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MONOTHIO- AND MONOSELENO-CARBAMATE COMPLEXES

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CONTENTS

ABBREVIATIONS

R_2mtc	*N*,*N*-Disubstituted monothiocarbamate anion
R_2dtc	*N*,*N*-Disubstituted dithiocarbamate anion

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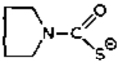
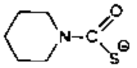
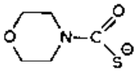
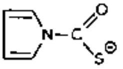
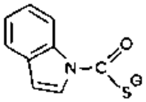
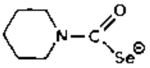
Pyrmtc	
Pipmtc	
Mormtc	
Ptc	
Iltc	
dmsc	*N*, *N*-Dimethylmonoselenocarbamate
desc	*N*, *N*-Diethylmonoselenocarbamate
dbsc	*N*, *N*-Di-n-butylmonoselenocarbamate
dpse	
Ph	C_6H_5
Az	Azobenzene
Pip	Piperidine
Pyr	Pyrrolidine
Py	Pyridine
Bipy	Bipyridine
Acac	Acetylacetonate
THF	Tetrahydrofuran
C–N	The $X_2C–NR_2 (X = S, O, Se)$ bond

A. INTRODUCTION

The coordination chemistry of monothiocarbamate ligands is in its infancy and only within the past ten years has some understanding of the properties of these ligands been gained. In contrast, the related dithiocarbamates have been under study for well over seventy years. There remains a remarkable interest in dithiocarbamate ligands, as indicated in two recent reviews [1,2]; the monothiocarbamates promise to provide an equally rich chemistry.

Prior to 1970, except for one study by Fredga [3], reports of monothiocarbamate chemistry dealt exclusively with their use as analytical reagents. The early investigations of the past decade were designed largely to compare the mono- to the dithiocarbamates and to determine the stereochemical effects of replacing a sulfur with an oxygen atom. It became clear almost immediately that the properties of the monothiocarbamate ligands and complexes differ greatly from those of the corresponding dithiocarbamates.

In this chapter the chemistry of monothiocarbamates as ligands will be reviewed in its entirety through early 1982. The chemistry of the closely related monoselenocarbamates is presented separately in section E.

B. GENERAL SYNTHETIC PROCEDURES FOR MONOTHIOCARBAMATES

(i) Ligands

The most common synthetic procedure for *N*,*N*-disubstituted monothiocarbamate ligands involves the treatment of carbonyl sulfide, OCS, with a secondary amine to provide an ammonium salt [4–6], as shown in the equation

$$2\ R_2NH + OCS \rightarrow [R_2NH_2]^+[R_2NCOS]^-$$

The most frequently used solvents for the reaction are diethylether and ethanol. High yields of the pure salts precipitate directly from the ethereal solutions in many cases. With ethanol as a solvent, the salts usually can be precipitated in pure form by addition of acetone or ether. In some cases the neat amines have been treated with OCS at reduced temperatures to provide the ammonium monothiocarbamate.

The majority of the studies have involved the following secondary amines: *N*,*N*-dimethylamine, *N*,*N*-diethylamine, *N*,*N*-dipropylamine, piperidine and pyrrolidine. As a general rule the solubility of monothiocarbamate complexes increases with increasing size of the alkyl substituents. The piperidine and pyrrolidine derivatives often provide complexes that have optimal stabilities and solubilities for chemical investigations [6].

Sodium salts may be obtained by reaction of OCS with a secondary amine in ethanolic solutions of NaOH [7]. Alternatively the sodium salts can be obtained by treatment of the ammonium salts with NaH in benzene [8].

Potassium salts of monothiocarbamate ligands derived from the aromatic amines indole and pyrrole have been obtained by treatment of the amine with potassium metal in THF under argon, followed by reaction with OCS [9]. Similar procedures were used to make a ligand derived from indoline.

In general the ammonium and alkali metal salts provide reasonably stable starting materials (when dry) for the synthesis of a wide variety of metal complexes.

(ii) Complexes

Most of the complexes reported to date have been prepared by the metathetical reaction of a monothiocarbamate salt with a transition metal salt in a polar non-aqueous solvent and only a few examples of other synthetic procedures can be cited. All of the complexes reported thus far involve ligands of the type $R_2NC(=O)S^-$ ($R \neq H$). It would be of interest to investigate complexes of the type $M(RHNC(=O)S)_x$.

Metal dialkylamides have been shown [10,11] to react with OCS to form monothiocarbamates in what presumably is an insertion reaction

$$M(NR_2)_4 + 4\ OCS \rightarrow M(OCSNR_2)_4$$

where M = Th, U, Ti, Zr and R = Me, Et, i-Bu. There seems to be little advantage to this technique, as the reactions are violently exothermic.

A unique and interesting procedure for the synthesis of $Fe(Me_2mtc)_3$ has been reported by Nakajima et al. [12]. Bis(*N,N*-dimethylcarbamolyl) disulfide was reacted with $Fe_2(CO)_9$ to give what was thought to be $[Fe(Me_2mtc)_2]_n$ as an insoluble polymeric material. Oxidation of this material with elemental S or Se provided $Fe(Me_2mtc)_3$. The utility of this type of synthetic approach should be investigated further.

Finally, the tin derivatives $Me_3Sn(R_2mtc)$ have been used as a starting material [13] for several organometallic complexes, as illustrated by the reaction

$$Me_3Sn(R_2mtc) + Mn(CO)_5Br \rightarrow Mn(CO)_5(R_2mtc) + Me_3SnBr$$

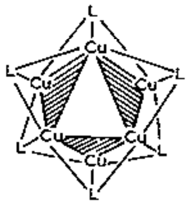
The monothiocarbamate complexes present much greater synthetic challenges than do the dithiocarbamates. Reactions that proceed quickly and cleanly in dithiocarbamate chemistry often fail when R_2mtc is substituted for R_2dtc. For example, K_2PtCl_4 reacts readily with $Na(R_2dtc)$ in aqueous solution to provide $Pt(R_2dtc)_2$ in high yields. The monothiocarbamates fail to react under similar conditions [14]. The need for additional synthetic studies is clear.

C. COMPLEXES OF *N,N*-DIALKYL- AND *N,N*-DIARYLMONOTHIOCARBAMATE LIGANDS

(i) Group I

The earliest reports in the area of monothiocarbamate coordination chemistry involved monovalent coinage metals. The major emphasis was on the degree of polymerization, since the low solubilities suggested structures different from the analogous dithiocarbamates.

In 1950 Fredga [3] described the synthesis and characterization of cuprous diethylmonothiocarbamate. It was noted that monothiocarbamates may exhibit different reactivities from those of dithiocarbamates, since both Cu(I) and Cu(II) dithiocarbamate complexes were isolable, but the Cu(II) complex



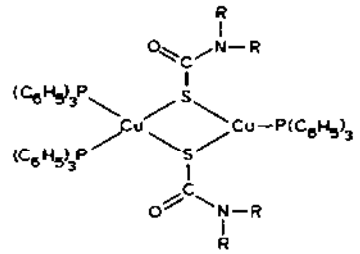


Fig. 1. Representation of the structure of $[Cu(R_2mtc)]_6$. Each ligand, L, is bonded to three different copper(I) ions.

Fig. 2. Proposed structure of the unsymmetrical dimers $Cu_2(R_2mtc)_2[(C_6H_5)_3P]_3$.

of Et_2mtc could not be isolated. Based on molecular weight measurements, Fredga concluded that $Cu(Et_2mtc)$ was a hexamer. This formulation was supported by Akerstrom, who reported the synthesis and solubility properties of $[Cu(R_2mtc)]_x$ (R = Me, Pr, Bu, i-Bu and i-amyl) [15]. Molecular weights were determined in chloroform and the value of x was shown to be concentration dependent, but always between 4 and 6.

The structure of $[Cu(Pr_2mtc)]_6$ was solved subsequently in an X-ray study that confirmed the hexameric nature of the compound [16]. As shown in Fig. 1, $[Cu(Pr_2mtc)]_6$ contains an almost regular octahedron of Cu(I) centers. The ligands are located over six faces of the octahedron with an oxygen from each ligand coordinated to a Cu(I) atom, while each sulfur bridges two Cu(I)

TABLE 1

Selected average bond distances in monothiocarbamate complexes (Å)

Compound	M–S	M–O [a]	M–N	C–O [a]	C–N	C–S	Ref.
$Zn(Pipmtc)\cdot 2Pip$	2.304		2.076	1.24	1.36	1.75	29
$[Cu(Pr_2mtc)]_6$	2.23	2.08		1.25	1.36	1.81	16
$[Ag(Pr_2mtc)]_6$	2.46	2.37					22
$[Ni(Bu_2mtc)_2]_6$	2.441	2.079		1.227	1.364	1.775	64
$[Ni(Pr_2mtc)_2]_6$	2.44	2.08		1.25	1.35	1.77	63
$Co(Pyrmtc)\cdot 2Pyr$	2.584	2.157	2.134	1.283	1.342	1.735	51
$Fe(Me_2mtc)_3$	2.413	2.073		1.278	1.329	1.733	42
$Ti(Et_2mtc)_4$	2.587	2.088		1.275	1.333	1.721	34
$Ti(Et_2mtc)_3Cl$	2.477	2.078		1.283	1.342	1.732	37
$Zr(Et_2mtc)_4$	2.679	2.190		1.275	1.339	1.727	34
$[UO_2(Pr_2mtc)_2(OEt)]$	2.871	2.39		1.26	1.36	1.72	73
$[UO_2(Et_2mtc)_2(OEt)]$	2.866	2.39		1.27	1.33	1.73	72
$Ni(Ptc)_2Py_2$	2.451	2.091	2.054	1.243	1.401	1.694	84

[a] Monothiocarbamate oxygen.

atoms. Each copper atom has non-planar, three-fold coordination. Relevant bond distances are included in Table 1.

Nakajima et al. [17] have investigated the reactions of $[Cu(R_2mtc)]_6$ ($R = Et$, Me) with tertiary phosphines and have isolated the adducts $(Ph_3P)_3Cu_2(R_2mtc)_2$, $(MePh_2P)_3Cu_2(Me_2mtc)_2$, and $(MePh_2P)_2Cu(Me_2mtc)$ as pure compounds. The first compound is thought to be an unsymmetrical dimer (Fig. 2). Molecular weight studies coupled with proton magnetic resonance and conductivity measurements suggest that in solution the dissociation reactions

$$(Ph_3P)_3Cu_2(R_2mtc)_2 \rightarrow Ph_3P + (Ph_3P)_2Cu_2(R_2mtc)$$

and

$$(Ph_3P)_3Cu_2(R_2mtc)_2 \rightarrow (Ph_3P)_2Cu(R_2mtc) + \tfrac{1}{2}\left[(Ph_3P)_2Cu_2(R_2mtc)_2\right]$$

take place. At low temperatures the unsymmetrical dimer is the most abundant species. Addition of free phosphine to $(Ph_3P)_3Cu_2(R_2mtc)_2$ leads to the formation of the symmetrical, sulfur-bridged dimer $(Ph_3P)_4Cu_2(R_2mtc)_2$. The unsymmetrical dimer derived from $MePh_2P$ behaves similarly. These results are analogous to those obtained in studies involving the interaction of Cu(I) halides with tertiary phosphines [18,19]. The NMR results suggest that there is restricted rotation around the C–N bond in the R_2mtc complexes of Cu(I) (vide infra).

Monothiocarbamates of Cu(II) have not been reported since the ligand appears to be readily oxidized by Cu(II). Thus, the reaction of indoline-*N*-carbothioate with $CuBr_2$ produces a Cu(I) species and bis(indolinylcarbomyl) disulfide [20]. Copper(II) dithiocarbamates are known and well characterized [21].

Like copper, silver(I) forms polymeric monothiocarbamate complexes. The structure of $[Ag(Pr_2mtc)]_6$ was determined and found to be isostructural with the corresponding Cu(I) complex [22]. Again, an octahedral arrangement of Ag(I) atoms prevails in the hexameric species and there are no chelate rings in the molecule.

The formation of phosphine adducts of Ag(I) monothiocarbamates has also been studied [23]. Reaction of $[Ag(R_2mtc)]_6$ ($R = Me$, Et) with one equivalent of Ph_3P produced $Ph_3PAg(R_2mtc)$. Reaction with $MePh_2P$ gave only the 2 : 1 adduct $(MePh_2P)_2Ag(R_2mtc)$. Observed molecular weights of the 1 : 1 adducts were 8–58% higher than expected depending on concentration, indicating some association in solution. On the other hand, the observed molecular weights of the 2 : 1 adducts were significantly lower than the calculated values, suggesting partial dissociation of phosphine.

Again proton NMR spectra of these complexes indicate that there is hindered rotation about the C–N bond; however, at −90° additional peaks were observed, suggesting the presence of additional species in solution. The equilibria

$$Ph_3PAg(R_2mtc) \rightleftarrows \tfrac{1}{2}\ [Ph_3PAg(R_2mtc)]_2 \rightleftarrows \tfrac{1}{4}\ [Ph_3PAg(R_2mtc)]_4$$

were proposed to account for these results. Also reported was the unusual complex $(Ph_3P)_3Ag_2(Et_2mtc)_2$, which also dissociates in solution. The structure suggested involves two thiocarbamates bridging the Ag atoms through sulfur analogous to the proposed structure of $(Ph_3P)_3Cu_2(R_2mtc)_2$ (Fig. 2). Mixed Cu(I)–Ag(I) thiocarbamate complexes of the type $CuAg(R_2mtc)_2$ (R = Me, Et) have been prepared along with the phosphine adducts $(Ph_3P)_3CuAg(R_2mtc)_2$ and $(MePh_2P)_4CuAg(R_2mtc)_2$ [24]. The mixed-metal complexes were obtained as crystals from equimolar mixtures of $[Cu(R_2mtc)]_6$ and $[Ag(R_2mtc)]_6$. That the crystals are well defined molecules rather than mixtures was shown by melting point measurements and X-ray powder diffraction studies. The mixed-metal complexes appear to be isostructural with the parent silver and copper hexamers. NMR studies indicate that the triphenyl phosphine adduct is an unsymmetrical dimer with bridging thiocarbamates similar to that shown in Fig. 2. Whether Cu(I) or Ag(I) occupies the four-coordinate position was not determined. In solution the complexes are thought to undergo partial rearrangement, as follows

$$2\,(Ph_3P)_3CuAg(R_2mtc)_2 \rightleftarrows (Ph_3P)_3Cu_2(R_2mtc)_2 + (Ph_3P)Ag(R_2mtc) + (Ph_3P)_2Ag(R_2mtc)$$

Addition of excess Ph_3P gave $(Ph_3P)_4Cu_2(R_2mtc)_2$ and $(Ph_3P)_2Ag(R_2mtc)$.

The mixed-metal adduct of $MePh_2P$ partially dissociates in solution to give $(MePh_2P)_3CuAg(R_2mtc)_2$. Addition of excess phosphine provided $(MePh_2P)_4Cu_2(R_2mtc)_2$ and $(MePh_2P)_2Ag(R_2mtc)$.

Binary monothiocarbamates of gold are unknown, but complexes of the type $R_3PAu(R_2mtc)$ have been reported [25]. These compounds are monomeric, at least in chloroform. Based on the position of a broad, strong band near 1595 cm^{-1} in the IR spectrum, it was concluded that the oxygen of the monothiocarbamate ligand is not coordinated (see section F).

Proton NMR spectra of $(R_3P)Au(R_2mtc)$ were recorded at several temperatures for the dimethyl and piperidyl derivatives. At $-30°$ rotation around the C–N bond is slow relative to the NMR time scale. Eyring plots for the hindered rotation were used to derive the associated thermodynamic constants. Values of $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ are given in Table 2. Comparison of the data for the two compounds shows that the R-group has a substantial effect on the rotation. Since both compounds contain monodentate ligands, no comparison of effects of bonding mode on the rotation was possible. The derived thermodynamic parameters are similar to those found for analogous dithiocarbamate complexes [26].

TABLE 2

Thermodynamic constants for C–N bond rotation ($\Delta G^{\neq}$ and $\Delta H^{\neq}$ in kcal mol^{-1}; $\Delta S^{\neq}$ in e.u.)

Compound	Solvent	$\Delta G^{\neq}$ (300 K)	$\Delta H^{\neq}$ (300 K)	$\Delta S^{\neq}$ (300 K)	Ref.
$(\mathrm{Ph_3P})\mathrm{Au}(\mathrm{Me_2mtc})$	$\mathrm{CDCl_3}$	15.8	15.8	0.0	25
$(\mathrm{Ph_3P})\mathrm{Au}(\mathrm{Pipmtc})$	$\mathrm{CDCl_3}$	15.2	10.8	−14.7	25
$(\mathrm{Ph_3P})\mathrm{Au}(\mathrm{dmsc})$	$\mathrm{CDCl_3}$	16.4	19.2	9.2	25
$(\mathrm{Ph_3P})\mathrm{Au}(\mathrm{dpsc})$	$\mathrm{CDCl_3}$	15.4	10.7	−15.7	25
$(\mathrm{CH_3})_3\mathrm{Sn}(\mathrm{Me_2mtc})$	$\mathrm{C_6H_{14}}$	16.4	16.4	0.2	79
$(\mathrm{CH_3})_3\mathrm{Sn}(\mathrm{Me_2mtc})$	$\mathrm{CHCl_3}$	16.6	19.3	9.1	79

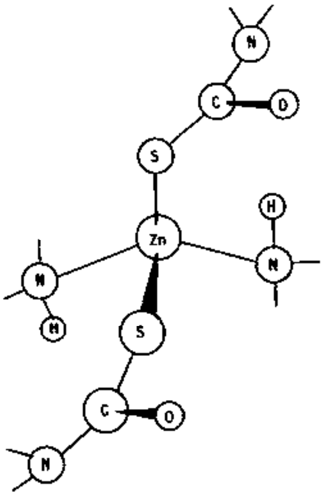
(ii) Group II

McCormick and Greene [27] have reported on complexes of Group II elements with pyrrolidyl and piperidyl monothiocarbamates. In general these compounds are of very limited solubility, but molecular weight determinations were possible for $\mathrm{Cd(Pipmtc)_2}$ and $\mathrm{Zn(Pipmtc)_2}$, which clearly are polymeric. Since the observed molecular weights were concentration dependent it was difficult to determine the exact degree of polymerization; however, the Zn(II) and Cd(II) compounds appeared to be dimeric and trimeric, respectively.

The $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ frequencies of the Zn(II) and Cd(II) compounds may be indicative of coordinated oxygen atoms, although this conclusion is tenuous on the basis of IR evidence alone (see section F).

The IR spectrum of the Hg(II) compound exhibited a band at 1575 cm^{-1} which was assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$. The high frequency of this band suggests that only the sulfur atom of the ligand is coordinated to the Hg(II) atom, as might be expected.

The structural details of the binary group II monothiocarbamates remain unknown. However $[\mathrm{Zn(Pipmtc)_2}]_x$ was found to react with piperidine to form the monomeric compound $\mathrm{Zn(Pipmtc)_2(Pip)_2}$ as white crystals, and the results of an X-ray diffraction study of this compound were published [28,29]. The oxygen atoms of the monothiocarbamate ligands are not coordinated. The Zn atom is in a pseudo-tetrahedral environment with two monothiocarbamate sulfurs and two piperidine nitrogens in the coordination sphere, as shown in Fig. 3. This was the first structure reported for a monothiocarbamate in which the oxygens are not coordinated. Yet, bond distances within the ligand are nearly identical to corresponding distances found in the polymeric Cu(I) [16], Ag(I) [22], and Ni(II) [30] structures. Thus it appears that the structural parameters of this ligand are almost indepen-



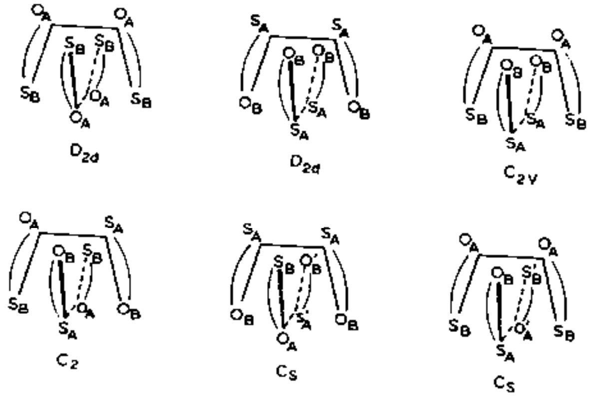


Fig. 3. Coordination geometry and bonding in $Zn(Pipmtc)_2(Pip)_2$.

Fig. 4. Representation of mmmm dodecahedral stereoisomers of $[M(R_2mtc)_4]$ complexes. (Reproduced with permission from ref. 33.)

dent of bonding mode. The C–O and C–N bond distances of 1.24(1) Å and 1.36(1) Å, respectively, compare well with the values found in organic amides where considerable multiple bond character exists in the C–N bond [31]. The C–S bond distance of 1.75(1) Å is longer than that for the same bond in dithiocarbamates where multiple bond character is known to be important. In fact the C–S bond distance in the monothiocarbamates approaches that of a C–S single bond as calculated by summing the covalent radii (1.81 Å).

(iii) Group III

Monothiocarbamate complexes of the Group III metals have not been reported.

(iv) Group IV

Monothiocarbamate complexes of Hf have not been reported. Chisholm and Extine [11] prepared $M(R_2mtc)_4$ (M = Ti, Zr; R = Me, Et) by insertion of carbonyl sulfide into the M–N bonds of $M(NR_2)_4$. A more complete study of these complexes was carried out by Fay and co-workers to determine whether there is sorting of oxygen and sulfur donors among inequivalent sites in these dodecahedral complexes, which were prepared from the metal halides and alkali metal monothiocarbamates [32–34]. Of the six

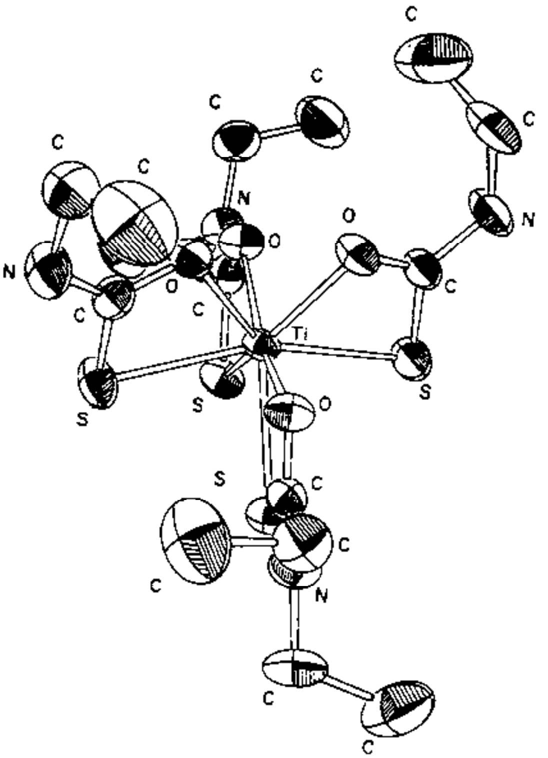


Fig. 5. Structural model of $Ti(Et_2mtc)_4$. (Reproduced with permission from ref. 34.)

possible mmmm isomers it was determined that the C_{2v} isomer is the most important species (Fig. 4).

This conclusion was reached on the basis of NMR and dipole moment measurements. Four methyl resonances attributable to the four inequivalent methyl groups in the C_{2v} configuration were observed at −104°. The structure was confirmed by three dimensional X-ray diffraction studies on $Ti(Et_2mtc)_4$ and $Zr(Et_2mtc)_4$ which are essentially identical [34]. The structure (Fig. 5) is surprising since Orgel's rules [35] predict that sorting of sulfurs and oxygens between A and B type sites should take place. Instead, two sulfurs were found in A sites and two were found in B sites. It was suggested that S- - -S interactions might force all four sulfurs to be on the same side of the molecule. However, the long S · · · S distances in the Zr(IV) complex argue against this possibility. Subsequently it was suggested that since no sulfur atoms were directly opposed a *trans* influence might be an important factor in determining the stereochemistry of these two molecules. However, the *trans* influence may be too complicated to invoke in a dodecahedral system [36].

Perhaps the most interesting and important aspect of this work is the conclusion that Ti(Et_2mtc)$_4$ and Zr(Et_2mtc)$_4$ may be added to the small list of eight-coordinate complexes that are stereochemically rigid on the NMR time scale. Two processes were detected by temperature dependent NMR spectral studies. At −84°C a metal-centered rearrangement of methyl groups between A and B sites occurred and at +30°C rotation about the C–N bond took place. Below 30°C, two resonances were observed corresponding to methyl group proximity to sulfur or oxygen. Below −84°C four resonances were observable owing to the rigidity of the dodecahedral complex.

The synthesis and stereochemistry of (R_2mtc)$_3$TiCl compounds have been reported [37]. The metal is seven coordinate and pentagonal bipyramidal in structure. The Cl atom occupies an axial position and two of the three bidentate monothiocarbamate ligands are equatorial. The third monothiocarbamate spans an axial and an equatorial site (Fig. 6). As in the eight coordinate Ti(R_2mtc)$_4$ complexes, all the sulfurs are mutually *cis*. Bond distances within the ligands are nearly identical to those found in Ti(R_2mtc)$_4$.

The rearrangement of this molecule was studied in solution by NMR spectroscopy. Two processes were postulated to explain the spectra: scrambling of monothiocarbamates among the all equatorial-ligand and the equatorial-axial sites and rotation about the C–N bond. At −86.2°C four resonances were observed with relative intensities of 1:2:2:1. As the

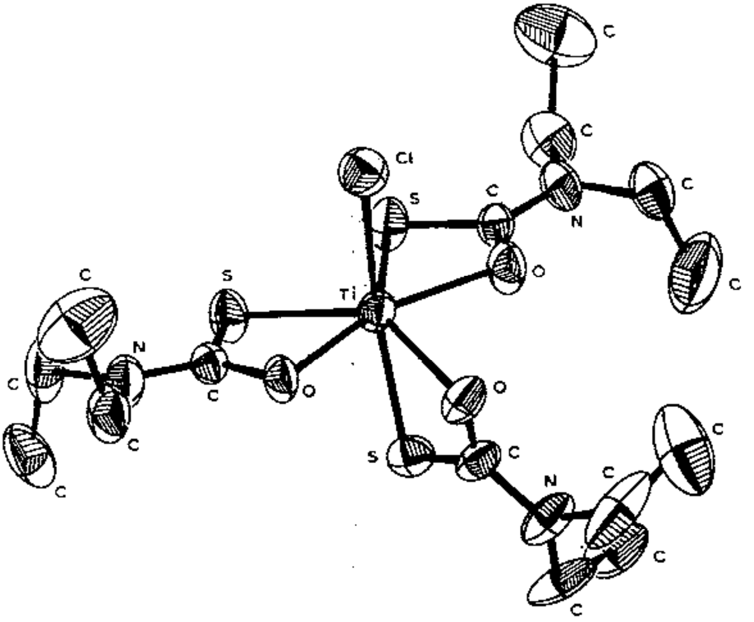


Fig. 6. Structural model of Ti(Et_2mtc)$_3$Cl. (Reproduced with permission from ref. 37.)

temperature was raised to −20°C this pattern coalesced to provide two resonance lines of equal intensity. A further temperature increase to 110°C resulted in a single resonance line. The low temperature process was attributed to ligand scrambling. If C–N rotation were the low temperature process, two resonances would indeed be expected. However, the intensities would be in the ratio 1 : 2 since all-equatorial and equatorial-axial ligands would still be distinguishable. Since the two peaks are of equal intensity, the only feature that distinguishes methyl groups is their proximity to S or O atoms. Warming of the compound to 110°C enhances rotation about the C–N bond and only one resonance is observed. It was proposed that the low temperature rearrangement did not involve breaking of metal–ligand bonds, but rather that it proceeded through a capped octahedral intermediate. This intermediate would render all monothiocarbamates equivalent on the NMR time scale.

(v) Group V

Only one monothiocarbamate complex of the Group V metals has been mentioned in the literature. The electrochemical properties of $(\eta^5\text{-}C_5H_5)_2V(\text{Pyrmtc})$ were alluded to briefly by Bond et al. [38], but the synthesis of the compound was not included in the report.

The Group V metals should receive additional study as it is to be expected that additional examples of oxygen coordination from the monothiocarbamate ligand will be found. It is conceivable that a complex bonded monodentately through oxygen might be observed.

(vi) Group VI

Monothiocarbamates of Cr and W have not been reported.

McCormick and co-workers reported the reactions of Na(Pyrmtc) with $Mo_2(Ac)_4$, MoO_2Cl_2, Na_2MoO_4, $MoCl_4(Py)_2$, $Mo(CO)_6$ and $MoBr_2(CO)_3$-Bipy [7]. In every case except that of $Mo_2(Ac)_4$ the products lacked monothiocarbamate ligand, as determined by IR spectroscopy. The bright red and extremely air sensitive product of the $Mo_2(Ac)_4$ reaction was assigned a molybdenum acetate type of structure based on mass spectral and IR evidence. Other structural studies were precluded because of the low solubility and high reactivity of the complex. An IR spectrum was recorded and the $\nu(C\overset{-}{-}N)$ band (see section F) was observed at 1500 cm^{-1}. This very low value suggests a bridging mode for the ligand.

Tanaka and co-workers [39] have synthesized and studied the electrochemical behavior of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(Me_2mtc)$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$-$(Me_2mtc)$ in CH_3CN and CH_2Cl_2 as solvent. The dicarbonyl was obtained

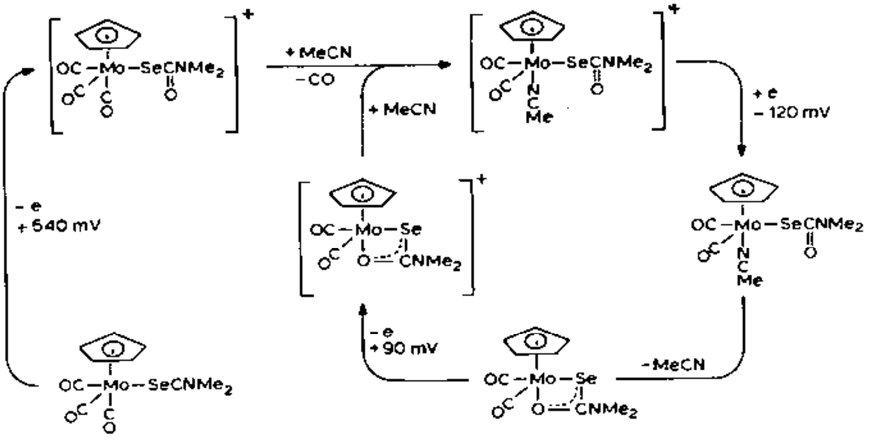


Fig. 7. Electrochemical properties of $[Mo(XOCNMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = S, Se). Although monoselenocarbamate is shown in the figure, the scheme applies equally well to the monothiocarbamate. (Reproduced with permission from ref. 39.)

from the thermolysis of the tricarbonyl, which is thought to involve monodentate Me_2mtc ($\nu(C=O) = 1600\ cm^{-1}$). The unstable oxidized form of the dicarbonyl is stabilized by acetonitrile to give $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(Me_2mtc)(CH_3CN)]^+$, which can be reduced to the original dicarbonyl complex with liberation of acetonitrile. The tricarbonyl complex is also subject to one electron oxidation to give electron deficient $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(Me_2mtc)]^+$, which eliminates CO to form $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(Me_2mtc)(CH_3CN)]^+$. This electrochemistry is summarized in Fig. 7.

(vii) Group VII

Monothiocarbamate complexes of Tc and Re are unknown.

Organometallic complexes of Mn(I) containing monothiocarbamates were synthesized and characterized by Tanaka et al. [40]. The complex $Mn(CO)_5(Me_2mtc)$ was formed by reaction of the ammonium salt of dimethyl monothiocarbamate with $Mn(CO)_5Br$. This compound has also been produced from the reaction of $Mn(CO)_5Br$ with $Me_3Sn(Me_2mtc)$ [13]. The IR spectrum of $Mn(CO)_5(Me_2mtc)$ exhibits a strong band near 1600 cm^{-1}, which was assigned to $\nu(C=O)$ for a non-coordinated monothiocarbamate oxygen. Attempts to close the chelate ring (with CO expulsion) by thermolysis were carried out. During thermolysis of $Mn(CO)_5(Me_2mtc)$ the band at 1603 cm^{-1} slowly gave way to a new band at 1540 cm^{-1}. This new band resulted from loss of CO with concomitant closing of the chelate ring to give

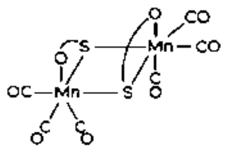


Fig. 8. Proposed structure of $[Mn(CO)_3(R_2mtc)]_2$ complexes.

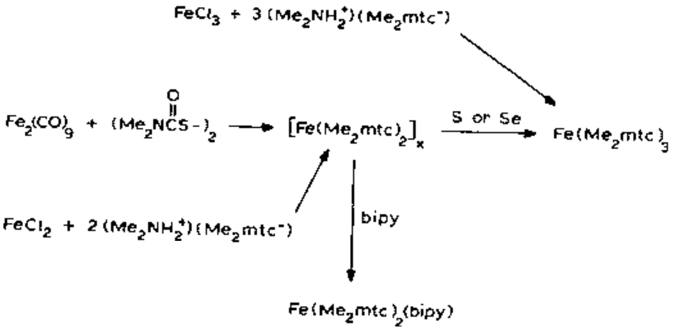


Fig. 9. Synthetic scheme for $Fe(Me_2mtc)_3$ and related complexes.

the unstable $Mn(CO)_4(Me_2mtc)$. The NMR spectrum taken during thermolysis showed, initially, one broad methyl peak that gave way to two sets of sharp doublets upon heating of the sample. The broad singlet characterizes $Mn(CO)_5(Me_2mtc)$ while the doublet results from $Mn(CO)_4(Me_2mtc)$. This may indicate that rotation about the C–N bond is more restricted in the bidentate than in the monodentate coordination mode. This contrasts to the earlier studies of Pd(II) [23] and Au [25] complexes which indicated that the nature of the R group in R_2mtc was more important than the bonding mode of the ligand. The unstable $Mn(CO)_4(Me_2mtc)$ continued to decompose by further loss of CO to give the dimeric species $[Mn(CO)_3(Me_2mtc)]_2$, which was isolated. In agreement with Abel and Dunster [13] the dimer was assigned the structure shown in Fig. 8 based on appearance of six ν(CO) bands in the IR spectrum.

The corresponding dithiocarbamates, thioselenocarbamates, diselenocarbamates, and monoselenocarbamates show only three ν(CO) bands and consequently are thought to have an alternate, but related, structure. It is not clear why the thiocarbamates should favor structure B.

(viii) Group VIII—iron triad

Complexes of Ru and Os have not been reported.

Iron monothiocarbamate complexes have received considerable attention. In 1976 Nakajima et al. [12] published the synthesis of Fe(II) and Fe(III) *N*,*N*-dimethyl monothiocarbamates (Fig. 9).

The iron(II) species, $Fe(Me_2mtc)_2$, was formulated as an air-sensitive polymeric compound based on its low solubility, but molecular weight determinations were not made. The IR spectrum showed a band at 1545 cm^{-1}. The iron(III) species, Fe(Me$_2$mtc)$_3$, which was said to be somewhat sensitive to moisture or oxygen, exhibited a similar band at 1540 cm^{-1}. Magnetic susceptibility measurements on Fe(Me$_2$mtc)$_3$ were reported to be consistent with Curie–Weiss behavior over the 80–300 K range and the magnetic moment was indicative of a high-spin state. It also was suggested that there is an antiferromagnetic interaction below 1.7 K, similar to that observed for Fe(Et$_2$dtc)$_2$I [41]. The magnetic moment of Fe(Me$_2$mtc)$_2$(Bipy) decreased from 5.34 to 5.00 B.M. in the interval 300 to 84 K. This variation was interpreted in terms of distortion from cubic symmetry and/or spin–orbit coupling.

In 1977 McCormick and co-workers [7] reported the synthesis of deep red Fe(R$_2$mtc)$_3$ (R = Pyr, Me, Pip) from anhydrous FeCl$_3$ and (R$_2$NH$_2$)$^+$-(R$_2$mtc)$^-$ in mixed acetone/benzene as solvent. The compound was said to be extremely air sensitive. The IR spectra were consistent with bidentate coordination (see Section F). Ahmed and Ibers [42] published the structure of Fe(Me$_2$mtc)$_3$. The tris bidentate arrangement of ligands in this complex was confirmed, as shown in Fig. 10. An important aspect of this work was the determination of the twist angle ϕ, which is described as the angle between the triangle formed by the three sulfur atoms and the parallel triangle described by the three oxygen atoms. In a trigonal prismatic

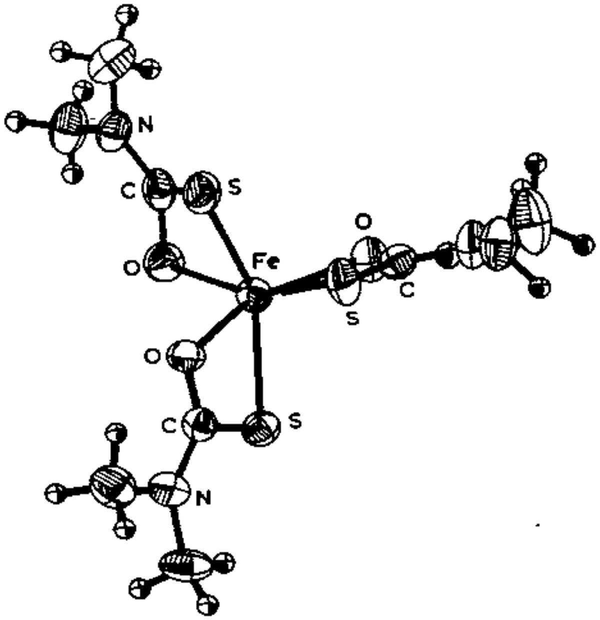


Fig. 10. Structure of Fe(Me$_2$mtc)$_3$. (Reproduced with permission from ref. 42.)

arrangement the donor atoms are eclipsed and $\phi = 0°$. For a trigonal antiprismatic (or pseudo-octahedral) arrangement $\phi = 60°$. For $Fe(Me_2mtc)_3$, ϕ was found to be 33.2°, intermediate between the two extremes. Since the monothiocarbamate and dithiocarbamates possess such similar structures, it was concluded that the intermediate geometry found in the dithiocarbamate complexes of Fe(III) cannot be ascribed simply to the presence of an S_6 core.

The magnetic properties of the Fe(III) monothiocarbamates clearly are of great interest because of their relationship to the dithiocarbamates, which exhibit a ^2T (low spin, $S = \frac{1}{2}$) $\rightleftarrows$ ^6A (high spin, $S = \frac{5}{2}$) spin equilibrium process [43]. Kunze et al. [44] reported that $Fe(R_2mtc)_3$ (R = Me, Et, i-Pr, Pyr, or Pip) have room temperature magnetic moments greater than 5.7 B.M., consistent with a high spin $S = \frac{5}{2}$ ground state. Only $Fe(Me_2mtc)_3$ and $Fe(Et_2mtc)_3$ exhibited non-Curie behavior typical of a spin equilibrium process. With respect to $Fe(Me_2mtc)_3$ this conclusion clearly differed from the report of Nakajima et al. [12]. In addition, Kunze et al. [44] did not specifically emphasize the extreme moisture sensitivity observed by previous workers [7,12] and, in fact, used hydrated ferric salts in their synthesis and isolated $Fe(Et_2mtc)_3$ as a dihydrate. Variable temperature Mossbauer parameters also were reported. The room temperature spectra ($S = \frac{5}{2}$ state predominating) were fit as singlets with positive isomer shifts ranging from 0.59 mm s^{-1} to 0.63 mm s^{-1} relative to sodium nitroprusside. $Fe(Pyrmtc)_3$ remained high spin to 80 K with the isomer shift increasing to 0.83 mm s^{-1}. Measurements below 80 K were not carried out.

Recently Perry et al. extended the previous magnetic and spectroscopic studies to 4.2 K [45], with emphasis on $Fe(R_2mtc)_3$ (R = Me, Et) since these two complexes had previously been shown to exhibit non-Curie behavior. The ethyl derivative was reported in the second study to have been obtained in anhydrous form, although it was pointed out that the two forms have similar magnetic properties at a given temperature.

The low temperature data obtained for $Fe(Et_2mtc)_3$ support the view that a spin equilibrium process exists, the $S = \frac{1}{2}$ state becoming increasingly populated with decreasing temperature. At 8.6 K the magnetic moment dropped to 1.22 B.M., which is below the spin-only value. This unusual behavior was attributed to weak intermolecular antiferromagnetic exchange interactions.

The low temperature magnetic studies [45] on $Fe(Me_2mtc)_3$ have revealed additional complications, as the results obtained were dependent on the particular preparation. Two preparations having indistinguishable IR spectra and elemental composition gave room temperature moments of 5.81 B.M. and 5.98 B.M. which dropped to 4.46 B.M. (6.9 K) and 5.75 B.M. (8.9 K), respectively. Thus, one preparation provided data consistent with a spin-equilibrium process and the other preparation gave a compound that remained high-spin. This very peculiar phenomenon probably accounts for the discrepancies in the earlier reports [12,44] on the magnetic properties of this compound.

Additional low temperature (to 4.5 K) Mossbauer results were reported for $Fe(R_2mtc)_3$ (R = Et, Me) in the crystalline modification that exhibits spin-equilibrium characteristics. At 4.5 K both compounds exhibited quadrupole split doublets. The increase in quadrupole splitting parallels the increase in ^2T population with decreasing temperature, as expected and as observed in corresponding spin equilibrium $Fe(R_2dtc)_3$ systems. It was also observed that $Fe(R_2mtc)_3$ and $Fe(R_2dtc)_3$ complexes are similar in that the Mossbauer spectra do not display separate high- and low-spin signals at temperatures where the ^6A and ^2T states are equally populated; instead, spectra that appear to be an average of the two spin states were obtained. This possibly reflects intersystem crossing rates that are faster than the Mossbauer transition time scale.

Low temperature (12 K) frozen glass ESR spectra also were reported [45] for several of the $Fe(R_2mtc)_3$ complexes, and in all cases signals (g = ca. 4.3) characteristic of high-spin iron(III) with maximum rhombicity (E/D = 1/3) were obtained. This observation may indicate that the spin-equilibrium phenomenon is induced by solid-state lattice effects and is not transferred to the solid solution state or, alternatively, that the ESR spectra represent decomposition products. The latter possibility is reasonable in view of the known instability of $Fe(R_2mtc)_3$ complexes in solution [7,12,44].

The $Fe(R_2mtc)_3$ complexes present substantial experimental challenges because of their solution sensitivity [44], their susceptibility to oxidation or hydrolysis [7,12], and the apparent variety of crystalline modifications that can be obtained [45]. This last point should be investigated further.

An electrochemical investigation [46] of $Fe(R_2mtc)_3$ (R = Me, Et, i-Pr, Pip, Pyr) showed that the compounds gave quasi-reversible cyclic voltammetric waves between −0.3 and −0.4 V (relative to SCE), which formally corresponds to reduction of Fe(III) to Fe(II). The $Fe(R_2mtc)_3$ compounds are almost identical to the corresponding $Fe(R_2dtc)_3$ complexes [47] in their electrochemical behavior.

Some interest has been shown in the organometallic iron complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(R_2mtc)$. This type of complex (R = Pyr) was first synthesized by Springsteen et al. [7] from Na(Pyrmtc) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and was formulated as having a monodentate R_2mtc ligand, bonded through sulfur. Attempts to close the chelate ring with concomitant expulsion of CO by thermal and photochemical methods were unsuccessful. In the dithiocarbamate series it is possible to close the chelate ring [48]. Bussetto et al. [49] have synthesized $(\eta^5\text{-}C_5H_5)Fe(CO)_2(R_2mtc)$ from carbamoyl derivatives as follows:

$$(C_5H_5)Fe(CO)_2CONHR + OCS \rightarrow (C_5H_5)Fe(CO)_2(R_2mtc) + CO$$

where R = Me, Et. The reaction is slow, but it provides a new route to mtc complexes. Nagao et al. [50] have prepared $(\eta^5\text{-}C_5H_5)Fe(CO)_2(Me_2mtc)$ from $(Me_2NH_2)^+(Me_2mtc)^-$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(OCMe_2)]BF_4$. The complex undergoes one electron oxidation to form $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}(Me_2mtc)^+$, which is thought to be unstable in solution.

(ix) Group VIII—cobalt triad

Complexes of iridium have not been reported, and there are only a few reports of cobalt and rhodium complexes.

The first cobalt complex to be reported was the mixed-ligand Co(II) species $[Co(pyr)_2(Pyrmtc)_2]$, the structure (Fig. 11) of which was determined by X-ray methods [51]. The dark blue complex contains bidentate non-bridging R_2mtc ligands incorporated in a highly distorted octahedral coordination geometry. The Co–O bond distance of 2.157 Å is long in comparison to that found for terminal oxygen donors in six-coordinate acetylacetonate structures [52] and other similar complexes [53]. The Co–O bond appears to be quite weak, and structural changes appear to take place when the complex

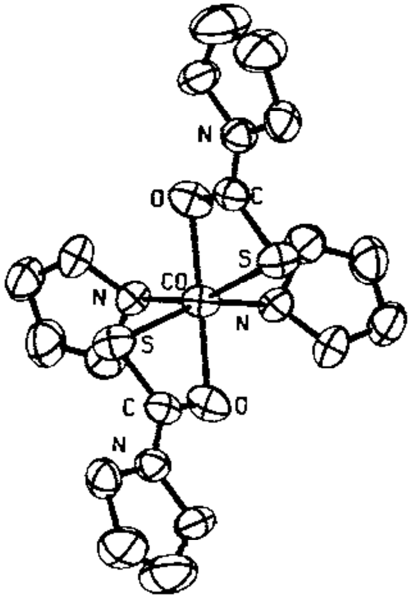


Fig. 11. Structure of $Co(Pyrmtc)_2(Pyr)_2$.

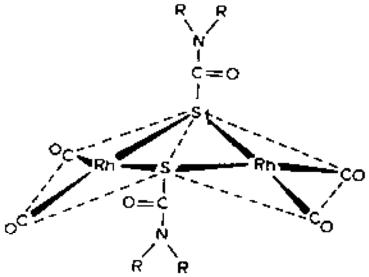


Fig. 12. Proposed structure of $[Rh(CO)_2(R_2mtc)]_2$. (Reproduced with permission from ref. 58.)

dissolves in even weakly polar solvents. The IR spectrum, electronic spectrum and magnetic moment (4.82 B.M. at 300 K) are consistent with the structure shown in Fig. 11.

The other known cobalt complexes are mixed ligand species of the type $Co(acac)_2(R_2NH)(R_2mtc)$ (R = Pyr, Pip, Mor) in which the R_2mtc ligand is thought to be monodentate and bonded to the Co(III) center through sulfur to provide a CoO_4SN chromophore [54]. The morpholine and pyrrolidine derivatives are thought to be *cis*, whereas NMR evidence indicates that the piperidine derivative is in a *trans* configuration.

The differences between R_2mtc and R_2dtc ligands are most obvious in cobalt chemistry. For example, it is well known that salts of *N,N*-dialkyldithiocarbamates react readily with Co(II) in aqueous solution to give stable, octahedral cobalt(III) dithiocarbamate complexes and thiuram disulfide ($R_2NC(=O)S-S(O=)CNR_2$) [55]. Analogous complexes of the form $Co(R_2mtc)_3$ have not been reported in spite of efforts to prepare them [56]. It is suggested that R_2mtc ligands are less likely to stabilize high oxidation states than are the corresponding R_2dtc ligands [57]; this difference probably results from the weak donor properties of the oxygen atom in R_2mtc ligands.

An air sensitive rhodium compound of the type $(Ph_3P)_2Rh(CO)(Pipmtc)$ has been prepared [25] from sodium or ammonium salts of Pipmtc and $(Ph_3P)_2Rh(CO)Cl$. If the phosphine is $(C_6H_{11})_3P$, no reaction occurs, which reflects the bulkiness of the cyclohexyl group. The Pipmtc ligand is thought to bond to Rh through sulfur.

Other rhodium monothiocarbamates were reported by Krankovits et al. [58]. These dimeric complexes of the form $(R_2mtc)_2Rh_2(CO)_4$ (R = Et, Pyr, Pip) are considered to have the structure shown in Fig. 12. This structure is suggested by the $\nu(C\dot{=}O)$ frequency of ca. 1660 cm^{-1}, corresponding to uncoordinated oxygen in the R_2mtc ligands, and by the observation of three bands attributable to ν_{CO} in the terminal carbonyl region. The terminal carbonyl bands are similar to those exhibited by dimeric $Rh_2(CO)_4Cl_2$ [59]. The dimeric structure is cleaved by the addition of excess amine to give square planar anions of the type $Rh(CO)_2(R_2mtc)_2^-$. Addition of Ph_3P results in the formation of $(Ph_3P)_2Rh(CO)(R_2mtc)$.

(x) Group VIII—nickel triad

Complexes of Ni(II), Pd(II) and Pt(II) have been reported; in fact, monothiocarbamate complexes of metals in this family have received more attention than any of the others.

Early reports by Krankovits et al. [60], Willemse [61], and McCormick and Stormer [62] described the synthesis of two types of Ni(II) monothiocarbamates: $[Ni(R_2mtc)_2]_n$ and $Ni(R_2mtc)_2(R_2NH)_2$.

It was first reported by Krankovits et al. [60] that bands corresponding to a COS group vibration appear at 1610 cm^{-1} in $[Ni(Pyrmtc)_2]_n$ and 1618 cm^{-1} in $Ni(Pyrmtc)_2(Pyr)_2$, while a band corresponding to $\nu(C \overset{..}{-} N)$ was assigned at 1540 cm^{-1} and 1500 cm^{-1} for the same two compounds, respectively. The values for $\nu(C \overset{..}{-} O)$ were later shown to be too high. Willemse's [61] assignments of $\nu(C \overset{..}{-} O)$ at 1545 cm^{-1} and $\nu(C \overset{..}{-} N)$ at 1525 cm^{-1} in $[Ni(Pr_2mtc)_2]_n$ are more reasonable. Krankovits et al. [60] believed that the Ni(II) compounds were polymeric based on magnetic studies and optical reflectance data, which suggested an octahedral environment for the Ni atom. The degree of polymerization could not be ascertained since the low solubility of $Ni(Pyrmtc)_2$ precluded molecular weight determinations.

The propyl compound $[Ni(Pr_2mtc)_2]_n$ [61] was sufficiently soluble for molecular weight determinations. While it was later shown to be incorrect, the data suggested that this compound was approximately pentameric [62]. The bis-pyridine adduct, $Ni(Pr_2mtc)_2(Py)_2$, on the other hand, was shown to be monomeric in solution.

The R_2mtc (R = Me, Et, Pr, Bu, Pyr, Pip) complexes of Ni(II) were reported independently by McCormick and Stormer in 1972 [62]. The purpose of the study was to compare monothiocarbamates to dithiocarbamates since the gross steric requirements of the ligands and the size of the chelate rings should remain essentially constant. Therefore, any observed differences between mono- and dithiocarbamate complexes should reflect the differing donor properties of oxygen and sulfur atoms. Based on magnetic studies and electronic spectral measurements McCormick and Stormer [62] suggested that the structure of $[Ni(Pr_2mtc)_2]_n$ is different from the structure of $Ni(Pr_2dtc)_2$, which is diamagnetic and planar. It also was shown that the propyl and butyl complexes dissociate readily in organic solvents to provide concentration dependent experimental molecular weights. It was concluded that the propyl and butyl complexes are hexameric and pentameric, respectively, and IR spectra were interpreted in terms of coordinated oxygen and sulfur atoms. It was proposed [62] that $[Ni(Pr_2mtc)_2]$ is a cyclic hexamer in the solid state in which oxygen is coordinated, sulfur bridges adjacent nickel centers, and the nickel atoms are approximately octahedral. The structure was confirmed by two independent X-ray studies which showed that both $Ni(Pr_2mtc)_2$ [63] and $Ni(Bu_2mtc)_2$ [64] are novel hexamers having the structure shown in Fig. 13a. The nickel(II) centers in the Ni_6 ring system form a slightly puckered configuration, somewhat analogous to the chair conformation of cyclohexane, as indicated in Fig. 13b. The NiO_2S_4 chromophores are remarkably octahedral and the Ni–Ni distances are ca. 3.4 Å. A variable temperature magnetic study of $Ni(R_2mtc)_2$ (R = Pr, Bu, Pyr, Pip) [65] has been interpreted in terms of weak ferromagnetic exchange

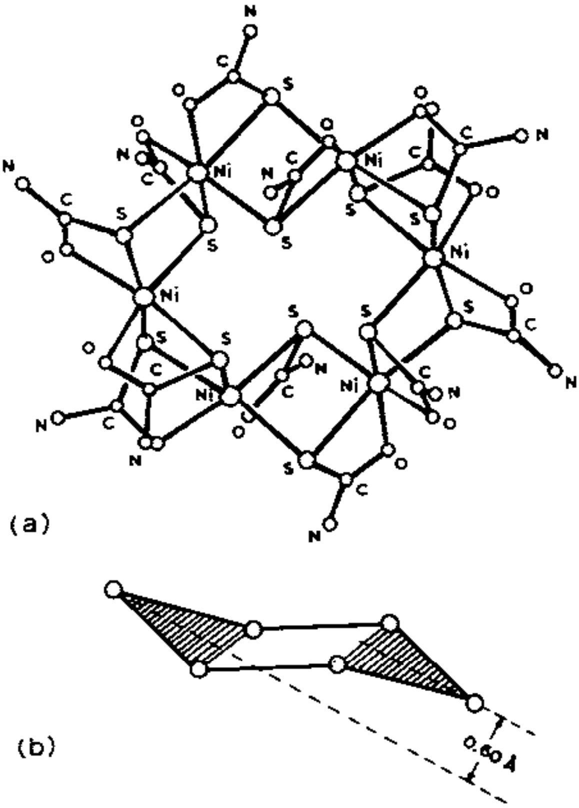


Fig. 13. (a) Structural model of hexameric $[Ni(R_2mtc)_2]_6$ complexes: R groups on N atoms not shown. (b) Arrangement of Ni atoms in the hexameric structure. (Reproduced with permission from ref. 30.)

coupling between neighboring nickel ions [65]; however, there are large differences between the room temperature magnetic moments reported in this work and those reported elsewhere [61,62]. For example, McCormick and Stormer [62] and Willemse [61] report values of 3.18 B.M. and 3.31 B.M., respectively, for $[Ni(Pr_2mtc)_2]$, while Krankovits et al. [60] report a value of 3.59 B.M. (all at room temperature). It seems clear that additional magnetic susceptibility measurements should be made on carefully purified materials in order to confirm the ferromagnetic exchange coupling.

Bright green amine adducts of the type $Ni(R_2mtc)_2(A)_2$ (A = Py, Pyr) are readily formed when the $Ni(R_2mtc)_2$ oligomers are treated with amine [60–62]. These adducts are considered to be monomeric octahedral complexes containing simple chelated monothiocarbamate ligand from which the amine can be removed quantitatively, e.g. heating the samples in vacuo regenerates the parent $Ni(R_2mtc)_2$ [62].

McCormick and Greene [66] have reported the results of solution studies of the reactions of $Ni(R_2mtc)_2$ (R = Me, Pr) with a wide variety of amines. Primary amines gave either octahedral bis or tetrakis amine adducts, the latter presumably containing monodentate monothiocarbamate ligands. Unhindered primary amines gave primarily bis adducts with small equilibrium amounts of pentacoördinate adducts of the type $Ni(R_2mtc)_2$(amine). Aromatic amines yield bis adducts with the exception of 2,6-lutidine, which provides equilibrium mixtures of $Ni(R_2mtc)_2$(amine) and (at high amine/Ni ratios) $Ni(R_2mtc)_2(\text{amine})_2$. The PMR contact shifts and A_i values were reported for the amine protons.

It was concluded that the $Ni(R_2mtc)_2$ oligomers are attacked by amines, as is the case with other similar nickel complexes such as $Ni(R_2dtc)_2$, but that the steric properties of the amine play an important role in defining the nature of the adduct.

McCormick and Stormer [67,68] have investigated the nature of $Ni(R_2mtc)_2$ (R = Pr, Bu) in benzene, since the original molecular weight determinations [62] suggest that fragmentation of the hexamers occurs even in non-coordinating solvents. These studies show that benzene solutions (ca. 10^{-3} M) contain a variety of nickel species at room temperature. One would predict that cleavage of the cyclic hexameric structure (Fig. 13a) to give a "linear" hexamer would render 2 of the 6 nickel ions five-coordinate (assuming that there is no coordination by solvent) and that any additional cleavage would increase the fraction of five-coordinate chromophores. Spectroscopic and magnetic studies confirm that this is the case, and that cleavage of the oligomer increases with increasing temperature and dilution [68].

It is clear that the cyclic hexamer is fragile and easily ruptured. Some of the small differences found among the previous reports dealing with the solid-state properties of $Ni(R_2mtc)_2$ complexes may reflect the vagaries of isolation procedures in which variable fractions of non-cyclic (and consequently, non-octahedral) fragments are precipitated along with *cyclo*-$[Ni(R_2mtc)_2]_6$.

Simple binary complexes of Pd(II) and Pt(II) with monothiocarbamates are not well known. Anions of the formula $M(R_2mtc)_4^{2-}$ (M = Pd, Pt; R = Pyr, Pip) have been isolated as quaternary ammonium salts [69,70]. These diamagnetic monomeric complexes almost certainly contain R_2mtc^- bonded to Pt or Pd through the sulfur donor only. Reaction of $[Pd(Pyrmtc)_4]^{2-}$ with triphenylphosphine yields yellow, monomeric $Pd(R_2mtc)_2(Ph_3P)_2$. A wide variety of compounds of this type can be prepared easily from $PdCl_2$, R_2mtc^- and Ph_3P [69]. The IR spectra of the phosphine adducts exhibit bands in the 1565 cm^{-1} to 1584 cm^{-1} region, the position of which is consistent with bonding of the R_2mtc ligand through sulfur only. Based on NMR spectral evidence, it was suggested that the phosphine groups are *trans*. These complexes appear to be square planar with *trans* phosphine atoms and *trans* monothiocarbamate sulfurs completing the coordination around the Pd(II) atom.

The *cis*-$(Ph_3P)M(R_2mtc)_2$ (M = Pd, Pt; R = Pyr) complexes were synthesized by McCormick and co-workers [7] from *cis*-$(Ph_3P)_2MCl_2$ and Na(Pyrmtc). Even though the physical properties of the *cis* and *trans* isomers differed somewhat, the IR spectra were virtually identical.

Three new types of Pd(II) monothiocarbamate complexes were reported in 1977 [71], some of which contained both mono- and dithiocarbamates coordinated to Pd. The compounds have the formulas: $[(Ph_2dtc)Pd(R_2mtc)_2Pd(Ph_2dtc)]$ (**I**), $Pd(R_2mtc)(R'_2dtc)(Ph_3P)$ (**II**) and $Pd(Az)(R_2mtc)$ (**III**) (R = Me, Pyr, Pip; R′ = Ph, Et, Bu). Complexes **I** and **III** were formed by reaction of the appropriate monothiocarbamate salt with the chloro-bridged dimers $(ClPdAz)_2$ or $[(ClPd(R_2dtc)]_2$.

The $Pd(Az)(R_2mtc)$ compounds are monomeric and appear to have the monothiocarbamate coordinated in a bidentate manner, as suggested by $\nu(C \overset{..}{-} N)$, which is located around 1550 cm^{-1}. A band assigned to νPd–O was assigned near 550 cm^{-1}.

The monothiocarbamates in the dimeric compound $[(Ph_2dtc)Pd(R_2mtc)_2Pd(Ph_2dtc)]$ appear to be monodentate since $\nu(C \overset{..}{-} O)$ in these compounds is located near 1650 cm^{-1}. The proposed structure is shown in Fig. 14. When this dimer is reacted with triphenylphosphine, monomeric compounds with the formula $Pd(R_2mtc)(Ph_2dtc)(Ph_3P)$ result. These complexes have monodentate monothiocarbamate ligands bonded through sulfur.

Variable temperature ^1H and ^{13}C NMR spectra were recorded for all three classes of Pd compounds. An interesting aspect of these studies is the behavior of the mixed monothiocarbamate-dithiocarbamate compound $(Ph_2dtc)Pd(Me_2mtc)_2Pd(Ph_2dtc)$. At low temperature four methyl signals were observed in the ^1H spectrum. As the temperature was increased, two of the signals decreased in intensity while the other two increased in intensity (finally resulting in two peaks of equal intensity at 50°C). As the tempera-

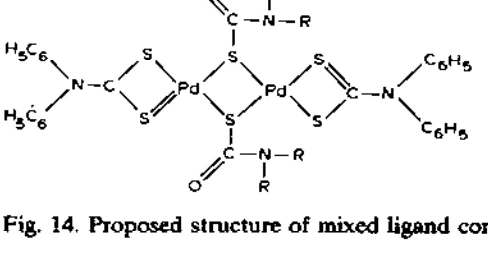


Fig. 14. Proposed structure of mixed ligand complexes $[Pd(R_2dtc)(R_2mtc)]_2$.

ture was increased further, the two remaining peaks coalesced. These observations were explained by invoking two different phenomena. The low temperature process (room temperature to 50°C) is the establishment of a dimer–monomer equilibrium

$$(Ph_2dtc)Pd(R_2mtc)_2Pd(Ph_2dtc) \rightleftarrows 2(Ph_2dtc)Pd(R_2mtc)$$

As the monomer becomes predominant (at higher temperatures), only the methyl signals of the bidentate monothiocarbamate group in the monomer can be observed in the NMR spectrum. When the temperature is raised above 50°C, rotation around the C–N bond is sufficient to cause the two methyl signals to coalesce. These conclusions were confirmed by the ^{13}C NMR measurements. Equilibrium constants and thermodynamic data for both the dimer–monomer equilibrium and the hindered rotation were obtained. The conclusion drawn is that the nature of the alkyl substituents on the monothiocarbamate ligands is more important than the bonding mode in determining the activation energies for rotation about the C–N bond.

Mixed monoselenocarbamate and monothiocarbamate complexes of Pd are discussed in section E.

(xi) Lanthanides and actinides

Monothiocarbamate complexes of lanthanide elements have not been reported.

The monothiocarbamates $M(R_2mtc)_4$ ($M = Th$, U) were among the first complexes synthesized [10] that involved this type of ligand. The authors were interested largely in the synthetic applicability of CXY (X = S, O, Se; Y = S, O, Se) insertion reactions with metal dialkyl amides and extensive characterizational work was not carried out.

More recently there has been some work on uranyl complexes of the type $[R_2NH_2][UO_2(R_2mtc)OR']$ (R = Me, Et, Pr; R′ = Me, Et) [72–74], which can be easily prepared as stable solids by treating $UO_2Cl_2 \cdot H_2O$ with R_2mtc in alcoholic solutions. The stability of these alkoxide complexes toward air

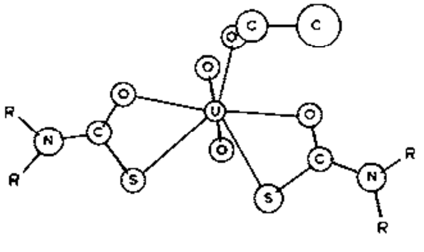


Fig. 15. Structural model of alkoxybis(*N,N*-dialkylmonothiocarbamato)dioxouranate(VI) anion.

and moisture is unusual. X-ray crystallographic studies on the complexes with R = R′ = Et [72] and R = Et, R′ = Pr [73] show that both compounds consist of a five-coordinate equatorial plane perpendicular to the O–U–O axis in which the sulfur atoms of the chelated monothiocarbamate ligands are in *cis* positions with the alkoxide oxygen occupying the fifth equatorial position (Fig. 15). These complexes represent an interesting example of three types of uranium–oxygen linkages in a single molecule. These complexes have been further characterized by extensive IR and X-ray photoelectron spectroscopy [74].

Another recent entry in the uranium monothiocarbamate series is $(\eta^5\text{-}C_5H_5)_2U(Et_2mtc)_2$, which was prepared by treating $(\eta^5\text{-}C_5H_5)_2U(NEt_2)_2$ with OCS in pentane [75]. The compound is monomeric and spectroscopic data are consistent with a bidentate coordination mode. The coordination geometry is pseudooctahedral with the $\eta^5\text{-}C_5H_5$ groups occupying *cis* positions. The complex shows dynamic solution behavior, and the observed NMR spectra can be explained by assuming that there is rapid metal-centered rearrangement coupled with slow C–N bond rotation.

(xii) Main group metals

Detailed investigations of main group metal complexes of monothiocarbamate ligands are limited largely to Tl and Sn.

The complexes $Tl(R_2mtc)$ (R = Et, Pyr) were synthesized and characterized by NMR, mass spectral and IR techniques [76]. The ethyl derivative was shown to be dimeric in chloroform solutions, but additional structural characterization has not been reported.

The trimethyltin derivative $Me_3Sn(Me_2mtc)$ was synthesized [77] by carbonyl insertion according to the reaction

$$Me_3SnNMe_2 + OCS \rightarrow Me_3SnOSCNMe_2$$

Subsequently this and related compounds were investigated [78–80] extensively by NMR techniques, primarily to determine the extent to which there is restricted rotation around the C–N bond. Representative data are given in Table 2. Structures involving four- and five-coordinate tin as well as polymeric assemblages have been proposed.

Tanaka et al. [81] have reported the synthesis of $Me_2Sn(R_2mtc)L$, where L is a monoseleno-, thioseleno-, or diselenocarbamate. Based on IR measurements it was suggested that the carbamates are bidentate.

The most complete study of tin complexes was carried out by Crosby et al. [82]. Compounds of the types $R_2Sn(R'_2mtc)_2$ and $Ph_3Sn(R'_2mtc)$ (R = alkyl, aryl; R′ = Me, Et) were synthesized and shown to be monomeric non-electrolytes. Proton NMR results indicate that the $R_2Sn(R'_2mtc)_2$ complexes contain non-linear dialkyltin(IV) moieties and that the *N*-alkylsubstituents in the R'_2mtc ligands are magnetically non-equivalent. Variable temperature proton NMR experiments were conducted on $Me_2Sn(Me_2mtc)_2$. The spectra of two isomeric species were observed with coalescence occurring at −30°C to give a single species that exhibited restricted rotation about the C–N bond. It was suggested that the $R_2Sn(R'_2mtc)_2$ compounds involve six-coordinate Sn in which the oxygen donors of the monothiocarbamate ligand are more weakly bonded than are the sulfur donors.

Infrared studies of $Ph_3Sn(R_2mtc)$ suggested a distorted trigonal bipyramidal structure with oxygen as the axial donor atom.

D. MONOTHIOCARBAMATES DERIVED FROM AROMATIC AMINES

A new class of monothiocarbamates has recently been reported by Bereman and co-workers [9,83,84]. The ligands are derived from aromatic amines that preclude the resonance form $\rangle N^+{=}C\langle\genfrac{}{}{0pt}{}{O^-}{S^-}$. Since the variability of bonding modes may be related in part to this resonance form (see section F), it was suggested that new examples of coordination chemistry were likely, as had been demonstrated for the dithiocarbamates derived from these same amines [85]. The synthesis of the ligands is different from other monothiocarbamates, as polar solvents and potassium reduction are both necessary. The two new aromatic ligands derived from pyrrole (Ptc) and indole (Iltc) seem to show parallel chemistry. Table 3 summarizes all the complexes prepared. Infrared data suggest the presence of bidentate ligands in all of the complexes except for $Ni(Ptc)_2(Ph_3P)_2$, which is thought to involve coordination through sulfur.

It is clear that new types of coordination compounds arise from these types of monothiocarbamate ligands. For example, the $Pt(Ptc)_2$ compound is the only example of a simple four coordinate monothiocarbamate of Pt(II). In addition the Ni(II) complex "$Ni(Ptc)_2 \cdot 1.5$ THF" was shown by a detailed magnetic susceptibility study to be a dimer containing one paramagnetic and one diamagnetic Ni(II) center. Two uncoordinated THF molecules are located in the crystalline lattice. It has been suggested that these new ligands parallel the chemistry of the thiobenzoate anion [86].

The crystal structure of $Ni(Ptc)_2Py_2$ shows bidentate ligands with C–N bond distances (see Table 1) that are much longer than those found in other monothiocarbamate complexes. In addition, the C–S distances (see Table 1) are shorter than is typical for other monothiocarbamate complexes. These results are consistent with the idea that the resonance form above is not important in a description of the electronic structure of this new class of ligand.

TABLE 3

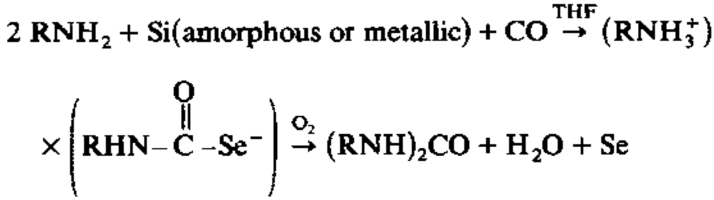
Complexes derived from aromatic amines

"$Ni(Ptc)_2 \cdot 1.5THF$"
$Pd(Ptc)_2$
$Pt(Ptc)_2$
$Cd(Ptc)_2$
$Ni(Ptc)_2(Py)_2$

$Mo_2(Ptc)_4 \cdot 2THF$
$Ni(Ptc)_2(Ph_3P)_2$
$Ni(Iltc)_2$
$Zr(Iltc)_2$
$Mo_2(Iltc)_4 \cdot 2THF$

E. MONOSELENOCARBAMATES

Monoselenocarbamates have received much less attention than have the corresponding monothiocarbamates owing to the difficulties associated with the chemistry of selenium. Sonoda and co-workers [87,88] reported the first examples of selenocarbamates as intermediates in a new synthesis of ureas, as shown below.



$$2\ RNH_2 + Si(\text{amorphous or metallic}) + CO \xrightarrow{THF} (RNH_3^+) \times \left(RHN-\overset{\overset{\displaystyle O}{\|}}{C}-Se^- \right) \xrightarrow{O_2} (RNH)_2CO + H_2O + Se$$

While no physical data were reported, the authors claim to have prepared the R = n-butyl, n-hexyl, n-octyl, cyclohexyl and benzyl intermediates, as well as compounds derived from ethylenediamine and piperidine.

The first [89] use of monoselenocarbamates as ligands was in the syntheses of Sn derivatives that were formulated as follows: $(CH_3)Sn(dmsc)_2$, $(CH_3)Sn(dmsc)_2$, $(CH_3)_2ClSn(dmsc)$, $(CH_3)_2ClSn(dmsc)$, and $(CH_3)_2Sn(dmsc)$. The ν(C=O) frequency reported for the first four compounds was 1590 cm^{-1}, which was taken to indicate that the monoselenocarbamates are coordinated in a bidentate fashion, while the value of 1620 cm^{-1} for $(CH_3)_3Sn(dmsc)$ was taken to mean that the ligand was monodentate, coordinating only through the Se donor. It was apparent that the Sn–O coordination in the entire series was weak.

Tanaka and Tanaka [90–92] also reported the first transition metal complexes of a monoselenocarbamate: $(Ph_3P)_2M(dbse)_2$ (M = Ni, Pd, Pt). Molecular weight measurements in chloroform indicated that the species dissociate in solution. The observation of free triphenylphosphine and the concentration dependence of the relative intensities of IR bands associated with the monodentate and bidentate dbsc suggest the following equilibria.

$$(Ph_3P)_2M(dbsc)_2 \overset{\text{dilution}}{\rightleftharpoons} 2\ Ph_3P + M(dbsc)_2$$

Monodentate ligand Bidentate ligand

An NMR study of the Pd and Pt complexes in a dilute solution led to the conclusion that the bidentate complexes exist in a *trans* configuration [91]. The Ni(II) complex reacts with CO to yield $(Ph_3P)_2Ni(CO)_2$ and the diselenide $[SeC(O)NEt_2]_2$. Mixed monoselenocarbamate–dithiocarbamate or monoselenocarbamate–selenothiocarbamate complexes of Pt contain only monodentate monoselenocarbamates [93].

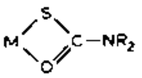
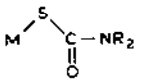
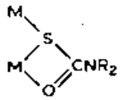
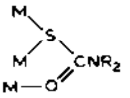
A gold complex, Ph_3PAuL and a Rh complex, $Ph_3PRh(CO)L$, (L = dmsc or desc) have been shown to contain monodentate selenocarbamate [25]. Similarly, $Mn(CO)_5L$ (L = dmsc) contains a monodentate selenocarbamate [40]. This latter complex loses CO upon heating (110°C) to yield $Mn(CO)_4L$, which contains a bidentate ligand. Under additional heating (140°C) dimerization occurs to yield $[Mn(CO)_3L]_2$ where the Se atom acts as a bridging group (a bridging bidentate ligand). The copper dimers, $(Ph_3P)_3Cu_2L_2$ (L = dmsc, desc) have also been shown [17] to contain bridging Se atoms, but in this case the oxygen atom is not coordinated (a bridging monodentate ligand). The monomeric Cu and Ag complexes; $(MePh_2P)_2ML$ (L = dmsc, desc; M = Cu, Ag) have been prepared [23]. Interestingly, the Ag complex loses a phosphine in solution suggesting that the selenium ligand then coordinates in a bidentate fashion

Even though early work in this field suggested that monoseleno- and monothiocarbamate ligands might have similar electronic structures [25], an electrochemical study of a series of iron complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(X(O)CNMe_2)$ (X = S, Se) shows clearly that the Se ligand is a better base than is the S analogue [50]. A Mo(II) complex with the same stoichiometry, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(dmsc)$, as well as a complex with 3 carbonyls, has also been shown to undergo one electron oxidation [34]. These two species apparently contain bidentate and monodentate ligand, respectively. Yet, the one electron oxidation product is the same, i.e. $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(dmsc)(CH_3CN)]^+$.

F. STRUCTURE AND INFRARED SPECTRA

The structural studies reported to date unequivocally establish that there are at least four bonding modes for monothiocarbamate ligands. These are shown below.

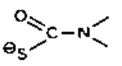
As pointed out by Rao and co-workers [94], in those cases where the monothiocarbamate ligand is bonded monodentately through sulfur the metal ions are soft acids (class b), whereas in those cases where the ligand is bidentate the metals are hard acids (class a). Thus the HSAB concept seems to offer a reliable guide to structure and bonding for this class of compounds. It should be noted, however, that the chelate bite of 2.6 Å in monothiocarbamate complexes is ca. 0.3 Å smaller than in the corresponding dithiocarbamates. The small bite may play a role in the determination of structure in some instances.

It should also be noted that in all of the reported structures the sulfur atoms of the monothiocarbamate ligands are located *cis*. This is the case for the vast majority of complexes containing sulfur in a bidentate ligand (thio-β-diketones [95], for example). The reason for maximization of S · · · S contact is not certain. Steffan and Fay [34] have presented indirect evidence from their studies of Ti(Et$_2$mtc)$_4$ and Zr(Et$_2$mtc)$_4$ that maximization of S · · · S contact cannot be attributed to weakly attractive S · · · S interactions. Numerous other factors such as *trans* effects, crystal packing forces, steric effects and even solubility probably play some role.

There was much early interest in the IR spectra of monothiocarbamate complexes, particularly as they relate to bonding mode and to the electronic structure of the ligands. In much of the reported work a characteristic strong band is mentioned in the range 1500–1600 cm^{-1}. This band has been referred to as the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band in the present review. The exact location of this band has been used by several workers as a criterion for establishing whether monothiocarbamates are bonded in a mono- or bidentate fashion [94]. The appearance of $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ above 1545 cm^{-1} has been taken to indicate that the ligand is bonded monodentately through sulfur; values below 1545 cm^{-1} are considered to be characteristic of bidentate ligands. This criterion is valid in the majority of complexes studied to this point; however, there are exceptions [51], and structural inferences based solely upon IR data must be viewed with caution.

The $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band corresponds to the well known "thioureide" band in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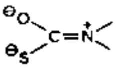
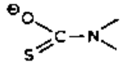

II


III

dithiocarbamates [1,2], and it reflects the importance of canonical form **II** in a valence-bond description of the electronic structure of monothiocarbamate ligands. That is, to the extent that form **II** is important in describing monothiocarbamate ligands, the C–N bond will have a bond order greater than one and the corresponding stretching frequency will be intermediate between ν(C–N) and ν(C=N).

There is ample evidence to support the postulate that canonical form **II** is of importance. Numerous NMR studies, both quantitative (Table 2) and qualitative, show that rotation around the C–N bond is restricted. This clearly is consistent with the concept of a bond order greater than one. The qualitative conclusions mentioned above regarding the nature of the band in the region 1500–1600 cm^{-1} have been confirmed by a normal coordinate analysis through which it was shown that the band arises from what can essentially be considered as a coupled [C=O + C=N] stretching mode. Again, the importance of canonical form **II** is emphasized. Finally, the results of the X-ray structural studies (Table 1) are fully consistent with the NMR and IR studies. Of primary importance is the C–N bond distance, which is found to be ca. 1.33 Å. This distance is comparable to the corresponding distance in dithiocarbamate complexes, where it is well established that there is appreciable multiple character in the C–N bond.

The relative importance of canonical forms **I** and **III** is difficult to assess. Based on electronegativity arguments one would expect **III**, with negative charge residing on oxygen, to be more important than **I**, with negative charge residing on sulfur. However the chemical properties of monothiocarbamate ligands, particularly the tendency of the sulfur moiety to bridge, suggest that the sulfur donor has considerable "mercaptide" character, consistent with form **I**.

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