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1,2-DITHIOLENE COMPLEXES OF TRANSITION METALS

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I. Introduction

Over the past two decades there has been a phenomenal increase in the study of the chemistry of transition metal complexes containing sulfur ligands. There are a number of reasons for this, the major one being the revitalization of the chemistry of the unsaturated sulfur donor chelates. These were used as early as the 1930s as analytical reagents for various metals (*32*, *154*). The interest in complexes of these ligand systems now embraces areas ranging from purely academic syntheses to large-scale industrial production. Almost every available physical technique has been utilized for the elucidation of the molecular and electronic structures and the kinetics manifested in these systems.

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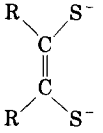
The spiraling interest in the complexes of sulfur donor ligands has prompted number of excellent and frequently exhaustive reviews. Discussions by Livingstone (*127*), Harris and Livingstone (*128*), and Jørgensen (*95*) cover sulfur ligands in general. Reviews by Gray (*69*), McCleverty (*139*), Schrauzer (*175*), and Hoyer (*77*) have dealt with the chemistry of 1,2-dithiolene complexes in great depth.

Other reasons for the expansion of the field of dithiochelate chemistry have undoubtedly included the correlations of model complexes with biological systems containing transition metal-to-sulfur bonds and the numerous commercial uses of the compounds. The patent literature abounds with examples of the uses of these compounds, and they include applications as vulcanization accelerators for rubbers, highly specific analytical reagents, chromatographic supports, high-temperature wear-inhibiting additives in lubricants, polarizers in sunglasses, polymerization catalysts, catalytic inhibitors, oxidation catalysts, semiconductors, fungicides, pesticides, mode-locking additives in neodymium lasers, and fingerprint developers in criminal investigations. This list is by no means exhaustive, but exemplifies the diversity of the applications of these complexes.

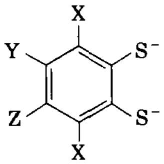
II. 1,2-Dithiolate Ligands and Synthetic Routes

One of the main reasons for the vast increase of interest in the chemistry of transition metal–sulfur complexes over the past 15 years has been the discovery of the novel complexes formed from the unsaturated 1,2-dithiols. These ligands form five-membered unsaturated chelate rings in the metal complexes. There are two main types of ligand that fall into the category of 1,2-dithiolates: the substituted and unsubstituted ethane-1,2-dithiolates (I) and the substituted and unsubstituted benzene-1,2-dithiolates (II).



(I)

$R = H, CF_3, CN$, alkyl, aryl

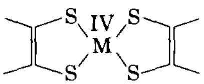


(II)

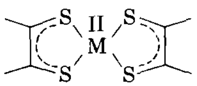
$X = Y = Z = H, CH_3, F, Cl$
$X = Y = H$
$X = H$
$Z = CH_3$
$Y = Z = CH_3$

The interest in these complexes has sprung mainly from the inability to assign formal oxidation states to the transition metal, the discovery of a very rare structural form, the trigonal prism, in the tris complexes, the facile one- and two-electron transfer reactions they undergo, and the five- and six-coordinate and organometallic adducts that they form.

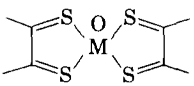
The difficulty of assigning formal oxidation states in these complexes according to the traditional rules of valence has introduced conflicting nomenclature, e.g., in the planar $MS_4C_4R_4$ complexes (III)–(V). Three different limiting structures are possible in which the metal could have the formal oxidation states shown:



(III)

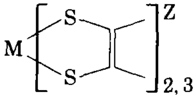


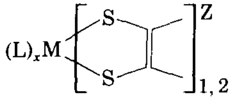
(IV)

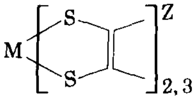


(V)

Structure (V), the bis dithioketone, is unlikely to be stable, as zerovalent metal complexes are not usually planar. Dithiolate dianions were previously considered to stabilize high valence states (*124*, *131*), but this has since been discounted (*172*). Ligands in complexes of type (III), the dithiolato dianions, exist in complex anions, such as $Pt[S_2C_2(CN)_2]_2^{2-}$. In the neutral complexes, however, the ligand is usually considered to be in a state intermediate between (III) and (V), having a delocalized ground state. Schrauzer (*172*) has proposed that complexes regarded as having delocalized ground states, i.e., the intermediate structure (IV), be termed "dithienes" and the dianions "dithiolates." McCleverty (*139*), however, used "dithiolene" to denote metal complexes of the type:



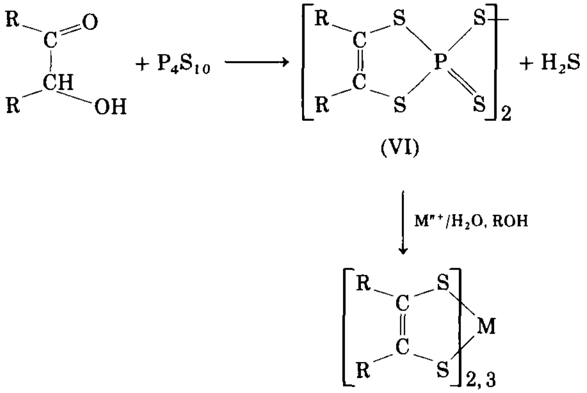




This terminology, although vague at times, does not imply any particular formal oxidation state or structure.

The 1,2-dithiolene complexes were first reported in the 1930s in the analytical studies of Clark and co-workers, who used toluene-3,4-dithiol and chlorobenzene-3,4-dithiol as reagents for zinc, cadmium, mercury, and tin (*32*, *154*). It was not until the late 1950s and the early 1960s that the interest in 1,2-dithiol ligands moved most markedly from their analytical uses to their coordination chemistry.

In 1962, Schrauzer and Mayweg (*175*), while attempting to catalytically produce thioaromatics, carried out a reaction between solid nickel sulfide and diphenylacetylene. From this they isolated an unusual, intensely green solid, the nickel dithiolene, $[Ni(S_2C_2Ph_2)_2]$. This method gave low yields, and the synthesis of dialkyl and diaryldithiolenes was later accomplished by allowing an acyloin or a benzoin to react with phosphorus pentasulfide in refluxing xylene or dioxane to produce a dithiophosphoric ester (VI). Addition of a solution (usually aqueous or alcoholic) of a metal salt and subsequent heating produces the dithiolene complex (VII).

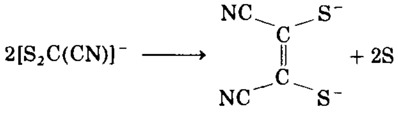


(VI)

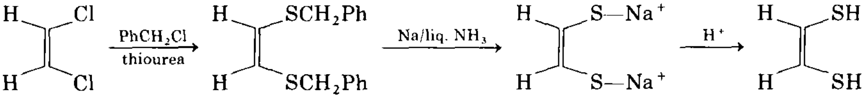
(VII)

This provides a very versatile synthetic route to the neutral dithiolene complexes, as many acyloins are available commerically or can readily be produced, but the unsubstituted complex (R = H) could not be obtained by this method (*196*).

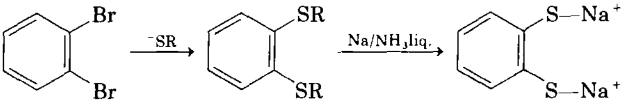
Also in 1962, Gray and co-workers (*70*) reported metal complexes derived from the *cis*-1,2-dicyano-1,2-dithiolate (maleonitriledithiolate, mnt) dianion. The latter was previously synthesized by Bähr and Schleitzer (*5*, *6*) by dimerizatation of sodium dicyanodithioformate in water for 24 hours via a spontaneous desulfinization. Improved yields were reported for the same reaction in refluxing chloroform for 8 hours (*128*).



Many metal complexes derived from the mnt ligand have been prepared and studied. This introduced the second major synthetic route to dithiolene complexes, i.e., from the dianionic 1,2-dithiolates. Thus, the parent unsubstituted ligand *cis*-1,2-ethylenedithiol was prepared by Schrath and Peschel (*171*). They obtained the dibenzyldithioether from *cis*-1,2-dichloroethylene, benzyl chloride, and thiourea in refluxing ethanol. By making the dithioether react with sodium in liquid ammonia, the benzyl groups were cleaved, forming the disodium salt of the dianion. Acidification produced the free dithiol:

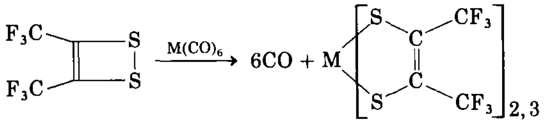


Metal complexes are easily produced by reaction of the dianion with the respective metal salts (*23*). The aryl-1,2-dithiolenes have also been prepared by reaction of the dianions with metal salts. Toluene-3,4-dithiol and quinoxaline-2,3-dithiol are available commercially, and treatment with potassium in alcohol liberates the dianion. Benzene-1,2-dithiol and its derivatives have been prepared in a similar manner to the *cis*-1,2-ethylenedithiol. *o*-Dibromobenzene is treated with copper ethyl- or *n*-butylmercaptide to yield the 1,2-dithioethers. Sodium/liquid ammonia cleavage of the alkyl groups produces the disodium dithiolate salt (*1*).

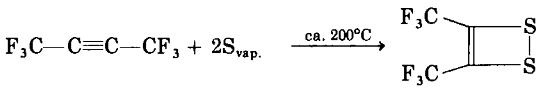


More recently, benzene-1,2-dithiol has been obtained in high yield from the diazotization of *o*-aminophenol in glacial acetic acid, which gives 1,2,3-benzodithiazole, followed by heating with carbon disulfide in an autoclave to give 1,3-benzodithiol-2-thione, which is decomposed in alkaline solution to give the product (*82*). The tetrachlorobenzene-1,2-dithiol is obtained via an iron complex. Hexachlorobenzene is made to react with iron powder and sodium sulfide in refluxing DMF, and $[Fe(S_2C_6Cl_4)_2]_n^0$ is precipitated by treatment with base. The free dithiol is liberated by boiling the complex with zinc oxide (*145*).

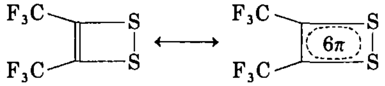
The third major synthetic route to dithiolene complexes is via the reaction of low-valent metal compounds (usually containing carbonyl or phosphine ligands) with the heterocyclic bistrifluoromethyldithiete (*108*),



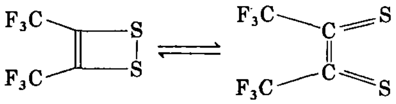
The ligand was first produced by the reaction of 1,1,1,4,4,4,-hexafluorobut-2-yne with boiling sulfur (*119*) to yield a yellow liquid that boils at 95°–96°C. It is in equilibrium with a dimer that is more stable at room temperature; at the temperature of the reaction, however, the monomer is more stable:



The high thermal stability of the dithiete is explained by partial aromaticity as the ring system has 6 π-electrons (*120*):



The formation of metal complexes from bistrifluoromethyldithiete probably takes place via the very reactive dithioketonic form (VIII), as molecular orbital calculations (*172*) suggest that the difference in stability between the two forms is quite small and they could exist in equilibrium.

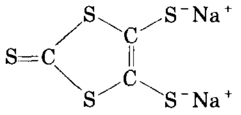


(VIII)

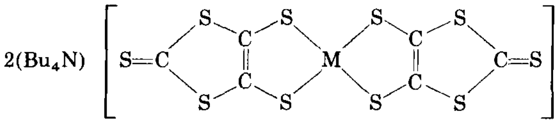
An electron diffraction study of the molecular structure of the dithiete in the vapor phase (*73*) has shown insignificant difference between it and its transition-metal complexes. This does not suggest that complex formation is accompanied by any great change in bond character in the S—C≡C—S moiety. The driving force for the rupture of the S—S bond in complexation must be the formation of two M—S bonds.

The discovery that facile one- and two-electron transfer reactions are major properties of the dithiolene complexes led to the syntheses of the various reduced and oxidized forms of existing complexes. The wealth of electrochemical redox data available for these complexes has been used to determine redox methods of synthesis. Oxidation and reduction have been achieved by a number of different oxidizing and reducing agents or by electrochemical methods. The commonest oxidizing agents are air, oxygen, iodine, and in special cases the powerful one-electron oxidizing agents $[Ni(tfd)_2]^0$ or $[Fe(tfd)_2]^0$. Common reducing agents include hydrazine, borohydride, zinc in pyridine, *o*- and *p*-phenylenediamine, alkali metal alkoxides, amalgams, and sometimes even weakly basic solvents, such as ketones and alcohols, have reduced the complexes, such as $[Ni(tfd)_2]^0$.

A number of interesting and novel dithiolene ligand systems have been developed recently. Of these, the dimercaptodithiolene (IX) is of interest, as there is potential for forming mixed 1,1- and 1,2-dithiolate polymeric complexes even though, to date, only the 1,2-dithiolene metal complexes (X) have been prepared (*184*). The ligand (IX) is obtained together with $SC(SNa)_2$ by treating carbon disulfide with sodium in DMF. Benzylation of the ligand has also been carried out.



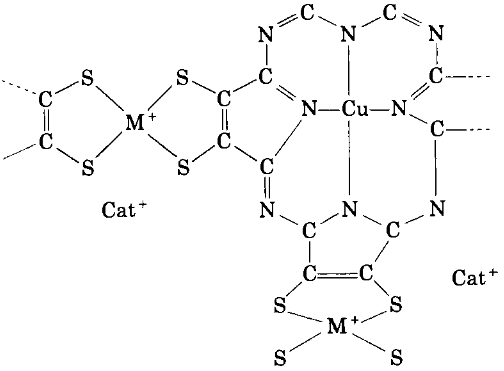
(IX)



(M = Cu, Ni, Zn, Pd, Pt)

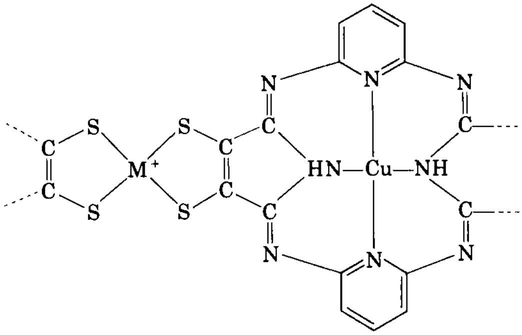
(X)

Mixed-ligand complexes have been obtained by refluxing a neutral complex with a dianionic species or two equivalent monoanions. The rate of ligand exchange is found to be dependent upon the solvent, the temperature, and the nature of the ligands (*52*). Very interesting and novel mixed-metal polymeric catalyst matrices have been evolved that contain dithiolene, porphorin, acetamide, and carboxylate units (XI-XIII) (*99*).

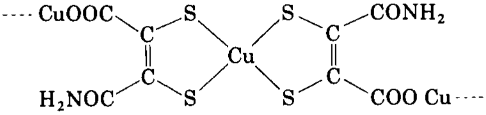


M^+	Cat^+
Cu^{3+}	NMe_4^+
Fe^{3+}	NMe_4^+
Cu^{2+}	Cu^{2+}

(XI)



(XII)



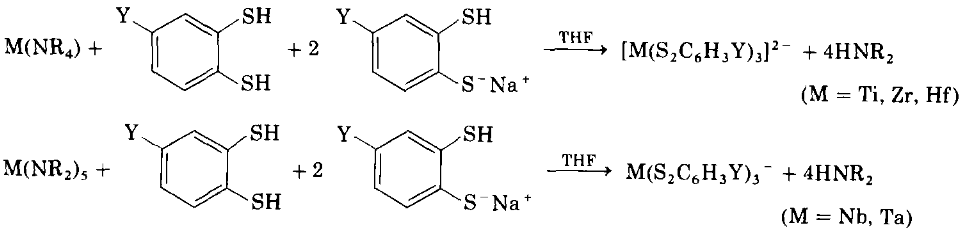
(XIII)

These systems possess unique chemical and physical properties.

III. Transition-Metal Complexes

A. TITANIUM, ZIRCONIUM, AND HAFNIUM

Few complexes of the early transition metals, apart from vanadium, have been reported (*129*, *151*). The inability to synthesize these complexes can be traced to the lack of a suitable preparative method. Early attempts to obtain dithiolene complexes of the early transition metals by known synthetic procedures invariably led to failures except in several notable cases (*183*, *202*). The difficulties were eventually overcome by Takats and Martin, who used the metal amides, $[M(NR_2)_x]$, as starting materials (*13*, *134*). Thus, $(R_4E)_x[M(S_2C_6H_3Y)_{3,2}]$ (R_4E = Ph_4As, Et_4N, Et_2H_2N, Bu_4N; M = Ti, Zr, Hf and $x = 2$; M = Ta or Nb and $x = 1$; Y = H or CH_3) were prepared by the following reactions:



A variety of coordination geometries have been noted, and structural studies (*13*, *42*) indicate that the niobium complex is trigonal prismatic and the isoelectronic zirconium complex has a structure intermediate between trigonal prismatic and antiprismatic or octahedral. The exceptions mentioned above are the successful preparations of $[Ti(S_2C_6Cl_4)_3]^{2-}$ (*202*) and $[Ti(mnt)_3]^{2-}$ (*183*). A distorted trigonal prismatic geometry has been suggested for $[Ti(mnt)_3]^{2-}$, and this complex is unstable in solution.

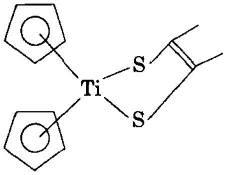
Polarographic results (*134*) show that the dithiolene complexes of the early transition metals undergo facile one-electron transfer reactions, but their electron transfer properties are more limited than in previously studied compounds (*179*). The ligands in these complexes are described as being close to the dithiolate structure, $C_6H_4S_2{}^{2-}$ and can be considered to be stabilizing a net highly positive charge on the metal ions (*134*).

Although the unsubstituted complexes of the early transition metals with the 1,2-dithiolenes have proved to be difficult to isolate, the cyclopentadiene-substituted complexes have been prepared quite easily by several workers (*109*, *115–117*, *128*, *141*, *142*). The generalized reaction is:

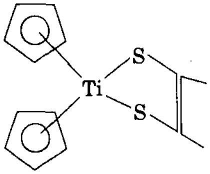
$$[\pi\text{-}Cp_2MCl_2] + \overset{\frown}{S\,S} \rightarrow [Cp_2M(\overset{\frown}{S\,S})]$$

where M = Ti, Zr, Co, Rh, Fe, W, Mn; and $\overset{\frown}{S\,S}$ = mnt^{2-}, $S_2C_2H_2{}^{2-}$, $S_2C_6H_4{}^{2-}$, $S_2C_6Cl_4{}^{2-}$, $S_2C_2H_3Me^{2-}$.

Some monocyclopentadiene- and nitrosyl-containing products have also been obtained by varying the starting material and the amount of ligand. Thus, $\pi-Cp_2TiCl_2$ reacts with 1, 2, and 3 mol of $(S_2C_6Cl_4)^{2-}$ to give $(\pi\text{-}Cp_2Ti(S_2C_6Cl_4))$, $[\pi\text{-}CpTi(S_2C_6Cl_4)_2]^-$, and $[Ti(S_2C_6Cl_4)_3]^{2-}$, respectively (*141*). A crystal structure determination of $[\pi\text{-}Cp_2Ti(S_2C_2H_2)]$ showed that the central titanium atom was tetrahedrally coordinated by the two sulfur atoms and the cyclopentadiene centroids with the TiS_2 plane folded out of the $S_2C_2H_2$ plane at an angle of 46.1° (*121*). The ^1H NMR spectra of $[\pi\text{-}Cp_2Ti(S\text{—}S)]$ ($S\text{—}S = S_2C_2H_2{}^{2-}$, $S_2C_6H_4{}^{2-}$, $S_2C_6H_3Me^{2-}$) complexes are temperature dependent (*116*), possibly representing the interconversion of the two identical conformers (XIV) and (XV) via an excited structure (XVI) in which the chelate ring is planar.



(XIV)



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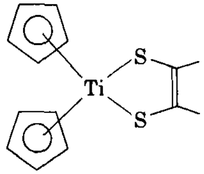
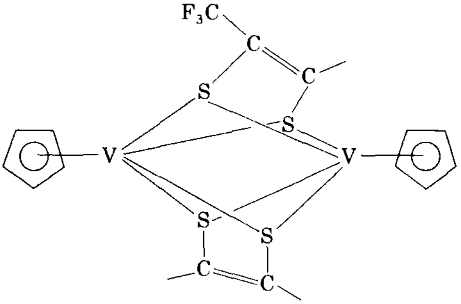


(XVI)

This is contrary to the planar structure generally proposed for metallocene dithiolene derivatives as characterized from NMR spectroscopic data (*139*).

B. VANADIUM, NIOBIUM, AND TANTALUM

In the past few years very few reports concerning the chemistry of complexes of the vanadium triad with 1,2-dithiolene ligands have appeared. The new complexes of niobium and tantalum were described in the preceding section. The preparation of violet-colored $(Ph_4As)_2[V(mnt)_3]$ have been reported and the $[V(mnt)_3]^{2-}$ dianion possess a distorted octahedral coordination geometry (*183*). Reaction of VO^{2+} and $VO_3{}^{2-}$ with $Na_2(mnt)$ in hot water produces five-coordinate $VO(mnt)_2{}^{2-}$ and a small amount of $[V(mnt)_3]^{2-}$ (*201*). Yields of the latter were improved by boiling the mixture for several hours. Reduction with hydrazine produces $[V(mnt)_3]^{3-}$ which reverts to $[VO(mnt)_2]^{2-}$ on aerial oxidation. $[V(S_2C_6Cl_4)_2]^{2-}$ was isolated from the reaction of VCl_3 or $VO(SO_4)_2$ with $K_2S_2C_6Cl_4$ in aqueous solution (*201*). As with titanium, a number of cyclopentadiene-substituted complexes of vanadium with 1,2-dithiolene ligands have been synthesized. The simplest and most common method employs the use of $[\pi\text{-}Cp_2VCl_2]$ and an alkali metal salt of the ligand in polar solvents (*28*, *118*). The patent literature contains the synthesis of neutral metal chelates containing one, two, or three $S_2C_2(CF_3)_2$ groups (*107*), and a series of π-cyclopentadiene-substituted complexes, [π-CpM(tfd)] (M = V, Cr, Mo, Co, Ni) have been prepared by refluxing the bistrifluorodithiete with a suitable π-cyclopentadiene metal carbonyl complex in a hydrocarbon solvent. These compounds, and the [$M(tfd)_3$] complexes, were found to be effective antiknock additives in petrol and oxidizers and were used in criminal investigations for the development of fingerprints. An exploration of the electrochemistry of bridged bimetallic species reveals examples of systems that reduce or oxidize to give stable radical anions or cations, respectively (*54*). Included in this study is [π-CpV(tfd)]$_2$ which has the proposed dimeric structure:



A saturated dichloromethane solution containing $NbOL_3$ (HL = 8-hydroxyquinoline) treated with $S_2C_6H_3Me^{2-}$ produces $O[NbL_2(S_2C_6H_3Me)]_2$ (*84*).

The electron spin resonance (ESR) spectra of magnetically dilute samples of $[VO(mnt)_2]^{2-}$ and $[V(mnt)_3]^{2-}$ have been analyzed in terms of molecular orbital descriptions of the electronic structures of the complexes (*4*, *123*). The results indicate that in both dianions the metal have more electron density than the formal oxidation state of (IV) would imply. One study proposed a reassignment of the ground state of $[V(mnt)_3]^{2-}$ dianion, the unpaired electron being in the metal's $3d_{xy}$ orbital. Steifel and Kwik, however, proposed that the ESR parameters for $[V(mnt)_3]^{2-}$ could be interpreted in terms of a $^2A_1$ ground state in D_3 symmetry, the unpaired having substantial d_{z^2} orbital character.

C. CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Complexes of this group of elements with 1,2-dithiolenes have been prepared and studied extensively: Molybdenum, in particular, has received much attention because of the use of molybdenum–sulfur complexes in modeling biological systems, such as xanthine oxidase and nitrogenase. The early work on these complexes has been covered in detail (*139*).

The simple, stoichiometric complexes of the elements that are formed under normal conditions are usually the tris species. With the ligands $(mnt)^{2-}$, $(S_2C_6Cl_4)^{2-}$, and $(S_2C_6H_3Me)^{2-}$, the tris complexes of chromium, molybdenum, and tungsten have been prepared as part of the series described in the preceding section (*183*, *202*). From physical measurements $[Cr(mnt)_3]^{3-}$ has octahedral symmetry and $[Cr(mnt)_3]^{2-}$ has distorted octahedral symmetry. Assignment of geometry of the dianionic complexes of molybdenum and tungsten is in doubt, and the possibility of trigonal prismatic coordination cannot be eliminated. In addition, Nyholm and co-workers prepared a series of complexes derived from tetrafluorobenzene-1,2-dithiol (*26*): $(Bu_4N)[Cr(S_2C_6F_4)_2]$ and $(Et_4N)_2[Mo(S_2C_6F_4)_3]$, for example. The diamagnetism of the formally assigned Mo(IV) complex suggests a trigonal prismatic structure. The four-coordinate geometry of the Cr(III) complex contrasts with the preferred octahedral geometry and is rather unusual. Hoyer and co-workers described the molybdenum and tungsten tris complexes of the ligand *o*-xylene-3,4-dithiol (*59*, *81*) and with $S_2C_2H_2{}^{2-}$ and mnt^{2-}, during studies of the electronic and X-ray photoelectron spectra of the complexes. The known $Cr(tfd)_3$ complex has been found to be useful in cathode depolarization compositions for electrochemical cells (*133*). Methylation of $[W(S_2C_2Ph_2)_3]^{2-}$ with CH_3I results in $[W(S_2C_2Ph_2)_2]\cdot(S(Me)S(Me)C_2Ph_2)^{2-}$ being formed as an olive-green solid (*178*). The complex was characterized by physical measurements and by reaction with *cis*-$Ph_2PCH{=}CHPPh_2$(Vpp) and sulfur-alkylated $PhSMeC{=}CMeSPh$. Further methylation proved to be unsuccessful. The chromium, molybdenum, and vanadium complexes could not be isolated, and the $[Re(S_2C_2Ph_2)_3]^-$ complex was only methylated at one sulfur atom, i.e., purple $[Re(S_2C_2Ph_2)_2(S(Me)SC_2Ph_2)]$ was formed. The outcome of this reaction has been discussed in terms of the electronic structure of the trisdithiolene complexes.

Crystal and molecular structures of $(Ph_4As)_2[M(mnt)_3]$ (M = Mo, W) reveal that the complexes are isomorphous and almost isostructural (*21*). They are among the few examples that, by all criteria, find themselves close to midway between octahedral and trigonal prismatic limiting geometries. The structural dimensions reveal a closeness to "dithiolate" character.

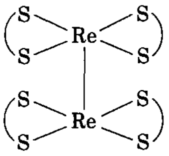
A number of oxomolybdenum complexes containing 1,2-dithiolene ligands have been formulated and studied. From the reaction of oxyanion salts of molybdenum with $Na_2(mnt)$, five-coordinate $[MoO(mnt)_2]^{2-}$ has been isolated (*201*), and voltammetric studies indicate the presence of a monoanionic species. The six-coordinate nitrosyls $[M(NO)_2(mnt)_2]^{2-}$ (M = Mo, W), which were shown to have *cis*-octahedral structures (*35*), are prepared by treatment of $[M(NO)_2Cl_2]_n$ with Na_2mnt. The chromium analog is obtained by similar treatment of $[Cr(NO)_2(NCMe)_4]^{2+}$ (*33*). The related complexes $[M(NO)_2(S_2C_6Cl_4)_2]^{2-}$ are prepared similarly. All the complexes undergo a one-electron oxidation to the corresponding monoanions.

As with the other early transition metals, the complexes of the chromium triad containing π-cyclopentadiene groups and 1,2-dithiolene ligands have been studied in some detail (*109*, *128*, *141*). Thus, Köpf and Kutoglu (*117*, *122*) prepared π-$Cp_2M(S_2C_2H_2)$ and $[\pi$-$Cp_2M(S_2C_6H_4)]$ (M = Mo, W) from Cp_2MCl_2 and $NaS_2C_2H_2$ in ethanol and $C_6H_4S(H)S(H)$ with Et_3N in benzene. $[\pi$-$Cp_2M(S_2C_6H_4)]$ was found to exist in two conformations statistically distributed in the crystals and differing by the staggered and eclipsed arrangement of the two π-cyclopentadiene rings. In both cases the molecule possesses a mirror plane bisecting the two cyclopentadiene rings as well as the chelate and benzene rings. The geometry about the molybdenum atom is considered to be a distorted tetrahedron. π-Cyclopentadiene rings can be cleaved from the molybdenum atom, and this is used to synthesize $[Mo(tfd)_3]^{2-}$ and $[Mo(S_2C_6Cl_4)_3]^-$ with $S_2C_2(CF_3)_2$ and $S_2C_6Cl_4{}^{2-}$. Analogous reactions with Na_2mnt and $(tdf)^{2-}$ have been reported (*90*, *206*). The reactions proceed in stages and $[CpMo(S—S)]_2{}^-$, $[CpMoI(NO)(S—S)]$, and $[CpMo(NO)(S—S)_2]$ with $P(OPh)_3$ afford $[CpMo(NO)(P(OPh)_3)(S—S)]$, with $[CpMo(S—S)(NO)_2]$ being produced originally. Voltammetric studies reveal that all species except the dimers could be oxidized in a reversible one-electron step, but only $[Mo(S_2C_6Cl_4)_3]^-$ was isolated. A number of 1,1- and 1,2-dithio-mixed ligand complexes of molybdenum and tungsten may be prepared by oxidative decarbonylation of $(Bu_4N)[M(CO)_2I]$ in the presence of both ligands (*18*).

Crystal structure determinations of $[\pi$-$CpM(S_2C_6H_4)]$ (M = Mo, W) show much the same features, the $S_2C_6H_4$ groups being inclined at 8° in the WS_2 plane and 9° in the MoS_2 plane (*53*, *122*). Knox and Prout determined the structure of $[\pi$-$Cp_2Mo(tdt)]$ and found a similar structure with no evidence that the lone-pair of electrons on sulfur is involved in Mo—S π-bonding (*114*). A detailed investigation of the structural geometry of $(Ph_4As)_2[CpMo(mnt)_2]$ revealed that the metal atom is seven-coordinate, being linked by two bidentate dithiolate ligands and a formally tridentate cyclopentadiene ligand (*30*).

D. Manganese, Rhenium, and Technitium

Until 1969 the only reported complexes of 1,2-dithiolene ligands with the manganese triad were $[Mn(mnt)_2]^{2-}$, $[Re(mnt)_2]_2^{-}$ which was derived from $[Re_2X_8]^{2-}$ ($X = Cl^-$, Br^-) and believed to retain the Re-Re structure:



$[Mn(mnt)_3]^{2-}$, $[Re(S_2C_6H_3Y)_3]$ ($Y = H$, CH_3), $Re(S_2C_2Ar)_3^-$ ($Ar = Ph$, p-MeC_6H_4), and $[Re(S_2C_2H_2)_3]$.

In recent years the number of complexes in this group has increased only slightly. Reports cited in previous sections (*123*, *183*, *202*) contain details of new complexes of the manganese triad with 1,2-dithiolenes. In addition, McCleverty and co-workers carried out a voltammetric study of the complex previously formulated as $[Re(mnt)_2]_2^{2-}$ and reassigned it as a $[Re(mnt)_2]_4^{4-}$ species that undergoes one-electron reduction and two-electron oxidation processes. Oxidation of $[Re(mnt)_3]^{2-}$ with iodine afforded the new complex $[Re(mnt)_2]^-$, which may be voltammetrically reduced to the dianion (*36*). Recently, very few papers concerning carbonyl derivatives of the manganese dithiolenes have appeared. A whole series of $[Mn(CO)_4(S—S)]^-$ ($S—S = mnt^2$, i-mnt^{2-}, $S_2C_6Cl_4^{2-}$, tdt^{2-}) were originally prepared by McCleverty and co-workers (*34*) from reaction of $Mn(CO)_5Br$ with the respective ligands. Action of phosphines on $[Mn(CO)_4(mnt)]^-$ produces $[Mn(mnt)_3]^{2-}$ and some decomposition. A transient green color was observed when $[Mn(CO)_4(mnt)]^-$ was allowed to react with NO, but the product, which may have been $[Mn(NO)(mnt)_2]^{2-}$, was not isolated. With $Na_2S_2C_2H_2$ in acetone/methanol, $[Mn(CO)_5Br]$ gives the deep-red, volatile complex $[Mn_2(CO)_6(S_2C_2H_2)]$ (*110*). On addition of Lewis-base ligands in inert solvents, dark red-brown substitution products of the type $[Mn_2(CO)_4L_2(S_2C_2H_2)]$ ($L = PPh_2$ or $P(Me_2N)_3$) and yellow-brown monoadducts $[Mn_2(CO)_6(S_2C_2H_2)L]$ [$L = PR_3$, $0.5(Ph_2PCH_2CH_2PPh_2)$, or NH_3] are formed. Hoyer and co-workers (*78*) have produced the monoanionic species $[Mn(S_2C_2H_2)py]^-$, $[Mn(S_2C_2H_2)]^-$, and $[Mn(S_2C_6H_2(CH_3)_2)_2py]^-$ as part of a general study of the mixed-ligand complexes of manganese, iron, cobalt, palladium, and platinium.

The methylation of $[Re(S_2C_2Ph_2)_3]$ to form

$$\{Re(S_2C_2Ph_2)_2[SS(Me)C_2Ph_2]\}$$

was described in the preceding section. Some interest has been shown in the π-cyclopentadiene-containing manganese dithiolene complexes. The novel complexes $[\pi\text{-}C_5H_4RMn(NO)(S{-}S)]^Z$ (R = H or Me; Z = 0 or −1; S—S = mnt^{2-}, tdt^{2-}, $S_2C_6Cl_4{}^{2-}$) have been prepared and investigated electrochemically (*142*). They were found to exist as part of a three-membered electron transfer series, Z = +1, 0, −1. Treatment of $[\pi\text{-}CpMn(NO)(CO)_2]PF_6$ the monoanionic species (*143*). With tdt^{2-}, $S_2C_6Cl_4{}^{2-}$(S—S), the neutral species $[\pi\text{-}CpMn(NO)(S{-}S)]$ were formed. Even in the presence of a large excess of the dithiolene ligands, the π-Cp—Mn bond was not cleaved. Another report provides evidence for the formation of $[Mn(NO)(S{-}S)_2]^{2-}$ (S—S = Tdt^{2-} or $S_2C_6Cl_4{}^{2-}$) and $[Mn(NO)(mnt)(S_2C_6Cl_4)]^{2-}$. $[Mn(NO)(mnt)_2]^{2-}$ is also produced by treating $MnCl_2$ with Na_2mnt and NO or by reaction of $[Mn(mnt)_2]^{2-}$ with NO.

A recent application of Mn $Mn(mnt)_2$ is as a catalyst in the formation of high-molecular-weight poly(phenylene oxides). The complex is usually produced and used *in situ* (*96*). A study of the spectrophotometric and voltammetric properties of $[ML_3]$ (M = Re, Mo, W, Te; L = tdt^{2-}) with organic basis appears to be the only account of a 1,2-dithiolene complex of technitium (*104*).

E. IRON, RUTHENIUM, AND OSMIUM

The chemistry of iron–1,2-dithiolene complexes has been studied exhaustively. In the past few years, however, interest has been channeled mainly into physicochemical studies of existing systems; as a result, literature concerning the synthetic chemistry of iron–dithiolene systems has become relatively sparse. The major concentration of synthetic effort has been directed toward the synthesis of carbonyl derivatives, ferredoxin models, and adducts of the existing complexes. Apart from early reports (*139*) of $[Ru(S_2C_2Ph_2)_2]$, $[Ru(mnt)_3]^{3-}$, and $[Os(S_2C_2Ph_2)_2]$ the chemistry of ruthenium and osmium dithiolene complexes is relatively unknown. The only recent reports are of the reaction of $Ru_3(CO)_{12}$ with $(CF_3)_2C_2S_2$ at 100°C to give an impure, orange-colored, carbonyl adduct and at higher temperatures to give a green, impure, carbonyl-free material (*152*). Addition of EPh_3 (E = P, As, or Sb) produces $[Ru(CO)_n(ER)_3)_{3-n}(tfd)]$ and

$[Ru(EPH_3)(tfd)_2]$, respectively, suggesting that the green complex may be of the form $[Ru(tfd)_2]_2$, which is similar to the iron analog. Two different molecular conformers are known for the orange and violet isomers of the square pyramidal $[(Ph_3P)_2Ru(CO)(tfd)]$ and solution studies suggest that the former is thermodynamically favored (*15*). This isomerism is contrary to the usual behavior of pentacoordinate species (*76*). Osmium(VI) reacts with excess quinoxaline-2,3-dithiol in acidified DMF/H_2O solutions to form 1:2 and 1:4 complexes (*91*).

The pure dithiolene complexes of iron, which were synthesized in the late 1960s consisted of those with $S_2C_6Cl_4{}^{2-}$ and $S_2C_6F_4{}^{2-}$. These, together with the mnt^{2-} complex, were prepared, as part of the series of complexes described in earlier sections (*123*, *183*, *202*). The novel complexes of several $[M(mnt)_{2,3}]^{2-,3-}$ anions, [M = Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Ag(II), and Sn(IV)] are readily precipitated with a polymeric cation prepared from *N*-methyllutidium iodide and terepthaldehyde (*132*, *186*). The pure dithiolenes of iron and cobalt are normally dimeric, with the metal atom in a five-coordinate environment of sulfur atoms (Fig. 1). Holm and co-workers (*10*) interpreted the spectral, magnetic, and electrochemical properties of the $[M(S{-}S)_2]_2$ (M = Co, Fe; S—S = tdt^{2-}, mnt^{2-}, and tfd^{2-}) complexes and systemized them as part of the series $[M(S{-}S)_2]_2{}^0$, $[M(S{-}S)_2]_2{}^-$, $[M(S{-}S)_2]_2{}^{2-}$, and $[M(S{-}S)_2]_2{}^{4-}$.

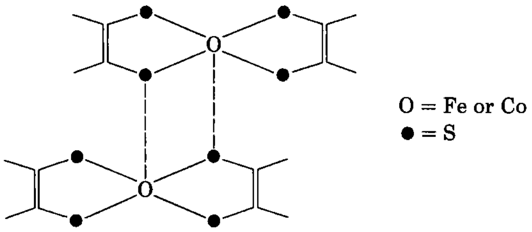


FIG. 1. Pure dithiolene of iron and cobalt.

The mixed dithiolate complexes $[Fe(R_2dtc)(mnt)_2]^{2-}$ (R = Me or Et), $[Fe(R_2dtc)_2(mnt)]^-$, and $[Fe(S_2C{=}X)(mnt)_2]^{3-}$ (X = $C(CN)_2 \cdot C(CN)$, CO_2Et, $CHNO_2$, $N(CN)$, or $C(CN)CONH_2$) have been prepared as salts of $(Ph_4P)^+$ and studied polarographically (*8*). The trianions are oxidized in a one-electron step, the half-wave potentials showing a dependence on the nature of X. $[Fe(i\text{-}mnt)(mnt)_2]^{2-}$ may be further oxidized, and $[Fe(R_2dtc)_2(mnt)]$ may be irreversibly reduced to the dianion. Aerial oxidation of $[Fe(i\text{-}mnt)(mnt)_2]^{3-}$ produces the dianion. Mixed-ligand complexes, $[Fe(S_2CNR^1R^2)_2(mnt)]$ (R^1R^2 = Et_2 and Et, Ph) result when $[Fe(S_2CNR^1R^2)_2]$ and Na_2mnt are mixed, followed by oxidation by air or Cu(II) in acetonitrile (*162*). Both complexes exhibit singlet–triplet equilibria and are stereochemically nonrigid, as shown by variable temperature ^1H-NMR spectroscopy. At lower temperatures there is an inversion process, the most likely mechanism for which is twisting about the pseudo-3-fold axis, and at higher temperatures the process of rotation about the C—N bond is observed.

The dimeric iron dithiolene complexes, $[Fe_2(CO)_6(S_2C_2R_2)]$, have the ability to form sulfur-rich, tetrameric $[FeS(S_2C_2R_2)]_4$ complexes by reaction with S_8 in refluxing xylene. These complexes with $R{=}CF_3$ have been shown to undergo four voltammetric, one-electron processes (*148*), and on dissolution in basic solution the dianion is formed. Reaction of the dianion with the neutral species gives the paramagnetic monoanion $[FeS(S_2C_2(CF_3)_2)_2]_4^-$ and with PPh_3 affords $[Fe(PPh_3)(S_2C_2(CF_3)_2)_2]^-$. The corresponding diphenyldithiolene complex (R = Ph) is reducible in three one-electron steps, and the monoanion may be obtained from the neutral species by a hydrazine reduction. The trinuclear compound, $[Fe_3S_2(tfd)_4]$ is a product of the sulfuration reaction, and it is reduced in two one-electron steps. Similarities have been drawn between these sulfur-rich complexes and ferredoxins, such as in the report of a nonenzymic model for nitrogen fixation (*198*). Significant amounts of ammonia are produced by treatment of $[Mo(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ with $[FeS(S_2C_2Ph_2)]_4^{n-}$ ($n \geqslant 4$). This is the first example of ammonia produced by direct reduction of a relatively stable nitrogenyl complex in a model system of the ferredoxin structural type. Reaction of $(CF_3)_2C_2S_2$ with $Fe(CO)_5$ in the presence of H_2S yields a black crystalline complex of empirical formula $Fe_3(tfd)_4S_6H_2$, which when dissolved in hydrocarbon solvents, exhibits many of the properties of reduced iron–sulfur proteins (*166*). ESR spectra of the compound in frozen solution, in the presence of isopropyl disulfide are similar to reduced adrenodoxin and putidaredoxin and indicate the presence of one unpaired electron per two iron atoms. ENDOR experiments show that the unpaired electron resides almost exclusively on an Fe-S center. In the series $[Fe_4S_4(mnt)_4]^{n-}$ (n = 0, 1, or 2), however, the overall electronic structure is very similar in all three cases, and magnetically perturbed Mössbauer spectra suggest that in the paramagnetic monanion the unpaired electron is highly delocalized over the dithiolene ligands and is not primarily associated with the (Fe_4S_4) core (*17*). The structure of $[FeS(S—S)]_4^{2-}$ systems consists of a cubanelike iron sulfide array of Fe_4S_4 clusters (Fig. 2). Mössbauer data for this, and the monoanion and neutral species have been compared with data for various ferredoxins (*16*).

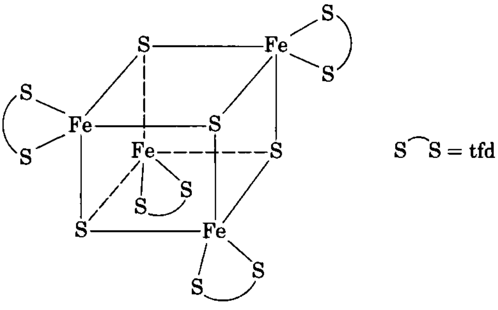
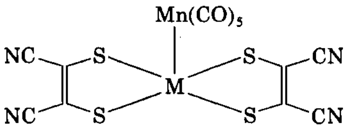


FIG. 2. Structure of $[FeS(S—S)]_4^{2-}$.

The positive value of V_{ZZ} derived from the Mössbauer spectrum of $(Ph_4As)_2\ [FeS(tfd)]_4$ is consistent with distorted trigonal bipyramidal coordination where the bonding electrons are probably the primary origin of the electric field gradient as is expected for in-plane bonding.

Considerable attention has been paid to the reactions of dimeric iron and cobalt dithiolenes with Lewis bases. The five- or six-coordinate products are formed by cleavage of the dimeric until followed by subsequent coordination of the Lewis base to the vacant coordination sites. The mechanism for the reaction is thought to proceed via an associative route (S_N2), but a small dissociative contribution cannot be ruled out (*188*). In acetonitrile, however, $[Fe(mnt)_2]^-$ is believed to be monomeric (*10*), and reactions with bidentate ligands, e.g., phen, bipy, en, dmg, have been shown to yield low-spin six-coordinate products (*140*, *209*). McCleverty and co-workers (*140*, *146*, *150*) have made a wide variety of iron and cobalt dithiolenes react with Lewis bases and nucleophiles, such as phosphines, arsines, stibines, amines, phosphites, phenylisocyanate, and azide, and have isolated a large number of complexes and identified several unstable species. Hoyer and co-workers (*78*) isolated a similar series of complexes with $S_2C_2H_2^{2-}$ and o-$(CH_3)_2C_6H_2S_2^{2-}$ as the dithiolene ligands. Novel complexes containing labile Mn—Fe and Mn—Co bonds are formed when $[Fe(mnt)_2]^-$ and $[Co(mnt)_2]^-$ are treated with $[Mn(CO)_5]^-$ in THF (*93*) (Fig. 3).



M = Fe, Co

FIG. 3. Complexes containing labile Mn—Fe and Mn—Co bonds.

The adducts $[Fe(diphos)(S—S)_2]^Z$, $[Fe(PEtPh_2)(S—S)_2]^Z$ [Z = −1; S—S = mnt^{2-}, tfd, $(S_2C_6Cl_4)^{2-}$; $Z = 0$, S—S = $S_2C_2Ph_2$, $S_2C_2(4\text{-}MeC_6H_4)_2$ or $S_2C_2(4\text{-}MeOC_6H_4)_2$], and $Fe(diphos)(mnt)_2$ are prepared by oxidation of the diiron with iodine (*146*). Complexes of Fe, Co, and Ni dithiolenes with chelating diarsine and diphosphines have also been reported (*147*). Holm and Eaton (*55*) used the carefully selected *p*-$Ph_2PC_6H_4PPh_2$, *trans*-$Ph_2P(H)C{=}C(H)PPH_2$ (DPPE), and Ph_2PC $CPPh_2$ ligands to prepare a new series of diphosphine bridged binuclear complexes of iron and cobalt. $[Fe(S_2C_2Ph_2)_2]$ has been used as a completely artificial, nonenzymic catalyst, modeling ferredoxin activity. By the use of inorganic reductants, amino acids were synthesized via biogenic-type CO_2 fixation. The α-ketoacid products were successfully converted to the corresponding α-amino acids on treatment with pyridoxamine (*156, 157*).

$[Fe(mnt)_2]^-$, $[Fe(mnt)_3]^{2-}$, and $[Fe(tfd)_2]_2{}^{2-}$ are found to activate molecular oxygen and are excellent catalysts for the autoxidation of PPh_3 by atmospheric oxygen (*57, 140*). Of the first two complexes $[Fe(mnt)_3]^{2-}$ is found to be the most efficient catalyst (*140*). The $(Bu_4N)[(Ph_3PO)Fe(tfd)_2]$ complex that was isolated in such a reaction had been previously formulated as a phosphine complex, and has the structure shown in Fig. 4.

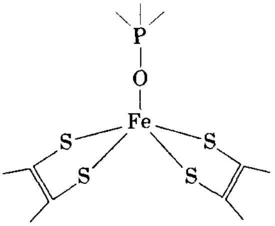


FIG. 4. Structure of $(Bu_4N)[(Ph_3PO)Fe(tfd)_2$ complex.

Electrochemical studies on a series of bis(diaryl-1,2-dithiolene) complexes indicate that the compounds are part of a four- and possibly five-membered electron transfer series, $[Fe(NO)(S_2C_2Ar_2)_2]^Z$ ($Z = -2, -1, 0, +1, (+2)$) (*149*). The $E_{1/2}$ values of the couple depend upon the substituents Ar, but they have very little effect on the nitrosyle stretching frequency.

$$[Fe(NO)(S_2C_2Ar_2)_2]^z + e^- \rightleftharpoons [Fe(NO)(S_2C_2Ar_2)_2]^{z-1}$$

In recent years attention has been paid to the syntheses of novel carbonyl-containing complexes of iron dithiolenes. $[Fe_2(CO)_6(XR)_2]$

(X = S, R = Me, Ph; X = Se, R = Ph) reacts with ($S_2C_2(CF_3)_2$) in pentane/benzene to yield a deep-green tetrameric $[Fe(XR)(CO)(tfd)_2]_4$ species in $CHCl_3$ and the dimer in acetone (*144*). The *S*-tetramer is shown by X-ray crystallography to be $[Fe_2(\mu\text{-}SMe)_3(CO)_6]^+[Fe(tfd)_4]^-$ (*94*). Reaction of $Fe_2(CO)_9$ with $S_2C_2(CF_3)_2$ under carefully controlled conditions produce an extremely reactive volatile violet solid, $[Fe(CO)_3(tfd)_2]_2$, while $Fe_3(CO)_9S_2$, $Fe(CO)_5$, and $Fe_3(CO)_{12}$ with $S_2C_2(CF_3)_2$ yield $[Fe_3S_2(tfd)_2]_4$, $[Fe_2S_2(tfd)_2]_4$, $[Fe_2(CO)_6(tfd)_2]$, and $[Fe(tfd)_2]$, respectively. Physical characterization and chemical reactivity of $[Fe(CO)_3(tfd)]$, the initial product of the reaction between $Fe(CO)_5$ and $S_2C_2(CF_3)_2$, have been reported by Miller and Balch (*152*). Reaction of $Fe_2(CO)_9$ with *cis*-1,2-ethylenedithiolate in methanol solution results in the hydrogenation of the double bond of the ligand giving the saturated derivative $[Fe(CO)_6(S_2C_2H_4)]$ (*110*).

Reactions of aryldiazonium tetrafluorobroates with $[Fe(CO)_3(PR_3)_2]$, $[Fe(mnt)_2]^-$, $[Fe(cyst)H_2]^{2+}$, and $[Fe(CO)_2(cystH)_2]$ results in ligand abstraction yielding arenediazophosphonium salts and *S*-(arenediazo)-cysteine or the N_2 extrusion product or ArS(CN)C=C(CN)SAr (*27*). Nucleophilic sulfur is suggested as a site for the activation and reduction of complexed dinitrogen in biological nitrogen fixation. Evaporation of a filtered dichloromethane solution of $Fe(tfd)_2$ by a stream of CO gives a quantiative yield of square pyramidal $[Fe(tfd)_2(CO)]$ (*153*). Similarly structured $[(\pi\text{-}Cp)Fe(tfd)_2]$ results from the treatment of $[(Cp)\text{-}\mu_3\text{-}Fe(CO)]_4$ with bistrifluorodithiete.

The rapidity of substitution reactions at a metal atom surrounded by a porphyrin or corrin group seems to be connected with the π-delocalization and a strong in-plane ligand field. The substitution

$$[M(S_2C_2Ph_2)X] + L \rightarrow [M(S_2C_2Ph_2)_2L] + X$$

reactions of five-coordinate neutral dithiolene complexes [M = Fe or Co; X and L = PR_3 or $P(OR)_3$] are likewise several orders of magnitude faster than normal. The kinetics of a series of reactions of this type are reported by Sweigart and co-workers (*188*). Although unusual for five-coordinate species, the mechanism followed by this reaction is probably mainly associative even though the existence of nonzero intercepts in the plots of k_{obs} v S (nucleophile) in the cobalt series suggest a contribution from a dissociative pathway. Steric effects are apparently important in determining the relative rates of nucleophilic substitution in these compounds. For $[M(tfd)_2X]^Z$ complexes [M = Fe, Co; X = PR_3, $P(OR)_3$; Z = 0, 1] the mechanism is associative for $Z = 0$ and dissociative for $Z = -1$ (*187*). The predominance of the associative mechanism is noted in the substitution reactions of $[M(mnt)_2X]^-$ complexes [M = Fe, Co; X = PR_3, $P(OR)_3$], and a purely dissociative pathway is definitely excluded (*190*). Replacement of bidentate groups (X = bipy, phen, diphos, vpp) by PBu_3^n proceeds via a dissociative mechanism. In each case the rates of reaction of the iron complexes are orders of magnitude faster than those of the corresponding cobalt species.

F. COBALT, RHODIUM, AND IRIDIUM

The ditholene complexes of cobalt and iron have frequently been studied in association. Much of the synthetic chemistry covered in previous sections (*123, 183*), like that of iron, has concentrated mainly on the syntheses of Lewis base, nitrosyl, and organometallic adducts. A new series of planar bis- and octahedral tris quinoxaline-2,3-dithiol (QDT) complexes of cobalt have been synthesized, and $Co(QDT)_3^{2-}$ is the first example of a trisdianionic cobalt dithiolene species to be isolated (*61, 62*). Hoyer and co-workers (*79, 80*) have presented an account of the synthesis and structural characterization of a series R^+ $M(S_2C_2H_2)_2^-$ (M = Co, Ni, Pd, Cu; R = Et_4N or Ph_4As), the physical and chemical properties of which indicate considerable electronic delocalization in the ground state. The same workers have also studied cis- and trans-isomerism exhibited by the Ni(II), Pd(II), and Pt(II) bis- and the Co(III), Rh(III), and Ir(III) trisdithiolene complexes derived from the *S*-alkyl-2-alkyl mercaptoethylene ligands (*71*).

There have been a number of physicochemical studies, particularly using magnetic methods, on the square-planar benzene- and toluene-dithiolato cobalt(III) systems because of the unique spin-triplet ground states not previously observed in square-planar systems (*159, 196*). Many of the dithiolenes of cobalt, like those of iron, are dimeric and possess structures analogous to that shown in Fig. 1. In acetone solution the $[Co(mnt)_2]_2^{2-}$ exists in this dimeric form. Kinetic studies of the reaction of this species with PPh_3, $AsPh_3$, py, and phen have shown that the mechanism involves a rapid equilibrium between the dimer and the monomer, the reaction of Lewis base with the monomer being the rate-determining step (*194*). With the potentially bidentate phen ligand, the kinetics correspond to a two-stage process in which the formation of a square-pyramidal adduct of $[Co(mnt)_2]^-$ and unidentate phen is followed by concurrent chelate ring formation and the necessary stereochemical reorganization around the metal atom to permit cis-chelation. From a structural study of $[Co(S—S)_2(phen)]^-$ systems

(S—S = tdt, mnt), it is concluded that bonding in the two complexes appeared to be similar and that differences in the equilibrium for the

$$[\mathrm{Co(S{-}S)_2}]^- + \mathrm{phen} \rightleftharpoons [\mathrm{Co(phen)(S{-}S)_2}]^-$$

two complexes are primarily due to differences in the relative stabilities of the original bis-substituted complexes (*105, 161*). Another kinetic study investigated the reactions of $[\mathrm{Co(mnt)_2PPh_3}]^-$ with en, bipy, phen, mnt, $^{2-}$*i*-mnt^{2-}, and $\mathrm{P(OPh)_3}$ and of $[\mathrm{Co(mnt)_2(L{-}L)}]^{n-}$ (L—L en, bipy, phen, mnt^{2-}) with $\mathrm{Bu_3P}$ and $\mathrm{Ph_3P}$ (*83, 189*), and indicate that associative and dissociative pathways contribute significantly to the overall mechanism as shown in Fig. 5.

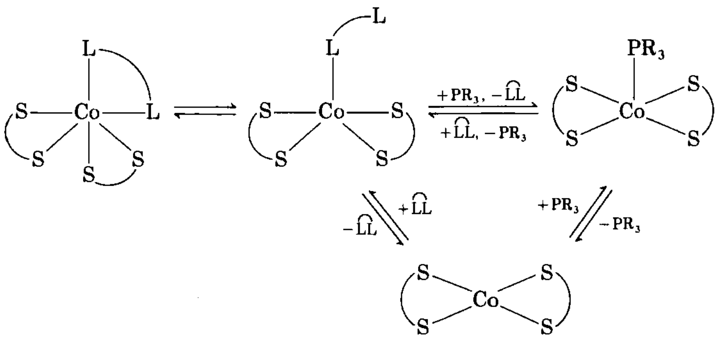


FIG. 5. Overall mechanism in the reactions of $[\mathrm{Co(mnt)_2PPh_3}]^-$ with en, bipy, phen, mnt,$^{2-}$ i-mnt,$^{2-}$ and $\mathrm{P(OPh)_3}$ and of $[\mathrm{Co(mnt)_2(L{-}L)}]^{N-}$(L—L en, bipy, phen, mnt^{2-}) with $\mathrm{Bu_3P}$ and $\mathrm{Ph_3P}$.

The formation of five- and six-coordinate complexes from Lewis-base addition to cobalt dithiolenes has followed much the same pattern as that outlined for iron (*78, 83, 188*). In addition, Balch (*9*) found that in ligand exchange of [Co(S—S)L] (S—S = tfd, mnt; L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$) the presence of additional base serves to retard the rate of attainment of equilibrium, but it does not affect the position of the equilibrium. Cobalt dithiolene systems have been the subject of kinetic investigations because of their relative kinetic inertness. An ESR study of the reaction of $[\mathrm{Co(S_2C_2Ph_2)_2}]$ with $\mathrm{P(OEt)_3}$, $\mathrm{PEt(OEt)_2}$, and $\mathrm{PEt_2(OEt)}$ in acetone indicates that one molecule of base is introduced into an axial position, and subsequently a second molecule enters trans to the first, followed by rearrangement to the cis structure (*193*). A similar series of reactions with $\mathrm{PCl_3}$, $\mathrm{PCl_2(OR)}$, $\mathrm{PCl(OR)_2}$, and $\mathrm{P(OR)_3}$ give only five-coordinate complexes. Dance (*43*) is responsible for an elaborate voltammetric study of the coordination reactions of pyridine with $[Co(mnt)_2]^Z$ ($Z = -2, -1$) complexes and proposes the following summary for the system:

$$\begin{tikzcd}
{[Co(mnt)_2]^-} \arrow[r, shift left, "+L"] \arrow[d, shift left, "+e"] & {[Co(mnt)_2L]^-} \arrow[l, shift left] \arrow[r, shift left, "+L"] \arrow[d, shift left, "+e"] & {[Co(mnt)_2L_2]^-} \arrow[l, shift left] \arrow[d, shift left, "+e"] \\
{[Co(mnt)_2]^{2-}} \arrow[r, shift left, "+L"] \arrow[u, shift left, "-e"] & {[Co(mnt)_2L]^{2-}} \arrow[l, shift left] \arrow[r, shift left, "+L"] \arrow[u, shift left, "-e"] & {[Co(mnt)_2L_2]^{2-}} \arrow[l, shift left] \arrow[u, shift left, "-e"]
\end{tikzcd}$$

Dance and Miller (*48, 49*) reported various amine adducts of $[M(mnt)_2]^{2-}$ and $[M(tfd)_2]_2{}^{2-}$ (M = Fe, Co). Monoadducts, $[M(mnt)_2L]^-$, are high spin; $S = 3/2$ for Fe, $S = 1$ (possibly 0) for Co. At room temperature only Co forms six-coordinate bis-amine adducts, $[Co(mnt)_2L_2]^-$, which are diamagnetic and exist as two steroisomers, one of which is cis-octahedral; the one insoluble pyridine adduct is $[Co(mnt)_2(py)_2]^-$. $[Fe(tfd)_2]_2{}^-$ with ethylenediamine and other bidentate amines produces amine-bridged binuclear species. $[Co(mnt)_2(amine)]^-$ readily forms $[Co(mnt)_2(amine)_2]^-$ provided there is minimal steric hindrance of the amine, while $Fe(mnt)_2(amine)^-$ shows no evidence of further coordination with any monodentate amine. Dance and co-workers have also made a detailed investigation of the catalysis by $[Co(mnt)_2]_2{}^{2-}$ of the thiol autoxidation reaction

$$2PhCH_2SH + O_2 \rightarrow PhCH_2SSCH_2Ph + H_2O_2$$

in acidic acetonitrile solution buffered with $PhMe_2N/PhMe_2NH^+ ClO_4{}^-$ (*45, 46*). Results indicate that $[Co(mnt)_2]_2{}^{2-}$ remains dimeric in the buffered system and does not coordinate to oxygen alone, but does coordinate to base-activated thiol, which then promotes oxygen coordination. The function of the dithiolene complex catalyst is to activate both reductant and oxidant by coordination and transmit one electron from the former to the latter.

The π-cyclopentadiene derivatives of cobalt and rhodium dithiolenes have been prepared by the methods described in previous sections. The crystal structure of π-CpCo(mnt) shows that the cobalt atom is pentacoordinate with a formally tridentate π-Cp group and a bidentate mnt^{2-} group (*193*). Reaction of the $Co_3(CO)_9CY$ (Y = Cl or Me) cluster compound with $S_2C_2(CF_3)_2$ gives the novel cluster $[Co_3(CO)_3(tfd)_3CY]$ (*144*). Trinuclear $[Co(CO)(tfd)]_3$ is obtained by reaction of $Co_2(CO)_8$ with $S_2C_2(CF_3)_2$ and undergoes one-electron reduction to the monoanion and oxidation to the monocation. This compound could exist as some complex cationic/dianionic form similar to $[Fe_2(\mu\text{-SMe})(CO)_6]^+$ $[Fe_2(tfd)_4]^-$ described earlier.

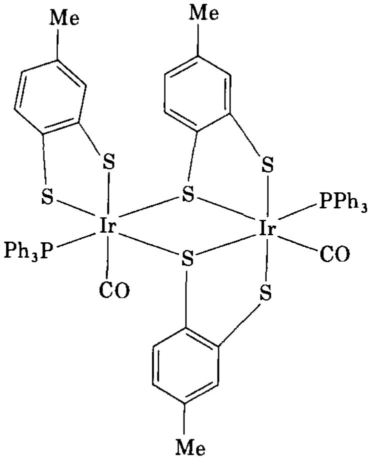
The synthetic chemistry of the pure and organometallic dithiolene complexes of rhodium and iridium has developed significantly in recent years. Both $[Rh(mnt)_2]_n^{n-}$ ($n \geqslant 1$) and $Rh(mnt)_3^{2-}$ have been isolated from the reaction of $Rh_2(OAc)_4$ and $Na_2(mnt)$ (*37*). cis-Dicarbonyls $[Rh(CO)_2(S\text{—}S)_2]^{-2}$ ($S\text{—}S = mnt^{2-}$, tdt^{2-}, $i\text{-}mnt^{2-}$) are prepared by treatment of $[Rh_2(CO)_2Cl_2]_2$ with the appropriate dithiolate dianion and there is evidence for the existence of $[Rh(CO)_2(S_2C_6Cl_4)]^-$. $[Rh(CO)_2(mnt_2)]$ reacts with phosphines, phosphites, and $S_2C_2(CF_3)_2$ to form $[Rh(CO)\text{—}(PR_3)(mnt)]^-$, $[RhP(OPh)_3mnt]^-$ and $[Rh(mnt)(tfd)]_n^{n-}$ ($n \geqslant 1$), respectively. Treatment of $[M(CO)(PPh_3)_2Cl]$ (M = Rh or Ir) with $S_2C_2(CF_3)_2$ affords $[M_2(PPh_3)_2(tfd)_3]$.

The addition of alkyl halides to the Rh(I) complex $[Rh(CO)(PPh_3)(mnt)_2]$ produces Rh(III) acyl species:

$$[Rh(CO)(PPh_3)(mnt)_2]^- + RX \rightarrow [RhX(COR)(PPh_3)(mnt)]$$

and for RX = EtI the structure of the product is square pyramidal (*29*). Heating solutions of the acyl species in THF or dichloromethane results in migration of the R group from acyl carbon to one of the sulfur donors of the mnt ligand to give S-alkylated rhodium(I) complexes.

Addition of toluene-3,4-dithiol (H_2L) to [IrHCl(HL)(CO)], in which the ligand is bonded unidentately, and a novel dithiolene complex, $[Ir_2L_3(CO)_2(PPh_3)_2]$ (*181*). X-Ray analysis (*106*) shows the last complex to have the novel structure:



Stiddard and Townsend (*185*) observed that reaction of tetrafluro-benzene-1,2-dithiol with *trans*-[IrX(CO)(PPh$_3$)$_2$] (X = Cl, Br) in benzene gives pale yellow [Ir(H)(X)(SC$_6$F$_4$SH)(CO)(PPh$_3$)$_2$] adducts. Refluxing the mixture, however, produces a deep red solution from which [IrH(S$_2$C$_6$F$_4$)(CO)PPh$_3$)$_2$] is eventually isolated. It is suggested for the [Ir(H)(X)C$_6$F$_4$CS(SH)(CO)(PPh$_3$)$_2$] complex that hydrogen bonding (Fig. 6) is involved and that elimination of HX under more vigorous conditions produces the dithiolene complexes.

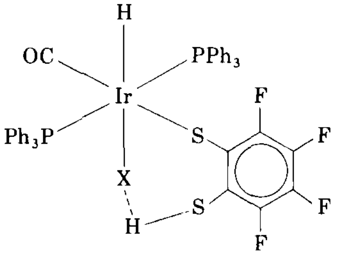


FIG. 6. Hydrogen bonding producing the dithiolene complex.

Recently, Eisenberg and Van Derveer produced a series of novel Rh(I) organometallic dithiolenes (*197*). Thus, reaction of [Rh(diene) (μ—Cl)]$_2$ (diene = cyclooctadiene or norbornadiene) with Na$_2$mnt in ethanolic hydrazine produces [Rh(diene)(mnt)]$^-$, isolated as the Bu$_4$N$^+$ salt. Reaction of this complex with CH$_3$I or PhCH$_2$X (X = Br or I) in ethanol produces [RH(diene)(mnt)R] (R = CH$_3$ or PhCH$_2$), and dynamic behavior is observed in the temperature-dependent ^{1}H-NMR spectra of the complexes. X-Ray structural analysis reveals that the complexes are methylated at the sulfur atoms and have pyramidal geometry and the ^{1}H-NMR spectral behavior is probably best explained by inversion about the pyramidal center.

G. NICKEL, PALLADIUM, AND PLATINUM

As with dithiolene complexes of other groups, the synthetic chemistry of the pure complexes of nickel, palladium, and platinum has been restricted in recent years, but some nickel complexes are shown in Table I. The square-planar species (Bu$_4$N)$_2$ [M(QDT)$_2$] (R = Ni, Pd, Pt, Cu, Zn) have been isolated by using the analytical reagent quinoxaline-2,3-dithiol (QDT) (Fig. 7) as a ligand (*191*). The physicochemical properties of the compounds closely resemble the related mnt complexes, and ESR spectral studies indicate that the ligand is S,S-bonded.

TABLE I

RECENT DITHIOLENE COMPLEXES OF NICKEL

Complex[a]	Melting point (°C)	Color	References
$(Bu_4N)_2[Ni(QDT)_2]$	204-5	Purple	(*191*)
$(Et_4N)[Ni(S_2C_2H_2)_2]$	176	Brown	(*79*)
$(Ph_4As)[Ni(S_2C_2H_2)_2]$	—	—	(*79*)
$(Bu_4N)[Ni(S_2C_6F_4)_2]$	144	Black	(*123*)
$(M(PPh_3)_2)_2[Ni(mnt)_2]$ (M = Cu, Ag)	—	—	(*40*)
$(Ag(PPh_2Et)_2)_2[Ni(mnt)_2]$	—	—	(*40*)
$[Ni(mnt)_2]^{3-}$	—	Green	(*155*)
$[Ni(tfd)_3]^{3-}$	—	—	(*67*)
$(KOS)_2[Ni(mnt)_2]$	197.5-8.5	Black	(*51*)
$(KOS)_2[Ni(tfd)_2]$	—	Brown	(*51*)
$(KOS)[Ni(S_2C_2Ph_2)_2]$	208.5-10.0	Red	(*51*)
$(Ferrocinium)[Ni(tfd)_2]$	—	—	(*130*)
$Cs[Ni(tfd)_2]$	150	—	(*130*)
$(Perylene)_2[Ni(mnt)_2]$	—	Black	(*204*)
$(Perylene)[Ni(tfd)_2]$	—	Black	(*204*)
$(Pyrene)[Ni(tfd)_2]$	—	Black	(*204*)
$(TTF)[Ni(tfd)_2]$	—	Black	(*75, 103*)
$(TTF)_2[Ni(S_2C_2H_2)_2]$	—	Black	(*88*)
$(TTF)[Ni(mnt)_2]$	—	Black	(*208*)
$(Phenoxazine)[Ni(tfd)_2]$	—	Brown	(*64*)
$(Phenothiazine)[Ni(tfd)_2]$	—	Brown	(*64*)
$(TCNQ)[Ni(tfd)_2]$	—	—	(*22*)
$(Q)[Ni(tfd)_2]$	—	—	(*22*)
$(C_7H_7)[Ni(tfd)_2]$	189.5-191	Green-black	(*205*)

[a] KOS = 1-ethyl-4-carbomethoxypyridinium cation; TTF = tetrathiafulvalene, i.e., 2,2′-bi-1,3-dithiolylium cation; TCNQ = 7,7,8,8,-tetracyanoquinodimethane; Q = 2,3-Dichloro-5,6-dicyano-p-benzoquinone.

$(Bu_4N)_2[Ni(QDT)_2]$, however, is more stable to oxidation than the corresponding $(Bu_4N)_2[Cu(QDT)_2]$, which is the reverse trend to that observed in mnt^{2-} complexes. The monoanionic bistetrafluorobenzene-1,2-dithiolatonickelate complex has been isolated as the Bu_4N^+ salt (*123*), and the dianionic tris complex of platinum with the same ligand was also prepared; slight antiferromagnetic behavior has been

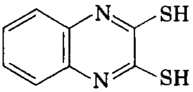


FIG. 7. The analytical reagent quinoxaline-2,3-dithiol (QDT).

noted for the nickel complex. Hoyer and co-workers (*71*, *79*) have been responsible for the synthesis of the nickel, palladium, and platinum complexes of the parent ligand, ethylene-1,2-dithiol and its S-substituted derivatives. More recently, Coucouvanis and co-workers isolated the mixed metal complex $[M(PR_3)_2]_2[Ni(mnt)_2]$ ($M = Ag, Cu$; $R_3 = Ph_2Et, ph_3$) and have determined their structure (*41*). Wing and Herrmann (*74*) studied the reaction of $[Ni(tfd)_2]$ with several 1,1-dithiolates and found that centrosymmetric mixed-ligand dimers of the type shown in Fig. 8 are produced. The reactions appear to proceed via either a preliminary redox process or formation of a highly polarized donor–acceptor complex. Dimers are also found to be formed in the mixed-ligand complexes of Cu, Zn, Co, Pd, and Pt with dithiocarbonates. Xanthates are also found to react in the same way as, but more slowly than, the dithiocarbonates.

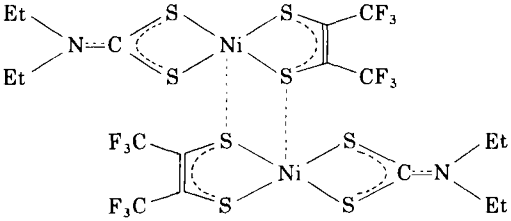


FIG. 8. Centrosymmetric mixed-ligand dimer.

The existence of more highly reduced species at large negative potentials in the electron-transfer series of metal-dithiolene systems has been largely overlooked. Recent reports by Geiger and co-workers, however, describe the generation of the green $[Ni(mnt)_2]^{3-}$ from the dianion by controlled-potential electrolysis at a mercury pool (*63*, *66*, *67*, *155*). The green dimethoxymethane and acetonitrile solutions of the trianion are extremely air sensitive and revert to the organe dianion upon exposure to traces of oxygen. The solid complex has not been isolated, but the trianion is characterized electrochemically and by its ESR spectrum, which exhibits a single resonance with $g = 2.116$. The data favor a d^9, or Ni(I) formulation for the metal in $[Ni(mnt)_2]^{3-}$. Similar results are reported for the $[Ni(tfd)_2]^{3-}$ complex, which has been generated electrochemically.

The kinetics of substitution reactions of nickel bisdithiolato complexes with dithiolate nucleophiles have been studied in aqueous solution at 25°C using stopped-flow techniques (*160*). Several five-coordinate intermediates are detected, and their stabilities have been estimated. In order to substantiate model calculations that suggest considerable delocalization of negative charge onto the four sulfur atoms of the $[Ni(S_2C_2R_2)_2]^{2-}$ dianions, Schrauzer and Rabinowitz (*177*) have shown that the sulfur atoms in $[M(S_2C_2R_2)_2]^{2-}$ (M = Ni, Pd, or Pt) possess nucleophilic character. On reaction with alkylating agents new, neutral, diamagnetic 1,4-S,S-diakylated complexes of composition $[M[(SR)SC_2R_2]_2]$ are obtained. The complexes show no tendency to undergo reversible oxidation or reduction and are remarkably resistant to attack by acids and bases.

During the course of investigating the physical properties of complexes containing the $(S_2C_2H_2)^{2-}$ ligand, a sharp contrast is observed between $[Ni(S_2C_2H_2)_2]$ and $[M(S_2C_2R_2)_2]$ (M = Pd or Pt) both in the electrical conductivity in the solid state and in the nature of the powder X-ray diffraction patterns. Single-crystal X-ray structural determinations show the palladium and platinum complexes to be isostructural. The molecular units in each case are an approximately square-planar arrangement of sulfur atoms about the metal, with two $MS_4C_4H_4$ units in eclipsed relationship joined by a Pd–Pd (279 pm) and Pt–Pt (274.8 pm) bonds, respectively, in a dimeric structure (Fig. 9) (*19*). They represent the first proved examples of metal–metal bonded bisdithiolenes.

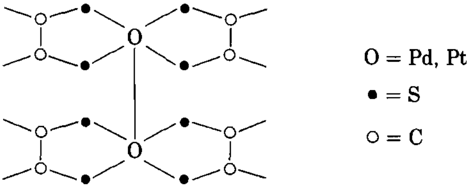
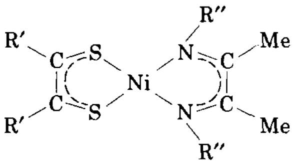


FIG. 9. Dimeric structure which represents the metal–metal bonded bisdithiolenes.

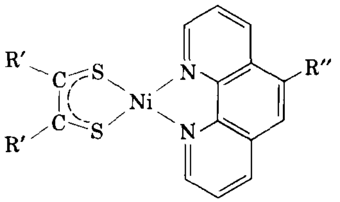
The X-ray photoelectron spectra of $(Et_4N)[M(mnt)_2]$, $(Et_4N)_2[M(mnt)_2]$, $[M(S_2C_2Ph_2)_2]$, $(Et_4N)[M(S_2C_2Ph_2)_2]$, and $(N_2H_5)_2[M(S_2C_2Ph_2)_2]$ (M = Ni, Pd, or Pt) have been used to determine the binding energies of sulfur $(2p_{3/2,1/2})$, nickel $(2p_{3/2})$, palladium $(3d_{5/2})$ and platinum $(4f_{7/2})$ (*136–138*), and Hoyer and co-workers (*125*) have carried out a similar study on $[Ni(S_2C_2H_2)_2]^{0,-1}$ their S-alkylated derivatives, and their copper analogs. The results are discussed in a later section.

The semiconductor properties and piezoresistance of crystals of $[M(S_2C_2R_2)_2]$ complexes have been studied (*11*, *167*). The resistivities lie between 10^3 and 10^5 cm at 25°C and depend upon the chelate structure, the metal ion, and the ligand substituents. With the same R substituents a linear correlation was found to exist between the first half-wave polarographic potential and the resistivity. This suggested that electron transport takes place in the lowest unoccupied π-molecular orbitals of the complexes, in accord with the proposed electronic structure of the complexes. Hall-effect measurements identified the majority of charge carriers as being negative species. The corresponding rhenium complex (R = Ph) was found to be the best conductor of all, indicating that the unpaired electron must be in a molecular orbital delocalized over the whole molecular complex. Among the trigonal prismatic complexes studied, V, Cr, Mo, and W had resistivities between 10^{12} and 10^{14} cm.

McCleverty and Orchard synthesized a series of nickel dithiolene adducts, containing chelating diarsine, diphosphine, and related ligands (*147*). Miller and Dance (*47–49*) have studied the reactions of several iron, cobalt, and nickel dithiolenes with a wide variety of amines and diimmines. The following series of complexes have been prepared (*47*).



R′ = CF_3; R″ = Ph, p-$MeOC_6H_4$, m-ClC_6H_4
R′ = CN; R″ = Ph, p-$MeOC_6H_4$, N = CHPh

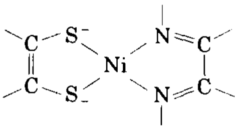


R′ = CF_3; R″ = H, NO_2
R′ = Ph; R″ = H

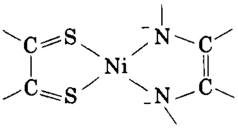
They are all intensely colored, diamagnetic, high- melting-point solids. Electrochemical studies reveal the following electron transfer series:

$$[\mathrm{Ni(S{-}S)(N{-}N)}]^+ \xrightleftharpoons{e^-} [\mathrm{Ni(S{-}S)(N{-}N)}] \xrightleftharpoons{e^-} [\mathrm{Ni(S{-}S)(N{-}N)}]^- \xrightleftharpoons{e^-} [\mathrm{Ni(S{-}S)(N{-}N)}]^{2-}$$

Electronic spectra show bands characteristic of the parent ligand complexes. The electronic ground state may be represented as



being the principal resonance form, and the excited state contains more of the form



Dance and Miller (*50*) have also allowed nickel, copper, and cobalt dithiolenes to react with weak nucleophiles and discovered the reaction to proceed by initial nucleophilic substitution of a dithiolene ligand followed by reduction of the oxidized complex leading to overall disproportionation stoichiometry.

Organometallic adducts of the nickel group dithiolenes have been thoroughly investigated. The cyclopentadiene complexes have been prepared and studied as for other metals (*206*). Wing and co-workers (*7*, *206*) have been concerned with the oxidative addition of olefins, dienes, and cyclodienes to [Ni(tfd)$_2$]. Structural studies of the adduct with norbornadiene suggests that the olefin suffers a two-electron oxidation, that two C—S bonds are formed between the reactants and that one of the norbornadiene double bonds had been transformed into a single bond. The sulfur atoms are in the exo-configuration (Fig. 10). A mechanism for the reaction was proposed after consideration of the Woodward–Hoffman rules (*7*). Schrauzer has also considered the addition of norbornadiene to [Ni($S_2C_2Ph_2$)$_2$] (*174*). Reactions of other olefins with other nickel triad dithiolenes have been reported. An X-ray study of the cycloaddition products of [Ni($S_2C_2H_2$)$_2$] with various dienes confirmed that the products formed by olefins and dienes are closed structural relatives and show a tetradentate ligand coordinated to square-planar nickel (*3*). Reactions of nickel and palladium olefin complexes with dithiolene ligands in the absence of oxygen has produced the metal dithiolene–olefin adducts (*200*). The crystal structure of the 1:1 adduct formed between [Pd($S_2C_2Ph_2$)$_2$] and cyclohexa-1,3-diene shows that a 1,8-cycloaddition

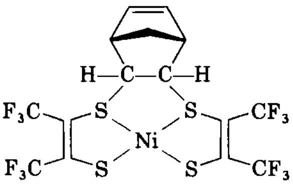
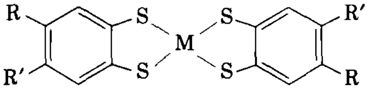


FIG. 10. Sulfur atoms in the exo-configuration.

reaction occurs between the donor and the acceptor, resulting in the two new C—S bonds (*31*).

Novel applications of the nickel group dithiolenes have been cited in the recent patent literature. The image dyes of color-photography recording materials and textile dyes can be stabilized to the effects of ultraviolet and visible radiation by use of $\{Ni[S_2C_2(C_6H_4OMe)_2]_2\}$ as an additive (*182*). Coating materials containing the structure



R = Cl, Br, I
R' = H, Cl, Br, I
M = Ni, Pd, Pt

have been used as selective absorbers of near-IR radiation (*192*). $[Ni(S_2C_2(C_6H_4NMe_2)_2)_2]$ is several times more stable than a standard iodopentacarbocyanine dye used for Q-switching and mode locking neodymium–glass lasers (*165*, *199*). Novel complexes of the decaborane (*172*) ligand containing dithiolene ligands have been synthesized (*180*) by displacement reactions, e.g., $[Pd(B_{10}H_{12})(mnt)]^{2-}$ from $[Pd(B_{10}H_{12})(PPh_3)_2]$ and

$$[Ir(B_{10}H_{12})(CO)(PPh_3)_2]^- + mnt^{2-} \rightarrow [Ir(B_{10}H_{12})(CO)(mnt)(PPh_3)]^{3-} + [Ir(B_{10}H_{12})(mnt)(PPh_3)_2]^{3-}$$

Complexes between electron acceptors and electron donors have been studied extensively. Electrically conducting donor–acceptor complexes between nickel dithiolenes and various organic cations, such as perylene, pyrene (*204*), tropylium ion (*86*), tetrathiofulvalence (*24*, *25*, *85*, *86*, *88*, *103*, *207*, *208*), quinones (*22*), pyridinium cations (*51*), ferrocinium (*130*), phenoxazine (*64*), tetrathiotetracene (*65*), and others (*20*, *179*) have been prepared and studied in considerable detail.

H. COPPER, SILVER, AND GOLD

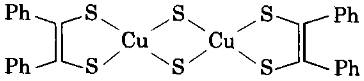
The complexes of copper with 1,2-dithiolenes were studied extensively during the early intensive development of the chemistry of 1,2-dithiolene complexes. Since 1969, however, the literature on the synthesis of new copper-containing dithiolenes has become less abundant, probably because the complexes show little tendency to form Lewis-base or organometallic adducts. Complexes of copper have usually appeared only in general papers in which a series of first-row transition metal complexes have been prepared. Thus, $[Cu(S_2C_6F_4)_2]^{2-}$ (*123*), $[Cu(S_2C_2H_2)_2]^{2-}$ (*79*), $[Cu(QDT)_2]^{2-}$, and $[Cu(QDT)_2]^-$ (*191*) have been prepared by methods outlined previously. The ESR spectrum of $(Bu_4N)[Cu(QDT)_2]$ indicates that the ligand is S,S-bonded.

The syntheses of mixed 1,1- and 1,2-dithiolates of copper have attracted some attention in recent years. An electron-transfer series of the complexes $[M(mnt)(S_2CNBu^n)_2]^{Z-}$ (M = Ni, Cu, or Au) has been investigated (*195*). The monoanionic ($Z = 1$) species have been obtained for nickel and copper, and the neutral species ($Z = 0$) for copper and gold. Voltammetric data show that these complexes exist as part of a two-membered, reversible, one-electron transfer series, $Z = 0$ or -1. The $E_{1/2}$ values are intermediate between those for complexes with unmixed ligands. Hermann and Wing (*74*) produced similar mixed-ligand complexes of copper by ligand exchange reactions of $[Cu(tfd)_2]$ and $[Cu(S_2CX)_2]$ ($X = NR_2$ or OR) and with diethyldithiocarbamate as a ligand dimers are formed similar to the analogous nickel complex (Fig. 8). Reiche (*164*) has studied reactions of numerous ligands with the copper(I) species, $[Cu(PPh_3)_3Cl]$, and when the reaction is carried out using tdt^{2-} the stable $[Cu(tdt)_2]^{2-}$ complexes are isolated, not the expected $[Cu(tdt)(PPh_3)_2]^-$. Recent work on sulfur-containing copper complexes has been concerned mainly with physicochemical studies, particularly the ESR spectra and magnetic properties of copper(II), formally a d^9 system.

Maleonitriledithiolato-4-diacetyldi-(4-methoxyanil) copper

[Cu(mnt)(acma)]

has been studied by ESR spectral methods in liquid and frozen solutions in order to explain the bonding situation in sulfur and nitrogen mixed chelates (*122*). Covalency parameters indicate that the unpaired electron is delocalized in the direction of the sulfur-containing ligands. Japanese workers (*135*) have prepared a sulfur-bridged copper dithiolene:



and characterized it by several physical methods. Like its manganese analog, $Cu[Cu(tdt)_2]$ and other copper dithiolenes have been used as a catalyst for the oxidative polymerization of penols (*97*, *98*, *100–102*).

The chemistry of silver 1,2-dithiolenes is virtually nonexistent apart from one general report (*72*) of the production of $[AgL_2(ClO_4)]$ [$n = 1$, 2; L = various thioethers and $C_2H_2(SH)_2$, H_2mnt, H_2tdt, $C_6H_4(SH)_2$, and $o\text{-MeC}_6\text{H}_3(\text{SH})_2$]. There is undoubted scope for expansion in this field. The 1,2-dithiolene complexes of gold, like those of copper, were synthesized in the 1960s. A new, higher-yield route has been developed to the formally gold(II) complex, $[\text{Au(mnt)}_2]^{2-}$, which involves electron exchange between Au(I) and Au(III) (*158*). The reaction seems to be specific for mnt^{2-}, since there is no evidence for a similar reaction with other unsaturated sulfur-donor ligands:

$$\{[(\text{PhCH}_2)_2\text{S}]\text{Au}^{\text{I}}\text{X}[(\text{Ph}_2\text{CH}_2)_2\text{S}]\text{AuX}_3\} + 2\text{Bu}_4\text{NBr} + 2\text{Li}_2(\text{mnt}) \xrightarrow{\text{THF/MeOH}} (\text{Bu}_4\text{N})_2[\text{Au(mnt)}_2] \quad (\text{X} = \text{Cl or Br})$$

Bergendahl and Waters (*14*) have prepared and characterized the pseudo Au(II) complexes $[(\text{Ph}_3\text{E})\text{Au(mnt)}]$ (E = P, As) and describe their relationship with the authentic $\text{Au(mnt)}_2{}^{2-}$ system. The complexes were reassigned as $[(\text{Ph}_3\text{E})_2\text{Au}]^+[\text{Au(mnt)}_2]^-$, a mixed Au(I)–Au(III) complex. The green mixed-ligand complexes $\{\text{Au(mnt)}[\text{S}_2\text{CN}(\text{Bu}^n)_2]\}$ and $\{\text{Au(tdt)}[\text{S}_2\text{CN}(\text{Bu}^n)_2]\}$ have been prepared as described earlier (*195*), and the crystal structure of the former confirms the formulation as presented (*14*), the gold atom having approximately square-planar coordination.

Like the analogous copper complexes, the formally gold(II) 1,2-dithiolenes have been the subject of ESR spectral studies (*170*). This is of particular interest owing to the rarity of formal Au(II) complexes. Results indicate that the complex $[\text{Au(mnt)}_2]^{2-}$ is best described as a gold(III) species with a radical anion ligand. The inability of most ligands to possess this form may explain the rarity of gold(II) complexes.

Complexes similar to those described in the nickel section have been formed from $[\text{M(tfd)}_2]$ and $[\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ (M = Cu, Au) and tetrathiofulvalene and magnetic and ESR studies provide the first unambiguous evidence for a spin-Pierels transition, a spin-lattice dimerization phenomenon, occurring below a transition temperature (*87*, *89*).

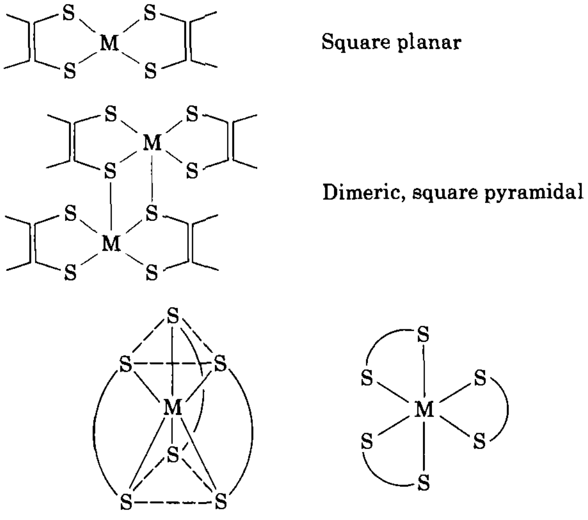
IV. Physical Studies

A variety of physical techniques have been used to structurally and electronically characterize transition metal 1,1- and 1,2-dithio compounds. Much information has been documented in these numerous studies, and some examples of the kind of information that can be obtained are mentioned in the following sections.

A. X-RAY STRUCTURAL STUDIES

The structural systematics of the 1,1- and 1,2-dithiolato complexes of the transition metals has been the subject of an excellent review by Eisenberg (*56*). The wide variety of structural types exhibited by these compounds is quite remarkable, and as a result the interest in structural aspects of these species has maintained at a very intense level. The number of studies, varying in degrees of refinement, which have appeared in the literature since 1969 is appreciably large. In many cases these have been systematic confirmations of structures postulated from other physical techniques, but in some cases they have revealed new and totally unexpected stereochemistries. A number of structure determinations by X-ray methods have been discussed or mentioned in previous sections.

Four basic structural types are known for the "pure" dithiolenes (Fig. 11).



Trigonal prismatic Octahedral

FIG. 11. "Pure" dithiolenes.

The neutral trisdithiolenes $M(S_2C_2R_2)_2$ (M = V, Cr, Mo, W, Re) are trigonal prismatic with delocalized electronic structures and the S—C bond distances indicate considerable multiple bond character. These complexes have the metal in its most oxidized form and the structure is ligand-preferred whereas the octahedral structure is metal preferred.

The intermediate oxidation states exhibit a recently discovered "in-between" geometry, e.g., $(Ph_4As)_2[M(mnt)_3]$ *(21)* (M = Mo, W). It is also significant that, amidst this great structural variety in the 1,2-dithiolene complexes, the bite of the ligand varies from only 303 to 315 pm. A study on the structures of an isoelectronic series of tris(benzenedithiolene) complexes of the early transition metals $[Zr(S_2C_6H_4)_3]^{2-}$, $[Nb(S_2C_6H_4)_3]^{-}$, and $[Mo(S_2C_6H_4)_3]$ revealed trigonal prismatic geometry for the Zr complex *(134)*. The observed structural trends (Fig. 12) appear to be associated with the charge on the complex and the metal *d*-orbital energies.

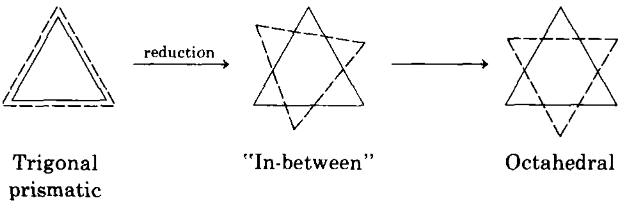


FIG. 12. Trigonal prismatic geometry.

Finally, the first examples of dimeric metal–metal bonded 1,2-dithiolenes were discovered by Browall and co-workers *(19)* in the complexes $[M(S_2C_2H_2)_2]_2$ (M = Pd, Pt). The arrangement of sulfur atoms about the metal is approximately square planar with two $M(S_2C_2H_2)_2$ eclipsed units joined by Pd–Pd (279 pm) or Pt–Pt (274.8 pm) bonds. The dimers have distorted cubic arrangement of sulfur atoms with the metal atoms pulled in toward each other from the centers of two opposite faces (Fig. 9). This is believed to be the first crystal structure determination of any bis-1,2-dithiolene complex of palladium or platinum.

B. INFRARED SPECTRAL STUDIES

Three absorption bonds are usually characterized in the infrared spectra of the bis-1,2-dithiolenes; $\nu(\mathrm{C}\overset{..}{=}\mathrm{C})$ at ca. 1400 cm^{-1} and $\nu(\mathrm{C}\overset{..}{=}\mathrm{C})$ at ca. 1110 cm^{-1} and ca. 860 cm^{-1}. The frequencies vary little with the metal but do depend upon the nature of the substituents. On reduction of neutral species to the monoanion $\nu(\mathrm{C}\overset{..}{=}\mathrm{C})$ increases and $\nu(\mathrm{C}\overset{..}{=}\mathrm{S})$ decrease. In the dianions the dithiene, $\nu(\mathrm{C}\overset{..}{=}\mathrm{S})$, bands usually disappear that can be considered to be a result of conversion of the ligand to the dithiolato dianions. The neutral dimeric cobalt and iron dithiolenes show lower-intensity bands, and the two $\nu(\mathrm{C}\overset{..}{=}\mathrm{S})$ bands are split. In the neutral tris complexes $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ occurs at higher frequencies than in the bis complexes, and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ has a more complicated structure. As the dithioketonic nature of the ligands is decreased $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ increases and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ decreases. Fresco and Siimann discussed anomalies in the assignation of IR active vibrations, from normal coordinate analysis, of $[\mathrm{M(S_2C_2Me_2)_2}]$ (M = Ni, Pd, Pt), $[\mathrm{Ni(S_2C_2H_2)_2}]$, and $[\mathrm{Ni(S_2C_2Ph_2)_2}]$, and bonding in the chelate rings is interpreted on the basis of stretching-force constants (*60*). Isotopic substitution of nickel has been used in ten complexes of the type $[\mathrm{Ni(S_2C_2R_2)_2}]^x$ (R = H, Ph, $\mathrm{CF_3}$, CN; $x = 0, -1, -2$) in order to assign Ni—S stretching modes. Normal coordinate analysis on all ten complexes gives force constants as well as providing theoretical band assignments (*169*).

C. ESR SPECTRAL AND MAGNETIC STUDIES

These techniques have been used extensively for the electronic and structural characterization of paramagnetic, ferromagnetic, and antiferromagnetic complexes. The amount of work that has been undertaken and the various implications derived from the experimental data are very extensive, and for brevity this section will consider only selected examples of the use of the techniques in the field of transition metal–sulfur chemistry. In many cases the ESR and magnetic parameters have been used to give preliminary structure and bonding evidence.

McCleverty has outlined the ESR spectral properties of the transition metal dithiolenes in considerable detail (*139*). Complexes having a doublet ground state are particularly amenable to study by ESR, although the assignment of a ground state may not be a trivial operation. Recently, two ESR studies of the $\mathrm{V(mnt)_3}^{2-}$ complex as single crystals in diamagnetic hosts have led to a reassignment of the ground state in terms of $^2A_2$ state in D_3 symmetry (*4*, *84*). The orbital bearing the unpaired electron has been shown to have substantial metal d_z2 character although the covalency is quite high. In complexes containing unpaired electrons that are delocalized onto orbitals primarily of ligand character, the ESR technique has been immensely useful. The ESR spectrum of the formally gold(II) complex, $\mathrm{Au(mnt)_2}^{2-}$, has been measured in several host crystals over a range of temperatures (*158*), and these results are consistent with a ground-state hole configuration $(B_{1g})^2(\mathrm{Ag})$ in D_{2n} symmetry. The B_{1g} orbital in square-planar d^9 complexes is normally half-filled; the Ag orbital is primarily ligand-based. The complex was therefore better described as a gold(III) complex with a radical anion ligand. Unusual antiferromagnetic exchange interactions have been observed from isotropic magnetic susceptibility data of the dimeric $[Fe(tfd)_2]_2$ (*44*). A recent study of the trigonal prismatic $[Re(S_2C_2Ph_2)_3]$ and $[Re(tdt)_3]$ have shown that they are characteristic of S-containing organic radicals and that the unpaired electron resides in a nonbonding orbital derived from the ligand π-orbitals. An electronic ground-state configuration of $(3a_1{}^1)(4e^1)(2a_2{}^1)$ has been derived for these complexes (*2*).

A large asymmetry parameter observed for $[Cu(mnt)_2]^{2-}$ is due to a strong in-plane π-bond (*203*). A single-crystal ESR study of $Bu_4N[Pd(mnt)_2]$ interprets ^{105}Pd and ^{33}S hyperfine splitting in terms of a $^2B_{3g}$ electronic ground state in which the half-filled out-of-plane molecular orbital is extensively delocalized over the ligands (*111–113*). The covalent character of the cobalt sulfur bond in phosphine adducts of $[Co(S_2C_2Ph_2)_2]$ is unaffected by the substituents on phosphorus (*168*).

D. ELECTRONIC SPECTRAL STUDIES

Electronic spectral studies of bidentate S-containing ligands have been reviewed in considerable detail (*39*, *95*, *139*), and the major use of the technique is in assignment of electronic and stereochemical structures to the complexes. In spite of the numerous studies in this field, the interpretation of the spectra are still far from being totally clear. π-bonding and electronic delocalization have wide and varying effects on the results, and high nephelauxetic effects are invariably observed. Another cause of the difficulty in assigning spectra is the presence of low-lying high intensity charge-transfer bonds (metal–ligand or ligand–ligand), which frequently mask the *d–d* bands. When *d–d* bands have been assigned, they usually have had anomalously high intensities due to borrowing of intensity from the charge-transfer bands.

E. X-RAY PHOTOELECTRON SPECTRAL (XPS) STUDIES

The ionization energies of electrons can be determined by XPS by means of the Einstein relationship,

$$E_i = h\nu - E_e$$

where E_i is the ionization energy, $h\nu$ is the X-ray energy, and E_e is the kinetic energy of the ejected photoelectron. The actual core electron-binding energy, which is closely related to the ionization energy, is influenced by the local electron density surrounding the atom and by the structural arrangement of other atoms within the solid. The core electron-binding energies of a central atom varies as the valence electron density of the atom is charged through a series of different bonding conditions. XPS has been used to gain new physical data of substantial significance for understanding the bonding in transition metal dithiolenes, as the metal and sulfur binding energies can be related to the charges on the atoms. Grim and co-workers (*136–138*) have determined binding energies for the metal and sulfur atoms in $[M(mnt)_2]^{-1,-2}$ and $[M(S_2C_2Ph_2)_2]^{0,-1,-2}$ (M = Ni, Pd, Pt). Their results are shown in Table II.

TABLE II

METAL AND SULFUR BINDING ENERGIES (eV) IN $[M(S_2C_2R_2)_2]^{z-}$

		M = Ni		M = Pd		M = Pt	
R	*Z*	Ni(2*p*3/2)	S($2p\frac{1}{2}3/2$)	Pd(3*d*5/2)	S($2p\frac{1}{2}3/2$)	Pt(4*f*7/2)	S($2p\frac{1}{2}3/2$)
Ph	0	852.9	161.1	336.4	161.9	71.5	161.8
Ph	−1	852.5	160.8	335.9	161.2	71.2	161.1
Ph	−2	852.8	160.5	335.8	161.3	71.1	161.3
CN	−1	853.1	161.3	335.3	161.1	71.2	161.8
CN	−2	853.1	161.4	335.8	161.2	71.5	161.8

Initially the data were interpreted in terms of Ni being assigned a formal oxidation state of 0 with the additional charge residing on the ligands (*136*); originally postulated from a comparison with the binding energies of other Ni(0) species. A study of over 100 Ni compounds (*138*) showed that the binding energies of the Ni(II) compounds overlap with those of Ni(0) compounds and that the electronegativity of the ligand can affect the binding energies significantly. The $S(2p\frac{1}{2}, \frac{3}{2})$ binding energies decrease in the series $[Ni(S_2C_2Ph_2)_2]^z$ ($z = 0, -1, -2$), which indicates that the charge resides largely on the sulfur atoms. The trend in the Pd and Pt complexes begins in the same way but then remains essentially constant. The sulfur binding energies are very low, indicating high electron density on the sulfur atoms. In the mnt complexes, however, metal and sulfur binding energies are essentially constant, which may indicate that in gaining an electron the extra negative charged is delocalized over the electronegative cyanide group. The absence of fine structure in the XPS of the paramagnetic monoanions is additional evidence for the unpaired electron residing primarily on the ligand, as other paramagnetic Ni compounds show broad lines and shake-up satellites in their XPS. The overall results provide additional weight to the argument for considering the metal as formally M(II) with the extra negative charge residing essentially on the ligands and demonstrates the valence electron delocalization in the complexes.

Hoyer and co-workers (*125*) measured the XPS of $[M(S_2C_2H_2)_2]^n$ (M = Cu or Ni; $n = 0$ or -1) and found the charge at the sulfur atoms dependent on the total charge on the complexes. Alkylation at the S atoms caused a decrease of the charge density at the coordinated atom. The same group also drew similar conclusions for the trisdithiolenes of Mo (*58*). It appears from the binding energies that the greater the localization of charge on the S atoms, the lower the binding energy.

F. MÖSSBAUER SPECTRAL STUDIES

To date, Mössbauer spectral studies of the bidentate S-chelates have been limited to the iron complexes. Complexes containing other Mössbauer-active nuclides have yet to be studied even though the Au^I systems present unique opportunities for studying pure trans effects of sulfur ligands in two-coordinate species.

Correlations of Mössbauer data with stereochemical rearrangements in the mixed-ligand complexes $[Fe(R_2dtc)_2(S_2C_2R_2)]^z$ have been studied recently (*163*), and the spectra of the $z = -1$, 0 complexes consist of a symmetrical quadrupole doublet, suggestive of spin interconversion rates in excess of 10^7 S^{-1} for the neutral species. Temperature-dependent Mössbauer techniques have been used in a study of $(Ph_4P)[Fe(mnt)_3]$ over a wide range of temperatures (*12*); a large quadrupole splitting was observed, indicating strong distortion from cubic symmetry. Conclusions concerning the ground-state formalization showed it to be an almost pure d_{xy} hole, well separated from higher states, contrary to previous assignments derived from ESR data (*38*).

The cluster compounds $(Ph_4As)^{n+}[Fe_4S_4(tfd)_4]^{n-}$ ($n = 0$, 1, or 2) are characterized by positive electric field gradients and near-zero asymmetry parameters. Furthermore, in each case the flux densities at the ^{57}Fe nuclear sites are similar to applied field values, demonstrating the delocalization of the additional electrons onto the dithiolene ligands (*17*) and the equivalence of the four iron atoms. Useful data derived from the Mössbauer spectra of iron dithiolene complexes has been related to empirical bonding parameters (*75*).

G. ELECTROCHEMICAL STUDIES

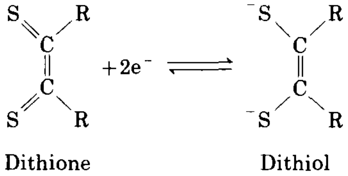
The growth of the chemistry of 1,2-dithiolene complexes is partly due to the discovery of facile reversible one- and two-electron transfer reactions exhibited by these species. A systemization of the pertinent electrochemical data has greatly extended the synthetic chemistry of this class of compounds. McCleverty (*139*) considered the electrochemistry of the 1,2-dithiolene complexes in great detail and attempted to standardize the $E_{1/2}$ values with respect to a standard acetonitrile–Standard Calomel Electrode (SCE) scale. Electrochemical studies have used most techniques available to investigate these reactions. These include ac, dc, and pulse polarography, linear sweep, pulse and cyclic voltammetry, chronopotentiometry, controlled potential, and exhaustive electrolysis.

The interest in the electrochemistry of 1,2-dithiolenes has been maintained at an intense level in recent years, particularly in synthetic and characterization studies (*47*, *54*, *55*, *142*, *191*). Chronopotentiometry and linear-scan voltammetry have been used to demonstrate that the oxidation of $[Ni(mnt)_2]^{2-}$ and the reduction of $[Ni(mnt)_2]^-$ were diffusion controlled in the presence of Et_4NClO_4 and that neither species was electroactively adsorbed onto the Pt electrodes (*126*). Electron transfer series have been shown to exist in the mixed-ligand complexes containing, 1,1- and 1,2-dithio ligands (*195*). The $E_{1/2}$ values were intermediate between those for the complexes with unmixed ligands.

A series of previously unreported gold(III) bisdithiolene complexes have been generated by polarography, and controlled potential electrolysis and the half-wave potentials of the reactions were correlated with the variations in the ESR parameters (*92*).

Paramagnetic $[M(mnt)_2]^{3-}$ complexes (M = Ni, Pd, Pt), have been generated by reversible cyclic voltammetry and ac polarography of the corresponding $[M(mnt)_2]^{2-}$ species (*66*, *67*, *155*). They are characterized as d^9 metals with the unpaired electron consisting of contribution from the d_{xy} metal orbitals and in-plane *s*-orbitals with the palladium complex showing greater covalent character than the nickel species. The reduction of $[Pt(mnt)_2]^{2-}$ proceeds by two successive one-electron processes, and arguments are presented that suggest an electronic ground state differing from the nickel and palladium analogs. This is just one example of the uniqueness of dithiolene systems and how they must be examined individually.

The recent discoveries that 1,1- and 1,3-dithiochelates undergo successive reversible one-electron transfer reactions have established that reversible behavior is not confined to those metal chelates with what Schrauzer (*173*) termed "even" π-electron character, notably the 1,2-dithiene systems. It had been suggested that the "odd" π-electron systems, which cannot exhibit dithione and dithiol forms, e.g., 1,1- and 1,3-dithiochelates, would possess slightly different properties and structures from those of 1,2-dithiolene, which can exhibit such structures, viz.



In the case of the "odd" ligands the electrochemical processes appear to be mainly metal-centered; even though Golding and Lehlonen (*68*) have suggested that the redox processes in the dithiocarbamates take place through the nitrogen atom of the ligand, the orbitals involved are primarily of metal character. In the "even" 1,1-electron systems the redox processes appear to involve orbitals of predominantly ligand character.

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