Chapter - 1
CHAPTER-1

INTRODUCTION AND SCOPE OF THE PRESENT INVESTIGATION.

There has been a prodigious upsurge of knowledge in the chemistry of transition metal sulfur complexes. This is amply reflected in the increased documentation on novel complex syntheses, on the formation of interesting organometallic molecules, and in the field of bio-inorganic chemistry.

A major class of sulfur containing ligands is obtained by the general reaction of carbon disulfide with various nucleophiles. The 1,1-dithioacids are obtained by the addition of uninegative nucleophiles to carbon disulfide under a variety of experimental conditions. They are used as pharmaceutical and analytical agents, fungicides and rubber vulcanisation accelerators.\textsuperscript{1,2} Stabilisation of transition metals in high oxidation states, extensive electron transfer series and such other structural, magnetic and spectroscopic properties have served to make 1,1-dithio complexes, especially the dithiocarbamates, the focus of attention among sulphur donor ligand complexes.
1.1. 1,1-Dithio ligands

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

\[
\begin{align*}
Z^- + CS_2 & \longrightarrow Z-C- \\
Z^{2-} + CS_2 & \longrightarrow Z= C
\end{align*}
\]

(1) (II)

(where I and II are the deprotonated forms of the dithio acid and dithiol respectively)

A wide variety of ligands is thus available by merely varying the nucleophile.

1.1.1. Dithiocarbamates

When carbon disulfide reacts with either aliphatic or aromatic, primary or secondary amines, dithiocarbamate salts are formed\(^3\) according to the scheme:

\[
2R_2NH + CS_2 \longrightarrow [R_2NH_2]^+[R_2NCSS]^- 
\]

By using an alkali metal hydroxide \textit{in situ} as a proton acceptor, the alkali metal dithiocarbamate salts, having various degrees of hydration may be obtained\(^5\).

\[
R_2NH + CS_2^+ MOH \longrightarrow R_2NCSS^- M^+ + H_2O 
\]
The dithiocarbamates derived from primary amines are unstable and in the presence of bases, are converted into the isothiocyanates. Although the disubstituted dithiocarbamates are more stable, they tend to decompose under acidic conditions.

1.1.2. O-Alkylcarbonodithioates (Xanthates)

O-Alkylcarbonodithioates are formed by nucleophilic addition of an alkoxide ion to carbon disulfide.

\[ M^+RO^- + CS_2 \rightarrow RO-C=S^+ (M^+ = \text{an alkali metal ion}) \]

Acidification of the alkali metal salts produces the unstable carbonodithioic acids (xanthic acids).

1.1.3. Alkyl trithiocarbonates (thioxanthates)

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

\[ M^+RS^- + CS_2 \rightarrow RSCS_2^- M^+ \]

Air oxidises these salts to disulfides, and unstable thioxanthic acids are formed upon acidification.
11.4. Dithiocarboxylic acid

The reaction of CS\(_2\) with a Grignard reagent gives dithiocarboxylic acid\(^{11}\).

\[
\text{R-MgX + CS}_2 \rightarrow \text{R-C-S-MgX} \rightarrow \text{R-C-SH}
\]

The dithiocarboxylic acids are relatively unstable, possess unpleasant odours, and tend to be oxidised to disulfides. An interesting dithiocarboxylic acid, 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (HACDA), is formed by the reaction of cyclopentanone with carbon disulfide and ammonia followed by acidification\(^{12}\).

It is also possible to prepare 2-alkylaminocyclopent-1-ene-1-dithiocarboxylic acid by reacting HACDA with the corresponding alkyl amine\(^{13}\).

Dithiocarbamate, 1,1-ethenedithiolate, trithiocarbonate dithiophosphonate, dithiophosphate, dithioarsinate, dithioarsenate are some of the other 1,1-dithio ligands.
Metal complexes of 1,1-dithio ligands.

Our present study is on the synthesis and characterisation of some metal complexes of dithiocarbamates, xanthates, and 2-aminocyclopent-1-ene-1-dithiocarboxylate (ACDA) and its N-alkyl derivatives.

1.2. Dithiocarbamato complexes

Dithiocarbamates are strong complexing agents and give rise to a large number of interesting complexes with metal ions. The fascinating chemistry of such complexes has been repeatedly reviewed by several workers. The analytical aspects of dithiocarbamate chemistry have been reviewed by Glew and Schwaab, Ul'ko and Hulanicki, and their structural aspects have been reviewed by Eisenberg. The reviews by Coucouvanis, and Burns et al. cover the major facets of dithiocarbamato metal complexes and related systems and are particularly invaluable. Important and useful reviews such as: *Dithiocarbamates of Transition Group Elements in Unusual Oxidation States* by Willemse et al., *Reactions of Complexes of Dithiocarbamate and Related Ligands* by Steggerda et al. and *Electrochemistry and Redox Behaviour of Transition Metal Dithiocarbamates* by Bond and Martin merit special mention.
12.1. Simple dithiocarbamate complexes

A. Syntheses

Dithiocarbamato metal complexes are usually prepared by the reaction of sodium dithiocarbamates with metal halides in aqueous media. Copper(II) dithiocarbamate complexes are reported to have been prepared by the oxidation of metal with tetraalkyl thiuram disulfides in chloroform or benzene. Further, treatment of metal oxide with the sodium salts of the dithiocarbamate also results in dithiocarbamato complexes. Copper(II) dithiocarbamates are obtained by treating Cu(I) oxide with the sodium salts of the ligands in an inert atmosphere. Inert atmosphere is required in the synthesis of Mn(II), Co(II) and Fe(II) dithiocarbamate complexes also, as these complexes are easily oxidised to the corresponding metal(III) complexes in the presence of air. However, in these cases, pure M(III) complexes can be prepared by passing air through an aqueous solution containing the sodium dithiocarbamate and metal(II) salts.

Dithiocarbamato complexes of titanium cannot be prepared by the reactions of dithiocarbamate salts with simple titanium salts. Bradley and coworkers synthesised a series of tetrakis(dithiocarbamates) of Ti(IV), Zr(IV) and Hf(IV) by an insertion reaction of CS$_2$ with metal amine, M(NR$_2$)$_4$, complexes. The CS$_2$ insertion reaction has also been used to prepare morpholine-4-carbonodithioate complexes of the first row transition metal ions.
Metal dithiocarbamates are generally water insoluble. But they are soluble in non-polar solvents like benzene, chloroform and nitrobenzene. The complexes are stable in dry conditions; however, the easily oxidisable complexes like Mn(II), Co(II) and Fe(II) dithiocarbamates are stable only under inert atmospheres.

B. Physico-chemical studies

1. Infrared spectra

The interpretation of the infrared spectra of dithiocarbamate complexes of transition metals has aroused considerable interest. There are three relevant regions in the spectra of dithiocarbamate complexes. They are the 1450-1550 cm\(^{-1}\), the 950-1050 cm\(^{-1}\) and the 350-400 cm\(^{-1}\) regions.

The 1450-1550 cm\(^{-1}\) region is associated primarily with the "thioureide" band. The presence of an absorption band around 1500 cm\(^{-1}\) is accepted as arising from a polar structure such as shown that below:

\[ \text{R}_2\text{N}^+\text{C} \equiv \text{S}^- \]

The increasing electron donating character in alkyl group would stabilize this structure and increase the \( \nu(\text{C-N}) \). The thioureide band for the dimethyl derivative is always observed to occur at a higher frequency than in the diethyl derivative\(^{30}\). Some workers
have assigned the higher value of $\nu_{C-N}$ to the greater inductive effect of the methyl groups. However, bonding arguments solely based on the inductive effects are not rigorous. The higher value of $\nu_{(C-N)}$ for the methyl derivative could be due to electron release through hyperconjugation. It was also suggested that kinematic effects$^{31}$ due to increasing mass of the alkyl group may also be responsible for the change in $\nu_{(C-N)}$.

Normal coordinate analysis of $[\text{Cr}(R_2\text{dtc})_3]$ complexes have been carried out by Brown et al.$^{31}$, who observed that the $\nu_{(C-N)}$ frequency decreased with increase in the mass of the alkyl groups. The masses of the alkyl substituents also were found to affect the mixing of asymmetric N-alkyl and the symmetric C-S modes.

The region 950-1050 cm$^{-1}$ is associated with the C-S stretching frequency, and according to Ugo and Bonati$^{32}$ the presence of only one band in this region indicates completely symmetrical bidentate bonding of the ligand. Two bands in this region, arising from the uncomplexed (C=S) and the complexed (C-S) groups, indicate monodentate bonding. The Ugo-Bonati criterion has been verified by other workers$^{33-35}$. Brinkhoff and Grotens$^{35}$ have made a detailed compilation of the absorptions in the 900-1050 cm$^{-1}$ region for a number of complexes with both symmetrically bound bidentate $R_2(dtc)$ ligands and complexes with monodentate $R_2(dtc)$ ligands$^{34}$. The studies conclusively show that while two bands are observed in that region for the $M(R_2\text{dtc})_n$
complexes with symmetrically bound bidentate \( \text{R}_2\text{dtc} \) ligands, three bands are observed for complexes with asymmetrically bound monodentate ligands. It appears that the splitting of the \( \nu(\text{C-S}) \) vibration would occur also with unsymmetrical bidentate bonding. It is suggested\(^{31}\) that monodentate bonding should be assumed only if the splitting exceeds 20 cm\(^{-1}\).

The third important region is around 350-400 cm\(^{-1}\), where \( \nu(\text{M-S}) \) should occur. In the far infrared spectra of \( \text{N,\text{N}} \)-dialkyldithiocarbamate complexes, a strong band is always observed in the region 345-410 cm\(^{-1}\) which is absent in the free ligand and so this was assigned to \( \nu(\text{M-S}) \). Similar assignments were made for \( [\text{Co(\text{Me}_2\text{dtc})}_3]^{36} \) and \( [\text{Fe(\text{Et}_2\text{dtc})}_3]^{36} \). These assignments are supported by normal coordinate analyses which predicted \( \nu(\text{Pt-S}) \) at 378 cm\(^{-1}\) for \( \text{Pt(H}_2\text{dtc})_2 \)\(^{37}\) and a \( \nu(\text{Ni-S}) \) at 410 cm\(^{-1}\) for \( \text{Ni(Me}_2\text{dtc})_2 \)\(^{38}\).

2. Electronic spectra

Shankaranarayana and Patel\(^{39}\) discussed the spectra of dithiocarbamates. They observed three types of bands in these compounds which they assigned to \( n \rightarrow \pi^* \), \( \pi \rightarrow \pi^* \), and \( n \rightarrow \sigma^* \) transitions. The first of these transitions undergoes a hypsochromic shift with increasing solvent polarity, while the other two shift to lower energies as the polarity of the solvent increases. Although these assignments are similar to those done by Janssen\(^{40}\), some uncertainty exists as to the nature of the
n→σ* band which, according to Janssen could be due to another π→π* transition.

Although the electronic spectra of dithiocarboxylates have been studied by several investigators\textsuperscript{1,41-44}, uncertainties exist in the interpretation of these spectra. The uncertainty is mainly due to the π-bonding effect associated with the dithiocarbamate and other dithio ligands. An additional cause of difficulty in assigning the spectra are the low energy-high intensity charge transfer absorptions which often mask the weaker absorptions due to d-d transitions. Jorgensen\textsuperscript{45} in his study of the electronic spectra of dithio complexes, used the parameter Δ, expressing the difference between σ and π antibonding effects, certain square-planar low spin d\textsuperscript{6} complexes, to determine the relative position of the ligands in the spectrochemical series. Jorgensen\textsuperscript{46} also determined the spectrochemical position of the dithio ligands in the octahedral complexes as: Br<sup>-</sup> < Cl<sup>-</sup> < Dtp<sup>-</sup> < F<sup>-</sup> < dtc<sup>-</sup> < EtXant<sup>-</sup> < H<sub>2</sub>O < R<sub>2</sub>S<sup>-</sup> < NH<sub>3</sub> < SO<sub>3</sub><sup>2-</sup> < NO<sub>2</sub><sup>-</sup> < CN<sup>-</sup>.

In addition to the d-d and intraligand absorptions, the spectra of the dithio complexes often contain intense absorptions which are not found in the spectra of the free ligands. Such absorptions have been assigned to charge transfer transitions. Jorgensen\textsuperscript{45} assigned these bands to a L→M transition, while Gray and coworkers\textsuperscript{47} assigned similar bands in dithiocarbamate complexes to a M→L charge transfer.
3. Magnetic Measurements

The titanium dithiocarbamates are reported to be diamagnetic and are the complexes of Ti(IV), Vanadyl and Cr(III) dithiocarbamate complexes exhibit $\mu_{\text{eff.}}$ values of 1.7 to 1.8 BM and 3.8 to 3.9 BM respectively. Mn(III) dithiocarbamates, without any exceptions, exhibit the spin only value of 4.9 BM expected for four unpaired electrons.

Cambi and coworkers$^{48-51}$ prepared a large number of Fe(III) dithiocarbamate complexes and studied their magnetic properties. The unusual variation of these properties as a function of temperature, as well as a function of the substituents on the nitrogen, was attributed to an equilibrium between high and low spin magnetic states. In 1963, Brown$^{52}$ reinvestigated magnetic susceptibility of these complexes and confirmed the findings of Cambi et al. Furthermore, he studied the equilibrium between the $^2T_2$ and $^6A_1$ states and attempted to correlate the infrared and UV-visible spectra of these compounds with their magnetic properties. Martin and coworkers$^{53-54}$ have also studied this system in detail. Martin and White$^{55}$ have compiled an extensive review on spin cross-over systems.

All the Ni(II) dithiocarbamates are diamagnetic due to their square planar geometries. The magnetic susceptibilities of the Cu(R$_2$dtc)$_2$ are indicative of the presence of one unpaired electron.
4. ESR studies

A number of ESR studies on transition metal dithiocarbamato complexes has been reported. Most of the ESR studies are centered on the copper(II) complexes, as they exhibit relatively uncomplicated magnetic properties and are ideal for theoretical calculations. ESR parameters for the \( [\text{Cu}(R_2\text{dtc})_2] \) complexes in frozen solutions or in host lattices of \( [\text{Ni}(R_2\text{dtc})_2] \) or \( [\text{Zn}(R_2\text{dtc})_2] \) have been obtained for various guest/host ratios. The parameters have been used together with the electronic spectral data for the calculation of M.O. coefficients. Such parameters have been obtained for the \( [\text{Ag}(R_2\text{dtc})_2] \) and \( [\text{Au}(R_2\text{dtc})_2] \) complexes. The studies show that, in general, covalency in the M-S bonds increases strongly on going from copper to silver to gold and that the metal 3d character of the MO of the unpaired electron decreases from 50% in \( [\text{Cu}(\text{Et}_2\text{dtc})_2] \) to 26% in \( [\text{Ag}(\text{Et}_2\text{dtc})_2] \) and 15% in the homologous Au(II) complex. The bonding parameters have also been calculated for the complex, bis(pyrrole-N-carbodithioato)-copper(II), and these values indicate strong covalency in the in-plane \( \sigma \) bonding and moderate covalency in the in-plane and out-of-plane \( \pi \) bonding. The moderate out-of-plane \( \pi \) bonding is intriguing in view of the fact that the extent of ligand conjugation appears minimal for this ligand when compared to other dithiocarbamate ligands.

5. Crystal structure studies

The crystal structure of \( [\text{Ti}(\text{Et}_2\text{dtc})_4] \) has been determined. Two independent molecules exist in the asymmetric unit and both
contain an eight coordinate Ti(IV) ion and the chelating Et\textsubscript{2}dtc ligands. The coordination geometry of the TiS\textsubscript{8} core in both the molecules is very close to dodecahedral.

Deviation from octahedral symmetry in [Mn(Et\textsubscript{2}dtc)\textsubscript{3}] was confirmed by X-ray structural study which showed that the [MnS\textsubscript{6}] chromophore exhibited an appreciable distortion from D\textsubscript{3} point symmetry, which was attributed to the large Jahn Teller distortion expected for high spin d\textsuperscript{4} complexes\textsuperscript{70}. An interesting crystallographic study of the [Fe(Et\textsubscript{2}dtc)\textsubscript{3}] complex at two different temperatures, 297 and 79\textsuperscript{0}K has been reported\textsuperscript{71}. The contraction of the FeS\textsubscript{6} core of the isomer in the low spin state at 79\textsuperscript{0}K (μ\textsubscript{eff.}=2.2 BM) has been demonstrated. The hypothesis of Ewald\textsuperscript{72} et al. that the S\textsubscript{2}C=N resonance form is more important in the low spin complexes is marginally supported: In the high temperature-"high-spin" structure, the C-N is 1.337(6)Å and the C-S is 1.708(4)Å; while that in the low temperature-"low spin" structure, the corresponding distances are 1.323(4) and 1.721(2)Å. Further, it has also been reported that in the case of Fe(III) dithiocarbamates that μ\textsubscript{eff.} values are found to increase with increase of Fe-S distance\textsuperscript{72,73}.

The crystal structure study of [Cu(Me\textsubscript{2}dtc)\textsubscript{2}] revealed that the complex possesses a centre of symmetry, with the copper atom octahedrally coordinated to six sulphur atoms. The studies also revealed that the two Cu-S bonds are longer than the other four\textsuperscript{74-76}.
6. Electrochemical studies and redox behaviour

Electrochemical studies of dithiocarbamates at mercury electrodes have been conducted. Generally redox behaviour associated with a ligand is very much dependent on the nature of the electrode, the solvent and the experimental conditions used. During such studies, the mercury complexes form at the mercury electrode, which suggests that oxidation of the electrode occurs in preference to oxidation of the dithiocarbamate ligand. A comprehensive study of the electrochemistry of the first row transition metal dithiocarbamates in non-aqueous media has shown that reversible redox processes are common and that the measured potentials are dependent on both the metal and the alkyl groups in dithiocarbamate complexes. Many workers have since confirmed that ferric dithiocarbamates are readily oxidised and reduced by electrochemical methods in a range of solvents. Mn(III) dithiocarbamates undergo a relatively facile oxidation in acetone with half-wave potentials in the range +0.25 to +0.53V vs. Ag/AgCl (0.1M LiCl in acetone) reference electrode. The reduction of Mn(R₂dtc)₃ at a platinum electrode in acetone or dichloromethane is a facile, one electron process occurring at E₁/₂ values in the range +0.06 to -0.23V vs. Ag/AgCl. The electrochemical behaviour of nickel dithiocarbamates has also been studied.

The electrochemical studies reported point to the following clear observations.
1. Electrochemical data for dithiocarbamate complexes are consistent with the concept of strong \( \sigma \)-donor properties dominant over weak \( \pi \)-back donation thereby producing complexes that are relatively easy to oxidise and conversely hard to reduce.

2. Low oxidation state complexes are reactive species and are therefore not readily isolable as stable solids.

3. Electrochemical measurements have established that the oxidation and reduction potentials for dithiocarbamates of Cr(III), Mn(III), Fe(III) and Co(III) display an almost identical dependence upon the \( R_1 \) and \( R_2 \) substituents. The redox potentials of the complexes are dominated by electron density at the metal centre rather than by differences in electronic configuration of the metal ion.

1.2.2. Mixed Ligand dithiocarbamate complexes

Only few investigations have been reported on mixed ligand complexes involving dithiocarbamates. \(^{89-96}\). Masakazu Kita \textit{et al.} have prepared mixed dimethyl dithiocarbamato Co(III) complexes containing ethylenediamine (en), of the type [Co(Me\(_2\)dtc)\(_x\)(en)\(_{3-x}\)]\(^{(3-x)+}\) (\( x = 1, 2 \)), by oxidizing an aqueous solution containing Co(II) ions and en with tetramethyl thiuram disulphide. \(^{92}\) By similar oxidation reactions mixed ligand Co(III) complexes containing dithiocarbamate and phosphine ligands have also been prepared. \(^{93}\).\(^{15}\)
π-Acceptor ligands are well known for their ability to stabilize low oxidation states. Addition of π-acceptor ligands such as bipyridine to electrochemically reduced solutions of M(R_2dtc)_n complexes leads to the isolation of stable mixed dithiocarbamato complexes^{97-104}. Tsipis et al. have synthesised mixed ligand complexes of Fe(III) dithiocarbamates by reacting stoichiometric amounts of the appropriate chloro complex, [Fe(R_2dtc)_2Cl]_7, and a salt of R_2dtc in chloroform-acetone or chloroform-alcohol solutions^{105}. However, this work seems to be in contradiction with the studies reported by Pignolet et al.^{106} and Kostanski and Magas^{107}. Pignolet et al. has reported on proton NMR studies which indicated that, the ligand exchange (or metathesis) in the reaction:

\[
\text{Fe}(R_2\text{dtc})_3 + \text{Fe}(R_2'\text{dtc})_3 \rightarrow \text{Fe}(R_2\text{dtc})_2(R_2'\text{dtc}) + \text{Fe}(R_2\text{dtc})(R_2'\text{dtc})_2
\]

(where R_2dtc and R_2'dtc are two different dithiocarbamate ions)

was slower than the intramolecular isomerization. The mixed complexes formed reach equilibrium within a few minutes. Kostanski and Magas have studied the exchange reaction between [Fe(Et_2dtc)_3] and radioactive NaEt_2dtc in dioxan and dimethylformamide and they found that the reaction rate was too fast to be measured at 20°C using radio tracer techniques. These two studies indicate that tris(dithiocarbamato)iron(III) complexes
are relatively labile. Therefore the mixed ligand complexes reported by Tsipis et al. might well be only a mixture of complexes. This work was repeated by Duffy, who found that the mixed ligand complexes reported by Tsipis et al. were mixtures of varying quantities of all possible metathetical products. The results of his study also indicate that the presence of a halide ion is not necessary for ligand exchange to take place.

Synthetic procedures of some mixed ligand dithiocarbamate complexes are indicated in the Table 1.1.

TABLE 1.1 Some mixed ligand complexes of dithiocarbamates

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Synthesised by</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ([\text{Ti}(\text{R}_2\text{dtc})_3\text{X}](\text{R}=\text{Me}, \text{i-Pr} \text{ or i-Bu}; \text{X}=\text{Cl or Br}))</td>
<td>(\text{TiX}_4 \text{ with NaR}_2\text{dtc in CH}_2\text{Cl}_2)</td>
<td>109,110</td>
</tr>
<tr>
<td>2. (\text{Cr}(\text{R}_1\text{R}_2\text{dtc})_2(\text{R}_1\text{R}_2\text{dtcO})) ((\text{R}_1=\text{R}_2=\text{Me or Et}))</td>
<td>(\text{NaR}_1\text{R}_2\text{dtc with K}_2\text{Cr}_2\text{O}_7)</td>
<td>111</td>
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<tr>
<td>3. ([\text{Fe}(\text{R}_2\text{dtc})_2\text{X}]) ((\text{R}=\text{Me or Et}))</td>
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<td>112</td>
</tr>
<tr>
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<td>(\text{FeCl}_3 \text{ or FeBr}_3 \text{ with benzoic-dithiocarbamic anhydrides in acetone})</td>
<td>113</td>
</tr>
<tr>
<td>Complexes</td>
<td>Synthesised by</td>
<td>Ref.</td>
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<tr>
<td>-------------------------------------------------------------------------</td>
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<td>$[\text{Fe}($Et$_2$dtc$)_2\text{Cl}]$</td>
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<tr>
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</tr>
<tr>
<td>($\text{R}_1\text{R}_2=$Me or Et; $\text{R}_1=$Me,$\text{R}_2=$Bz; $\text{R}_1\text{R}_2=$Pyrr.; $\text{R}_1=$Me,$\text{R}_2=$Ph; $\text{R}_1\text{R}_2=$Pip)</td>
<td></td>
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<td>$[\text{Fe}($R$_1$R$<em>2$dtc$)(</em>\text{MNT}$)] ($\text{R}_1\text{R}_2=$Et; $\text{R}_1=$Me, $\text{R}_2=$Ph)</td>
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<tr>
<td>Complexes</td>
<td>Synthesised by the reaction of</td>
<td>Ref.</td>
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<tr>
<td>10. $(n\text{-Bu}_4\text{N})\text{Ni}(\text{MNT})(n\text{-Bu}_2\text{dtc})$</td>
<td>$(n\text{-Bu}_4\text{N})_2\text{Ni}(\text{MNT})_2$ with $\text{[Ni}(n\text{-Bu}_2\text{dtc})_2]$ in boiling acetonitrile</td>
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<tr>
<td>$(L=\text{Py or Pic}, R=\text{Me or Et}, R_2=\text{Pip})$</td>
<td></td>
<td></td>
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<tr>
<td>12. $[\text{Cu}(R_2\text{dtc})X]$</td>
<td>$\text{CuX}_2$ with solutions of $[\text{Cu}(R_2\text{dtc})_2]$</td>
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<tr>
<td>$(X=\text{Cl, Br or NO}_3)$</td>
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<tr>
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</table>
1.2.3 Dithiocarbamato complexes in unusual higher oxidation states

A. Syntheses.

Higher oxidation state complexes are generally 1:1 electrolytes and contain the cation, \([M(R_2dtc)_n]^+(n=3\text{ when } M=Mn(IV), Fe(IV), Co(IV) \text{ or } Ni(IV) \text{ and } n=2 \text{ when } M=Cu(III))\); and they can be isolated only when the anion is large. However, some copper(III) complexes are found to be non-electrolytes and have the general formula, \([Cu(R_2dtc)X_2]\), where \(X=Cl\) or \(Br\). The complexes are generally prepared by the oxidation of metal dithiocarbamates. A number of such complexes have been synthesised. Synthetic procedures of some of the complexes are indicated in the Table 1.2.

Table 1.2. Some dithiocarbamato metal complexes in higher oxidation states

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Synthesised by the reaction of</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ([Mn(Et_2dtc)_3]BF_4)</td>
<td>([Mn(Et_2dtc)_3]) with (BF_3)</td>
</tr>
<tr>
<td>2. ([Fe(R_2dtc)_3]BF_4)</td>
<td>([Fe(R_2dtc)_3]) with (BF_3)</td>
</tr>
<tr>
<td>3. ([Fe(Pyrrdtc)_3]ClO_4)</td>
<td>([Fe(R_2dtc)_3]) with (Fe(ClO_4)_3) (6H_2O)</td>
</tr>
<tr>
<td>4. ([Fe(Et_2dtc)_3]PF_6)</td>
<td>([Fe(Et_2dtc)_3]) with an acidic solution of (K[PF_6])</td>
</tr>
<tr>
<td>Complexes</td>
<td>Synthesised by the reaction of</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>5. $[\text{Fe}(R_1R_2\text{dtc})_2(\text{MNT})]$  (R_1=\text{Et or Ph}; R_2=\text{Et or Me})) (X=\text{CN or CF}_3)</td>
<td>$[\text{Fe}(R_1R_2\text{dtc})_2]$ with the $\text{Na}_2\text{MNT}$ followed by successive oxidation with copper(II)</td>
</tr>
<tr>
<td>6. $[\text{Co}(\text{Et}_2\text{dtc})_3]\text{BF}_4$</td>
<td>$[\text{Co}(\text{Et}_2\text{dtc})_3]$ with $\text{BF}_3$</td>
</tr>
<tr>
<td>7. $[\text{Ni}(\text{Bu}_2\text{dtc})_3]\text{Br}$</td>
<td>$[\text{Ni}(\text{Bu}_2\text{dtc})_2]$ with $\text{Br}_2$</td>
</tr>
<tr>
<td>8. $[\text{Cu}(\text{R}_2\text{dtc})_2]^+X$ (X =\text{I}_3^-, [\text{FeCl}_4]^-) or $[\text{ClO}_4^-]^-)</td>
<td>$[\text{Cu}(\text{R}_2\text{dtc})_2]$ with $\text{I}_2$, $\text{FeCl}_3$ or $\text{Fe(ClO}_4)_3\cdot6\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>9. $[\text{Cu}(\text{Bu}_2\text{dtc})X_2]$ (X=\text{Cl or Br})</td>
<td>$[\text{Cu}(\text{Bu}_2\text{dtc})_2]$ with $\text{Cl}_2$ or $\text{Br}_2$</td>
</tr>
<tr>
<td>10. $[\text{Cu}_3(\text{Bu}_2\text{dtc})_2]\text{(MBr}_3\text{)}_2$ (M=\text{Zn, Cd or Hg})</td>
<td>$[\text{Cu}($n-$\text{Bu}_2\text{dtc})_2]$ with $\text{MBr}_2$ and $\text{Br}_2$ in stoichiometric amounts</td>
</tr>
</tbody>
</table>
B. Physico-chemical studies

1. Infrared spectra

Infrared spectra of the higher oxidation state complexes are almost similar to those of the simple dithiocarbamate complexes; however, substantial shift to higher frequencies is observed for the bands due to $\nu$(C-N) and $\nu$(M-S). The C-N and M-S stretching frequencies of some of these complexes are given in the Table. 1.3

Table 1.3. The C-N and Cu-S stretching frequencies of some copper dithiocarbamate complexes in cm$^{-1}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(C-N)</th>
<th>$\nu$(Cu-S)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(Bu$_2$dtc)$_2$]</td>
<td>1500</td>
<td>352</td>
<td>1</td>
</tr>
<tr>
<td>[Cu(Bu$_2$dtc)Cl$_2$]</td>
<td>1585</td>
<td>404</td>
<td>132</td>
</tr>
<tr>
<td>[Cu(Bu$_2$dtc)Br$_2$]</td>
<td>1580</td>
<td>396</td>
<td>135</td>
</tr>
<tr>
<td>[Cu$_3$(Bu$_2$dtc)HgBr$_3$]$_2$</td>
<td>1511</td>
<td>1548</td>
<td>397</td>
</tr>
<tr>
<td>[Cu$_3$(Bu$_2$dtc)CdBr$_3$]$_2$</td>
<td>1510</td>
<td>1549</td>
<td>397</td>
</tr>
<tr>
<td>[Cu$_3$(Bu$_2$dtc)ZnBr$_3$]$_2$</td>
<td>1512</td>
<td>1548</td>
<td>398</td>
</tr>
</tbody>
</table>

It is interesting to note that two C-N and two Cu-S stretching frequencies are observed for the complex $[\text{Cu}_3(\text{Bu}_2\text{dtc})_6][\text{Cd}_2\text{Br}_6]$ and the appearance of these bands are
correlated with the presence of copper atoms in different oxidation states, +2 and +3. The increase in $\nu_{C-N}$ of the higher oxidation state complex with respect to the simple dithiocarbamato complexes is due to an additional $\pi$ electron flow from the nitrogen atom to the sulphur atoms caused by the electron withdrawing property of the metal in the higher oxidation state, and the increase in $\nu_{M-S}$ has been attributed to the removal of an electron from an antibonding molecular orbital composed mainly of metal and sulphur orbitals. However, such an explanation is plausible only if there is no significant change in the geometry of metal-sulphur core.

2. Electronic spectra

The higher oxidation state dithiocarbamate complexes exhibit high intensity charge transfer bands which usually obscure the d-d bands. Therefore, the information about stereochemistry are rarely available from the electronic spectra. However, the spectra of such complexes resemble those of the corresponding isoelectronic lower oxidation state complexes: Thus the spectra of the Cu(III), Ni(IV), Fe(IV) and Mn(IV) dithiocarbamate complexes are almost similar to those of the Ni(II), Co(III), Mn(III) and Cr(III) dithiocarbamate complexes respectively. It was generally found that the 10 Dq values of the higher oxidation state complexes are greater than those of the corresponding lower oxidation state complexes.
3. Magnetic measurements

This is considered as the best and easy technique to know the oxidation state of a metal complex. By means of this technique, the oxidation state of the metals in the complexes formed by the oxidation of metal dithiocarbamates was determined. The red \([\text{Cu} (\text{Et}_2\text{dtc})\text{Cl}_2]\) complex obtained by the oxidation of \(\text{Cu} (\text{Et}_2\text{dtc})_2\) with chlorine is found to be diamagnetic as expected for a square planar \(d^8\) complex. The complexes obtained by the oxidation of Ni(II) and Mn(III) dithiocarbamate complexes were found to have \(\mu_{\text{eff.}}\) values of 0.7 BM and 3.7 BM respectively which are in agreement with the higher oxidation state of these metals.

The tris(dithiocarbamato)iron(IV) complexes have magnetic moments of 3.2 - 3.4 BM at room temperature, which is slightly lower than those expected for a spin paired \(d^4\) electron configuration in an octahedral environment. The magnetic behaviour of \([\text{Co} (\text{cy}_2\text{dtc})_3]\text{BF}_4\) is similar to that of the isoelectronic iron(III) dithiocarbamates and has a magnetic moment of 3.48 BM which is in between the value expected for a high spin and a low spin complex.

4. Crystal structure studies

X-ray crystal structure studies have been done for many higher oxidation state complexes. Generally M-S bond is found to be shorter than that found in the normal dithiocarbamate complexes.
For example, Cu(III) complexes show a remarkable shortening of the Cu-S distances with respect to those in Cu(Et$_2$dtc)$_2$. The Cu-S distance in [Cu(Et$_2$dtc)$_2$] is 2.3Å while that in [CuBr$_2$(Bu$_2$dtc)] is 2.19Å.

The crystal structure study of an interesting mixed oxidation state complex of copper, [Cu$_3$(Bu$_2$dtc)$_6$][Cd$_2$Br$_6$], has been carried out. The evidence for the existence of copper in +2 and +3 oxidation states has been clearly obtained from the X-ray studies. The complex contains [Cu$_3$(Bu$_2$dtc)$_6$]$^{2+}$ cation (Fig.1.1.) and

![Schematic structure of the [Cu$_3$(n-Bu$_2$dtc)$_6$]$^{2+}$ trimer.](image-url)
[Cd₂Br₆]²⁻ anion. The ion [Cu₃(Bu₂dtc)₆]²⁺ is centrosymmetric containing three[Cu(Bu₂dtc)₂] units. The central[Cuᴵᴵ(Bu₂dtc)₆] is sandwiched between two[CuᴵᴵΙ(Bu₂dtc)₂] layers. The Cu(II) unit is planar, centrosymmetric, with Cu-S distances of 2.30Å and 2.35Å, which are not significantly different from those in Cu(Et₂dtc)₂.

The centrosymmetric copper atom has, apart from the four Cu-S bonds already mentioned, two longer Cu-S bonds at 2.88Å; thus reaching a pseudo-octahedral coordination, which is not unusual for a d⁹ configuration. The other two equivalent[Cu(Bu₂dtc)₂] units are in slightly deformed planes with much shorter Cu-S distances (2.22Å).


O-Alkylcarbonodithioates are more usually known as xanthates. The name xanthate is derived from the Greek word "xanthos" (meaning blond), and was coined by Zeiss in 1815, because the copper complexes that he isolated had a characteristic yellow colour. Information on the metal complexes of xanthates is available in some of the reviews on 1,1-dithio complexes. Like dithiocarbamates, xanthates also form simple type of complexes. However, xanthates are more prone to form polymeric complexes. Polymeric metal xanthates are usually the result of bridging through the bidentate xanthate moiety (ie M-S-C-S-M bridge). The tendency for polymerisation is particularly pronounced in the complexes of zinc, cadmium and mercury. In the case of haloxanthate complexes, the possibility of polymer formation through halogen bridges might be expected.
A. Syntheses

Xanthate complexes are generally prepared by reacting metal salts with potassium alkyl xanthates in aqueous media. However, in the case of the complexes of readily oxidisable metal ions like Co(II), Mn(II) and Fe(II), inert atmosphere conditions are required. Anionic complexes like $[\text{Mn(}\text{EtXant})_3]^-$ and $[\text{Fe(}\text{EtXant})_3]^-$ are formed, when KEtXant and the metal(II) salts are allowed to react in 1:3 ratio, and they can be precipitated as the Et$_4$N$^+$ salt. Many mixed ligand complexes of xanthates are also synthesised by reacting the xanthate complexes with ligands such as pyridine, picolines etc. Some of the xanthate complexes of metals synthesised are given in the Table 1.4.

B. Physico-chemical studies

1. Infrared spectra

Infrared spectra of metal xanthates have been studied by several workers. Chat et al.\textsuperscript{154,155} suggested that contribution of the resonance form (c) (Fig.1.2) to the total structure in xanthate complexes is only very little. But according to Nakamoto and coworkers\textsuperscript{156}, the contribution of this form is not so little.
Table 1.4. Some metal complexes of xanthates

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Synthesised by the reaction of</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. [VO(RXant)₃]  (\text{R} = \text{Et}, \text{i-Pr or i-Bu})</td>
<td>(\text{VOSO}_4) with KRXant</td>
<td>146</td>
</tr>
<tr>
<td>2. [VO(i-PrXant)L₂] (\text{L} = \text{Py or Pip}) (\cdot\text{5H}_2\text{O})</td>
<td>[VO(i-PrXant)₂] with the amines</td>
<td>146</td>
</tr>
<tr>
<td>3. [Cr(RXant)₃] (\text{R} = \text{He, Et or L-menthyl})</td>
<td>KRXant with CrCl₃</td>
<td>147-149</td>
</tr>
<tr>
<td>4. [Mn(EtXant)₂]</td>
<td>MnCl₂ with KExXant in aqueous medium under (\text{N}_2) atmosphere</td>
<td>144</td>
</tr>
<tr>
<td>5. [Mn(EtXant)₂bipy]</td>
<td>Mn(EtXant)₂ with bipy</td>
<td>144</td>
</tr>
<tr>
<td>6. [Fe(RXant)(Py)₂] (\text{R} = \text{Me or Et})</td>
<td>[Fe(RXant)₃] with Py</td>
<td>150</td>
</tr>
<tr>
<td>7. [Co(L)(EtXant)₂] (\text{L} = 1,10\text{ Phen or} \ 2,2'\text{-bipy})</td>
<td>(\text{M(L)(H}_2\text{O)}₄)²⁺ with KExXant</td>
<td>159</td>
</tr>
<tr>
<td>8. [CoL₂(EtXant)₂] (\text{L} = \text{Py or Pic})</td>
<td>[Co(EtXant)₂] with Py or Picolines (Pic)</td>
<td>151</td>
</tr>
<tr>
<td>9. [Ni(EtXant)₂Py₂]</td>
<td>[Ni(EtXant)₂] with Py</td>
<td>152</td>
</tr>
<tr>
<td>10. [Cu(PPh₃)(EtXant)]</td>
<td>((\text{PPh}_3)\text{Cu} (\mu-S₂\text{CSCH}_2\text{SCS}_2)\text{Cu} (\text{PPh}_3)_2) with (\text{CH}_2\text{Cl}_2/\text{ethanol})</td>
<td>153</td>
</tr>
</tbody>
</table>
The contribution of the resonance form (c) for bidentate complexes is determined by two factors: 1) the electron releasing tendency of the alkyl group and 2) the electron withdrawing tendency of M. The O-R group, unlike the -NR₂ group, is weakly electron releasing, and therefore in the xanthate complexes, the contribution of the resonance form (c) is determined by the extent to which M-S σ bonds are effective in drawing off electrons from the sulphur atoms and promoting a drift of electrons from oxygen to sulphur. Factor 2 is often much less effective, hence the relative contribution of the resonance form (c) is considerably less than that of dithiocarbamate complexes. This is further evidenced by the ability of nickel(II) xanthates to form adducts with Lewis bases. This is due to the fact that sulphur atoms of the resonance form (a) and (b) are not completely able to donate electrons into a nonbonding molecular orbital containing the 4Pz function of the metal, and as a result, this molecular orbital is available for interaction with bases. This tendency of the complexes to form base adducts decreases as the contribution of the resonance form (c) increases.
Several attempts\textsuperscript{158} have been made to assign C-O group frequencies in xanthate compounds, but the situation is complicated by the lack of agreement concerning C=S vibrational assignments; for which frequency ranging from 850-1550 cm\textsuperscript{-1} have been reported. Entirely different conclusions concerning the C=S and C-O group frequencies have appeared in the literature. For example, Little \textit{et al.}\textsuperscript{159} assigned the bands in the region 1020-1070 cm\textsuperscript{-1} to $\nu$(C=S) and the band around 1200 cm\textsuperscript{-1} to C-O stretching frequency; whereas Sankaranarayana and Patel\textsuperscript{39} have assigned the bands in the region 1200-1260 cm\textsuperscript{-1} and 1010-1037 cm\textsuperscript{-1}, to $\nu$C=S and $\nu$C-O respectively. Assignments of such group frequencies with any degree of exactness would be somewhat futile, since the C=S and C-O motions are highly coupled and sensitive to environment changes. Thus the normal C-O vibrational frequencies can be expected anywhere between 1000 cm\textsuperscript{-1} and 1250 cm\textsuperscript{-1}.

An intense band in the range 1250-1325 cm\textsuperscript{-1} in the spectra of some transition metal complexes of EtXant and MeXant has been assigned to a C-O stretching vibration. The position of this C-O band increases in the order: Cr(III) < Co(III) < Ni(II) < Pd(II) < Pt(II). The band near 1115 cm\textsuperscript{-1} is assigned to the second C-O stretching in these complexes\textsuperscript{157}.

2. Electronic spectra

Electronic spectra of xanthate complexes have been studied by a number of investigators\textsuperscript{1}. Because of the low energy-high
intensity charge transfer absorptions, weaker absorptions due to d-d transitions are often masked\textsuperscript{1}.

Nature of the spectra of the xanthate complexes is almost like that of the dithiocarbamate complexes in non-coordinating solvents. For example $[\text{Ni}(\text{EtXant})_2]$ and $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ have bands almost at the same position in chloroform\textsuperscript{42}. However, the spectra are different in coordinating solvents like DMSO, DMF, Py etc. This is because of the strong interactions of the nickel xanthate complexes with the Lewis bases\textsuperscript{160}.

A general discussion of axial interactions in nickel(II) dithiochelate complexes has been given by Coucovanis and Fackler\textsuperscript{160}. In general the nickel dithio complexes vary substantially in their ability to interact with Lewis bases. This capacity seems to be closely related to the electronic properties of the ligands as a whole rather than to the donor atoms alone. Thus xanthate, dithiophosphate and dithiophosphinate complexes interact strongly with bases. The nickel(II) dithiocarbamates exhibit intermediate behaviour that appears to vary depending on the nature of the substituent R groups in $\text{NR}_1\text{R}_2$. Ability of the dithio complexes of nickel(II) to form adducts with bases increases in the order: xanthates $\rightarrow$ dithiophosphinates $\rightarrow$ dithiophosphates $\rightarrow$ dithiocarbonates $\rightarrow$ dithiolenes\textsuperscript{161}. 
3. Magnetic measurements

Magnetic moments have been reported for a number of xanthate complexes. The copper complexes are diamagnetic, and are in the +1 oxidation state. The Ni(II) complexes also are diamagnetic and hence square planar structures have been assigned for these complexes. However, the adducts formed by the Ni(II) complexes with bases like pyridine are found to be paramagnetic, and this has been attributed to the change in stereochemistry from square planar to octahedral structure. The magnetic behaviour of the tris(xanthate) complexes of Fe(III) are different from the Fe(III) dithiocarbamates. The iron(III) xanthate complexes are of low spin type and exhibit a magnetic moment value around 2.7 BM. However, the magnetic moment values indicate that a spin-equilibrium exists with the majority of the molecules in the low spin state.

4. Crystal structure studies

The structure of a few metal xanthate complexes have been analyzed by single crystal X-ray diffraction techniques.

The crystal structure study of the \([\text{Cr}(\text{EtXant})_3]^{164}\) reveals that the metal is in a distorted octahedral environment provided by the six sulphur atoms of the bidentate ligands. The rather short \(S_2C-O\) bond of 1.297\(\text{Å}\) is thought to be an indication of considerable double-bond character of this bond. The contribution
of the resonance form (c) to the structure of the ligand is considered to be ~30% concomitant with this short bond is the unusually long bond between the oxygen atom and the first carbon atom of the ethyl group (1.471Å) The lengthening of the O-C₂H₅ bond, is also found in the structure of the {Cd(EtXant)₂-Phen}¹⁶⁵ and [Fe(EtXant)₃]¹⁶⁶,¹⁶⁷ complexes.

14. Metal complexes of ACDA

In the past 15-20 years, a number of metal complexes of chelating species containing sulphur and nitrogen donor atoms have been reported. Stimulus for this work has been due to diverging reasons: The ligand systems having soft sulphur and hard nitrogen atoms are chemically very versatile. With transition metal ions, they form a wide variety of compounds that display interesting properties and structures. In some of the complexes, both nitrogen and sulphur atoms are involved in the bond formation to the metal; while in some others, metal ions display preference for bond formation either with nitrogen or with sulphur.

An interesting ligand belonging to this group is the deprotonated form of 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (ACDA). The metal complexes of this ligand have been studied by several workers with a view to elucidate the bonding sites of this ligand. A series of complexes of the type M(ACDA)₂ (where M=Ni(II), Co(II), Pt(II), Zn(II) or Cd(II)) were synthesised and studied by Pattanaik and Sen¹⁶⁸. They have reported that bonding to
these metal ions occur through amino nitrogen and deprotonated thiol sulphur. Nag and Joardar have also studied Ni(II), Pd(II) and Pt(II) chelates of ACDA\textsuperscript{169}. In the case of these complexes also bonding was reported to occur through amino nitrogen and one of the sulphur atoms of ACDA. They could also get the evidence for the formation of the Ni(II) complex with pyridine.

Thomas and Poveda\textsuperscript{170} have also investigated ACDA complexes with divalent Co, Ni, Cu, Zn, and Cd, ions, and according to them the bonding is exclusively through the sulphur atoms. Studies by Choi and Wasson also reveal that nitrogen atom of the ligand is not involved in the bonding to the metal\textsuperscript{171}.

A. Syntheses

The metal complexes are synthesised by reacting ethanolic solution of HACDA with metal salts. The complexes are also prepared by reacting an aqueous solution of the ammonium salt of ACDA with metal salts. The complexes obtained from these two procedures showed difference in colour in the case of Ni(II), Pd(II) and Pt(II) complexes and this was attributed to geometrical isomerism\textsuperscript{169}. Synthesis of a few more metal complexes of ACDA and its derivatives have been reported in the literature\textsuperscript{170-176}.

B. Physico-chemical studies

1. Infrared data

Three or more bands in the 3400-3000 cm\textsuperscript{-1} region were observed for the ACDA complexes. The ammonium salt shows bands at
3390, 3260, and 3080 cm$^{-1}$. The band at 3080 cm$^{-1}$ has been attributed to the NH$_4^+$ ion. The bands at 3390 and 3260 cm$^{-1}$ have been assigned to asymmetric and symmetric NH$_2$ stretching frequencies. Shifts of these bands to lower frequencies were generally observed upon coordination. In the absence of other data this was taken to indicate NH$_2$ coordination. However, the electronic effects can profoundly influence N-H stretching frequencies and conjugation of the amino group with the cyclopentene ring could lead to a similar result$^{171}$ (Fig.1.3). If coordination results in an increase in the C-N $\pi$-bond order and a concomitant decrease in the $\pi$-electron density on the nitrogen atom, the shift of the N-H stretching frequencies to lower wave numbers is expected. Mason$^{177}$ has demonstrated that there is a correlation between $\nu$(NH) and $\pi$-electron densities calculated using Huckel Molecular Orbital (HMO) theory, $\nu$(NH) decreases with decreasing $\pi$-electron density.

![Fig. 1.3. Delocalization scheme for ACDA.](image-url)
Tentative assignments for the infrared spectra of ACDA complexes have been discussed by Pattnaik and Sen. The bands which appear in the region 300-400 cm$^{-1}$ on complexation has been attributed to metal-sulfur stretching frequencies.

2. Electronic spectra

$\text{NH}_4^+ \text{ACDA}$ contains two chromophore systems:

\[ \begin{array}{c}
\text{S} \\
\text{C-S} \\
\text{C=C} \\
\text{NH}_2
\end{array} \]

and exhibit two distinct absorption bands with very high intensity, one at 25570 cm$^{-1}$ which has been assigned to the $n\rightarrow\pi^*$ band of the thiocarbonyl group and another at 32700 cm$^{-1}$ has been attributed to the conjugation effect of the chromophores. Almost similar absorption spectra are exhibited by the complexes of d$^{10}$ metal ions$^{171}$. The electronic spectra of $[\text{VO(ACDA)}_2]$, $[\text{Cu(ACDA)}_2]$, and $[\text{Ni(ACDA)}_2]$ in DMSO and solid state are virtually the same indicating that structural change does not occur in DMSO solution. The electronic spectrum of the planar $[\text{Ni(ACDA)}_2]$ complex also is unaffected by changes in solvent coordinating power. The spectrum of $[\text{Ni(ACDA)}_2]$ is very similar to previously reported spectra of the nickel(II) dithiocarboxylates$^{178}$; whereas the electronic spectrum of $[\text{Cu(ACDA)}_2]$ closely resembles those reported for copper(II) dithiocarbamates and copper(II) cyclopentadienedithiocarboxylate. The spectrum is interpretable in terms of a planar $D_{2h}$ CuS$_4$ chromophore$^{171}$. 
15. Scope of the present investigation

The metal complexes of dithiochelates, especially dithiocarbamates, have a wide range of applications: Their analytical and pharmacological properties, fungicidal activity as well as their ability to function as accelerators in rubber vulcanisation processes have made them a very important class of inorganic compounds. A deeper insight into the basic chemistry of the metal-dithio complexes is indispensable for a proper understanding of the processes involved. It was therefore considered worthwhile to synthesise some new metal complexes of dithio ligands and study their physicochemical properties.

The work presented in this thesis is mainly concerned with the metal complexes isolated from the interactions of benzoic-dithiocarbamic anhydrides with metal halides. In an earlier investigation\textsuperscript{125}, bis(dithiocarbamato)-$\mu$-dichlorodiconcopper(II) complexes were synthesised by the reaction of mixed benzoic-dithiocarbamic anhydrides with copper(II) chloride. It was felt that these type of complexes could serve as the starting material for the synthesis of new and novel mixed ligand complexes of dithiocarbamates. The ligand selected for interaction was ACDA. It is an interesting ligand having dual possibility of bonding between the metal atom and the ligand. Although the complexes of ACDA have been reported earlier, the contradictory reports\textsuperscript{168-171} on the nature of bonding in these complexes
warranted a further investigation on these complexes and hence a study on these type of complexes was undertaken. As the solubilities of the ACDA complexes in common organic solvents are very low, we have used the N-isopropyl derivative of this ligand. The complexes of this derivative of ACDA have not been investigated earlier. The observed higher solubilities of these complexes as compared to that of ACDA complexes have enabled us to study the solution electronic spectra and also the NMR spectra of the complexes (These studies are described in Chapter III and the studies on the mixed ligand complexes are described in Chapter IV).

Another interesting reaction that has been probed into is that between mixed benzoic-xanthic anhydrides and the copper(II) chloride. The complexes isolated from these reactions are of the type $[\text{Cu}_2(\text{RXant})\text{Cl}]$. (Studies on these complexes are presented in Chapter V). Besides we have explored the interactions of mixed benzoic-dithiocarbamic anhydrides with $\text{HgX}_2$ and have isolated the complexes of the type $[\text{Hg}(\text{R}_2\text{dtc})\text{X}]$. Analytical and spectral studies, in these cases, revealed that the structure of these complexes are similar to that of the complex reported by Chie Chung$^{179}$, which was obtained by reacting thiuram disulphides with $\text{HgI}_2$ (These studies are described in Chapter VI).

Yet another interesting aspect of our investigations has been the interaction of mixed benzoic-dithiocarbamic anhydrides with
CuBr$_2$ in different solvents. Reaction with acetone gave complexes with no definite stoichiometry. However, we have isolated interesting complexes of the type [Cu$_3$(R$_2$dtc)$_6$]Cu$_2$Br$_6$ from the reactions in diethyl ether. Our studies revealed that they have structures similar to the complex, [Cu$_3$(Bu$_2$dtc)$_6$]Cd$_2$Br$_6$], which was prepared by Golding et al.$^{126}$ by the reaction of CdBr$_2$ and Br$_2$ with [Cu(Bu$_2$dtc)$_2$] (These studies are presented in Chapter VII). Further we have also probed the interactions of Cu(R$_2$dtc)$_2$ with SOCl$_2$ in benzene, with a view to synthesising the thionyl chloride adducts; but this resulted in the formation of copper(III) dithiocarbamate complexes (This work is presented in Chapter VIII).