the following type. Iron(IV) and iron(II) complexes containing dithiocarbamate ligands have also been produced electrochemically (*270, 272–274*). $[Fe(Et_2dtc)_3]$ exhibits reversible, one-electron oxidation and reduction steps. This method of synthesizing

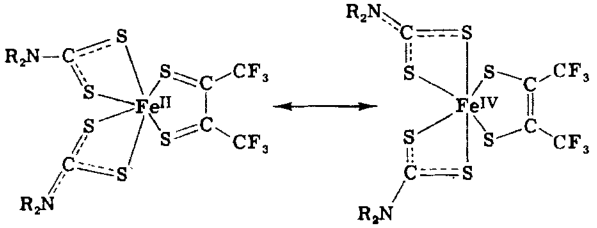


$$[Fe(Et_2dtc)_3]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Fe(Et_2dtc)_3] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe(Et_2dtc)_3]^-$$

$[Fe(Et_2dtc)_3]BF_4$ has the advantage that the product is completely free from by-products and is isolable in yields of 90%. The relationship between $E_{1/2}$ values and electronic structures has been described in terms of ${}^6A_1$ – ${}^2T_2$ crossover equilibrium (*273*). The rate of e^- transfer between $[Fe(Me_2dtc)_3]$ and $[Fe(Me_2dtc)_3]BF_4$ has been measured by ^2H-NMR, line-broadening experiments (*275*). Mössbauer-spectral data have been published (*276*) for a series of (R_2dtc) complexes of iron(IV).

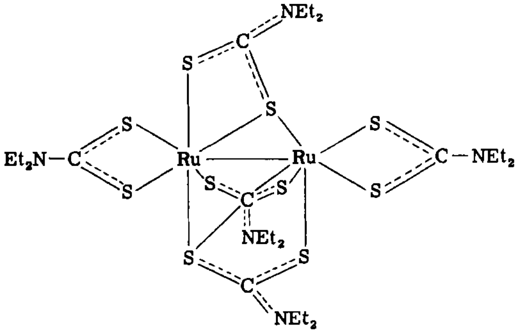
A report of cationic, mixed-ligand complexes of iron(III) containing dithiocarbamate ligands appeared recently (*277*). The complexes, $[FeL(R_2dtc)_2]^+$ (L = CNR, diphos, or PPh_3) were obtained by reaction of L with $[Fe(R_2dtc)_3]^+$, involving a ligand-displacement reaction (*277*).

A number of mixed 1,1-dithiolato and 1,2-dithiolene complexes of iron have been prepared and characterized (*278–280*), namely, $[Fe(R^1R^2dtc)_2(S_2C_2X_2)]$ (R^1 = Et, or Ph; R^2 = Et, or Me; X = CN, or CF_3). They are formed on treating the bis(dithiocarbamato)iron complex with the Na_2mnt, followed by successive oxidation with copper(II) in air in MeCN (*278*). Alternatively, the 1,2-dithiolene complex can be treated with the dithiocarbamate ligand, followed by sulfite reduction (*279, 280*). The complexes have room temperature magnetic moments of $\sim 2.5\mu_B$, indicating low-spin iron(III). The crystal structure of $[Fe(Et_2dtc)_2(tfd)]$ shows FeS_6 coordination of distorted octahedral symmetry, and two limiting, nonequivalent valence-bond structures can be drawn for this complex (ignoring the relatively trivial resonance of the dithiocarbamate ligand).



dithioketonic form dithiolene form

Relatively few complexes of ruthenium with 1,1-dithio ligands are known. The earlier, sparse reports of these complexes are included in Coucouvanis's review (*1*). Only two tris(dithiocarbamato) complexes of ruthenium have been reported, the $[Ru(Et_2dtc)_3]$ complexes by reaction of K_2RuCl_6 with NaR_2dtc in water (*281*), and the $[Ru(Et_2dtc)_3]BF_4$ complex by reaction of the former complex with BF_3 in the presence of air (*282*). However, a recent crystal-structure determination (*283, 284*) of a complex has shown that the product from this reaction is $[Ru_2(Et_2dtc)_5]BF_4$, a Ru(III) species (**XIX**). The complex contains a Ru–Ru bond and two types of bridging dithiocarbamate ligand. The nature of one of the bridging dithiocarbamate ligands is novel, as no other structures studied to date contain this ligand bonding in this mode. Duffy and Pignolet, and Pignolet (*285, 286*) studied the ^1H-NMR spectrum and crystal structure of $[Ru(Et_2dtc)_3]$, which is intermediate between trigonal antiprismatic and trigonal prismatic, approximating to D_3 symmetry, and is stereochemically nonrigid. The only other pure,



(XIX)

1,1-dithio complex of ruthenium prepared (*287*) is $(Ph_4As)_3[Ru(\textit{i}\text{-}mnt)_3]$.

A number of ruthenium(II) complexes have been prepared. Cole-Hamilton and Stephenson isolated *cis*-$[Ru(Me_2dtc)_2L_2]$ (L = PPh_3, PMe_2, Ph, $PPhMe_2$, or $P(OPh)_3$) from Ru(II) and Ru(III) tertiary phosphine and phosphite complexes with $NaMe_2dtc$, and found that they undergo rearrangements (*288*).

New dithiocarbamato and *O*-alkyl dithiocarbonato derivatives $[M(S{-}S)_2(PPh_3)_2]$, $[M(S{-}S)_2(CO)(PPh_3)]$, $[MH(S{-}S)(CO)(PPh_3)_2]$ (M = Ru, or Os; S—S = R_2dtc, or RXant; R = Me, or Et), $[OsCl(R_2dtc)(CO)(PPh_3)_2]$ and $[IrH_2(S{-}S)(PPh_3)_2]$ have been prepared by treating the appropriate chloro or carboxylato complexes with sodium salts of the ligand (*289*). "Insertion" of CS_2 into the metal–hydrogen bonds has been employed (*438*) in synthesizing a range of new dithioformato complexes of Ru, Os, and Ir, including $[MX(S_2CH)(CO)(PPh_3)_2]$,(two)—$[MX(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(CO)(PPh_3)_2]$ (M = Ru, or Os; X = Cl, Br, or $OCOCF_3$), $[M(S_2CH)_2(PPh_3)_2]$,$[IrCl_2(S_2CH)(PPh_3)_2]$, $[MH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(CO)(PPh_3)_2]$, and $[Ru(RN{-}CH{-}S)_2(PPh_3)_2]$.

An electrochemical study of several Et_2dtc complexes of Ru(III) and Ru(IV), including $[(CO)Ru(dtc)_2]$, $Ru(dtc)_3$, and $ClRu(dtc)_3$, using dc, ac, and cyclic, voltammetric techniques in solvents MeCN, Me_2Cl_2, and propylene carbonate has been very recently reported (*290*).

The dimeric $[Ru_2N(Et_2dtc)_4]Cl$ was prepared by Griffith and Pawson (*441*). An organometallic, Ru(II) adduct $[Ru(Me_2dtc)_2(1,5\text{-}COD)]$ (1,5-COD ≡ bicyclo[2.2.1]hepta-2,5-diene) was produced by Powell (*292*). Other organometallic derivatives have been synthesized (*293, 294*) by CS_2 insertion into · Ru bonds in such complexes as $[RuCl(CO)(PCy_3)_2(H)]$ and $[RuH_4(PPh_3)_3]$. The product of the latter reaction, $[Ru(S_2CH)_2(PPh_3)_2]$, has been characterized as a dithioformato complex (*295*). A number of Ru(II) carbonyl complexes containing dithiocarbamate ligands were prepared by treating a solution of a ruthenium carbonyl with a solution of the particular dithiocarbamate, e.g., $[Ru(Et_2dtc)_2(CO)]$ (R = Et or Me) and $[Ru(Bz_2dtc)_2(CO)_2]$.

Most of the reports of osmium complexes containing 1,1-dithio ligands are concerned in the use of dithiocarbamate complexes for the analytical determination of the metal (*296*); a violet color forms when OsO_4 and NaR_2dtc are mixed in aqueous solution (*84*).

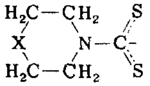
Addition of CS_2 to $[OsHCl(CO)(PCy_3)_2]$ gives two different products, depending upon the conditions employed. In benzene, the product β-$[OsCl(HCS_2)(CO)(PCy_3)_2]$ is indicated on the basis of infrared data [ν(C–S) bands at 917 and 790 cm^{-1}], whereas, if the reaction is conducted in the solid state, an additional product $[OsHCl(CS_2)(CO)(PCy_3)_2]$, containing terminally S-bonded CS_2 [ν(C–S) = 1510 cm^{-1}] was isolated (*294*).

The reactions of *mer*$[OsCl_3(PMe_2Ph)_3]$ with Me_2dtc^-, $MePS_2^-$, $Ph_2PS_2^-$, and EtXant have been studied, and some of the products isolated included (*297*) *cis*-$[Os(PMe_2PH)_2(Me_2dtc)_2]$, *mer*-$[Os(PMe_2Ph)_3(Me_2dtc)]$, *fac*-$[OsCl(PMe_2Ph)_3(Me_2dtc)]$, *fac*-$[Os(OEt)(PMe_2Ph)_3(Me_2dtc)]$, and $[Os(PMe_2Ph)_2(Me_2dtc)(EtXant)]$. From measurements of the ionic products of the sparingly soluble R_2dtc (R = Et, Bu^n, or Bz)·Os^{IV} complexes $[OsO_2(R_2dtc)_2]$, it has been concluded that these species are of high stability (*298*).

F. Cobalt, Rhodium, and Iridium

The 1,1-dithio complexes of cobalt have been studied extensively (*1*). Most of the literature is concerned with Co(III) compounds, as the complexes with divalent cobalt are extremely air-sensitive and have only been synthesized in acidic solution under rigorously deoxygenated conditions. The recent complexes of cobalt with 1,1-dithio ligands are listed in Table III, together with some of their physical properties.

Recently, Preti and co-workers (*291*) prepared Co(II) complexes with piperidine (pipdtc), thiomorpholine (Timdtc), and *N*-methylpiperazine-4-carbodithioate (Me-Pzdtc) (**XX**).



X = CH_2-pipdtc;
X = S-Timdtc;
X = NCH_3-Me-pzdtc.

(XX)

TABLE III

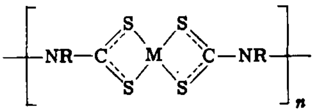
1,1-DITHIOCHELATES OF Co[a,b]

Compound	Melting point (°C) (d = decomp)	Color
$[Co(pipdtc)_2]$	350	Green
$[Co(Me\text{-}Pzdtc)_2]$	304	Green
$[Co(Thiomorphdtc)_2]$	350	Green
$[Co(C_6H_8NS_2)_2]$	350d	Brown
$[Co(Morphdtc)_3]$	—	—
$[Co(EtSxant)_3]$	—	—
$[Co(PrSxant)_3]$	—	—
$[Co(BuSxant)_3]$	—	—
$[Co(Et_2NCH_2)_2HCS_2)]$	Oil	Green
$[Co(Et_2\overset{+}{N}HCH_2)_2NCS_2)]Cl_6$	Decomp.	Green
$(Et_4N)_2[Co(C_5H_4CS_2)_2]$	—	Brown
$[Co(Me_2dtc)_3]BF_4$		
$[Co(Et_2dtc)_3]BF_4$		
$[Co(Pr^i_2dtc)_3BF_4$		
$[Co(cyclohexyl_2dtc)_3]BF_4$		Green
$[Co(MeBzdtc)_3]\cdot 2\ H_2O$	—	—
$[Co_2(Me_2dtc)_5]BF_4$	—	—
$[Co_2(Et_2dtc)_5BF_4$	—	—
$[Co_2(Bz_2dtc)_5]BF_4$	—	—
$[Co_2(pyrrolidyldtc)_5]BF_4$	—	—
$[Co_2(MeBu^ndtc)_5]BF_4$	—	—
$(Ph_2I)_3[Co(S_2CNCN)_3]$	72d	Yellow-green
$Co[Co(S_2C{=}CHNO_2)_2]$	—	—
$(Bu_4N)_2[Co(S_2C{=}C(CN)_2]$	157–164	—

[a] D. H. Brown and D. Venkappaya, *J. Inorg. Nucl. Chem.* **35,** 2108 (1973).

[b] P. Thomas and O. Poveda, *Z. Chem.* **10,** 153 (1971).

These complexes are stable (presumably to aerial oxidation), which is, perhaps, surprising, in view of the fact that the analogous complexes of iron(II) could not be isolated, oxidation to iron(III) taking place in each case. A number of interesting poly(bisdithiocarbamate) complexes of cobalt(II) and nickel(II) (**XXI**) have been prepared and

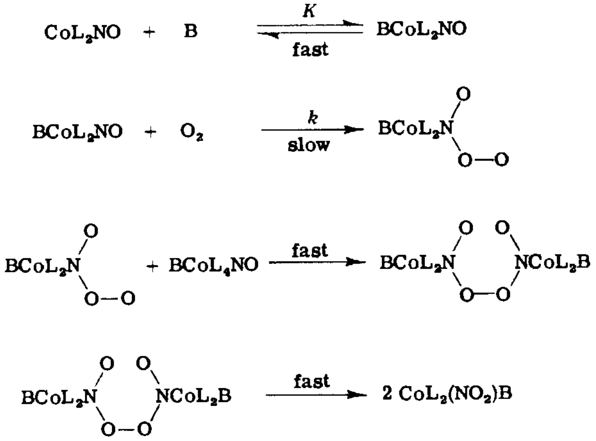


M = Co, or Ni; R = $(CH_2)_2$, $(CH_2)_6$, or $(C_6H_4{-}C_6H_4)$

(**XXI**)

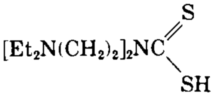
their IR spectra studied (*299*). In addition, some suggestions concerning the nature of the bonding in cobalt(II) and nickel(II) xanthates have been made (*300*).

The 1,1-ethylenedithiolate ligands appear to stabilize cobalt(II) species. Thus, Lewis and Miller (*113*) synthesized $Co[Co(S_2C{=}CHNO_2)_2]$ and $(Bu_4N)[Co(S_2C{=}C(CN)_2)]$, and found them to be active insecticides. The disodium salt of cyclopentadienedithiocarboxylic acid reacts with $CoBr_2$ in anhydrous acetonitrile, from which can be isolated (*301*) $[Et_4N]_2[Co(C_5H_4CS_2)_2]$, of D_{2h} symmetry. The dinegatively charged 1,1-dithiolate ligands are probably more effective in stabilizing a cobalt(II) complex than the uninegative dialkyldithiocarbamate ligands. Cobalt nitrosyl complexes have been known for some time (*302*). A three-dimensional structure determination of the complex $[Co(NO)(Me_2dtc)_2]$, and an improved synthesis have been reported (*303*). The coordination geometry about the cobalt atom is tetragonal pyramidal, with the NO group at the apex, and the Co atom situated 52 pm "above" the basal plane of the four sulfur atoms. The NO group is disordered in such a way that the oxygen atom alternatively lies above one or other of the Co–S bonds of the same dithiocarbamate ligand. The reaction of this complex with oxygen in the presence of pyridine or a phosphine (B) resulted (*304*) in the formation of complexes of the type $[Co(Me_2dtc)(NO_2)(B)]$. From kinetic data, the following mechanism was proposed.



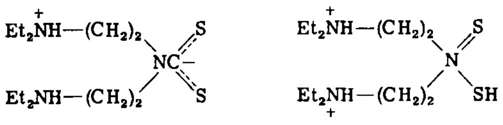
The two major methods used for the synthesis of cobalt(III) dithiocarbamates are (*a*) treatment of a cobaltous salt with aqueous NaR_2dtc in the presence of air, or (*b*) oxidation of a cobalt(II) salt with tetraalkyldithiuram disulfides. In recent years, a complex with morpholine-4-carbodithioate (Mdtc), $[Co(Mdtc)_3]$, has been prepared and characterized (*44*); the reaction involved formation of an adduct with the parent base, morpholine, followed by CS_2 insertion. Complexes of Ti(IV), VO^{2+}, Cr(III), Mn(III), Ni(II), Cu(I), Zn(II), and Cd(II) were prepared by the same method.

The alleged preparation of the supposed cobalt(II) complex $Na[Co(Et_2dtc)_3]$ described by D'Ascenzo and Wendlandt (*305*) has been repeated by Holah and Murphy (*306*), who identified the product as $[Co(Et_2dtc)_3]$. Complexes of cobalt(III), nickel(II), and palladium(II) salts with cationic, dithiocarbamate ligands have been synthesized (*307*). Reaction of the secondary amine $(Et_2N(CH_2)_2)_2NH$ with CS_2 produces



$[Et_2N(CH_2)_2]_2NC\genfrac{}{}{0pt}{}{\diagup S}{\diagdown SH}$

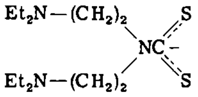
(L), the IR spectrum of which indicated that it exists in a zwitterionic form. Thus, reaction of L with one mole, or two moles, or protonic acid produces L^+ and L^{2+}, respectively (**XXII**).



(L^+) (L^{2+})

(XXII)

Reaction with one mole of base produces the dithiocarbamato anion, L^- (**XXIII**).



(L^-)

(XXIII)

Complexes $[Co(L^-)_3]$ and $[Co(L^+)_3]Cl_6$ have been obtained. The presence of a positive charge on the dithiocarbamato ligand has little effect on the coordination properties of the ligands or complexes, except for an alteration of solubility characteristics. It is surprising that work on these zwitterionic, sulfur-containing ligands does not appear to have been extended, as they are potential, biological-model systems. The complexes $[Co(RSXant)_3]$ (R = Me, Et, Pr^n, Bu^t, and Bz) and $[Co(RSXant)_2(SR)]_2$ (R = Et, or Pr^n) have been reported (*308*), and the elimination of CS_2 from the tris(thioxanthato) complexes to give the dimers has been directly confirmed, and the reaction found to be first-order. The structure of the solid ethyl thioxanthato dimer was found to be centrosymmetric, with bridging SEt groups, and ^{1}H-NMR-spectral data indicated that this structure also exists in solution. The structure of tris(ethylthioxanthato)cobalt(III)·$Co(S_2CSEt)_3$ shows Co–S (mean) = 226.6 pm, and LS–Co–S (mean) = 76.2°. The discrepancy between these results (*309*) and those previously reported (*310*) led Li and Lippard (*309*) to suggest that the earlier determination had, in fact, been performed on the chromium(III) analog. Villa *et al.* (*311*) also redetermined the structure of the compound, and found it to be isostructural with the chromium(III) complex, and the apparent discrepancies between the previously reported Co–S distance and the spectroscopic data have been explained. The single-crystal structure of the arylxanthate complex of cobalt(III), $[Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3]$, shows that the pseudooctahedral CoS_6 unit has (*312*) a mean Co–S distance of 227.0(6) pm. The structure is quite similar to that of the aliphatic analog $[Co(S_2COEt)_3]$ reported by Merlino (*442*).

Cobalt(III) complexes containing mixed chelating ligands have been produced. Reaction of potassium bis[biuretocobaltate(III)], $K_2[Co(bi)_2]$ with R_2dtc^- or $Rxant^-$ at 0° produces (*313*) the blue–violet $[Co(bi)_2(S—S)]^{2-}$ ion (S—S = R_2dtc or RXant). If the reaction is performed above 0° in the presence of water, the products are $[Co(bi)_2(S—S)_2]^-$ and biuret.

A number of complexes of cobalt(III) with 1,1-dithiolato ligands are known. Since 1969, however, only the isolation and reactions of the first dithiocarbimate complex of cobalt(III), $[Ph_2I]_3[Co\ S_2CN(CN)_3]$, the diphenyliodonium tris(N-cyanodithiocarbimato)cobaltate salt, has been reported (*314*). Pyrolysis of this compound showed that the reactive sites in the anion are the coordinated sulfur atoms of the same ligand. Partial reduction of the metal ion to cobalt(II), and liberation of PhS_2 and PhI, occur simultaneously. In pyridine, ligand phenylation occurs, but the arylated ligand decomposes. In pyridine, nonarylated ligands dissociate into thiocyanate, accompanied by reduction to cobalt(II).

Several complexes with cobalt in the unusually high oxidation state of (+4) were reported (*198, 202, 280*) in 1974. All of the complexes reported were prepared by reaction of $[Co(R_2dtc)_3]$ with BF_3 or Et_2OBF_3 in the presence of air. The complexes were formulated (*202, 280*) as $[Co(R_2dtc)_3]BF_4$ (R = Me, Et, Pr^i, or cyclohexyl), but Hendrickson and Martin (*198*) suggested that dimeric $[Co_2(R_2dtc)_5]BF_4$ (R_2 = Me_2, Et_2 pyrrolidyl, $MeBu^n$, or Bz_2), Co(III) complexes, form that are analogous with the ruthenium(III) complex discussed earlier.

The dynamic stereochemistries of M(dtc)$_3$ and [M(dtc)$_3$] (M = Fe, Co, or Rh) complexes have been studied (*315*). The cobalt complex is nonrigid, but the mechanism of optical inversion could not be determined. The Rh complex is stereochemically rigid up to 200°. The optical inversion of $(+)_{546}$ [Co(pyr-dtc)$_3$] in chloroform has been studied, by loss of optical activity, by polarimetry (*316*).

The diene complex [(diene)Rh(dtc)] [diene = $(C_8H_{14})_2$, or 1,5-cod] is oxidized in the presence of an excess of dtc to [Rh(dtc)]. One of these ligands can be replaced (*317*) by HCl, to give [Rh(dtc)$_2$Cl]$_2$. The preparation of other [Rh(dtc)$_3$] complexes derived from cyclic amines has also been reported (*318*). Treatment of [(cod)Rh(MeCN)$_2$]$^+$ with [NO]PF$_6$ yields green [Rh(NO)(MeCN)$_4$](PF$_6$)$_2$. The dtc complexes were found to exhibit low N–O stretching-frequencies, e.g., 1545 cm^{-1} for [Rh (NO)(Me$_2$dtc)$_3$]PF$_6$ (*319*).

The literature concerning the preparation of 1,1-dithio complexes of rhodium and iridium is relatively sparse. Wilkinson and co-workers (*320, 321*) reported that replacement of chloro groups in tertiary phosphite complexes of rhodium with various alkali-metal dithio-acid salts produces [Rh(Me$_2$dtc)$_3$], [Rh(R$_2$dtc)$_3$(PPh$_3$)] (R = Me, or Et), [Rh(Me$_2$dtc)(PPh$_3$)$_2$], [Rh(Me$_2$dtc)(CO)PPh$_3$], [Rh(Me$_2$dtc)$_3$(CO)PPh$_3$], and (Rh(Et$_2$dtc)$_2$(PPh$_3$)$_2$]BF$_4$. [Rh(CO)(PRh$_3$)(Me$_2$dtc)$_3$] contains two monodentate and one bidentate dithiocarbamate ligands, and [Rh(PPh$_3$)(Me$_2$dtc)$_3$] contains one monodentate ligand and two bidentate ligands. Recently Cole-Hamilton and Stephenson produced a series of new dithiocarbamate and xanthate complexes by the same route (*322*), and postulated a detailed mechanism for the overall reaction.

The crystal and molecular structure of K[RhCl$_2$(S$_2$CO)(PMe$_2$PH)$_2$]·3H$_2$O show that there are two independent anions per unit cell, with crystallographic C$_i$(I) symmetry. They are essentially identical, and the planar dtc ligands have (*323*) Rh–S = 237 pm, C–S = 172.5 pm, C–O = 125 pm; S–Rh–S = 73.5°, S–C–S = 111°, and S–C–O = 125°.

The new air-stable complex [Rh(PPh$_3$)(Et$_2$dtc)$_2$]BF$_4$ was prepared (*324*) by treating Rh_2^{4+} with Et$_2$dtc$^-$ and PPh$_3$. The rhodium(IV) complexes [Rh(R$_2$dtc)$_3$]BF$_4$ were prepared during the work with the cobalt(IV) and ruthenium(IV) complexes (see earlier). Rhodium carbonyl derivatives containing dithiocarbamate ligands have been prepared by Abel and Dunster (*179*).

The first report (*325*) of iridium(III) dithiocarbamate complexes appeared in 1973. The procedure is straightforward, consisting in addition of an excess of NaR$_2$dtc to sodium chloroiridate in aqueous methanol. On being kept for several days, an orange–yellow precipitate forms. Eleven complexes (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^u, amyl, cyclohexyl, pyrrole, piperidine, and $EtOH_2$) were isolated in this way. Reaction of $[Ir(CO)(PR_3)Cl]$ with $\{(CF_3)C{=}CS_2\}_2$, and subsequent isolation of the product, $[Ir(CO)(PR_3)_2(Cl)\{S_2C{=}C(CF_3)_2\}]$, represent the first reported preparation of an iridium or rhodium complex with a 1,1-dithiolene ligand (*326*). The crystal structure of $[Ir(Et_2dtc)_3)]$ shows the complex to be isostructural (*327*) with the cobalt(III) analog having a mean Ir–S of 236 pm.

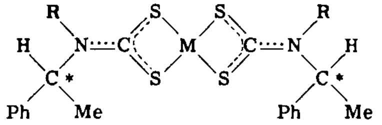
G. Nickel, Palladium, and Platinum

The chemistry of complexes of members of the nickel triad with 1,1-ligands has been studied extensively (*1*).

Nickel 1,1-dithio complexes with the metal in the unusually low oxidation state of +1 have been prepared by Garif'yanov and Luchkina (*328*), who studied the esr spectra of $[Ni(NO)(S_2CX)]$ (X = NEt_2, or OEt), and observed a signal, g = 2.103, in toluene solution. Using ^{61}Ni-enriched samples, hyperfine structure was observed, and the structure is probably square or tetragonal pyramidal. $[\pi\text{-}CpNi(PBu_3)_2]Cl$ reacts with RCS_2^- (R = Ph, Et, or Bz), to form $[\pi\text{-}CpNi(PBu_3)_2(SC(S)R)]$, which, on treatment with HCl, yields (*329*) $[\pi\text{-}CpNi(SCR)]$. The complex is a Ni(I) species, and was found to revert to the intermediate complex on treatment with PBu_3 in hexane.

The nickel(II) dithiocarbamate complexes are neutral, water-insoluble, usually square-planar, species, and they have been studied extensively by a range of physical techniques. The usual methods for the synthesis of dithiocarbamate complexes have been employed in the case of Ni(II), Pd(II), and Pt(II). In addition, McCormick and co-workers (*330, 331*) found that CS_2 inserted into the Ni–N bonds of $[Ni(aziridine)_4]^{2+}$, $[Ni(aziridine)_6]^{2+}$, and $[Ni(2\text{-}methylaziridine)_4]^{2+}$ to afford dithiocarbamate complexes. The diamagnetic products are probably planar, but they have properties typical of dithiocarbamate complexes, and IR- and electronic-spectral measurements suggested that they may be examples of N,S-, rather than S,S-, bonded dithiocarbamates. The S,S-bonded complexes are however, obtained, by a slow rearrangement in methanol. The optically active *N*-alkyl-*N*(α-phenethyl)dithiocarbamates of Ni(II), Pd(II), and Cu(II) (**XXIV**) have been synthesized, and the optical activity was found to be related to the anisotropy of the charge-transfer transitions (*332*).

An interesting, halogen-exchange reaction takes place when $[Ni(Et_2dtc)_2]$ is refluxed in 1,2-dichloroethane with an excess of α,α′-dibromo-*o*-xylene and α-bromo-α′-chloro-*o*-xylene. The products, α,α′-



M = Cu, Ni, or Pd; R = H, Et, Pr^n, or Bz; and
* denotes optically active carbon atom.

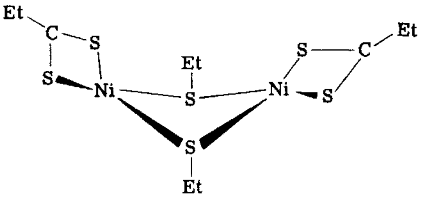
(XXIV)

dichloro-*o*-xylene and some α-bromo-α'-chloro-*o*-xylene, were not found, however, in the absence of $[Ni(Et_2dtc)_2]$, or when $[Ni(Etxant)_2]$ was used. Red–violet $[Ni(Et_2dtc)_2Br(Bu_3^nP)]$ and dark-violet $[Ni(Et_2dtc)_2Cl(PPh_3)]$ have been prepared by reaction of the respective nickel halide, phosphine, and $NaEt_2dtc{\cdot}3H_2O$ in ethanol (*333*).

Resonance-Raman spectra of Cu(II) and Ni(II) diethyldithiocarbamates have been reported recently (*334*). Both spectra show the preferential intensity enhancement of four bands in the M–S stretching- and SCS, SCN, MSC, and SMS bending-regions at 367–157 cm^{-1}. A thermodynamic study of the addition of pyridine or 4-Me-pyridine to bis(penthiobenzato)nickel(II) and $[Ni(Bz_2dtc)_2]$ in C_6H_6 solution showed that the variation of base-adduct stabilities of the NiS_4 complexes with four-membered chelate rings is due primarily to entropy effects (*335*). A correlation between isotropic contact shifts and Taft σ^* values for some pyridine-base adducts of nickel(II) bis(*o*-alkyldithiocarbonates) and bis(β-diketonates) has been found (*350*). Several X-ray crystallographic, structural determinations of nickel(II) dithiocarbamate complexes have been performed in recent years (*236, 244*). Thus, the structures of $[Ni(R^1R^2dtc)_2]$ ($R^1 = R^2 =$ Me (*344*), Pr^i (*343*), Pr^n (*135, 137*), H (*336*); R^1 = Me, R^2 = Ph (*341*); R^1 = H, R^2_2, = Pr^i (*343*); $R^1R^2 = (CH_2)_4$ (*342*); and $R^1R^2 = (CH_2)_6$ (*338*) have been determined. Deviations from planarity in the coordination plane were explained by crystal packing and hydrogen-bonding interactions (*344, 336*). The structure of *cis*-bis(diisopropyldithiocyanate)nickel(II) is the first example of the cis configuration in complexes of this kind. The adoption of a cis stereochemistry is due to the strong hydrogen-bonding between the HN hydrogen atom and the sulfur atoms in the neighboring molecules (*343*). Fackler *et al.* (*345*) recently prepared three classes of unsymmetrical dithiocarbamate complex of the nickel triad elements: (*i*) $M(R_2dtc)\ (PR_3)X$ (M = d, or Ni; R = Bu^t, or Et; R = alkyl, or aryl; X = Cl, Br, I, SCN, or SR); (*ii*) $Pt(R^1R^2dtc)(PMe_2Ph)_2X$ (R^1 = Me; R^2 = Ph; X = Cl,BPh_4, or PF_6); and (*iii*) $(R^1R^2dtc)_3$. In the first two classes, magnetic nonequivalence can be observed in the ^1H-NMR spectra of the liquids, whereas, in the third class, both cis and trans isomers are observed. For the Ni(II) compounds, partial halide exchange appears to be responsible for the observation of magnetically equivalent R groups in structurally nonsymmetric dtc complexes in the presence of free phosphine, or upon increase in temperature.

The nickel(II) xanthate complexes are diamagnetic, square planar species that are slightly soluble in water, the solubility decreasing with increasing size of the hydrophobic alkyl groups. The position of the $^1A_g \rightarrow {}^1B_{1g}$ transition in these complexes indicates that the thioxanthate ligands have smaller ligand field-splitting potentials than the corresponding xanthates (*1*).

The only new complexes of Ni(II) containing only xanthate ligands to have been reported in the recent literature include (*160*) the aryl xanthate complex $[Ni(S_2COC_6H_4\text{-}4\text{-}tert\text{-}Bu)_2]$. The palladium(II) analogs $[Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2]$ have also been studied by single-crystal, X-ray crystallography. The coordination about both the Ni(II) and Pd(II) complex is planar, with the phenyl ring approximately perpendicular to this plane (*160*). Only one report of the formation of thioxanthate complexes of Ni(II) has appeared (*256*). $[Ni(S_2CSR)_2]$ (R = Et, Pr, or Bu) were prepared by reaction of S_2CSR^- with a nickel(II) salt in ethanol. Attempts to crystallize the ethyl complex from $CHCl_3\text{-}Et_2O$ gave a dimeric complex, $[Ni(S_2CSEt)(SEt)]_2$, which was found to contain two equivalent, square planar NiS_4 species; the -SEt groups bridge the two nickel atoms (**XXV**). The short Ni–Ni distance (276 pm) may indicate the presence of the first example of metal–metal bond in a binuclear Ni(II) complex. A kinetic study of the spontaneous elimination of CS_2 to afford $[M(S_2CSR)(SR)]_2$ (M = Ni^{II}, Pd^{II}, or Pt^{II}) and $[M(S_2(CSR)_2(SR)]_2$ [M = Co(III), or Fe(III)] was undertaken by Fackler and co-workers (*346, 347*). Radioactive labeling of the mercaptide sulfur atom of the thioxanthate complexes showed that it forms the bridge in the dimeric complexes.



(XXV)

The majority of the work on xanthates of divalent nickel has, in recent years, been centered on the formation of base adducts with $[Ni(Rxant)_2]$. Carlin and Siegel (*348*) and Daktenieks and Graddon (*349*) reported the formation of paramagnetic $[Ni(Etxant)_2B_2]$ or $[Ni(Et_2xant)_2B]$, where B = pyridine, 4-methylpyridine, bipyridyl, or

2,9-dimethyl-1,10-phenanthroline. An additional study showed that [Ni(EtXant)$_2$] forms 1:2 adducts with pyridine and 4-picoline in nitrobenzene solution (*350*). Furthermore, Carlin and Siegel (*348*) observed that pyridine derivatives lacking an α-substituent form only the [Ni(Etxant)$_2$B$_2$] adduct, but α-substitution led to steric hindrance at the coordination site. Triphenylphosphine and other bulky bases formed only a monoadduct [Ni(Etxant)$_2$B]. Steric hindrance and the amount of electron density on the metal ion were found to have important effects on the thermal stability of the adducts (*351*). The effect of replacing pyridine by 4-methylpyridine is to increase the stability constant of the adduct about fivefold; this is due to the greater base-strength of 4-methylpyridine. 2,2′-Bipyridine forms a bidentate-bound adduct, and the large adduct-formation constants (K > 10^5) shows a typical, chelate effect (*352*). Base-adduct formation in nitrobenzene was also studied by ^{1}H-NMR spectroscopy (*353*), and the equilibrium constant for the reaction

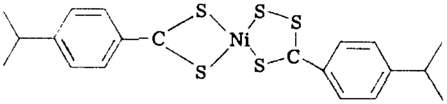
$$[\mathrm{Ni(Etxant)_2}] + 2\,\mathrm{B} \overset{K}{\rightleftharpoons} [\mathrm{Ni(Etxant)_2B_2}]$$

may be related to the NMR-spectroscopic parameters $\Delta\nu_0$ (observed isotropic shift in the presence of Lewis base), $\Delta\nu_\mathrm{p}$ (isotropic shift of 1:2 adducts), and α (= $\Delta\nu_\mathrm{o}/\Delta\nu_\mathrm{p}$, the degree of interaction)

$$K = [\{\mathrm{Ni(Etxant)_2B_2}\}]/[\{\mathrm{Ni(Etxant)_2}\}][\mathrm{B}]^2 = \alpha/(1 - \alpha)([\mathrm{B}] - 2\,\alpha[\{\mathrm{Ni(Etxant)_2}\}])^2$$

The equilibrium constants thus determined were found to be smaller than those previously reported, no doubt due to the use of a polar solvent. In three papers by Kruger and Winter (*354–356*), two polymorphs of the adduct of [Ni(Etxant$_2$] with 4,4′-bipyridine were reported, one of which is capable of forming clathrate compounds by trapping a molecule of cyclohexane, C_6H_6, Et_2O, Me_2CO, $CHCl_3$, CCl_4, or cyclopentadiene. The 1,10-phenanthroline adduct also forms 1:1 clathrates with C_6H_6, C_6H_3Me, $CHCl_3$, and C_6H_5Cl. The inclusion compounds are formed from solutions of the respective solvents, or from solvent vapors. The same workers also successfully isolated the first two adducts of [Ni(Etxant)$_2$] with oxygen as the donor atom. Bright-green, 2:1 adducts of [Ni(Et$_2$xant)$_2$] with DMSO and pyridine *N*-oxide were isolated. A most interesting reaction that takes place in the thermal decomposition of nickel xanthates is the formation of olefins (*357*).

The chemistry of the dithiocarboxylate complexes of nickel(II) has been investigated extensively. Interest in recent years has been mainly in the further investigation of the "sulfur-rich" species, the perthiocarboxylates, and the unusual structures discovered in the dithiocarboxylate complexes (*359*). The violet complex formed by reaction of [Ni(C$_6$H$_5$CS$_2$)$_2$] with sulfur or polysulfide, [Ni(C$_6$H$_5$CS$_2$)$_2$]$_2$, originally formulated as a disulfide-bridged, nickel(II) dimer, has been reformulated (*358*) as the monomeric perthiocarboxylate complex on the basis of physical and chemical similarities with the analogous bis(dithiocumato)nickel complex (**XXVI**).



(XXVI)

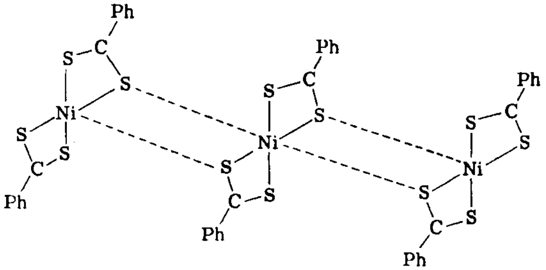
The large dihedral angle between the plane of the "sulfur-rich," chelate ring and that of its attached benzene ring is striking, and suggests a decreased, π-electron interaction in this ligand compared with the dithiocumate ligand bonded to the same nickel atom. Photochemical reaction of sulfur with $[Ni(S_2CC_6H_4CHMe_2)_2]$ produces the same complex (**XXV**). Treatment of the "sulfur-rich" species with Ph_3P results in specific removal of the sulfur atom adjacent to the carbon atom in the Ni–S–S–C linkage (*360*). This had been observed in a mass-spectrometric study of $[Ni(S_2CPh)(S_3{}^{34}SCPh)]$, which was formed (*361*) from the addition of ^{34}S-enriched sulfur to $[Ni(S_2CPh)_2]$. Spectrophotometric and NMR-spectroscopic, kinetic studies of "sulfur-rich" dithioarylates of Ni(II), Pd(II), Pt(II), and Zn(II) indicated S-atom mobility in these complexes (*362*). The kinetic data for the reaction of PPh_3 with $[Ni(S_2CC_6H_4CMe_2)(S_3CC_6H_4CMe_2)]$ are consistent with a mechanism that involves kinetically controlled attack of PPh_3 on the complex at the sulfur atom adjacent to the carbon atom in the disulfide linkage.

A crystal-structure determination on $[Ni(PhCH_2CS_2)_2]$ showed evidence of a Ni–Ni bond (Ni—Ni distance, 256 pm) in a bridging, acetate-cage, binuclear complex (*363*). Each nickel atom is 5-coordinate and is in a tetragonally distorted, square-pyramid; spectroscopic evidence for a Ni–Ni bond has been obtained (*364*). The polarized crystal spectra showed more bands than predicted for a mononuclear, diamagnetic, square-planar nickel(II), and the spectra are indicative of substantial overlap of the d-orbitals between the two nickel atoms. The bis(dithiobenzation)nickel(II) complex was found to exhibit unusual spectrochemical behavior (*365*).

In nickel and palladium dithiobenzoato complexes, four-membered chelate rings are formed (*366*), whereas, in the corresponding phenyldithio acetates $[M_2(S_2CCH_2Ph)_4]$, the dithio ligands act as bridging groups between the two metal atoms, with the formation of binuclear units (*367*). The molecular structure of the latter compounds shows that each metal atom is coordinated to four sulfur atoms and to the other metal atoms in a square-pyramidal geometry. Other evidence for a metal–metal bond was obtained from a comparison of the metal–sulfur distances with those in nickel and palladium square-planar complexes having comparable bond-angles about the sulfur and the metal. The bis-pyridine adduct, $[Ni(PhCH_2{\cdot}CHS_2)_2(py)_2]$ has been prepared, and the X-ray structure showed monomeric units consisting of distorted octahedrons about the nickel atoms, with the pyridine molecules cis-coordinated (*368*). This is in contrast to the nickel–nickel-bonded bridging of binuclear structures found (*363*) in tetrakis(phenyldithioacetate)dinickel(II).

The infrared spectra have been reported for polycrystalline samples of $[Ni(S_3CPh)_2]$ and $[Zn(S_3CPh)_2]$. The nickel compound has two molecules per unit cell on sites of C_i symmetry, and assignment of a weak absorption at 655 cm^{-1} to $\nu(S{-}S)$ has been made (*369*).

An X-ray crystal-structure determination (*370*) revealed that mixed, nickel coordination exists in the trimeric complex, $[Ni(S_2CPh)_2]_3$. The trimeric structure is similar to that found (*371*) in $[Pd(PhCS_2)]$. The structure contains one molecule of type A linked centrosymmetrically through short Ni–S bridges to two molecules of type B, the three molecules being closely parallel (**XXVII**). Bonamico and co-workers (*372*) also determined the crystal structure of bis(dithiopivalato)nickel(II), $[Ni(C_5H_9S_2)_2]$.



(XXVII)

Nickel(II) complexes with most of the 1,1-dithiolate ligands are known. Recently, the new complexes, $K_2[Ni(S_2C{=}CHNO_2)_2]$ (*113, 373*), $[Ag(PPh_3)_2]_2[Ni(i\text{-mnt})_2]$ (*374*), and $(Ph_2BzPh)_2[Ni(DED)_2]$ (*375*) have been prepared and studied. The complex $[Ph_2I]_2[Ni(S_2CNCN)_2]$ was prepared as part of a study of iodonium salts of complex anions (*376*). Pyrolysis phenylated the two sulfur atoms of the same ligand, as verified by the isolation and identification of *N*-cyanophenyldithiocarbimate, $(PhS)_2CNCN$. As a result of phenylation, the configuration about Ni changed from planar to octahedral, resulting in a polymeric species.

Rate constants for the substitution reactions of square-planar dithiophosphates and dithiocarbonate complexes of Ni(II), Pd(II), and Pt(II), with ethylenediamine and cyanide ion as nucleophiles, have been measured in methanol. The results were compared with those obtained in previous investigations, and interpreted in terms of the stabilities of 5-coordinate species that are formed prior to substitution (*377*).

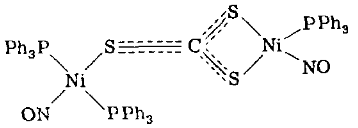
The preparation and chemistry of nickel trithiocarbonate complexes have been studied in detail, and both $[Ni(CS_3)_2]^{2-}$ and $[Ni(CS_4)_2]^{3-}$ have been isolated (*379*). Shul'man and co-workers (*379*) reprepared the known $[Ni(NH_3)_3(CS_3)]$and $[Ni(en)_3]CS_3$, and the kinetics of the reaction of Ni(II) with the trithiocarbonate ion in methanol was studied; the results confirmed the previously proposed ion-pair mechanism (*380*).

$$Ni^{2+} + CS_3^{2-} \rightarrow NiCS_3$$

$$NiCS_3 + CS_3^{2-} \rightarrow Ni(CS_3)_2^{2-}$$

$$Ni(CS_3)_2^{2-} + CS_3^{2-} + 1/2\ O_2 \rightarrow Ni(CS_3)(CS_4)^{2-} + COS_2^{2-}$$

A re-examination of $[Ni(CS_3)(NH_3)_3]$ showed (*381*) it to be $[Ni(NH_3)_6][Ni(CS_3)_2]$. An interesting, dimeric nitrosyl complex containing a bridging CS_3^{2-} group (**XXVII**) was prepared in 100% yield by Brunner (*382*) by prolonged (30 h) reaction of $BaCS_3$ with $[(Ph_3P)_2Ni(NO)I]$ in ethanol.



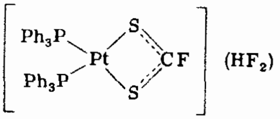
(XXVIII)

The electronic spectra of a range of dithio- and perthiocarboxylatonickel(II) complexes and their pyridine adducts show the presence of a variety of structures in solution, but complete interpretation of the spectra was prevented by lack of a complete MO treatment of these complexes (*378*).

Recent literature contains work in which complexes of nickel(IV) with 1,1-dithio ligands have been isolated. Brinkhoff (*383*) successfully oxidized $[Ni(Et_2dtc)_2]$ to $[Ni(Et_2dtc)_3]I_3$ with iodine, and detected a nickel(III) species in $[Ni(Etxant_2X]$ (X = Cl, or Br) by epr spectroscopy during the oxidation of $[Ni(Etxant_2]$ with chlorine and bromine. $[Ni(R_2dtc)_3]X$ ($X = ClO_4^-$ and $FeCl_4^-$) is prepared by reaction of $[Ni(R_2dtc)_2]$ with $Fe(ClO_4)_3$ and $FeCl_3$, respectively (*270*) Solozhenkin and Kopitsaya (*384*) detected by epr a paramagnetic, nickel(III) dithiocarbamate species formed from oxidation of $[Ni(R_2dtc)_3]$ with tetramethylthiuram disulfide at the boiling point of benzene, no spectrum is obtained, owing to oxidation of Ni(III) to Ni(IV). Brinkhoff and co-workers (*385*) had previously reported a similar reaction, and the isolation of [Ni(Bu$_2$dtc)$_3$X], which they characterized as an octahedral Ni(IV) species. Structurally, the coordination in [Ni(Bu$_2$dtc)$_3$]$^+$ is similar to that in the [Ni(Etxant)$_3$]$^-$ anion, containing high-spin nickel(II). Nigo and co-workers (*386*) isolated [Ni^{IV}(Et$_2$dtc)$_2$]Br$_2$ by oxidation of [Ni(Et$_2$dtc)$_2$] with Br$_2$ in CS$_2$ solution. On the basis of spectroscopic and polarographic data, the complex was characterized as a very rare example of a low-spin, nickel(IV) species having a planar, chelate structure. [Ni(Bu$_2$dtc)$_2$] reacts with I$_2$ at −30° in ether, to give Ni[Bu$_2$dtc)$_2$I], although the magnetic moment of the complex (1.33 B.M.) is somewhat low for low-spin nickel(III); epr evidence indicated square-pyramidal coordination (*387*). Very recently, Lachenal (*388*) and Hendrickson *et al.* (*389*) studied the oxidation and reduction processes for Ni(II) and Ni(IV) dithiocarbonate complexes. Lachenal (*388*) prepared [Ni(Et$_2$dtc)$_3$]BF$_4$ by an electrochemical method. The [Ni(R$_2$dtc)$_3$]$^+$ cations react with isocyanides or phosphines to form [NiL$_2$(R$_2$dtc)]$^+$ or [Ni(diphos)(R$_2$dtc)]$^+$. Reaction with PPh$_3$ produces (*390*) [Ni(R$_2$dtc)$_2$], Ph$_3$PS, [Ph$_3$PC(=S)NR$_2$]$^+$, and some [Ni(PPh$_3$)$_2$(R$_2$dtc)$_2$]$^+$.

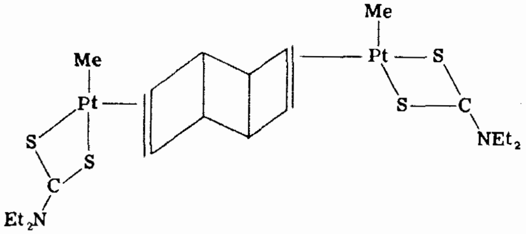
McCleverty and Harrison recently studied (*391*) the reaction of [Ni^{IV}(dtc)$_2$]cations with various Lewis bases, and found that treatment of [Ni(R$_2$dtc)$_3$][PF$_6$] R = Et, or Bu^n) with Lewis bases [L = CNR^1 (R^1 = Pr^i, Bu^t, or *p*-C$_6$H$_4$Cl), *p*-MePH$_2$ or ½ dppe] gave [NiL$_2$ (R$_2$dtc)]PF$_6$, and, when L = CNR^1, the thiuram disulfide was isolated. Reaction with PPh$_3$ yielded PPh$_3$S, [PPh$_3${C(NR$_2$)S}]PF$_6$ and Ni(dtc)$_2$, with the isolation of only very low yields of [Ni(PPh$_3$)$_2$(R$_2$dtc)][PF$_6$].

Considerably less is known about the chemistry of palladium and platinum 1,1-dithio complexes. Of late, there has been only one report that dealt with the synthesis of a large number of palladium dithiocarbamates (*392*). Twenty-five yellow palladium dithiocarbamate complexes were obtained by reaction of PdCl$_2$ with NaR$_2$dtc in methanol solution. Several other reports have appeared in which a few dithiocarbamate complexes of palladium were synthesized. Thus, the novel [Pd{(OH)$_2$dtc}$_2$], which is soluble in water, was isolated (*393*). The synthesis of optically active palladium(II) complexes of *N*-alkyl-α-phenethyldithiocarbamates, similar to (**XXIV**), via the reaction between the optically active amine, CS$_2$, and PdCl$_2$, has been described. From ORD and CD spectra, it has been established that the vicinal contribution of a remote, asymmetric carbon center could give rise to optical activity of the d—d transitions of palladium (*394*). Carbon disulfide has been shown to insert into the Pt–F bond of [PtF(PPh$_3$)$_3$]HF$_2$, and X-ray studies indicated the structure (**XXIX**).



(XXIX)

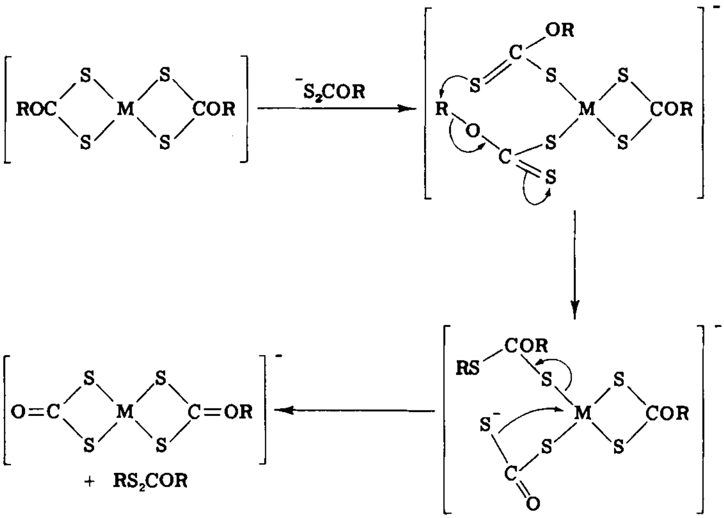
The mixed complexes of the type $[M(mnt)(R_2dtc)]^-$ (M = Pd, or Pt; R = Et, Bu, or Ph) have been prepared, and voltammetry in CH_2Cl_2 revealed that the complexes undergo one-electron oxidation; the values of the half-wave potentials are intermediate between those of the unmixed complexes (*395*). The halide-substituted complexes $[MX_2(Bu_2dtc)_2]$ (M = Pd, or Pt; X = Br, or I) have been prepared by Willemse and co-workers (*396*) and the platinum complex was isolated as cis and trans isomers. ESCA measurements showed the trans isomer to be a Pt(IV) species. With tetrabutylthiuram disulfide, these complexes give $[M(Bu_2dtc)_3]X$. A novel dimeric complex (**XXX**) is formed (*397*) from the reaction of $NaEt_2dtc$ with $[Pt(CH_3)(\pi\text{-}1,5\text{-cyclooctadiene})L]PF_6$ (L = 4-Mepy, $AsPh_3$, PPh_3, $p\text{-}NCC_6H_4OCH_3$, or CNEt).



(XXX)

The reaction of $[M(S—S)_2]$ complexes ($S—S^-$ = R_2dtc, Rxant; M = Pd, Pt) with tertiary phosphines occurs by a stepwise cleavage of the M–S bonds to generate the 4-coordinate compounds $[M(S—S)_2PR_3]$ and $[M(S—S)(PR_3)_2](S—S)$, which respectively exhibit unidentate/bidentate and bidentate/ionic modes of bonding of the dithioacid groups (*398, 399*). Reactions of platinum(II) xanthates with the xanthate ion (*400*) produce a series of compounds, $Ph_4As[Pt(Rxant)_3]$ (R = Et, or Pr^i), $Ph_4As[M(S_2CO)(Rxant)]$ (R = Et, Pr^i, or Me; M = Pr, or Pd), and $(Ph_4As)_2[Pt(S_2CO)_2]$, and the following scheme was proposed for the formation of the second type of complex.

Very few studies on complexes of palladium and platinum with 1,1-dithiolato ligands have been reported recently. The electronic absorption spectra of the Et_2dtc complexes of Pd and Pt, as well as Zn, Cu, Fe, Co, and Mn, have been measured in MeCN, EtOH, and *n*-heptane, with diffuse-reflectance spectra also being determined (*401*). In 1969 and



SCHEME 5

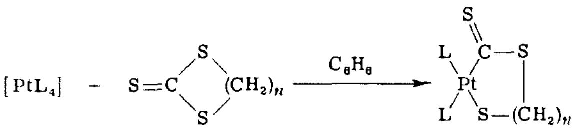
1970, the first, stable, transition-metal dithiocarbonate (CS_2O) complexes were reported (*402, 403*).

Reaction of the complexes $[PtS_2(COR)_2]$ with $K[S_2COR]$ ($R = Et$, or Pr^i), followed by the addition of $[AsPh_4]Cl$, generates $[AsPh_4][Pt(S_2COR)_3]$. Variable-temperature ^1H-NMR studies indicated rapid unidentate–bidentate exchange at ambient temperature. When the palladium(II) analog $[Pd(S_2COEt)_2]$ reacts with $K[S_2COEt]$ and $[AsPh_4]Cl$, the main product is $[AsPh_4][Pd(S_2COEt)]$. Reaction of $[Pt(S_2COR)_2]$ with $K[S_2COR]$ (R = Me, or CH_2Ph) and $[AsPh_4]Cl$ generates $[AsPh_4][Pt(S_2CO)(S_2COMe)]$ or $[AsPh_4]_2[Pt(S_2CO)_2]$, both of which gave $[PtL_2(S_2Co)]$ on addition of various Lewis bases L (L = PPh_3, PMe_2Ph, or ½ dppe) (*404*).

Facile replacement of the unidentate $[S_2PPh_2]^-$ group by X^-, to give $[PdX(PR_3)(S_2PPh_2)]$, occurs when $[Pd(PR_3)(S_2PPh_2)_2]$ (PR_3 = PPh_3, or PMe_2Ph) reacts with an excess of AgX in acetone (X = Cl, Br, I, or SCN). Similar reactions with $[Pt(PR_3)(S—S)_2]$ ($S—S^-$ = $[S_2PPh_2]^-$ or $[Etdtc]^-$) are not very efficient, and a better, general method of synthesizing $[MX(PR_3^-)(S—S)]$ complexes (M = Pd, or Pt; X = Cl, Br, or I; $S—S^-$ = $[S_2PMe_2]^-$, $[Etdtc]^-$, $[Pr_2^i$ dtc], or $[S_2COEt]^-$) is be reaction of equimolar amounts of $[\{MX_2(PR_3)\}_2]$ and alkali-metal dithioacid salts (*405*). Prolonged reaction of $[Pd(S_2PMe_2)_2]$ with an excess of $PPh_2(OR)$(R = Me, or Et) in either $MeCl_2$ of benzene gives the 4-coordinated complex $[Pd(S_2PMe_2)_2(PPh_2O)\{PPh_2(OH)\}]$, shown by spectroscopic evidence and X-ray structural analysis to contain the symmetrically hydrogen-bonded $Ph_2 \cdot POHOPPh_2$ ligand (*406*).

Bis complexes of pyrrole-*N*-carbodithiolate (L) with Pt(II), Pd(II), and Co(II), as well as Cu(II), have been reported. A mixed chlorine-ligand complex of Pt(IV), $[PtCl_2L_2]$, was also prepared. Infrared spectra of these complexes indicated an exocyclic single C–N bond, as opposed to similar complexes containing other dithiocarbamate ligands (*407*).

The reactions of platinum(II) complexes $[Pt(L)Cl_3]^-$, $[Pt(L)_4]Cl_2$ (L = NH_3, or py) with an excess of aqueous Na_2CS_3 yield $[Pt(L)CS_3]$ and $[Pt(L)_3CS_3]$; heating the latter results (*408, 409*) in the formation of $[PtCS_3]$ and $[Pt(py)_2CS_3]$. Trithiocarbonates, $(CH_2)_nCS_3$ (n = 2, or 3), oxidatively add to $[PtL_4]$ (L = PPh_3, or PPh_2Me) to yield (*410*) cis complexes as shown (**XXXI**).

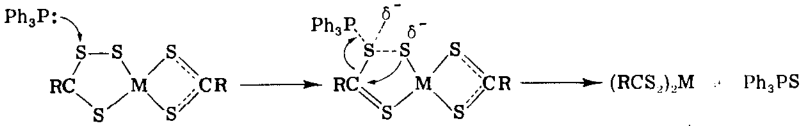


(XXXI)

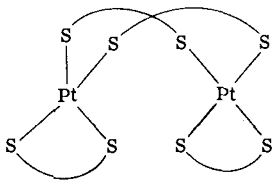
The first example of the synthesis of a novel metallodithiocarbonylate ligand complex, $[Cl(Ph_3P)_2Pt(CS_2)Pt(Ph_3P)_2]BF_4$, has been reported (*411*). $[L_2Pt\{(CF_3)_2C{:}CS_2\}]$ (L = PPh_3, or PPh_2Me) complexes have been prepared by reaction of low-valent platinum–phosphine complexes with the ligand (*326*). A novel synthesis of platinum dithiocarbimidato complexes was recently evolved (*412*) by Haszeldine and coworkers: $[Pt(S_2O{=}NR^1)(PPh_3)_2]$ complexes (R^1 = Ph, or Me) were obtained in 30–60% yields by a sulfur abstraction-reaction between $[PtR(PPh_3)_2]$ (R = $CH_2{:}C{:}C{:}CH_2$, or $CF_3CH{=}C{=}CH_2$), $[Pt(PPh_3)_4]$, or $[Pt(PhNCS)(PPh_3)_2]$ and R′NCS, to yield crystalline products $[Pt(S_2C{=}NR')(PPh_3)_2]^+CF_3CO_2^-$. Kinetics and mechanisms of substitution reactions of platinum dithiolato complexes $[Pt(S{-}S)_2]^{2-}$($(S{-}S)^{2-}$ = $S_2C{:}C(CN)_2^{2-}$, mnt^{2-}, $S_2C{=}CHNO_2$, $S(O)C{=}C(O)S^{2-}$, $NC{-}N{=}CS_2$, and $NC(Ph)C{:}CS_2^{2-}$) with both unidentate and bidentate nucleophiles have been studied in aqueous solution (*413*). Reactions were found to be second-order overall (first-order in substrate, and first-order in nucleophile). The results permit a comparison of the relative reactivities of dithiolato complexes of Ni, Pd, and Pt. Except for $[Pt\ S(O)C{:}C(O)S_2]^{2-}$, two steps were observed for the substitution reactions with CN_3^-, the first step being substitution of one dithiolato ligand by two CN^- ions, and the second, the substitution of the second dithiolato ligand.

NMR spectra have been used for comparing the solution structure of Pt[Bu$^i_2$dtc]$_2$ (PMe$_2$Ph$_2$) with its solid-state structure. The low-temperature, solution structure is that of the cation [Pt(Bu$^i_2$dtc) (PMePh)$_2$]$^+$ with a free dithiolate anion, compared to the structure of the crystalline solid, which is *trans*-PtS$_2$P$_2$. The structure of Pt(S$_2$CO)(Ph$_3$P)$_2$] and the diphos analog show a *cis*-PtS$_2$P$_2$ coordination *(414)*.

The isolation, separation, and chemistry of dithio- and perthioarylcarboxylate complexes of Ni(II), Pd(II), and Pt(II) were reported in two complementary reports *(381, 415)*. The perthiocarboxylate complexes have also been obtained by oxidative addition of sulfur to the dithiocarboxylic acid complexes. The abstraction of the sulfur atom adjacent to carbon by PPh$_3$ was again observed, and rationalized as follows.



X-Ray structural analysis of [Pt(dithiocumato)$_2$] revealed a dimeric structure containing two bridging and two terminal dithiocarboxylate ligands (**XXXII**). The proximity of the two platinum atoms (278 pm) suggested that a Pt–Pt bond may be present *(415)*.



(XXXII)

H. Copper, Silver, and Gold

The complexes of the 1,1-dithio ligands with the Group I transition metals have been studied in considerable detail, and have been extensively reviewed by Coucouvanis *(1)*. Interest in the synthetic chemistry of these complexes has been maintained over recent years, but a large proportion of the work on these complexes has been concerned with physical studies, particularly by esr spectroscopy.

Solid-state, esr spectra of [Cu(Et$_2$dtc)] and [Cu{S$_2$P(OPr^i)$_2$}$_2$] dissolved in coordinating and noncoordinating solvents have been compared with single-crystal and powdered samples diluted with the corresponding complexes of divalent nickel and zinc. With noncoordinating solvents, the ESR spectra are similar to those obtained from the solid samples, where weak self-association is present. On the basis of the results of this study, it was suggested that in the ground state the unpaired electron is in a hybrid orbital of the $dx^2 - y^2$, dz^2, and 4s atomic orbitals of copper (*416*). The effect of varying the solvent, and the temperature, on esr parameters and linewidths of $[Cu(Et_2dtc)_2]$ have been reported (*417*). An esr study of the Cu(II) complex of pyrrole-*N*-carbodithiolate, taken together with the optical transition for this complex, showed a very covalent σ and π metal–sulfur bond (*407*).

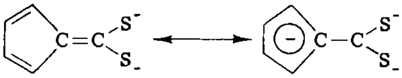
Dithiocarbamate complexes of copper have been sythesized at a high rate. Reports of new complexes include the morpholine-4- (*44*), thiomorpholine, *N*-methylpiperazine-4-, and piperidine- (*291*) dithiocarbamates. Novel, polymeric complexes of the type $\{Cu(pipdtc)_2\}\,(CuBr)_n$ ($n = 4$, or 6) and $\{Cu(pipdtc)_2\}\,(CuCl)_4$ have been prepared by reactions of $[Cu(pipdtc)_2]$ with the respective copper halide in $CHCl_3$–EtOH (*418*). The crystal structures of the polymers are known to consist of sheets of individual $[Cu(pipdtc)_2]$ molecules linked to polymeric CuBr chains via Cu–S bonds. A series of copper(I) dtc complexes have been the subject of a ^{63}Cu and ^{65}Cu NQR-spectral study (*440*).

Unlike 2-thiazolidinethione and its simpler derivatives, the 3-alkyl-5-hydroxy-5-(1,2,3,4-tetrahydroxy-*n*-butyl)-2-thiazolidine thiones [which are specific, photometric reagents for Cu(II)] undergo rearrangement in the presence of Cu(II) ions, to form complexes of dithiocarbamate. The analytical specificity is explained by the inability of most other metal ions to effect this rearrangement (*419*).

Oxidation of copper dithiocarbamate complexes of Cu(I) with chlorine or bromine yields paramagnetic compounds with the composition $CuX_3(R_2dtc)$, in which the copper has a formal oxidation-state of (IV), but the structure of these compounds is obscure (*385*). The synthesis and crystal structures of $[Cu_2(Et_2dtc)_2Cl_2]$ and $[Cu_3(Et_2dtc)_2Cl_3]$ have been reported. The latter is an example (*420*) of a complex containing the unusual mixed valence Cu^{II} and Cu^{I}. Both Cu(I) and Cu(III) are present in complexes of the type $[Cu_7Br_7(Bu_2dtc)_2]$, $[Cu_5Br_5(Pr_2dtc)_2]$, $[Cu_5Br_5(Et_2dtc)_2]$, and $[Cu_3Br_3(Me_2dtc)_2]$. The Cu(III) is present in the $[Cu(dtc)_2]^+$ cation, and the Cu(I) is in the haloanion (*421*). $[Cu(R_2dtc)_2]ClO_4$ and $[Cu(R_2dtc)_2]FeCl_4$ have been prepared (*270*) by reaction of $FeCl_3$ and $Cu(ClO_4)_2$ with copper dithiocarbamate, and the reaction of $Cu(Bu_2dtc)_2$, MBr_2 (M = Zn, Cd, or Hg), and bromine in stoichiometric quantities, or the reaction of $[M(Bu_2dtc)_2]$ and $[Bu_4bitt][Cu_2Br_6]$ (Bu_4bitt = 3,5-bis-(*N,N*-dialkyliminium)-1,2,4-trithiolane) $[Cu_3(Bu_2dtc)_6][MBr_3]_2$. The cadmium-complex cation contains one copper atom having distorted octahedral geometry, the other being square pyramidal; the anion is $Cd_2Br_6^{2-}$. ESR measurements (*422*) suggested that the unpaired electron is localized on one copper atom, and that the cation is best described as $[\{Cu^{III}(Bu_2dtc)_2\}_2\{Cu^{II}(Bu_2dtc)_2\}]^+$. The $[Cu(Pr^n_2\,dtc)_2]$ species is dimeric in the solid state, the copper atoms having tetragonal-pyramidal coordination (*423*); $[Cu(PhMedtc)_2]$ is monomeric, and isostructural with its nickel(II) analog.

The crystal structure of $[Cu(Me_2dtc)_2]$ shows that it possesses a center of symmetry, with the copper octahedrally co-ordinated to six S atoms, two Cu–S bonds being longer than the other four (*424*). Choi and Wasson (*425*) showed that there is only Cu–S bonding in $[Cu(acdc)_2]$ (acdc = 2-amino-1-cyclopentadienyl-1-dithiocarboxylate).

Of late, few complexes of copper with 1,1-dithiolate ligands have appeared. A red–brown, air-sensitive complex with the new, cyclopentadiene-dithiocarboxylate ligand was readily obtained by reaction with $CuBr_2$ in degassed THF or acetonitrile (*426*), and NMR data indicated a large amount of charge residing on the cyclopentadiene ring system, but, from esr and electronic-spectral data, it was concluded that, as expected, the out-of-plane π-bonding was much more covalent than that in the copper dithiocarbamate systems. The in-plane π- and σ-bondings were similar. As the out-of-plane bond is anti-bonding in character, and is very covalent, the bonding molecular orbital is similar, indicating that the dithiolate is a strong, π-bonding ligand. The delocalization of charge onto the ring system can be shown as follows.



2-Aminocyclopentene-1-dithiocarbamic acid (LH) forms a series of complexes, ML_2(M = Ni^{II}, Co^{II}, or Cu^{II}), in which the ligands are S,S-bonded (*427*). Diethanoldithiocarbamic acid forms $Cu[(HOC_2H_4)_2NCS_2]_2$, which is a monomeric, planar, CuS_4 chromophore in solution, but Cu · · · S interaction probably occurs between neighboring molecules in the solid state (*428*).

A number of complexes of copper with 1,1-dithiolenes are known; they are interesting, inasmuch as they form (*1*) polynuclear species, e.g., $[Cu_4(i\text{-mnt})_3]_2^{4-}$. Recently, a copper(III) complex of 1,1-dicarboethoxy-2-ethylenedithiolate (DED^{2-}) was prepared (*375*) by oxidation of aqueous solutions of $K_2[Cu(DED)_2]$ with a 10–15% excess of Cu(II) or H_2O_2, and of $(BzPh_3P)_2[Cu(DED)_2]$ with I_2. The possibility of this system as a model for the Cu^{III}/Cu^{I} system in D-galactose oxidase has been pointed out. Lewis and Miller (*113*) also prepared $M[Cu(S_2C{:}CHNO_2)_2]$ (M = Cu, or Zn) and $Cu[Cu\{S_2C{:}C(CN)_2\}_2]$, and found that they are effective insecticides.

A variety of 1,1-dithio complexes of silver are known, but, lately, there have been few reports concerning the chemistry of these species. However, the chemistry of the gold 1,1-dithio complexes has been probed in depth. The preparation of a series of dithiocarbamate complexes of Au(III) was reported by Van der Linden (*429*). Thus, $Au(R_2dtc)_2^+ X^-$ (R = H, Me, Et, Pr^n, Bu^n, or Ph; X = Br, ClO_4, PF_6, $AgBr_2$, or BPh_4), $[Au(tdt)_2]$, and $[Au(mnt)_2]$ have been prepared. It was found that, in the solid state, some of the anions have a distinct effect on the C–N stretching-frequency that is absent in $CHCl_3$ solution. X-Ray studies showed that, in some cases, the anion is near to the nitrogen atom of the cation and the effect on the ν(C–N) is due to polarization of the C–N bond. The infrared and ^{1}H-NMR spectra of $[(PPh_3)_2Cu(Et_2dtc)]$ have been studied (*430*).

The complexes of Ph_3P and Cu(I)- and Au(I)-dithiocarbamates have been reinvestigated (*431*). An equilibrium

$$(Ph_3P)_2M(R_2dtc) \rightleftharpoons (Ph_3P)M(R_2dtc) + Ph_3P$$

was indicated by the results, and the complexes originally formulated as $[(Ph_3P)_2M]^+[R_2dtc^-]$ may not be constituted as indicated. The Au(III) complexes $[Au(Bu_2dtc)_2]Br$ and $[Au(Bu_2dtc)_2]^+[AuBr_4]^-$ have been prepared and characterized (*432*). A spectrophotometric study (*393*) showed the formation of $[Au(R_2dtc)Cl_2]$, $[Au(R_2dtc)_2Cl]$, and $[Au(R_2dtc)_3]$ by reaction of Au(III) species with R_2dtc^- in acidic solution. The Bergendahls (*433*) studied the equilibrium of Au^{III}/Au^{I} and Ag^{II}/Ag^{III} systems with Bu_2dtc^-,

$$[(Bu_2dtc)_3M] \rightleftharpoons [M(Bu_2dtc)_2] + 0.5\,[Bu_2NCS_2]_2$$

and the esr spectra support the formation of the paramagnetic species $[Au(Bu_2dtc)_2]$ from mixtures of $LiBu_2dtc$ and $[AuBr_4]^-$. The structure of $[Au(Pr^ndtc)_2]_2$ is dimeric with tetragonal-pyramidal coordination at the Au atom (*434*); $[Au(Bu^idtc)_2]_2$ is known to be dimeric. The valence state, $5d^{10}$, of Au(I) is quite stable, and would not be expected to favor homonuclear Au–Au bonds. Many heteronuclear Au–metal bonds are known, but substantial electronegativity differences are involved. Nevertheless, the length of the Au–Au bond in $[Au(Bu_2dtc)_2]_2$ is 276 pm, compared with 288 pm in metallic gold, and is less than the span of the sulfur atoms in the ligands. The sulfur atoms are twisted out of the plane that the Au and carbon atoms form. From the Raman spectrum of this complex (*435*), an estimated bond-order of about one-fourth of its value in Au_2^0 was derived for Au–Au. The metal–metal interaction was understood to be due to charge transfer from the dithiocarbamate ligands to the Au(I) ions, with the partial formation of an Au_2^0 bond.

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