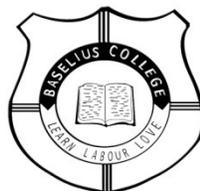


***SYNTHESIS AND CHARACTERISATION OF MIXED LIGAND
DITHIOCARBAMATO COMPLEXES OF Ni(II) AND Cu(II)***

**MINOR PROJECT WORK
UNDER
UNIVERSITY GRANTS COMMISSION 2014-2016**

**A MINOR PROJECT WORK OF JINU MATHEW
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BASELIUS COLLEGE
KOTTAYAM**

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2014**



DECLARATION



I hereby declare that the project work entitled "*SYNTHESIS AND CHARACTERISATION OF MIXED LIGAND DITHIOCARBAMATO COMPLEXES OF Ni(II) AND Cu(II)*" is a bonafide work carried out in the Department of Chemistry, Baselius college, Kottayam under minor UGC project of XII plan.

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INTRODUCTION

There has been a prodigious upsurge of knowledge in the chemistry of transition metal complexes with sulphur donor ligands. A major class of sulfur containing ligands is obtained by the general reaction of carbon disulphide with various nucleophiles. Carbon disulphide enters into reaction with a variety of nucleophiles. Its reaction with nucleophiles RO-, RNH- and R₂N- are of considerable interest; the products in these cases are o-alkyldithiocarbonates (xanthates), N-monoalkyldithiocarbamates and N,N-dialkyldithiocarbamates respectively. Dithiocarbamate anions are strong complexing agents and give rise to a large number of chelate complexes with metal ions.

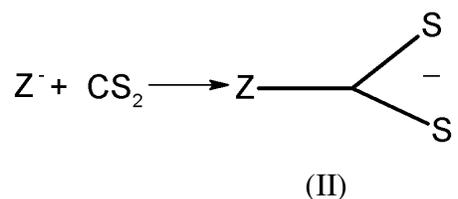
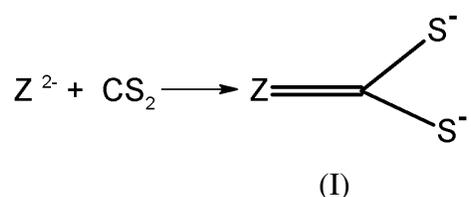
Dithiocarbamates have considerable industrial and technological significance and have a variety of uses. Organic dithiocarbamate have received much attention due to their pivotal role in agriculture¹ and their intriguing biological activities². Recently they are used in the synthesis of ionic liquids³. Their chelating properties allow them to be used as antidotes against nickel and copper poisoning (Wilson's disease)⁴, in analytical determination of heavy metals, in waste water treatment and as rubber vulcanization accelerators. In the field of medicine these compounds also find application in the treatment of chronic alcoholism⁵ and in fungi and bacteria related diseases, and they have also received some attention as potential auxiliaries in oncological chemotherapy and in the prevention of arteriosclerosis. Diethyl dithiocarbamate are known to inhibit the activity of Cu/Zn-superoxide dismutase (SOD) through the withdrawal of copper from the protein both in vivo and invitro⁶, and their chelating property with copper has made them strong inhibitors of NF-κB signalling pathway⁷. Some dialkyl-substituted dithiocarbamates have proved to be an efficient anti-alkylating, anti-HIV and froth-floatation agents⁸. Therefore, there is a continuing interest in the synthesis of new dithiocarbamates and their complexes.

1.1. Dithiocarbamate

It is not clear when dithiocarbamate was first synthesized, but certainly they have been known for at least 150 years, Debus reported the synthesis of dithiocarbamic acids as early as 1850. The first synthesis of transition metal dithiocarbamate complex is also unclear, however, in

a seminal paper in 1907, Delepine reported on the synthesis of a range of aliphatic dithiocarbamate and also salts of di-iso-butyl dithiocarbamate with transition metals including chromium, molybdenum, iron, cobalt, nickel, zinc and gold. He also noted that while dithiocarbamate salts of alkali and alkaline earth metals are water soluble, those of transition metals, p- block metals and lanthanides were precipitated from water to give salts soluble in ether and chloroform and even in some cases in benzene and carbon disulphide.

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

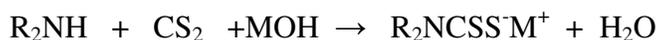


I and II are the deprotonated forms of the dithio acid and dithiol respectively

A wide variety of ligands are thus available by merely varying the nucleophile. When carbon disulphide reacts with either aliphatic/ aromatic primary or secondary amines, dithiocarbamate salts are formed according to the scheme:



Ammonium and trialkylammonium salts (NH_4^+ , R_3NH^+), which are synthetically useful, can be prepared by the reaction of carbon disulphide and an amine in dry ethanol or diethyl ether with excess ammonia or trialkylamine⁹. Alkali metal dithiocarbamate are obtained by treating primary and secondary amines with carbon disulphide in the presence of NaOH, KOH or n-BuLi.



This method has the advantage that only one equivalent of amine is required, and consequently it is more efficient than the original method when expensive amines are employed as substrates. The dithiocarbamates derived from primary amines are unstable and are converted into the isothiocyanates in the presence of bases. Although the disubstituted dithiocarbamates are more stable, they tend to decompose under acidic conditions.

Facile reactions with a metal salt, often via simple metathesis, yield the corresponding, metal dithiocarbamate. The stability of such complexes is renowned and readily explained by the significant contribution of resonance form (b) to the overall electronic structure (Fig.1) ensuring that this anion is a very effective ligand for metals.

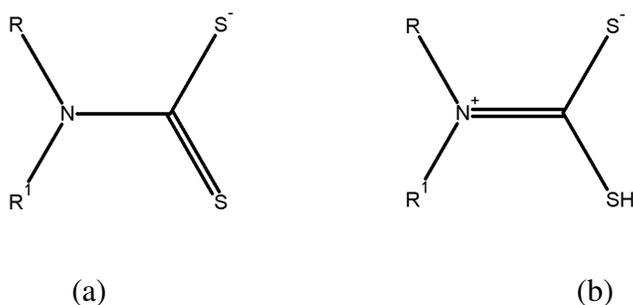


Figure 1: Resonating structures of dithiocarbamate

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. Dithiocarbamate salts have variable stability. Purification is achieved by crystallization but the yield can be very disappointing since the salts may decompose, particularly in the case of monoalkyl dithiocarbamate salts, which are unstable and decompose to yield isothiocyanates in basic solution. The mechanism for the formation of dithiocarbamate salts has been investigated, and the rate of formation is inversely proportional pH^{10} .

Although the sulphur atom of dithiocarbamate possesses σ donor and π back donation capability, there is an additional π electron flow from nitrogen to sulphur via planar delocalized π orbital system. This effect results in strong electron donation and hence more electron density on the metal leading to its next higher oxidation state. Dithiocarbamates are strong complexing agents and give rise to a large number of interesting complexes with metal ions.

The dithiocarbamate group has been found to act as a uninegative bidentate ligand, coordinating through both sulfur atoms¹¹. Both four- and six-coordinated complexes of a number of transition metal ions have been isolated. The possible modes of coordination of dithiocarbamate are shown in Fig. 2.

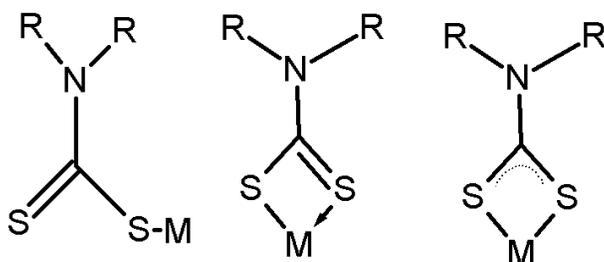


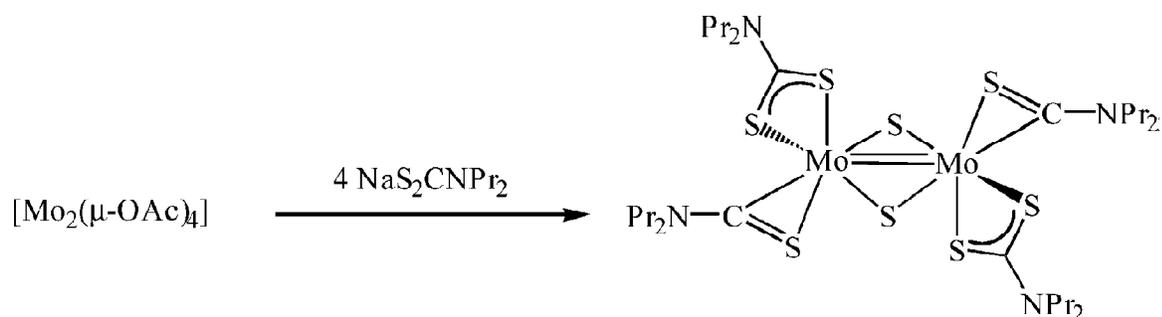
Figure 2: Modes of coordination of dithiocarbamate

In anisobidentate mode metal to sulphur bonds are not equivalent, so they exhibit only bidentate mode possibility. The dithiocarbamate ligand forms a negative anion, with delocalized π electron, which is able to form neutral chelate rings in complexes of the form: $M(dtc)_n$ (n = oxidation state of the metal).

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 Schwaab¹², Ul'ko¹³ and Hulanicki¹⁴ and their structural aspects have been reviewed by Eisenburg. The reviews by Coucouvanis, and Burns et al. cover the major facts of dithiocarbamate metal complexes and related systems and are particularly invaluable.

Earliest work on dithiocarbamate complexes were done by Von Braun¹⁵ and Delepine. Information about dithiocarbamate can also be seen on several reviews on sulphur complexes¹⁶. Chemistry of dithiocarbamate and other dithioacids complexes has been reviewed by Coucouvanis¹⁷.

Dithiocarbamates are an important class of ligand, being capable of stabilising transition metals in a wide range of oxidation states. In majority cases, they act merely as non-sterically demanding ancillary ligands. However, under certain circumstances the ligand can behave in a non-innocent fashion, as in the case of the following reaction:



This reaction can be viewed as an oxidative–addition reaction. Increasing number of examples of the non-innocent behavior¹⁸ of dithiocarbamates has been reported in the last few years. The majority cases involve the cleavage of one (or both) of the sulfur–carbon bonds. A number of other different types of non-innocent behavior have also been found. These include the addition of dithiocarbamates to unsaturated ligands and the insertion of the unsaturated groups into metal–sulfur bond(s) of dithiocarbamates.

Ability of dithiocarbamate (dtc) ligands to stabilize a wide range of oxidation states and their associated metal centered electrochemistry¹⁹ are the key factors in their applications. Matthew et al.²⁰, for the first time, explored the use of dithiocarbamate in stabilizing the formation of gold nanoparticles via strong S-Au interaction and combination of steric and electrostatic repulsion between ligand shell of nanoparticles preventing agglomeration. They are found to be stable even after a few months' storage in air. The relative ease with which dithiocarbamate ligand can be incorporated into a variety of inorganic, organic and biological

frameworks offer an exciting opportunity for the future fabrication of novel surface modified nanoparticles materials. Later in 2009, Edward et al.²¹ synthesized polyfunctional variants of dithiocarbamate ligand using piperazine dithiocarbamate and explored the use of such species to the emerging field of gold nanoparticles. Recently an effective protocol was established for the synthesis of silver nanoparticles by using dithiocarbamate derivatives as the protecting ligand²².

The use and potential utility of tin/organotin dithiocarbamate compounds were reviewed by Edward²³. Tin dithiocarbamates have also proven useful as precursors for SnS nanoparticles. New Sn(IV) dithiocarbamate complexes were synthesized by Juan et al., which can be used to sense the presence of O-donor anions at very low concentration by the displacement of metal coordinated dithiocarbamate²⁴.

The iron(II) and iron(III) dithiocarbamates have been studied for their spin crossover phenomenon²⁵, radical traps for NO²⁶ and as antioxidants and pro-oxidants in biological systems²⁷. Studies on spin cross over in iron(III) systems have been very fascinating for past 3 decades²⁸⁻²⁹. As early as 1931 Cambi and coworkers prepared iron(III)N,N-dialkyldithiocarbamates, the first compounds reported to exhibit a spin equilibrium. Rickard et al.³⁰ studied several tris(N,N-dialkyldithiocarbamato)iron(III) complexes and rate of exchange between high and low spin state were estimated to be greater than 10^7 s^{-1} . Effective magnetic moment of these complexes shows wide variation ranging from the high spin to the low spin values. The changes in μ_{eff} values with temperature reveal that there is “an equilibrium between 2 magnetically isomeric forms”³¹. Later this hypothesis was re-examined by Merrithew et al. for dicyclohexyl, dimethyl, and diisopropyl dithiocarbamates to determine whether the temperature dependence of Mossbauer spectra is consistent with the above hypothesis³². The spectra never show the presence of 2 doublets which would be expected if 2 spin states were in equilibrium. The problem of accounting for unusual magnetic behaviour of $[\text{Fe}(\text{R}_2\text{dtc})_3]$ could be better explained in terms of spin mixed state.

Sonal et al.³³ synthesised four asymmetrically substituted tris(*N*-alkyl,*N'*-hydroxyethylthiocarbamato)iron(III) complexes, $[(\text{OHCH}_2\text{CH}_2)\text{RNCS}_2]_3\text{Fe}$ (where R=CH₃, C₂H₅, *n*-C₃H₇ or *n*-C₄H₉) and their variable temperature Mössbauer spectral and magnetic

moment studies suggest that all the complexes tend to become nearly low spin at 77 K. Room temperature Mössbauer spectra of all the complexes exhibit an asymmetric doublet which could be resolved into two doublets corresponding to high and low spin states in equilibrium. Also the rare occurrence of iron (III) in an $S=3/2$ ground state and the unusual coordination of iron atom have made chlorobis(dithiocarbamato)iron(II) complexes an interesting series for study³⁴. In addition an investigation of $[\text{FeCl}(\text{Et}_2\text{dtc})_2]$ has shown a ferromagnetic transition in this chelate at 2.43K³⁵. Electronic properties of Fe(III) bis and tris dithiocarbamates are continuing to be an area of immense research.

Crystallographic analysis of diorganotin dithiocarbamates²³, $\text{R}_2\text{Sn}(\text{S}_2\text{CNR}_2)_2$ are interesting in terms of structural diversity. These complexes show four distinct structural motifs. Of these 3 motifs are related to each other with two asymmetrically coordinating dtc ligand. Crystal structure of $[\text{Cu}(\text{Pdtc})_2]_2$ (Pdtc=Pyrrolidine dithiocarbamate) and $[\text{Cu}(\text{Ppdtc})_2]_2$ ³⁶ has shown that it possess a centre of symmetry with Cu(II) ions having distorted square pyramid coordination sphere. The basal coordination positions are occupied by 4 sulphur atoms belonging to the two dtc ligands. Crystal structure of $[\text{Zn}(\text{Pdtc})_2]$ (= pyrrolidinedithiocarbamate)⁷ was examined. The complex is dinuclear with a centre of symmetry and Zn²⁺ has distorted tetrahedral environment.

Copper(II) dithiocarbamate complexes are reported to have been prepared by the oxidation of metal with tetra alkyl thiuram disulphide in chloroform or benzene. Copper(I) dithiocarbamates are obtained by treating copper(I) oxide with the sodium salts of the ligands in an inert atmosphere. Inert atmosphere is required in the synthesis of Mn(II), Co(II) and Fe(II) dithiocarbamate complexes also, as these complexes are easily oxidized to the corresponding metal(III) complexes in the presence of air³⁷. 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. Heavy metal dithiocarbamates can be obtained by adding soluble salt of a heavy metal to the solution of a sodium or ammonium salt of the required dithiocarbamic acid. Aromatic amines react less readily with carbon disulphide, and dithiocarbamate salts from these substrates are best prepared under anhydrous conditions using strong bases such as NaH in THF or KOH in DMSO³⁸.

During the past few years, it has been shown that dithiocarbamate ligands are excellent candidates for crystal engineering as well as for the preparation of macrocycles, cages, catenanes and nanoparticles. These compounds are being investigated to gain insight into the nature of the sulfur-metal bond in many biomolecules. Amino acids and their derivatives are attractive ligands due to their importance in biological systems and have been widely studied. Many proteins have cysteine and methionine residues and hence dithiocarbamate derivatives of α -amino acids may be valid models for the study of the coordination of proteins to metal ions. The complexes formed between metal ions and dithiocarbamate derivatives of amino acids have been reported.

Properly designed amino acid dthc ligand have been employed for the generation of macrocyclic assemblies having a double calyx shaped conformation [Jorge Cruz, Manuel Carillo et.al.; *Inorg.Chem.*2008,47,9874-9885]. Most of the reported dithiocarbamate derivatives of amino acids contain the dithiocarbamate functionality at the N-terminus of the amino acids, where the NH₂ group of an amino acid is involved in forming the dithiocarbamate moiety. Saha et.al.[2012] have synthesized unnatural α -amino acids containing dithiocarbamate side chains.

1.2 PHYSICO-CHEMICAL STUDIES

As the present work deals with IR spectra, electronic spectra and magnetic measurements, the discussion is confined to these techniques only.

1.2.1. 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 950-1050cm⁻¹ and the 350-400cm⁻¹ region.

Chatt, Duncanson and Venanzi³⁹ have found that dithiocarbamate complexes exhibit a band of medium intensity in the region 1480-1550cm⁻¹, that is between the ranges for C-N and C=N. This band has been assigned to a CN stretching mode where the CN bond order is between 1 and 2 due to the sort of resonance shown in Fig. 3.

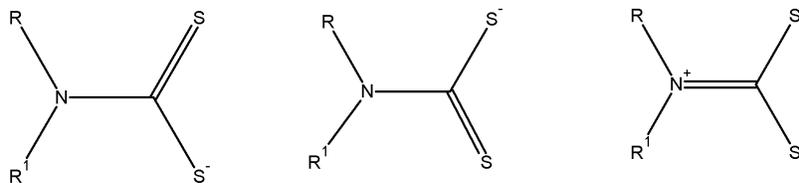


Figure 3: Resonating forms

Evidence for the intermediate order of the C-N bond has been provided by a crystallographic study⁴⁰ of $\text{NOCo}[\text{S}_2\text{CN}(\text{CH}_3)_2]$, where it was shown that the bond in question was 1.3\AA while those bonds between the methyl groups and the tertiary nitrogen atom were 1.5\AA ; the position of the C-N stretching frequency in this particular compound was 1544 cm^{-1} .

The increasing electron donating character in alkyl group would stabilize this structure and increase the $\nu(\text{C-N})$. The thioureide band for the dimethyl derivative is always observed to occur at a higher frequency than in the diethyl derivative. Some workers have assigned the higher value of $\nu(\text{C-N})$ to the greater inductive effect of the methyl groups. However, bonding arguments solely based on the inductive effects are not rigorous. The higher value of $\nu(\text{C-N})$ for the methyl derivative could be due to the electron release through hyper conjugation. It was also suggested that kinematic effects due to increasing mass of the alkyl group may also be responsible for the change in $\nu(\text{C-N})$. It was found that generally the frequency of C-N stretching is influenced by the stereochemistry of the complex (and probably the oxidation state of the metal) and that it apparently follows the order planar > tetrahedral > octahedral.

Normal coordinate analysis of $[\text{Cr}(\text{R}_2\text{dtc})_3]^{41}$ complexes have been carried out by Brown et al.⁴² who observed that the $\nu(\text{C-N})$ 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 $950\text{-}1050\text{ cm}^{-1}$ is associated with the C-S stretching frequency, and according to Ugo and Bonati⁴³ 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 workers⁴⁴. Brinkoff and Grotens⁴⁵ have made a detailed compilation of the absorption in the $900\text{-}1050\text{ cm}^{-1}$ region for a number of complexes

with both symmetrically bound bidentate ligands and complexes with monodentate ligands⁴⁶. 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 $\nu(C-S)$ vibrations would occur also with unsymmetrical bidentate bonding. It is suggested that monodentate bonding should be assumed only if the splitting exceeds 20 cm^{-1} . Studies on $Cu(II)$ complexes with piperidine dithiocarbamate⁴⁷ had shown that presence of different heteroatom in piperidine ring influence the $\nu(C-S)$ and $\nu(C-N)$ vibrations which decreases in the order $pipdtc(=piperidine\ dithiocarbamate) > N\text{-mepipdtc}(=methylpiperidine) > Pzdtc > Morpdtc > Timdtc$ ligand. The position of methyl group on piperidine ring also influences $\nu(C-S)$ and $\nu(C-N)$ vibrations which decreases as $2\text{-mepipdtc} > 3\text{-mepipdtc} > 4\text{-mepipdtc}$ ⁴⁸.

The third important region is around $350\text{-}400\text{ cm}^{-1}$, where $\nu(M-S)$ should occur. In the far infrared spectra of N,N -dialkyldithiocarbamate complexes, a strong band is always observed in the region $345\text{-}410\text{ cm}^{-1}$, which is absent in the free ligand and so this was assigned to $\nu(M-S)$. Similar assignments were made for $[Cu(Pdtc)]^{49}$ and $[Cu(Mordtc)_3]^{50}$. These assignments are supported by normal coordinate analysis which predicted $\nu Pt-S$ at 378 cm^{-1} for $[Pt(H_2dtc)_2]$ and $\nu(Ni-S)$ at 410 cm^{-1} for $[Ni(Me_2dtc)_2]^{51}$

1.2.2 Electronic spectra

Shankaranarayana and Patel⁵² discussed the spectra of dithiocarbamate. 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 Janssen⁵³, some uncertainty exists as to the nature of the $n \rightarrow \sigma^*$ band which, according to Janssen could be due to another $n \rightarrow \pi^*$ transition.

The electronic spectra of crystalline bis(diethyldithiocarbamato)nickel(II) complex had been studied in detail by R.Dingle⁵⁴. Although the electronic spectra of dithiocarbamate complexes have been studied by several investigators⁵⁵⁻⁵⁶, uncertainties exist in the interpretation of these spectra. The uncertainty is mainly due to the π bonding effect associated with the

dithiocarbamate and other dithio ligands. An additional cause of difficulty in assigning spectra are the low energy high intensity charge transfer absorptions which often mask the weaker absorption due to d-d transition. Jorgensen⁵⁷ in his study of the electronic spectra of dithio complexes used the parameter Δ , expressing the difference between σ and π antibonding effects, in certain square planar low spin d^8 complexes, to determine the relative position of the ligands in the spectrochemical series. Jorgensen 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 which are not found in the spectra of the free ligands. Such absorptions have been assigned to charge transfer transitions. Jorgensen⁵⁷ assigned these bands to $L \rightarrow M$ transitions, while Gray and coworkers assigned similar bands in dithiocarbamate complexes to an $M \rightarrow L$ charge transfer. A series⁵⁸ of Ir(I) N,N-diethyl dithiocarbamate complexes were prepared and the electronic spectra shows concentration dependant with low energy bands appearing with increasing concentration. Dilute solutions exhibit absorption maximum around 400nm.

1.2.3. Magnetic measurements

Vanadyl and Cr(III) dithiocarbamate complexes exhibit μ_{eff} values of 1.7 to 1.8BM and 3.8 to 3.9 BM respectively. Cambi and co-workers prepared a large number of Fe(III)dithiocarbamate complexes and studied their magnetic properties³¹. 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 equilibrium between high and low spin magnetic states. Martin and White⁵⁹ 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.

1.3. MIXED LIGAND DITHIOCARBAMATE COMPLEXES

There has been growing interest in the formation of mixed ligands chelates involving ligands containing different functional groups and transition metals of different oxidation states (Samus et al 2006 and Manov et al.2004)⁶⁰⁻⁶¹. Coordination compounds with mixed ligands are

of considerable importance in the field of metalloenzymes and are known to possess various biological activities (Rai et al.2005)⁶². Hence a large number of mixed ligand complexes with various transition metals are known (Mahapatra et al.1986 and Rai et al.2006). The complexes formed between metal ions and dithiocarbamate derivatives of aminoacids have been reported. Although there are numerous reports on transition metal complexes of dithiocarbamate derived from aminoacids, information on the corresponding mixed ligand complexes of nickel(II) is still very scanty.

Castillo et al.⁶³ found that complexes of Ni(II) with derivatives of branched and cyclic aminoacids have a near square planar geometry around Ni(II) ion coordinated through sulphur atom of dithiocarbamate moiety. Nickel(II) amino acid dithiocarbamates complexes of the composition $[\text{Ni}(\text{AA}(\text{dtc})(\text{PPh}_3)(\text{NCS})]$, $[\text{Ni}(\text{AA}(\text{dtc})(\text{PPh}_3)(\text{CN})]$ and $[\text{Ni}(\text{AA}(\text{dtc})(\text{PPh}_3)]\text{ClO}_4$ ⁶⁴, {(AA(dtc)=dithiocarbamate) derivative from amino acids i.e. glycine (glydtc), L-iso-leucine (i-leudtc) and L-proline (prodtc) were synthesized. Bhagwan et.al.⁶⁵ proved stabilization of higher oxidation state of metals by dithiocarbamate by synthesising and characterizing Mn(III) mixed ligand complexes containing dithiocarbamate and glycine as ligands.

Mixed ligand complexes of nickel(II) with substituted phosphine and dithiocarbamate derived from α amino acid have been reported⁶⁴. 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.

Martin and White⁶⁶ had prepared a series of monohalogenobis(N,N-dialkyldithiocarbamato)iron(III) complexes (Fig. 4) by vigorously shaking benzene solution of tris(N,N-dialkyldithiocarbamato) iron(III) with minimum quantity of concentrated aqueous hydrohalic acid. These complexes are reported to be susceptible to hydrolysis by hydroxylic medium such as water or alcohol. If an excess hydrohalic acid is used for precipitation, unnecessary moisture is introduced, which is difficult to be removed. Thus critical care has to be taken during the preparation of these complexes by the procedure of Martin and White.

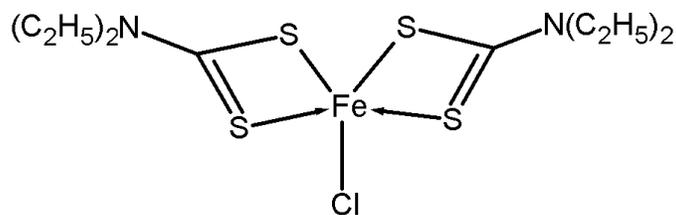


Figure 4: Monochlorobis(dithiocarbamato) iron (III)

Interaction of mixed benzoic – dithiocarbamic anhydride with anhydrous ferric chloride in acetone media yield the monochlorobis(dithiocarbamato)iron(III) complexes⁶⁷. In the case of its reaction with cupric chloride in acetone a black crystalline powder is separated out on slow evaporation at room temperature⁶⁸. These complexes have been characterized chemically and a dimeric structure (Fig. 5) has been assigned to them. The direct reaction of sodium dialkyl dithiocarbamate with cupric chloride does not give these chlorides bridged complexes, but give only the simple copper dithiocarbamate.

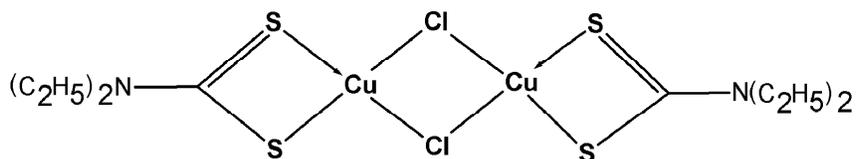


Figure 5: bis(diethyldithiocarbamato)-μ-dichlorodicopper(II)

Masakazu Kita et al. have prepared mixed dimethyldithiocarbamato Co(III) complexes containing ethylenediamine, of the type $[\text{Co}(\text{Me}_2\text{dtc})_x(\text{en})_{3-x}]^{(3-x)+}$. Mixed ligand Fe(III) dithiocarbamato complexes of general formula $\text{Fe}(\text{R}'_2\text{dtc})_2[\text{R}_2\text{dtc}]$ have been prepared and characterised⁶⁹. Mixed chelate (salen)(pyrrolidine-dtc)Fe(III)⁷⁰ complexes in which both Schiff base and a dithiocarbamate group are present have been synthesised by Petridis et al., but the crystal structure and stereochemistry are not yet known. New mixed ligand complexes of Fe and Cu was reported by Manoussakis et al.⁷¹ containing Schiff base of N,N-diethylaminodithiocarbamate as ligand with the aim of enhancing the biological action of dithiocarbamate ligand. Attempt to synthesize mixed ligand complex of zinc, $[\text{Zn}(\text{Pdtc})(\text{MSC})]^-$ by Mariam et al.⁷ resulted in $[\text{Zn}(\text{Pdtc})_2]$.

The coordination chemistry of sulphur ligands has been extensively studied and has shown a unique variety of structures with most of the transition metals in different oxidation states. The mixed ligand complexes of transition metal containing ligands with N, S and N, S, O donors show interesting stereochemical and electrochemical properties. The demand for cheaper and more efficient processes in the industry necessitated a major explosion of research in the area of synthetic chemistry to develop new systems that can act as catalyst. However, the use of sulphur ligands in reactions catalyzed by transition metals is still relatively unexplored compared with other ligands. Dithiocarbamate coordinated to rhodium⁷²⁻⁷³ and titanium⁷⁴ been studied as catalyst precursors in the hydrogenation of olefins.

1.4. SCOPE OF THE PRESENT INVESTIGATION

It has always been a challenge to synthesise pure solid mixed ligand complexes containing dithiocarbamate ligands, as their structural, electronic and magnetic properties are expected to be distinct from those of the simple dithiocarbamate complexes. The main objective of the present investigation is to synthesise mixed ligand complexes of copper(II) and nickel(II) containing the dithiocarbamate ligand and the Schiff base. The following strategies were adopted for the synthesis:

- Reaction of simple dithiocarbamate complexes of nickel (II) with SAAP.
- Reaction of simple SAAP complexes of nickel(II) with dithiocarbamate ligand derived from various amino acid
- Reaction of bis(dithiocarbamate)- μ -dichlorodicopper(II) with VAAP and VAAPy

Chapter 2

EXPERIMENTAL TECHNIQUES

Details about the general reagents used, the procedure adopted for the preparation of ligands and various physic-chemical techniques employed in the elucidation of structure of the complexes are given in this chapter.

2.1. Reagents

The metal salts used are, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, GR) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, GR). The other reagents used are: morpholine (Aldrich), carbon disulphide (Merck), barium hydroxide (Merck), sodium hydroxide (Merck), alanine, glycine, methionine, benzoyl chloride (Merck), salicylaldehyde (Aldrich), 3-aminopyridine (Aldrich), 2-aminophenol, vanillin. The solvents employed are either of 99% purity or purified by known procedures.

2.2. Preparation of starting materials for the synthesis of complexes

2.2.1. Sodium Dithiocarbamates

Sodium salt of diethyldithiocarbamate (Et_2dtc) and morpholine-N-carbodithioate (mordtc) was prepared by the general procedure given below:

A 500 ml three-necked flask was equipped with a separating funnel, electric stirrer and air condenser. An aqueous solution of NaOH (20g, 0.5 moles) and 0.5 mole of amine were taken in the flask. This was cooled in a freezing mixture of ice and salt. CS_2 (31 ml, 0.5 moles) was added drop wise from the separating funnel and the mixture was stirred for about 2 hours. The solid separated out was washed several times with petroleum ether and recrystallised from water.

2.2.2. Barium dithiocarbamates

The dithiocarbamate derivatives of α -amino acid such as glycine, alanine and methionine have been synthesized following a method similar to that described by Musil and Irgolic⁷⁵.

The amino acid (50mmole) was reacted with an aqueous solution of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (55mmole) and the resulting suspension was magnetically stirred until total solution is achieved. In order to overcome the precipitation of barium carbonate, the presence of air was

avoided. Acetone (50ml) was then added followed by carbon disulphide(60mmole) dropwise. Formation of the barium salt occurs according to the reaction.



The solution was kept at 0^oc for 12 hours. Addition of ethanol resulted in a white precipitate, which was filtered and washed with diethyl ether. The product was further purified by dissolving it in water and reprecipitating with ethanol.

2.2.3. Mixed benzoic-dithiocarbamic anhydrides

These anhydrides have the general formula Y-C(S)-S-COC₆H₅ (where Y=Et₂N-, Me₂N-, C₄H₈N-). They were prepared by adopting the procedures of the earlier workers⁷⁶⁻⁷⁷ .

Benzoyl chloride (11.6 g, 0.1 moles) was added to ice cold aqueous solution containing 0.1 mole of the appropriate sodium dithiocarbamate. A 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 diethyl ether.

These mixed anhydrides decompose on keeping to the corresponding amides with the loss of CS₂. Further these decompositions are reported to be enhanced by light. Therefore, the anhydrides were prepared afresh every time for subsequent synthesis work.

2.2.4. Schiff base derived from salicylaldehyde and 3-aminopyridine (SAAP)

Salicylaldehyde (2.3ml, 0.02mol) and the amine (2g, 0.02mol) both dissolved in methanol were refluxed for 2 hrs. From the resulting solution the solvent is evaporated to almost half in a water bath. Yellowish orange residue obtained is filtered and washed with methanol.

2.2.5. Schiff base derived from vanillin and 3- aminopyridine(VAAPy)

Vanillin (1.5g, 0.01moles) and 3-amino pyridine (0.1g, 0.01 moles) was dissolved in methanol and then refluxed for 2 hours. The solvent is allowed to evaporate and the crystals obtained after 2 days was washed with ether, dried over anhydrous CaCl_2 .

2.2.6. Schiff base derived from vanillin and 3-amino phenol(VAAP)

The Schiff base was prepared as described by Raman et al; 2004⁷⁸. Vanillin (1.5g, 0.01 mole) and 2- amino phenol (2g,0.01 moles) was dissolved in 20ml ethanol. The mixture was then refluxed for 3 hours and the product obtained was filtered, washed with water and dried over anhydrous CaCl_2 .

2.3. Elemental Analysis

2.3.1. Estimation of metal ions:

For all the complexes, the organic part of the complexes was completely eliminated before the estimation of the metals. A uniform procedure was adopted for this purpose. A known weight of the complex was digested with concentrated nitric acid and the resulting solution was evaporated to dryness. This was repeated for 3-4 times. The formed metal nitrate was dissolved in water and made up to a known volume, and this solution was used for the estimation of metal ion using Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer.

2.3.2 Sulphur Estimation

For sulphur estimation the complexes were fused with Na_2CO_3 and Na_2O_2 and the resulting sulphate was determined gravimetrically as barium sulphate⁷⁹.

2.3.3. CHN analysis

Microanalysis for carbon, hydrogen and nitrogen in the synthesised ligand and complexes were done on an Elementar model Vario EL III at Sophiscated Test and

Instrumentation Centre (SAIF), Kochi. These results give an idea about the composition of the ligands and complexes and provide a method to determine the structure of the complexes.

2.4. Physical and Spectral Measurements

2.4.1. Conductivity Measurements:

The molar conductance of the complexes in DMF (10^{-3}) solution was measured at 298 K with a Systronic model 303 direct-reading conductivity bridge.

2.4.2. Electronic Spectral Measurements:

Electronic spectra were recorded in chloroform solution were recorded on a Thermoelectron Nicolet evolution 300UV-Vis spectrophotometer.

2.4.3. Infrared Spectral Measurements:

The FTIR spectra provide valuable information regarding the structure of the complex and the nature of the functional groups present. Infrared spectral data were obtained with a Thermo Nicolet, Avatar 370 FTIR Spectrometer in the frequency range 400-3000 cm^{-1} using KBr pellet.

CHAPTER-III

STUDIES ON THE SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF SOME DITHIOCARBAMATO COMPLEXES OF Ni(II) AND Cu(II)

3.1. INTRODUCTION

Dithiocarbamate ligands are known to exhibit high coordination ability to transition metals with the small bite angle ($\sim 2.8\text{-}2.9\text{\AA}$) of the ligand facilitating its stabilization under a variety of reaction conditions. Several interesting mixed ligand (dithiocarbamato)iron(III) complexes were synthesised and studied by PMR technique⁷⁶. However, only few mixed ligand dithiocarbamato complexes have been isolated and studied.

Several metal complexes of dithiocarbamates derived from α -amino acids have been reported. The simultaneous presence of the dithiocarbamate and the carboxylic group make these ligands very interesting as they can display variable coordination mode. Mixed ligand complexes involving aminoacid dithiocarbamates, substituted phosphines and Ni(II) have been reported

The whole chapter is divided into three sections. Section A deals with the studies on the synthesis of mixed ligand complex of nickel (II). Section B involve the studies towards the synthesis of mixed ligand complex of copper (II).

3.2. SECTION A: Towards the Synthesis of mixed ligand dithiocarbamato complexes of nickel (II)

3.2.1 Experimental

3.2.1.1. Materials:

Details regarding reagents and preparation of dithiocarbamate and mixed benzoic dithiocarbamate are given in chapter II.

3.2.1.2. Synthesis of nickel(II)-dithiocarbamate complex.

A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5mmole) in methanol was added dropwise to an aqueous solution of the barium salt (1mmole) of the corresponding dithiocarbamate ligand. The light green colour of the original nickel(II) solution immediately darkens indicating the fast formation of new compound..It was stirred for two hours. An olive green precipitate obtained is filtered, washed with methanol and dried over anhy. CaCl_2 .

3.2.1.3. Reaction of $[\text{Ni}(\text{RR}'\text{dtc})_2]$ with SAAP

SAAP (3mmol, 0.59g) and sodium hydroxide (3mmol, 0.12g) in methanol was stirred for half an hour. This was slowly added to a mixture of $\text{Ni}(\text{RR}'\text{dtc})_2$ (2mmole) [$\text{RR}'\text{dtc}$ is a general notation for- $\text{S}_2\text{C-NR-HC}(\text{R}')\text{COO}^-$, glydtc, metdtc and aladtc] and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1mmole) in chloroform(25ml) and ethanol(25ml) and it was refluxed for three hours. The resulting solution was filtered and set aside to evaporate. After 4 days a yellowish green solid separated which was filtered, washed with methanol and dried over anhydrous CaCl_2 .

3.2.2 Result and discussions

The analytical data (Table.3.1) for the complexes obtained by the reaction of $\text{Ni}(\text{RR}'\text{dtc})_2$ with SAAP, shows that the complexes have the formula $[\text{Ni}(\text{SAAP})\text{dtc}]$. The complex $\text{Ni}(\text{RR}'\text{dtc})_2$ was olive green and $[\text{Ni}(\text{SAAP})\text{dtc}]$ was yellowish green in colour. They were found to be stable in air .They were partially soluble in methanol, acetone, chloroform, and acetonitrile. The low molar conductance values in DMF (Table.3.2) suggest that complexes are non electrolytes.

Table 3.1. Analytical data of the complexes

Complexes	Analytical data. Found (calculated) %					Colour
	C	H	N	S	Cu	
$[\text{Ni}(\text{glydtcH})_2]$	20.06 (20.07)	1.90 (2.25)	8.00 (7.80)	35.69 (35.70)	16.40 (16.34)	Olive green
$[\text{Ni}(\text{aladtcH})_2]$	25.17 (24.82)	3.20 (3.12)	7.34 (7.24)	33.09 (33.13)	15.20 (15.16)	Olive green

[Ni(metdtcH) ₂]	28.36 (28.41)	3.88 (3.97)	5.51 (5.52)	37.94 (37.92)	11.53 (11.57)	Olive green
[Ni(glydtcNa)SAAP]	42.00 (42.08)	2.81 (2.83)	9.79 (9.82)	14.91 (14.98)	13.65 (13.71)	Yellowish green
[Ni(aladtNa)SAAP]	43.52 (43.47)	3.20 (3.19)	9.51 (9.50)	14.55 (14.51)	13.30 (13.28)	Yellowish green

Table 3.2. Conductance data

Complexes	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
[Ni(glydtcH) ₂]	3
[Ni(aladtH) ₂]	4
[Ni(metdtcH) ₂]	13
[Ni(glydtcNa)SAAP]	12
[Ni(aladtNa)SAAP]	2
[Ni(metdtcNa)SAAP]	5

3.2.2.1. Electronic Spectra

The electronic spectral bands and their assignments are given in Table 3.3. In the case of dithiocarbamate complexes the low energy high intensity charge transfer band often mask the weaker absorption due to d-d transition. Most of the dithiocarbamate complexes show bands at approximately 260, 285 and 350 nm⁷¹. Although precise assignments of these bands are yet to be determined the band near 260 and 285 nm are due to intraligand $\pi \rightarrow \pi^*$ transitions mainly located on N-C=S and S-C=S group. The bands near 350 nm is due to charge transfer transition⁶⁹

Table: 3.3. Electronic Spectra of the Cu(II) Complexes

Complexes	Absorption maxima (nm)	Band assignments
[Ni(glydtcNa)SAAP]	263 nm	Intraligand transition
	266 nm	Intraligand transition

	306 nm	Intraligand transition
	380 nm	charge transfer
[Ni(aladtcNa)SAAP]	259nm	Intraligand transition
	290nm	Intraligand transition
[Ni(metdteNa)SAAP]	240nm	Intraligand transition
	320nm	Intraligand transition
	380nm	Charge transfer

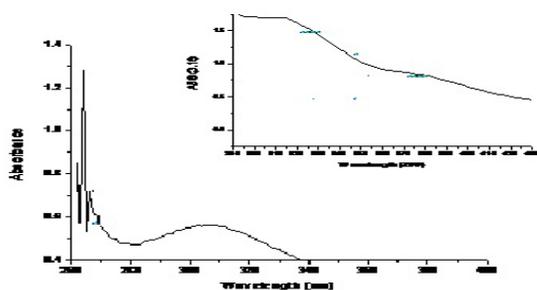


Fig.3A: UV-Visible spectrum of [Ni(glydteNa)SAAP]

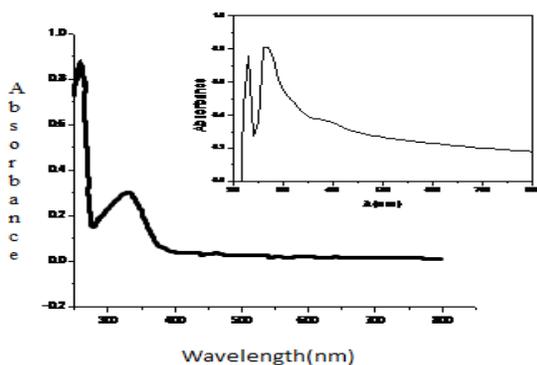


Fig.3B. UV-Visible spectrum of [Ni(aladtcNa)SAAP]

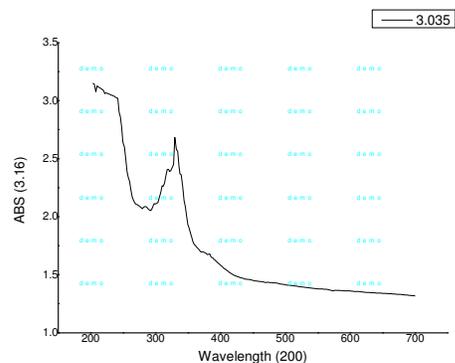


Fig.3C: UV-Visible spectrum of [Ni(metdtcNa)SAAP]

3.2.2.2. Infrared spectra of complexes

The infrared spectral data of the complexes are tabulated in Table 3.4. The tentative assignments given in the table are based on published work on dithiocarbamate⁷⁷⁻⁷⁸. The spectra of the mixed ligand complexes exhibit bands due to both the constituent ligands. Some of the characteristic bands of both the ligands appear in the same region, makes the assignment of such bands often difficult.

The complexes show IR absorption band in the 1500-1450 cm^{-1} range. These bands were assigned to carbon – nitrogen bonds of NCSS^- moiety⁷⁹. For all the complexes $\nu(\text{NCS}_2^-)$ lies between 1430-1500 cm^{-1} , which is in between the values expected for a single bond (1350-1250 cm^{-1}) and double bond ($\nu=1680-1640 \text{ cm}^{-1}$) suggesting a considerable double bond character of the C-N bond in the dithiocarbamate group. As the double bond character is more pronounced in the complexes (higher frequency) than that in ligands, it can be concluded that the ligand is coordinated via the 2 sulphur atoms⁸⁰. A second region between 950-1100 cm^{-1} is associated with $\nu(\text{CSS}^-)$ vibration and has been effectively used in differentiating between monodentate and bidentate ligands⁸⁰. The spectra of the complex shows a single band at 995 cm^{-1} which indicates a symmetrical bidentate coordination in the complexes. Methionine mixed ligand complex does not show any characteristic peak of Schiff base. It may be due to bulky nature of both methionine dithiocarbamate and the Schiff base ligand.

Table: 3.4. IR spectral data of Ni(II) complexes

complexes	b) $\nu_{(C2-N)}$	a) $\nu_{(C1-N)}$	$\nu_{(COO^-)}$		$\nu_{C=S}$		$\nu_{C=N}$ azomethane
			$\nu_{(asymm)}$	$\nu_{(sym)}$	$\nu_{(asym)}$	$\nu_{(sym)}$	
[Ba(aladtc) ₂].3H ₂ O	1090	1484	1568	1398	1001	716	-
[Ni(aladtc) ₂]	1081	1406	1521	1367	1009	721	-
SAAP	-	-	-	-	-	-	1609
[Ni(glydteNa)SAAP]	1124	1461	1527	1410	1032	663	1650
[Ni(aladtcNa)SAAP]	1152	1459	1527	1328	1124	660	1651
[Ni(metdteNa)SAAP]	1126	1462	1527	1385	1033	661	-

a) C₁ of dithiocarbamate group b) C₂-C α with respect to carboxylic group

The bands originated by the carboxylate groups are different for the free ligand and the complexes. As the free dtc has been isolated as barium salt, two bands are recorded at 1568cm⁻¹ and 1398cm⁻¹ due to asymmetric and symmetric stretching modes of carboxylate group. In the mixed ligand complex the two bands characteristic of carboxylic group are observed at 1527cm⁻¹ ($\nu_{asym\ COO^-}$) and 1328cm⁻¹ ($\nu_{sym\ COO^-}$). This shows that carboxylic group is not involved in coordination. Also a band at 1608cm⁻¹ indicates presence of carboxylic group as it's sodium salt. The NCCOO⁻ moiety of aminoacid is responsible for the band at 1152cm⁻¹ which indicates that the C-N bond length in S₂CN moiety of alanine derivative is shorter than C-N bond of the NCCOO⁻ group. In the spectra of mixed ligand a broad band at 3330cm⁻¹ is due to $\nu_{(O-H)}$ and a band at 3230cm⁻¹ is ascribed to $\nu_{(N-H)}$.

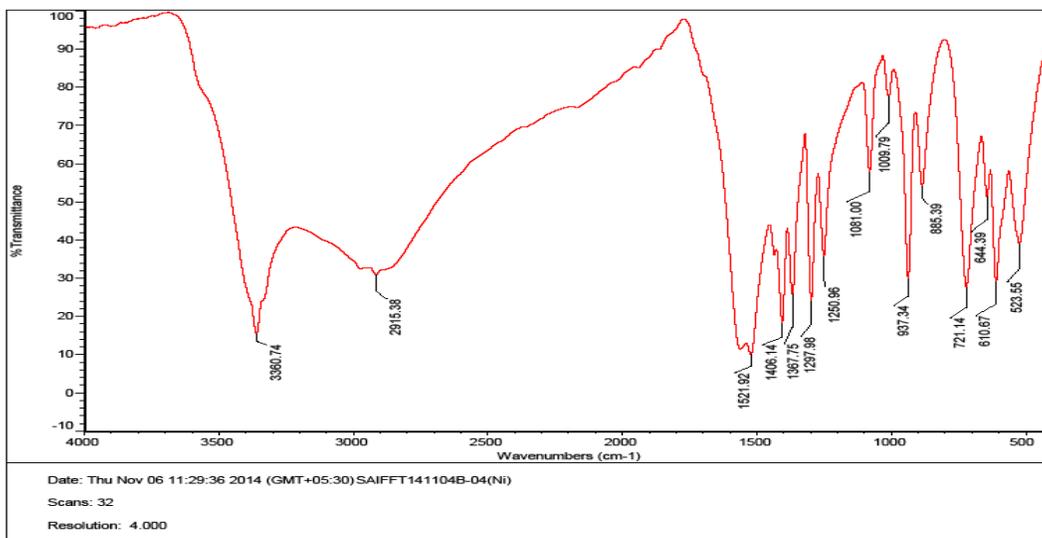


Fig3D: IR spectrum of SAAP

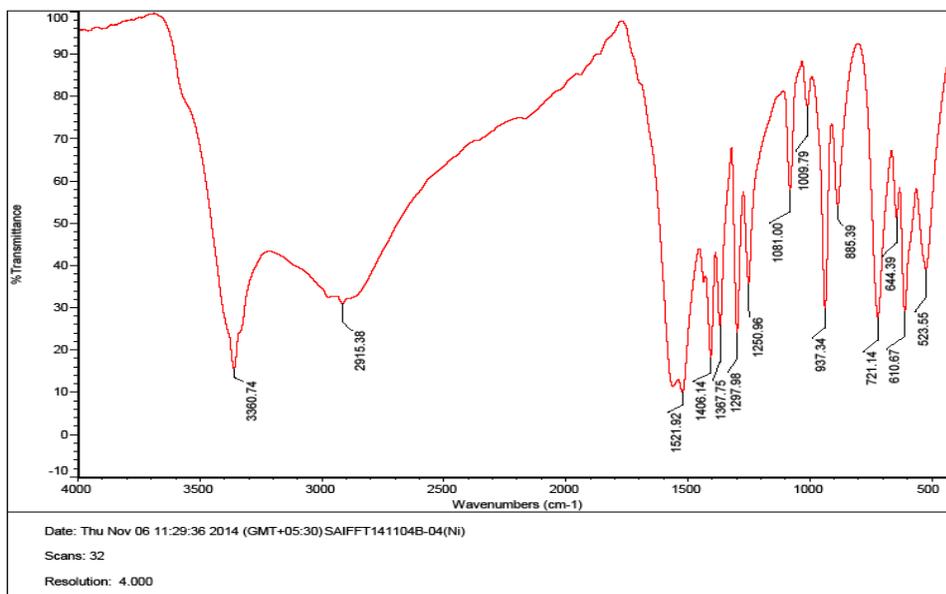


Fig.3E: IR spectrum of the nickel dithiocarbamate complex

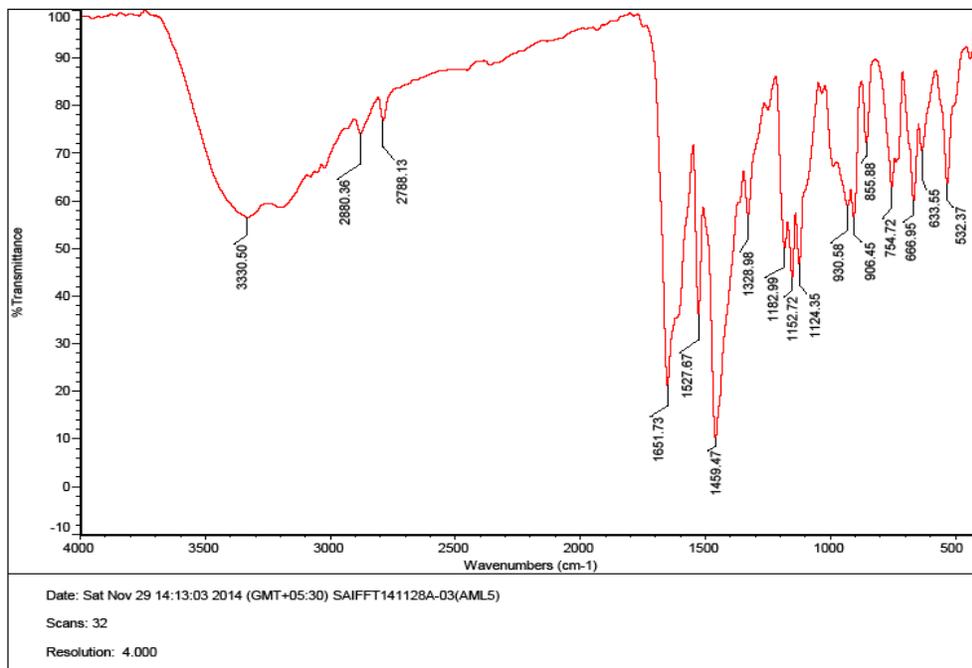


Fig.3F: IR Spectrum of [Ni(aladtc Na)SAAP]

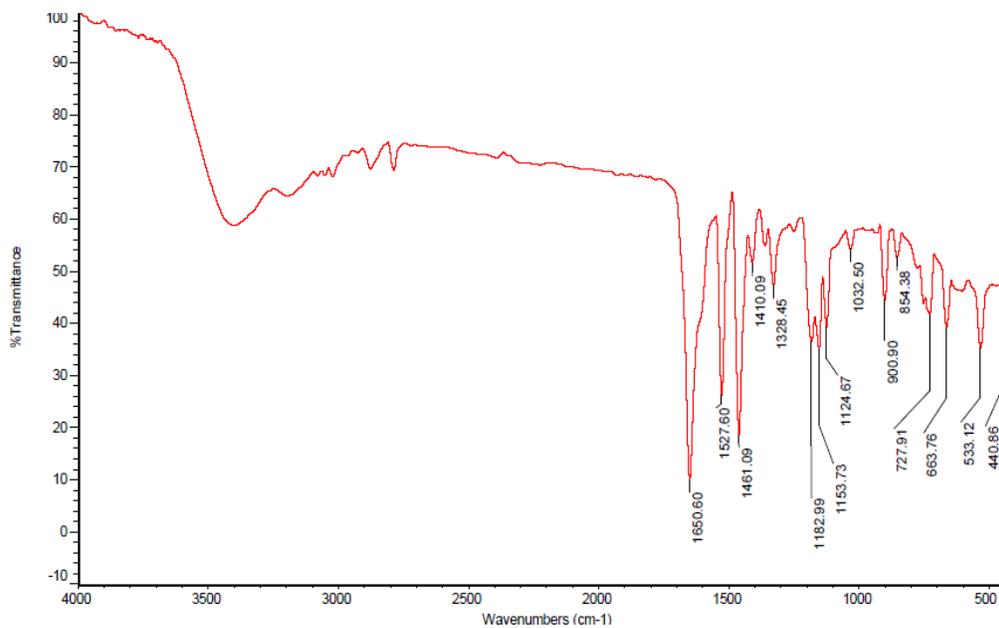


Fig.3G: IR Spectrum of [Ni(glydte Na)SAAP]

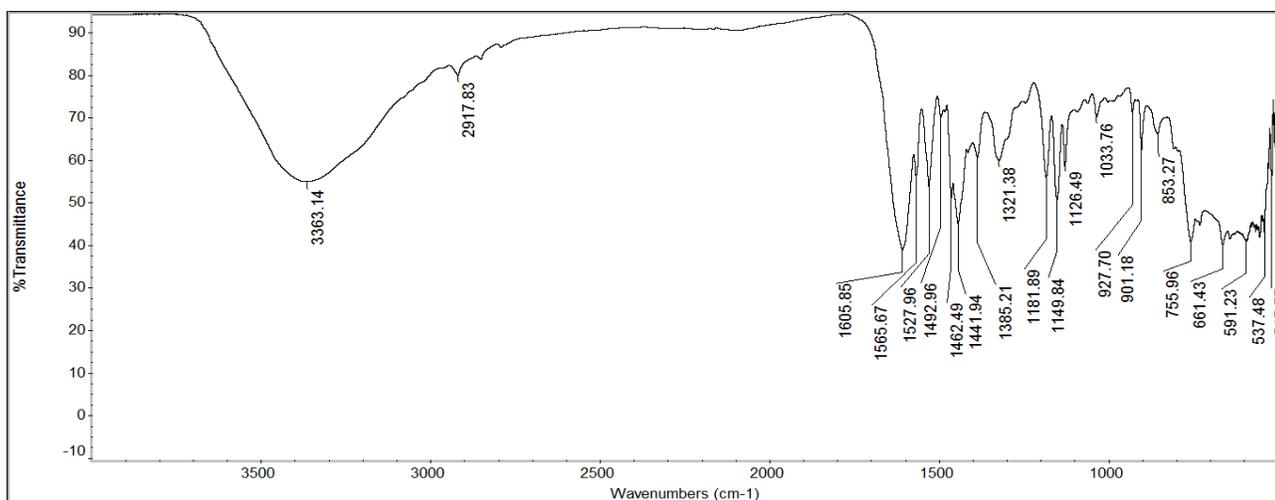
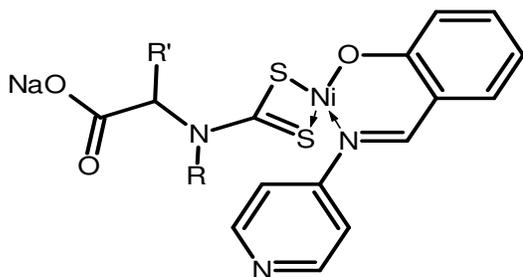


Fig.3H:IR Spectrum of [Ni(metdtc Na)SAAP]

Based on the above analytical and spectral data it was clear that the dithiocarbamate ligand is coordinated to metal via both the sulphur atom and Schiff base is coordinated through the azomethine nitrogen and phenolic oxygen atom. The tentative structure of [Ni(SAAP)RR'dtc] is: (Fig.3I).



3.3. SECTION B: Towards the Synthesis of mixed ligand dithiocarbamate complexes of copper(II)

3.3.1 Experimental

3.3.1.1. Materials:

Details regarding reagents and preparation of dithiocarbamate and mixed benzoic dithiocarbamate are given in chapter II.

3.3.1.2. Synthesis of [Cu(mordtc)₂]

The complex was prepared by reacting aqueous solution of Namordtc (2mmol, 0.97g) and CuCl₂.4H₂O (1mmol, 0.17g). The dark brown complex separated out was filtered, washed several times with cold water and dried over anhydrous calcium chloride.

3.3.1.3. Synthesis of bis(morpholine-N-carbodithioato)-μ-dichlorodicopper(II)

Bis(morpholine-N-carbodithioato)-μ-dichlorodicopper(II) was prepared by mixing CuCl₂.2H₂O(1.7g, 0.01mol) and the freshly recrystallised benzoic– morpholine-N-carbodithioic anhydride (0.02 moles) both dissolved in minimum quantity of acetone. The chloro complex separated out as a black crystalline powder. The smell of benzoyl chloride was noted during the preparation. The complex was filtered, washed with diethyl ether and dried in vacuum over P₂O₅.

3.3.2. Synthetic routes for the synthesis of mixed ligand complexes of copper(II):

3.3.2.1. Reaction of [Cu(mordtc)₂] with VAAP:

[Cu(mordtc)₂] (1mmol, 0.36g) and VAAP (1mmol, 0.19g) both dissolved in methanol was stirred for 2 hr. The product obtained was separated, washed with methanol and dried over anhydrous calcium chloride.

3.3.2.2. Reaction of [CuCl(mordtc)]₂ with VAAP :

SAAP (3mmol, 0.59g) and sodium hydroxide (3mmol, 0.12g) in methanol was stirred for half an hour. To this bis(morpholine-N-carbodithioato)-μ-dichlorodicopper(II) (1mmol,0.52g) in methanol was added drop wise with stirring and it was stirred for 4hrs.The greenish brown residue obtained was separated, filtered and washed with methanol.

3.3.2.3. Reaction of $[\text{CuCl}(\text{mordtc})]_2$ with VAAPy :

VAAPy (3mmol, 0.59g) and sodium hydroxide (3mmol, 0.12g) in methanol was stirred for half an hour. To this bis(morpholine-N-carbodithioato)- μ -dichlorodicopper(II) (1mmol, 0.52g) in methanol was added drop wise with stirring and it was stirred for 4hrs. The greenish brown residue obtained was separated, filtered and washed with methanol.

3.3.3. Result and discussions

The starting complexes bis(morpholine-N-carbodithioato)copper(II) and bis(morpholine-N-carbodithioato)- μ -dichlorodicopper(II), were analysed. The analytical data (Table 3.5), conductance data (Table 3.6), electronic spectra (Table 3.7 and Figs. 3I), infrared spectra (Table 3.8 and Fig. 3J, 3K, 3L, 3M) of these complexes agrees well with data reported for these complexes in the literature.

The following methods were used for the synthesis of mixed ligand dithiocarbamate complexes of copper (II): 1) reaction of simple dithiocarbamate complexes of copper(II) with Schiff bases, and 2) reaction of bis(dithiocarbamate)- μ -dichlorodicopper(II) with Schiff bases. The complex isolated from the reaction of $[\text{Cu}(\text{mordtc})_2]$ with VAAP was analysed. The analytical data (S:33.09, Cu:16.12), electronic spectrum and IR spectrum confirm that the compound isolated was the starting complex, $[\text{Cu}(\text{mordtc})_2]$. This clearly suggests that VAAP is not coordinated to the metal centre and this method cannot be adopted for the synthesis of mixed ligand dithiocarbamate complex of copper (II).

The analytical data (Table 3.5) for the complexes obtained by the reaction of bis(dithiocarbamate)- μ -dichlorodicopper(II) with SAAP, shows that the complexes have the formula $[\text{Cu}(\text{SAAP})\text{dte}]$. The complex $[\text{Cu}(\text{VAAP})\text{mordtc}]$ was blackish brown and $[\text{Cu}(\text{VAAPy})\text{mordtc}]$ was greenish brown in colour. They were found to be stable in air. They were partially soluble in methanol, acetone, chloroform, and acetonitrile and soluble in DMF and DMSO. The low molar conductance values in DMF (Table 3.6) suggest that complexes are non electrolytes.

Table 3.5. Analytical data of the complexes

Complexes	Analytical data. Found (calculated) %				
	C	H	N	S	Cu
[Cu(mordtc) ₂]	29.84 (30.95)	4.17 (4.16)	6.32 (7.22)	33.09 (33.05)	16.12 (16.38)
[Cu(VAAPy)(mordtc)]	47.60 (47.61)	4.50 (4.44)	9.24 (9.25)	14.09 (14.12)	13.95 (14.00)
[Cu(VAAP)(mordtc)]	48.52 (48.76)	4.29 (4.31)	5.85 (5.99)	13.53 (13.70)	13.49 (13.58)

Table 3.6. Conductance data

Complexes	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
[Cu(mordtc) ₂]	4
[Cu(mordtc)Cl] ₂	12
[Cu(VAAP)(mordtc)]	21
[Cu(VAAPy)(mordtc)]	14

3.3.3.1. Electronic Spectra

The electronic spectral bands and their assignments are given in Table 3.3. In the case of dithiocarbamate complexes the low energy high intensity charge transfer band often mask the weaker absorption due to d-d transition. Most of the dithiocarbamate complexes show bands at approximately 260, 285 and 350 nm. Although precise assignments of these bands are yet to be determined the band near 260 and 285 nm are due to intraligand $\pi \rightarrow \pi^*$ transitions mainly located on N-C=S and S-C=S group. The bands near 350 nm is due to charge transfer transition⁶⁹

Table: 3.7. Electronic Spectra of the Cu(II) Complexes

Complexes	Absorption maxima (nm)	Band assignments
[CuCl(mordtc)] ₂	345	Intra ligand
[Cu(VAAP)(mordtc)]	268 432	Intra ligand Charge transfer
[Cu(VAAPy)(mordtc)]	264	Intra ligand

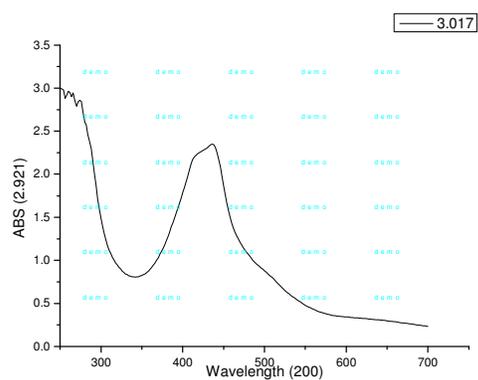


Fig.3J: Electronic spectra of [Cu(VAAP)mordtc]

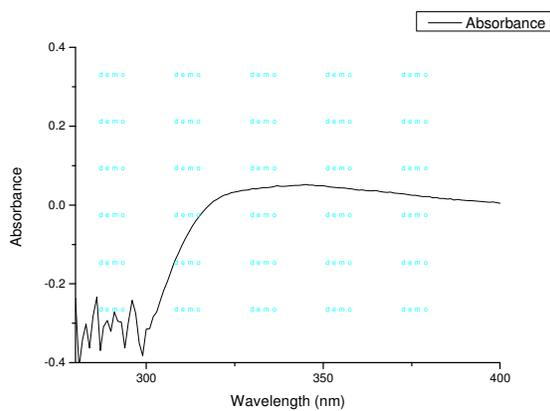


Fig3K: Electronic spectra of [Cu(VAAPy)mordtc]

3.3.3.2. Infrared spectra of complexes

The infrared spectral data of the complexes are tabulated in Table 3.4. The tentative assignments given in the table are based on published work on dithiocarbamate⁷⁷⁻⁷⁸. The spectra of the mixed ligand complexes exhibit bands due to both the constituent ligands. Some of the characteristic bands of both the ligands appear in the same region, makes the assignment of such bands often difficult.

The complexes show IR absorption band in the 1500-1450 cm^{-1} range. These bands were assigned to carbon-nitrogen bonds of NCSS^- moiety¹⁷. For all complexes (ν_{NCS_2}) lies between 1440-1618 cm^{-1} , which is in between the values expected for a single bond ($\nu=1350-1250\text{cm}^{-1}$) and double bond ($\nu=1680-1640\text{cm}^{-1}$) suggesting a considerable double bond character of C-N bond in the dithiocarbamate group. The high vibrational frequencies of this band in the mixed ligand complexes indicate a partial double bond character of the C-N group arising from mesomeric drift of electron from the dithiocarbamate moiety towards the Cu(II) ion center.

A second region between 950-1100 cm^{-1} is associated with $\nu(\text{CSS})^-$ vibration and is diagnostic in describing the mode of sulphur coordination to the metal atom. Usually 2 bands close to 1000 and 660 cm^{-1} respectively, have been assigned to the stretching vibration of CS_2 group. These bands have been assigned to the ν_{asymm} and ν_{symm} modes of the CS_2 group. In the spectra of complex a single band appears in this region due to the greatest contribution of resonance form (RN^+CS_2^-) in the sulphur atom has symmetrical bidentate coordination to metal atom¹⁸

All these facts suggest that a monohalogeno complex was formed as the precursor of the mixed ligand complex, which is similar to that prepared by Martin and white¹⁹. They have already assigned a square pyramidal structure for these complexes from X-ray crystal studies. The 1277 cm^{-1} band in the ligand has been assigned to the $\nu_{(\text{C-O})}$ phenolic stretching vibration. In the complexes the band shifts to higher frequency by *ca* 12 cm^{-1} indicating the participation of phenolic oxygen atom in the coordination. The azomethine ($\nu_{\text{C=N}}$) stretching frequency in the mixed ligand is at a higher frequency than that of free ligand indicating bonding to the metal through imine group. A band at 954 is assigned to M-N bond which was absent in the ligand.

Table 3.8. Infrared spectral data of Cu (II) complexes.

Complexes	$\square_{\text{C-N}} (\text{cm}^{-1})$	$\square_{\text{C-S}}(\text{symm})$	$\square_{\text{C-O}} (\text{a})$	$\square_{\text{O-H}}(\text{b})$	$\square_{\text{C-O-O}}$	$\square_{\text{C=N(azomethine)}}$
[Na(mordtc)]	1417	1018	-	-	1105	-
[Cu(mordtc) ₂ Cl ₂]	1492	1028	-	-	-	-
VAAP	-	-	1277	3406	-	1581
VAAPy	-	-	1277	3376	-	1594
[Cu(VAAP)mordtc]	1481	1071	1307	3432	1108	1640
[Cu(VAAPy)mordtc]	1433	1023	1311	3427	1110	1645

a) phenolic C-O bond

b) phenolic O-H

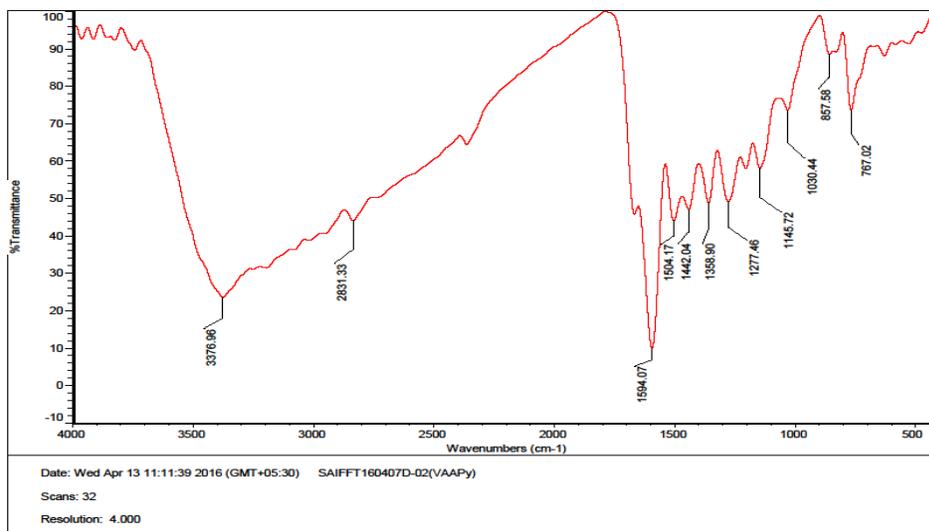


Fig.3L:IR Spectrum of VAAPy

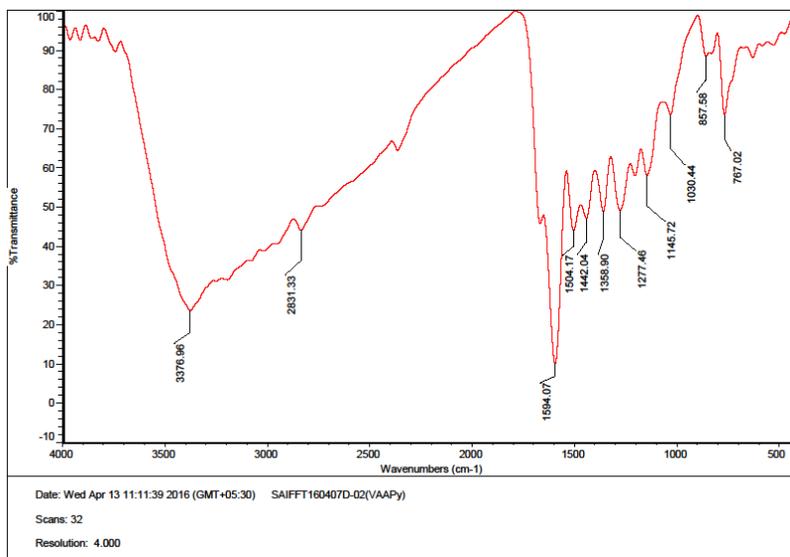


Fig.3M: IR Spectrum of VAAP

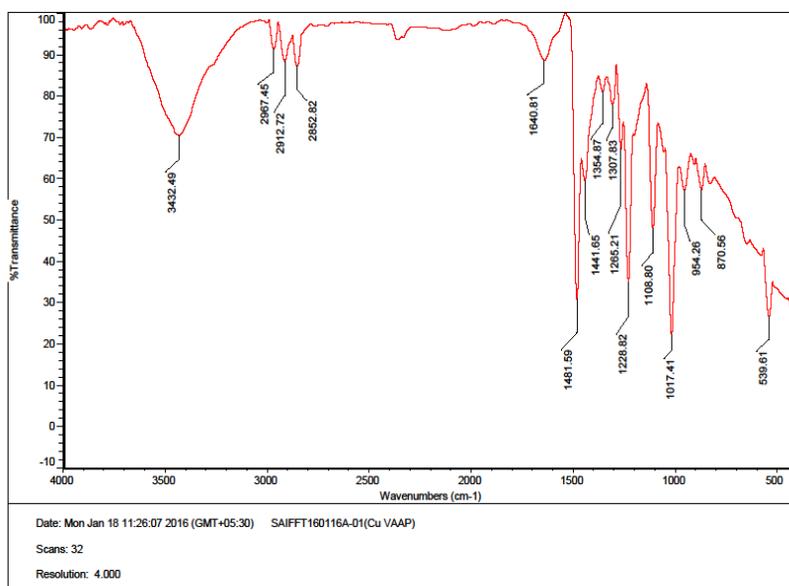


Fig.3N: IR Spectrum of [Cu(VAAP)mordtc]

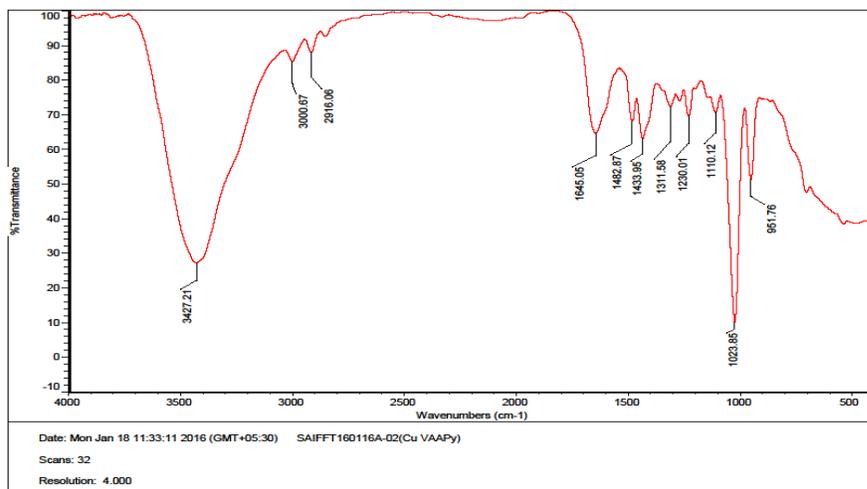
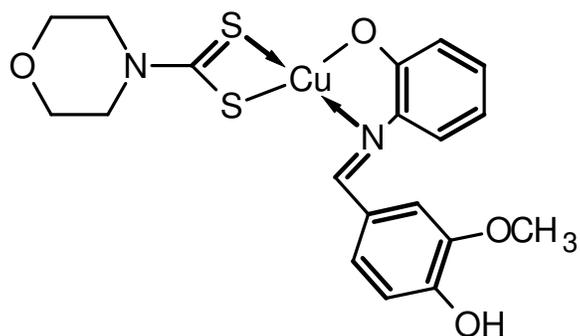


Fig.3O: IR Spectrum of [Cu(VAAPy)mordtc]

Based on the above analytical and spectral data it was clear that the dithiocarbamate ligand is coordinated to metal via both the sulphur atom and Schiff base is coordinated through the azomethine nitrogen and phenolic oxygen atom. The tentative structure of [Cu(VAAP)mordtc] and [Cu(VAAPy)mordtc] is: (Fig.3N)



3.4 SUMMARY AND CONCLUSIONS

The thesis mainly deals with the studies on our attempts to synthesize mixed ligand dithiocarbamate (dtc) complexes of nickel(II) and copper(II). It is divided into three chapters. The first chapter of the thesis presents a discussion on the synthesis, physico-chemical techniques used for the characterization, structural aspects and applications of dithiocarbamates and their complexes. The scope of the present investigation is also outlined in this chapter. Details about the reagents used, synthetic procedures for the dithiocarbamate ligands, Schiff base ligand, and mixed benzoic-dithiocarbamic anhydrides and the various physico-chemical techniques used to characterise the complexes are given in Chapter II.

Chapter III is divided into two sections: section A and section B. Section A deals with the studies on the synthesis of mixed ligand dithiocarbamate complexes of nickel(II). Our attempts to prepare the complexes by reacting nickel dithiocarbamate complex with the Schiff base derived from salicylaldehyde and 3-aminopyridine(SAAP) was successful, we could isolate stable mixed ligand complexes with the empirical formula $[\text{Cu}(\text{RR}'\text{dtc})(\text{SAAP})]$. IR spectral data of the complexes suggest bonding of the two sulphur atoms of the dtc ligand and azomethine nitrogen and phenolic oxygen of the Schiff base ligand.

Section B deals with the studies on the synthesis of mixed ligand dithiocarbamate complexes of copper(II). Our attempts to prepare the complexes by reacting bis(dithiocarbamate)copper(II) with the Schiff base derived from vanillin and 3-aminopyridine(VAAP) met with failure. However, by reacting bis(morpholine-N-carbodithioato)- μ -dichlorodicopper(II) with Schiff base, we could isolate a stable mixed ligand complexes with the empirical formula $[\text{Cu}(\text{mordtc})(\text{Schiff base})]$.

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