STUDIES ON SOME METAL COMPLEXES OF DITHIO LIGANDS

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By

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NOVEMBER 1990

DEDICATED

TO MY

BELOVED FATHER

DECLARATION

Certified that the work presented in this thesis is based on the original work done by me under the guidance of Dr. K. K. Mohammed Yusuff, Reader, Department of Applied Chemistry, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for the award of any degree.

Mathew

Cochin 682022
November 28, 1990

E. J. Mathew

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of research work carried out by the author under my supervision in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

Dr. K. K. MOHAMMED YUSUFF
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PREFACE

The thesis deals with our studies on the synthesis and elucidation of structure of some metal complexes of dithio ligands, such as the dithiocarbamates, xanthates and 2-aminocyclopent-1-ene-1-dithiocarboxylate and its N-alkyl derivatives.

The thesis is divided into eight chapters. The Chapter I is a general discussion on the metal complexes of 1,1-dithio chelate complexes, that are relevant to the study and the scope of the present investigation. The experimental techniques, reagents, procedural details, instrumental methods etc. employed for the synthesis and characterisation of the complexes are described in Chapter II.

2-Aminocyclopent-1-ene-1-dithiocarboxylate (ACDA) is an interesting ligand, because of its potential dual capability of bonding between the metal and the ligand. Since the earlier reports on the complexes of ACDA contain contradictory ideas on the nature of its bonding, it was thought worthwhile to undertake a detailed and systematic study of these type of complexes. As the ACDA complexes have very low solubilities in solvents like chloroform, we have used the isopropyl derivative of ACDA as the ligand. The increased solubility of these complexes has made it possible to investigate their NMR and solution electronic spectra.

The complexes of this ligand have not yet been reported in the literature, and the studies on these complexes are described in Chapter III.

We have synthesised some new mixed ligand complexes of dithiocarbamates by reacting bis(dithiocarbamato)-μ-dichloro dicopper complexes (obtained by the reaction of mixed benzoic dithiocarbamic anhydride and copper(II) chloride) with ACDA or its N-alkyl derivatives. The isolation and characterisation of these complexes are reported in Chapter IV.

Interactions of metal halides with the mixed anhydrides formed from benzoylchloride and xanthates have also been investigated. Novel complexes of the type, $[Cu_2(RXant)Cl]$ (R=i-Bu, i-Pr, n-Bu or n-Pr)) have been isolated from the reaction of copper(II) chloride and the mixed anhydride, and these reactions appear to be like the clock reactions reported in the literature. The synthesis and structural elucidation of these complexes are presented in Chapter V.

Chapters VI, VII and VIII deal with the characterisation of the complexes of the type $[Hg(R_2dtc)X]$ (X=Cl, Br or I), $[Cu_3(R_2dtc)_6][Cu_2Br_6]$ and $[Cu(R_2dtc)Cl_2]$ (R_2=Me_2, Et_2, Pip, Morph or Pyrr) respectively, synthesised by simple and novel routes, different from those reported earlier.

The work described in this thesis has been published/ is under publication as indicated below:

1. "Reaction of mixed benzoic-dithiocarbamic anhydrides with mercury(II) halides", K. K. M. Yusuff and E. J. Mathew, Synth. React. Inorg. Met. -org. Chem., 19(1), 15-22 (1989).

2. "Reaction of mixed benzoic-carbonodithioic anhydrides with copper(II) chloride", E. J. Mathew and K. K. M. Yusuff, Abstracts, Paper No: 57, 77th Indian Science Congress, Cochin, 1990.
3. "Reactions of mixed benzoic-dithiocarbamic anhydrides with copper(II) bromide" (Communicated).
4. "Synthesis of new mixed ligand complexes of copper(II) dithiocarbamates" (Communicated).
5. "2-Isopropylaminocyclopent-1-ene-1-dithiocarboxylato complexes of chromium(III), manganese(III), iron(III), cobalt(III), nickel(II) and copper(I)" (Communicated).

ABBREVIATIONS

Å	Angstrom
BM	Bohr Magneton
IR	Infrared
NMR	Nuclear magnetic resonance
ESR	Electron spin resonance
χ	Magnetic susceptibility
ε	Molar extinction coefficient
ν	Stretching
δ	Deformation
ρ	Wagging
s	Symmetric
as	Asymmetric
en	Ethylenediamine
Phen	1,10-phenanthroline
Py	Pyridine
bipy	Bipyridine
Cy	Cyclohexyl
Pip	Piperidine
Morph	Morpholine
Pyrr	Pyrrolidine
R_2dtc	Dialkyl and diaryl dithiocarbamate anion
Pipdtc	Piperidine N-carbodithioate anion
Morphdtc	Morpholine-N-carbodithioate anion

Pyrrdtc	Pyrrolidine-N-carbodithioate anion
R_4tds	Tetraalkyl thiuram disulphide
RXant	Alkylxanthate anion
Me	Methyl
Et	Ethyl
i-Pr	Isopropyl
i-Bu	Isobutyl
n-Pr	n-Propyl
n-Bu	n-Butyl
sec-Bu	sec-Butyl
ACDA	2-Aminocyclopent-1-ene-1-dithiocarboxylate anion
i-PrACDA	2-N-isopropylaminocyclopent-1-ene-1-dithiocarboxylate anion
n-BuACDA	2-N-isobutylaminocyclopent-1-ene-1-dithiocarboxylate anion
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
salen	Bis-(salicylaldehyde)ethylenediimine
THF	Tetrahydrofuran
MNT	Maleonitriledithiolate
Cp	Cyclopentadienyl anion

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Chapter - 1

CHAPTER-1

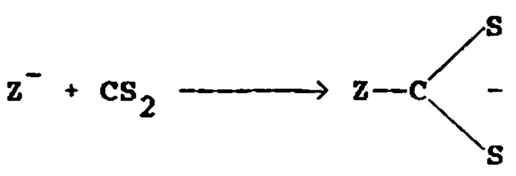
INTRODUCTION AND SCOPE OF THE PRESENT INVESTIGATION.

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[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.



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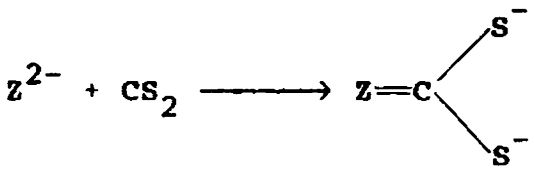


(II)

(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[3,4] according to the scheme:

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

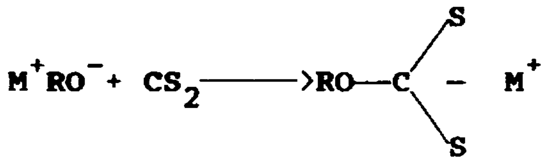
By using an alkali metal hydroxide *in situ* as a proton acceptor, the alkali metal dithiocarbamte salts, having various degrees of hydration may be obtained[5].

$$R_2NH + CS_2 + MOH \longrightarrow R_2NCSS^-M^+ + H_2O$$

The dithiocarbamates derived from primary amines are unstable and in the presence of bases, are converted into the isothiocyanates[6]. Although the disubstituted dithiocarbamates are more stable, they tend to decompose under acidic conditions[7].

1.1.2. O-Alkylcarbonodithioates (Xanthates)

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



(M^+ = an alkali metal ion)

Acidification of the alkali metal salts produces the unstable carbonodithioic acids(Xanthic acids)[8].

1.1.3. Alkyltrithiocarbonates (thioxanthates)

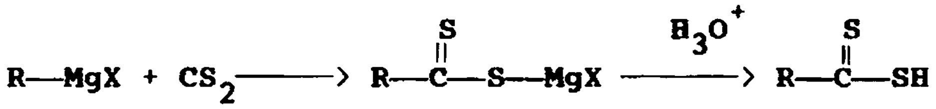
The alkali metal salts of the thioxanthates are formed by a method analogous to that used for the xanthates. Alkali metal mercaptides react with carbon disulfide to form thioxanthate salts[9].

$$M^+RS^- + CS_2 \longrightarrow RSCS_2^-\ M^+$$

Air oxidises these salts to disulfides[10], and unstable thioxanthic acids are formed upon acidification.

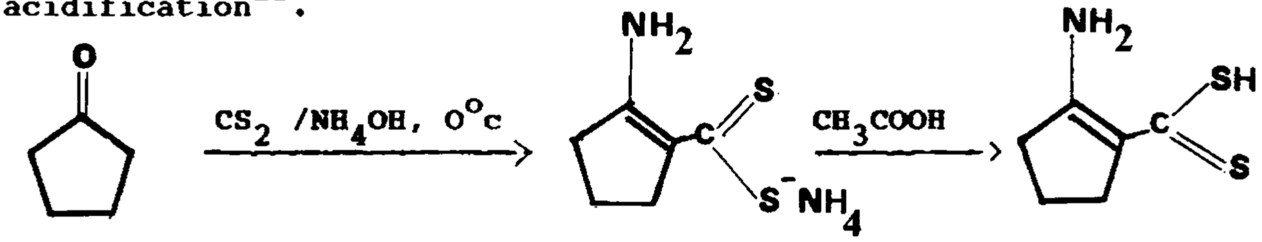
1.1.4. Dithiocarboxylic acid

The reaction of CS_2 with a Grignard reagent gives dithiocarboxylic acid[11].



$$R{-}MgX + CS_2 \longrightarrow R{-}\overset{\overset{S}{\|}}{C}{-}S{-}MgX \xrightarrow{H_3O^+} R{-}\overset{\overset{S}{\|}}{C}{-}SH$$

The dithiocarboxylic acids are relatively unstable, possess unpleasant odours, and tend to be oxidised to disulfides. An interesting dithioic 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].

Dithiocarbimate, 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,[14] Ul'ko[15] and Hulanicki[16], and their structural aspects have been reviewed by Eisenberg[17]. The reviews by Coucouvanis[18], and Burns *et al.*[19] 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.*[20], *Reactions of Complexes of Dithiocarbamate and Related Ligands* by Steggerda *et al.*[21] and *Electrochemistry and Redox Behaviour of Transition Metal Dithiocarbamates* by Bond and Martin[22] merit special mention.

1.2.1. 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[23]. 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[24]. 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 coresponding metal(III) complexes in the presence of air[25]. 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[26-28] 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[29].

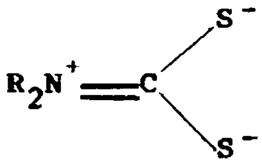
Metal dithiocarbamates are generally water insoluble. But they are soluble in non-polar solvents like benzene, chloroform and nitrobenzene. The complexes are stable in dry conditions; however, the easily oxidisable complexes like Mn(II), Co(II) and Fe(II) dithiocarbamates are stable only under inert 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:



The increasing electron donating character in alkyl group would stabilize this structure and increase the ν(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 νC-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 ν(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 ν(C-N).

Normal coordinate analysis of $[Cr(R_2dtc)_3]$ complexes have been carried out by Brown *et al.*[31], who observed that the ν(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 $M(R_2dtc)_n$

complexes with symmetrically bound bidentate R_2dtc ligands, three bands are observed for complexes with asymmetrically bound monodentate ligands. It appears that the splitting of the ν(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 ν(M-S) should occur. In the far infrared spectra of N,N-dialkyldithiocarbamate complexes, a strong band is always observed in the region 345-410cm^{-1} which is absent in the free ligand and so this was assigned to ν(M-S). Similar assignments were made for $[Co(Me_2dtc)_3]$[36] and $[Fe(Et_2dtc)_3]$[36]. These assignments are supported by normal coordinate analyses which predicted ν(Pt-S) at 378 cm^{-1} for $Pt(H_2dtc)_2$[37] and a ν(Ni-S) at 410 cm^{-1} for $Ni(Me_2dtc)_2$[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 uncertainity exists as to the nature of the

$n \rightarrow \sigma^*$ band which, according to Janssen could be due to another $\pi \rightarrow \pi^*$ transition.

Although the electronic spectra of dithiocomplexes have been studied by several investigators[1,41-44], uncertainities exist in the interpretation of these spectra. The uncertainity 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[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^8 complexes, to determine the relative position of the ligands in the spectrochemical series. Jorgensen[46] also determined the spectrochemical position of the dithio ligands in the octahedral complexes as: $Br^- < Cl^- < Dtp^- < F^- < dtc^- < EtXant^- < H_2O < R_2S^- < NH_3 < SO_3^{2-} < NO_2^- < CN^-$.

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[45] assigned these bands to a L—>M transition, while Gray and coworkers[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 $\mu_{eff.}$ 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 $Cu(R_2dtc)_2$ 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[18,56-64]. 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 $[Cu(R_2dtc)_2]$ complexes in frozen solutions or in host lattices of $[Ni(R_2dtc)_2]$ or $[Zn(R_2dtc)_2]$ have been obtained for various guest/host ratios[65,66]. 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 $[Ag(R_2dtc)_2]$ and $[Au(R_2dtc)_2]$ 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 $[Cu(Et_2dtc)_2]$ to 26% in $[Ag(Et_2dtc)_2]$ 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 σ bonding and moderate covalency in the in plane and out-of-plane π bonding[58]. The moderate out-of-plane π 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 $[Ti(Et_2dtc)_4]$ has been determined[69]. Two independent molecules exist in the asymmetric unit and both contain an eight coordinate Ti(IV) ion and the chelating Et_2dtc ligands. The coordination geometry of the TiS_8 core in both the molecules is very close to dodecahedral.

Deviation from octahedral symmetry in $[Mn(Et_2dtc)_3]$ was confirmed by X-ray structural study which showed that the $[MnS_6]$ chromophore exhibited an appreciable distortion from D_3 point symmetry, which was attributed to the large Jahn Teller distortion expected for high spin d^4 complexes[70]. An interesting crystallographic study of the $[Fe(Et_2dtc)_3]$ complex at two different temperatures, 297 and 79°K has been reported[71]. The contraction of the FeS_6 core of the isomer in the low spin state at 79°K ($\mu_{eff.}$=2.2 BM) has been demonstrated. The hypothesis of Ewald[72] *et al.* that the $S_2C{=}N$ 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 $\mu_{eff.}$ values are found to increase with increase of Fe-S distance[72,73].

The crystal structure study of $[Cu(Me_2dtc)_2]$ 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[74-76] .

6. Electrochemical studies and redox behaviour

Electrochemical studies of dithiocarbamates at mercury electrodes have been conducted.[77-80] 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[81] 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[82]. 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[83]. The reduction of $Mn(R_2dtc)_3$ at a platinum electrode in acetone or dichloromethane is a facile, one electron process occuring at $E_{1/2}$ 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[84-88].

1. Electrochemical data for dithiocarbamate complexes are consistent with the concept of strong σ-donor properties dominant over weak π-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 *et al.* have prepared mixed dimethyldithiocarbamato Co(III) complexes containing ethylenediamine (en), of the type $[Co(Me_2dtc)_x(en)_{2-x}]^{(3-x)+}$ (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].

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, $[Fe(R_2dtc)_2Cl]$, 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:

$$Fe(R_2dtc)_3 + Fe(R_2'dtc)_3 \longrightarrow Fe(R_2dtc)_2(R_2'dtc) + Fe(R_2dtc)(R_2'dtc)_2$$

(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[108], who found that the mixed ligand complexes reported by Tsips *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

Complexes	**Synthesised by the reaction of**	**Ref.**
1. $[\mathrm{Ti(R_2dtc)_3X}]$ (R=Me, i-Pr or i-Bu; X=Cl or Br)	$\mathrm{TiX_4}$ with $\mathrm{NaR_2dtc}$ in $\mathrm{CH_2Cl_2}$	109,110
2. $\mathrm{Cr(R_1R_2dtc)_2(R_1R_2dtcO)}$ ($R_1=R_2$=Me or Et)	$\mathrm{NaR_1R_2dtc}$ with $\mathrm{K_2Cr_2O_7}$	111
3. $[\mathrm{Fe(R_2dtc)_2X}]$ (R=Me or Et)	Benzene solution of $[\mathrm{Fe(R_2dtc)_3}]$ with HX	112
4. $[\mathrm{Fe(R_2dtc)_2X}]$ ($X=Cl^-$ or Br^-; R=Me or Et;R=Pip, Morph or Pyrr)	$\mathrm{FeCl_3}$ or $\mathrm{FeBr_3}$ with benzoic-dithiocarbamic anhydrides in acetone	113

Complexes	Synthesised by the reaction of	Ref.
5. [Fe(Et$_2$dtc)$_2$Cl]	[Fe(Et$_2$dtc)$_3$] with CHCl$_3$ or C$_6$H$_5$Cl in the presence of UV lhght	114
6. [Fe(R$_2$dtc)$_2$NO] (R=Me or Et)	NaR$_2$dtc with FeSO$_4$.7H$_2$O and NO$^+$ in an inert atmosphere	115,116
7. [Fe(Salen)(R$_1$R$_2$dtc)] (R$_1$=R$_2$=Et,n-Bu, Pyrr or Pip)	FeCl$_3$ with Salen anion and dithiocarbamate ligands	117,118
8. [Fe(R$_1$R$_2$dtc)(TFD)] (R$_1$=R$_2$=Me or Et; R$_1$=Me,R$_2$=Bz; R$_1$R$_2$=Pyrr.; R$_1$=Me,R$_2$=Ph; R$_1$R$_2$=Pip)	[Fe(R$_2$dtc)$_2$] and TFD in THF solution	119
9. [Fe(R$_1$R$_2$dtc)(MNT)] (R$_1$=R$_2$=Et; R$_1$=Me, R$_2$=Ph)	[Fe(R$_1$R$_2$dtc)$_2$] and MNT in THF and subsequent oxidation by Cu(II) ions in acetonitrile	120

Complexes	Synthesised by the reaction of	Ref.
10. $(n\text{-}Bu_4N)Ni(MNT)(n\text{-}Bu_2dtc)$	$(n\text{-}Bu_4N)_2Ni(MNT)_2$ with $[Ni(n\text{-}Bu_2dtc)_2]$ in boiling acetonitrile	121
11. $[CuCl(R_2dtc)L]$ and $[CuCl(R'dtc)L]$ (L=Py or Pic, R=Me or Et, R_2=Pip)	$[Cu(R_2dtc)Cl]_2$ with pyridines or picolines (Pic)	122
12. $[Cu(R_2dtc)X]$ (X=Cl, Br or NO_3)	CuX_2 with solutions of $[Cu(R_2dtc)_2]$	123
13. $[Cu(Et_2dtc)Cl]_2$	$CuCl_2.2H_2O$ and $[Cu(Et_2dtc)_2]$ in a benzene-ethanol (3:1 mixture)	124
14. $[Cu(Et_2dtc)Cl]_2$	Cu(II) chloride with benzoic-dithiocarbamic anhydrides in acetone	125

1.2.3 Dithiocarbamato complexes in unusual higher oxidation states

A. Syntheses.

Higher oxidation state complexes[20] are generally 1:1 electrolytes and contain the cation, $[M(R_2dtc)_n]^+$ (n=3 when M=Mn(IV), Fe(IV), Co(IV) or Ni(IV) and n=2 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

Complexes	Synthesised by the reaction of	Ref.
1. $[Mn(Et_2dtc)_3]BF_4$	$[Mn(Et_2dtc)_3]$ with BF_3	126
2. $[Fe(R_2dtc)_3]BF_4$	$[Fe(R_2dtc)_3]$ with BF_3	127
3. $[Fe(Pyrrdtc)_3]ClO_4$	$[Fe(R_2dtc)_3]$ with $Fe(ClO_4)_3\ 6H_2O$	128
4. $[Fe(Et_2dtc)_3]PF_6$	$[Fe(Et_2dtc)_3]$ with an acidic solution of $K[PF_6]$	127

Complexes	Synthesised by the reaction of	Ref.
5. $[Fe(R_1R_2dtc)_2(MNT)]$ $(R_1$=Et or Ph; R_2=Et or Me) X=CN or CF_3)	$[Fe(R_1R_2dtc)_2]$ with the Na_2MNT followed by successive oxidation with copper(II)	129
6. $[Co(Et_2dtc)_3]BF_4$	$[Co(Et_2dtc)_3]$ with BF_3	130,131
7. $[Ni(Bu_2dtc)_3]Br$	$[Ni(Bu_2dtc)_2]$ with Br_2	132,133
8. $[Cu(R_2dtc)_2]^+X$ $(X = I_3^-, [FeCl_4]^-$ or $[ClO_4]^-)$	$[Cu(R_2dtc)_2]$ with I_2, $FeCl_3$ or $Fe(ClO_4)_3.6H_2O$	134,126
9. $[Cu(Bu_2dtc)X_2]$ (X=Cl or Br)	$[Cu(Bu_2dtc)_2]$ with Cl_2 or Br_2	132,135
10. $[Cu_3(Bu_2dtc)_6][(MBr_3)_2]$ (M=Zn,Cd or Hg)	$[Cu(n\text{-}Bu_2dtc)_2]$ with MBr_2 and Br_2 in stoichiometric amounts	136,140

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 ν(C-N) and ν(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}

Complex	ν(C-N)		ν(Cu-S)		Ref.
$[Cu(Bu_2dtc)_2]$	1500		352		1
$[Cu(Bu_2dtc)Cl_2]$		1585		404	132
$[Cu(Bu_2dtc)Br_2]$		1580		396	135
$[Cu_3(Bu_2dtc)_6][CdBr_3)_2]$	1511	1548	360	397	136
$[Cu_3(Bu_2dtc)_6][HgBr_3)_2]$	1510	1549	360	397	136
$[Cu_3(Bu_2dtc)_6][ZnBr_3)_2]$	1512	1548	362	398	136

It is interesting to note that two C-N and two Cu-S stretching frequencies are observed[136] for the complex $[Cu_3(Bu_2dtc)_6][Cd_2Br_6]$ and the appearance of these bands are correlated with the presence of copper atoms in different oxidation states, +2 and +3. The increase in νC-N of the higher oxidation state complex with respect to the simple dithiocarbamato complexes is due to an additional π 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 νM-S has been attributed to the removal of an electron from an antibonding molecular orbital composed mainly of metal and sulphur orbitals[21]. However, such an explanation is plausible only if there is no significant change in the geometry of metal-sulphur core[137].

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[126,129,132]. 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[133].

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 techniqe, the oxidation state of the metals in the complexes formed by the oxidation of metal dithiocarbamates was determined. The red [Cu(Et$_2$dtc)Cl$_2$] complex obtained by the oxidation of Cu(Et$_2$dtc)$_2$ with chlorine is found to be diamagnetic[132] 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 $\mu_{eff.}$ values of 0.7 BM[138] and 3.7 BM[139] 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[127]. The magnetic behaviour of [Co(cy$_2$dtc)$_3$]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[131].

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$(Et_2dtc)_2$. The Cu-S distance in [Cu$(Et_2dtc)_2$] is 2.3Å while that in [$CuBr_2(Bu_2dtc)$] is 2.19Å.

The crystal structure study of an interesting mixed oxidation state complex of copper, [$Cu_3(Bu_2dtc)_6$][Cd_2Br_6], has been carried out. The evidence for the existance of copper in +2 and +3 oxidation states has been clearly obtained from the X-ray studies. The complex contains [$Cu_3(Bu_2dtc)_6$]$^{2+}$ cation (Fig.1.1.) and

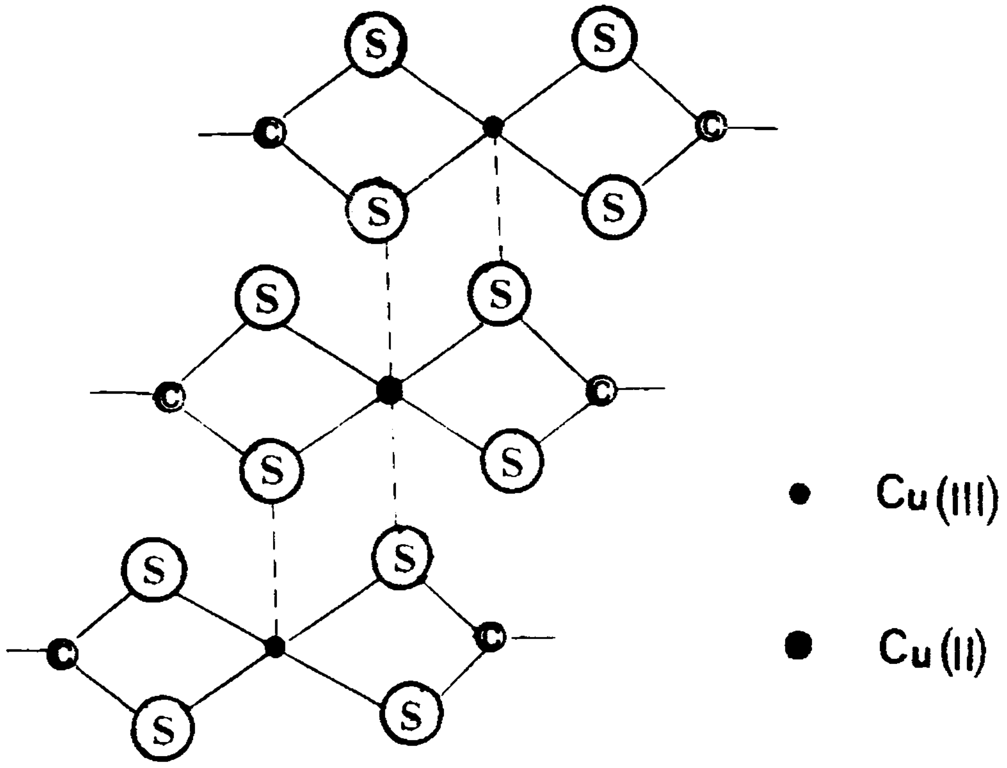


Fig. 1.1. Schematic structure of the [$Cu_3(n\text{-}Bu_2dtc)_6$]$^{2+}$ trimer.

$[Cd_2Br_6]^{2-}$ anion. The ion $[Cu_3(Bu_2dtc)_6]^{2+}$ is centrosymmetric containing three $[Cu(Bu_2dtc)_2]$ units. The central $[Cu^{II}(Bu_2dtc)_6]$ is sandwiched between two $[Cu^{III}(Bu_2dtc)_2]$ 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 $Cu(Et_2dtc)_2$. 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 d^9 configuration. The other two equivalent $[Cu(Bu_2dtc)_2]$ units are in slightly deformed planes with much shorter Cu-S distances (2.22Å).

1.3. O-Alkylcarbonodithioate (Xanthate) complexes of metals.

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[141] 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[1,18,19]. 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[142]. In the case of haloxanthate complexes, the possibility of polymer formation through halogen bridges might be expected[143].

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 $[Mn(EtXant)_3]^-$ and $[Fe(EtXant)_3]^-$ 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_4N^+ 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.

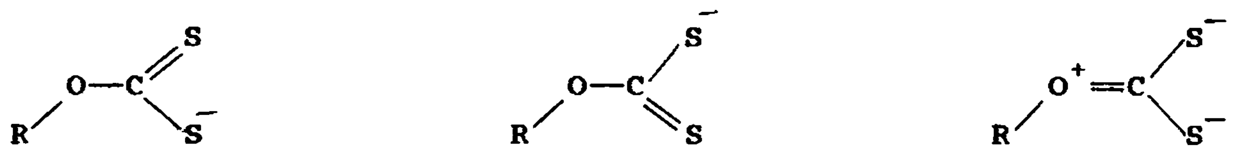
B. Physico-chemical studies

1. Infrared spectra

Infrared spectra of metal xanthates have been studied by several workers. Chat *et al.*[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[156], the contribution of this form is not so little.

Table 1.4. Some metal complexes of xanthates

Complexes	Synthesised by the reaction of	Ref.
1. $[VO(RXant)_3]$ (R=Et, i-Pr or i-Bu)	$VOSO_4$ with KRXant	146
2. $[VO(i\text{-}PrXant)L_2].5H_2O$ (L=Py or Pip)	$[VO(i\text{-}PrXant)_2]$ with the amines	146
3. $[Cr(RXant)_3]$ (R=Me, Et or L-menthyl)	KRXant with $CrCl_3$	147-149
4. $[Mn(EtXant)_2]$	$MnCl_2$ with KEtXant in aqueous medium under N_2 atmosphere	144
5. $[Mn(EtXant)_2bipy]$	$Mn(EtXant)_2$ with bipy	144
6. $[Fe(RXant)(Py)_2]$ (R=Me or Et)	$[Fe(RXant)_3]$ with Py	150
7. $[Co(L)(EtXant)_2]$ (L=1,10 Phen or 2,2'-bipy)	$[M(L)(H_2O)_4]^{2+}$ with KEtXant	159
8. $[CoL_2(EtXant)_2]$ (L=Py or Pic)	$[Co(EtXant)_2]$ with Py or Picolines (Pic)	151
9. $[Ni(EtXant)_2Py_2]$	$[Ni(EtXant)_2]$ with Py	152
10. $[Cu(PPh_3)(EtXant)]$	$(PPh_3)Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$ with CH_2Cl_2/ethanol	153



(a) (b) (c)

Fig. 1.2. Resonance forms of xanthate complexes.

The contribution of the resonance form (c) for bidentate complexes is determined by two factors[157]: 1) the electron releasing tendency of the alkyl group 2) the electron withdrawing tendency of M. The O-R group, unlike the -NR_2 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[1].

Several attempts[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^{-1} have been reported. Entirely different conclusions concerning the C=S and C-O group frequencies have appeared in the literature. For example, Little *et al.*[159] assigned the bands in the region 1020-1070 cm^{-1} to ν(C=S) and the band around 1200 cm^{-1} to C-O stretching frequency; whereas Sankaranarayana and Patel[39] have assigned the bands in the region 1200-1260 cm^{-1} and 1010-1037 cm^{-1}, to νC-S and νC-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^{-1} and 1250 cm^{-1}.

An intense band in the range 1250-1325 cm^{-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^{-1} is assigned to the second C-O stretching in these complexes[157].

2. Electronic spectra

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

Nature of the spectra of the xanthate complexes is almost like that of the dithiocarbamate complexes in non-coordinating solvents. For example $[Ni(EtXant)_2]$ and $[Ni(Et_2dtc)_2]$ have bands almost at the same position in chloroform[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[160].

A general discussion of axial interactions in nickel(II) dithiochelate complexes has been given by Coucovanis and Fackler[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 NR_1R_2. Ability of the dithio complexes of nickel(II) to form adducts with bases increases in the order: xanthates ~ dithiophosphinates ~ dithiophosphates > dithiocarbonates > dithiolenes[161].

3. Magnetic measurements

Magnetic moments have been reported for a number of xanthate complexes[144]. 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[145], 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[162] 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[163].

4. Crystal structure studies

The structure of a few metal xanthate complexes have been analyzed by single crystal X-ray diffraction techniques[18,19].

The crystal structure study of the $[Cr(EtXant)_3]$[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 1.297Å 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 $O-C_2H_5$ bond, is also found in the structure of the $[Cd(EtXant)_2-Phen]$[165] and $[Fe(EtXant)_3]$[166,167] complexes.

1.4. 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 preferance for bond formation either with nitrogen or with sulphur.

An ineresting 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 bondig 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 Pattnaik and Sen[168]. 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[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[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[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[169]. Synthesis of a few more metal complexes of ACDA and its derivatives have been reported in the literature[170-176].

B. Physico-chemical studies

1. Infrared data

Three or more bands in the 3400-3000 cm^{-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 π-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 ν(NH) and π-electron densities calculated using Huckel Molecular Orbital (HMO) theory, ν(NH) decreases with decreasing π-electron density.

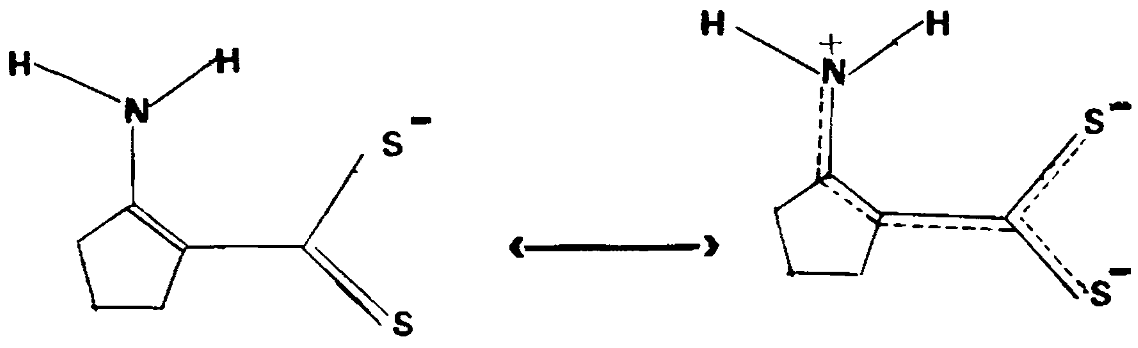
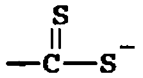


Fig. 1.3. Delocalization scheme for ACDA.

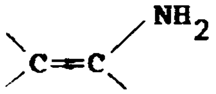
Tentative assignments for the infrared spectra of ACDA complexes have been discussed by Pattnaik and Sen. The bands which appear in the region 300-400 cm^{-1} on complexation has been attributed to metal-sulfur stretching frequencies.

2. Electronic spectra

NH_4^+ ACDA contains two chromophore systems:



$-C(=S)-S^-$



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 $[VO(ACDA)_2]$, $[Cu(ACDA)_2]$, and $[Ni(ACDA)_2]$ 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 $[Ni(ACDA)_2]$ complex also is unaffected by changes in solvent coordinating power. The spectrum of $[Ni(ACDA)_2]$ is very similar to previously reported spectra of the nickel(II) dithiocarboxylates[178]; whereas the electronic spectrum of $[Cu(ACDA)_2]$ 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].

1.5. 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[125], bis(dithiocarbamato)-μ-dichlorodi-copper(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[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 descibed 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 $[Cu_2(RXant)Cl]$. (Studies on these complexes are presented in Chapter V). Besides we have explored the interactions of mixed benzoic-dithiocarbamic anhydrides with HgX_2 and have isolated the complexes of the type $[Hg(R_2dtc)X]$. 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 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 $[Cu_3(R_2dtc)_6][Cu_2Br_6]$ from the reactions in diethyl ether. Our studies revealed that they have structures similar to the complex, $[Cu_3(Bu_2dtc)_6][Cd_2Br_6]$, which was prepared by Golding *et al.*[126] by the reaction of $CdBr_2$ and Br_2 with $[Cu(Bu_2dtc)_2]$ (These studies are presented in Chapter VII). Further we have also probed the interactions of $Cu(R_2dtc)_2$ 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).

Chapter - 2

CHAPTER II

EXPERIMENTAL TECHNIQUES

Details about the general reagents used, the procedures adopted for the preparation of the ligands and various physico-chemical techniques employed in the elucidation of structure of the complexes are given in this chapter . Procedural details regarding the synthesis of the metal complexes are given in the appropriate chapters.

2.1. Reagents

The following metal salts were used:
$CrCl_3.6H_2O$ (BDH,AR); $MnCl_2.4H_2O$ (E.Merck,AR); $FeCl_3$ (Merck, GR); $CoCl_2.6H_2O$ (E.Merck, GR); $NiCl_2.6H_2O$ (BDH,GR); $CuCl_2.2H_2O$ (BDH,GR); $CuBr_2$ (Aldrich, 99% pure); $HgCl_2$ (E.Merck, GR); $HgBr_2$ (Aldrich, 98% pure) and HgI_2 (E.Merck, GR).

Dimethylamine (40% aqueous solution), diethylamine, piperidine, pyrrolidine, morpholine, carbon disulphide, cyclopentanone, isopropanol, isobutanol, n-propanol, n-butanol, sodium hydroxide, potassium hydroxide, 25% ammonia solution , thionyl chloride, benzoylchloride and other reagents used for the present work are commercially available (BDH or E.Merck) chemicals of 99% purity. The solvents employed are either of 99% purity or purified by known laboratory procedures before use[180].

Preparation of starting materials for the synthesis of complexes.

2-Aminocyclopent-1-ene-1-dithiocarboxylic acid (HACDA)

The reagent was prepared following a modified procedure[13] of Takeshima *et al.*[12]. Cyclopentanone (22.2ml, 0.25 mole) and 25% aqueous ammonia (100ml) were taken in a stoppered conical flask. The flask was cooled to ~ 0°C by keeping it in a bath containing a freezing mixture of ice and salt. Carbon disulphide (15ml, 0.25 mole) was then added slowly with constant stirring to this cooled solution. The flask was shaken in an automatic shaker for eight hours, while keeping the same in the freezing bath. Ammmonium salt of HACDA was separated as a yellow solid, which was filtered and washed with diethylether. The ammonium salt is not stable at room temperature; it losses ammonia on standing. The acid form is more stable than its ammonium salt, and was prepared by dissolving the crude product in water and slowly neutralising with 2N acetic acid under ice-cooling. The yellow crystals separated were collected, washed with water and dried over anhydrous calcium chloride.

Alkyl derivatives of HACDA

Alkyl derivatives of HACDA were prepared by the transamination reaction[13] of HACDA. HACDA (7.9 g) and alkylamine, (9ml of i-PrNH$_2$ or 10ml of n-BuNH$_2$) were dissolved in methanol

(100 ml). This solution was refluxed for one hour. After cooling the solution to room temperature, water (200 ml) was added, and the solution was filtered to remove any solid impurities. To this filtrate, 2N acetic acid was added till the yellow product was separated. The crude product was then recrystallised from acetone.

Sodium dithiocarbamate

Sodium salts of dimethyl dithiocarbamate (Me_2dtc), diethyldithiocarbamate, (Et_2dtc), morpholine-N-carbodithioate, (Morphdtc), piperidine-N-carbodithioate (Pipdtc) and pyrrolidine-N-carbodithioate (Pyrrdtc) were prepared by the general procedure[5] given below:

A 500ml three-necked flask was equipped with a separating funnel, electric stirrer and an air condenser. An aqueous solution of sodium hydroxide (20g, 0.5mole) and 0.5mole of the amine were taken in the flask. This was cooled in a freezing mixture of ice and salt. Carbon disulphide (31 ml, 0.5mole) was added dropwise from the separating funnel and the mixture was stirred for about two hours. The solid that separated out was washed several times with petroleum ether and recrystallised from water.

Potassium carbonodithioates (xanthates)

Potassium salts of isobutylxanthate (i-Buxant), isopropylxanthate (i-PrXant), n-butylxanthate (n-BuXant) and n-propylxanthate (n-PrXant) were prepared by the general procedure[181] given below:

Potassium hydroxide pellets (11.2g, 0.2 mole) was mixed with an excess of the appropriate alcohol, R-OH (~ 0.6mole) (R=i-Bu, i-Pr, n-Bu or n-pr). The reaction mixture was refluxed for three hours in a 500ml round bottomed flask. The potassium alkoxide solution was transferred into a 500ml beaker and cooled by placing in a freezing mixture of ice and salt . Carbon disulphide (12ml, 0.2mole) was added drop by drop with stirring till the precipitation was complete. The precipitated potassium xanthate was filtered and washed with diethylether.

Mixed benzoic-dithiocarbamic anhydrides

These compounds have the general formula $Y\text{-}C(S)\text{-}S\text{-}COC_6H_5$ (where $Y=Me_2N-$, Et_2N-, C_4H_8N-, $C_5H_{10}N-$, OC_4H_8N-), were prepared by adopting the procedures of the earlier workers.[182,183] Details about the preparation are given below:

Benzoylchloride(11.6 g, 0.1 mole) was added to ice cooled aqueous solution containing 0.1mole of the appropriate sodium dithiocarbamate. An yellow oily layer was formed immediately. On vigorous shaking for a few minutes, yellow crystals of mixed benzoic-dithiocarbamic anhydride separated out. The crude product was washed a few times with distilled water and finally with methanol. It was further purified by crystallisation from a mixture of n-hexane and diethylether.

These mixed anhydrides decompose on keeping to the corresponding amides with the loss of carbon disulphide. Further these decompositions are reported to be enhanced by light.[182] Therefore, the anhydrides were prepared afresh everytime for subsequent synthetic work.

Mixed benzoic-xanthic anhydrides

The mixed benzoic-xanthic anhydrides having the general formulae $R{-}O{-}C(S){-}S{-}COC_6H_5$; were prepared by the procedure reported in the literature[184]: Potassium alkylxanthate (0.1 mole) was dissolved in water and crushed ice was added. To this was added benzoylchloride (11.6ml, 0.1mole) drop by drop with vigorous shaking. The benzoylated product was extracted into the diethylether medium and dried using anhydrous sodium sulphate. The ether solution was filtered and the anhydride was separated as a yellow liquid by the evaporation of ether in vacuum.

2.2. Elemental analysis

Estimation of metal ions

In all the cases, the organic part of the complexes were completely eliminated before estimation of metals. A uniform procedure (except for the mecury complexes) was adopted for this purpose. A known weight of the complex (0.1-0.5mg) was treated with concentrated nitric acid (25ml) and bromine in carbon tetrachloride (20ml). This mixture was kept for more than three hours. It was then evaporated to dryness on a water bath and converted to its sulphate by fuming with few drops of sulphuric acid two or three times. The resulting metal sulphate was dissolved in water, and this solution was used for the analysis of metal.

Metal analyses were carried out using standard procedures[185]. Chromium in the solution was estimated using standard ferrous ion solution, after oxidising to dichromate using potassium persulphate and a little silver nitrate (catalyst). Manganese and nickel were estimated by EDTA method using Eriochrome Black T as indicator. A back titration procedure was adopted for the estimation of nickel. Iodometric method was employed for the estimation of copper in the complex.

Gravimetric procedures were adopted for the estimation of iron and nickel. Iron in the complex was estimated by precipitating the metal with ammonia solution and igniting the resulting hydroxide to the ferric oxide. Cobalt was estimated by precipitating it as $[Co(Py)_2(SCN)_2]$ using ammonium thiocyanate and pyridine.

Halogen content was determined by peroxide fusion of the sample, followed by volumetric estimation using Volhard's method. The percentage of nitrogen present in the ligand and also in the complexes was determined by Kjeldahl's method. For sulphur estimation, the complexes were fused with Na_2CO_3 and Na_2O_2 and the resulting sulphate was determined gravimetrically as barium sulphate.

2.3. Physical measurements

Conductivity measurements

The molar conductance of the complexes in nitrobenzene was determined at 28$\pm$2^{o}C using a ELICO PR 9500 conductance bridge with a dip type cell and a platinum electrode. The concentration of the solutions used were about 10^{-3}M.

Magnetic susceptibility measurements

The measurements were carried out using solid samples at room temperature, 28$\pm$2^{o}C, on a Gouy type balance. The Gouy tube was standardised using $Hg[Co(SCN)_4]$, as recommended by Figgis and Nyholm [186]. The effective magnetic moment, was calculated using the equation,

$$\mu_{eff.} = 2.84\ (\chi_M^{corr.} T)^{1/2}\ BM$$

where $X_M^{corr.}$ is the molar magnetic susceptibility corrected for diamagnetism of other atoms in the complex using Pascals constants[187] and T is the temperature (in ^{o}K).

EPR spectral measurements

The EPR spectra of a few complexes in chloroform were obtained at room temperature using Varian E-112 X/Q band EPR spectrometer . Samples are taken in capillary tubes for the measurements. Spectra were calibrated using diphenylpicrylhydrazyl (DPPH) as a field marker.

Electronic spectral measurements

Electronic spectra were recorded in solutions (in the cases of soluble complexes) or in the solid state by a mull technique following a procedure recommended by Venanzi *et al.*[188] Mull spectra were recorded as follows. Samples were prepared in nujol and smeared over Whatman filter paper No.1. Reference filter paper was prepared by smearing a drop of nujol. The two filter paper bits were placed in the two windows of the spectrometer and the spectra were scanned in the desired region. Solution spectra were recorded using matched one cm quartz cells. The spectra were recorded on a Hitachi U-3410 spectrophotometer or on a Shimadzu UV-160A spectrophotometer.

Infrared spectral measurements.

Infrared and far infrared spectra of the complexes were recorded on Perkin Elmer 983 recording spectrometer. The spectra were recorded in the infrared region with the samples distributed in potassium bromide matrix and in the far infrared region with the samples smeared on polyethylene films.

Proton NMR spectral measurements

The proton nuclear magnetic resonance spectra of complexes, which have got sufficient solubility in chloroform, were taken in $CDCl_3$ using Hitachi R-600 FT NMR spectrophotometer. Tetramethylsilane (TMS) was employed as an internal reference.

Chapter - 3

CHAPTER III

2-ISOPROPYLAMINOCYCLOPENT-1-ENE-1-DITHIOCARBOXYLATO COMPLEXES OF CHROMIUM(III), MANGANESE(III), IRON(III), COBALT(III), NICKEL(II) AND COPPER(I)

3.1. INTRODUCTION

The sulphur-nitrogen containing ligands are biochemically important[189]. Metal complexes of sulphur containing amino acids are considered as models of metal sulphur proteins. The sulphur nitrogen chelating ligand, 2-aminocyclopent-1-ene-1-dithiocarboxylic acid shows a marked antifungal action against various fungi[190-192]. This type of ligands finds use in analytical chemistry as gravimetric reagents and cation exchangers.

The bonding sites of 2-aminocyclopent-1-ene-1-dithiocarboxylate (ACDA) ligand are the nitrogen atom of the amino group and the sulphur atoms of the dithio group. Therefore, one can expect N,S coordination or S,S coordination in these complexes. Pattnaik and Sen[168], and Nag and Joardar[169] claim that ACDA makes use of both sulphur and nitrogen donor centres for bonding to the metal. However, Thomas and Poveda[170], and Choi and Wasson[171] are of the opinion that only sulphur atoms are involved in the bonding. The difference of opinion among the earlier workers has prompted us to undertake a detailed study of these type of complexes . Due to the limited solubilities of ACDA complexes in common organic solvents, their ^1H NMR spectra and electronic spectra in solution could not be studied properly. The solubility is expected to be increased by using N-alkyl substituted derivatives of ACDA as the ligand, which can be prepared by transamination reaction of ACDA[13]. It was therefore considered worthwhile to synthesise and study some 3d-transition metal complexes of 2-isopropylaminocyclopent-1-ene-1-dithiocarboxylate (i-PrACDA) ligand. We have synthesised the chromium(III), manganese(III), cobalt(III), iron(III), nickel(II) and copper(I) complexes of i-PrACDA. The complexes of this ligand have not been reported earlier. In this chapter, the synthesis, spectral and magnetic behaviour of these complexes are described.

3.2 EXPERIMENTAL

Materials:

Details about the reagents used and the synthesis of i-PrACDA are given in Chapter II.

Synthesis:

The complexes of chromium, manganese, iron and cobalt were prepared by the general method given below:

A solution of the metal chloride (0.01mole - 2.66g of $CrCl_3.6H_2O$, 1.98g of $MnCl_2.4H_2O$, 1.62g $FeCl_3$ or 2.4g of $CoCl_2.6H_2O$) was prepared in methanol (100 ml). To this, i-PrACDA (6g, 0.03mole) dissolved in methanol (150 ml) was added. The mixture was refluxed on a water bath for one hour. It was then cooled to room temperature. The complex formed was filtered, washed with methanol and ether and dried over anhydrous calcium chloride. Yield: 60-70%

The complexes of nickel and copper were prepared in the same way using 0.01 mole of the metal chloride (2.4g of $NiCl_2.6H_2O$ or 1.7g of $CuCl_2.2H_2O$) and 0.02 moles of i-PrACDA.

Characterisation

Details about the characterisation techniques are given in Chapter II.

3.3 RESULTS AND DISCUSSION

The formation of the present complexes take place only on refluxing the solution containing i-PrACDA and the metal salt. In the case of dithiocarbamate complexes, complex formation takes place immediately on mixing the aqueous solution of sodium dithiocarbamate ligand with metal salt solution. This often results in the the formation of a mixture of complexes in +2 and +3 oxidation states in the case of easily oxidisable transition metal ions like cobalt(II) and manganese(II) ions. Therefore, in these cases pure metal(II) complexes can be prepared only by conducting the reaction in an inert atmosphere. For preparing the pure metal(III) complexes, a stream of air has to be passed through the reaction medium. However, for i-PrACDA, Mn(III) and Co(III) complexes were obtained even without passing air through the system. This might be due to the following facts:

i) The complexation takes place only under refluxing conditions.

ii) Under such conditions the interaction with oxygen in the air is possible.

Results of elemental analyses are given in Table 3.1. The analytical data show that empirical formulae agree with $[M(i\text{-}PrACDA)_3]$ for the chromium, manganese, iron and cobalt complexes, $[Ni(i\text{-}PrACDA)_2]$ for the nickel complex and [Cu(i-PrACDA)] for the copper complex.

The complexes are soluble in non-polar solvents like chloroform, benzene, nitrobenzene etc. and are much more soluble than the correspoding complexes formed by the ACDA ligand. However the [Cu(i-PrACDA)] does not have sufficient solubility to record ^1H NMR spectrum. The low solubility indicates a polymeric nature for this complex. It was also found that these complexes are quite stable and can be kept for a longer period without decomposition.

3.3.1 Electrical Conductance

The conductance data of the complexes are presented in Table 3.2. It may be seen from the table that all the complexes are non-electrolytes in nitrobenzene.

3.3.2 Magnetic measurements

The magnetic moment values of the complexes at room temperature are also given in Table 3.2.

The magnetic properties of the octahedral chromium(III) complexes are generally uncomplicated. All such complexes must

Table 3.1 Analytical data of the i-PrACDA complexes

Complex	N(%) Found (Calc.)	M(%) Found (Calc.)	S(%) Found (Calc.)
$[Cr(i\text{-}PrACDA)_3]$	6.40	8.03	29.65
$[C_{27}H_{42}CrN_3S_6]$	(6.50)	(8.04)	(29.73)
$[Mn(i\text{-}PrACDA)_3]$	6.43	8.39	29.50
$[C_{27}H_{42}MnN_3S_6]$	(6.47)	(8.45)	(29.60)
$[Fe(i\text{-}PrACDA)_3]$	6.42	8.48	29.52
$[C_{27}H_{42}FeN_3S_6]$	(6.46)	(8.58)	(29.56)
$[Co(i\text{-}PrACDA)_3]$	6.44	8.97	29.35
$[C_{27}H_{42}CoN_3S_6]$	(6.43)	(9.01)	(29.42)
$[Ni(i\text{-}PrACDA)_2]$	6.14	12.82	28.12
$[C_{18}H_{28}Ni\ N_2S_4]$	(6.15)	(12.89)	(28.16)
$[Cu(i\text{-}PrACDA)]$	5.33	24.25	24.43
$[C_9H_{14}CuNS_2]$	(5.35)	24.27)	(24.49)

Table.3.2 **Molar conductance and magnetic moment values of the i-PrACDA complexes**

Complex	Molar conductance in nitrobenzene* $ohm^{-1}cm^{2}mole^{-1}$	$\mu_{eff.}$ in BM at 28 ± 2° C
$[Cr(i\text{-}PrACDA)_3]$	2.4	3.9
$[Mn(i\text{-}PrACDA)_3]$	1.0	5.0
$[Fe(i\text{-}PrACDA)_3]$	2.1	5.1
$[Co(i\text{-}PrACDA)_3]$	1.5	Diamagnetic
$[Ni(i\text{-}PrACDA)_2]$	2.8	"
$[Cu(i\text{-}PrACDA)]$	1.6	"

* Concentration = 10^{-3} mole lit^{-1}.

have three unpaired electrons irrespective of the strength of ligand field. In the absence of any orbital contribution, the magnetic moment value should be very close to the spin-only value of 3.87 BM[187]. The $[Cr(i\text{-}PrACDA)_3]$ complex exhibits magnetic moment value of 3.9 BM which suggests an octahedral structure for the complex.

Nearly all manganese(III) complexes are octahedral and high-spin with magnetic moment values close to the spin-only value of 4.9 BM (expected for 4 unpaired electrons)[187]. The present complex of manganese exhibits a $\mu_{eff.}$ value of 5.0 BM which suggests that the complex is an octahedral high-spin manganese(III) complex.

For the high spin iron(III) complexes, the magnetic moment values are always very close to the spin only value of 5.9 BM. The low spin complexes with $t_{2g}^{5}e_{g}^{0}$ configuration usually have considerable orbital contributions to their magnetic moments at room temperature and have $\mu_{eff.}$ values of ~ 2.3 BM. The i-PrACDA complex of iron(III) exhibits a magnetic moment of 5.1 BM. This value is in between the magnetic moment valu expected for a high-spin and a low-spin iron(III) complex, and might be due to spin cross over phenomenon. This phenomenon is known to occur in the case of dithiocarbamato iron(III) complexes. Cobalt(III), nickel(II) and copper(I) complexes were found to be diamagnetic. The diamagnetic nature of the Co(III) complex indicates that the complex is a low-spin octahedral complex, while that of the Ni(II) complex reveals that the complex has a square planar structure. The magnetic behaviour of the copper complex is in agreement with the +1 oxidation state of the metal.

3.3.3 Electronic spectra

The electronic spectra of the complexes were recorded in chloroform solution. The electronic spectral bands along with their probable assignments are given in Table 3.3.

$[Cr(i\text{-}PrACDA)_3]$

With hardly any exceptions, the chromium(III) complexes are hexacoordinate and have either octahedral or distorted octahedral structures. Three spin allowed transitions: $^4A_{2g} \longrightarrow {}^4T_{2g}(F)$, $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$, and $^4A_{2g} \longrightarrow {}^4T_{1g}(P)$ are expected for these complexes. In $[Cr(i\text{-}PrACDA)_3]$, the band due to $^4A_{2g} \longrightarrow {}^4T_{1g}(P)$ was not observed; probably, this might have been masked by the high intense charge transfer bands and the band at $22500 cm^{-1}$ can be assigned to $^4A_{2g} \longrightarrow {}^4T_{2g}(F)$ transitions. The shoulder band at $25600 cm^{-1}$ might be due to the $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ transition[193].

$[Mn(i\text{-}PrACDA)_3]$

Only one spin allowed absorption band ($^5E_g \longrightarrow {}^5T_{2g}$) is expected for octahedral manganese(III) complexes. These complexes generally give rise to fairly intense crystal field bands, which probably results from combination of factors, namely a fairly covalent metal-ligand bond, low symmetry components to the ligand field and fairly low lying charge transfer bands. In the $[Mn(i\text{-}PrACDA)_3]$ complex three d-d bands are observed. This clearly

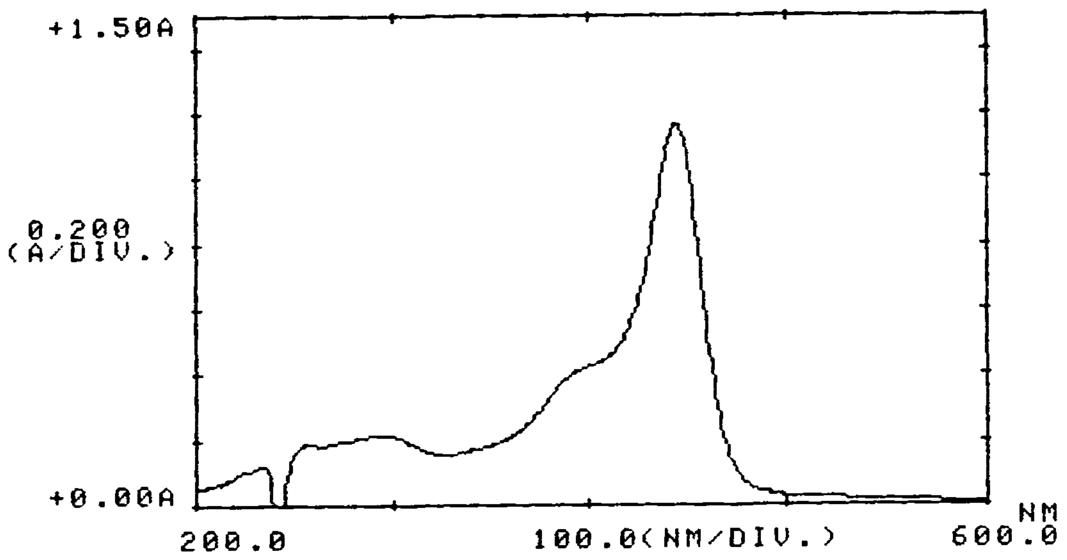


Fig. 3.1. Electronic spectra of [Cr(i-PrACDA)$_3$] in chloroform.

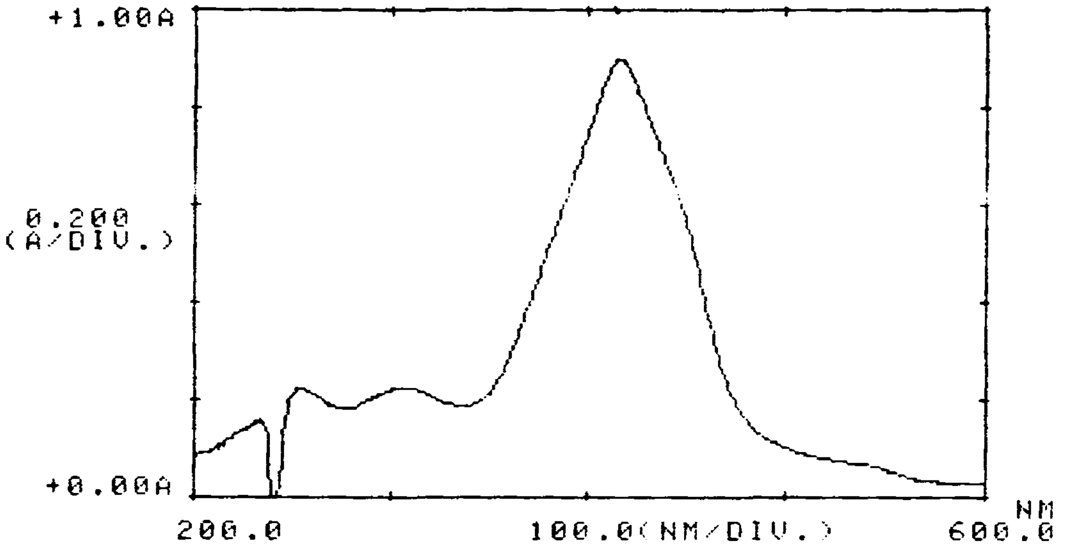


Fig. 3.2 .Electronic spectra of [Mn(i-PrACDA)$_3$] in chloroform.

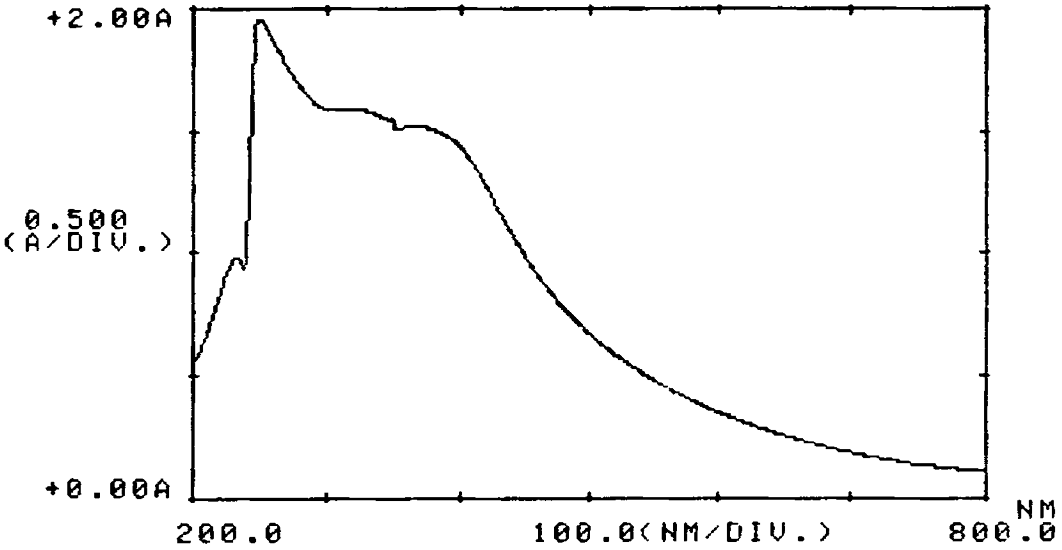


Fig. 3.3 Electronic spectra of [Fe(i-PrACDA)$_3$] in chloroform.

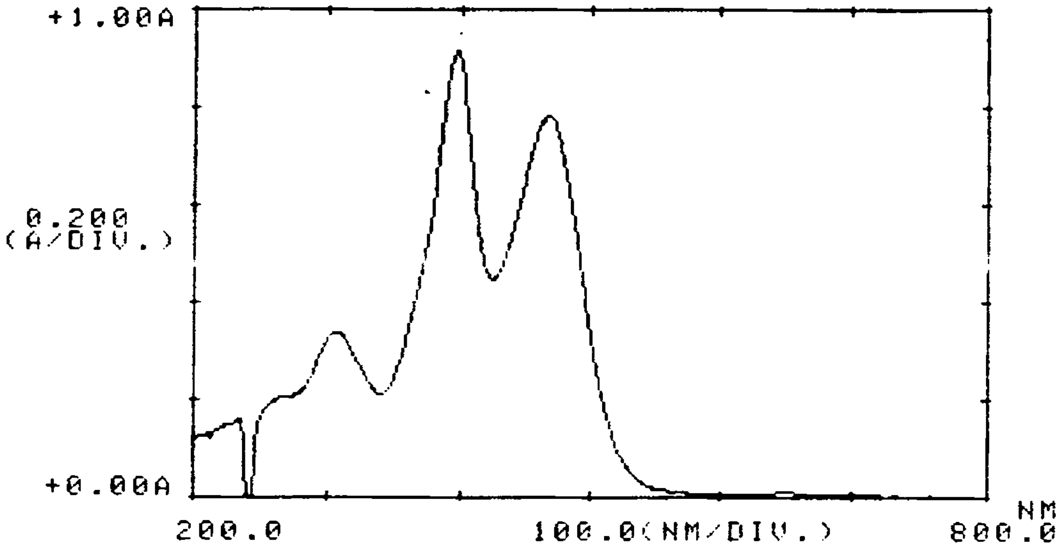


Fig. 3.4 Electronic spectra of [Co(i-PrACDA)$_3$] in chloroform.

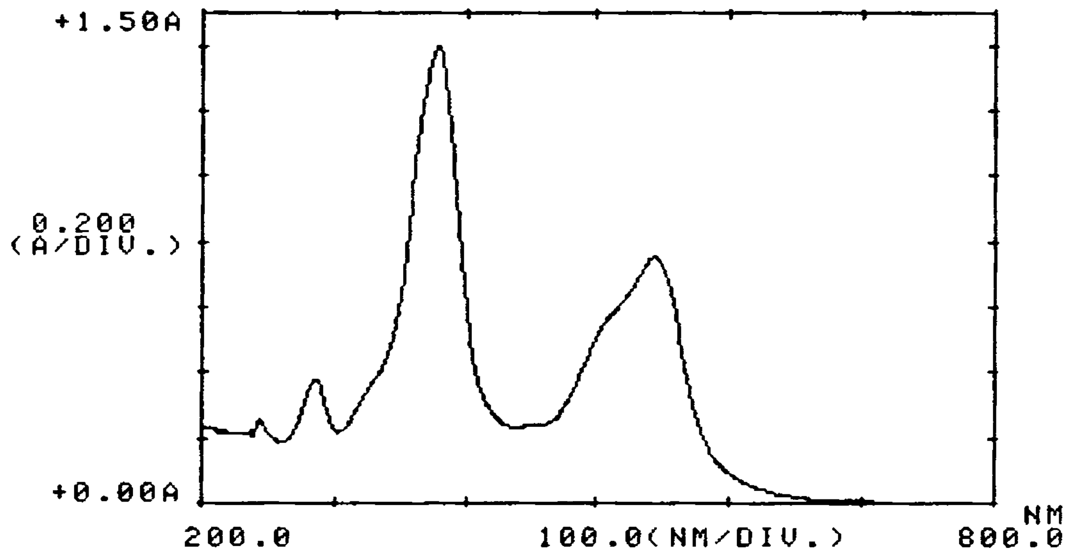


Fig. 3.5 Electronic spectra of [Ni(i-PrACDA)$_2$] in chloroform.

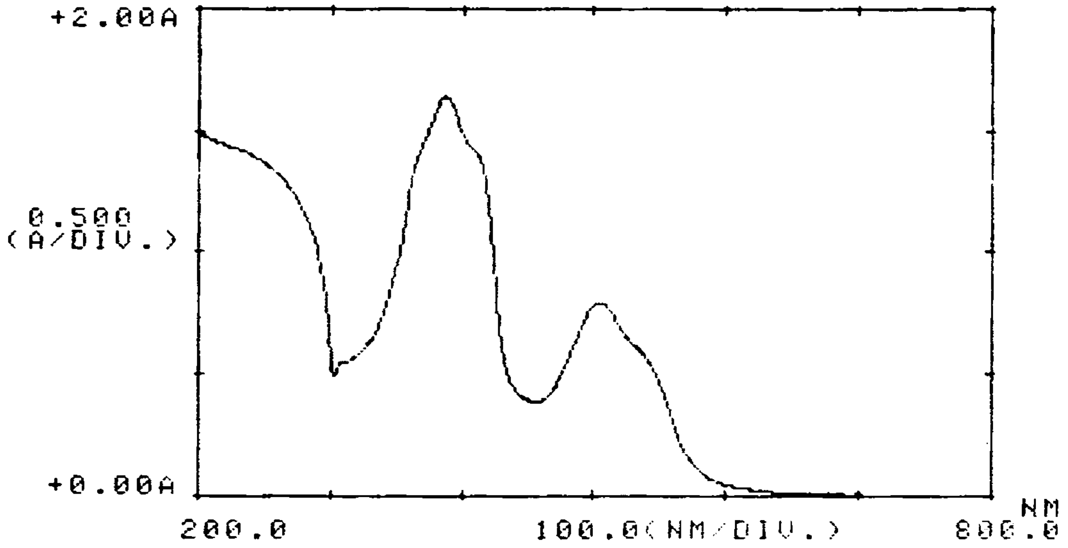


Fig. 3.6 Electronic spectra of [Ni(i-PrACDA)$_2$] in pyridine.

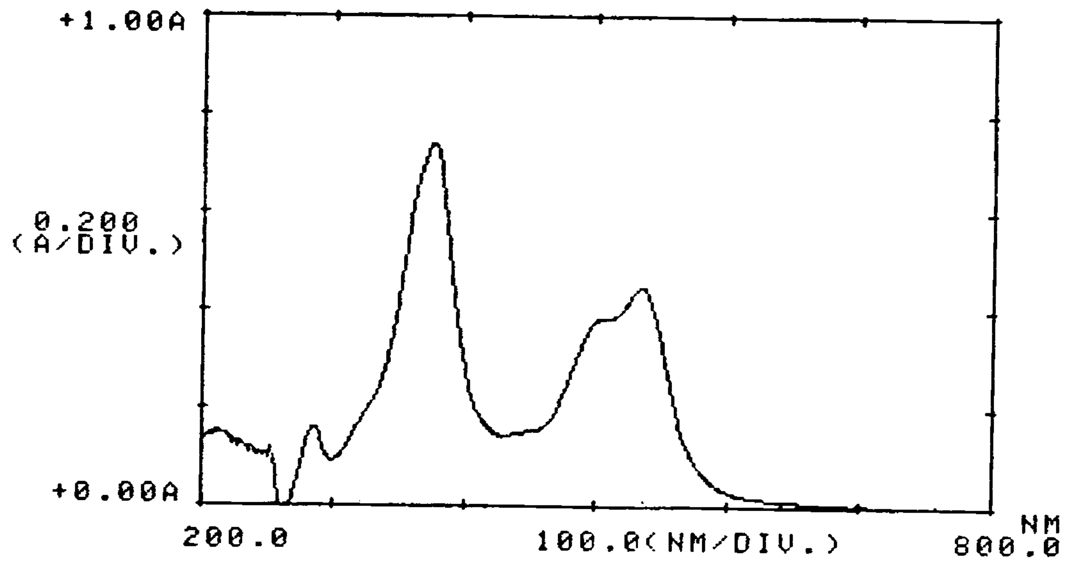


Fig. 3.7 Electronic spectra of [Ni(i-PrACDA)$_2$] in DMSO.

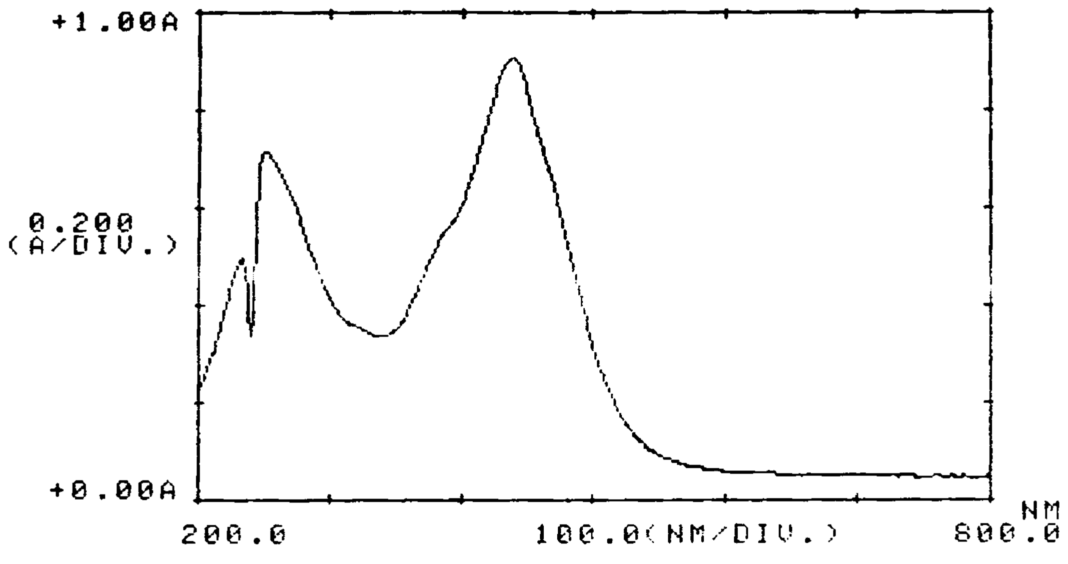


Fig. 3.8 Electronic spectra of [Cu(i-PrACDA)] in chloroform.

Table 3.3. Electronic spectral data of the i-PrACDA complexes in $CHCl_3$

Complex	Absorption maxima (cm^{-1})	log ε	Tentative assignments
[Cr(i-PrACDA)$_3$]	42700	3.15	Intraligand transition
	38900	3.50	Charge transfer transition
	33900	3.42	"
	25600 (sh)	3.71	$^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ transition
	22500	4.12	$^4A_{2g} \longrightarrow {}^4T_{2g}(F)$ transition
[Mn(i-PrACDA)$_3$]	42700	3.40	Intraligand transition
	35200	3.51	Charge transfer transition
	32900	3.56	"
	25800 (sh)	3.98	$^5B_1 \longrightarrow {}^5A_2$ transition
	24000	4.16	$^5B_1 \longrightarrow {}^5B_2$ transition
	22400 (sh)	4.07	$^5B_1 \longrightarrow {}^5B_2$ transition
[Fe(i-PrACDA)$_3$]	40000	3.44	Intraligand transition
	31200	3.32	Charge transfer transition
	27200	3.31	"

contd...

Complex	Absorption maxima (cm^{-1})	log ε	Tentative assignments
[Co(i-PrACDA)$_3$]	42500	3.23	Intraligand transition
	32500	2.77	Charge transfer transition
	25200	3.21	"
	21400	3.13	$^1A_{1g} \longrightarrow {}^1T_{2g}$ transition
	15600 (sh)	2.81	$^1A_{1g} \longrightarrow {}^1T_{1g}$ transition
[Ni(i-PrACDA)$_2$]	·42900	3.70	Intraligand transition
	35000	3.96	Charge transfer transition
	26400	4.52	"
	18400	4.26	$^1A_{1g} \longrightarrow {}^1B_{1g}$ transition
[Cu(i-PrACDA)]	42900	3.37	Intra ligand transition
	39800	3.52	Charge transfer transition
	22800	3.61	"

suggests that Jahn-Teller distortions occur in this complex. The present complex might be considered to have a symmetry C_2.

The band observed at 24000cm^{-1} in the present complex may be assigned to the $^5B_1 \longrightarrow {}^5B_2$ transitions. The highest energy transition $^5B_1 \longrightarrow {}^5A_1$ seems to have masked by the charge transfer bands, and the other transitions, $^5B_1 \longrightarrow {}^5B_2$ and $^5B_1 \longrightarrow {}^5A_2$ appear as shoulder bands at 22400 and 25800 cm^{-1} respectively[194].

$[Fe(i\text{-}PrACDA)_3]$

The ground state term is the orbital singlet ^6S in high spin complexes. It cannot be split by crystal field of any symmetry. The absence of any other spin sextet terms requires that all transitions in high spin d^5 complexes are spin forbidden as well as Laporte forbidden; thus they will generally be very weak. Further because of the greater oxidising power of iron(III), ligand to metal charge transfer bands often obscure the very low intensity bands[195]. No d-d transitions are observed in the complex. Such transitions are rarely observed in 6-coordinate FeS_6 species, since the strong Fe-S charge transfer absorption will obscure such weak bands.

$[Co(i\text{-}PrACDA)_3]$

The low-spin octahedral ground term is $^1A_{1g}$ and there are two relatively low lying spin allowed transitions to $^1T_{1g}$ and $^1T_{2g}$. The bands observed in the spectra of $[Co(i\text{-}PrACDA)_3]$ at 15600 cm^{-1} and 21500 cm^{-1} can be assigned to $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$ transitions respectively. The band at 25600 cm^{-1} can be assigned to the charge transfer band and that at 41600 cm^{-1} can be assigned to intraligand transitions[196].

[Ni(i-PrACDA)$_2$]

Nickel(II) ion is prone to form 4-coordinate diamagnetic square planar complexes, especially with stronger ligand fields. Such complexes typically have a single band in the region 15000-25000cm^{-1}. A second, more intense band may be seen near 23000-30000cm^{-1} which is often charge transfer in origin. Only one d-d band was noticed. The band at ~ 18400 cm^{-1} can be assigned to the transition $^1A_{1g} \longrightarrow {}^1B_{1g}$. The band at 26400$cm^{-1}$ and 35000cm^{-1} can be attributed to charge transfer bands and the band at 42900cm^{-1} is due to the intraligand transitions[197].

The spectra of the nickel(II) complex have also been recorded in other solvents like DMSO and pyridine (*vide* Fig. 3.5-3.7). Nature of the spectra indicates some interaction of the nickel(II) complexes with pyridine. Such interactions are seen in xanthate and dithiobenzoate complexes.

[Cu(i-PrACDA)]

The complex does not exhibit any d-d bands as expected for Cu(I)complexes. The charge transfer band observed at 22800 cm^{-1} suggests that this complex has some similarity with the dithiocarbamate complexes. A similar band at 22900 cm^{-1} is observed in the spectra of [Cu(Et$_2$dtc)$_2$] which is the basis of a well known method for the spectrophotometric determination of copper with Na^+Et_2dtc[198].

It is ineteresting to note that i-PrACDA appears to have parallel reactivity to that of the xanthates and dithiobenzoates. The similarity is seen in the following aspects:

1. The i-PrACDA acts as a reducing agent towards Cu(II) ions
2. Its Mn(II) and Co(II) complexes are not stable and gets easily oxidised to M(III) complexes in presence of air.
3. The Ni(II) complex of i-PrACDA strongly interacts with the Lewis bases like pyridine. However, its ability to form adducts seems to be in between that of the xanthates and dithiocarbamates.

3.3.4 Infrared spectra

The infrared spectral data of the ligand and the complexes are given in the Table.3.4. The assignments of the bands have been done based on those carried out by earlier workers[168-176] for the ACDA complexes.

The IR spectrum of the free ligand exhibits a broad band at 2490 cm^{-1} which can be assigned to νS-H. This band disappears in the infrared spectra of the complexes, indicating that the deprotonation of the thiol group has taken place and the bonding has occured through the sulphur atom.

The νN-H is found in the spectrum of the free ligand at 3080 cm^{-1}. The lower value for νN-H is due to the strong intramolecular hydrogen bonding. In the spectra of the complexes, νN-H is seen at a higher frequency (~3210 cm^{-1}). The increase in νN-H can be attributed to the breaking of the hydrogen bonding on complexation of the ligand through the sulphur atoms. The νN-H

Table. 3.4 Infrared spectral data of i-PrACDA and its complexes

I	II	III	IV	V	VI	VII	Tentative assignments
3080w	3210m	3210m	3210m	3210m	3210m	3210m	νN-H
2990s	2980m	2980m	2980m	2980m	2980m	2990m	νC-H
2920s	-	-	-	-	-	-	
2490s	-	-	-	-	-	-	νS-H
1575s	1570s	1560s	1570s	1560s	1570s	1555s	δCNH
1470s	1480s	1480s	1480s	1480s	1480s	1480s	$\nu C=C+\delta CH_2$
1370m	1390s	1390s	1375s	1380s	1390s	1380s	
1330s	1325s	1330s	1325s	1325s	1330s	1330s	νC-N+νC-S
1265m	1270m	1270m	1280m	1265m	1270m	1270m	νC-S+νC-N
1155s	1160m	1160m	1170m	1160m	1155m	1155m	
1115w	1110w	1115w	1120w	1110w	1130w	1130w	ρCH_2
1060w	1065w	1065w	1070w	1060w	1060w	1060w	
1020w	1010m	1010m	1005m	1010m	1010m	1010m	
950m	950m	950m	960m	940m	960m	950m	$\nu_{as}CSS$
905m	900m	900m	910m	910m	920m	910m	
870m	865m	685m	870m	860m	870m	865m	
765s	800s	810s	805m	820s	810s	820s	νC-S
-	670s	665s	670s	665s	670s	670s	

s = strong; m = medium; w = weak; vw = very weak

I=i-PrACDA; II=$[Cr(i\text{-}PrACDA)_3]$; III=$[Mn(i\text{-}PrACDA)_3]$; IV=$[Fe(i\text{-}PrACDA)_3]$;

V=$[Co(i\text{-}PrACDA)_3]$; VI=$[Ni(i\text{-}PrACDA)_2]$; VI=[Cu(i-PrACDA)].

Contd....

I	II	III	IV	V	VI	VII	Tentative assignments
515vw	524s	519s	510s	580s	584m	592s	
-	430w	411w	436m	480m	527m	531s	
-	390w	391w	392m	390m	384m	442w	
410m	362s	369s	-	380s	380s	413w	
355sh	350s	347s	348s	350s	349m	369s	νM-S
325m	321w	321w	322w	320w	319w	319w	
-	296m	308w	290w	290w	293w	305w	
-	270m	266w	270w	270w	268w	268w	
-	240m	237m	234w	-	237m	241w	

s = strong; m = medium; w = weak; vw = very weak

I=i-PrACDA; II=[Cr(i-PrACDA)$_3$]; III=[Mn(i-PrACDA)$_3$]; IV=[Fe(i-PrACDA)$_3$];

V=[Co(i-PrACDA)$_3$]; VI=[Ni(i-PrACDA)$_2$]; VI=[Cu(i-PrACDA)].

modes should have shifted in the reverse order, if the coordination of the ligand had occured through the amino nitrogen. This fact is reflected in the δCNH values: The δCNH in the spectrum of the free ligand appears around 1575 cm^{-1} and this value decreases to 1560 cm^{-1} in the spectra of the complexes. The higher value of δCNH in the free ligand is due to the hydrogen bonding. The decrease in δCNH in the complexes is due to the disappearance of hydrogen bonding[156]. Similar observations have been made for many ammine complexes.

There is a strong band at 766 cm^{-1} in the spectrum of the free ligand which is seen to be shifted to ~805 cm^{-1} in the case of the complexes[157]. This band can be assigned to νC-S and the increase in C-S stretching frequency on complexation might be again due to the breaking of the hydrogen bond. Further, the appearance of a single band in the region 700-850 cm^{-1} in the present complexes indicates that both the sulphur atoms are taking part in the bonding. Thus inferences obtained from the infrared spectra are clearly in favour of S-S bonding.

Further evidence for M-S bonding is obtained from the far infrared spectra of the complexes. A strong band is seen in the region 300-400 cm^{-1} which can be attributed to νM-S[156]. In the case of the Mn(III) complex two strong bands due to νMn-S are seen, one at 369 and 347 cm^{-1} which might have resulted from the Jahn-Teller distortions.

More information about the bonding sites may be obtained from the EPR spectra of the complexes. If the bonding takes place through the nitrogen atom, hyperfine splittings due to nitrogen would have observed in the spectra. As the present copper complex is diamagnetic and all the other complexes are EPR silent at room temperature, the information about this aspect was not obtained. However, we could record the EPR spectra of a few mixed ligand complexes of ACDA or its N-alkyl derivatives. The spectra did not show any hyperfine splittings due to the nitrogen atom (*vide* discussions in Chapter IV). Further, conclusive evidences for the non-involvement of the nitrogen atom was obtained from the ^{1}H NMR spectra of the complexes.

3.3.5 ^{1}H NMR spectra

The H NMR spectra of the metal complexes of ACDA have not been studied in $CDCl_3$ due to their limited solubilities in this solvent. All the reported NMR studies of ACDA complexes have been carried out in a coordinating solvent[171], DMSO-d_6. The higher solubilities of i-PrACDA complexes in chloroform have enabled us to record their spectra in $CDCl_3$. The ^{1}H NMR spectrum of the copper complex could not be taken due to the lack of proper solubility. The ^{1}H NMR data of the complexes are given in Table 3.5.

The CH_2 protons at the C_3 and C_5 positions experience more shielding than the protons at the C_4 position, and have almost the same chemical shifts.

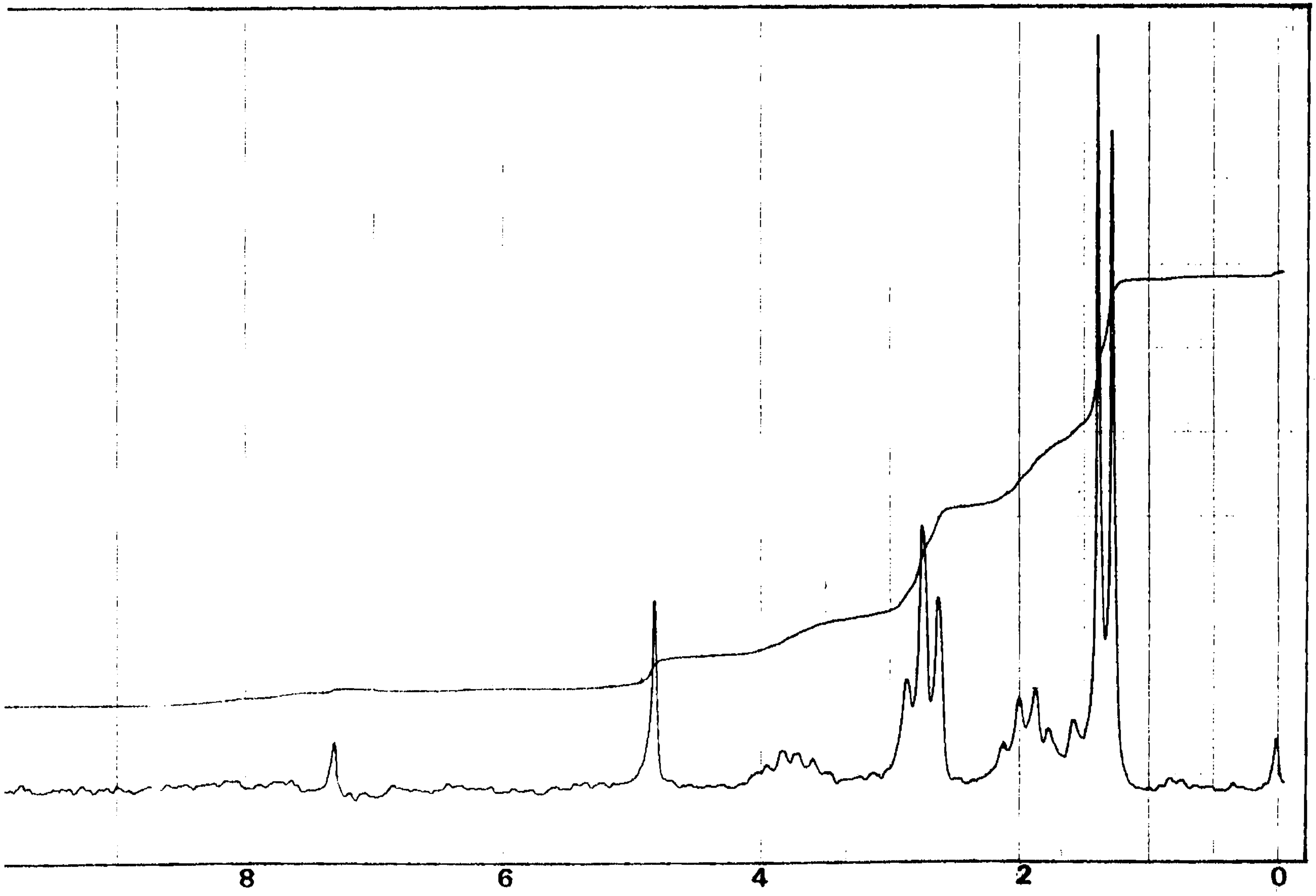


Fig. 3.9 Proton NMR spectra of i-Pr HACDA ligand in $CDCl_3$.
(0-10 ppm.)

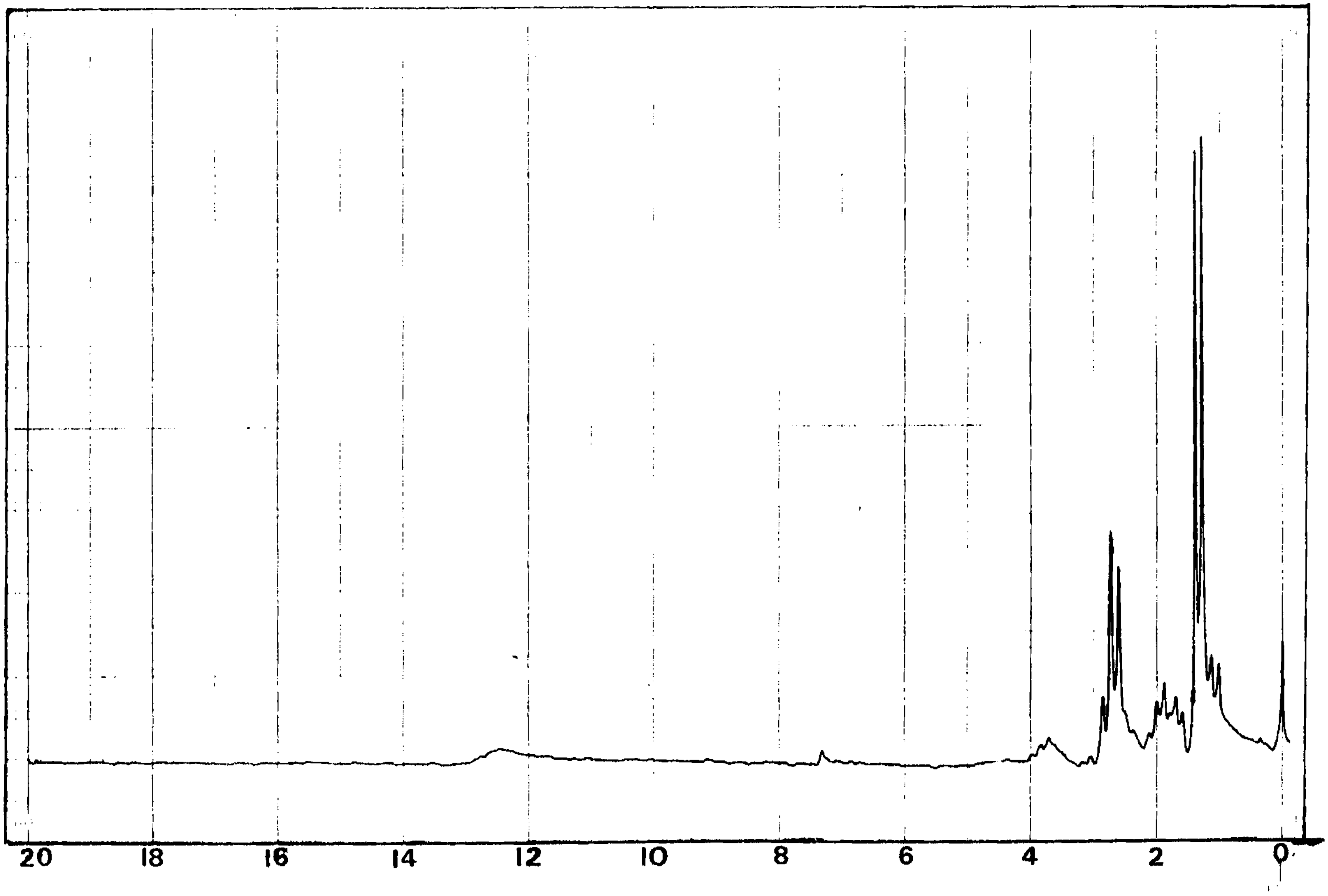


Fig. 3.10 Proton NMR spectra of i-Pr HACDA ligand in $CDCl_3$.
(0-20 ppm.)

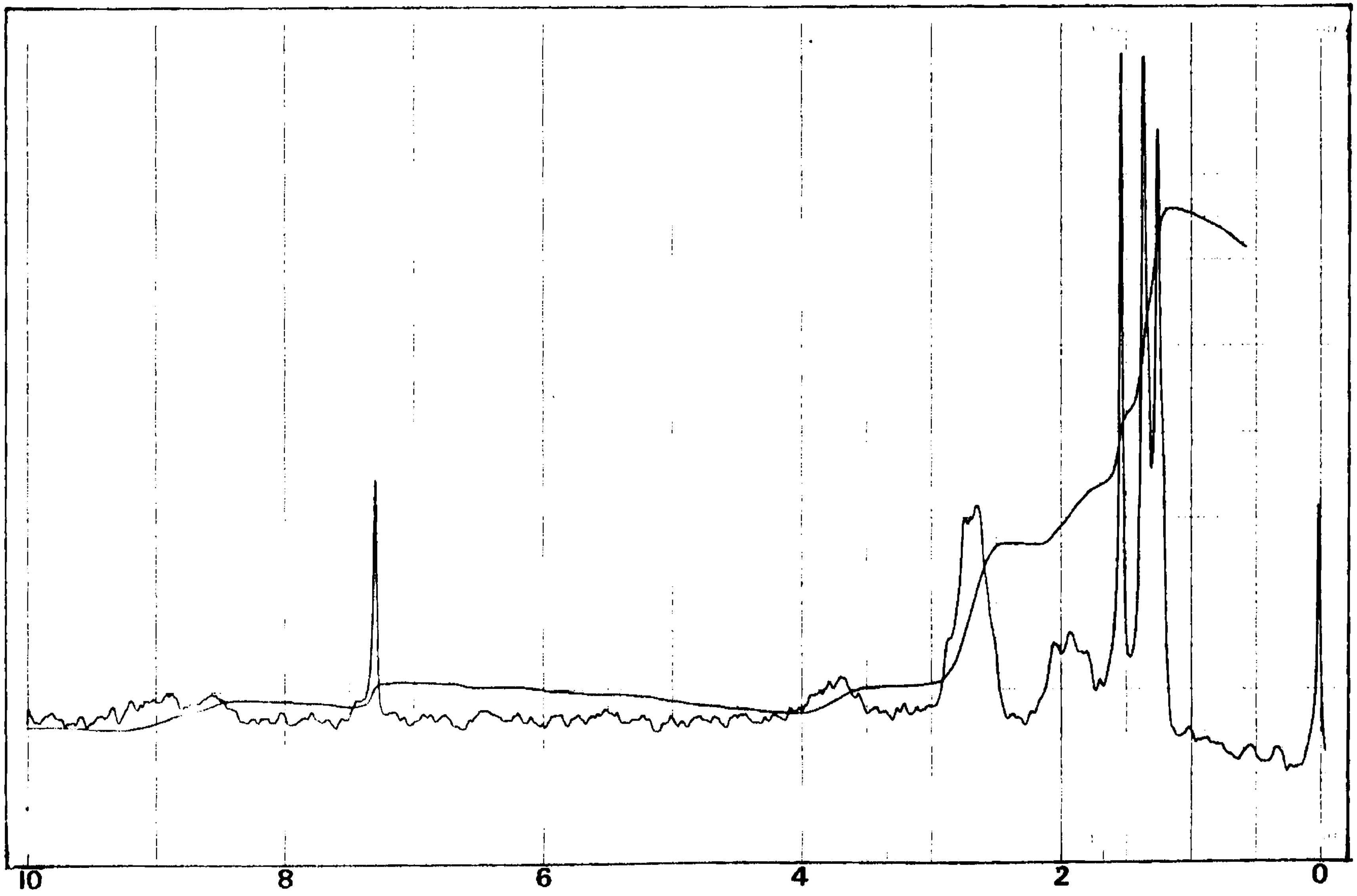


Fig. 3.11 Proton NMR spectra of [Ni(i-PrACDA)$_2$] in CDCl$_3$.

Table 3.5 ^1H NMR data for i-PrACDA and its complexes in $CDCl_3$ (*vide* Fig.3.12)

Complex	Chemical shift (δ) values in ppm					
	CH_3	CH	CH_2		NH	SH
			C_4	C_3&C_5		
i-PrACDA	1.35d	3.75h	1.85p	2.85t	12.4s,br	4.8s
[Cr(i-PrACDA)$_3$]	1.30br	3.70br	1.85br	2.25br	8.80s,br	-
[Mn(i-PrACDA)$_3$]	1.35v.br	3.60br	1.90br	2.60br	8.50s,br	-
[Fe(i-PrACDA)$_3$]	1.30v.br	3.70br	1.85br	2.70br	8.50s,br	-
[Co(i-PrACDA)$_3$]	1.30d.br	3.70br	1.85br	2.70br	8.80br	-
[Ni(i-PrACDA)$_2$]	1.30d.br	3.75br	1.95br	2.75t,br	8.80s,v.br	-

d-doublet, h-heptet, p-pentet, s-singlet, br-broad, v.br-very broad

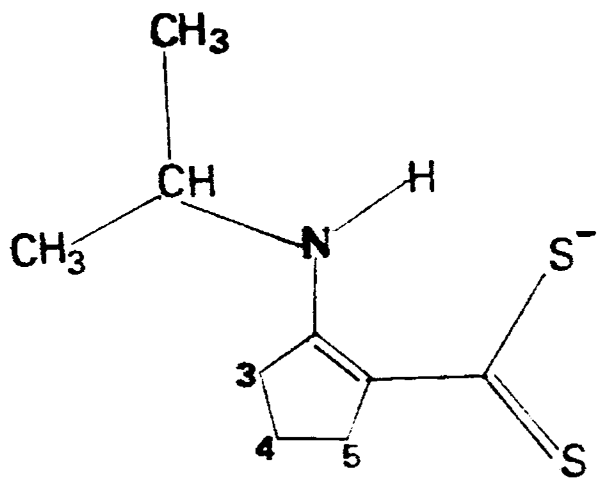


Fig 3·12 i-PrACDA

The signal of the -SH proton appears at δ 4.8 ppm in the spectrum of the ligand. This signal is absent in the spectra of the complexes indicating the removal of the -SH proton and formation of M-S bond.

Another major change observed on complexation is that the -NH proton signal which appears as a broad singlet at δ 12.4 ppm for the ligand is shifted to δ 8.6ppm in the spectra of the complexes. This large upfield shift has been attributed to the coordination of the nitrogen to the metal ion by some workers in the case of the ACDA complexes. This cannot be right and this fact would become more clear, if we consider the signals due to the CH proton of the isopropyl group. If the N atom had been involved in the bonding, then considerable shift might have occured for this proton also. But the signals due to the CH proton appear in the spectra of both the ligand and the complexes almost at the same position. Therefore the observed NH proton shift in the case of the complexes is not due to the involvement of the nitrogen atom in the bonding, but due to the breaking of the intramolecular hydrogen bonding between the NH proton and sulphur atom of the dithiocarboxylic acid group of the free ligand.

Thus spectroscopic (IR, electronic and ^{1}H NMR) evidences are in favour of the bidentate bonding of the dithio group to the metal.

Chapter - 4

CHAPTER IV

NEW MIXED LIGAND COMPLEXES OF COPPER(II) DITHIOCARBAMATES

4.1 INTRODUCTION

Mixed ligand complexes of dithiocarbamates are of particular interest because of the following reasons: (i) their structural and electronic properties are possibly distinct from those of the simple dithiocarbamate complexes, (ii) they are regarded as models for metalloenzyme-substrate complexes.

Solid mixed ligand complexes of copper(II) dithiocarbamates have been synthesised by reacting the bis(dithiocarbamato)-μ-dichloro-dicopper(II) complexes with pyridine or picolines[122]. The synthesis of these complexes have prompted us to use these chlorine bridged complexes as the starting material for the synthesis of some new mixed ligand complexes. We have isolated some interesting mixed ligand complexes by reacting this chloro complexes with 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (ACDA) or its N-alkyl derivatives. The syntheses and structure elucidation of such complexes are described in this chapter.

4.2 EXPERIMENTAL

Materials

Details about the reagents and preparation of dithiocarbamates, ACDA and its alkyl derivatives are given in Chapter II.

Synthesis:

Bis(dithiocarbamato)-μ-dichloro-dicopper(II) complexes

All the complexes were prepared by the general method given below: $CuCl_2.2H_2O$ (1.7g, 0.01mole) and the appropriate, freshly recrystallised benzoic-dithiocarbamic anhydride (0.02mole), both dissolved in minimum quantity of acetone, were slowly mixed. The chloro complexes separated out as a black crystalline powder. The smell of benzoylchloride was noted during the preparation. The complex was filtered, washed with diethylether and dried in vacuum over P_2O_5.

Synthesis of the mixed ligand complexes

[Cu(Me_2dtc)(ACDA)]

ACDA (1.58g, 0.01mole) was dissolved in methanol (100ml). To this yellow coloured solution, the black complex, $[Cu(Me_2dtc)Cl]_2$ (2.19g, 0.005mole), was added and thoroughly mixed. The complex dissolved and the colour of the solution immediately changed to red. The solution was then filtered to remove any solid particles, and the filtrate was refluxed on a water bath for one hour. The red coloured product separated out from the solution was filtered, washed with methanol, acetone and ether and dried over anhydrous calcium chloride.

[Cu(Pipdtc)(n-BuACDA)] and [Cu(Pipdtc)(i-PrACDA)]

These complexes were obtained in the same way as [Cu(Me_2dtc)(ACDA)] using $[Cu(Pipdtc)Cl]_2$ (2.64g, 0.005mole) and n-BuACDA (2.15g, 0.01mole) or i-PrACDA (2.0g, 0.01mole).

[Cu(Morphdtc)(i-PrACDA)] and [Cu(Morphdtc)(n-BuACDA)]

These complexes were also made in the same way as [Cu(Me_2dtc)(ACDA)] using $[Cu(Morphdtc)Cl]_2$ (2.60g, 0.005mole) and i-PrACDA (2.0g, 0.01mole) or n-BuACDA (2.15g, 0.01mole).

Characterisation

Details about the characterisation techniques are given in Chapter II.

4.3 RESULTS AND DISCUSSION

Analytical data of the complexes are given in Table 4.1. The data show that the complexes have the empirical formula [Cu(R_2dtc)L] (where R_2=Me_2, Pip or Morph: L=ACDA, i-PrACDA or n-BuACDA). Even when the $[Cu(R_2dtc)Cl]_2$ and L were mixed in different ratios (1:2.2, 1:2.5, 1:3 etc), the complexes with the same composition, [Cu(R_2dtc)L], were obtained. This suggests that the present complexes are pure mixed ligand complexes and not a mixture of complexes.

All the complexes are red in colour. They are stable and can be kept for a longer period without decomposition. The complexes are only slightly soluble in chloroform, and hence good ^1H NMR spectra could not be recorded in these cases.

4.3.1 Conductance measurements

The molar conductances of the complexes are given in Table 4.2. The values suggest that the complexes are non-electrolytes in nitrobenzene.

Table.4.1 Analytical data of the mixed ligand complexes of Cu(II)

Complex	N(%) Found (Calc.)	Cu(%) Found (Calc.)	S(%) Found (Calc.)
[Cu(Me_2dtc)(ACDA)]	8.18	18.52	37.40
[$C_9H_{14}CuN_2S_4$]	(8.19)	(18.58)	(37.50)
[Cu(Pipdtc)(n-BuACDA)]	6.35	14.48	29.25
[$C_{16}H_{26}CuN_2S_4$]	(6.41)	(14.54)	(29.33)
[Cu(Morphdtc)(n-BuACDA)]	6.28	14.41	29.18
[$C_{15}H_{24}CuN_2OS_4$]	(6.38)	(14.47)	(29.20)
[Cu(Morphdtc)(i-PrACDA)]	6.56	14.93	30.18
[$C_{14}H_{22}CuN_2OS_4$]	(6.61)	(14.98)	(30.24)
[Cu(Pipdtc)(i-PrACDA)]	6.59	15.02	30.32
[$C_{15}H_{14}CuNS_4$]	(6.64)	(15.05)	(30.38)

4.3.2 Magnetic measurements

The magnetic behaviour of the complexes has been studied and $\mu_{eff.}$ values are tabulated in Table 4.2. All the complexes exhibit a $\mu_{eff.}$ value of 1.9 BM at 28±2°C. The magnetic data clearly establish +2 oxidation state for copper in these complexes. The data indicate absence of any metal-metal interactions and also excludes the possibility of these complexes to have a tetrahedral structure[187]. (The $\mu_{eff.}$ values for tetrahedral copper(II) complexes would be around 2.2 BM)

4.3.3 Electronic spectra

The electronic spectral bands and their assignments are tabulated in Table 4.3. The electronic spectra of the present mixed ligand complexes do not differ much from that of simple copper(II) dithiocarbamate complexes. On this basis, a structure similar to that of the copper(II) dithiocarbamate may be assigned to the present complexes[194].

4.3.4 Infrared spectra

The infrared spectral data of the complexes are tabulated in Table 4.4. The tentative assignments given in the table are based on published work on ACDA and dithiocarbamates.

The spectra of the complexes exhibit bands due to both the constituent ligands. In the spectra of [Cu(Me$_2$dtc)(ACDA)], all the bands due to Me$_2$dtc and ACDA are observed: The νN-H and δNH_2

Table 4.2 Molar conductance and magnetic data of the mixed ligand complexes of Cu(II)

Complex	Molar conductance in nitrobenzene* $ohm^{-1}\ cm^2\ mole^{-1}$	$\mu_{eff.}$ in BM at 28 ± 2^o C
[Cu(Me_2dtc)(ACDA)]	1.8	1.9
[Cu(Pipdtc)(n-BuACDA)]	1.1	1.8
[Cu(Morphdtc)(n-BuACDA)]	1.7	1.9
[Cu(Morphdtc)(i-PrACDA)]	0.8	1.9
[Cu(Pipdtc)(i-PrACDA)]	0.9	1.9

* Concentration = 10^{-3} mole lit^{-1}.

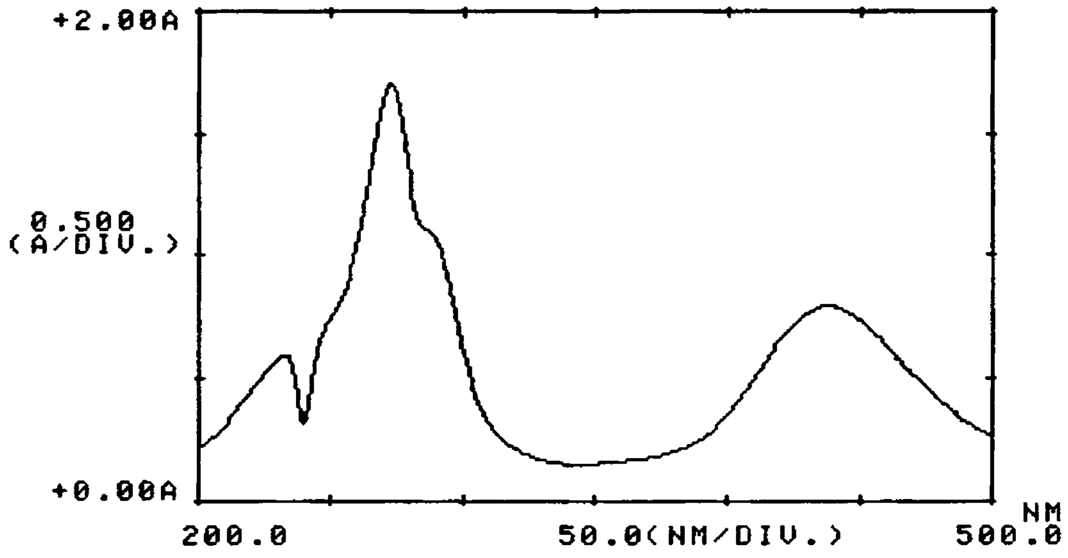


Fig. 4.1 Electronic spectra of [Cu(i-PrACDA)(Pipdtc)].

Table 4.3 Electronic spectral data of mixed ligand complexes of Cu(II).

Complex	Absorption maximum, cm^{-1}	log ε	Tentative assignments
	41800	4.90	Intraligand transition
	39000	4.78	"
[Cu(Me_2dtc)(ACDA)]	36500	5.34	"
	34600	5.15	"
	22250	5.10	Charge transfer transition
	41700	4.85	Intraligand transition
	39000 sh	4.72	"
[Cu(Pipdtc)(n-BuACDA)]	36400	5.28	"
	34500 sh	5.10	"
	22100	4.94	Charge transfer transition
	41600	4.83	Intraligand transition
	38900 sh	4.76	"
[Cu(Morphdtc)(n-BuACDA)]	36450	5.34	"
	34500 sh	5.20	"
	22200	5.10	Charge transfer transition
	41600	4.80	Intraligand transition
	39000 sh	4.74	"
[Cu(Morphdtc)(i-PrACDA)]	36400	5.30	"
	34500 sh	5.20	"
	22200	4.89	Charge transfer transition
	41600	4.83	Intraligand transition
	39000 sh	4.76	"
[Cu(Pipdtc)(i-PrACDA)]	36400	5.29	"
	34500 sh	5.17	"
	22200	5.08	Charge transfer transition

Table. 4.4 Infrared spectral data of the mixed ligand complexes of Cu(II)

I	II	III	IV	V	Tentative assignments
3360m					
	3180w	3180w	3180w	3180w	ν_{N-H}
3120vw	3120w	3120w	3100w	2960w	ν_{C-H}
2960w	2920w	2920m	2960m	2920m	
2840w	2840m	2840m	2840w	2840w	
2320w	2300w	2300v	2300w	2300w	
1620s	1570vs	1565vs	1570vs	1570vs	δ N-H
1505s	1495s	1475s	1475s	1495s	ν_{C-N}
1450s	1440s	1440m	1440m	1465s	
1380s	1385m	1390m	1385s	1380s	δ CH_2+ $\nu_{C=C}$
1320m	1340m	1340m	1325s	1325s	ν_{C-N}+ ν_{C-S}
1290m	1280m	1285m	1290m	1290m	
1280m	1250m	1260s	1265s	1265s	ν_{C-S} + ν_{C-N}

vs = very strong; s = strong; m = medium w = weak

I = [Cu(Me_2dtc)(ACDA);

II = [Cu(Pipdtc)(n-BuACDA);

III = [Cu(Morphdtc)(n-BuACDA);

IV = [Cu(Morphdtc)(i-PrACDA)

V = [Cu(Pipdtc)(i-PrACDA)

Contd.

I	II	III	IV	V	Tentative assignments
1240m	1230s	1225s	1225s	1230s	
1155m	1155m	1155m	1155m	1155m	
1120m	1130w	1105s	1105s	1105m	
1030w	1055w	1055w	1060m	1060w	ρ_{C-H}
1020w	1015w	1020s	1020s	1020w	
955m	990m	945w	940w	940m	$\nu_{as}C-S$
920m	970w	905s	905s	905s	
880w	900m	870w	870w	865w	
805s	780m	780m	790m	790m	ν_{C-S}
665w	690m	690m	690m	690m	
540m	510m	540s	540s	520s	
340s	345s	335s	340vs	350s	ν_{M-S}
270m	270m	290m	285m	260m	

vs = very strong; s = strong; m = medium w = weak

I = [Cu(Me$_2$dtc)(ACDA)]; II = [Cu(Pipdtc)(n-BuACDA)];

III = [Cu(Morphdtc)(n-BuACDA)]; IV = [Cu(Morphdtc)(i-PrACDA)]

V = [Cu(Pipdtc)(i-PrACDA)]

of the ACDA appear at 3360 cm^{-1} and 1620 cm^{-1} respectively. The νN-H band and δCNH bands appear around 3180 cm^{-1} and 1570 cm^{-1} respectively for the complexes with i-PrACDA and n-BuACDA. The νN-H bands appear at lower frequencies in the case of the free ACDA ligands. The shift to higher frequencies can only be attibuted to the breaking of the intramolecular hydrogen bonding and not due to the involvement of the nitrogen atom in the bonding (*vide* discussions in Chapter III).

The νC-N of the dithiocarbamate ligand is seen around 1500 cm^{-1} in the spectra of all the present complexes. Further bands due to νC-S of both type of ligands are also observed in the spectra of all the complexes. The number of bands observed in these regions have been used to distinguish between the bidentate and monodentate bonding[1]. In the case of the present complexes more than two bands are seen in both the νC-S region of the dithiocarbamate ligand (950-1050 cm^{-1}) and the νC-S region of the ACDA ligand (750-850 cm^{-1}). However this fact cannot be used for excluding the bidentate bonding of the ligands, as bands due to both the ligands may appear in the same region.

In the far IR region of the spectra, there is a strong band around 350 cm^{-1} which can be attributed to νM-S. It was not possible to identify from the spectra, νCu-S band due to the dithiocarbamate and νCu-S due to the ACDA ligands; probably they might appear in the same region.

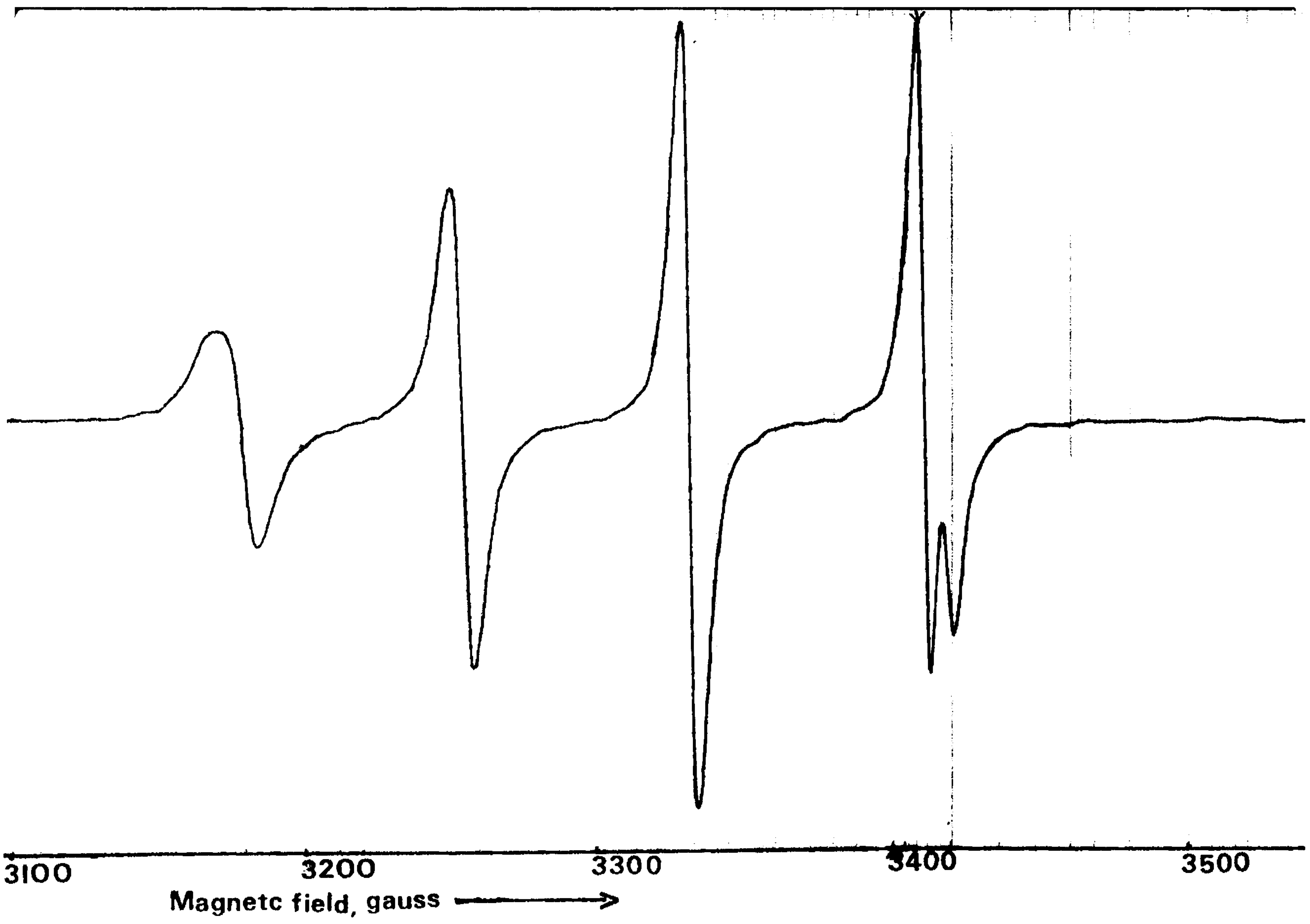


Fig. 4.2 ESR spectrum of [Cu(Pipdtc)(i-PrACDA)].

Table 4.5 ESR data for the mixed ligand complexes of Cu(II) in chloroform

Complex	g_o	A_o (in Gauss)
[Cu(Me$_2$dtc)(ACDA)]	2.041	74
[Cu(Pipdtc)(n-BuACDA)]	2.042	80
[Cu(Pipdtc)(i-PrACDA)]	2.040	80
[Cu(Morphdtc)(n-BuACDA)]	2.039	76
[Cu(Morphdtc)(i-PrACDA)]	2.043	76

4.3.5 ESR spectra

The ESR spectra of the complexes in chloroform solution were recorded. The g_o and A_o values of the complexes have been calculated and are given in Table 4.5

The ESR spectra of the complexes (*vide* Fig. 4.2) exhibit equidistant signals which are due to the coupling of the spin of the unpaired electron with nuclear spins of the copper atoms. The high field line is so narrow in the spectra that the hyperfine splitting due to ^{65}Cu becomes visible. No nitrogen hyperfine splitting was observed in the spectra, which indicates that the N-atom of the ACDA ligands is not involved in bonding. The g_o and A_o values of the present complexes are very similar to those reported for $[Cu(R_2dtc)_2]$. It may be noted here that the ESR parameters of $[Cu(ACDA)_2]$ and $[Cu(Et_2dtc)_2]$ have almost same values[171].

The g_o value for CuN_4 chromophore have values in the range 2.09-2.108, while that for CuN_2S_2 and CuS_4 chromophores are in the range 2.042-2.06 and 2.042-2.045 respectively[187]. The present complexes have almost the same g_o values (2.04) as that for CuS_4 core. Further A_o values (~ 80 G) are also in favour of a CuS_4 core for these complexes: A_o values for CuS_4, CuS_2N_2 and CuN_4 are in the range 75-82, 90-95, 84-102 G respectively. Thus the ESR spectra give strong support for bidentate bonding of both ACDA and dithiocarbamate ligands through sulphur atoms resulting in a CuS_4 chromophore.

Chapter - 5

CHAPTER V

REACTION OF MIXED BENZOIC-XANTHIC ANHYDRIDES WITH COPPER(II) CHLORIDE

5.1 INTRODUCTION

The reactions of benzoic-dithiocarbamic anhydrides with iron(III) halides, copper(II) chloride and mercury(II) halides have yielded interesting halogeno- dithiocarbamato complexes[113,125,199]. In this chapter, we are reporting the results of our studies on the interaction of benzoic-xanthic anhydrides with copper(II) chloride. Eventhough the reactions were tried with other metallic halides, it was only with copper(II) chloride we were able to isolate halogen containing xanthate (carbonodithioate) complexes with a definite stoichiometry. These type of copper(II) complexes containing xanthate and chlorine have not yet been reported in the literature.

5.2 EXPERIMENTAL

Materials:

Details about the reagents used and synthesis of mixed benzoic-xanthic anhydrides are given in Chapter II.

Synthesis:

All the complexes, were prepared by the same general method given below : $CuCl_2.2H_2O$ (1.7g, 0.01 mole) dissolved in minimum quantity of acetone and the freshly prepared benzoic-xanthic anhydride (slightly greater than 0.015 mole) dissolved in diethyl ether were mixed. This resulted in a bright green solution. After a certain period of time (approximately 45 minutes), the solution became dark brown and an orange red complex separated out.The complex was filtered off immediately, washed several times with dry diethylether and rapidly dried in vacuum over P_2O_5.

Characterisation

Details about the characterisation tachniques are given in Chapter II.

5.3 RESULTS AND DISCUSSION

The reaction between copper(II) chloride and benzoic-xanthic anhydride is very interesting and is almost like the clock reactions reported in the literature[199a]. The outstanding feature of clock reactions is the sudden appearance of a product some time after the initial mixing of reagents. In the present cases, the bright green solution formed after the mixing of the anhydride and cupric chloride becomes dark brown on keeping for a definite period of time (this happens around 45 minutes) with subsequent separation of an orange red compound. If the product is not separated immediately from the reaction medium, it will be contaminated with yellow copper(I) xanthates. In the case of benzoic-ethylxanthic anhydrides or its methyl derivative, separation of a compound takes place only after 14 hours and hence isolation of the complexes without contamination is difficult.

In a few instances, instead of a green solution, a yellow solution was formed and the compounds were not separated even after keeping the solution for a longer period. The condition for the formation of the green solution seems to depend upon the concentration of the reactants. During the course of the reaction, slow separation of benzoyl chloride, as indicated by its characteristic smell, was also noticed. Similar observations were made during the reaction of benzoic-dithiocarbamic anhydrides with copper(II), iron(III) and mercury(II) chlorides[113, 125, 199].

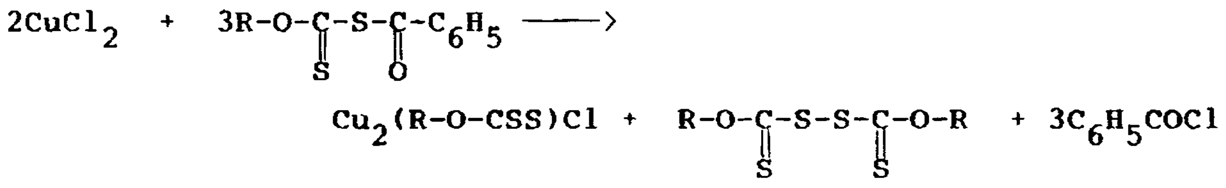
The analytical data (Table 5.1) for carbon, hydrogen, sulphur chlorine, and copper for these complexes establishes the empirical formula to be $[Cu_2(RXant)Cl]$ (R= isobutyl, sec-butyl, n-butyl, or isopropyl). The complexes on keeping slowly changes into a black solid. The infrared spectra of the decomposition product showed the absence of the xanthate ligands, and by elemental analysis it was found to have an approximate composition of cupric sulphide.

All the chloro xanthato complexes of copper were found to be insoluble in almost all the solvents like chloroform, nitrobenzene, ethyl alcohol and acetone. Furthermore, the complexes are diamagnetic in nature which suggest a +1 oxidation state for copper atoms in these complexes. Thus, during the formation of the complexes, copper is reduced from the +2 to the +1 oxidation state. Such type of reductions also take place during the reaction of alkali metal carbonodithioates with copper(II) salts[200]. Another product, dialkyl ester of thioperoxydicarbonic acid (dixanthogen) is also formed during the

Table 5.1 Analytical data of the chloroxanthate complexes of Cu(I)

Complex	Sulphur(%) Found (Calcd.)	Copper(%) Found (Calcd.)	Chlorine(%) Found (Calcd.)
[Cu$_2$(i-BuXant)Cl]	20.55	40.45	11.20
[$C_6H_9ClCu_2OS_2$]	(20.56)	(40.76)	(11.36)
[Cu$_2$i-PrXant)Cl]	21.40	42.60	11.70
[$C_4H_7ClCu_2OS_2$]	(21.53)	(42.68)	(11.90)
[Cu$_2$n-BuXant)Cl]	20.50	40.36	11.25
[$C_5H_9ClCu_2OS_2$]	(20.56)	(40.76)	(11.36)
[Cu$_2$sec-BuXant)Cl]	20.52	40.58	11.32
[$C_5H_9ClCu_2OS_2$]	(20.56)	(40.76)	(11.36)

reaction[200,201]. Based on these informations, we suggest the following reaction scheme for the formation of the present chloro carbonodithioato complexes of copper(I):



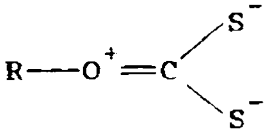
$$2CuCl_2 + 3R{-}O{-}\underset{\underset{S}{\|}}{C}{-}S{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \longrightarrow Cu_2(R{-}O{-}CSS)Cl + R{-}O{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}O{-}R + 3C_6H_5COCl$$

5.3.1 Electronic spectra

The solid state electronic spectra (Table 5.2) of the complexes only show one band in the visible region, which is around 22900 cm^{-1}. This high intensity band may be due to the charge transfer transition.

5.3.2 Infrared spectra

The infrared frequencies of the complexes are presented in the Table 5.3. The assignments given in the table are based on the spectral studies of xanthates by Watt and McCornick.[149] The νC-O and νC-S bands are quite sensitive to the environment, both with regards to the absorption frequency and intensity; hence assignments of these bands are often difficult. The shifts and splittings of the C-O band are observed in the spectra of many xanthate complexes, which suggest that the contribution of the resonance form (I)



(I)

Table 5.2 Electronic spectral data of the chloroxanthate complexes of Cu(I)

Complex	Absorption maximum cm^{-1}	Assignments.
[Cu_2(i-BuXant)Cl]	49100	Intraligand transition.
	44600	"
	40400	"
	34700	"
	22900	Charge transfer transition.
[Cu_2(sec-BuXant)Cl]	49000	Intraligand transition.
	44500	"
	40300	"
	34800	"
	22000	Charge transfer transition.
[Cu_2(i-PrXant)Cl]	49000	Intraligand transition.
	44600	"
	40200	"
	34700	"
	22700	Charge transfer transition.
[Cu_2(n-BuXant)Cl]	49000	Intraligand transition.
	44500	"
	40200	"
	34600	"
	22800	Charge transfer transition.

Table 5.3 Infrared spectral data of the chloroxanthate complexes of Cu(I)

I	II	III	IV	Tentative assignments
2960 w	2960 m	2980 s	2960 s	$\nu(CH_3)$
2920 w	2920 w	2920 w	2920 w	$\nu(CH_2)$
2300 m	2300 m	2300 m	2300 w	
1980 w	1970 w	1970 m	1970 w	
1740 m	1740 m	1740 m	1740 m	
1620 m	1640 w	1630 m	1640 vw	
1450 w	1500 s	1480 s	1450 m	$\delta(CH_3)$
1370 w	1370 m	1370 m	1370 m	
1210 s	1200 vs	1230 w	1220 m	νC-O
1020 s	1010 vs	1080 vs	1010 vs	$\rho(CH_3)$
960 m	960 vw	960 m	960 vw	
850 w	870 m	870 m	870 m	
810 w	820 vw	820 m	820 vw	ρCH_2
520 s	551 s	515 m	551 s	νC-S
450 w	470 s	462 s	518 s	
425 vw	410 s	413 m	438 s	δ(C-O-C)
346 s	340 m	350 w	345 m	νCu-S
306 vw	315 m	315 w	311m	
261 s	270 m	266 m	273s	νCu-Cl
210 w	240 m	235 m	237 m	

s =strong; m = medium; w = weak; vw = very weak

I = [Cu_2(i-BuXant)Cl] II = [Cu_2(i-PrXant)Cl]; III = [Cu_2(n-BuXant)Cl]

IV = [Cu_2(sec-BuXant)Cl]

is not inconsequential in the xanthate complexes (The contribution of this resonance form is considered as negligible by many workers[1]). When contribution of this form is not negligible, two C-O stretching frequencies are observed, one around 1270 cm^{-1} and the other around 1110 cm^{-1}. Relative contribution of this resonance form is determined largely by the electron withdrawing nature of the metal ion. As the copper in the resent complexes is in the +1 oxidation state, the contribution of this form will be very little and in such cases only one broad intense band will be observed at a frequency in between that due to C=O and C-O

The spectra of the present complexes exhibit a strong band around 1230 cm^{-1}, which can be assigned to νC-O. The medium band formed in the region 500-560 cm^{-1} can be assigned to C-S stretching frequencies, as these bands vary with regard to absorption frequency[156].

However, the far infrared spectra provide valuable information regarding the nature of the chlorine atoms in the complexes. The copper-chlorine stretching frequencies usually occur in the region 360-220 cm^{-1};these frequencies should be expected to lie near the upper limit for the terminal chlorine, while they should be near the lower limit for the bridged chlorine[1,156,202]. The intense band observed around 270 cm^{-1} in the present complexes of copper(I) can be attributed to the bridged chlorine atoms. The medium band around 360 cm^{-1} can be assigned to the Cu-S stretching frequencies.

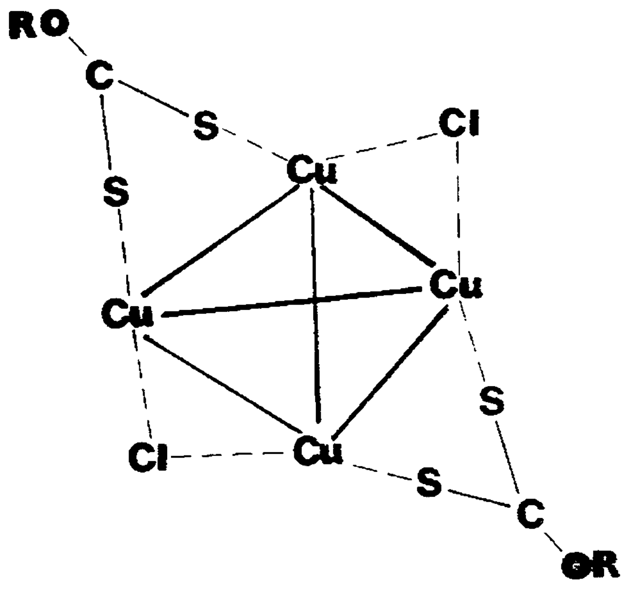


Fig. 5.1 Schematic diagram of the postulated cluster type structure of the chlorocarbonodithioatocopper(I) complex.

The analytical data, the diamagnetic nature and the presence of bridging chlorine may suggest a cluster type structure for these complexes as indicated in Fig. 5.1.

Such instances of copper atoms occupying the four corners of a tetrahedron are known in many cluster type copper(I) complexes[1,203]. However, the structure of the present copper(I) complexes can be confirmed only through X-ray crystal structure studies, which we could not undertake due to the lack of this facility in our institution.

Chapter - 6

CHAPTER VI

REACTION OF MIXED BENZOIC-DITHIOCARBAMIC ANHYDRIDES WITH MERCURY(II) HALIDES

6.1 INTRODUCTION

Reactions of mixed benzoic-dithiocarbamic anhydrides with iron(III) halides and copper(II) chloride have given interesting halogenodithiocarbamato complexes. This prompted us to carry out the reactions of these anhydrides with mercury(II) halides. From such reactions, we have isolated halogeno dithiocarbamato complexes of mercury(II), $[Hg(R_2dtc)X]$ (R_2=Et_2 or Pip; X=Cl, Br or I). A brief report of the synthesis of a similar complex with the composition $[HgCl(Et_2dtc)]$ appeared in 1950[204]. An iododithiocarbamato complex of mercury with a similar empirical formula $HgI(Et_2dtc)$, has been reported[179] in 1977. This complex was obtained by the reaction of HgI_2 and Et_4tds). Another complex $[HgI_2(Et_4tds)$ was also formed during the reaction. In this chapter the synthesis and characterisation of these type of complexes are described.

6.2 EXPERIMENTAL

Materials:

Reagents used and the preparation of mixed benzoic-dithiocarbamic anhydrides are described in Chapter II.

Synthesis:

All the complexes were prepared by the same general procedure. A solution of mixed benzoic-dithiocarbamic anhydride (slightly greater than 0.01mole) in acetone (50ml) was slowly added to a solution of mercury(II) halide (0.01mole) in acetone (200ml). The solution was stirred well. The complex separated as a white or cream coloured powder was filtered, washed with ether, and dried in a desiccator over anhydrous calcium chloride.

Characterisation

Details about the characterisation techniques are given in Chapter II.

6.3 RESULTS AND DISCUSSION

During the complex formation reaction between mixed benzoic-dithiocarbamic anhydrides and mercury(II) halides the benzoyl part of the mixed benzoic-dithiocarbamic anhydride is removed probably as benzoyl halides. The characteristic smell of benzoyl chloride was noted in the reaction of the anhydrides with mercury(II) chloride. Similar observations have been made during the reaction of mixed benzoic-dithiocarbamic anhydrides with Cu(II) chloride[125].

The halogeno dithiocarbamato mercury(II) complexes are white or cream coloured powders, which are moderately soluble in benzene, nitrobenzene, acetone, chloroform and carbon tetrachloride and are insoluble in ether. The complexes were found to be pure by TLC analysis using silica gel-G as the static

Table 6.1 Analytical data of the Hg(II) complexes

Complex	Hg(%) Found (Calcd.)	Halogen(%) Found (Calcd.)	S(%) Found (Calcd.)
[Hg(Et_2dtc)Cl]	51.60	9.02	16.48
	(52.19)	(9.23)	(16.69)
[Hg(Pipdtc)Cl]	50.20	8.78	15.90
	(50.61)	(8.95)	(16.18)
[Hg(Et_2dtc)Br]	46.40	18.25	14.55
	(46.78)	(18.64)	(14.95)
[Hg(Pipdtc)Br]	45.35	18.00	14.20
	(45.51)	(18.13)	(14.55)
[Hg(Et_2dtc)I]	41.88	26.27	13.18
	(42.16)	(26.67)	(13.48)
[Hg(Pipdtc)I]	40.75	25.67	12.90
	(41.12)	(26.02)	(13.15)

Table 6.2 Molecular weights and electronic spectral data of the Hg(II) complexes

Complex	Absorption maxima, cm^{-1}	Molecular weight	
		Found	Calcd. (for a monomer)
[Hg(Et$_2$dtc)Cl]	42900 28800 24200	724	384
[Hg(Et$_2$dtc)Br]	43000 28840 24250	800	428
[Hg(Et$_2$dtc)I]	42900 28900 24300	875	475.5
[Hg(Pipdtc)Cl]	43000 29000 24300	740	396
[Hg(Pipdtc)Br]	42900 29040 24360	810	440
[Hg(Pipdtc)I]	43000 29100 24380	940	487

Table 6.3 Infrared frequencies (in cm^{-1}) of Hg(II) complexes

I	II	III	IV	V	VI	Tentative assignments
-	-	-	3500w	3500w	3500w	
-	-	-	2975w	2975w	2975w	
2900m	2900m	2900m	2900vw	2900vw	2900w	
-	-	-	2375w	2375w	2375w	
1720m	1720m	1725m	-	-	-	
1520s	1525s	1525s	1525s	1520s	1520s	
1460s	1460s	1465s	1465s	1465s	1460s	νC-N
1375s	1380s	1380s	1380vw	1380vw	1370w	
1270w	1270w	1270w	1260s	1265s	1260vs	
1245w	1245m	1245m	1240s	1240s	1230w	
1140vw	1145vw	1145vw	1120w	1140m	1140vw	
1030w	1025m	1020m	1025vw	1025w	1020w	νC=S (Band III)
980m	985m	985m	975m	975m	980w	νC=S (Band II)
910m	905m	910m	905m	905m	905w	νCSS (Band I)
830w	830w	830w	840vw	840vw	840w	
535w	530m	530m	535s	530s	540w	
330s	335s	330s	340s	340s	340s	νM-S
265s	210s	-	270s	210s	-	νM-X

s =strong; m = medium; w = weak; vw = very weak
I=[Hg(Et_2dtc)Cl]; II=[Hg(Et_2dtc)Br];III=[Hg(Et_2dtc)I]; IV=[Hg(Pipdtc)Cl];
V=[Hg(Pipdtc)Br]; VI=[Hg(Pipdtc)I].

symmetrically bound bidentate dithiocarbamate ligands and complexes with monodentate dithiocarbamate ligands have appeared in the literature[35], and monodentate bonding is associated with a splitting of greater than 20 cm^{-1} between bands II and III[205]. For the halogenodithiocarbamate complexes of mercury, this splitting is found to be ~40 cm^{-1}.The complexes exhibit two νC-N bands: one at ~1460 cm^{-1} and other at ~ 1520 cm^{-1}. Similar observations has been made in the case of tris(diethyldithiocarbamato)nitrosylruthenium(III) for which there is definite proof for the presence of monodentate dithiocarbamate ligand[206]. The absence of band at ~1460 cm^{-1} has been used to rule out monodentate bonding of the dithiocarbamate ligands in the [MoNO(R_2dtc)$_3$] complexes. All these facts clearly suggest a monodentate bonding of the dithiocarbamate ligand in these complexes.

All the complexes exhibit a strong band around 340 cm^{-1} which can be assigned to the Hg-S stretching frequency[202, 207]. The chlorodithiocarbamato mercury(II) complexes exhibit a strong band around 260 cm^{-1} which may be due to the terminal Hg-Cl stretching frequency. The stretching frequencies involving bridging chlorine[208] should have occured below 200 cm^{-1}. The bromo complexes also exhibit a band around 210 cm^{-1} which may be due to the terminal Hg-Br vibration. Because of the similarities of the properties of iodo- dithiocarbamato mercury(II) complex and other halogeno dithiocarbamato mercury(II) complexes, a terminal iodine

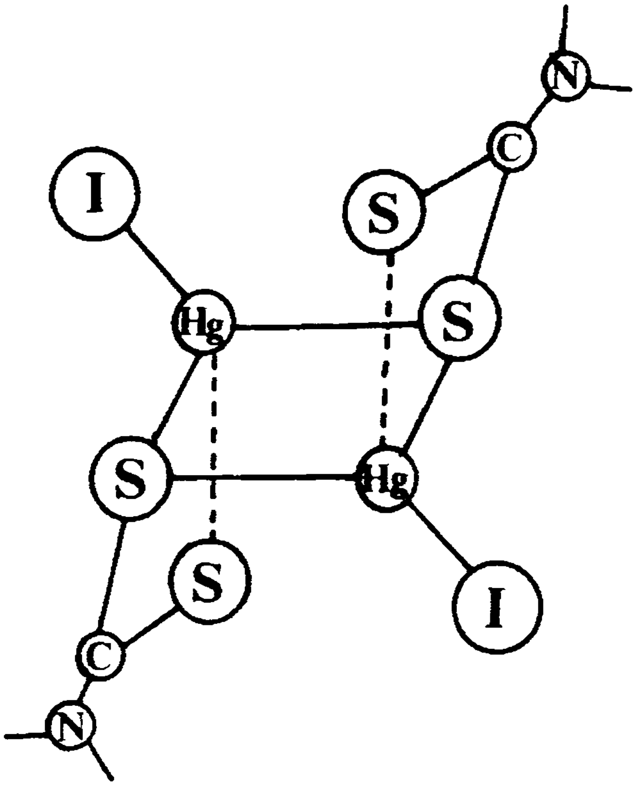


Fig. 6.1 Schematic structure of the $[HgI(Et_2dtc)]_2$ complex.

atom is presumed to be present in the iododithiocarbamato mercury(II) complexes also. This could not be verified as we were not able to record spectra below 200 cm^{-1}.

The indications of dimers in benzene and the presence of terminal halogen atom and monodentate dithiocarbamate ligand suggest that the complexes might have a structure similar to that of the iododiethyldithiocarbamatomercury(II) complex reported by Chie Chung[179].

Chapter - 7

CHAPTER VII

REACTIONS OF MIXED BENZOIC-DITHIOCARBAMIC ANHYDRIDES WITH COPPER(II) BROMIDE

7.1 INTRODUCTION

A series of bis(dithiocarbamato)-μ-dichlorodicopper(II) complexes have been prepared by reacting mixed benzoic-dithiocarbamic anhydride with copper(II) chloride in acetone[125]. But when this reaction was carried out with copper(II)bromide, analogous bromo complexes with definite stoichiometry were not obtained. It was thought that the solvent acetone has some destabilizing effect on the bromo complexes formed during the reaction. Therefore, the reaction was carried out in other solvents. While investigating the reaction in diethylether, we were able to isolate an interesting series of complexes in which copper atoms exist in +2 and +3 oxidation state. In this chapter the synthesis and characterisation of these complexes are described.

7.2 EXPERIMENTAL

Materials:

Details about the reagents used and preparation of mixed benzoic-dithiocarbamic anhydrides are given in chapter II. All the other reagents used were of Analar grade purity.

Synthesis:

All the complexes were prepared by the same general method given below:

Anhydrous $CuBr_2$ (1.1g, 0.005 mole) and the appropriate freshly recrystallised benzoic dithiocarbamic anhydride (0.006 mole), both dissolved in minimum quantity of diethylether, were mixed with stirring. An immediate complex formation was observed. The black crystalline complex was filtered off and washed with diethylether and dried in vacuum over P_2O_5.

Characterisation:

Details about the characterisation techniques are given in Chapter II.

7.3 RESULTS AND DISCUSSION

All the complexes are black crystalline solids. They are quite stable in dry atmosphere. They are insoluble in non-polar solvents like chloroform, diethylether and carbon tetrachloride, but have moderate solubility in acetone, acetonitrile, nitrobenzene, DMF and DMSO. Analytical data (*vide* Table 7.1) for copper, bromine, nitrogen and sulphur established the general empirical formulae of the complexes to be $[Cu_5(R_2dtc)_6Br_6]$ (R_2=Me_2, Et_2, Pip or Morph).

Analytical data, conductance and magnetic measurements and infrared and electronic spectral data furnish enough clues to suggest that the copper atoms in the present complexes are in a mixed oxidation state of +2 and +3, and also that the complexes contain two units of copper(III) dithiocarbamate and one unit of copper(II) dithiocarbamate and $Cu_2Br_6^{2-}$ species. The molecular formulae of the complexes may be shown as $[Cu_3(R_2dtc)_6]^{2+}[Cu_2Br_6]^{2-}$. A similar type of complex

TABLE 7.1 Analytical data of the mixed oxidation state complexes of copper

Complex (Empirical formula)	C(%) Found (Calc.)	H(%) Found (Calc.)	N(%) Found (Calc.)	Cu(%) Found (Calc.)	Br(%) Found (Calc.)	S(%) Found (Calc.)
$[Cu_3(Et_2dtc)_6]Cu_2Br_6$	21.26	3.48	4.92	18.70	28.35	22.75
$[C_{30}H_{60}Br_6Cu_5N_6S_{12}]$	(21.36)	(3.59)	(4.98)	(18.84)	(28.42)	(22.81)
$[Cu_3(Pipdtc)_6]Cu_2Br_6$	24.48	3.35	4.73	18.00	27.19	21.82
$[C_{36}H_{60}Br_6Cu_5N_6S_{12}]$	(24.58)	(3.44)	(4.78)	(18.07)	(27.26)	(21.87)
$[Cu_3(Pyrrdtc)_6]Cu_2Br_6$	21.44	2.77	4.98	18.85	28.58	22.92
$[C_{30}H_{48}Br_6Cu_5N_6S_{12}]$	(21.52)	(2.89)	(5.02)	(18.97)	(28.63)	(22.97)
$[Cu_3(Morphdtc)_6]Cu_2Br_6$	20.28	2.69	4.68	17.85	27.01	21.68
$[C_{24}H_{48}Br_6Cu_5N_6O_6S_{12}]$	(20.35)	(2.73)	(4.75)	(17.94)	(27.08)	(21.73)

$[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$ was synthesised by Cras et al[140]. by the reaction of $Cu(n\text{-}Bu_2dtc)_2$ with $CdBr_2$ and Br_2 in stoichiometric amounts. The X-ray crystal study of the complex has also been reported. This compound contains copper(II) dithiocabamate unit sandwiched between two copper(III) dithiocarbamate units with sulfur bridging between the copper atoms as shown in the Fig. 7.1.

7.3.1 Electrical conductance

The molar conductance values[209] for $10^{-3}M$ solution of 1:1 electrolyte in nitrobenzene are in the range 25-30 $ohm^{-1}\ cm^{2}\ mole^{-1}$; while those for 2:1 electrolytes are in the range 50-65 $ohm^{-1}\ cm^{2}\ mole^{-1}$. All the present complexes show a conductance value around 60 $ohm^{-1}\ cm^{2}\ mole^{-1}$, which suggests that the complexes acts as 2:1 electrolytes in nitrobenzene. The observed conductance may be due to the dissociation of the complex into two Cu(III) dithiocarbamate ions, one molecule of Cu(II) dithiocarbamate and one $[Cu_2Br_6]^{2-}$ ion, as indicated in the following equation:

$$[Cu_3(R_2dtc)_6]^{2+}[Cu_2Br_6]^{2-} \longrightarrow$$
$$2[Cu(R_2dtc)_2]^{+} + [Cu(R_2dtc)_2] + [Cu_2Br_6]^{2-}$$

Similar type of dissociation has been observed in the case of the complex, $[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$.

7.3.2 Magnetic measurements

All the complexes have a $\mu_{eff.}$ value of about 2.3 BM (Table 7.2). In order to get the contribution due to $[Cu_2Br_6]^{2-}$ unit, we

Table 7.2 Magnetic susceptibilities and magnetic moments of the mixed oxidation state complexes of copper

Complex	$\chi_M \times 10^6$ ($cm^3 mole^{-1}$)	$-\chi_D \times 10^6$ ($cm^3 mole^{-1}$)	$\chi_M' \times 10^6$ ($cm^3 mole^{-1}$)	$\mu_{eff.}$ in BM at 28 ± 2° C
$[Cu_3(Et_2dtc)_6][Cu_2Br_6]$	1375	811	2186	2.3
$[Cu_3(Pipdtc)_6][Cu_2Br_6]$	1617	763	2380	2.4
$[Cu_3(Pyrrdtc)_6][Cu_2Br_6]$	1614	776	2390	2.4
$[Cu_3(Morphdtc)_6][Cu_2Br_6]$	1400	780	2180	2.3
$(IPA)_2[Cu_2Br_6]$	333	327	660	1.3

χ_M = Molar susceptibility χ_M' = Corrected molar susceptibility

χ_D = Diamagnetic susceptibility

have synthesised $[(IPA)_2]^{2+}[Cu_2Br_6]^{2-}$ by the reaction of stoichiometric quantities of IPABr with $CuBr_2$ in alcohol[210] (where IPA= isopropyl ammonium cation) and measured its χ_M value at room temperature. The χ_M value of this compound was found to be 660 cm^3 $mole^{-1}$. Assuming nonmagnetic interaction between the cationic species, $[Cu_3(R_2dtc)_6]^{2+}$ and its anionic species $[Cu_2Br_6]^{2-}$, the χ_M values due to $[Cu_2Br_6]^{2-}$ species was subtracted from the χ_M value of the complexes. This gives a magnetic moment of 1.9 BM, which suggests the presence of only one unpaired electron in the cationic species $[Cu_3(dtc)_6]^{2+}$. This further indicates that out of the three copper atoms in the cationic species only one copper atom is in the +2 oxidation state and the other two are in the +3 oxidation state. A close similarity is seen in the magnetic moment value of the $[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$ (1.9 BM) and the corrected value for the cationic species of the present complexes suggesting similar structures for the cationic species of both the complexes.

7.3.3 Electronic spectra

The electronic spectral bands (solid state) and their assignments are given in the Table 7.3. As a low energy band is absent in the spectra of the complexes the possibility of tetrahedral structure can be excluded. The complexes show a charge transfer band around 22500 cm^{-1}. This indicates the presence of copper(II) dithiocarbamate unit in the present complexes as this band is observed in all the copper(II) dithiocarbamate complexes. Further, the complexes show a band

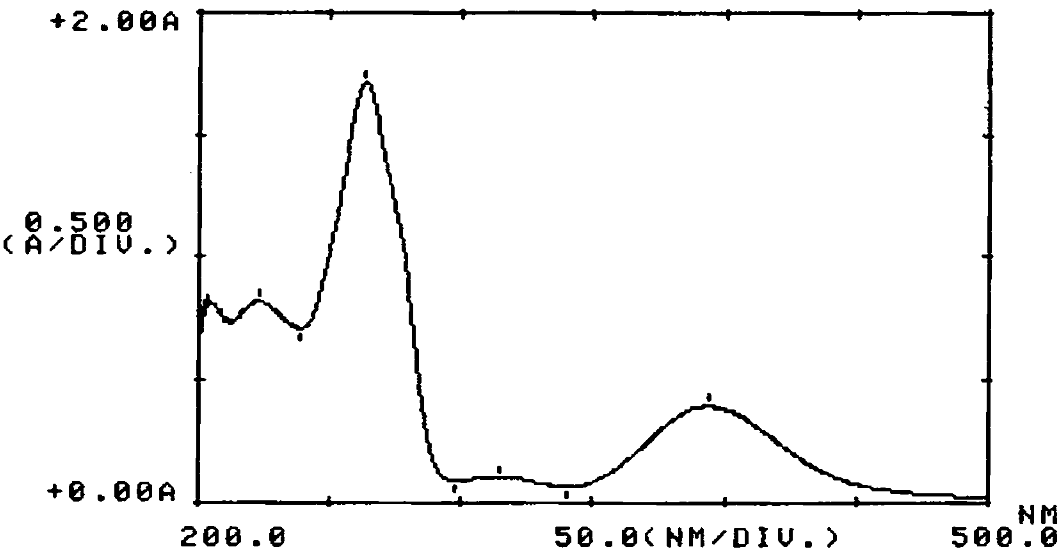


Fig. 7.1 Electronic spectra of $[Cu_3(Pipdtc)_6][Cu_2Br_6]$. (200-500 nm)

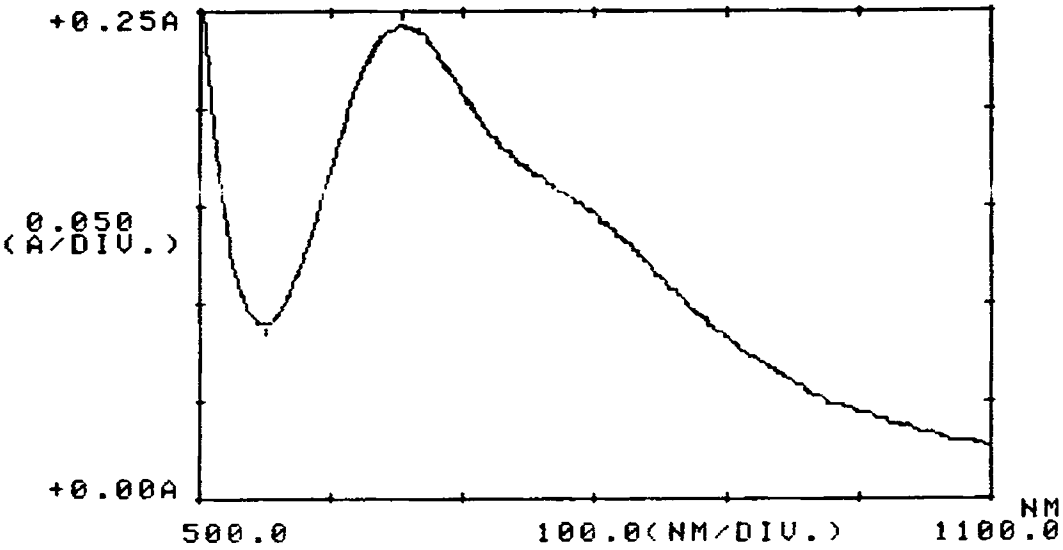


Fig. 7.2 Electronic spectra of $[Cu_3(Pipdtc)_6][Cu_2Br_6]$. (500-1100 nm)

Table 7.3 Molar conductance and electronic spectral data of the complexes

Complex	Molar conductance in nitrobenzene* $ohm^{-1}cm^{2}mole^{-1}$	Solid state electronic spectra Absorption maxima, cm^{-1}
$[Cu_3(Et_2dtc)_6][Cu_2Br_6]$	60	13700, 19000, 22700, 36400
$[Cu_3(Pipdtc)_6][Cu_2Br_6]$	65	13900, 19000, 23000, 36500
$[Cu_3(Pyrrdtc)_6][Cu_2Br_6]$	62	14700, 19000, 23300, 39000
$[Cu_3(Morphdtc)_6][Cu_2Br_6]$	60	14300, 19000, 22000, 37000

* Concentration = 10^{-3} mole $lit.^{-1}$

around 26000 cm^{-1} and a band around 14000 cm^{-1} which are exhibited more or less in these positions by $[Ni(R_2dtc)_2]$ and $[Cu(R_2dtc)_2]^+$. As Ni(II) is isoelectronic with Cu(III), these bands might have originated from the copper(III) dithiocarbamate unit. Further Ni(II) dithiocarbamates have square planar structures and hence the same stereochemistry can be assigned for copper(III) dithiocarbamate units. The band around 14000 cm^{-1} can be assigned to a $^1A_{1g} \longrightarrow {}^1B_{1g}$ transition. Furthermore, the complexes also show a shoulder band around 19000 cm^{-1}. This might be due to $[Cu_2Br_6]^{2-}$ species in the complexes as this band is observed almost at the same position in the electronic spectra of the complex, $(IPA)_2Cu_2Br_6{}^{2-}$.

7.3.4 Infrared spectra

The infrared spectral bands and the assignments of the relevant bands are given in Table 7.4. The most important criterion for a copper dithiocarbamate complex in mixed oxidation state is the presence of two C-N and two Cu-S stretching frequencies in the infrared spectrum of the complexes. In the spectra of the present complexes, two bands due to C-N stretching frequencies are observed, one around 1500 cm^{-1} and the other around 1540 cm^{-1}. This suggests the presence of copper(II) dithiocarbamate and copper(III) dithiocarbamate units in the complexes, as the 1500 cm^{-1} band is observed in the spectra of copper(II) dithiocarbamates and the 1500 cm^{-1} band is observed for the copper(III) dithiocarbamates. It is also observed that the intensity of the band around 1540 cm^{-1} is almost twice that of the

Table 7.4 Infrared spectral data of the mixed oxidation state complex of copper (in cm^{-1})

I	II	III	IV	Tentative assignments of the more relevant bands
2960w	2920w	2955w	2960w	
2920w	2840w	2920w	2925w	
2300w	2310w	2320w	2300w	
1540s	1545s	1540s	1540w	νC-N of the Cu(III) unit
1500m	1480s	1470m	1500m	νC-N of the Cu(II) unit
1430m	1440s	1440m	1430m	
1380w	1340m	1380w	1380w	
1350w	1345m	1340w	1355w	
1290m	1290m	1290m	1285m	
1260s	1265m	1270s	1260s	
1240s	1235m	1230s	1250s	
1210w	1200s	1210w	1210w	
1165w	1165w	1170w	1165w	
1100s	1110s	1100s	1110s	

v = strong; m = medium w = weak

I = $[Cu_3(Et_2dtc)_6]\ [Cu_2Br_6]$

II = $[Cu_3(Pipdtc)_6]\ [Cu_2Br_6]$

III = $[Cu_3(Pyrrdtc)_6]\ [Cu_2Br_6]$

IV = $[Cu_3(Morphdtc)_6]\ [Cu_2Br_6]$

Contd..

I	II	III	IV	Tentative assignments of the more relevant bands
1050m	1045m	1055m	1045s	
1020s	1010s	1025s	1025s	νCSS
995w	990w	990w	995w	
965w	970w	970w	965w	
875m	880m	880w	880m	
815w	810w	810m	820w	
70[illegible]m	675m	700m	710m	
650w	660w	650w	650w	
530s	525s	530s	520s	
440w	450w	430w	440w	
390s	390s	395s	400s	νCu-S of the Cu(III) unit
340s	340s	340s	335s	νCu-S of the Cu(II) unit
305m	310w	305m	310w	
290m	295m	290w	290w	
260w	265m	269w	260w	

v = strong; m = medium w = weak

I = $[Cu_3(Et_2dtc)_6]$ $[Cu_2Br_6]$ II = $[Cu_3(Pipdtc)_6]$ $[Cu_2Br_6]$

III = $[Cu_3(Pyrrdtc)_6]$ $[Cu_2Br_6]$ IV = $[Cu_3(Morphdtc)_6]$ $[Cu_2Br_6]$

band at 1500 cm^{-1}, which suggests that there are two copper(III) dithiocarbamate units and one copper(II) dithiocarbamate unit. The complexes exhibit the Cu-S stretching frequency due to the copper(II) dithiocarbamate at 360 cm^{-1} and that due to copper(III) dithiocarbamate at 410 cm^{-1}. Intensity relationship observed for νC-N is also seen in the case of νCu-S: The intensity of the band at 410 cm^{-1} is almost twice as that of the band at 360 cm^{-1}. This further confirms the presence of two copper(III) units and one copper(II) unit.

Mechanism of formation of the complexes

Mixed valence complexes are usually found in systems involving free radicals. So in the formation of these complexes, the involvement of free radicals are expected. The mechanism for the formation of the complexes is not very clear. However we suggest the following free radical mechanism:

$$4\,CuBr_2 \rightleftharpoons 2\,CuBr^+ + [Cu_2Br_6]^{2-}$$

$$C_6H_5-\underset{\underset{O}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-NR_2 + Br^- \longrightarrow C_6H_5COBr + R_2dtc^-$$

$$CuBr^+ + 2R_2dtc^- \longrightarrow [Cu(R_2dtc)_2] + Br^-$$

$$C_6H_5COBr \longrightarrow C_6H_5CO. + Br.$$

$$Cu(R_2dtc)_2 + Br. \longrightarrow Cu(R_2dtc)_2^+ + Br^-$$

$$2C_6H_5CO. \longrightarrow (C_6H_5CO)_2$$

$$2[Cu(R_2dtc)_2]^+ + [Cu(R_2dtc)_2] + [Cu_2Br_6]^{2-} \longrightarrow [Cu_3(R_2dtc)_6]^{2+}[Cu_2Br_6]^{2-}$$

Conclusion

Based on the above discussions a structure similar to the $[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$ can be assigned to the present complexes. A schematic diagram of the cationic species of this complex is given in the Fig. 1.2.

Chapter - 8

CHAPTER VIII

REACTION OF THIONYL CHLORIDE WITH BIS(DITHIOCARBAMATO)COPPER(II) COMPLEXES

8.1 INTRODUCTION

The synthesis and properties of a copper(III) complex, [$CuBr_2(Bu_2dtc)$], has been reported earlier by Beurskens[135] *et al*. The crystal structure of this complex shows a planar four coordination of the copper atom. Analogous chloro complexes were also reported. These copper(III) dithiocarbamato complexes are prepared by reaction of bromine or chlorine with either copper(II) or copper(I) dithiocarbamates. While investigating the reaction of thionyl chloride with copper(II) dithiocarbamates, we have found a simple and alternative route to the chloro dithiocarbamato complexes of copper(III). In this chapter, our studies on the synthesis and characterisation of these copper(III) complexes are described.

8.2 EXPERIMENTAL

Materials:

Details about the reagents and preparation of sodium dithiocarbamates are given in Chapter II.

Synthesis

All the complexes were prepared by the same general method given below:

Sodium salt of dithiocarbamate (0.02 mole- 0.36g of $Na^+Et_2dtc^-$; 0.35g of $Na^+Pipdtc^-$; 0.32g of Na^+Pydtc^- or 0.35g of $Morphdtc^-$) was dissolved in 100 ml water. Copper sulphate pentahydrate (0.01 mole; 0.25 g.) was dissolved in 50 ml water and this was added to the ligand solution with constant stirring. The copper(II) dithiocarbamate formed is extracted into the benzene layer by shaking with 50 ml portions of benzene in a separating funnel. The extracts were collected and was dried using anhydrous sodium sulphate. Thionylchloride in carbon tetrachloride was added drop by drop into the benzene solution with vigorous stirring. The dark brown colour of the solution changes gradually into red with immediate separation of a red complex. The complex formed was filtered, washed several times with carbon tetrachloride.

Characterisation

Details about the characterisation techniques are given in Chapter II.

8.3 RESULTS AND DISCUSSION

When thionyl chloride was added to a saturated solution of bis(dithiocarbamato)copper(II) complex in benzene a red complex was immediately precipitated out. The complexes decompose on exposure to moisture. However the compounds when kept in dry condition are very stable. In the presence of polar solvents such as acetone or ethanol, these compounds are readily decomposed to form the corresponding copper(II) dithiocarbamates.

Analytical data for copper, chlorine, nitrogen and sulphur, as summarised in Table 8.1, established the general empirical formulae of the complexes to be $[Cu(R_2dtc)Cl_2]$ ($R=Et_2$, Pip, Morph or Pyrr). The complexes are insoluble in almost all solvents. Therefore molar conductance values could not be determined.

8.3.1 Magnetic measurements

The molecular formula of the complexes suggest that the complexes are in the +3 oxidation state, and hence are of d^8 ions. The complexes of d^8 having square planar structure are usually diamagnetic. All the present complexes might have square planar structure, as they are diamagnetic. The small amount of residual paramagnetsm (~ 0.4 BM) could be due to the temperature independent paramagnetism. Such residual paramagnetism is observed in the square planar nickel(II) dithiocarbamate complexes. The complexes, therefore, must be in the +3 oxidation state.

8.3.2 Electronic Spectra

The electronic spectral data of these complexes are given in Table 8.2. The complexes exhibit bands around 14600 cm^{-1}, 27000 cm^{-1} and 27000 cm^{-1}. Thus the spectra of the present copper(III) complexes almost resemble those of the red coloured square planar Ni(II) complexes like $[CuCl_2(Bu_2dtc)]$, $[CuBr_2(Bu_2dtc)_2]$ etc.[194] The band at 14600 cm^{-1} may be assigned to $^1A_{1g} \longrightarrow {}^1B_{1g}$ transition.

Table 8.1 Analytical data of the Cu(III) complexes

Complex	N(%) Found (Calc.)	Cu(%) Found (Calc.)	Cl(%) Found (Calc.)	S(%) Found (Calc.)
[Cu(Et$_2$dtc)Cl$_2$]	4.80	22.42	28.15	22.58
[C$_5$H$_{10}$Cl$_2$CuNS$_2$]	(4.95)	(22.48)	(28.27)	(22.68)
[Cu(Pipdtc)Cl$_2$]	4.68	21.50	24.02	21.66
[C$_6$H$_{10}$Cl$_2$CuNS$_2$]	(4.75)	(21.56)	(24.06)	(21.76)
[Cu(Pyrrdtc)Cl$_2$]	4.89	22.58	25.18	22.74
[C$_5$H$_8$Cl$_2$CuNS$_2$]	(4.99)	(22.64)	(25.26)	(22.84)
[Cu(Morphdtc)Cl$_2$]	4.67	21.36	23.75	21.56
[C$_5$H$_8$Cl$_2$CuNOS$_2$]	(4.72)	(21.42)	(23.90)	(21.61)

Table 8.2 Magnetic and electronic spectral data of the Cu(III) complexes.

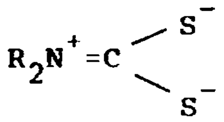
Complex.	Absorption maximam cm^{-1}	Assignments	$\mu_{eff.}$ in BM
$[Cu(Et_2dtc)Cl_2]$	43300	Intraligand transition	0.5
	27200	Charge transfer transition	
	14600	$^1A_{1g} \longrightarrow {}^1B_{1g}$	
$[Cu(Pipdtc)Cl_2]$	43200	Intraligand transition	0.4
	27200	Charge transfer transition	
	14600	$^1A_{1g} \longrightarrow {}^1B_{1g}$	
$[Cu(Morphdtc)Cl_2]$	43200	Intraligand transition	0.4
	27200	Charge transfer transition	
	14700	$^1A_{1g} \longrightarrow {}^1B_{1g}$	
$[Cu(Pyrrdtc)Cl_2]$	43300	Intraligand transition	0.4
	27200	Charge transfer transition	
	14600	$^1A_{1g} \longrightarrow {}^1B_{1g}$	

The band at - 27000 cm^{-1} is apparently due to charge transfer transitions and the band at - 43200 cm^{-1} can be attributed to the electronic transitions within the ligand.[135]

8.3.3 Infrared Spectra

Infrared spectral data of the complexes and its tentative assignments of the relevant bands are presented in Table 8.3.

On comparing the spectrum of dichlorocomplexes with its corresponding dithiocarbamate complexes, significant deviations are found in the C-N stretching frequencies. They occur around 1580 cm^{-1} in the chloro complexes, while they are around 1500 cm^{-1} in the copper(II) dithiocarbamates. In dithiocarbamato complexes, the presence of C-N stretching frequency around 1500 cm^{-1} is accepted as arising from a polar structure as given below,



and the contribution of this resonance form will be increased in the complexes with higher C-N stretching frequencies. Thus, the dichloro complexes, which show the C-N stretching frequencies around 1580 cm^{-1}, can be thought to have much higher contribution of this resonance form than that in the copper(II) dithiocarbamates.

The special feature of the dithiocarbamato ligand is an additional π electron flow from the nitrogen atom to the sulphur

Table 8.3 Infrared frequencies of copper(III) dithiocarbamato complexes

$[Cu(Et_2dtc)Cl_2]$	$[Cu(Pipdtc)Cl_2]$	$[Cu(Pyrrdtc)Cl_2]$	$[Cu(Morphdtc)Cl_2]$	Tentative assignments
3220w	3260w	3240w	3580w	
2980w	2940w	2960w	2920w	
1630w	1640w	1640w	1610w	
1585m	1585m	1580m	1580m	$\nu C=N$
1460s	-	-	1520m	
1440s	1440vs	1430vs	1435vs	
1380m	-	-	1380vw	
1350w	1350m	1340w	1340w	
1260m	1270w	1255w	1260m	$\nu C-N$
1210m	1230w	1235w	1240m	
1100w	1120vw	1160sh	1160s	
1080w	1080w	1090w	1100m	
1005w	1010w	990w	1020w	
-	960w	970vw	970m	$\nu_a C-S$
920w	940w	935vw	885w	
-	870vw	880vw	875w	
855w	850m	850w	850w	
730vw	710m	705w	720m	
605w	610s	600w	590m	

Contd....

$[Cu(Et_2dtc)Cl_2]$	$[Cu(Pipdtc)Cl_2]$	$[Cu(Pyrrdtc)Cl_2]$	$[Cu(Morphdtc)Cl_2]$	Tentative assignments
580m	560w	555w	550w	
500m	520m	515vw	520m	
460w	470w	465vw	470vw	
400s	405s	400s	410s	νCu-S
310s	305s	310m	305m	νCu-Cl
280w	295w	290w	280w	
260w	255w	250w	265w	
225w	220w	220w	220w	

atoms via a planar delocalised π orbital system. The net effect is a strong electron donation, resulting in a high electron density on the metal. The stability of the complexes is possible because of the high oxidation state of copper and also because of the presence of electron withdrawing chlorine ligands.

The far IR spectra of the complexes have been studied and the spectral data are presented in Table 8.3. The strong band seen around 310 cm^{-1} in the spectra of the present complexes may be due to Cu-Cl stretching vibration. The Cu-S stretching frequencies were observed around 400 cm^{-1} in all the present Cu(III) complexes where as this band is observed around 360 cm^{-1}in copper(II) complexes. This suggests that Cu-S bond has greater strength in the chloro complex. The increase in bond strength can be explained on the basis of M.O.scheme set up from the E.S.R. spectroscopic studies of $[Cu(Et_2dtc)_2]$. The studies indicated the unpaired electron to be situated in an antibonding σ orbital, which is mainly composed of the metal and sulphur orbitals. Upon the oxidation of $Cu(R_2dtc)_2$ to $[Cu(R_2dtc)Cl_2]$ this electron will be removed causing in an increase in Cu-S bond strength.

In the earlier preparations, chlorine gas was used for the oxidation of $[Cu(dtc)_2]$ to $[Cu(dtc)Cl_2]$. Eventhough thionylchloride is used in the present preparations, it appears that, here also chlorine is acting as the oxidising agent. Chlorine might have formed in the reaction medium by the interaction of thionyl chloride with oxygen of the atmosphere. We propose the following reaction scheme for the formation of the present copper(III) dithiocarbamato complexes:

$$SOCl_2 + 1/2\ O_2 \longrightarrow SO_2Cl_2$$

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

$$[Cu(R_2dtc)_2] + Cl_2 \longrightarrow [Cu(R_2dtc)Cl_2] + R_2dtc^-$$

Cases of thionylchloride acting as chlorinating agent are already known. The involvement of oxygen in such reactions has been noted by Pillai and Bhatt[211] in the chlorination of quinoxaline systems using thionyl chloride.

In the preparation of $[Cu(dtc)Cl_2]$ using chlorine gas, if correct stoichometry is not maintained, chances of forming other types of complexes like $[CuCl_3(R_2dtc)]$ in which copper has a final oxidation state of IV are also there. Where as the preparation of using thionyl chloride, $[Cu_2(dtc)Cl_2]$ complexes in good purity are obtained, even if the reactants are not added in the correct stoichometric quantities. This might probably due to the slow release of chlorine during the reaction.' Thus the present method appears to be a simple and more convenient alternative route to the dithiocarbamato copper (II) complexes.

SUMMARY

The thesis deals with the synthesis and characterization of some metal complexes of 1,1-dithio ligands such as dithiocarbamates, xanthates and 2-aminocyclopent-1-ene-1-dithiocarboxylate(ACDA) and its N-alkyl derivatives.

The thesis is divided in to eight chapters. Chapter I presents a general discussion on the metal complexes of 1,1-dithio chelate ligands. Scope of the present investigation is also described in this chapter. Chapter II gives detailed information concerning the actual experimental work.

Chapter III deals with the synthesis and magnetic and spectral behaviour of the isopropylaminocyclopent-1-ene-1-dithiocarboxylate (i-PrACDA) complexes of Cr(III), Mn(III), Fe(III), Co(III), Ni(II) and Cu(I). The empirical formulae of the complexes agree with $[M(i\text{-}PrACDA)_3]$ for the chromium, manganese, iron and cobalt complexes, [Ni(i-PrACDA)] for the nickel complex and [Cu(i-PrACDA)] for the copper complex. The complexes, except the copper complex, have moderate solubility in nonpolar solvents. The low solubility indicates a polymeric structure for the copper complex. The present complexes are found to be more soluble than the corresponding complexes formed by ACDA. The complexes behave as nonelectrolytes in nitrobenzene. Electronic spectra and magnetic behaviour suggest that the complexes of Cr(III), Mn(III), Fe(III), Co(III) are octahedral complexes and that of Ni(II) is square planar. Infrared and NMR studies revealed that the nitrogen atom of i-PrACDA is not involved in bonding . The properties of the present complexes are similar to that of the dithiobenzoates and xanthates.

Chapter IV is a discussion on the synthesis and characterisation of some new mixed ligand complexes containing dithiocarbamate and ACDA ligands . Five complexes have been synthesised by reacting bis(dithiocarbamato)-μ-dichloro dicopper(II) complexes with ACDA and its N-alkyl derivatives. They are [Cu(Me$_2$dtc)(ACDA)], [Cu(Pipdtc)(n-BuACDA)], [Cu(Pipdtc)(i-PrACDA)], [Cu(Morphdtc)(i-PrACDA)] and [Cu(Morphdtc)(n-BuACDA)]. All the complexes are red in colour. The complexes have $\mu_{eff.}$ values around 1.9 BM and behave as non-electrolytes in nitrobenzene. ESR, IR and electronic spectra of the complexes have been studied, and the spectral data suggest that the present mixed ligand complexes have structures similar to that of simple dithiocarbamate complexes.

In Chapter V, details about the isolation and characterisation of some chloroxanthato complexes of copper(I) are described. The complexes were synthesised by reacting mixed benzoic-xanthic anhydride with $CuCl_2$ in acetone. These reactions appear to behave like the clock reactions. The complexes have the general empirical formula, [Cu$_2$(RXant)Cl] (R=i-Bu, sec-Bu, n-Bu or i-Pr). The complexes are insoluble in almost all solvents indicating a polymeric structure for these complexes. The complexes are diamagnetic in nature. The far IR spectra indicate that the chlorine in these complexes acts as a bridging ligand. A cluster type structure has been suggested for these complexes.

Chapter VI deals with the characterisation of the complexes isolated from the reaction of mixed benzoic-dithiocarbamic anhydrides with mercury(II) halides. The complexes are of the type, $[HgX(R_2dtc)]$ (R_2=Et_2 or Pip, X=Cl, Br or I). The complexes are non-electrolytes in nitrobenzene. They are found to be dimeric in benzene solution. The IR spectra of the complexes indicate monodentate bonding for the dithiocarbamate ligand and absence of halogen bridges. Analytical and spectral studies, in these cases revealed that the structure of these complexes is similar to that of the reported dimeric complex, $[HgI(Et_2dtc)]_2$: This complex has terminal iodine atoms and two mercury(II) ions bridged by unidentate Et_2dtc ligand, and was obtained by reacting tetraethylthiuram disulphide with HgI_2.

Synthesis and characterisation of the complex isolated from the reactions of mixed benzoic-dithiocarbamic anhydrides with copper(II) bromide are presented in Chapter VII. The complexes are insoluble in solvents like chloroform, diethylether and carbon tetrachloride; but, they have moderate solubilities in acetone, methanol and nitrobenzene. The complexes are 2:1 electrolytes in nitrobenzene. The complexes are of the type, $[Cu_3(R_2dtc)_6]^{2+}[Cu_2Br_6]^{2-}$ (R_2=Me_2, Et_2, Pip or Morph). Analytical data, conductance and magnetic measurements and infrared and electronic spectral data furnish enough clues to suggest that the copper atoms in these complexes are in a mixed oxidation state of +2 and +3 , and also that complexes contain two units of Cu(III) dithiocarbamates and one unit of Cu(II) dithiocarbamate. A similar type of complex $[Cu_3(Bu_2dtc)_6]^{2+}[Cd_2Br_6]^{2-}$ was synthesised by Cras *et al.*[140] by the reaction of $[Cu(n\text{-}Bu_2dtc)_2]$ with $CdBr_2$ and Br_2 in stoichiometric amounts.

Chapter VIII deals with the synthesis and characterisation of complexes formed by the reaction of thionyl chloride with $[Cu(R_2dtc)_2]$ complexes. The complexes are of the type $[Cu(R_2dtc)Cl_2]$ ($R=Et_2$, Pip, Morph or Pyrr), and are insoluble in almost all solvents. Magnetic and spectral (IR and electronic) behaviour of the complexes suggest that these are copper(III) complexes.

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