CHAPTER - III

STRUCTURAL STUDIES OF METAL COMPLEXES OF 2,4 DIAMINO 5-CHLORO-THIAZOLE AND ITS SCHIFF BASE

Metal complexes of ligands containing nitrogen and sulphur attracted the attention of researchers because such metal ligand systems can serve as models with biological significance. A variety of metal complexes can be prepared in which preferred bonding site is either cyclic nitrogen or cyclic sulphur. This can happen in case of heterocycles containing both sulphur and nitrogen or any one of them. Many substituted heterocycles possess exocyclic coordinating sites and give metal complexes. Since such molecules mimic biologically important molecules, the structural and stereochemical aspects are equally important. Among the heterocycles thiazole has great importance and therefore, the metal complexes of substituted thiazoles deserve detailed study.

The present study involves synthesis and structural ellucidations of metal complexes of 2,4-diamino 5-chlorothiazole (DCT) and its Schiff base obtained by condensation with salicylaldehyde $[DCT\ (Sal)_2\ H_2]$. This has been done by chemical analysis, molecular weight determination, electrical conductivity study, spectroscopic studies including electronic absorption spectra, vibrational spectra and thermogravimetry.

3.1 Synthesis and Chemical Elemental Analysis

The details of preparation techniques of ligands DCT and its metal complexes and DCT $(Sal)_2 H_2$ and its metal complexes are already given in Chapter II. The results are given in Tables 3.1 and 3.2.

3.2 Physical Properties of DCT

DCT is an analog of ethylenediamine and easily forms well characterizable complexes with many metals. The ligand has a thiazole ring with aromatic character. The ligand molecule has enough flexibility to surround the metal ion either by involving the cyclic nitrogen or the cyclic sulphur for coordination to the metal ion with its available lone pair of electrons. The choice of heteroatom of course is governed by the metal under consideration. The π electron system of the ring also helps formation of stable metal complexes. In all cases except cobalt complexes reaction medium was strictly anhydrous hence none has water molecules of constitution or water of crystallization or absorbed water. In case of cobalt complexes both anhydrous and hydrated complexes were prepared.

All the metal complexes are microcrystalline, stable well characterizable materials, insoluble in water and moderately soluble in organic solvents like acetone, methanol and ethanol. Since the ligand is moderately bulky, high solubilities are not expected. If protected from moisture all the materials are quite stable over prolonged period. There was no change in composition, appearance and form over 18 months.

Physical Properties of the Schiff Base

Salicylaldehyde on condensation with DCT gives stable, well-characterizable, crystalline, cream coloured Schiff base (DCT $(Sal)_2 H_2$). This vic-hydroxy aldehydic Schiff base on deprotonation on reaction with metal ions gives well characterizable metal complexes. Each molecule of the ligand contains two hydroxy protons from two salicylaldehyde units and the choice of coordination is again either cyclic nitrogen or cyclic sulphur. The ligand molecule is fairly bulky and the solubilities even in acetone and ethanol are poor. The compounds are quite stable. Hydration of the Co(II) complexes gives pink coloured hydrated solids insoluble in water.

3.3 Molecular Weights of Metal Complexes

Rast's method was used for the determination of molecular weights of the ligand-metal complexes. Pure camphor was sublimed to give light weight crystalline sublimate which was thoroughly ground with weighed quantity of the complex and was quickly melted by immersion of the test tube in an oil bath at temperature higher than the melting point of camphor.

On a quick stirring a homoginious melt results and the diffusion of the colour in a clear transparent molten mass indicates that the complex is soluble in camphor. To avoid the loss of camphor by sublimation, the mixture is quickly cooled and the whole mixture is taken out with a spatula and weighed again to avoid the error due to loss of camphor. The molecular weights are entered in Table 3.1 and 3.2 along with calculated molecular weights. On attempting the determination of molecular weights of pink stable hydrated Schiff base cobalt complex, quick dehydration at the high temperature of molten camphor takes place and the complex reverts to dehydrated blue complex which is indicated by deep blue colour of melt and hence molecular weight of molecules containing water coordinated to Co (II) atom could not be determind.

The results are quite satisfactory as is indicated by the good agreement between experimental and calculated molecular weights.

3.4 Determination of Electrical Conductivity

Electrical conductivity (χ) of the complexes in both the series were determined in acetone medium because the complexes are not soluble in nitrobenzene. All the compounds show very poor conductivity and are very much below the values expected for ionised species of ionic compound [1].

This is in agreement with reported behaviour of the thiazole complexes [2,3].

The Schiff base complexes are not expected to give high electric conductivity, because free ions may not be found on dissolution. The observation are in agreement with this expectation as seen from conductance value, reported in Table No. 3.3

3.5 Magnetic Susceptibility

Magnetic susceptibility measurement of transition metal complexes were determined at room temperature and are given in Table 3.4

3.6 Electronic Absorption Spectroscopy

Electronic absorption spectroscopy plays an important role in structural studies of metal complexes. The d-orbitals of metal ions interact with ligand electrons and depending on the nature of the incoming ligand, the metal ion electrons i.e. d orbital electrons occupy the suitable molecular orbitals. Because of the symmetry condition dxy, dyz, dzx orbitals constitute a degenerate single level while dx^2-y^2, dz^2 constitute other degenerate level. As a result of it, d-d transition becomes possible and still Hund's rule is not broken. Transition metal chemistry which in other words can be most appropriately described as d orbital chemistry differs from pre and post-transition element chemistry which involves mearly S and P orbitals leading to σ , π and lone pair interaction. The non-degeneracy of the two groups of d-oribtals along with the consideration of nature of incoming ligand and distinction between axial or " in between axes " attacks give a much wider scope for structural variation and thus a innumerable stereo-chemical situations arise. With the advent of ligand field theory and crystal field theory, the interpretation of electronic absorption spectra has been well organised. Detailed explanation of spectral features can be provided with application of Orgel-diagrams and Tanabe-Sugano diagrams. In the light of further precision calculations by curve fitting techniques given by Konig [4] where more than one electron i.e. d^2 to d^8 or electron hole formalism for d^8 to d^2 cases involve inter-electron repulsion. With application of computers now it has become possible to enhance the capability of calculation interpretation of the spectra in much better way[5] .

The electronic absoprtion spectra involve a multitude of molecular energy processes such as σ and π bond formation long pair interactions such as $n \rightarrow \pi^*$ transitions and charge transfer phenomenon, d-d transition and generally d-d transition bands are extremely weak or very weak or moderately strong ($\epsilon < 100$ L $mole^{-1} cm^{-1}$) and cover NIR and U.V. region σ and π interaction involving S and P orbital generally occur UV region and are fairly strong bands.

In case, charge transfer is possible the energy matches with that of UV region. The absorption band in UV region are generally strong by 1 or 2 orders compared with those in visible region and charge transfer bands are still stronger by several orders. The electronic absorption band, because of several allied intractions, covers much wider energy regions and give broad absorption bands. Since symmetry allowed and forbidden bands occur near by many a times weaker bands become indistinguishable. Sometimes weak side bands and still weak shoulders appear. All these features must be studied by applying standard curve fitting procedure method, Gaussian analysis or by using suitable computer programmes.

From the above discussion one can tell that, although a bit tedious, straight forward interpretative procedure is not very difficult to evolve. In actual practice many a times there are several difficulties in making clearcut assignments. A successful search of the expected spectral details demanded by proposed structure, is possible if we seek the explanation for missing feature on theoretical grounds and apply all other available instrumental analytical arsenal of the structural chemist.

In present study the electronic absorption data of Co(II), Ni(II), Cu(II), Cr(III), Mn(II), Zn(II) and Cd(II) complexes are recorded, interpreted in the light of theory of transition metal complexes and plausable structures are assigned to them. The ligand and complexes for which the solubilities permit recording of solution spectra. The data are for solutions. The absorption spectral data and the calculated parameters and spectra curves are given in results and discussion.

For sparingly soluble Schiff base complexes the recorded spectra are in the reflectance mode.

3.7 Infrared Spectra

IR spectroscopy can be conveniently used for the study of involvment of certain functional groups in formation of ionic or covalent chemical bonds , coordination by donation of electron by electron rich atom like nitrogen, oxygen and sulphur. Finger print vibrational bands for various functional feature of the ligand as well as major to minor changes in the band positions resulting from over all metal ligand complexation processess. The interpretation of IR absorption bands can be done on the basis of evidences from the known reports from literature. However, more perfect analysis is possible by application of symmetry consideration and group theory wherever possible.

Infrared data and assignments as well as the spectra are given in results and discussion.

3.8 Structure of Co(II) complexes

Cobalt ion generally forms two series of complexes d^6 and d^7. The d^6 state is Co(III) with four unpaired electrons in high spin state and all paired electrons in spin-paired strong field case in the octahedral geometry. In the tetrahedral case the reversal of t2g, and eg levels may give spin-free weak field complex with four unpaired electrons and in spin-paired case two unpaired electrons are present. The corresponding change in magnetic character is a diagnostic feature. Generally preparation of d^6 Co(III) complexes passes through the oxidation using ~~by~~ air or oxidation by using H_2O_2. In strong field spin paired case theoretically an octahedral state will exist and will have one unpaired electron. In the tetrahedral geometry three unpaired electron must be present. In weak field case octahedral geometry will show three unpaired electrons, and in tetrahedral case there are three unpaired electrons.

This discussion gives theoretical aspects of ideal octahedral or tetrahedral geometries and incase the complexes are monomeric in nature. Any distinction may have its reflection in mainly spectral characteristics.

The complexes are fairly soluble in common organic solvents like acetone and ethanol, methanol and well defined absorption bands are trassed in visible region at around 25 kK. The charge transfer band begins to appear in NIR region that is 10000 to 26000 cm^{-1} (i.e. 10 - 4 kK). The absorption is very low and no absorption bands in NIR are observed for the solutions. However, reflectance spectra of the powders can be recorded to give all the bands. In case of tetrahedral complexes further opening to make available two additional coordination sites around central metal atom resulting in octahedral conversion is possible. This conversion from tetrahedral to octahedral species results in further opening of coordination sphere. This change is very easily visualized by a colour change from deep blue tetrahedral to faint pink octahedral state. The complexes reported in this project are high spin d^7 Co(II) complexes and on the basis of tabulated data if conclusively proves that the deep blue or green complexes are tetrahedral whereas the aqua-complexes are all octahedral in nature.

3.8.1 High spin Co(II) Complexes : d^7 State

High spin tetrahedral Co(II) has t_{2g}^{5} e_{g}^{2} configuration and its ground term corresponds to three unpaired electrons. high spin tetrahedral cobalt complexes absorb mainly in 5000-7000 cm^{-1} to 14000 - 16000 cm^{-1} region[6-13]. Three absorption bands may be expected which corrspond to $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ ($\nu 2$) and $^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$ ($\nu 3$) . Their intensities are $10 - 10^2$ L mol^{-1} cm^{-1} and $10^2 - 10^3$ L mol^{-1} cm^{-1}. The $^4T_{2g}(F) \leftarrow {}^4A_{g}(F)$ transition is very weak.

Marootrigiano et. al. studied the electronic spectra of tetrahedral Co(II) complexes of amines of type CoX2 (L^{2+}) (where X = Cl, Br, I)[14]. The complexes exhibit visible wavelength absorption ($\nu 3$) which occurs in the region 12000 cm^{-1} to 17000 cm^{-1} which is usually found for the tetrahedral Co(II) complexes. They also exhibit multiple absorption in the region 10000 to 5000 cm^{-1} ($\nu 2$) found for Co(II) in tetrahedral surroundings. Colton and Faut et.al.[15] studied the cobalt complexes which exhibit visible wave lengths absorption ($\nu 3$) at 1390 cm^{-1} to 16200 cm^{-1} which is a feature of the tetrahedral geometry. There is multiple absorption in the region 5300 cm^{-1} 7570 cm^{-1}. Forster studied the tetrahedral complexes $Co(etu)_4^{2+}$ in which $\nu 3$ band is at 13875 to 15720 cm^{-1} and multiple absorption in the region 6500 cm^{-1} [16]. Tomlinson studied Co(II) complexes $Co(dietu)_2Cl_2$ which exhibit 2 band at 14000 to 16400 cm^{-1} which is the characteristic of tetrahedral environment[17] Kennedy et.al. studied[18] the tetrahedral cobalt complexes which exhibit $\nu 2$ band at 13500 to 154700 cm^{-1} and ν_1 band at 7330 cm^{-1}.

Tetrahedral Co(II) complexes of Schiff's bases are less studied [19-22] as compared to octahedral ones. Biradar et.al. studied tetrahedral Co(II) complexes of Schiff's bases vanillydenemines [19] and showed that the electronic spectra exhibit two prominant bands at ~ 14750 cm^{-1} (ν_2) and ~7100 cm^{-1} (ν_1) in the visible and near infrared regions. Dey et.al. studied the tetrahedral Co(II) complexes of salicyliden-ethylenediamine [21] . The above discussion of electronic spectra together with magentic susceptibility data give the precise idea about the stereochemistry.

3.8.2 High spin octahedral d^7 complexes

High spin octahedral cobalt (II) complexes absorb mainly in two regions 8000 - 10000 cm^{-1} and 20000 cm^{-1} [23-29].
There absorption bands may be expected which correspond to $^4T_{2g} \leftarrow {^4T_{1g}}$, $^4T_{1g}(P) \leftarrow {^4T_{1g}}$ and $^4A_{2g} \leftarrow {^4T_{1g}}$. The band around 8000 cm^{-1} is usually assigned to $^4T_{2g} \leftarrow {^4T_{1g}}$ transition and its intensity is 1-10 L $mole^{-1}$ cm^{-1}. A second band observed around 20000 cm^{-1} is of intensity 5-40 L $mole^{-1}$ cm^{-1} and may be assigned to $^4T_{1g}$ (P) ← $^4T_{1g}$ transition, with a probable overlap of the spin forbidden bands due to the free ion ^2G and ^2H terms. The two electron transition $^4A_{2g} \leftarrow {^4T_{1g}}$ is normally not observed.

Ferguson et. al. studied the low temperature spectra of complexes of cobalt (II) with a large number of ligands [23]. They reported that the spectrum consists of symmetric band with shoulders on the high energy side and assigned them to spin forbidden transition. The $^4A_{2g} \leftarrow {}^4T_{1g}$ aband is very weak and occurs around 12000 cm^{-1}. In many cases where o organic ligands are used, the band due to $^4A2g^2 \leftarrow {}^4T_{1g}$ transitions is so weak that it is not observed because the tail of the ligand absorption band is intense eneough to cover it. In some cases spin forbidden bands on either sides of the spin allowed band are observed. The spin forbidden band appearing on the low energy side as a shoulder arises from ^2G term and the spin forbidden band appearing on the high energy side as a shoulder arises from ^2G, ^2H, ^2D and ^2P terms.

A few recent studies on octahedral cobalt(II) complexes are reviewed in the following paragraph [30-37]. Rao et. al. studied octahedral Co(II) complexes of some nitrogenous ligands viz. quinoline, isoquinoline and 3-methyl-pyridine [30]. The electronic spectra of the complexes exhibit bands at 8600 and 19700 cm^{-1} corresponding to the $^4T2g \leftarrow {}^4T_{1g}$ $^4T_{1g}(P) \leftarrow {}^4T_{1g}$. Sanghis et.al. studied the electronic spectra of octahedral Co(II) complexes derived from o-amino benzene sulphonic acid and 2-amino ethane sulphonic acid of Schiff's base.

base. Electronic spectra of complexes in benzene solution show two bands at ~ 15500 and at ~ 20200 cm^{-1} corresponding to the transition $^4A_{2g}$ (F) ← $^4T_{1g}$ (F) and $^4T_{1g}$(P) ← $^4T_{1g}$(F)[3 Rastogi et.al. studied the octahedral Co(II) complexes derived from Schiff bases of hydroxymethyl aminomethane and 2-amino-2-methylpropanediol. Reflectance spectra of the complexes exhibit bands at 20,000, 10,400 and 8,330 cm^{-1} (ν_3, ν_2 and ν_1) respectively[32]. Yamada et al. studied some octahedral complexes of Schiff's bases derived from 2-aminoethylpyridine and salicylaldehydes. The complexes exhibit bands ~ 10000 cm^{-1}, ~ 15000 cm^{-1} ~ 19000 cm^{-1} and 27000 cm^{-1}[33].

3.8.3 Ligand field theory of tetrahedral high spin d^7 complexes

The high spin configuration for t_{2g}^5 , e_g^2 resembles the pattern of d^2 cases. The correlation diagram for d^7 cases is comparable to that of d^2 and is inverse to that of d^3 case. Three spin-allowed transitions from the spin free ground state are expected. The approximate energies of these transitions are given by Lever[5] as below.

$^4T_2$ —— $^4A_{2g}$ 10 Dq ... (1)

$^4T_1$ —— $^4A_{2g}$ 6 Dq + 15 B ... (2)

$^4T_1$ —— $^4T_{2g}$ 8 Dq ... (3)

The energy level diagram is shown in fig. 3.1 . The half part of the Tanabe-sugano diagram incorporates allowed transitions involving ^4F and ^4P terms as well as weak forbidden transitions involving ^2G and ^2I terms. With the introduction of Tanabe-Sugano diagram [38,39] electronic spectra of coordinatio compounds, even the not-allowed transition levels could be explained. It is possible to determine tetrahedral ligand splitting parameters 10 Dq and the interelectronic repulsion parameters (Racah B and C parameters) can be directly calculated from the observed spectra. The main difficulties encountered in the study are as follows :

(1) Some times very strong charge transfer bands overlap the d-d transition bands.

(2) Some times the d - d transition bands are extremely weak and hence the location is difficult.

(3) Due to poor solubility of some complexes accurate recording of spectra is difficult.

(4) Near infrared spectrometry and reflectance measurement in NIR region are not within easy reach of all.

3.8.4 Racah parameters B and C

The interelectronic repulsion parameters are important electrostatic parameters in ligand field theory.

The Racah interelectronic parameters B and C are the functions of ligand, central metal ion and the sterochemistry. The crystal field intergral Dq describes the interaction of the central metal electrons with surrounding ligands, but the interrelation repulsion parameters (Racah B and C) are a measure of the interaction of the metal electrons among themselves. In any molecules or ion with more than one electron capable of attributing optical characters both the crystal field integral (Dq) and inter electron repulsion parameters (B and C) are simultaneously operating.

The Racah parameter C is approximately equal to 4B. But an accurate equation for d^7 case is given by lever[5].

$$C = 4.633B \qquad \ldots (13)$$

3.9 Results and Discussion

3.9.1 Electronic Spectra

3.9.1.a Cobalt (II) Complexes of DCT

Two bands are observed in the electronic spectra of Co(II) complexes which are specifically due to spin allowed transition.

$$^4T_1 \leftarrow {}^4A_2 \qquad 7500\ \text{cm}^{-1}$$

$$^4T_{1(P)} \leftarrow {}^4A_2 \qquad 16500\ \text{cm}^{-1}$$

These transitions are in agreement with tetrahedral geometry of Co(II) complexes. The representative spectra are shown in Fig. 3. . These bands observed in reflectance spectrum and its solution spectra show transitions at 14300, 15 15200 and 16500 cm^{-1}. The complexes of $CoBr_2$, $(OCoAc)_2$ and $Co(NO)_3$ show similar absorption bands.

Sacconi et al.[40] studied the tetrahedral $Co(Me_4en)e/2$ complexes. The absorption bands lie in the region 7250 - 10000cm^{-1} and 15400 - 17200 cm^{-1}. Prucurik et al.[41] studied the tetrahedral $Co(tu)_2$ c/2 complex, the absorption bands lie in the region 5300 - 7500 cm^{-1} and 13950 - 16200 cm^{-1}. Singh et al.[42]

studied the tetrahedral Co(II) complexes of, the absorption bands lie in the region 9000 - 5000 cm^{-1} and 16000 - 14000 cm^{-1}. John et al.[43] studied the tetrahedral Co(II) complexes of substituted taiazole, the absorption bands at 8076 cm^{-1} and 16450 cm^{-1}. Eilbeek et al.[44] studied the tetrahedral Co(II) complexes of thiazole, the absorption bands at 6349 - 8509 cm^{-1} and 15870 cm^{-1}. The values ν_3/ν_1, ν_2/ν_1 and ν_3/ν_2 calculated for the complexes are in agreement with the reported values of tetrahedral Co(II) complexes.

3.9.1.b Magnetic Susceptibility

The magnetic mement of the Co(II)complexes lie in the range 4.6 to 4.7 B. M.[42,44,45]. This supports tetrahedral or pseudotetrahedral geometry. In present study the values of magnetic moment were found in the range 4.3 to 4.7 B.M. These values suggest that Co(II) complexes have tetrahedral geometry. The values are given in Table 3.4

3.9.1.c Infrared Spectra

The infrared spectral data of DCT and its complexes are given in Table No. 3.5. The -NH band in the free ligand shifts
Schiffs to lower or higher frequencies. The ν(N-H) shift may be due to coordination to the central metal atom.

The Co(II) ~~metal~~ atom in the complexes in the present work are coordinated through exocyclic nitrogen because the ~~ni~~ nitrogen of the amine group is in sp^3 hybridization state, hence loosely holds its lone pair electrons as compared with the ring nitrogen which is present in sp^2 hybridization and lone pair of electrons of sulphur are involved in aromaticity of the ring and hence comparatively less available [42].

In case of Co(II) complexes the ν(N-HO) vibration at 3390 cm^{-1}, 3200 cm^{-1}. δ(N-H) deformation as same the ligand and (C-N) vibration also show the same frequency of ligand, (C-S) frequency similar to ligand. The ν(M-N) band at 315 cm^{-1}, 440 cm^{-1}, 425 cm^{-1} and 345 cm^{-1} [2,42,45,46]. The present cobalt complexes show the ν(M-N) bands at 315, 330, 360 and 345 cm^{-1}.

3.9.2 Schiff Base Complexes

3.9.2.a Electronic Spectra

Electronic spectra of Schiff bases show an intense charge transfer band at 26200 to 25000 cm^{-1}. Two bands are observed in the electronic spectra of Co(II) complexes which are due to spin allowed transition.

$^4T_2 \leftarrow {}^4A_2$ 7600 cm^{-1}

$^4T_{1(P)} \leftarrow {}^4A_2$ 13400 - 16000 cm^{-1}

These transitions are in agreement with tetrahedral geometry of the Co(II) complex. The electronic spectra are given in Fig. 3.2. These bands observe in reflectance spectra and its solution spectra shows bands at 14009 , 15000 and 16000 cm^{-1} . Saha et al. [47] studied tetrahedral Co(II) complexes of Schiff base which is derived from N-Benzylidene-5-(3)-Methylpyrazole 3(5)-carbohydrazide . The asborption bands lie in the region 8.3 - 9.1, 15.4 - 15.3 and 21.1 - 21.0 kK respectively.

Mahapatra et al. [48] studied tetrahedral Co (II) complexes of Schiff base derived from 2-Amino-5-phenyl-1,3,4-oxadiazole. The absorption bands lie in the region 83000, 15600 cm^{-1} attributed to $^4T_{1(F)} \leftarrow {}^4A_2$ and $^4T_{1(P)} \leftarrow {}^4A_2$ respectively. Cotton et al. [49] studied the tetrahedral complexes of Schiff base. The absorption bands lie in the region 7220 - 10000 cm^{-1} and 13890 - 15600 cm^{-1} respectively.

Dash et al.[50] studied the tetrahedral complex of Co(II). The band lie in the region 1800 - 25000 cm^{-1}. The values ν_3/ν_1, ν_2/ν_1 and ν_3/ν_2 calculated for the complex is in agreement with the reported values of tetrahedral Co(II) complexes[13,10, 47,50].

3.9.2.b Magnetic Susceptibility

The magenetic moment of the Co(II) complexes lies in the range 4.8 to 5.2 B.M.[51]. This supports the octahedral geometry for the complexes. Squar.planar quadri-coordinated Co(II) complexes may be either spin free or spin paired. There is no evidence for spin free Co(II) square-planar complexes. More et al.[52] showed that the octahedral complexes possess magnetic moment in range 4.8 to 4.7 B.M., whereas the tetrahedral complexes generally lies in the range 4.4 to 4.7 B.M.[53-54]. The present Co(II) complex shows magnetic 4.5 B.M. This indicates that the complex have tetrahedral geometry.

4.6? (Table 34)

3.9.2.c Infrared Spectra of Schiff Base

The presence of C=N frequency of 1620 to 1630 cm^{-1} is characteristic of all schiff base. The absence of free phenolic -OH group frequency at 3100 cm^{-1} may be due to intermolecular hydrogen bonding between the phenolic azomethine nitrogen and -OH group[55-56].

3.9.2 d Infrared Spectra of Complexes

The OH band in free ligand disappears in the complex thereby showing the band formation through oxygen of OH group and metal ion. The C=N frequency shift may be due to coordination to the central metal atom through nitrogen of azomethine group.

3.10 Octahedral Co(II) complexes of DCT and $DCT(Sal)_2H_2$ i.e.

$Co(DCT_2\ (H_2O)_2\ Cl_2)$

$CO(DCT(H_2O)_2\ Br_2)$ $Co(DCT(H_2O)_2\ (NO_3)_2\ )$ and

$Co(DCT(sal)_2\ (H_2O)_2Cl_2)$

Deep blue or green Co(II) complexes undergoes a distinct colour change to faint pink by direct reaction within water. Two moles of water can be added to CoL_2X_2 and $CoLX_2$ complexes and the blue or green coloured tetrahedral complexes $[CoL_2X_2]$ and $[CoL'X_2]$ changes to $[CoL_2\ (H_2O)_2Cl_2]$ and $[CoL'(H_2O)_2Cl_2]$ as octahedral species where L is DCT and L' is the tetradenate Schiff base.

In UV region high spin octahedral complexes show very weak transitions and hence the search for above bands in solution spectra is not successful. From the nature of reaction and the It is obvious the complexes are octahedral in nature.

Ligand Field Parameters of tetrahedral Co(II) complexes (cm^{-1})

$[Co(DCT)_2Cl_2]$, $[Co(DCT)_2Br_2]$, $[Co(DCT)_2(NO_3)_2]$ and $[Co(DCT(Sal)_2)Cl_2]$

		ν_1	ν_2	ν_3	Dq	B	C
I)	Expt	6600	15000	25000	805.0	1324.9	6138.2
II)	Expt	7500	14800	24800	722.4	1387.4	6427.8
III)	Expt	7400	14600	24200	698.2	1110.2	5143.5
IV)	Expt	7600	14600	24800	707.01	1092.9	5063.40

Ligand Field Parameter of tetrahedral Co(II) complexes (cm^{-1})

$[Co(DCT)_2Cl_2]$, $[Co(DCT)_2Br_2]$, $[Co(DCT)_2(NO_3)]$ and $[Co(DCT)(Sal)_2Cl_2]$

		ν_3/ν_1	ν_2/ν_1	ν_3/ν_2	Dq/B	B/C
I)	Expt	3.78	2.27	1.6	0.607	0.215
II)	Expt	3.30	1.9	1.6	0.52	0.2158
III)	Expt	3.27	1.9	1.6	0.62	0.2158
IV)	Expt	3.26	1.92	1.69	0.64	0.2158

3.11 Thermal Analysis

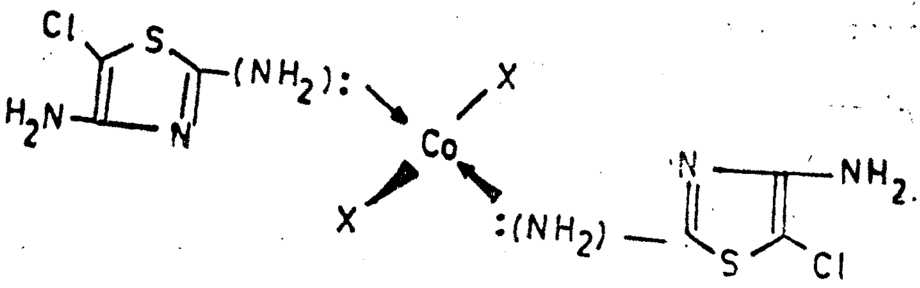
Thermal analysis is a useful analytical tool and it is possible to study serveral aspects such as association of water in the form of loosely coupled absorbed water, the molecules of water which are coordinated to central metal atom in aquocomplexes and the relation of the secondary ligands in the adduct. The ligands mostly break down and are lost and finally the residue left around 500°C is generally the oxide of the metal. Sometimes the complex can undergo sublimation and in such cases mass spectrometry is used. The thermal analysis of the metal complexes were carried out from the room temperature to 500°C. DTA mostly talks about two aspects; the first is heats of theremal decomposition reaction that is exothermic or endothermic nature of the theremal change. In addition to this DTA can throw light on phase changes and the associated energies.

The TGA curves are given in Fig.3.7. The Thermograms show no presence of water in blue green complexs. and so the profile of curves do not show any loss of free water. The ligands are completely lost between 200 to 340°C mainly leaving behind metal oxide. The calculated metal oxide percentage agree with loss of ligand obtained from thermogravimetic curve.

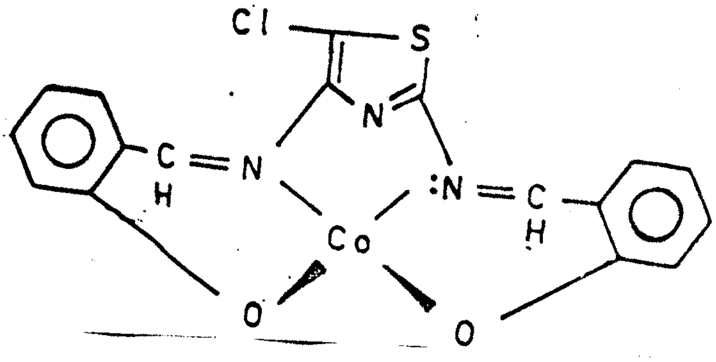
3.12 Electrical Conductivity

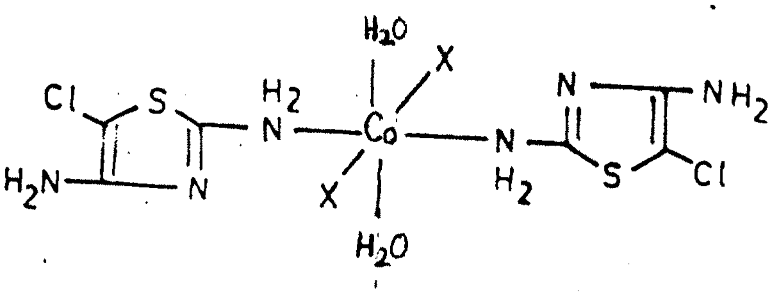
The complexes have fairly good solubility in many oxygenated solvents such as acetone and alcohol. The complexes shown very low conductivity (as given in Table). This indicates that all the complexes are molecular in nature.

In the light of above discussion. The tetrahedral geometry is proposed for the complexes on the basis of electronic spectra, Infrared spectra, magentic susceptibility measurements, and thermal analysis. The tetrahedral structure involves bonding through exocyclic nitrogen in DCT and in DCT $(Sal)_2H_2$ bonding through two phenolic -OH groups and coordination through two azomethine nitrogens. The structure of the complexes is as shown below.



Where $X = Cl, Br, NO_3$ or OAc





3.13 Structure of Ni(II) Complexes

The common oxidation state of nickel is +2 in simple salts and complexes in the form~~s~~ of solids as well as in solutions. The stereochemistry of nickel is fairly complicated and a clear cut analysis and ellucidation of structure is often a difficult work.

Nickel complexes generally form four, five or six coordinated species with octahedral, trigonal bipyramidal , square pyramidal, tetrahedral or square plan~~n~~ar structures and variations of multinuclear clusters.

Monomeric as weell as dimeric species commonly occur. Often it is difficult to clearly argue out one over the other. The issue becomes somewhat difficult because of several complicated equilibria which are temperature as well as concentration dependent.

3.13.1 Tetrahedral Complexes

Four coordinated ~~tetrahedral~~ complexes in tetrahedral symmetry, the d^8 configuration, gives rise to $3T_1(F)$ ground state. The electronic transition $3T_1(P) \leftarrow 3T_1(F)$ occurs in the visible region with values around 1000 L mole^{-1} cm^{-1}

and are expected to be strongly coloured, generally blue or green in colour. Regular tetrahedral Ni(II) complexes must have magnetic moment of about 4.2 B.M. at room temperature. If ideal geometry does not exist there is marked reduction to ~ 3.5 B.M. With further distortion lowering of magnetic moment to 3 B.M. is possible. This value matches with that expected for six coordinated complexes.

3.13.2 Square Planar Complexes

The preferred geometry for d^8 confugeration in four coordinated state is square -planar. Planar complexes of nickel are diamagnetic in nature. They are generally red, yellow or brown. Examples of such square-planar complexes are yellow $[Ni(CN)_4^{2-}]$ and yellow to brown $[Ni(PR_3)_2X_2]$ in which R is any alkyl group.

3.13.3 Octahedral Complexes

Ni(II) can have six as highest coordination number. These complexes are blue, purple or bright green. d^8 octahedral complexes are expected to have three allowed transitions in electronic spectra corresponding to $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ at 9 - 10 kK, 14 - 18 kK and 25 - 30 kK. Octahedral nickel complexes have two unpaired electrons giving magnetic moment ranging from 2.9 to 3.9 B.M.

3.13.4 Anomalous Properties of Ni(II) Complexes

Although in the above discussion Ni(II) complexes have been attributed specific geometries, in reality, the ideal geometries are less commonly observed. The observed properties of many complexes can be explained in term of anomalour behaviour. The additional stereochemical forms are observed in Ni(II) on partial dimerisation to give 5-coordinated square pyramidal structure. The nickel complexes obtained by reaction with DCT, $NiCl_2$, $NiBr_2$ and $Ni(NO_3)_2$ and Schiff's base $NiCl_2$ gave ochre yellow microcrystalline materials. The electronic spectra in acetone solution and reflectance mode for these complexes are shown in Fig. 3.2 A and B. The observed magnetic moment of these complexes indicated the possibility of a complex structure. The ring nitrogen donating the pair to nickel in the upper level and ring nitrogen from the upper ring donating a pair to nickel of lower level. This structure must be consistent with a moderate colour of complexes. Electronic spectra, the magnetic moment, infrared spectral data for these complexes are summarised in Tables 3.5 and 6, 3.4 and 3.7, 8 and 9.

A dimeric structure with five coordinated nickel is shown below. This explains the ochre yellow colour, low solubility, microcrystalline nature and magnetic moment of ~ 3.2 B.M.

Schiff base complex also has yellow colour and it can be assigned five coordinated square pyramidal dimeric structure.

The properties are consistant with those of DCT complexes of nickel (II).

3.13.5 Formation of Six Coordinated Aduct

Addition of ligands like pyridine, ethylenediamine, 2,2' bipyridyl and 1,10-phenanthroline give six coordinated octahedral nickel complexes. Here the DCT complex gives rise to a monomeric structure of the type $[\,M(L_2L\tfrac{1}{2})X_2]$. The products are either waxy pale green or yellow crystals. The very weak absorption band giving very low profile making it almost impossible to locate absorption bands indicates a symmetric substitution by 2 py molecules in axial positions. The IR spectra as shown in table 5 confirm to this view.

3.14 Theory of Square-Planar Complexes

Square Planar nickel (II) complexes are generally orange, yellow or red in colour. Some complexes have been reported to be purple or green in colour [57 - 64]. Generally, the complexes exhibit a strong absorption band in the visible region between 15000 and 25000 cm^{-1} and in many cases a second more intense band between 23000 and 30000 cm^{-1}. These bands correspond to $\nu 2$ and $\nu 3$ transitions respectively [65 - 69].

Square planar Ni(II) complexes of sulphur containing ligands show additional band in NIR region and is referred as ν_1[65]. Some amine complexes exhibit a very weak band ~ 11000 cm^{-1} in NIR region and may be due to spin-forbidden transition.

The distinction between the square planar and octahedral or tetrahedral coordination can be done on the basis of the fact that the prior does not absorb belwo 10000 cm^{-1}. This situation is due to the large crystal field splitting in the square planar complexes.

Spectra of the single crystals of some complexes have however shown bands below 10000 cm^{-1}, but these bands may be vibrational in nature. Several studied of the square-planar complexes have been reported[57 - 64] but clear cut generalisation is not so far possible. Parikh et al. studied Ni(II) complexes of Schiff's base derived from salicylaldehyde and diamine complexes which exhibit two shoulders at ~425 nm and 500 nm in the electronic spectra. There is no band beyond 600 nm[70]. Thakur et al. studied the Ni(II) complexes of type [Ni(L)PY)X] (where LH = Schiff's base derived from amino quinidine, PY = Pyridine and X = NO_3^- , Cl^-, Br^- or I^- and proposed a square planar structure. The complexes exhibit only one absorption band at 16000 cm^{-1} in electronic spectra[71].

A series of square planar bis ligand nickel (II) chelates with hydrazine-s-methyl dithiocarboxylate exhibit bands in the region 16000 to 27800 cm^{-1}. Schiff's bases exhibit bands in the region 16000 to 27800 cm^{-1} 72 - 76.

Iskander et al. studied Ni(II) complexes of Schiff's bases derived from hydrazine-5-methyldithiocarboxylate. The structure of complexes is consistent with square-planar geometry. The bands located at 450 and 565 nm in the electroni spectra can be assigned to $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1B_{1g} \leftarrow {}^1A_{1g}$ transitions in D_2h symmetry [77]. Nishida et al. studied square-planar Ni(II) complexes of macrocyclic Schiff's bases. The electronic spectral bands correspond to transitions $d_{xy} \leftarrow d_{yz}$, $d_{xy} \leftarrow d_{z^2}$ and $d_{xy} \leftarrow d_{x^2-y^2}$ with energies $\delta_1 - 3f_2 - 20F_4$, $\delta_2 - HF_2 - 15F_4$ and $\delta_3 - 35F_4$ respectively [77].

3.15 Ligand Field Theory of Square Planar d^8 Complexes

The ground state of square planar d^3 and d^8 system is $3A_{2g}$ state and order of excited state in both the configuration is the same i.e. spin allowed transition and the energy of transition are given by [80].

$^1B_{1g} \longleftarrow {}^1A_{1g}$ (ν_1)

$^1A_{2g} \longleftarrow {}^1A_{1g}$ (ν_2)

$^1E_g \longleftarrow {}^1A_{1g}$ (ν_3)

The configuration d^8 gives rise to two quartet terms 4F and $3P_1$ with 3F the ground terms and 3P being 15B higher in energy.

3.16 Racah Parameter B and C

The Racah interelectronic parameters B and C are the functions of ligand, central metal ion and the stereochemistry. The crystal field integral Dq describes the interactions of the central metal electron parameters are a measure of interaction of the metal electrons among themselves.

The Racah parameter C is approximately equal to 4B. But more accurate equation is given by Lever[66]

$C = 4.633B$

Free ion values of B and C are given in the following table for 1st row transitions.

Racah Parameter B and C

	Ion	B in cm^{-1}	C in cm^{-1}
$3d^2$	Ti^{++}	718	2629
	V^{3+}	861	4165
	Cr^{4+}	1039	4238
$3d^3$	Sc^{+}	480	-
	V^{2+}	766	2855
	Cr^{3+}	918	3850
	Mn^{4+}	1064	-
$3d^4$	Cr^{2+}	830	3430
	Mn^{3+}	1140	3675
$3d^5$	Mn^{2+}	1058	3901
	Co^{3+}	1100	-
$3d^7$	Co^{2+}	971	4366
$3d^8$	Ni^{2+}	1041	4831

If the B values for metal complexes are compared with the corresponding free ion values, a reduction B upon complexation is invariably noted. This implies both that the mean radial displacement of the d electrons has increased and that the effective charge experience by the electrons has decreased.

3.17 Results and Discussion

3.17.1 Nickel Complexes of DCT

3.17.1 a Electronic Spectra

The electronic spectra of Ni(II) complexes exhibit three bands at 8600 cm^{-1}, 13400 cm^{-1} and 20000 cm^{-1}. These three bands are attributed to ν_1, ν_2 and ν_3.

$^1B_g \leftarrow {}^1A_{1g}$ (ν_1) 8600 cm^{-1}

$^1A_{2g} \leftarrow {}^1A_{1g}$ (ν_2) 13400 cm^{-1} and

$^1E_g \leftarrow {}^1A_{1g}$ (ν_3) 20000 cm^{-1}

transitions respectively. These bands are observed in the reflectance mode and the solution spectra shows absorption band at 14700 cm^{-1} and 16000 cm^{-1}. The above results support five coordinated square-planar geometry for Ni(II) complexes. The complexes prepared from nickel bromide and nitrate show similar bands in reflectance as well as transmission in solution.

Goodgame et al. studied [79] the $Ni(Q)_2I_2$ complexes having square-planar structure. The absorption bands lies in the region 11000 cm^{-1}, 15430 cm^{-1} and 21750 cm^{-1} as ν_1, ν_2

and ν_3 respectively. Electronic spectra of square-planar Ni(II) complexes were studied by Lever [80]. The absorption spectra show square-planar characteristics and bands lie in the the region 11000 cm^{-1} (ν_1), 16160 cm^{-1}(ν_2) and 22730 cm^{-1} (ν_3).

Ferraro et al. studied [81] the square-planar $Ni(as\text{-}Et_2en)_2^{2+}$ complexes which gives absorption band ν_2 at 21390 cm^{-1}. Lever et al. [82] studied the $Ni(QX)_2I_2$ having square-planar geometry. The absorption bands ν_1, ν_2 and ν_3 lie in the region 11650 cm^{-1}, 17100 cm^{-1} and 26000 cm^{-1} respectively. Stephens et al. studied [83] the Ni(II) complexes $Ni(2\text{-}2\text{-}2tetN_4)^{2+}$, $Ni(2\text{-}3\text{-}2tetN_4)^{2+}$, $Ni(3\text{-}2\text{-}3\ tetN_4)^{2+}$ and $Ni(3\text{-}3\text{-}3\ tetN_4)^{2+}$ these complexes are square-planar. The absorption band, ν_2 lies in the region 21050 - 22520 cm^{-1}. In present study the absorption spectra of complexes are in agreement with the dimeric five coordinated square pyramided structure.

3.17.1 b Magnetic Moments

The octahedral and tetrahedral Ni(II) complexes have no degenerate ground state and no contribution from spin orbital coupling is expected. The magnetic moments in octahedral complexes lie in the range 2.9 to 3.06 B.M. [84 - 86]. In tetrahedral complexes the magnetic moments lie in the range 2.9 to 3.43 B.M. [87 - 88]. In present study, magnetic moments of the complexes lie in the range 3.05 to 3.09 B.M.

3.17.1 c Infrared Spectra

Infrared spectra of nickel halide complexes were studied by Singh. The shifting of (NH) frequencies from 3400 to 3335 cm^{-1} - 3440 cm^{-1} indicate that coordination is through exocyclic nitrogen. The metal nitrogen bands and M-X bands are at 280 cm^{-1} and 218 cm^{-1}, respectively. The C-N and C-S-C stretching frequencies are similar to ligand. Compbell et al. studied the nickel complexes of amino thizole. The shifting of (NH) frequency from 3370 to 3300 cm^{-1} indicate coordination through exocyclic nitrogen. The metal-nitrogen band is at 247 cm^{-1} and the (M-N) band is at 310 cm^{-1}. Infrared spectra of Ni(II) complexes were studied by Manhas et al. The IR spectra of complexes are similar to ligand but only expected donor site is tertiary nitrogen. In present study all complexes show (N-H) shift, It means that coordination site is exocyclic nitrogen as well as the ring nitrogen.

3.17.2 Schiff Base Complex

3.17.2 a Electronic Spectra

The electronic spectra of Ni(II) complexes exhibit three bands at 9000 cm^{-1}, 13400 cm^{-1} and 22000 cm^{-1}. These three bands attributed to ν_1, ν_2 and ν_3

${}^1B_1 \leftarrow {}^1A_{1g}$ (ν_1) 9000 cm^{-1}

${}^1A_{2g} \leftarrow {}^1A_{1g}$ (ν_2) 13400 cm^{-1} and

${}^1E_g \leftarrow {}^1A_{1g}$ (ν_3) 22000 cm^{-1}

transistions respectively. These bands are oobserved in the reflectance mode and its solution spectra shows band at 14000 and 16000 cm^{-1}. The above results support five coordinated square-planar geometry for Ni(II) complexes. Iskander et.al. studied [72] the square-planar Ni(II) complexes. The absorption bands are exhibited in the region 16000 to 27800 cm^{-1}. Bakul et al. studied [87] the Schiff's base complexes of Ni(II) having square-planar geometry. The absorption bands are shown at 16000 to 22000 cm^{-1}. The five coordinated square-planar Ni(II) complexes were studied by Ahmed et al. [88]. The absorption bands occur at 380 nm and 410 nm. The five coordinated square-planar Ni(II) complexes of Schiff's base reported by Holm [89]. Show the absorption bands at 14400 cm^{-1} and 17000 cm^{-1}.

Several researchers studied the Schiff's base complexes of Ni(II). The electronic absorption spectra shows the bands at 16000 to 22000 cm^{-1} 73 - 76. In the present study, the ratios ν_3/ν_1, ν_2/ν_1 and ν_3/ν_2 calculated for the complexes are in agreement with the reported values of square-planar Ni(II) complexes.

3.17.2 b Magnetic Susceptibility Measurement

In an octahedral field Nickel (II) has a non-degenerate ground state $^3A_{2g}$ (t_{2g}^6 eg^2) and no contribution from spin orbit coupling is expected. The measured moments are in the range 2.8 to 3.3 B.M., very close to spin only value of 2.83. Value of octahedral complexes are slightly above the spin only value arising due to slight mixing of multiplet excited state in which spin-orbit coupling is appreciable. Tetrahedral Ni(II) has a ground state $T_1(eg^4\ t^4{}_{2g})$ and a large orbital contribution to the moment is expected. As a result, even though both octahedral and tetrahedral Ni(II) complexes contain 2 unpaired electrons, tetrahedral complexes have magnetic moment ~ 4. B.M. compared to 3.3 B.M. or less, for octahedral complexes. For octahedral complexes μ values lie in the range 3.0 - 3.3 B.M. whereas for the tetrahedral complexes, they lie in the range 3.6 to 4.00 B.M.[90]. The Ni(II) square-planar complexes are diamagnetic in character [90]. Our complexes posses magnetic moment of the order of 3.2 B.M.

3.17.2 c Infrared Spectra of Schiff base Ni(II) Complex

The shift of phenolic -OH frequency and appearance of a weak band at 2900 cm^{-1} in the the infrared spectra of the ligands suggest the intramolecular hydrogen bonding between the hydroxyl hydrogen and nitrogen of the azomethine group forming a stable six membered ring 92 . The absence of the -OH frequency in the complexes suggests the metal oxygen bond formation. The C-O frequency at ~ 1280 cm^{-1} in the free ligand is shifted to higher frequency at 1320 cm^{-1} in the complex which supports the metal oxygen bond formation 92 - 95 . The $>C=N$ stretching frequency in the free ligand is observed at ~ 1630 cm^{-1} while that in the complex occurs at ~1580 cm^{-1}. This lowering of the $>C = N$ frequency in the complex suggests the coordination through the nitrogen of the azomethine group 92 - 95. The coordination of the nitrogen to the metal atom would be expected to reduce the electron density in azomethine group and cause a reduction in the $>C = N$ frequency.

In the present study a broad band ~ 280 cm^{-1} may be due to metal nitrogen vibrations.

3.17.2 d Electrical Conductivity

The complexes have fairly good solubility in many oxygenated solvents such as acetone and alcohol. The complexes of DCT and [DCT $(Sal)_2H_2$] show very low conductivity (as given in table). This indicates that all the complexes are molecular in nature.

3.18 Thermal Analysis

The temperature increases at the rate of 10°C per 3 min. The sample size is approximately 30-40 mgm. At 500°C most of the complexes decompose.

3.18.1 Ni(II) Complexes of DCT

A thermogram of Ni(II) complexes does not show any change upto 120°C, beyond 120°C there is continuous weight loss upto 360°C mainly due to loss of ligand and metal oxide remain behind. The thermal behaviour of complex exhibits a fairly complex phenomenon. The abrupt change in the thermogram from 120 to 360°C may be due to loss of ligand. The calculated metal oxide percentage agrees with loss of ligand.

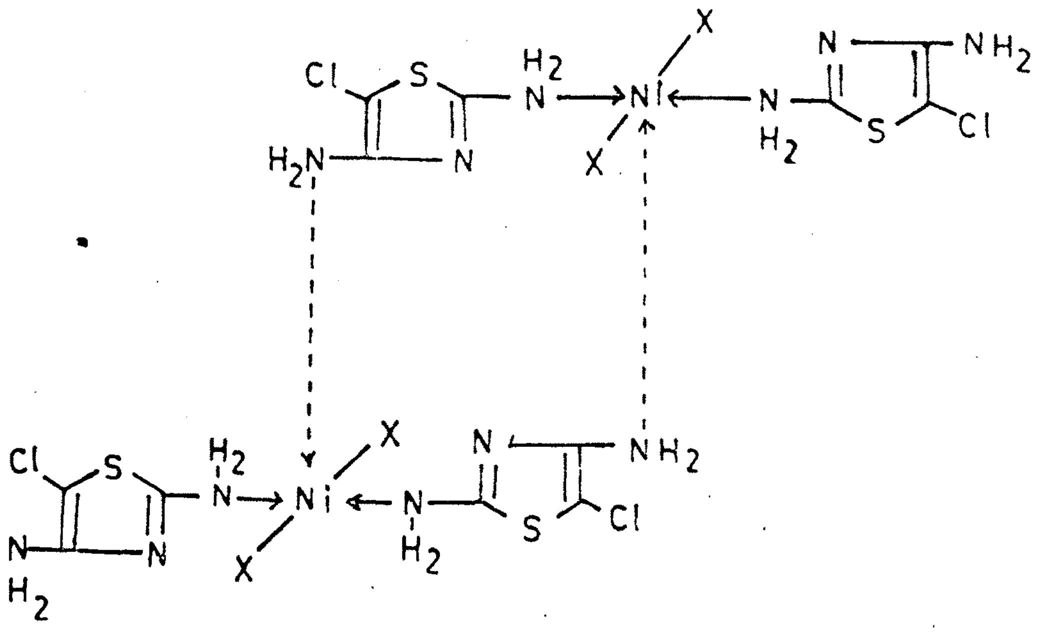
Ni(II) complex of DCT$(Sal)_2H_2$ shows similar thermogram. At 180 to 360°C there is loss of ligand and formation of nickel oxide beyond 360 upto 500 °C and the calculated metal oxide percentage agrees with loss of ligand obtained from thermogr~~amic~~vimetric curve.

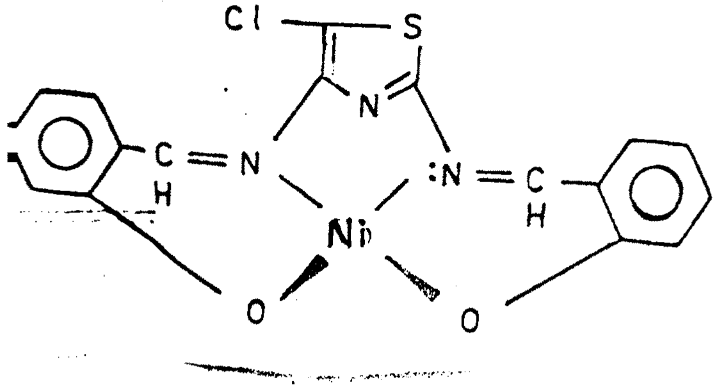
3.19 Adduct of the Nickel Complexes

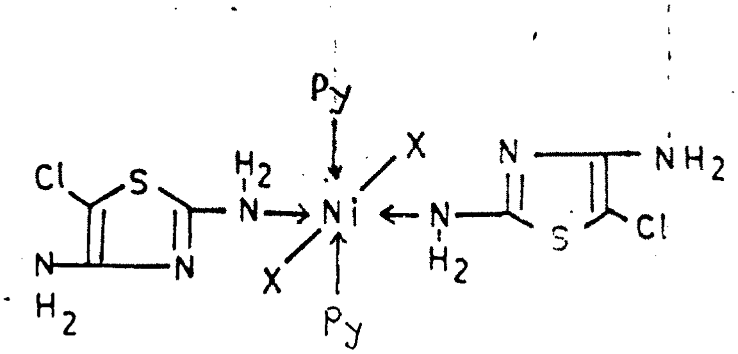
Several research workers studied the pyridine aduct complexes of Ni(II).

Assignment on pyridine aduct complexes of Ni(II) was done by Dave [96]. The ν(N-H) and C = N stretching frequency are at 3400, 3200 cm^{-1} and 1595, 1620 cm^{-1} of $-NH_2$ and C = N of Schiff's base and pyridine. Charalombous et al. [97] analysed the IR spectram of $Ni(H\text{-}Clquo)_2$ 2 Py and $Ni(S\text{-}meoquo)_2$ py complexes. The C = N stretching frequency was observed at 1603, 1530, 1500 cm^{-1} and 1505, 1550, 1500 cm^{-1} respectively. Marcotrigiano et al. analysed the spectra of $Ni(Ae\text{-}val)_2(Py)_2 \cdot 2H_2O$ complex. The ν(NH) and δ(NH) stretching and deformation occur at 3370, 3308 cm^{-1} and 1530 cm^{-1} [98]. El-Sharly and Charalamous et al. studied IR absorption of various pyridine adduct complexes [99-100] and assigned the C = N frequency to respective ligands.

In the light of above discussion, square-planar geometry is proposed for the complexes on the basis of electronic spectra, infrared spectra and magnetic susceptibility measurement. The square-planar dimeric structure of DCT and Schiff base, involves bonding through exocyclic nitrogen as well as ring nitrogen in DCT. In case of Schiff base bonding through two –OH phenolic groups and coordination through two azomethine nitrogen and two thiazole nitrogen may be present. Structures of the complexes are as shown below.







3.20 Structure of Cu(II) Complexes

Copper occurs in Cu(I), Cu(II) and Cu(III) state. But mainly the dipositive state is the most important one for copper. The well defined aqueous chemistry of Cu(II) and a large number of salts of various ions and its complexes are water soluble, exist in addition to a number of complexes.

The chemistry of copper complexes has been extensively studied. The interest in copper chemistry arises from the fact that it can take octahedral, square-planar or tetrahedral geometries and also forms polynuclear complexes. Its role as an essential micronutrient in plants and animals (as an essential micronutrient) is a subject of biochemical significance. Its action of controlling the iron metabolism and the enzyme activities necessitate a~~l~~ proper understanding of structure and reactivity.

In the present study near complexes of general type ML_2 (where L = DCT), ML (Where L = Schiff base) and M = Cu(II) have been prepared and charaterised by using analytical techniques. The molecular formula has been found on the basis of elemental analysis and molecular weight determination. Complexe prepared from schiff base is deep green and from DCT are pale blue in colour. The electronic spectral analysis has been used to assign the geometry. Infrared spectra, solution conductivity magnetic susceptibility measurement have been used for further characterization of the complexe. The complexes posses square-planar geometry.

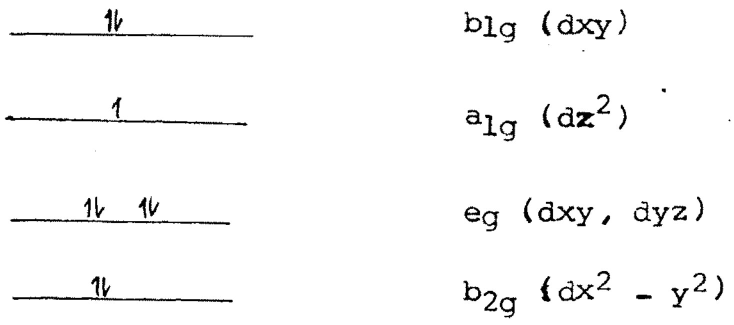
3.21 Theory of Copper Complexes

The bivalent Cu(II) has electronic configuration $3d^9$. Therefore the structure of the complex may be either distorted octahedral which in limit goes to square-planar configuration or tetrahedral.

Square-Planar Complexes

Complexes of square-planar stereochemistry with the configuration d^9 filled upto and including the A_{1g} orbital are with one unpaired electron in the big orbital. The ground term is $^2B_{1g}$. Excitation of one of the a_{1g} electrons to the big orbital gives the term $^2A_{1g}$.

Molecular orbitals



Square-planar complexes of bivalent copper are well established[101 -102]. In the spectrum of $Cu(acac)_2$, there are bands at $\sim$ 15000 cm^{-1} ($\epsilon = 38$) and $\sim$ 18000 cm^{-1} ($\epsilon = 53$) as well as bands of charge transfer at higher energy. The two bands may be assigned as

$$^2A_{1g} \leftarrow \quad ^2B_{1g} \qquad (a_{1g}^2\, b_{1g}^1 \rightarrow a_{1g}^1\, b_{1g}^2)$$

$$^2E_g \leftarrow \quad ^2B_{1g} \qquad (e_g^4 a_{1g}^2\, b_{1g}^1 \rightarrow e_g^3\, a_{1g}^2\, b_{1g}^2)$$

Belford et al. studied[103] the spectrum of $Cu(3\text{-}phacac)_2$ theres are bands at $\sim$ 19000 cm^{-1} and 20600 cm^{-1} bands of charge transfer at higher energy. Dudley et al. studied[104] the spectrum of $Cu(trien)_3 \not\subset (Clo_4)_2$ there are bands at 8000 cm^{-1} and 15000 cm^{-1} In the spectrum of $Cu(3\text{-}meacac)_2$ there are bands at 19200 cm^{-1} bands of charge transfer at higher energy and another bands at 15800 cm^{-1}, 14000 - 16000 cm^{-1} and 15500 cm^{-1} [105]. Radhakrishnan et al. studied square-planar Cu(II) complexes of Schiff's bases derived from 4-amino anti pyrine which exhibit a broad band 700 nm[107]. It is predicted that the complex may posses a distorted octahedral structure. Rastogi et al. studied the square planar Cu(II) complexes of Schiff bases derived from 2(2'amino-ethyl) pyridine which exhibit a band in the region 16000 - 16700 cm^{-1} ($^2E_g \leftarrow {}^2B_{1g}$) and shoulder in the region 19500 - 18000 cm^{-1} ($^2A_{1g} \leftarrow {}^2B_{1g}$) [113]. Shukla et al. showed that the square-planar Cu(II) complex of Schiff's bases which exhibit d-d transition band 680 nm[116]. Maztell et al. studied the square-planar complexes which exhibit a broad band in the visible region. The complexes were prepared by a templet reaction of amino alkylphosphoric acids or glyeylaminoalkyl phosphoric acids and salicylaldehyde with Copper(II) ion[115].

Lever et al. studied the square-planar complexes of Cu(II)[121]. The charge transfer band at 21000 cm^{-1}.

Square-planar complexes of Cu(II) reqpored by Weaver[122]. The charge transfer band at 22500 cm^{-1}.

3·22 Results and Discussion

3.22.1 Electronic Absorption Spectra

Electronic spectra of the present Cu(II) complexes exhibit two absorption bands, out of which one is in NIR region.

$^2A_{1g} \longleftarrow {}^2B_{1g}$ 7400 cm^{-1} and

$^2E_g \longleftarrow {}^2B_{1g}$ 9800 cm^{-1}.

The charge transfer band at 25000 cm^{-1}. These bands are observed in reflectance mode. These transitions are in agreement with square-planar geometry of Cu(II) complex.

3.22.2 Infrared Spectra

Infrared spectral data are given in table 3. Infrared spectra of substituted thiazole studied by Weaver [122]. The $\nu(M-N)$ frequency assigned at 285 cm^{-1} and $CuCl_2(4\ met)_2$ the $\nu(M-N)$ band at 305 cm^{-1}. Eilbeck et al. studied [123] infrared spectra of Cu(II) complexes. The $\delta(NH)$ vibration at 1449 cm^{-1} disappears at a neal band at 1412 - 1420 cm^{-1} and $\nu(NH)$ stratching vibration from 3480 to about 3300 cm^{-1} indicates that coordination througher aminogroup. Manhas et al. studied the Cu(II) complexes of aminothizole [124]. The spectral assignment shows that the tertiary nitrogen is involved in the bonding and entire spectra is similar to ligand. In the present complexe, the bonding through exocyclic nitrogen and metal-nitrogen bond observed at 308 cm^{-1}.

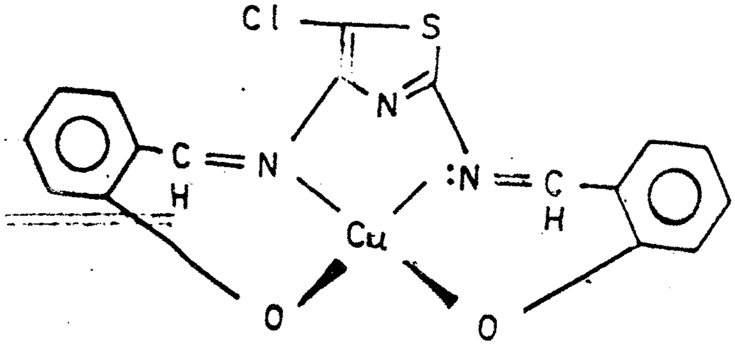
3.22.3 Magnetic Susceptibility

The Cu(II) complexes (d^9 case) have one unpaired electron. Hence the square-planar, tetrahedral or octahedral complexes show magnetic susceptibility ~ 1.9 B.M. [123, 125].

In case of square-planar Cu(II) complexes the unpaired electron of d^9 configuration is in the b_{1g} orbital giving a $^2B_{1g}$ term. may be expected to be some 15% above the spin only value. Amount of 1.9 B.M. is anticipated, independent of temperature[126]. In present study magnetic moment is 1.6 B.M. Magnetic susceptibility data given in table.

3.22.4 Schiff Base Complex

Electronic spectra of the present Cu(II) complexe exhibits two absorption bands; one band appears in NIR region at 7400 cm^{-1} and charge transfer band at 25000 cm^{-1}. These bands are observed in reflectance spectra and in agreement with square-planar structure. The structure is shown below.



Square-planar Cu(II) complexes of Schiff's bases are studied by several workers[106 120].

Shukla et al. showed the square-planar Cu(II) complex of Schiff base which exhibit d-d transition broad at ~ 680 nm [116]

3.22.5 Infrared Spectra

Infrared spectral assignments for the Cu(II) complexes are recorded in table. The representative spectrum is shown in fig.

The IR spectra of the Schiff's bases show a weak band at 2900 cm^{-1} instead of a strong band ~3100 cm^{-1} (due to phenolic -OH frequency). This may be due to the intramolecular hydrogen bonding between hydroxyl hydrogen and nitrogen of the azomethine group forming a stable membered ring [127]. The absence of OH frequency in the complexes suggests the formation of metal oxygen bond.

The Schiff's bases show a strong intense band at 1630 cm^{-1}. This may be due to $>C = N$ frequency. The $>C = N$ frequency in the complexes occur at 1580 cm^{-1}. The lowering of the $>C = N$ frequency in the complexes suggests the coordination through nitrogen atom of the azomethine group group [127 - 130]. The coordination through nitrogen to the central metal atom reduces the electron density of the nitrogen, hence the reduction in the $>C = N$ frequency in the complexes takes place.

The $C = O$ frequency at 1280 cm^{-1} in the Schiff's bases is shifted to higher frequency at 1320 cm^{-1} in the complexes. This shifting in the frequency suggests the formation of Copper oxygen bond [127 - 130].

As stated previously, the clear cut spectral analysis in IR is still not possible. Some clues on the basis of similarity between the structure of the amino acid complexes and Schiff's bases complexes give a certain degree of speculation. Low frequency bands observed in the present copper complex between 475 to 450 cm^{-1} may be due to $\nu(M-N)$ bond probably $\nu(M-O) + \nu(M-N$

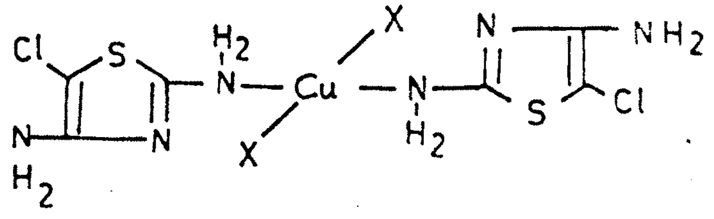
3.22.6 Thermal Analysis

A thermogram shows sliqut change from 60 to 120°C. This loss due to absorbed water. From 120 to 260°C a continuous weight loss indicating that formation of copper oxide upto 500°C. This thermal behaviours of cu complex exhibit complex phenomenon. A large change from 120 to 260°C may be due to loss of ligand and at 500°C complexes completely decomposed. The calculated metal oxide percentage agree with loss of ligand obtained from thermogramic curve. In Schiff base there is no loss upto 120°C from above there is continuous loss upto 380 °C. This thermal behaviour shows the complex phenomenon. At 120 to 380°C the complete loss of ligand and copper converted into oxide. The calculated metal oxide percentage agree with loss of ligand obtained from thermogramic curve.

3.22.7 Electrical Conductivity

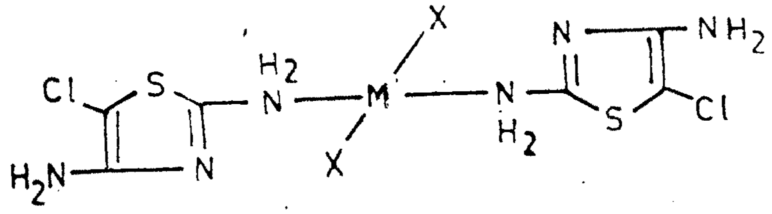
Both the complexes have good solubility in common organic oxyginated solvent such as acetone, ethanol and methanol. But complexes are non conducting in nature, hence there are molecular complexes.

In the light of above discussion a square-planar geometry is proposed for both complexes on the basis of electronic spectra, Infrared spectra and magnetic moment. A square-planar monomeric structure involve bonding through exocyclic nitrogen and in Schiff base bonding through -OH group and coordination through two azomethine nitrogen. The structure of Cu(II) complex is as shown below.



3.23 Complexes of Mn(II), Zn(II) and Cd(II)

The structures of Mn(II), Zn(II) and Cd(II) complexes are similar i.e. square-planar and except that Mn(II) has got single unpair electron in each of the five 'd' orbitals attributly a magnetic moment of 5.9 B.M. for both octahedral and tetrahedral geometries. The other part remains almost the same. Mn(II) complex shows electronic absorption band at 17000 cm^{-1}. Infrared spectral assignments are almost the same as in earlier cases and hence are not repeated. Electrical conductivity of solutions indicate non-ionic nature of the complex. The thermograms show features of the ligand loss giving ultimately the metal oxide. All these complexes may therefore, be assigned four coordinated square-planer structure given below.



3.24 Conclusion

The above studies indicate that structural chemistry of metal complexes of 2-4 diamino-5-chlarothiazole are interesting. The Co(II) complexes are tetrahedral in nature and hydration reactions add on two molecules of water yielding six coordinated octahedral complexes. The Ni(II) complexes are dimeric in nature and each unit represents five coordinated square pyramidal geometry. The Dimer breaks down on addition of secondary ligands like , pyridine, quinoline, Isoquinoline , 2-2 bypyridyl and 1-10 phenanthroline to give six coordinated octahedral species. The complexes of Cu(I) and Mn(II) are square-planar molecules and Sn(II) and Cd(II) complexes are diamagnetic square-planar molecules. The stereochemical changes in Ni(II) and Co(II) complexes, particularly the opening and expansion of the coordination sphere is an intenesting feature of the chemistry of the complexes studied in the project. The candidate intench to take up further work in this direction as an extension of the present project.

No.	Metal Salt used	Formula of the complex	Nature	Colour	Elemental Analysis *					Molecular Weight
					M %	S %	Cl %	Br %	N %	
1	-	DCT	Crystalline	-	-	21.01 (21.3)	23.04 (23.24)	- -	27.78 (27.9)	147 (149)
2	$CoCl_2$	$Co(DCT)_2Cl_2$	Crystalline	Blue	13.2 (13.8)	14.9 (15.04)	21.92 (20.98)	- -	20.03 (20.33)	413.5 (422.9)
3	$CoBr_2$	$Co(DCT)_2\ Br_2$	"	Greenish blue	10.9 (11.3)	12.04 (12.6)	13.6 (14.08)	- (31.7)	16.7 (16.60)	504.3 (512.7)
4	$Co(NO_3\ )$	$Co(DCT)_2(NO_3)_2$	"	Blue	13.20 (13.38)	14.8 (15.02)	16.20 (16.43)	- -	21.7 (21.87)	- (426.9)
5	$Co(OAC)_2$	$Co(DCT)_2(OAC)_2$	"	Blue	12.10 (12.23)	13.3 (13.7)	14.8 (15.02)	- -	17.8 (18.02)	466.01 (470.9)
6	$NiCl_2$	$Ni(DCT)_2Cl_2$	"	Ochre Yellow	10.10 (10.16)	11.30 (11.40)	20.97 (21.04)	- -	14.05 (14.9)	561.3 (572.6)
7	$NiBr_2$	$Ni(DCT)_2Br_2$	"	Ochre yellow	9.5 (9.6)	10.5 (10.8)	11.65 (11.82)	26.5 (26.66)	14.15 (14.18)	592.8 (600.8)
8	$Ni(NO_3)_2$	$Ni(DCT)_2(NO_3)_2$	"	"	8.95 (9.1)	10.09 (10.3)	11.01 (11.2)	- -	17.43 (17.9)	620.7 (623.6)
9	$Cu(OAC)_2$	$Cu(DCT)_2(OAC)_2$	"	Pale blue	14.2 (14.7)	15.01 (15.02)	16.01 (16.4)	- -	17.09 (17.7)	462.03 (475.5)
10	$CuCl_2$	$Cu(DCT)_2Cl_2$	"	"	13.01 (13.8)	15.01 (15.02)	20.9 (20.78)	- -	16.09 ((15.98)	426.8 (427.54)
11	$Cd(OAC)_2$	$Cd(DCT)_2(OAC)_2$	"	Greenish yellow	13.65 (13.77)	13.09 (13.5)	13.01 (13.2)	- -	15.5 (15.8)	529.3 (524.4)
12	$Zn(OA)_2$	$Zn(DCT)_2(OAC)_2$	"	Pale yellow	23.5 (23.8)	11.9 (12.09)	12.98 (13.2)	- -	15.59 (15.8)	472.6 (477.36)
13	$Cr(OAC)_3$	$Cr(DCT)_2(OAC)_3H_2O$	"	State gray	9.69 (9.54)	11.53 11.74	13.05 13.02	- -	15.69 15.4	540.33 545.01

* Values given in round brackets are calculated on the basis of proposed structure and formula.

Table 3.2 Elemental analytical data of Schiff base and its metal complexes

No.	Metal Salt	Formula of complex	Nature	Colour	M %	S %	Cl %	N %	Molecular Weight
					Elemental Analysis *				
1	-	$DCT(Sal)_2H_2$	Crystalline	Pale yellow	-	8.0 (8.01)	8.80 (8.92)	10.3 (10.5)	388 (392)
2	$CoCl_2$	$Co(DCT(Sal)_2)$	,,	Blue	11.7 (11.9)	6.25 (6.29)	20.30 (20.39)	8.27 (8.26)	508.9 (520.9)
3	$NiCl_2$	$Ni(DCT(Sal)_2)$	,,	Ochre yellow	11.01 (11.2)	6.01 (6.2)	20.32 (20.38)	8.31 (8.36)	508.6 (520.6)
4	$CuCl_2$	$Cu(DCT(Sal)_2)$	,,	Dirty gray	11.7 (11.9)	6.05 (6.4)	20.20 (20.19)	7.7 (7.9)	529.3 (525.5)
5	$CrCl_3$	$Cr(DCT(Sal)_2)$	,,	Slate gray	9.32 (9.43)	5.9 (5.92)	25.81 (25.86)	7.57 (7.62)	551.3 (549.01)
6	$MnCl_2$	$Mn(DCT(Sal)_2)$	,,	Buff colour	10.7 (10.67)	6.25 (6.29)	20.51 (20.54)	8.20 (8.26)	508.9 (510.9)
7	$ZnCl_2$	$Zn(DCT(Sal)_2)$	,,	Cream yellow	12.14 (12.5)	6.14 (6.15)	20.10 (20.12)	8.0 (8.05)	520.9 (527.3)

* Values given in round brackets are calculated on the basis of proposed structure and formula.

Table 3.3 Electrical conductivity data of Metal Complexes of DCT

Complex No.	Molar conductance k mole^{-1}	Nature
2	0.0091	Non conducting
3	0.0134	,,
4	0.0145	,,
5	0.0130	,,
6	0.0057	,,
7	0.0252	,,
8	0.0100	,,,
9	-	,,
10	-	,,
11	-	,,
12	-	,,
13	-	,,

Electrical conductivity data of Metal Complexes of $DCT(Sal)_2H_2$

Complex No.	Molar conductance k mole^{-1}	Nature
2	1.99	Non conducting
3	1.77	,,
4	0.99	,,
5	1.76	,,
6	1.46	,,
7	1.27	,,

Table 3.4 Magnetic susceptibility data for metal complexes of DC

Complex No.	μeff B.M.	No. of unpaired electron
2	4.5	3
3	4.7	3
4	4.6	3
5	4.3	3
6	3.06	2
7	3.03	2
8	3.09	2
9	1.62	1
10	1.59	1
11	3.04	4
12	Diamagnetic	-
13	„	-

Magnetic susceptibility data for metal complexes of $DCT(Sal)_2H_2$

Complex No.	μeff	No. of unpaired electron
2	4.6	3
3	3.21	2
4	1.87	1
5	4.8	4
6	2.73	2
7	Diamagnetic	-

Table 3.5 Infrared spectral data of 2,4–Diamino–5–Chloro thiazole. (Frequency in cm^{-1})

No.	Ligand	(N–H)	(N–H)	– C= N	C – Cl	C – N	Thiazole ring vibrations	Other observed vibrations
1	DCT	3380s 3260s 3155s	1695s	1580s	1110s	930s	1465s 1330s 1430s 1350m	835s, 750sh, 650s, 620s 510sh, 445w

Infrared spectral data of metal complexes

No.	Complex	(N–H)	(N–H)	– C = N	C – Cl	C – N	Thiazole ring vibration	Other observed ob vibrations
1	2	3390s 3300s 3210s	1700s	1630s	1110s	925s	1510s 1490m 1435s 1390s	830s, 705s, 670w, 645m, 570bd, 510sh, 470m, 445w, 315s, 290
2	3	3375s 3280s 3190s	1690s	1625s	1110s	925s	1500m 1470s 1420m, 1390s	835s, 750s, 700m, 650s, 620s, 480m, 440s, 360w, 330w, 290s
3	4	3380s, 3290s 3200s	1695s	1630s	110s	925s	1540m 1500s 1385bd	825s, 750s, 705s, 650m, 620w, 555bd, 500sh, 425sh, 360w, 290s,
4	5	3440bd 3400bd	1650s	1620s	1045s	–	1565s, 1395bd 1330s	835s, 745w, 660s, 525bd, 345s, 320w, 290s
				Ni(II) Complex				
1	6	3450s 3370s 3300bd,3190s	1700s	1615s	1090s	930s	1590s 1440s 1400s	835m, 720s, 670w, 560bd, 485s, 445w, 420w, 560w, 290s
2	7	3370bd 3245bd 3135s	1700s	1595s	1110s	930s	1460s 1440s 1390s	835s, 760bd, 650s, 625s, 510bd 445s, 510s, 290s
3	8	3460s 3338s 3330bd 3190s	1700s	1620s	1090s		1465s 1445s 1400s	835s, 710s, 665w, 645w, 550sh 490s, 440sh, 415sh, 360w, 290s
	9	3390bd 3290bd 3180bd	1670bd	1625s	1020s	950s	1520s 1480m 1400s	835s, 735s, 690m, 670m, 625m, 445s, 308s
	10	3370bd 3290bd	1675bd	1630s	1050s	955s	1530s 1470m 1430w, 1380s	835s, 730s, 680m, 650m 630m, 440s, 308s
	11	3370s 3245s 3180m	1690s	1610m	1110s	930s	1550s 1380s 1350m	835s, 822m, 750s, 645s 670w, 620w, 445s, 312s
	12	3380bd 3320bd	1630bd	1560s	1035s	930s	1520s 1400m 1450m 1330s	835s, 740w, 680s, 665w, 620m, 585m, 305s, 285s
	13	3370s 3270s 3185m	1695s	1580m	1085s	930s	1450m, 1545s 1470s 1415s	835s, 730s, 690m, 670m 620m, 527m, 280s

Table 3.6 Infrared spectral data of Schiff base (Frequency in cm^{-1})

obNo	Compound	- O-H	- C = N	C - Cl	Phenyl ring vibrations	Thiazole ring vibrations	Other observed vibration
	Ligand	2695bd	1620s	1105s	1590s	1465m, 1430m 1387m, 1350m	1225s, 928s, 740s, 650m, 618sh, 490m, 442m, 300w, 285s, 235m

Infrared spectral data of metal complexes (Frequency in cm^{-1})

obNo.	Complex	C - O	- C = N	C - Cl	Phenyl ring vibrations	Thiazole ring vibrations	Other observed vibration
2	Co(II)	1370s	1600s	1093s	1560s 1505s	1480s 1465s 1398m	1270w, 76w, 707s, 580w, 473w, 420m, 315s, 293s, 275s, 255s
3	Ni(II)	1386s	1610s	1090s	1575s 1505s	1480s 1440s 1400m 1438s	712s, 670w, 550m, 480w, 420w, 280s, 245m, 235m, 220s
4	Cu(II)	1385s	1600s	1090s	1555s 1510s	1470s 1425s	1275sh, 710s, 598s, 475s, 450w, 358w, 255s, 237s
5	Cr(III)	1385s	1590s	1095s	1550s 1507s	1465s 1430s	12502, 1173w, 895sh, 723m, 620s, 510s, 280s, 240m, 635m
6	Mn(II)	1385s	1590s	1095s	1565s 1503s	1465s 1430s	730m, 635w, 635sh, 620m, 520sh 495w, 260m, 220s
7	Zn(II)	1386s	1600s	1090s	1555s 1515s	1460s 1408s	1250sh, 755m, 590s, 470s, 440w, 404m, 380m, 270s, 240s, 220s

Where s = strong, m = medium, w = weak, sh = shoulder, bd = broad.

Table 3.7 Infrared spectral data of pyridine aduct of Ni(II) complex. (Frequency in cm^{-1})

Complex	(N–H)	(N–H)	– C=N	C – Cl	C – N	Thiazole and pyridine ring vibration	Other observed vibration
$NiL_2 2PyBr_2$	3360bd	1700w	1630sh	1090s	910bd	1540s, 1490s	1255w, 1200w, 1170m, 750
	3270bd		1600			1470m, 1430bd	670s, 600s, 490s, 425w,
	3150s					1335w	400w, 360w, 330w, 305w,
							280s
$NiL_2 2PyCl_2$	3540bd	–	1640	1155	985s	1580w	1220s, 1080s, 1040s,
	3400bd		1607			1490s	1010s, 945w, 880w, 760s
	3100w					1450s	700s, 670w, 630s, 435s,
							380w, 360w, 280s

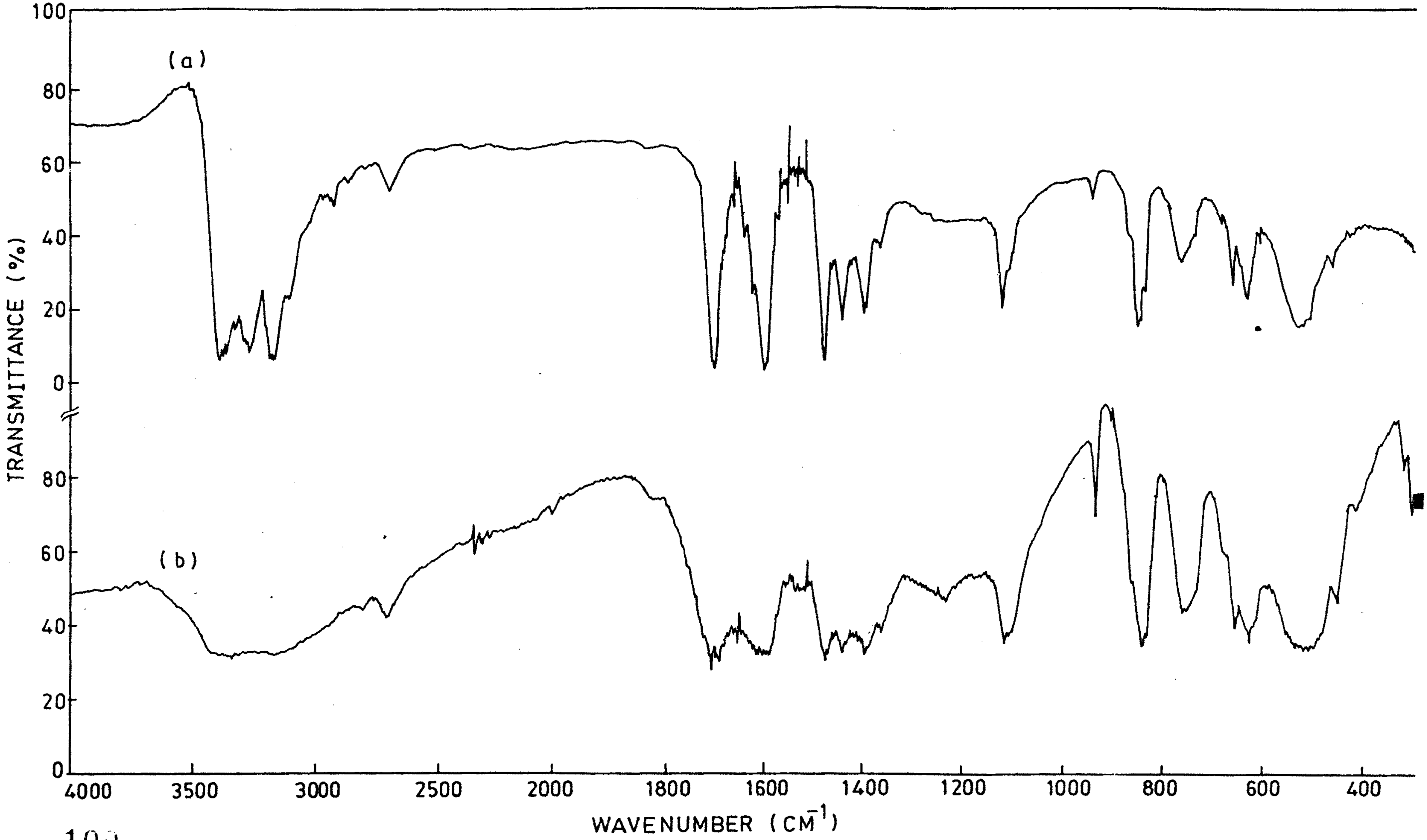


Fig. 3.1— INFRARED SPECTRA OF(a) 2,4-DIAMINO -5 CHLORO-THIAZOLE,(b) SCHIFF BASE .

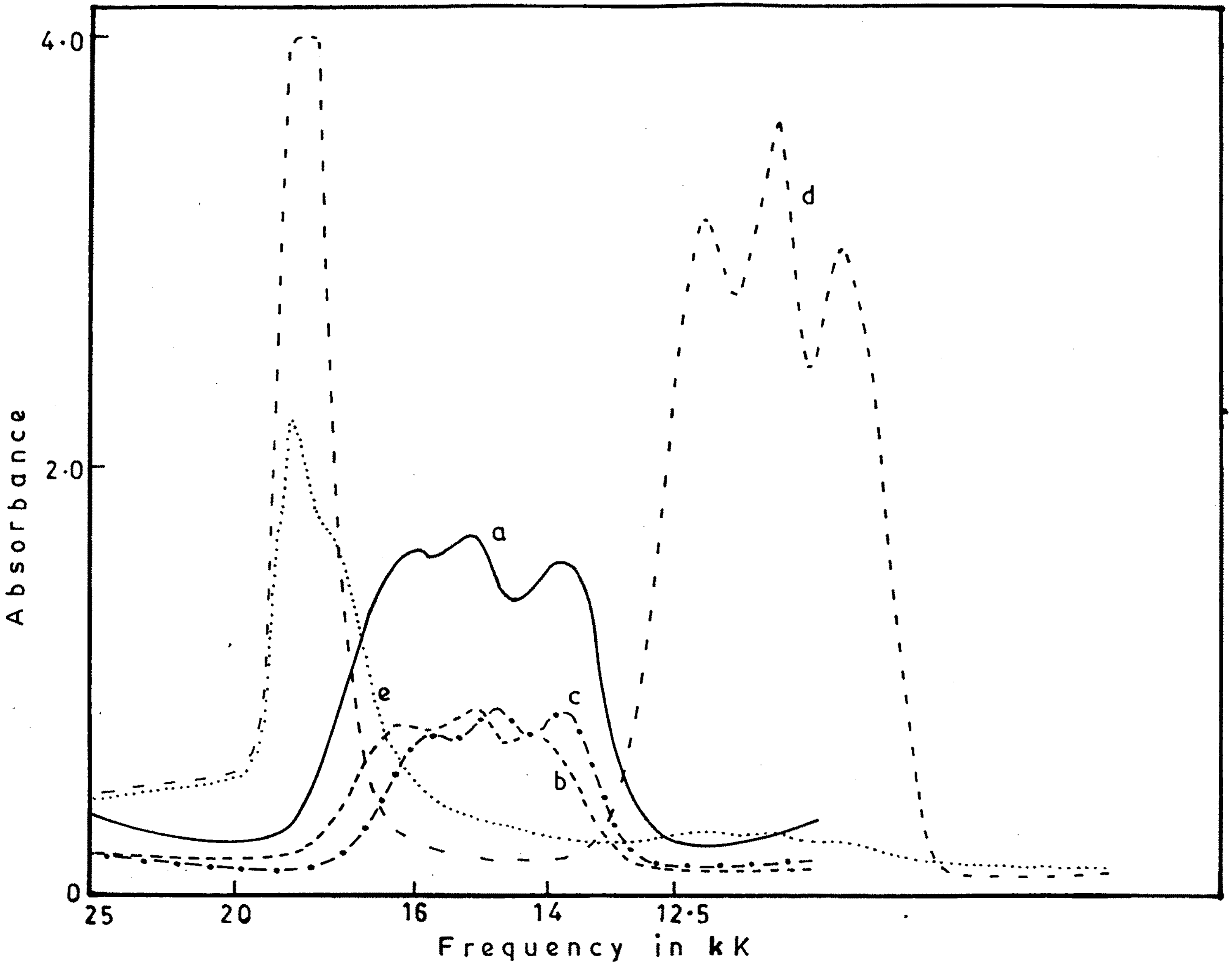


Fig.3.2A. ELECTRONIC SPECTRA OF (a) $[DCT]_2Co(II)(NO_3)_2$, (b) $[DCT]_2Co(II)Cl_2$, (c) $[DCT]_2Co(II)Br_2$, (d) $[DCT(sal)_2]Co(II)Cl_2$, (e) $[DCT]_2Co(II)OAc_2$.

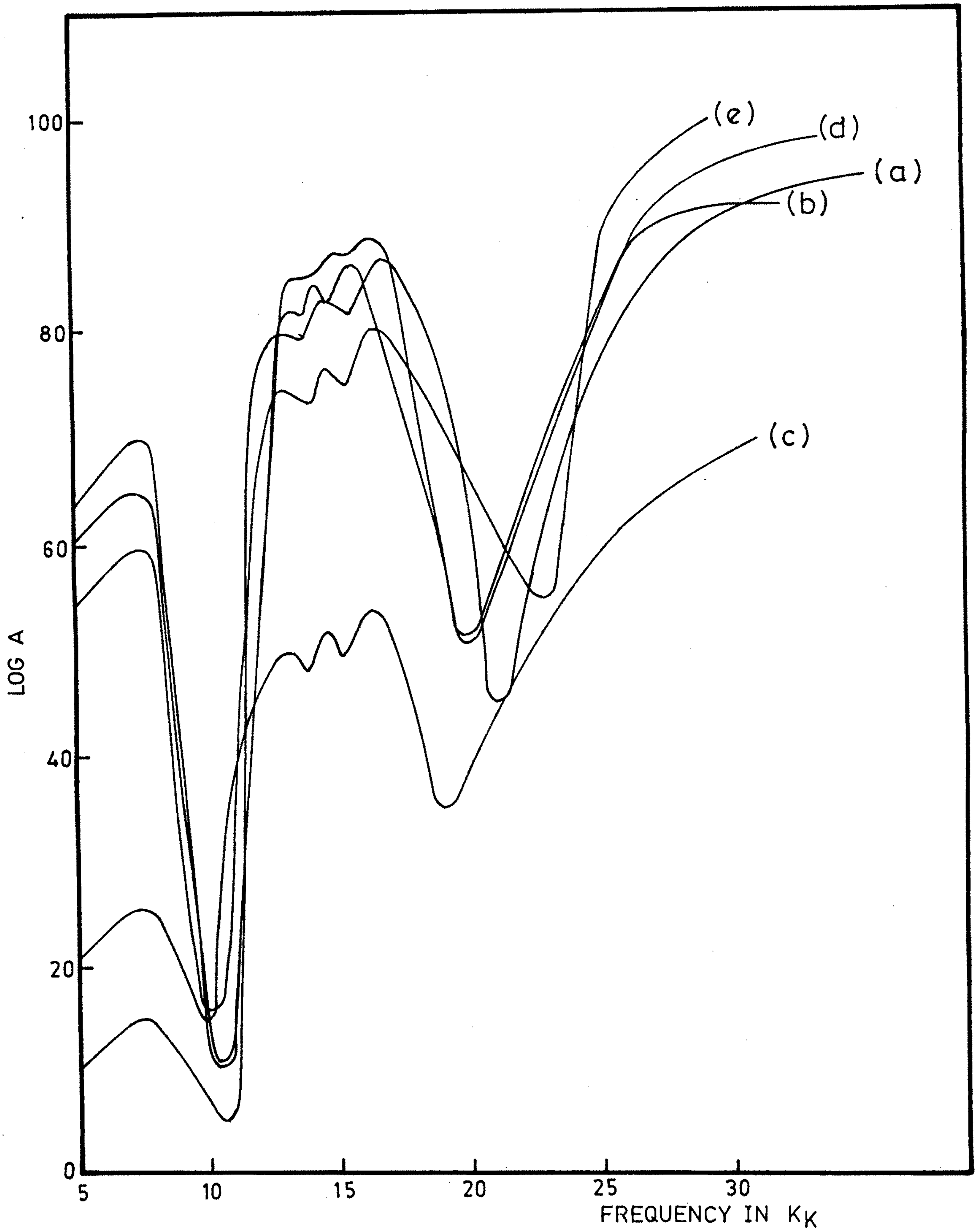


Fig. 3·2 B — REFLECTANCE SPECTRA OF (a) [DCT]$_2$Co(II) Cl$_2$, (b) [DCT]$_2$ Co(II) Br$_2$, (c) [DCT]$_2$ Co(II) (NO3)$_2$, (d) [DCT]$_2$ Co(II) OAC$_2$, (e) [DCT(sal)$_2$] Co(II) Cl$_2$.

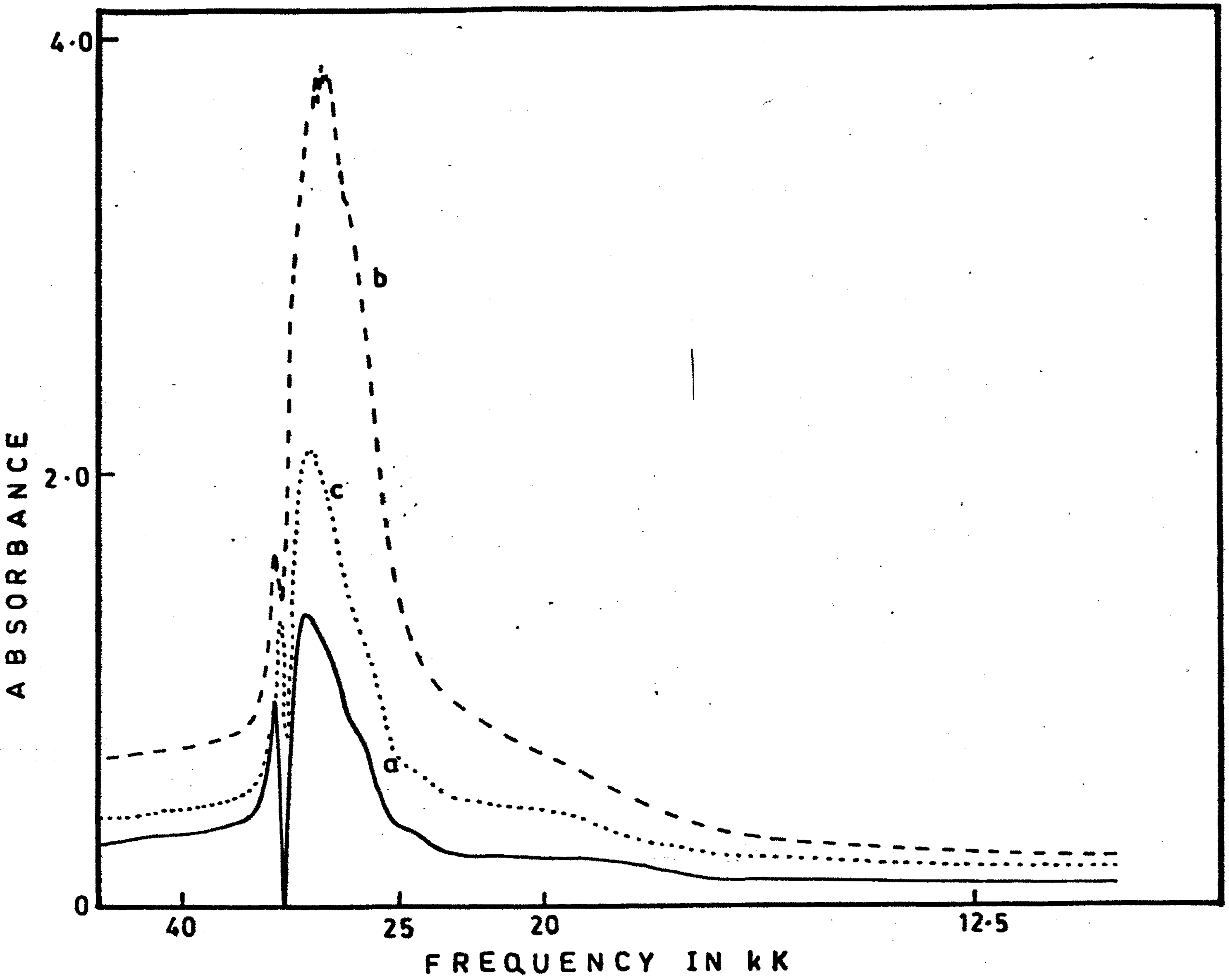


Fig.3.2.C-ELECTRONIC SPECTRA OF (a) $[(DCT)_2(H_2O)_2Br_2\ Co(II)]$

(b) $[DCT(sal)_2(H_2O)_2Cl_2\ Co(II)]$, (c) $[(DCT)_2(H_2O)_2Cl_2\ Co(II)]$.

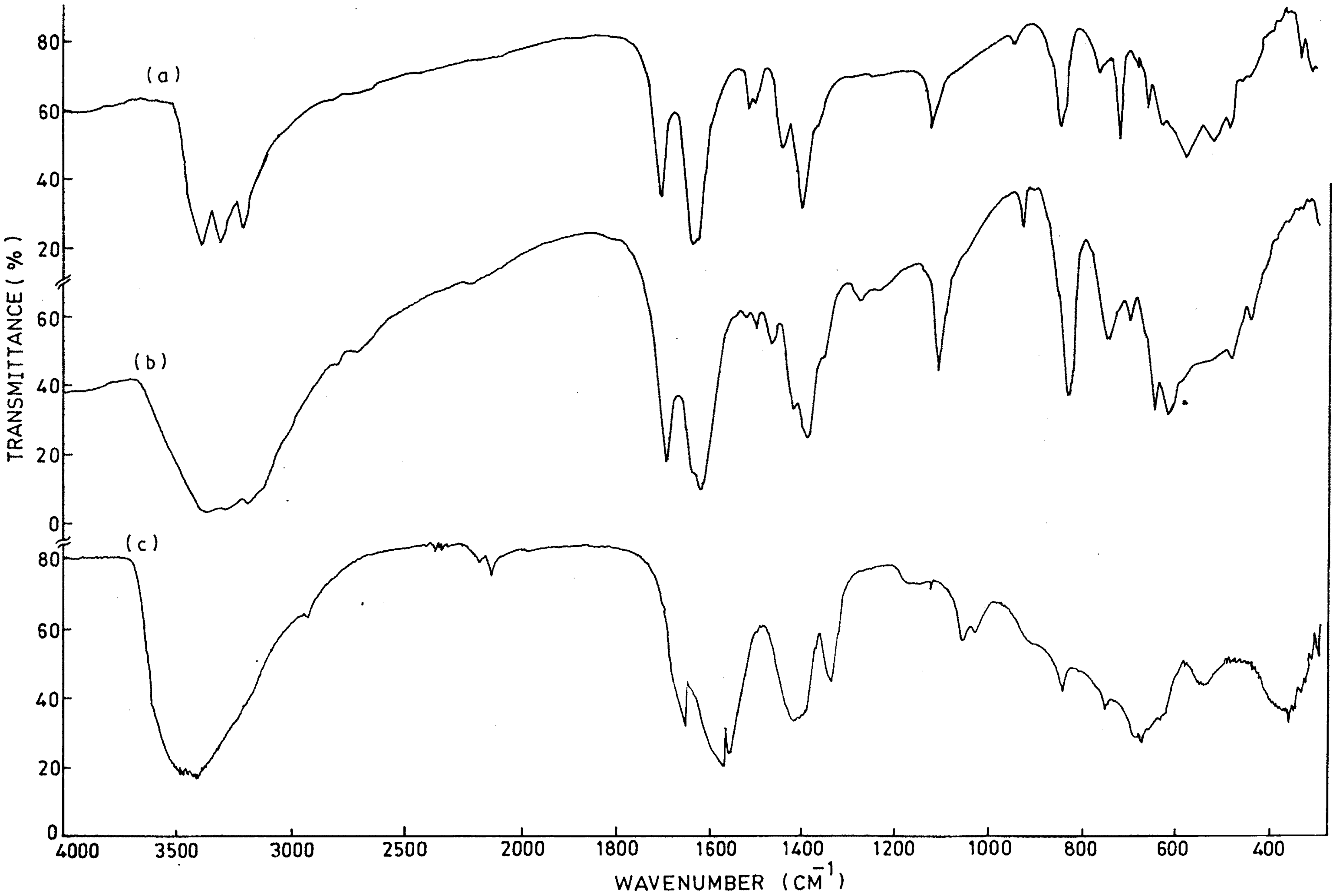


Fig. 3·3 — INFRARED SPECTRA OF (a) $[DCT]_2$ CO(II) Cl_2, (b) $[DCT]_2$ CO(II) Br_2, (c) $[DCT]_2$ CO(II) OAC_2.

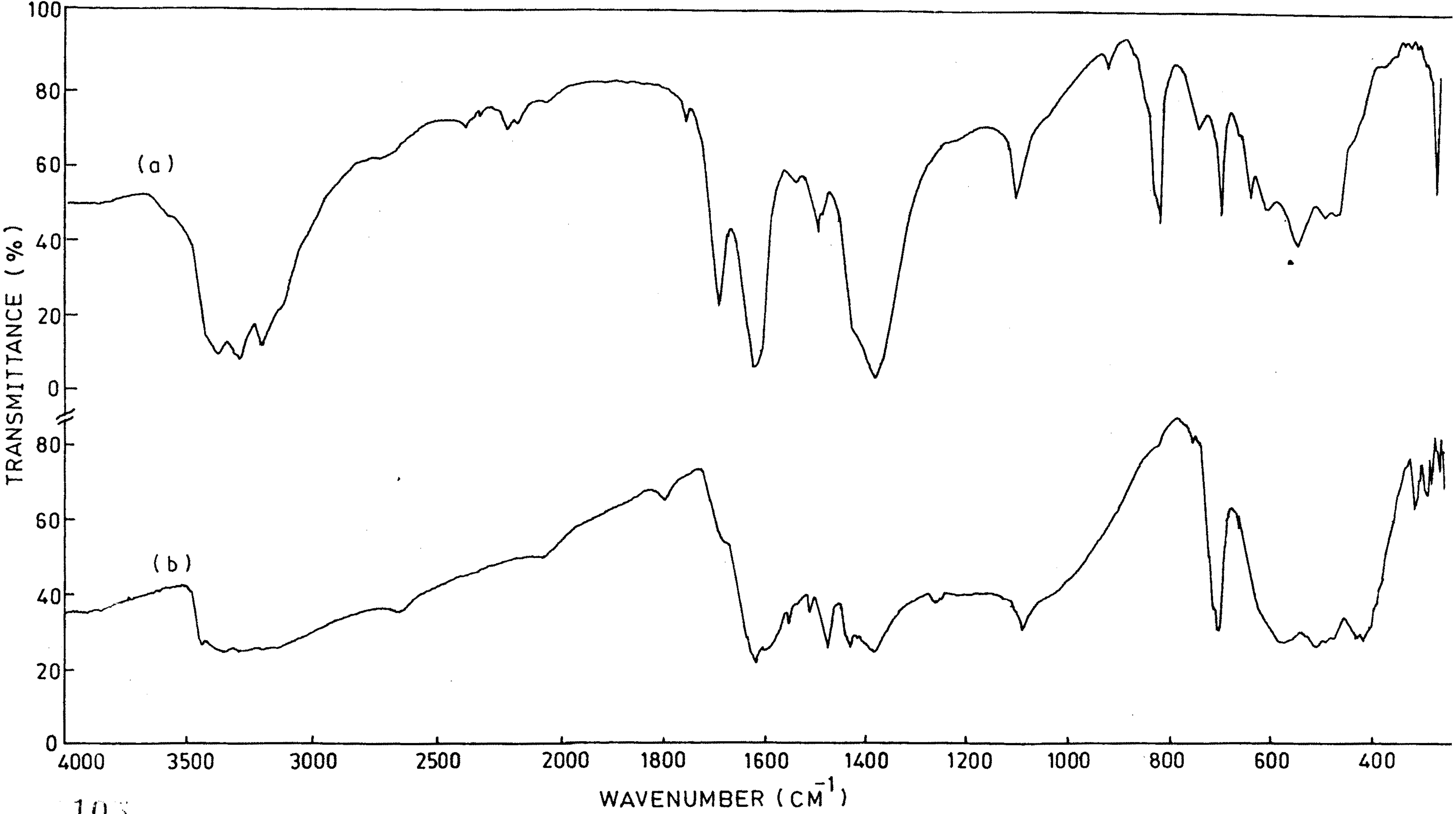


Fig. 3·3(a)-INFRARED SPECTRA OF (a) [DCT]$_2$ CO(II)(NO3)$_2$, (b) [DCT(sal)$_2$] CO(II) Cl$_2$.

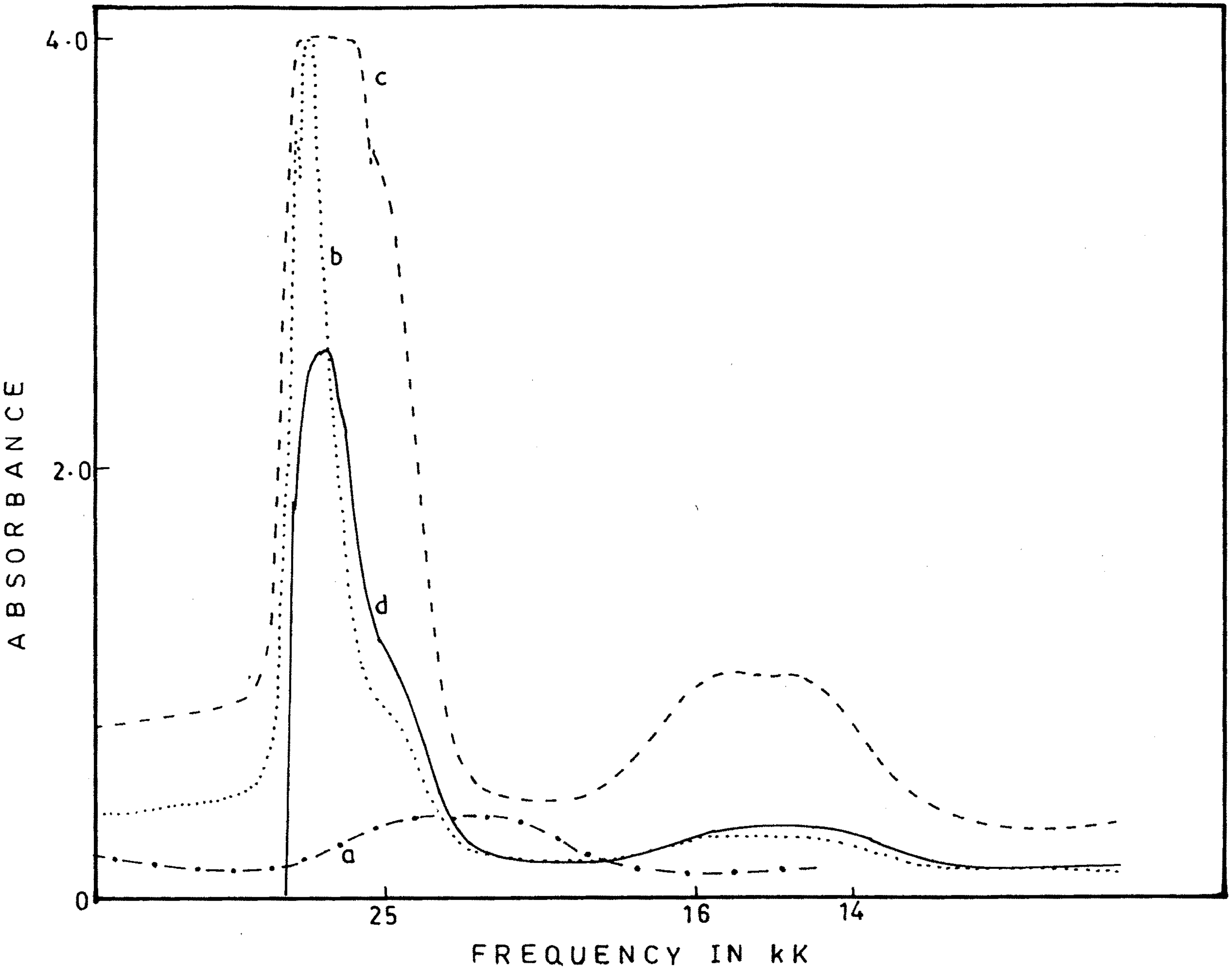


Fig.3.4A-ELECTRONIC SPECTRA OF (a) $[DCT]_2$ Ni(II) Cl_2, (b) $[DCT(sal)_2]$ Ni(II) Cl_2, (c) $[DCT]_2$ Ni(II) $(NO_3)_2$, (d) $[DCT]_2$ Ni(II) Br_2 .

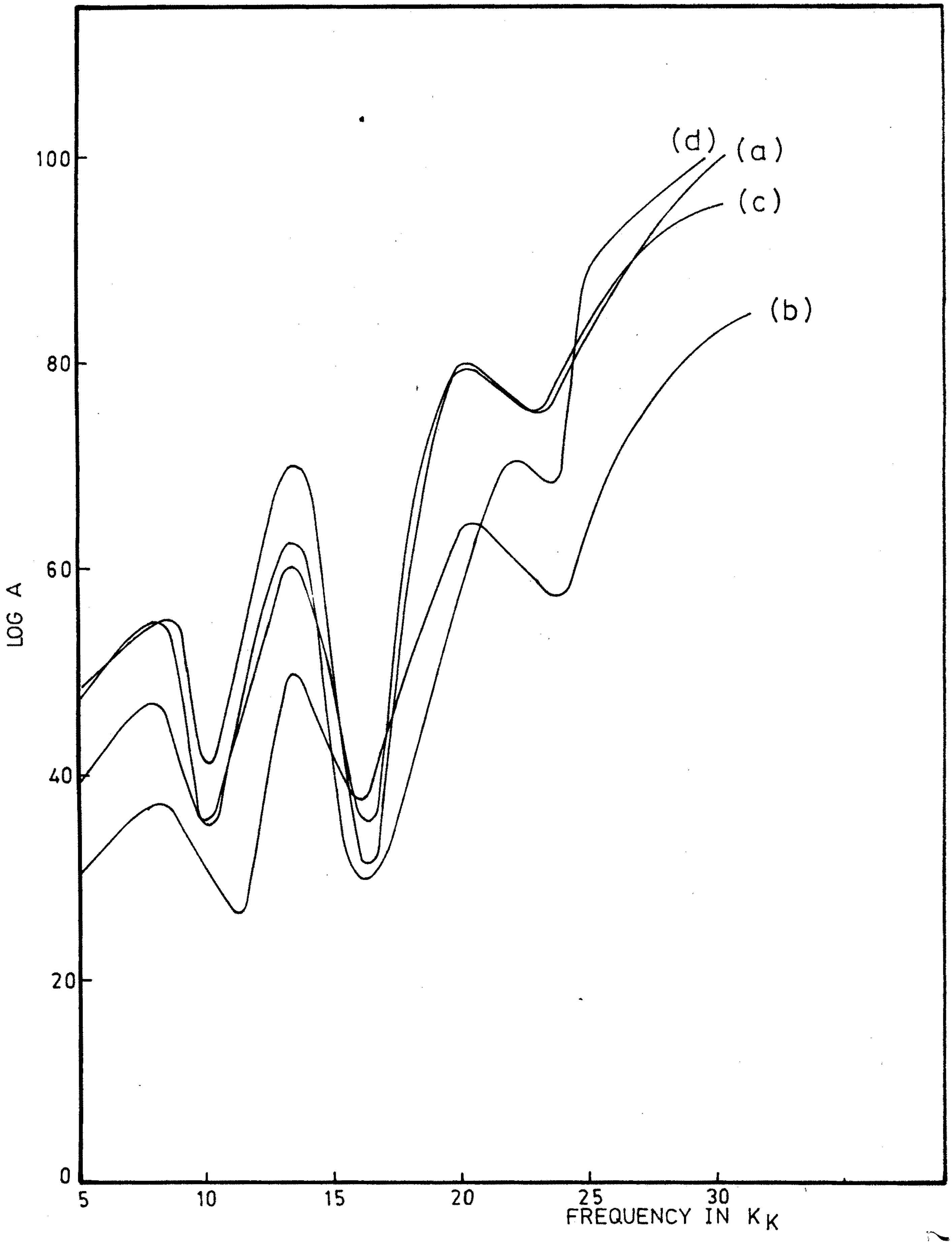


Fig. 3·4 B – REFLECTANCE SPECTRA OF (a) $[\mathrm{DCT}]_2\,\mathrm{Ni(II)}\,\mathrm{Cl}_2$, (b) $[\mathrm{DCT}]_2\,\mathrm{Ni(II)}\,\mathrm{Br}_2$, (c) $[\mathrm{DCT}]_2\,\mathrm{Ni(II)}\,(\mathrm{NO}_3)_2$, (d) $[\mathrm{DCT}(\mathrm{sal})_2]\,\mathrm{Ni(II)}\,\mathrm{Cl}_2$.

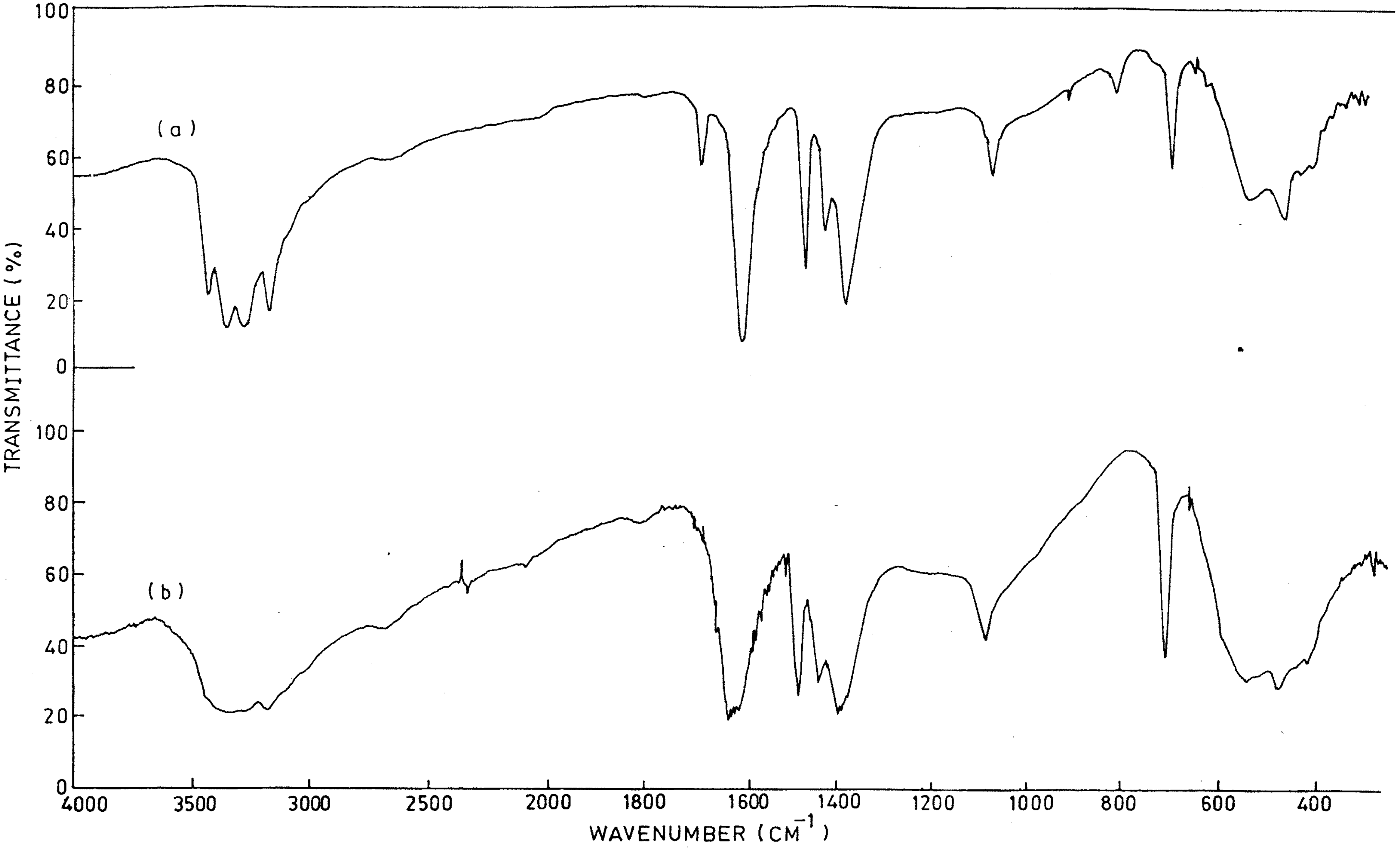


Fig. 3·5 — INFRARED SPECTRA OF (a) [DCT] Ni(II) Cl_2, (b) [DCT(sal)$_2$] Ni(II) Cl_2.

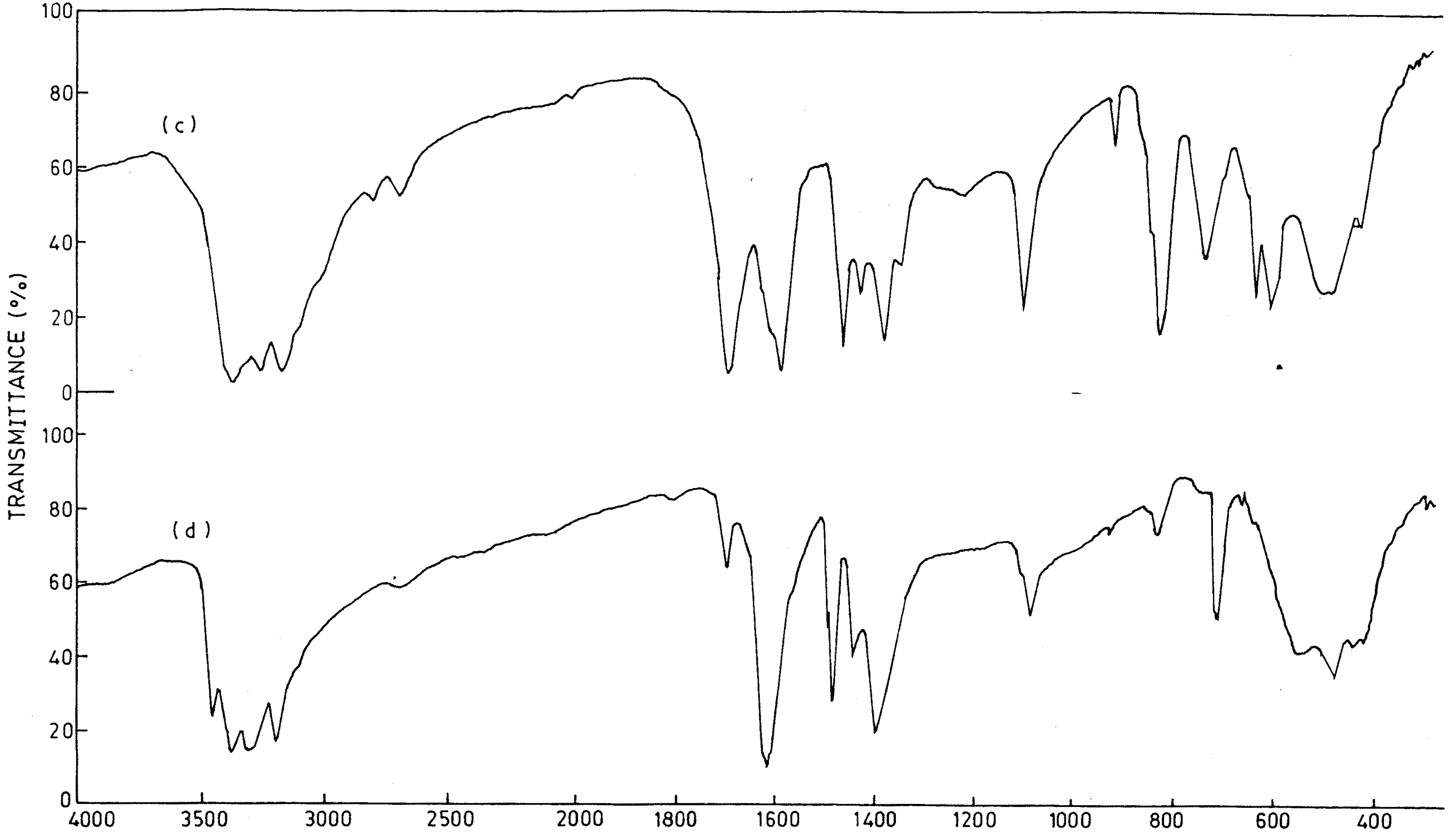


Fig.3.5(a)-INFRARED SPECTRA OF (c) [DCT] Ni(II) Br_2, (d) [DCT] Ni(II) $(NO3)_2$.

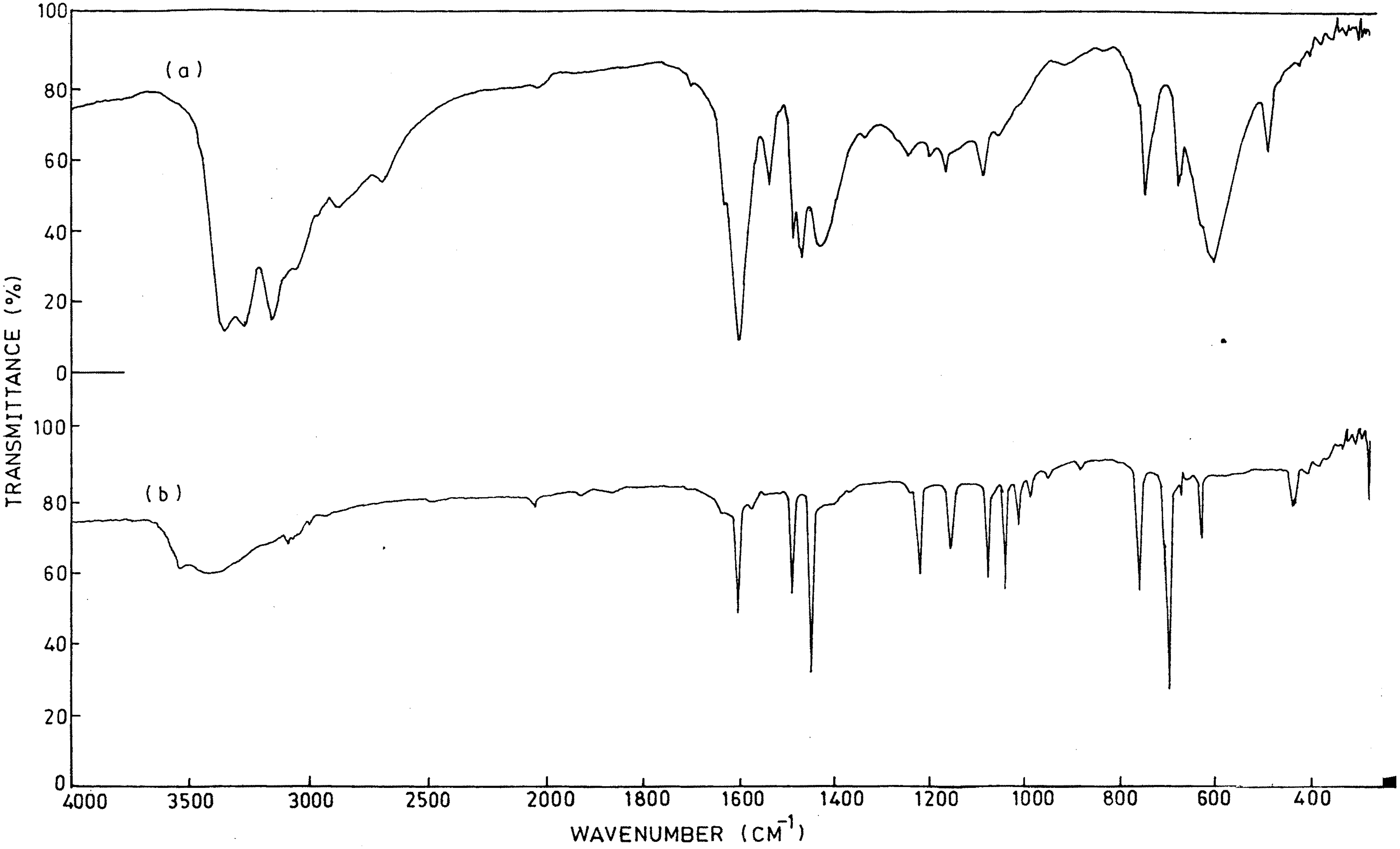


Fig.3·5(b)-INFRARED SPECTRA OF (a) [Ni(DCT$_2$ Py$_2$) Cl$_2$], (b) [Ni(DCT$_2$ Py$_2$) Br$_2$].

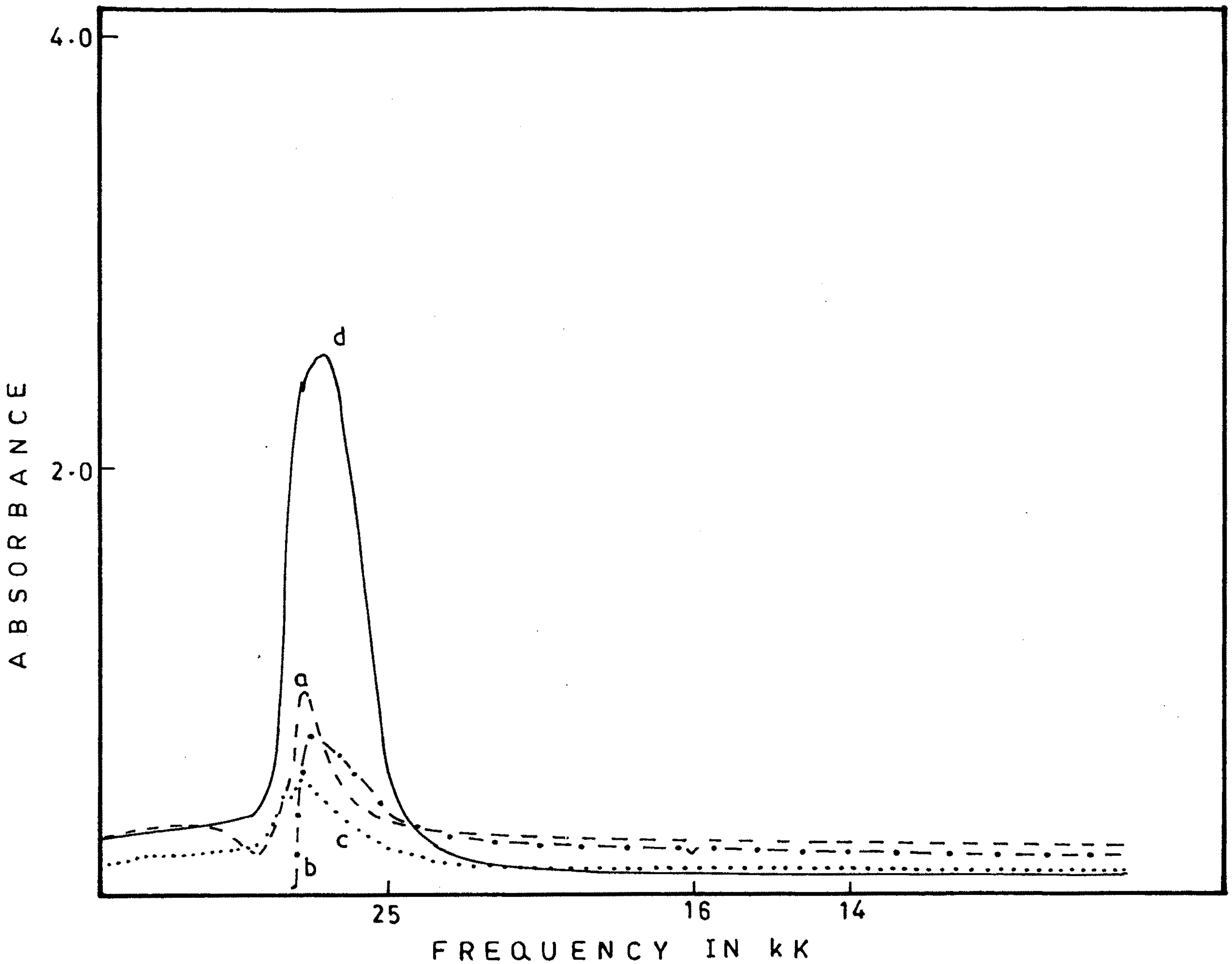


Fig 3.6-ELECTRONIC SPECTRA OF (a) $[DCT(sal)_2Cl_2]Cr(III)$,(b) $[DCT(sal)_2]Mn(II)Cl_2$ (c) DCT . (d) $[DCT(sal)_2]H_2$.

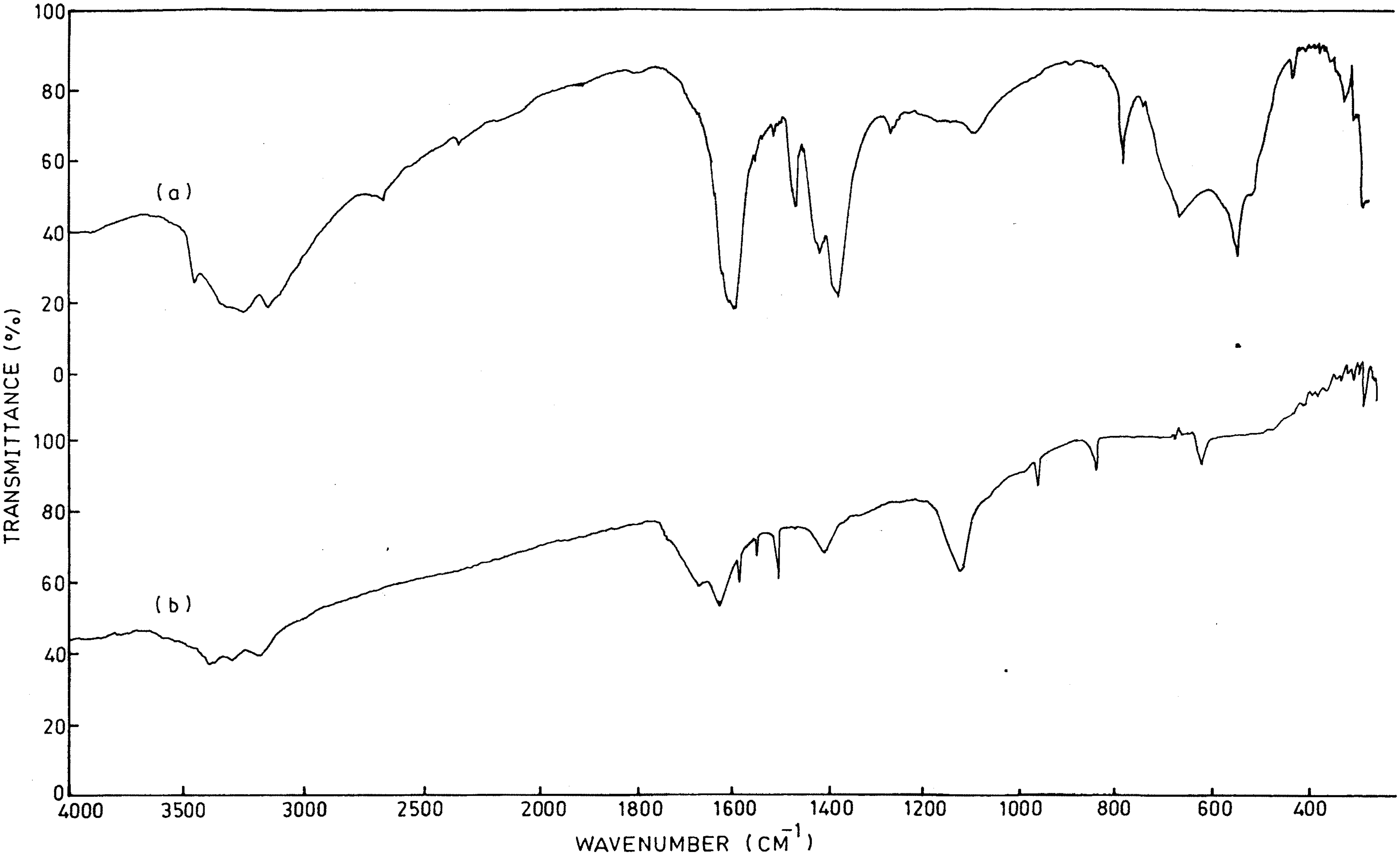


Fig. 3·7 – INFRARED SPECTRA OF (a) [DCT(sal)$_2$] Cu(II) Cl$_2$, (b) [DCT]$_2$ Cu(II) OAC$_2$.

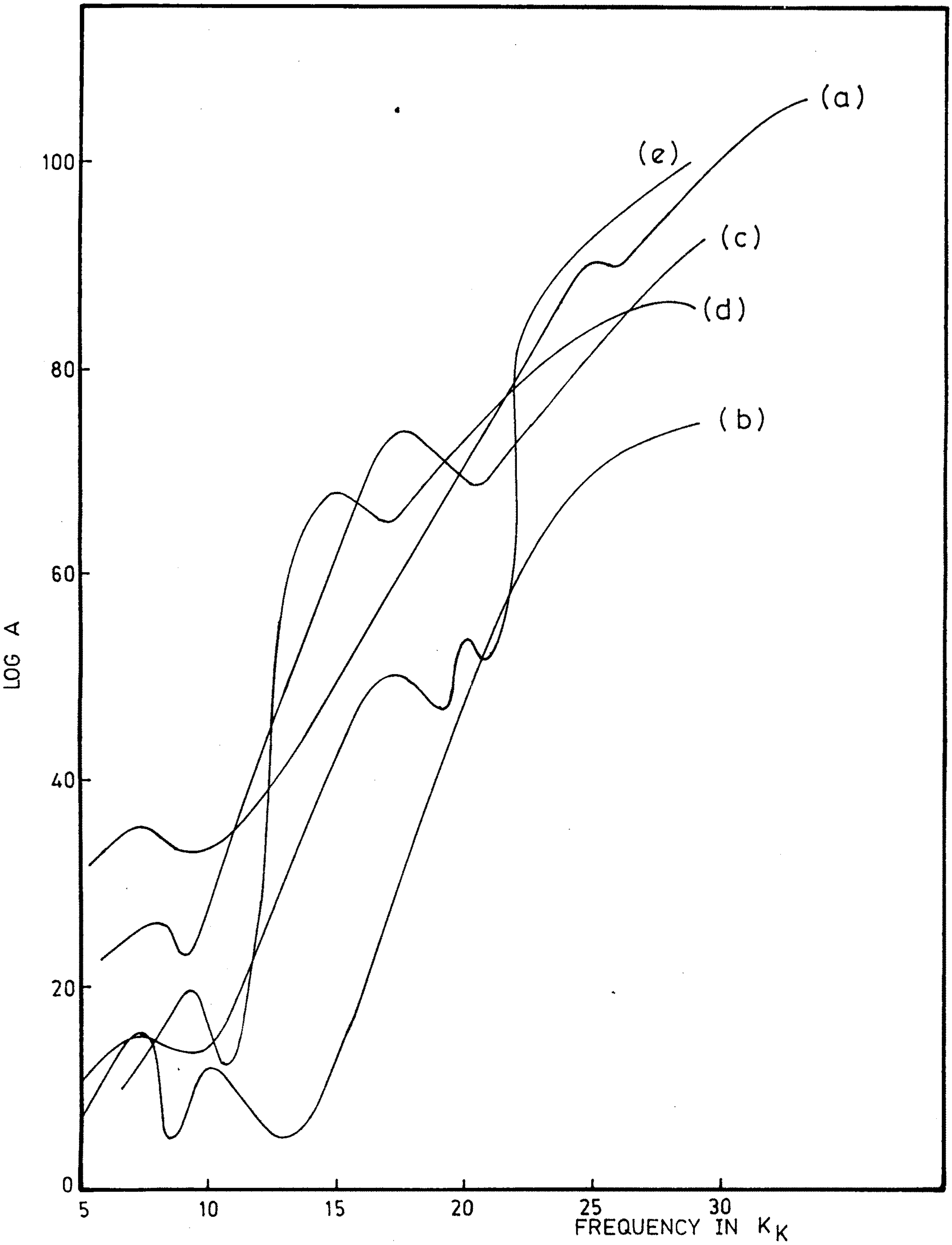


Fig.3·8 – REFLECTANCE SPECTRA OF (a) [DCT(sal)$_2$] Cu(II) Cl$_2$, (b) [DCT]$_2$ Cu(II) OAC$_2$, (c) [DCT]$_2$ Cr(III) OAC$_2$, (d) [DCT(sal)$_2$] Cr(III) Cl$_2$, (e) [DCT(sal)$_2$] Mn(II)Cl$_2$.

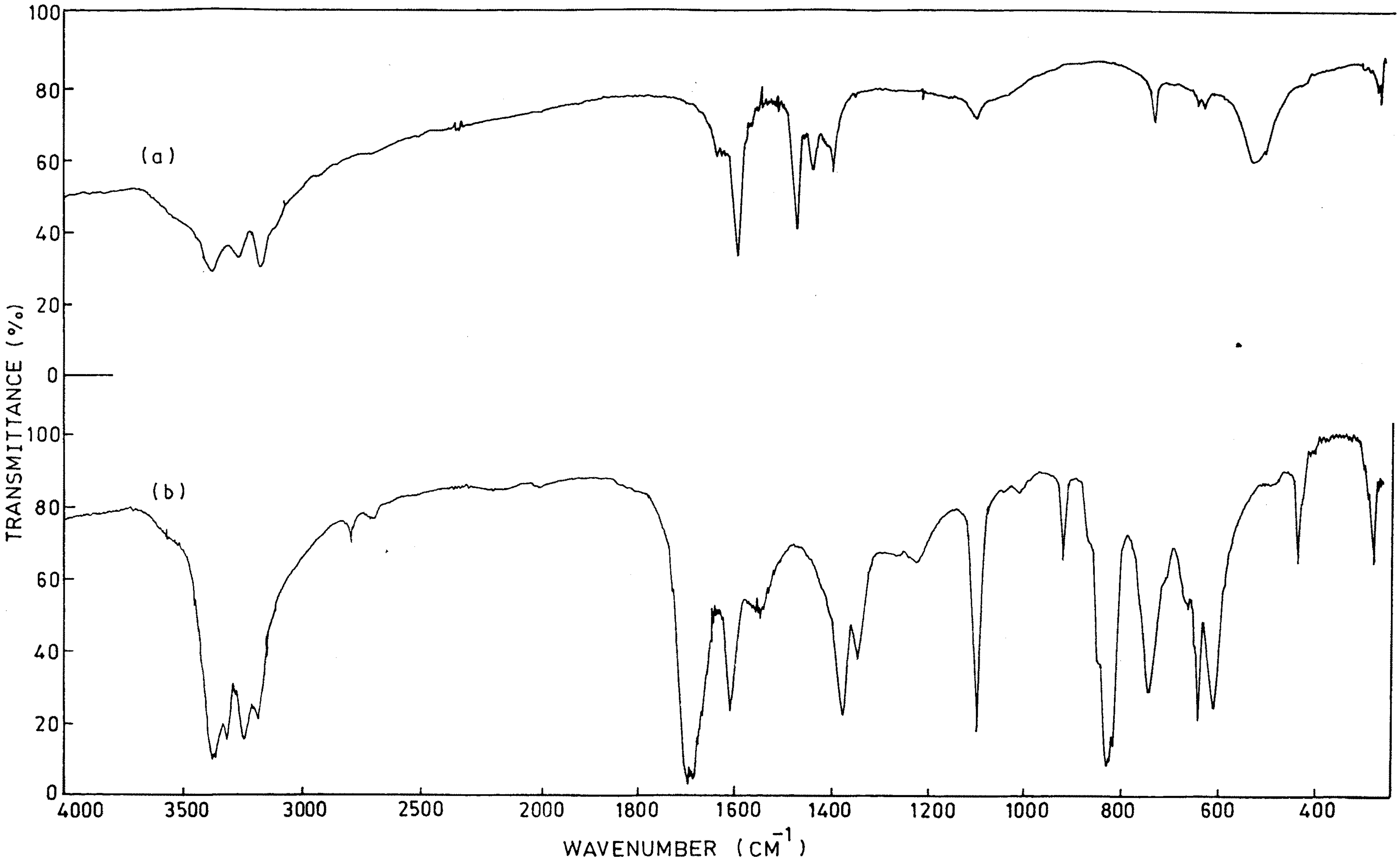


Fig. 3·9 – INFRARED SPECTRA OF (a) [DCT(sal)$_2$] Mn(II) Cl$_2$, (b) [DCT]$_2$ Cd(II) OAC$_2$.

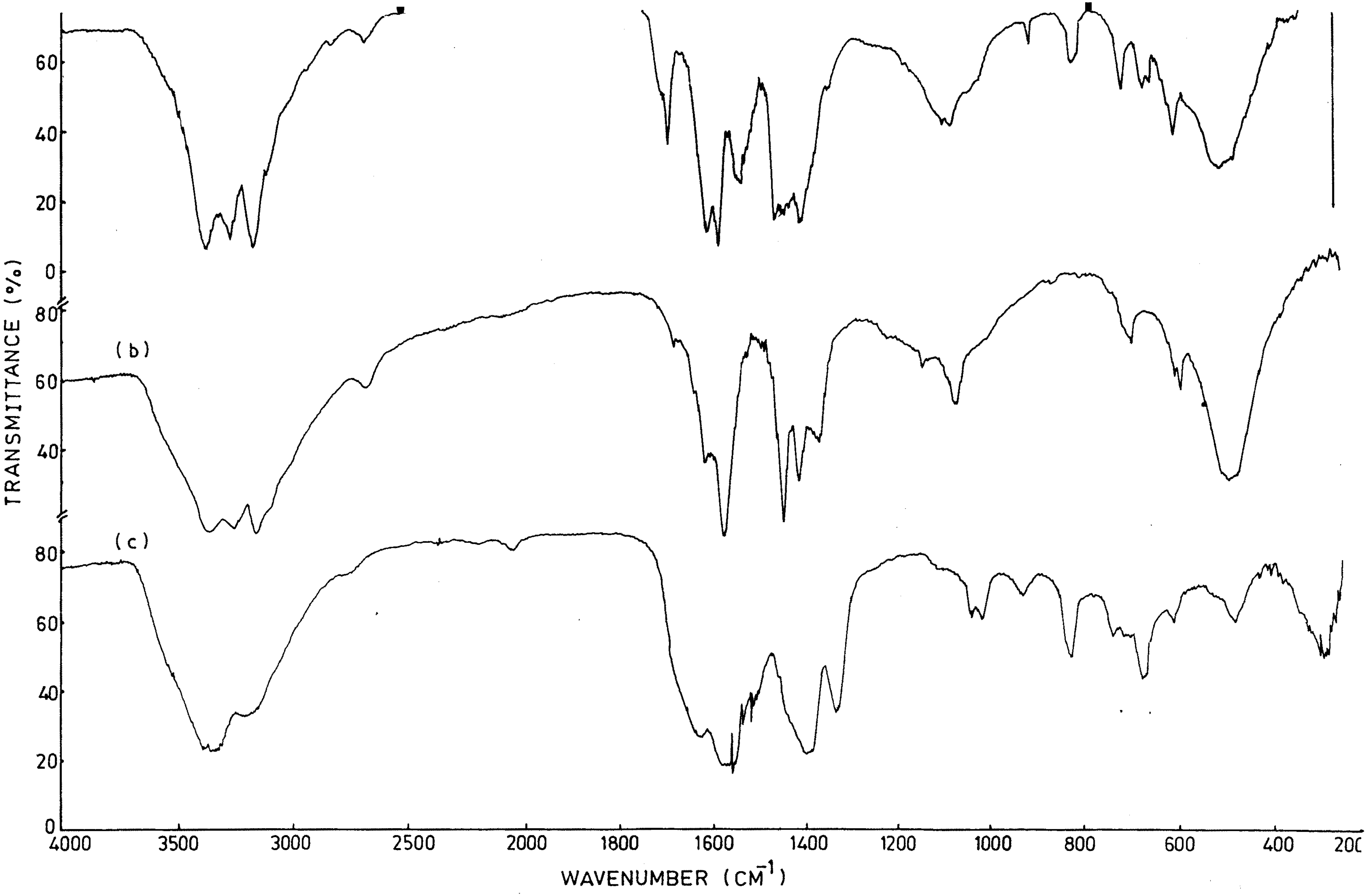


Fig. 3-9 — INFRARED SPECTRA OF (a) [DCT]$_2$ Cr(III) OAC$_3$, (b) [DCT(sal)$_2$] Cr(III) Cl$_3$, (c) [DCT]$_2$ Zn(II) OAC$_2$.

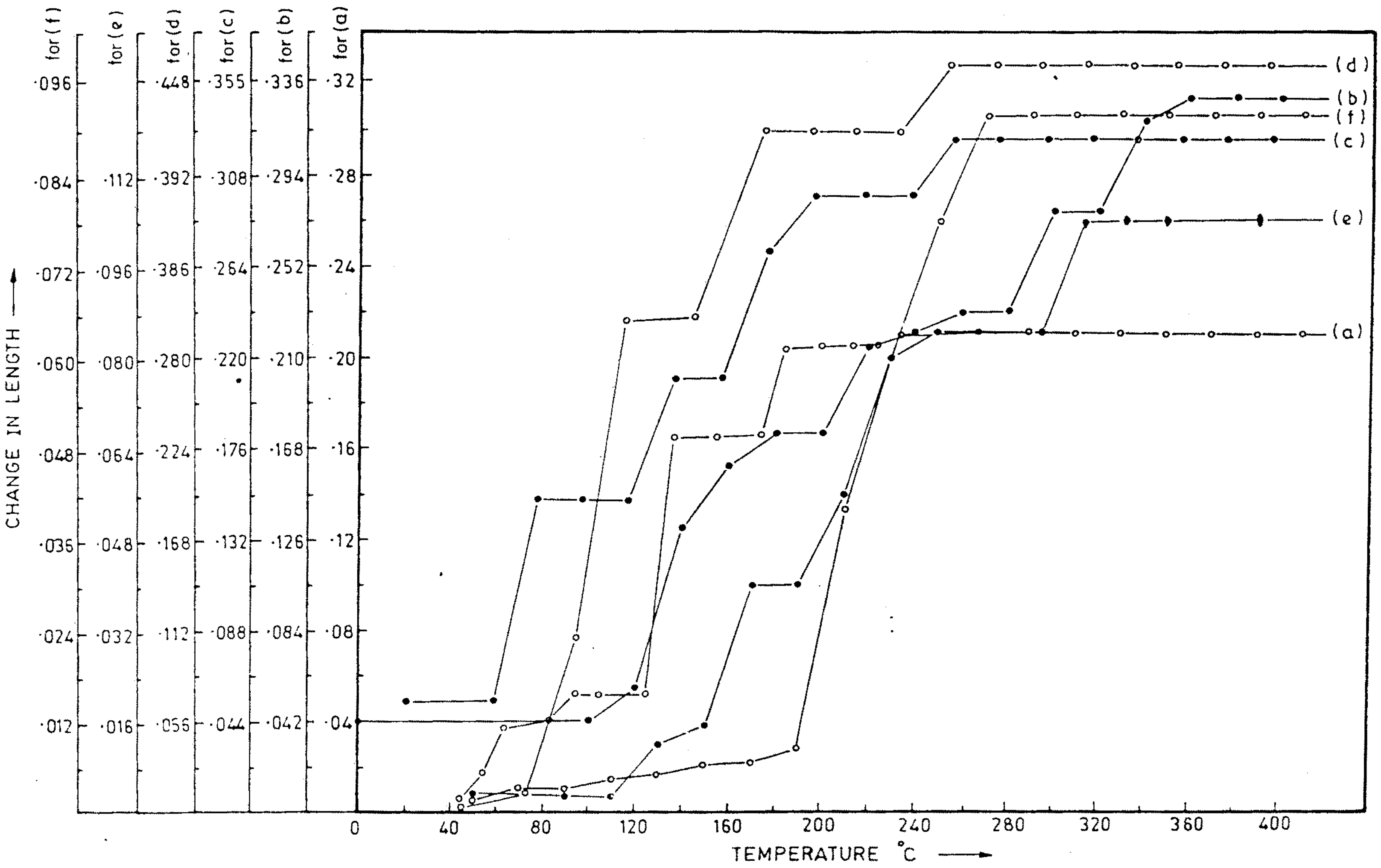


Fig. 3.10 – THERMOGRAM OF [DCT] COMPLEXES OF (a) Co(II), (b) Cr(III), (c) Cu(II), (d) Cd(II), (e) Zn(II), (f) Ni(II).

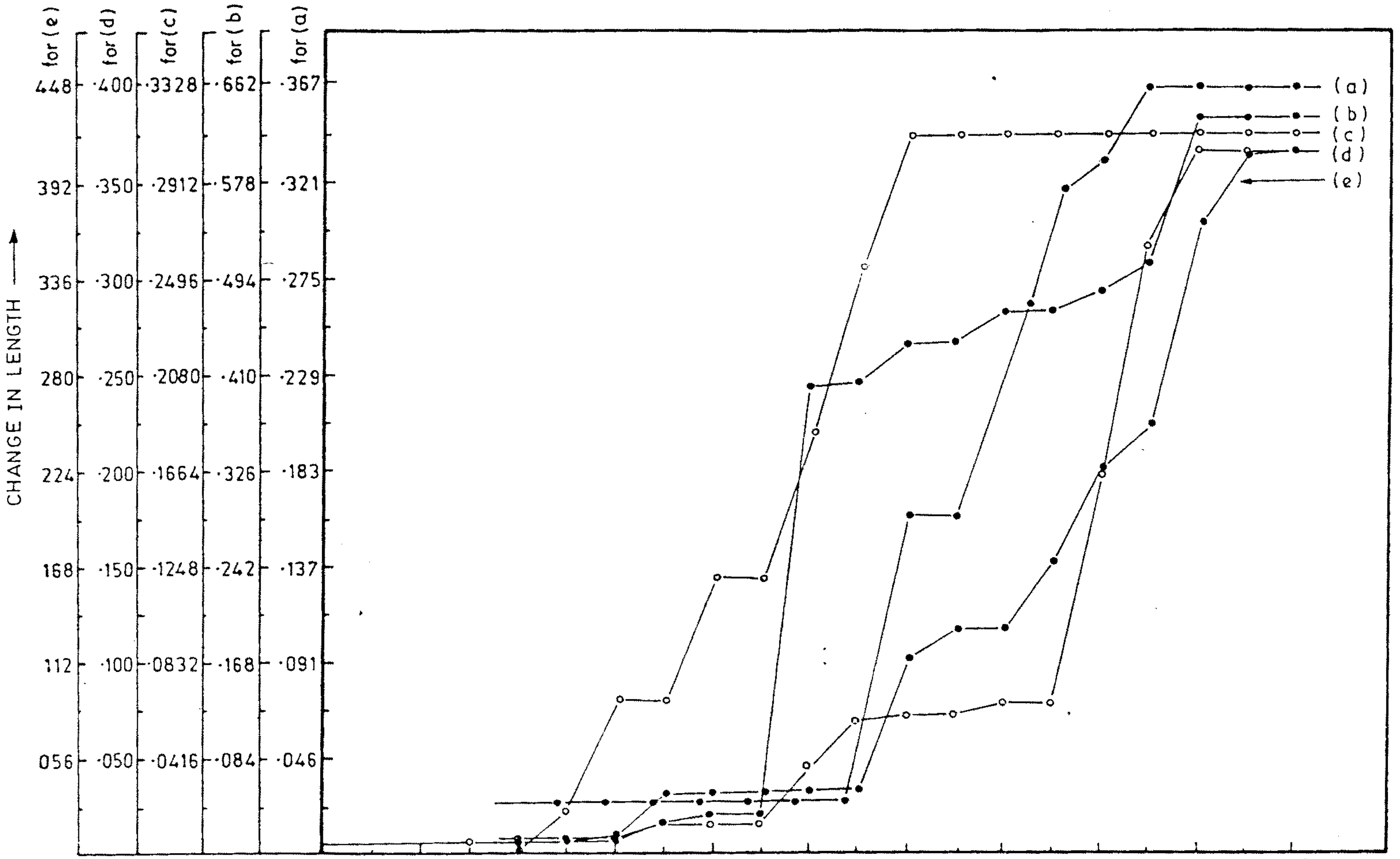


Fig. 3.10 — THERMOGRAM OF SCHIFF'S BASE COMPLEXES OF (a) Co(II), (b) Ni(II), (c) Cr(III), (d) Mn(II), (e) Cu(II).

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