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SYNTHESIS AND CHARACTERIZATION OF SOME MIXED LIGAND DITHIOOXAMIDE COMPLEXES OF TRANSITION METALS

BY

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1421 H.

To my Father,

My Mother,

And to my Brothers.

Acknowledgement

*First of all I do thank **Allah** for his bless to me and I pray for the best creation and messengers our **prophet Mohammad**, peace be upon him.*

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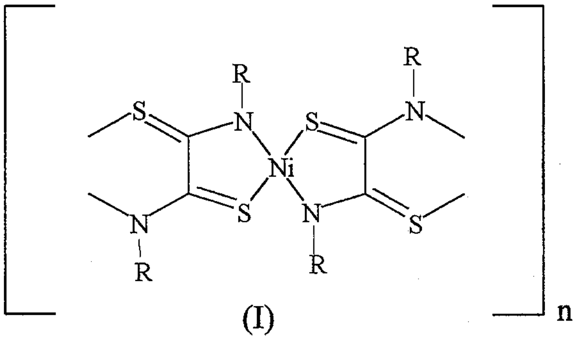
CHAPTER I

INTRODUCTION

INIRODUCTION

Dithiooxamide (rubeanic acid) has been widely used as an analytical reagent where it is found to provide a very sensitive spot test for the detection of Co, Ni and Cu(1) . This ligand (abbreviated hereinafter as dto) forms insoluble 1:1 with Cu(II) and Ni(II) that are thought to be polymeric and involve N-S bis-bidentate bridging behaviour(2). The dto and its mono- and disubstituted derivatives have a varied and interesting coordination chemistry(3) and their intense chromophore(4) have led to a number of applications(5), including an important imaging process(6). These ligands are exemplary of polyfunctional molecules that can, in principle, chelate in a variety of different ways, i.e they are flexidentate ligands.(7) Attention has been focused especially an their intensely coloured neutral polymeric(8) and cationic monomeric(9) complexes of Ni, Pd and Pt metals. The particular complex formed depends on the reaction conditions and the stoichiometry(3).

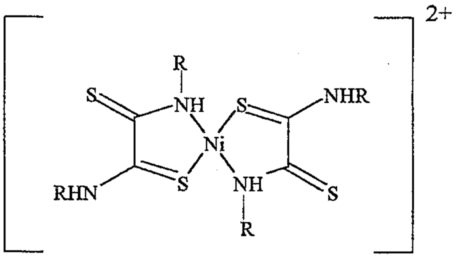
In the case of Ni (II), one equivalent of metal ion reacts with one equivalent of the ligand in neutral or weakly acidic media to give an insoluble 1:1 polymer. In this material the ligand is believed to bridge between two nickel atoms, coordinating to each metal atom through one sulfur and one nitrogen forming a five membered chelate ring(8,9,10) such as the structure below .



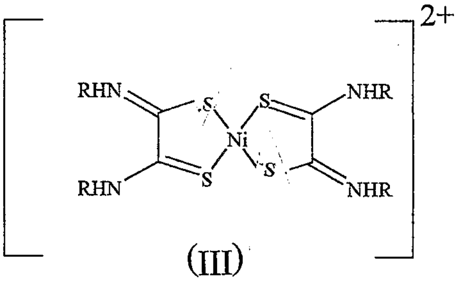
(I)

With two or more equivalents of the ligand and from strongly acidic media, salts of monomeric cationic Ni(II) complexes of general formula [Ni $(L_2)_2$]X_2 have been obtained(9,11) in this complex, the ligands were first believed to coordinate in a bidentate N,S(II) fashion forming a square planar complex(12,13). However another work suggested that the ligands are probably bound in an S,S fashion(III)(14,15).

Monomeric neutral complexes of unsubstituted and N-substituted



(II)



(III)

dto ligands, of the general formula $[M(LH)_2]$ have been reported for Pd(II) and Pt(II)(16). Crystallographic studies have confirmed S_4 coordination sphere about M(II) in these complexes(17). Unlike Pd and Pt, no monomeric neutral nickel complex of unsubstituted dto has been reported. Neutral Ni complexes have been reported only for N,N^1-disubstituted dto ligands such as N,N^1–diethyl-dto and N,N^1-dibenzyl dto (18). A crystallographic study of the neutral quinoxaline-

2,3-dithiol (or N,N'-1,2-phenylene-dto) complex showed an S_4 environment about Ni(II)(19).

Hurd et al,(20) prepared a low polymer of nickel with RRdto and stated that the size of the terminal structure of the complex depends on the method of preparation and purification, and that from about pH=1 to alkaline solutions the complex is formed by replacement of the amide hydrogen with nickel. The infrared spectra of Ni (RRdto) and Ni (dto) have been given, some fundamentals have been assigned and a polymeric structure with S,N coordination sites was proposed. Physical properties such as low solubility and the variable composition suggested that these compounds are polymeric. The magnitude of the magnetic susceptibility of these complexes has been explained with the idea that the polymeric structure consists of planar and octahedral conformations about the nickel atoms(21). Kaneka and Casey(21) stated that the octahedral geometry may arise from interaction between the nickel atoms and sulfur or nitrogen atoms in adjacent planes or coordination of water molecules.

NMR spectral studies(22), indicated that the planar dithiooxamide (dto) act as bidentate sulfur donor ligand with nickel(II). The infrared bands in the 330 cm^{-1} region were assigned to the ν Ni-S and only the most intense bands at 1500(νCN) and 850cm^{-1} region (νCS) have been mentioned, special attention has been given to the hydrogen bonding ability in the complexes of dto and its N-substituted derivatives and it was found that the ability of H-bond formation together with metal-ligand bond strength increase on passing from dto to RRdto and from iodide to the chloride compounds(14) the νNH_2 appeared as a very broad and intense band in the IR spectra of Ni (RRdto)X_2 with several sub-maxima, generally due to intermolecular H-bonding. The chloride compounds showed the strongest hydrogen bonds and had the highest ionic contribution in the thioamide group, so both νCN and δNH appeared the highest frequencies for the chloride complexes. In these complexes νCN and δNH are very near to each other and the outers could not distinguish between them(14).

On the other hand, Cu(II) gave square planar complexes having the formulae $Cu(LH_2)\ X_2$ and $Cu(LH_2)_2X_2$ where X= Cl, Br or ClO_4 with the planar dithiooxamides dto, Mdto and NNMdto, with Mdto = N-methyl dithiooxamide and NNMdto = N,N^1-dimethyldithooxamide. The ligands act as bidentate with S,S coordination in these complexes(23). The IR spectra of these complexes have been investigated with special attention to the low frequency region and to the influence of hydrogen bonding in the spectra. The hydrogen bonding ability was found to increase following the series:

$$\text{Dto} < \text{Mdto} < \text{NNMdto}, \text{ and}$$

$$ClO_4 < Br < Cl$$

This difference in the hydrogen bond strength was found to be much more pronounced in the $[Cu\ (LH_2)_2]\ X_2$ complexes than the $[Cu\ (LH_2)\ X_2]$ ones .

The work of Desseyn and his coworkers(24-28) , was extended to characterize some metal complexes of dithiomalonamide

($H_2NCSCH_2CSNH_2$) where they found that introducing a CH_2 group in this bidentate ligand between the two cis amide functions dramatically changes the behaviour of the ligand compared with dithiooxamide. The Ni(II) and Pd(II) complexes were described by Peyronel et al,(29) where they proposed S,N coordination for the cationic species and S,S coordination for the neutral complexes. Martin(30) reported on the Ni(II), Pd(II) and Pt(II) complexes of dithiomalonamide and other metals such as Zn(II), Cu(II) have been also reported (31,32) , Ray and Sathyarayana(33) proposed S,S coordination for the cationic species $[Ni(H_2A)] Cl_2$ in analogy with other metal complexes. De Beuklleer and Desseyn(34) prepared the Ni(II), Pd(II) and Pt(II) complexes with dithiomalonamide from acid media and found that cationic species of general formula $[M(H_2A)_2]X_2$ are formed C(X= Cl, Br,I,ClO_4). They studied the infrared and Raman spectral characteristics of the complexes and investigated the influence of both the central metal ion and the counter ion on the spectra.

Desseyn group expended their work to the preparation of Au(III) complexes with dithiooxamide(35). They stated that in acid media they got a complex having the formula [Au (dto) (dtoH)]Cl_2. In strong alkaline media, the N,N-disubstituted dithiooxamide formed a new type of complexes with formula $A[Au(L)_2]$ where A = Li, Na or K and LH_2 is DMdto or DEdto. They used IR and Raman spectroscopy and thermal analysis to study the complexes and concluded that all complexes have a square planar geometry around Au(III) and that in all cases the dithiooxamides act as bidentate ligands coordinating through both the two sulfur atoms forming chelate ring systems. For the complexes formed in acid media special attention was given to the effect of H-bonding on the infrared spectra while for the complexes obtained in alkaline media the influence of the alkali counter-ion is investigated. From the TG data it was concluded that the forces in the ionic lattice of the $A[Au(L)_2]$ complexes follow the series Li > Na > K.

Stootmaekers et al,$^{(36)}$ studied also the complexes of Cu(I) and Ag(I) with dithiooxamides they stated that both metal ions form complexes of formula $(MLH_2)X$ in acid media where L-dto, methyl dithiooxamide (Mdto) and N,N-dimethyldithiooxamides (Ddto). The authors concluded that, although all the complexes studied have the same formula, different structures, depending on the halogen and the ligand used, are formed as substantiated from thorough investigation of their vibrational spectra. The M (dto) X, (X= Cl, Br) complexes and Cu (Mdto) Cl were found to be binuclear with bridging halogens, while the ligand exhibits on S-cis structure. For the other complexes, the dithiooxamide has an S-trans conformation and polymeric structures are formed. In the case of Ag(dto)Cl, Ag(Mdto)Cl and Cu(dto)Cl terminal metal-halogen are present and trigonal coordination around the metal is proposed, while for Cu(dto) Br and the $Cu(LH_2)I$ complexes bridging halogens are present in the structure giving a tetrahedral coordination. Furthermore, 1:2 complexes of Cu(I) and dithiooxamides have been prepared and characterized by X-ray powder diffraction as well as vibrational spectroscopy$^{(37)}$. It was found that Cu(I) can form complexes with the formula $Cu(LH_2)_2X$

where X=CL or Br and LH_2 is an N,N^1-disubstituted dithiooxamides. Vibrational analysis, with IR and Raman techniques indicated the presence of an inversion centre in the structure of the prepared complexes that leads to the proposal of a very unusual six-coordinate structure for these compounds, with the two oxamide ligands having S-cis conformation coordinating to the same copper and halogen bridges between to different copper atoms. The authors tried to confirm the six-coordinate Cu(I) complex, which is unusual, but the powder diffraction together with the vibrational spectra could not prove the structure, instead a square-pyramidal five-coordinate structure was proposed.

El-Gahami(38) reported the divalent copper, nickel, cobalt and cadmium complexes of dithiooxamides as primary ligand and both di-hydroxyanthraquinone and tetrahydroxyanthraquinone as secondary ligands. The complexes were characterized by elemental analysis electrical conductance measurements as well as electronic and IR spectroscopy. The mixed ligand Cu(II), Ni(II) and Co(II) complexes were suggested to assume a distorted octahedral geometry while for the Cd(II) complex, a tetrahedral structure was proposed.

Mikhaiolov and Polovnyak(39) found that the complexation reaction occurring between mixed potassium Iron(III) hexacyanoferrate(II), KFe $[Fe(CN)_6]$ and dithiooxamide or its N,N`-diphenylsubstituted derivatives on thin gelatin layers proceeds according to pseudo-SN_1 mechanism. The complexation was found to occur after the dissociation of Fe(III) hexacyano-ferrate(II) in an alkaline medium.

Dithiooxamide was used as a bridging ligand in the preparation of binuclear Fe(III)-Fe(II) complexes(40) of the type $[Fe(Salen)_2dto]$-$2H_2O$, where Salen stands for bis(salicylidene)ethylenediamine. The complexes were studied by elemental analysis, IR and electronic spectra as well as magnetic measurements . A dimeric structure with an octahedral arrangement of Fe(III) was proposed. Some of the complexes have been characterized by temperature-dependent magnetic susceptibilities and an antiferromagnetic exchange interaction was found for the binuclear complex containing the dithiooxamides bridge.

Chemisorbed copper(II) and Co(II) complexes of dithiooxamide on aminopropyl bonded silica(41) were prepared and evaluated for the separation of light hydrocarbons (C_4 and below) by micro column gas chromatography (GC). All the columns appeared to be effective for the separation of C_1-C_4 saturates with reproducible retention times. In general, the sample components were retained longer on the metal containing packing presumably due to specific solute-metal interactions. The cobalt(II) complex of amino propylsilyl-dithiooxamides bonded phase showed better selectivity for the test solutes, particularly the C_2 hydrocarbons this result, which reflects the higher capability of cobalt(II) to form π-complexes with electron donor compounds than copper(II), showed a significant improvement in the separation of the C_2 hydrocarbons over molecular sieve 5A, alkyl bonded silica and copper(II) complexes of cyano-and mercaptopropyl bonded phase where ethane and ethylene eluted as a single peak. Thermal stability test showed that the columns could be operated at temperatures up to 200°C without any appreciable change in retention properties.

In the search of metal, especially Pt(II), complexes showing metallomesogenic properties, $[Pt(Rdto)_2]$ complexes were synthesized starting from cis-$[Pt(Me_2SO)\ CL_2]$(42). The coordination chemistry of long chain dithiooxamides which in some cases show a different behaviour with respect to R_2 dto bearing small substituents on nitrogen atoms was found to be interesting. The reactivity appeared related only in part to the lower basicity of the amide nitrogen atoms in diaryl with respect to dialkyl-dithiooxamides, and differently populated conformations of the complexes seem to play an important role. Mesophase formation for $[Pt(R_2Hdto)_2]$ with 3,4-dalkylsubstituents is suggested by polarising optical microscopy and differential scanning calorimetry.

Workman et al,(43) studied the monolayer properties of the amphiphilic N,N^1-bis(10,12-pentacosadiynyloxycarbonylmethyl) dithiooxamide at the air-water interface by measuring surface pressure-area isotherms. The amphiphile itself did not form stable monolayers on an aqueous subphase but when Cu(II) ions are added to the subphase a coordination polymer was formed, forming stable monolayers at the air-water interface. The monolayer stability was found to be strongly influenced by the counter ion, pH and temperature of the subphase. Electron microscopy showed that at a low surface pressure a monolyer of loosely packed islands is formed. The monolayer of the coordination polymer could be transferred onto solid substrates by a Y-type transfer. The presence of Cu(II) ions is confirmed by xps measurements and UV-visible spectroscopy showed a strong absorption at 370nm, indicating that a strong conjugated coordination polymer is formed at the air-water interface.

Sengupta et al,(44) studied the oxovanadium(IV) complexes with 14-membered macrocyclic ligands derived from dithiooxamides. Tentative structures have been proposed on the basis of elemental analysis, electrical conductance, magnetic measurements and spectral (IR, EPR, electronic) data. The X-band EPR spectra of all the complexes were recorded at room temperature and at liquid nitrogen temperature. The room temperature EPR spectra did not show anisotropy because of rapid tumbling of the molecules in solution but it is observed at liquid nitrogen temperature. The spectral studies suggested a square pyramidal geometry for the oxovanadium(IV) complexes.

Thermal studies on the complexes formed between monosubstituted dithiooxamides (Rdto) as well as disubstituted dithiooxamides (RRdto) with Cu(I) and Au(III) ions are recently reported(45). It was found that the neutral Au complexes decompose without formation of intermediates. The ionic $M^I[Au(L)_2]$ complexes, where M^1=Li,Na or K, are mainly stabilized by the lattice forces. In the complex $[Au(LH)Br_2]$ Br, the release of one HBr per molecule occurs in two steps to form the more stable[Au(L)Br_2] The neutral[Cu(LH_2)$_2$$X_2$] decompose to the more stable [Cu(LH)X]. The latter complex was found to disproportunate to form Cu LX polymers, Cu, ligand and HX.

Abou-Taleb et al,$^{(46)}$ prepared a series of Ni(II) complexes with unsymmetric NNSS quadridentate containing hydrazine carbothioamide residues by the nucleophilic displacement of one SCH_3 group from [(1-phenyl-1,2-ethanediylidenebis(S-methylhydrazinecarbodithioate)NNSS]$^{2-}$ Ni(II) with primary and secondary amines. The N-diethyl substituted complexes of palladium(II) and platinum(II) have been similarly prepared. The authors prepared also the mono hydrazine Ni(II) complex and discussed its condensation with acetylacetone and benzoylacetone to the corresponding pyrazoles. The electron impact mass spectral studies suggested a preferential displacement of the SCH_3 group on the carbon atom directly conjugated to the phenyl group. The infrared, ultraviolet and visible absorption spectra as well as proton NMR spectra of these complexes have been discussed.

Kopel$^{(47)}$ and his coworkers prepared some mixed ligand complexes of Ni(II) with dithiooxamide. The secondary ligands include triphenyl phosphine, diethyl dithiocarbamate and 2-amino thiophenol. The magneto-chemical and spectral properties of the prepared complexes have been discussed.. The X-ray crystal structure of [$(Pph_3)_2$Cu(dto)Ni(dto)Cu$(Pph_3)_2$] was solved. The sulfur atoms of dithiooxamides are coordinated to copper atoms, while nitrogen atoms

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form a square planar surrounding the nickel atoms. The authors suggested that the copper atoms were in an approximately tetrahedral environment.

Mixed ligand mononuclear complexes of the type $(Pph_3)_2MdtoX$, where M=Cu(I), Ag(I) and X=Cl or Br have been synthesized and characterized by elemental analysis and IR spectera(48) The X-ray crystallographic structure determination of the bromide complex has been reported. In these complexes, dithiooxamide was found to act as monodentate ligand through one sulfur atom coordinated to Cu. The coordination of Cu atom was suggested to be distorted tetrahedron with a Cu-Br distance of 2.48A° and Cu-S distance of 2.35A°.

Tight contact ion pairs of general formula $[Pt(R_2H_2dto)_2]\ X_2$ have been prepared(49) and their absorption spectra and luminescence properties (at room temperature in dichloromethane fluid solution at 77K in butyronitrile rigid matrix) have been studied (R = methyl, butyl, benzyl and X = Cl, Br). The absorption spectra of all the compounds are dominated by moderately strong Pt(dπ) / S(π) to dithiooxamide π* charge transfer (Pt/S ⟶ dtoCT) bands in the visible region ($\varepsilon = 10^4 to 10^5 M^{-1}cm^{-1}$). Absorption features are also present at higher energies due to π-π^* transitions centered in the dto ligands (ligand centered, LC). All the compounds exhibit an unstructured Luminescence band in fluid solution at room temperature, with the maximum centered in the 700-730nm range. The luminescence band are blue shifted about 4000 cm^{-1} on passing to the rigid matrix at 77 K. Luminescence is assigned to the triplet

Pt/S → dto CT excited states in all cases. The compounds exhibited a second higher-energy luminescence band at room temperature centered at 610nm, attributed to LC excited state. Charge transfer interactions between halides and dto ligands destabilize dto centered orbitals, affecting the energy of Pt/S → dto CT transitions and states. The X counterions and X → dto CT levels are proposed to play a role in promoting excited state conversion between LC and Pt/S → dto CT levels. The R substituents on the nitrogen atoms of the dto ligands influence the absorption and photophysical properties of the compounds, by affecting proximity of the ion pairs. The possibility to functionalize the R substituents may open the way to interface these luminescent compounds with desired substrates and to construct supramolecular assemblies.

Finally, Barnard and his coworkers(50) tried to answer the question "is dithiooxamide oxidized or reduced during complexation?". To answer this question, the authors studied the complexes formed between dto and various $[Mo(CO)_4(PR_3)_x]$ fragments as well as the dioxomolybdenum-dto complexes(51,52). Trends in the CO stretching frequencies led authors to an interesting assertion that $[Mo(CO)_4(R_4N_2C_2S_2)]$ and $[Mo(CO)_3(PR_3)(R_4{}'N_2C_2S_2)]$ species are Mo - dithione complexes whereas the $[Mo(CO)_2(PR_3)2\text{-}R4'N2C2S2)]$ is a Mo^{II}-dithiolene complex. On the other hand, from crystallographic data they could conclude that the short C - C bond length in the complex $[Mo(CO)_2(PBu_3)_2(C_5H_{10}N)_2C_2S_2)]$ and the observed planar chelate ring provide substantive evidence that the dithiooxamide ligand is present in its reduced thiolene form confirming the previous assignments.

Complexes of other sulfur-nitrogen donor ligands

Other ligands, related to Dithiooxamide, with sulfur, nitrogen and/or oxygen bonding sites are known. The derivatives of dithiocarbamate with amino acids are famous S,N donor ligands besides the importance of their complexes as models for some biological systems.

Dithiocarbamates the subject of considerable interest , because they are easily undergoing any different reactions , thus being useful when studying substitution reactions in cation bonded ligands or between ligands themselves. (53) Many proteins have systein and methionine residues and so dithiocarbamate derivatives of amino acids can be valid as models to study the coordination of proteins to metallic cations (54) .

The dialkyldithiocarbamates are easily synthesized through the reaction of the amine with carbon disulphide in basic medium however if an α-amino acid is used instead of an amine dithiocarbamte derivatives of α-amino acids are obtained with the general structure where simultaneous presence of the dithiocarbamate and the carboxylic groups makes these ligands very interesting as both can be coordinate to the metallic cation . (55)

Metal ditiocarbamates have been successfully used in agriculture for controlling insects and fungi in treatment of alcoholism and in estimation of copper. (55) Their range of application is covering fields as different as chemical industry biology and boichemistry . (56)

The barium dithiocarbamate drivatives of glycine, alanine, 2-amino buteric acid norvaline and norleucine have been synthesized (57) the salts are formed according to the following equation :

$$H_2CHRCOOH \xrightarrow[(2)\,CS_2]{(1)\,Ba\,(OH)_2} Ba[S_2CNHCH(R)COO]+2H_2O \quad (3)$$

The anions have been used to obtain the corresponding nickel (II) complexes in acidic form according to the following reaction .

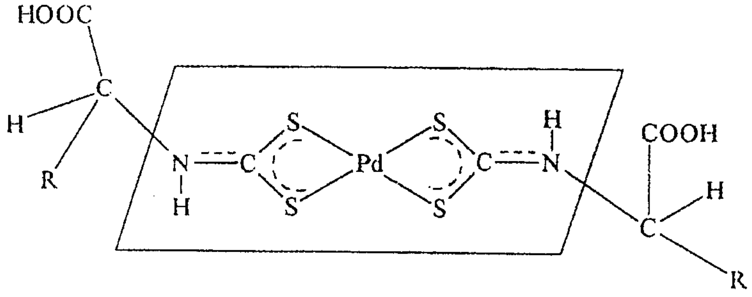
$$2Ba[S_2CNHCH(R)COO]+NiCl_2 \xrightarrow[2HCl]{Et_2}$$

$$Ni[S_2CNHCH(R)COOH]\ 2\ +2BaCl2 \qquad (4)$$

The complexes are diamagnetic and coordination takes place in a square planar geometry around the Ni (II) ion through sulphur atom of the dithiocarbamate .

Complexes of nickel (II) and copper (II) with aromatic dithiocarbamate have been reported by Macias et al.(58) Phenylglycine and phenylalanine react with CS, in a basic medium to yield the corresponding dithiocarbamates which react with Ni (II) and Cu (II) salts to form complexes of general formulae (Ni aadtc) and Cu(aadtc) respectively, where aadtc is the dithiocarbamate anion of the respective α-amino acid. It has been proposed that both series of complexes are diamagnetic and that the nickel (II) compounds are square planar. A reaction of the copper (II) in the complexes to the Cu (I) state occurs during synthesis .

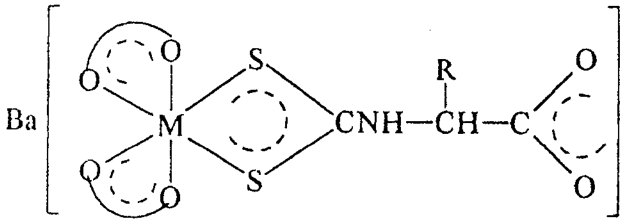
Complexes of Pd (II) with dithiocarbamate derived from α-amino acids (glycine alanine valine and leucine) have been also reported(59). The stoichiometry of the complexes are Pd : L = 1 : 2. The complexes have a distorted square planar structure with the ditiocarbamate acting as bidentate ligand through the sulphur atoms the carboxylic group is in the free acidic form .

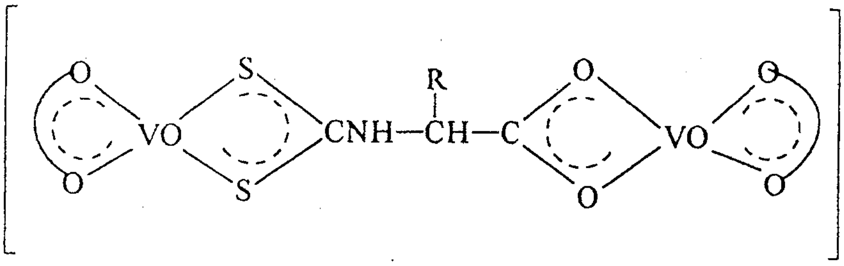


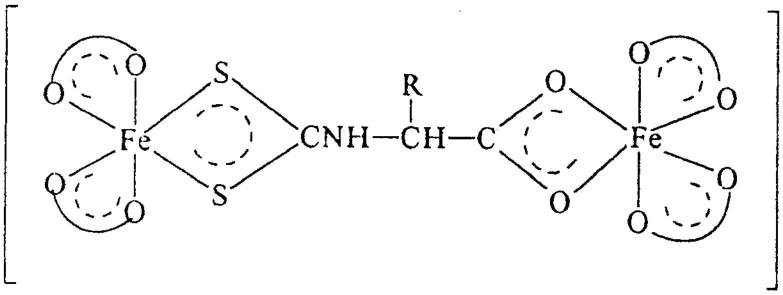
Where R=H, CH_3, CH(CH3)$_2$, CH_2-CH(CH_3)$_2$

Molybdenum(V) complexes of the general formula $[Mo_2O_4(aadtc)_2].2H_2O_2$ where aadtc = anion of dithiocarbamate derived from different amino acids have been prepared either by the raction of the ligands with molybdenum (V) chloride in an inert atmosphere or by reaction of sodium molybdate with dithionite in the presence of ligands in acidic medium. It has been found that the carboxylate group is in an acidic form without binding to the metal cation. The oxidation state of molybdenum ion Mo (V) has been confirmed by X-ray powder diffraction. (60)

Very few mixed ligand complexes containing dithiocarbamate ligand derived form α-amino acids have been reported in literature. (60) A number of mixed ligand complexes of general formula Ba[(M(acac)$_2$(aadtc)], [{VO(acac)}$_2$(aadtc)] and [{Fe(acac)$_2$}(aadtc)] where(aadtc = glycinlydithiocarbamate or alninyldihicarbamate, acac= acetylacetonate and M=Co(II) Ni(II)Cu(II) has been synthesized. An octahedral structure around the central metal ions has been proposed Vanadium (IV) and iron (III) complexes are supposed to be dimeric with the glycinly – and alaninyldithoicarbamates acting as a bridge as shown below :







M= Co(II), Ni(II), Cu(II); O⌒O = acetylacetonate anion; R= H or CH_3

Importance and application of the used metal ions

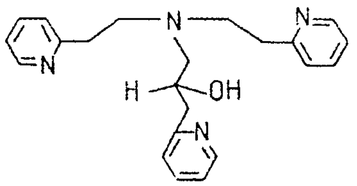
The metal ions used in the present thesis have a variety of application either in biological systems or in chemical industries. Co(II) is known in vitamin B_{12} which is found as the vitamin of the lowest concentration in the human body(61) .Nickel on the other hand was found to play an important role in biological systems (62). Studies on some hydrogenases indicate that the nickel center is surrounded by S, N and or O atoms, (63) where complexes with such combination of ligands can serve not only as models for some biological systems, but also can stabilize less usual oxidation states of Ni. (64) The blue copper proteins are a well – known class of copper containing proteins. These proteins are involved in electron transfer reactions and include azurine, plastocynine and stellacyanine. Many other proteins were found to contain Cu and Cu complexes . (65-67)

In addition to the above mentioned biological importance of Co, Ni and Cu; the ability of Ru (III) ion as catalytic oxidants is very important especially in the oxidation of primary and secondary alcohols .

The trinuclear complexes $[Ru_3OCO_2(R)_6L_3]^{n+}$ (R = Me, Et; L = H_2O, pph_3; n = 0, 1) have been used to oxidise primary alcohols to aldehydes and secondary alcohols to ketones with aerobic catalysts at 65° C and a considerable pressure of oxygen. High catalytic turnovers were observed under such condition for $[Ru_3O(CO_3Et)_36(pph_3)_3]$, over 24h but with $[Ru_3O(Pfb)_6(Et_2O)]$, (Pfb = perfluorobutyratate) alkenes may oxidise with aerobic catalysts cyclohexene to a mixture of the oxide ,the allylic alcohol and the ketone at 65° C .(68)

The catalytic oxidation has been studied using the cyclic voltammogram(69) of trans-[Ru(phen) $_2$ (OH_2) (OH)] (ClO_4)$_2$ (10^{-3}M) in 0.1 M CF_3CO_2H in presence of 2- propanol and indicated that the presence of a catalytic oxidation current was found beyond the couple Ru(IV)/Ru(III). Controlled potential electrolysis of this solution at 1.05 V vs. NHE (normal hydrogen electrode) produced acetone with over 85% current efficiency. No other organic product was formed however if the electrolysis was carried out at 1.25 V both the current efficiency and catalytic activity of the ruthenium complex decreases .

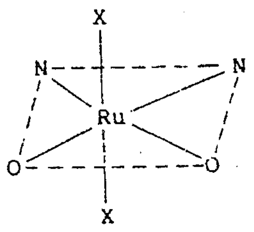
The cyclic voltammogram demonstrates the catalytic oxiation of isopropyl alcohol to acetone when the [Ru (N_4O) (OH_2)]$^{2+}$ [(N_4OH = bis-2(2-pyridylethyl) (2-hydroxy-2-(2-pyridyl)amine]. (70)



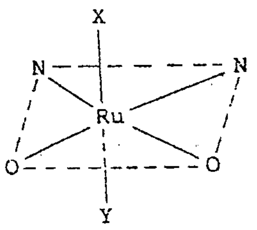
The complex is oxidised at a glassy carbon electrode and controlled potential electrolysis in 0.1 M $HClO_4$ and 0.1 M $NaClO_4$ at 1.2 V vs SCE (Saturated Calomel Electrode) in the presence of 2-propan of (1 M) and yielded acetone with turnover 12, over a period of 4.5 h. More importantly this ruthenim (III) complex provide a catalytic oxidation current that showed no sign of diminishing after several hours of continuous electrolysis .

It was found that [RuCl$_2$ (pph$_3$)$_2$ (acac)]oxidises alcohol in the presence of excess NMO, primary and secondary alcohols are oxidised to the corresponding aldehydes and ketones respectively. There is no oxidation by either NMO in the absence of the catalyst or reaction between the complex and the alcohols in the absence of NMO. The complex was found to be a good oxidant for alcohols compared with its osmium analogue [OsCl$_2$(pph$_3$)$_2$ (acac)] which showed weak oxidation for alcohols .(71)

The chelating ligands which are good σ-donors increase the electron density on the metal ion facilitating dioxygen binding. The dioxygen carriers so far studied simply include metal complexes of Schiff bases, prophyrins and macrocyclic ligands. (72-74) The cobalt (II) complexes with tetra and pentadentate Schiff bases have attracted much attention as used for separation of oxygen form air. (75) Oxygenation with molecular oxygen or H$_2$O$_2$ of ruthenim (III) Schiff base complexes , K(Ru^{III}(saloph))X$_2$] and [Ru^{III}(saloph))XY] gives the oxo-derivatives, ruthenium (V) oxocomplexes.(76)



X = Cl



Y = Imidazole or its derivatives.

However oxygenation studies of ruthenium (III) complexes derived from the Schiff bases HL of bis (Salicylaldehyde), ethylenedimine suggest the reversible binding of molecular oxygen (as shown below) to form ruthenim (IV) superoxo speices $[Ru^{IV}L(O_2)Y]^+$. (77, 78)

$[RuLXY]$ O_2 $[RuL(O_2)Y]^+ + X^-$

Cyclic voltammogram of [Ru(Salen)ClY],(Y-2-methyl imida zole) showed two redox wave at negative potential (-0.2 - 1.0 V) corresponding to Ru^V/Ru^{IV}.(79)

The $RuCl_3$/phIO system catalysed epoxidation of olefins and gave more than 10% of epoxide. Pyridine addition increases the yield and selectivity of epoxide. Spectral studies suggest that oxoruthenium (V) is the active oxidising species.(80) In the $RuCl_3$/hypochlorite or periodate systems, oxidative cleavage of double bonds occurs and a small proportion of epoxide (< 1%) is obtained .

The ruthenium (III) complexes $[Ru^{III}X_2(Asph_3)_2(HL)]$ (X = Cl, Br; HL = monoaino of Schiff bases formed from condensation of 2,3-dihydroxy benzldeyde and aniline or its o- and p-substituted derivatives) have been isolated characterized by spectroscopic technique and investigated by cyclic voltammetry. These complexes were found to be effective catalysts for oxidation of primary alcohols to aldehydes, secondary alcohols to ketones and 3,5-(di-(tert-butyl)) catechol to the corresponding o-benzoquione in the presence on N-methylmorrpholine N-oxide as co-oxidant .(83,84)

AIM OF THE WORK

The wide range of application of the dithiooxamide (dto) ligand in analystical chemistry(1), biochemistry and imaging processes(6) provides unambiguous importance of the study of its metal complexes. The ligand is multifunctional and can chelate metal ions in a variety of different ways including the formation of neutral polymeric and cationic monomeric(9) complexes. Coordination polymer networks based on multidentate ligands represent, on the other hand, a growing area of interest because they can be used as ionic exchangers and catalysts. They have also provided interesting examples of low-dimentional magenetic materials(85-88).

In view of these findings and due to the lack of studies regarding Co (II) and Ru (III) complexes with dto, as well as mixed ligand complexes involving these and other metal ions, it is thought of interest to present, in this thesis, a systematic study of the binary and mixed ligand complexes of Co(II), Ni(II), Cu(II) and Ru(III) with dto as primary ligand and 8–hydroxyquinoline, acetylacetone, o-pheylene-diamine, salicylic acid or thioacetamide as a secondary ligand. The study involve;

(a) Spectrophotometric determination of the stoichiometry of the binary and mixed ligand complexes liable to form in solution and evaluation of their apparent formtion constants.

(b) Synthesis of the solid complexes and their characterization using different tools, viz. elemental analysis, conductivity as well as electronic and IR spectral measurements with the aim to shed the light on the nature of interaction and bonding between the metal ions and the ligands.

(c) Investigation of the thermal properties of the complexes and kinetics of their decomposition.

CHAPTER II

Experimental

CHAPTER II

EXPERIMENTAL

Materials:

All solvents used in this thesis were of the analar grade (B.D.H or Merck products). Dithiooxamide (dto), used as primary ligand, was E. Merck product, its purity was checked by elemental analysis and IR spectra and was used as supplied.

Secondary ligands; o-phenylenediamine (o-phen),2,2`-bipyridyl (bipy), acetylacetone (acac), 8-hydroxyquinoline (8-HQ), thioacetamide (taa) and salicylic acid (sal) were all of the Analar grade (B.D.H. or Merck products) and used without further purification.

Reagent grade metal salts; $CoCl_2. 6 H_2O$, $Co(CH_3COO)_2 .4 H_2O$, $NiCl_2.6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $CuCl_2.2H_2O$, $Cu(CH_3 COO)_2 \cdot H_2O$, and $RuCl_3 .6H_2O$ have been used for the preparation of the solid complexes, and also for investigation of the complex formation in solution.

Solutions:

In order to investigate the possibility of complex formation in solution two different spectrophotometric methods have been applied, namely the molar ratio and continuous variation methods. For the purpose of using the molar ratio method a series of solutions was prepared in which the metal ion concentration was kept constant while the ligand concentration was varied to cover the ratios 2:1, 1:1, 1:2 and 1:3 (metal ion :ligand). Both the metal salt and ligand were dissolved in methanol.

For using the continuous variation method a series of methanolic solutions was prepared in which both the metal ion and ligand concentrations were varied while keeping the total molar concentration constant.

Spectrophotometric measurements for the determination of the stoichiometry of the complexes liable to form in solution and to evaluate their formation constants have been carried out at room temperature (~ 25°C).

Preparation of the complexes

(i) Binary complexes of Co(II), Ni(II)and Cu(II)with dto.

Two different methods were used for preparing the binary M(II) complexes with dto.

(a) In the first method a methanolic solution containing 3mmol of the M(II) salt was added to a solution of 6mmol of dto in methanol while stirring. The mixture was then refluxed for 2-4h depending upon the type of the metal salt and left overnight whereby a precipitate was formed. The precipitate was filtered, washed several times with small portions of cold methanol and with water and dried in vacuo over P_4O_{10} .

(b) In the second method, the acetate salt of the metal was used and the preparation was performed in an acid medium, as follows:

Three mmol of the metal(II) acetate was dissolved in a mixture of acetate + glacial acetic acid (1:1 by volume) were added to a solution containing 6m mol of dto dissolved in a mixture of acetone + acetion acid, in the same composition. The mixture was digested at about 70°C for about an hour while stirring and left at room temperature for ~ 25h. The formed precipitate was filtered, washed with acetic acid and acetone followed by washing with ether and dried in vacuo over P_4O_{10}.

(ii) **Binary Ru(III)- dto complex**

To a methanolic solution of 5mmol of $RuCl_3.6H_2O$, 5ml of 1:1 HCl were added in order to avoid the possibility of hydrolysis of the highly charged metal ion. The metal salt solution was then added to 10 m mol of dto dissolved in acetic acid + HCl (25 ml) while stirring. The stirring of the mixture was continued for about one hour and the mixture was left at room temperature for about 24h whereupon a precipitate is formed, the precipitated solid complex was filtered, washed with acetic acid, methanol and ether and dried in vacuo over P_4O_{10}.

(iii) **Mixed ligand complexes**

Two methods have been applied to synthesize the mixed ligand complexes depending upon the solubility of the binary complex in the common organic solvents:

(a) For soluble binary complexes, especially those prepared from the metal acetate salt. In this case 3 to 5 mmole of the binary complex were dissolved in warm methanol or ethanol and then added to a warm methanolic solution containing a slight excess than the equimolar amount of the secondary ligand while stirring. The mixture was kept warm and under stirring for about one hour, then left at room temperature for 24 hours whereupon a fine crystalline solid was separated. This was filtered, washed with acetic acid, methanol and finally with ether and kept in a desiccator over P_4O_{10}.

(b) When the binary complex was insoluble in water and common organic solvents equimolar amounts of the metal acetate, dto and the secondary ligand, dissolved each in a mixture of acetone and glacial acetic acid, were mixed on hot and while stirring. The mixture was digested at 60-70°C for 60 min with a constant stirring and then left at room temperature for a full day whereupon a solid was precipitated as fine crystals. This was filtered, washed with acetic acid, methanol and ether and dried in vacuo over P_4O_{10} for several days.

The prepared solid binary and ternary complexes were analyzed for their carbon, hydrogen and nitrogen contents. The cobalt, nickel and copper contents of the complexes have been also determined using the recommended procedure.

Determination of the metal content in the prepared complexes.

Determination of Co(II) and Ni(II)

1- About 0.03g of the Co(II) or Ni(II) complex are decomposed by adding 10 ml of conc. HCl + 5 ml of conc. HNO_3 and evaporating till nearly dryness. To ensure decomposition, the process was repeated using 5 ml conc. HCl.

2- The Decomposed sample was dissolved in 100ml doubly-distilled water and heated just to boiling, then allowed to cool to the room temperature. To this solution, 5-6 drops of freshly prepared murexide-NaCl mixture was added, followed by 10ml of 1M NH_4Cl Solution. Concentrated ammonia solution was then introduced dropwise until the pH was ~7.0.

3- The solution was titrated with 0.01M EDTA solution until the end point is approached, then the solution was rendered strongly alkaline by about 10ml of conc. NH_4OH solution and the titration was continued until the colour changed to wine-red (for cobalt) or bluish-violet (in the case of nickel).

Determination of Copper

1- A 0.03g sample of the copper complex was decomposed as described before for the cobalt and nickel complexes.

2- The diluted solution was neutralized with 2M Na OH solution using M.O as indicator to the first yellow colour.

3- To that solution 5ml of buffer PH5 solution were added, the resulting solution was heated to ~60°C, and 3 drops of PAN indicator (pyridylazo-2-naphthol) were added.

4- The solution was then titrated with EDTA till the colour change form red to yellow (end point).

Physical Measurements

Ultraviolet and visible spectra were recorded on a Varian 100S uv-vis spectrophotometer using 1-cm matched silica cells at room temperature (25°C).

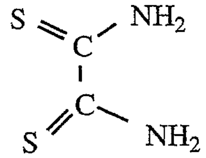
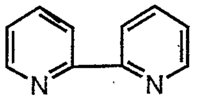
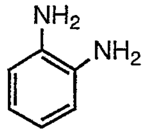
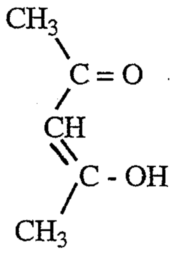
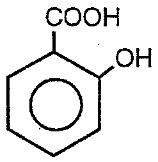
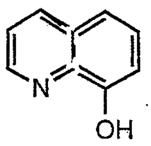
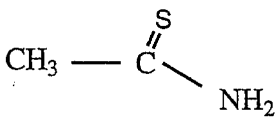
The infrared spectra of the ligand (dto), its binary and ternary complexes have been recorded as KBr discs using a Varian 450 spectrophotometer.

Conductivity measurements were performed using a Jenway 4310 Conductivity meter with an immersion cell (cell constant =

1.09). Thermal analysis was obtained by a Du Pont 2000 thermal analyzer in an air carrier. The heating rate was 10°/min .

Carbon, hydrogen and nitrogen analysis were performed in the microanalytical laboratories at the university of Assiut, Assiut, Egypt; *Istituto di chimica dei Materiali, Area Della Recirca di Roma,* Italy; and Department of Chemistry King Fahd University, Dammam, Kingdom of Saudi Arabia . The elemental analysis together with the results of metal analysis are given in Tables 14-17 (Chapter IV)

The ligands used in this thesis have the following structures:

Dithiooxamide		(dto)
2,2-Dipyridyl		(bipy)
o-Phenylenediamine		(o-phen)
Acetylacetone		(acac)
Salicylic acid		(Sal)
8-Hydroxyquinoline		(8-HQ)
Thioacetamide		(Taa)

CHAPTER III

Spectrophotometric Studies on the Binary Metal- Dithiooxamides and Mixed Ligand Complexes Formed in Solution

CHAPTER III

Spectrophotometric Studies on the Binary Metal-Dithiooxamides and Mixed Ligand Complexes Formed in Solution

The work given in this chapter is devoted to investigate the possibility of formation of binary metal dithiooxamide complexes in solution and also their mixed ligand adducts formed by using the secondary ligands, where such a study is not reported as evident from the literature survey given in the introduction .

The study involves a spectrophotometric investigation of the reaction of the Co(II) , Ni(II), Cu(II), and Ru(III) ions with dithiooxamide in solution and also some of the mixed ligand complexes formed in solution. It is aimed to determine the stoichiometry of the binary and ternary complexes liable to form in solution, and also to evaluate their apparent formation constants.

The uv-visible absorption spectra of methanolic solutions having 1:1 (metal ion : ligand) composition have been recorded. This is made with the intention to trace the ability of complex formation, in solution, from the reaction of dithiooxamide and each of the aforementioned metal ions; and to investigate the effect of the coordinated metal ion on the low energy electronic transition band of the ligand.

Figure 1 represents the recorded electronic absorption spectra of methanolic solutions of dto and its 1:1 complex solutions with Ni(II), Cu(II) and Ru(III) as representative examples. The blank used was methanol. In general, it is evident that the addition of metal ion into the ligand solution causes distinguishable changes. It could be easily recognized that there is either, a pronounced shift of the main band towards a longer wavelength (bathochromic shift in the case of Cu(II)), or a new band (or shoulder) is developed in the lower energy side of the main band of dto (Ni(II) and Ru(II)).

Such spectral changes can be attributed to the expected easier charge transfer interaction within the complexed ligand relative to the free one. This results from the high accepting character of the coordinating positively charged metal ion.

These spectral changes together with the observed instantaneous colour change on mixing solutions of the metal ions and dto clearly indicate an immediate formation of complexes in solution.

Determination of the Stoichiometry of the Complexes:

Metal complexes with organic ligands have usually, in general, selective absorption in the uv-visible region. This property is widely used to determine the stoichiometry of the complexes formed in solution as well as to evaluate their stability constants.

The spectrophotometric methods applied for the determination of the stoichiometry of the complexes, formed in solution, are the molar ratio method of Yoe-Jones(89) and Job`s continuous variation method(90). Generally, for purpose of using these two methods, the series of solutions mentioned in the experimental part (Chapter II) were prepared. The spectra of all solutions were recorded within the range 300-600 nm, where a solution containing the same concentration of the ligand as that of the complex solution was used as a blank.

Results of the molar ratio method:

The recorded spectra of the different complex solutions prepared for this method are shown in Figs. 2-5 for the binary complexes. The spectra are characterized by one main band in the visible region. On plotting the absorbance values at a selected λ_{max}, of all the complex solutions, against the molar ratio [dto] / [M^{n+}] the relationships given in Figs. 6-9 are obtained. It is evident that these relationships are characterized by one or two breaks located at the molar ratios [dto] / [M^{n+}] equal 1.0 and/or 2.0. This clearly indicates that the stoichiometric ratios of the complexes liable to form in solution from the reaction of the dto ligand with Co(II), Ni(II), Cu(II) and Ru(III) are 1:1 or 1:2 (M^{n+} : dto) depending on the type of the metal ion. The data used in plotting the absorbance-molar ratio ([dto] / [M^{n+}]) relationship for the various complexes investigated are reported in Tables 1-4.

On the other hand, Figs. 10-14, represent the spectra obtained for using the molar ratio method to determine the stoichiometry of some mixed ligand complexes involving Cu(II), dto and some secondary ligands such as bipyridyl(bipy), o-phenylenediamine (o-phen), acetyl acetone (acac), and thioacetamide (taa). It is noteworthy in this context that, because the binary complex of Cu-dto is reactive towards these secondary ligands, it is considered as the metal ion in the series of solutions prepared for this study. The relations shown in Figs.15-19 are those obtained for the formation of mixed ligand complexes in solution. These relations clearly indicate that the binary complexes are reactive toward the used secondary ligands forming mixed ligand adducts and also used to determine the ratio of secondary ligand to the binary complex. It is evident that 1:1 or 1:2 (binary complex: secondary ligand) mixed ligand complexes could be formed in solution.

Results of the continuous variation method

As an example, the continuous variation method has been applied on the binary complex of Cu(II) with dto. The recorded spectra of the different solutions prepared for this method are shown in Fig.20. On plotting the absorbance values at a fixed wavelength, of all the complex solutions, against the mole fraction of dto a curve was obtained as given in Fig.21. The maximum of this curve was found to correspond a mole fraction of the ligand equals 0.5 indicating the formation of 1:1 (Cu(II):dto) complex which is in confirmation to the result obtained by applying the molar ratio method as evident from Table 11.

Evaluation of the apparent formation constants of the metal complexes formed in solution

The two spectrophotometric methods, namely the molar ratio and continuous variation, that have been used in this thesis to establish the stoichiometry of the complexes formed in solution have been also utilized for the evaluation of their formation constants.

Within a certain, rather restricted, range the inflection point of the molar ratio plot and the maximum of the continuous variation plot can be, to a good advantage, used for the calculation of the formation constant of the complex. Thus if the metal ion (M^{n+}) and the ligand(X) are found to form a 1:1 complex (MX) and the total concentration of M^{n+} in solution is Cf, then that of the ligand X at the inflection point (or maximum) would virtually be Cf. If the concentration of MX is taken as C, then its absorbance would be the same as the absorbance Am, which is the limiting absorbance, that is reached only when a large excess of the ligand (X) is present in solution, corresponding to the maximum formation of the complex. Actually, the formation of a complex is not quite complete at the inflection point and so the absorbance A, at that point is smaller than Am. The value of A can be calculated from the intersection of the straight lines on both sides of the inflection point. For calculating the formation constant of a complex of the type (MX), one proceeds in the following manner:

The equilibrium existing in solution might be given as

$$M^{n+} + X \rightleftharpoons (MX)^{n+} \qquad (1)$$

For which the limiting absorbance Am, corresponds to the concentration of MX at full colour development, A corresponds to the concentration of the complex species existing in equilibrium. If C is the initial concentration of the metal ion , then at equilibrium we have :

$$[MX]=(A/Am).C \qquad (2)$$

$$[M] = C-[MX] = C\ (1-A/Am) \qquad (3)$$

From the equilibrium(I), the formation constant (Kf) of the complex is given by:

$$Kf = \frac{[MX]^{n+}}{[M]^{n+}\ [X]}$$

Substituting the values of [M] and [MX] from the relations (2) and (3) we get

$$Kf = \frac{(A/Am)\ C}{(1-A/Am)^2\ C^2} \qquad \text{or}$$

$$Kf = \frac{(A/Am)}{(1-A/Am)^2\ C} \qquad (4)$$

In the case of formation of MX_2 type complex, the value of the formation constant Kf, can be evaluated as follows:

$$M^{n+} + 2X \rightleftharpoons (MX_2)^{n+} \qquad (5)$$

$$[M^{n+}] = C - [MX_2] = C\,(1\text{-}A/Am) \qquad (6)$$

$$[X] = 2C\,(1\text{-}A/Am) \qquad (7)$$

$$[MX_2] = (A/Am)\,C \qquad (8)$$

Then

$$Kf = \frac{(1\text{-}A/Am)C}{[2C\,(1\text{-}A/Am)]^2\,(1\text{-}A/Am)\,C} \qquad \text{or}$$

$$Kf = \frac{A/Am}{4C^2\,(1\text{-}A/Am)^3} \qquad (9)$$

The Kf values obtained for the binary and mixed ligand complexes formed in solution have been calculated by applying equations(4) and (9) on the data of the molar ration and continuous variation methods. The obtained values are given in Tables 12 and 13.

Examination of the Kf values in Table 12 reveals that they decrease in the following order.

$$Ru^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+}$$

This is in agreement with the general order of stability reported by Irving and Williams(91) and also by Grinberg and Yatsimerski(92) which is based upon the increase in the ionic radius in the same direction. On the other hand. The relatively greater value of the formation constant of the Ni-dto complex reflects the fact that Ni(II) ions are preferred as “soft Lewis acid” to the dto molecules. This behaviour suggests the coordination of dto molecules through its sulfur atoms (soft Lewis base) to the nickel ions.

Regarding mixed ligand complexes, the data given in Table 12 reveal that the stability decreases on changing the secondary ligand according to the following order for 1:1:1 complexes:

ac.ac.> 8-HQ > bipy > o-phen

The above order indicates the greater affinity of Cu^{2+} ions towards oxygen donor ligands from one hand, and from the other hand both acac and 8-HQ which are usually coordinates to metal ions as monvalent bidentate ligands are expected to form more stable complexes than the neutral bidentate (bipy and o-phen) ligands(93,94) . Moreover, bipyridine ligand with extended π-electronic system is capable for back donation by the metal ion through π-bonding(95) forms more stable complexes with Cu^{2+} ions relative to the o-phenylenediammine ligand having no extended π-system.

Table1: Data of molar ratio method for Co(II)-dto complexes

[dto] / [Co(II)]	Absorbance
0.2	0.054
1.0	0.0755
1.4	0.0844
1.8	0.888
2.4	0.955
2.8	0.101

Table 2: Data of the molar ratio method for Ni(II)-dto complexes

[dto] / [Ni(II)]	Absorbance
0.2	0.027
0.6	0.066
1.0	0.0944
1.4	0.1277
2.0	0.194
2.6	0.255
3.2	0.311
3.6	0.383

Table 3: Data of the molar ratio method for Cu(II)-dto complexes

[dto] / [Cu(II)]	Absorbance
0.2	0.055
0.6	0.188
0.8	0.283
1.0	0.327
1.4	0.338
1.8	0.350
2.6	0.350

Table 4: Data of the molar ratio method for Ru(III)-dto complexes

[dto / [Ru(III)]	Absorbance
0.2	0.229
0.6	0.241
1.0	0.2475
1.4	0.250
1.8	0.2536
2.4	0.259

Table 5: Data of the molar ratio method for Cu(II)-dto-acac mixed ligand complexes.

[acac] / [Cu^{2+}]+[dto]	Absorbance
0.2	0.387
0.6	0.505
1.0	0.590
1.4	0.615
1.8	0.633
2.2	0.658

Table 6: Data of the molar ratio method for Cu(II)-dto-8-HQ mixed ligand complexes.

[8HQ] / [Cu^{2+}]+[dto]	Absorbance
0.2	0.387
0.6	0.505
1.0	0.590
1.4	0.615
1.8	0.633
2.2	0.658

Table 7: Data of molar ratio method for Cu(II)-dto-Taa mixed ligand complexes.

[Taa] / [Cu^{2+}]+[dto]	Absorbance
0.6	0.325
1.0	0.354
1.4	0.485
1.8	0.515
2.4	0.586
2.8	0.619

Table 8: Data of molar ratio method for Cu(II)-dto-Tsc Mixed ligand complexes.

[Tsc] / [Cu^{2+}]+[dto]	Absorbance
0.2	0.233
0.6	0.244
1.0	0.261
1.4	0.272
1.8	0.283
2.2	0.322
2.6	0.372

Table 9: Data of molar ratio method for Cu(II)-dto-o-phen Mixed ligand complexes.

[o-phen] / [Cu^{2+}]+[dto]	Absorbance
0.2	0.275
0.6	0.280
1.0	0.304
1.8	0.329
2.2	0.33
2.6	0.345

Table 10: Data of molar ratio method for Cu(II)-dto-bipy Mixed ligand complexes.

[bipy] / [Cu^{2+}]+[dto]	Absorbance
0.2	0.147
0.6	0.203
1.0	0.337
1.4	0.381
1.8	0.406
2.2	0.395
2.6	0.477

Table 11: Data of the continuous variation method for Cu(II)-dto complexes.

$[Cu(II)] \times 10^{-5}$	$[dto] \times 10^{-5}$	Mole fraction	Absorbance
1	9	0.9	0.033
2	8	0.8	0.105
3	7	0.7	0.108
4	6	0.6	0.25
5	5	0.5	0.35
6	4	0.4	0.288
7	3	0.3	0.222
8	2	0.2	0.147
9	1	0.1	0.088

Table 12: Apparent Formation (Kf) values for the binary complex.

Complex	Kf
Ni(dto)	7.00×10^{7}
Co(dto)	1.86×10^{3}
Ru(dto)	2.27×10^{4}
Cu(dto)	5.05×10^{3}
Cu(dto)	5.52×10^{3} *

* Calculated form Continuous Variation

Table 13: Apparent Formation Constant (Kf) values for the Mixed complexes.

Complex	Kf
Cu(dto) (acac)	4.42×10^4
Cu(dto)(8-HQ)	1.37×10^4
Cu(dto) (bipy)	1.22×10^4
Cu(dto)(o-phen)	4.05×10^4
Cu(dto)(Taa)$_2$	4.50×10^6

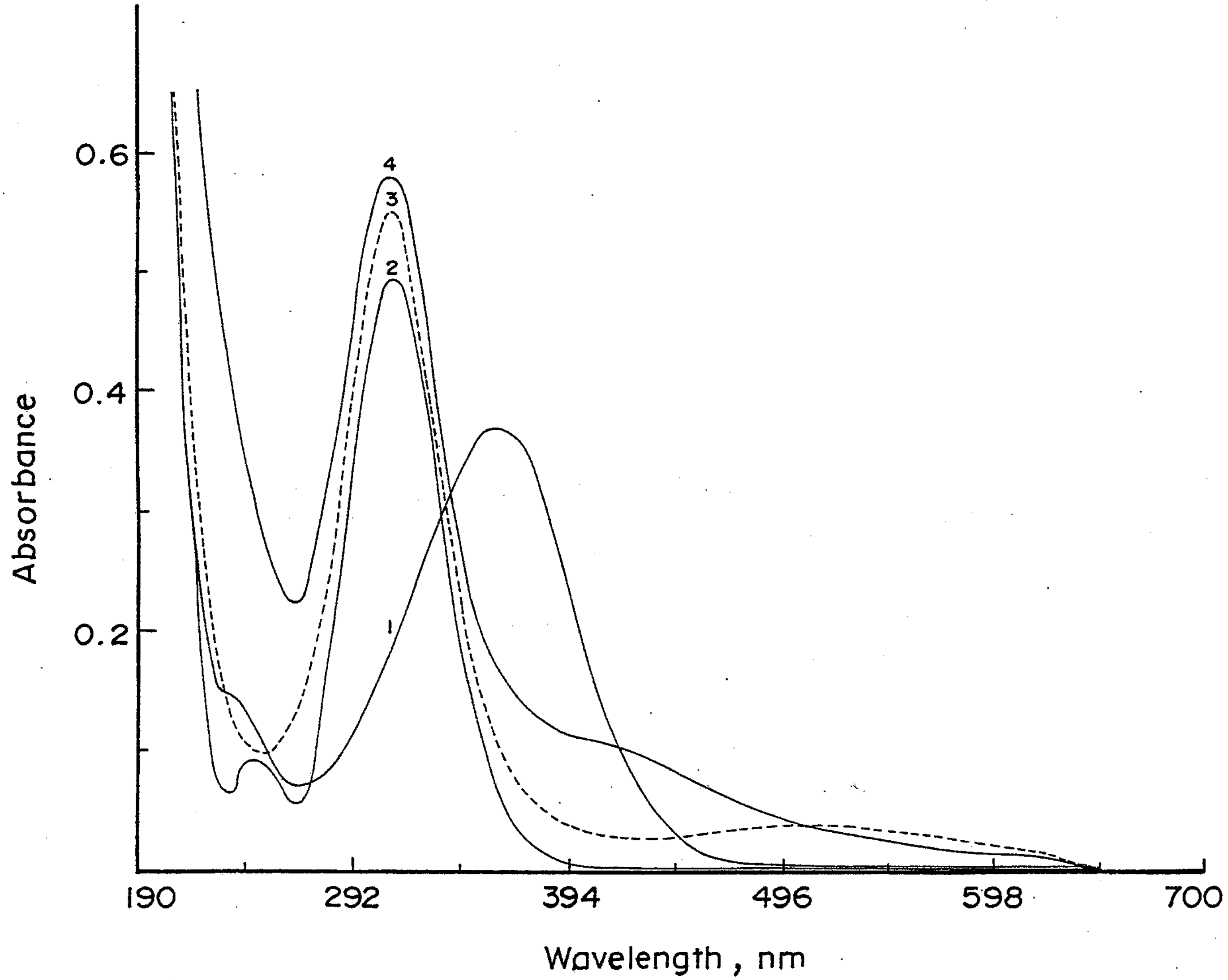


Fig. 1. Absorption spectra of dto and its 1:1 metal complex solutions

1- Cu(II) + dto, 2-Free dto, 3-Ni(II) + dto, 4- Ru (III) + dto

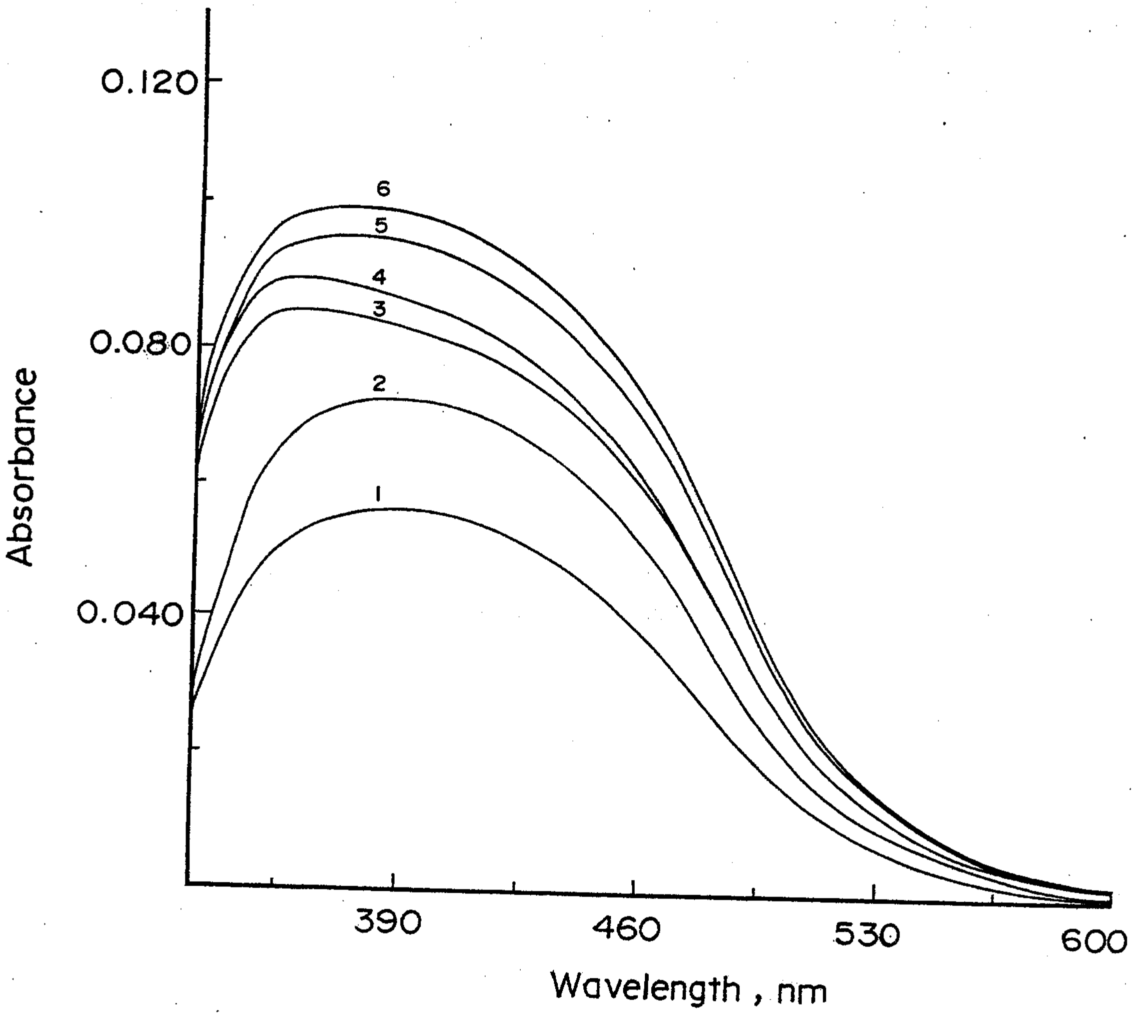


Fig. 2. **Absorption spectra of the Co^{II}-dto complex solutions**

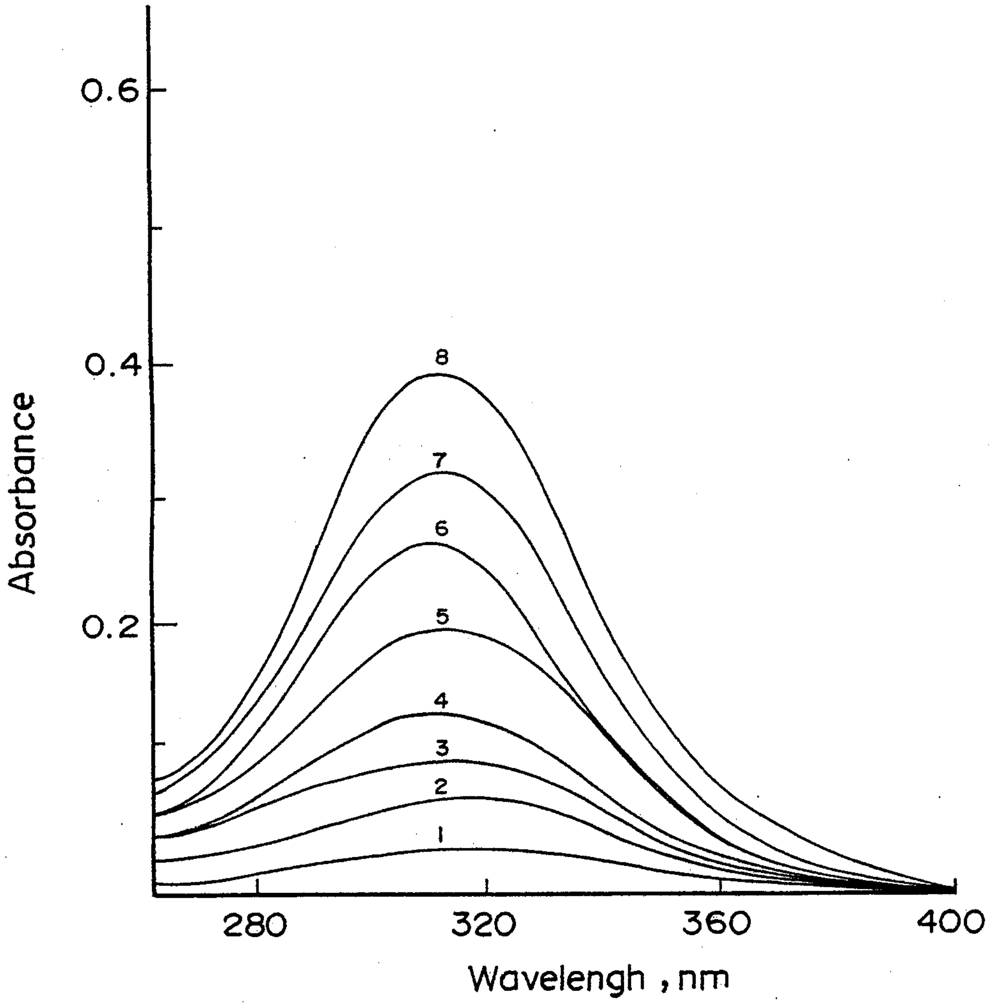


Fig. 3. Absorption spectra of the Ni^{II}-dto complex solutions

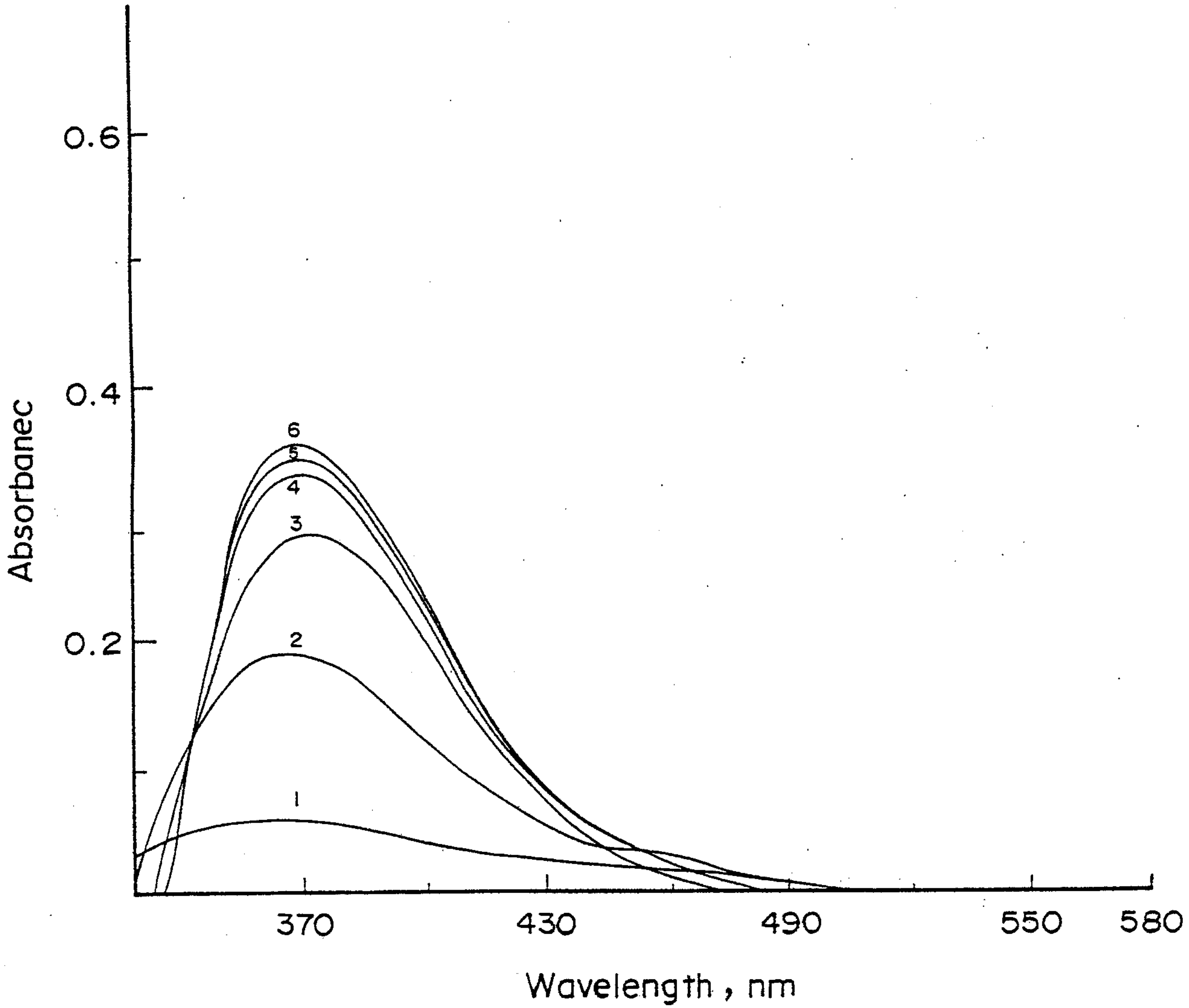


Fig. 4. Absorption spectra of the Cu^{II}-dto complex solutions

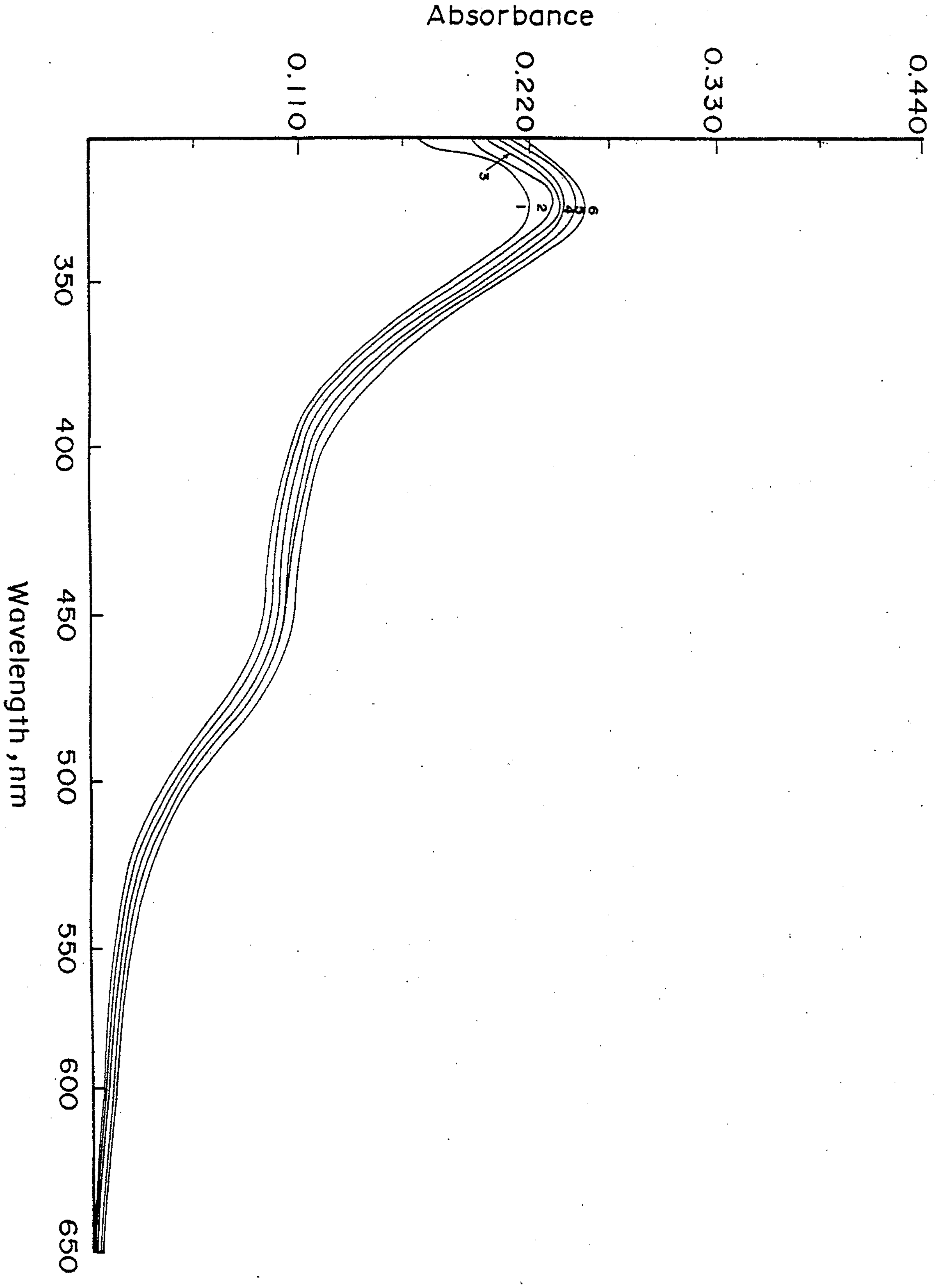


Fig. 5. Absorption spectra of the Ru^{III}-dto complex solutions

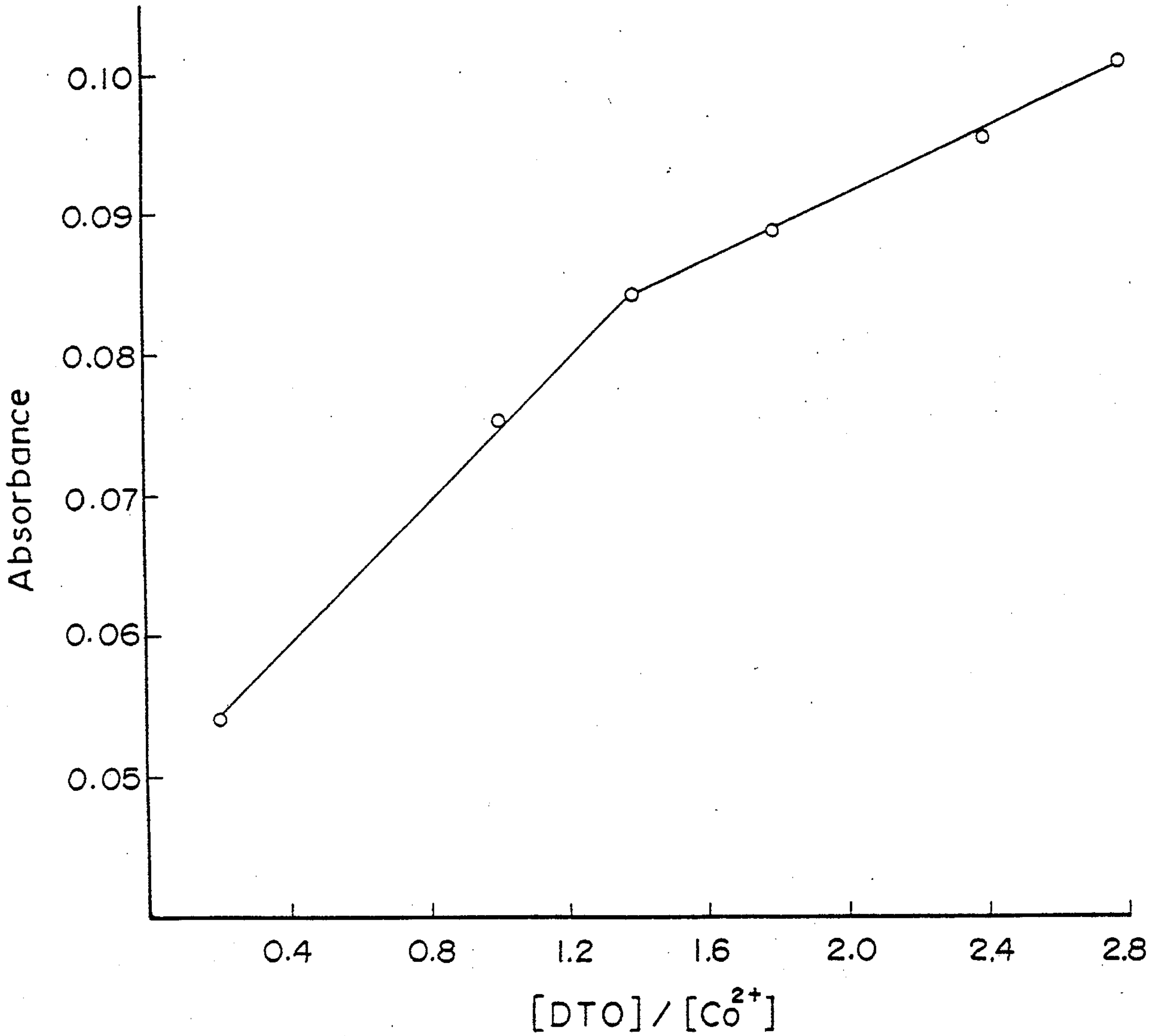


Fig. 6. Molar ratio plot of the Co^{II}-dto complex

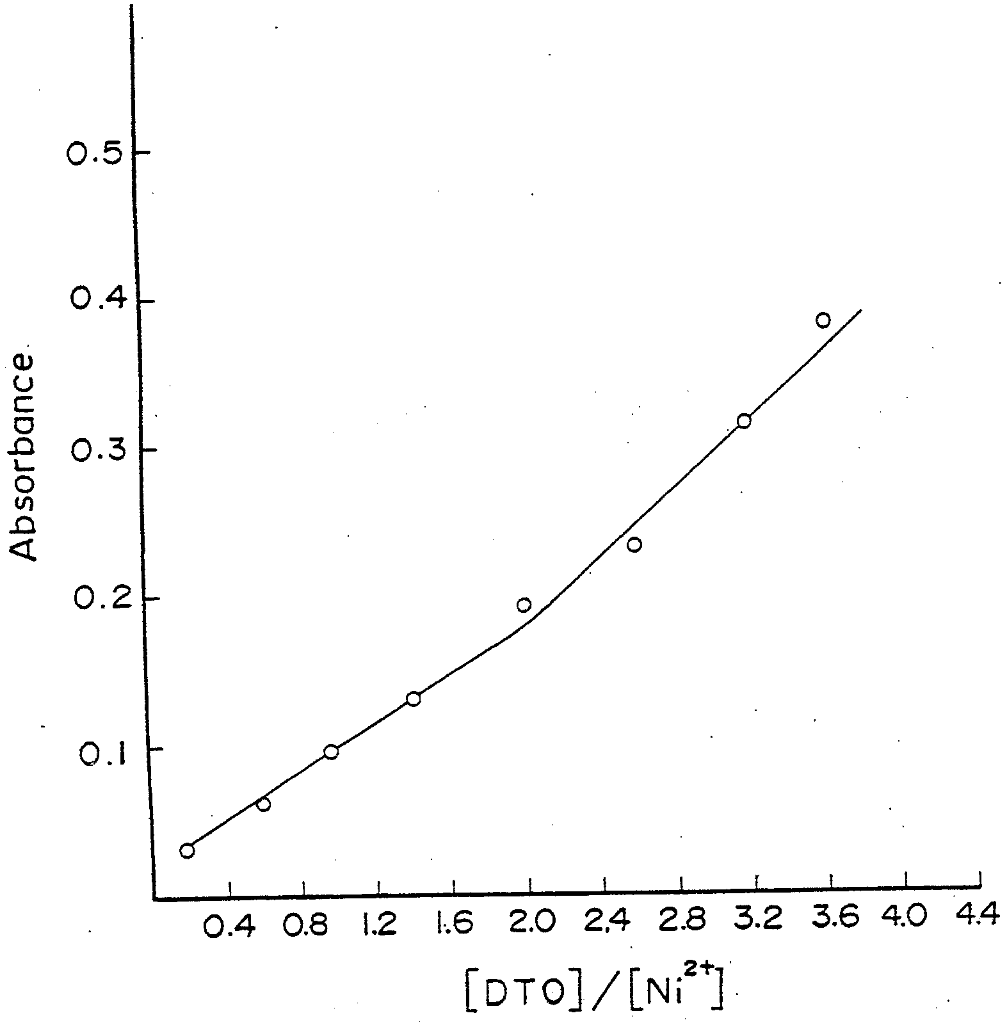


Fig. 7. Molar ratio plot of the Ni^{II}-dto complex

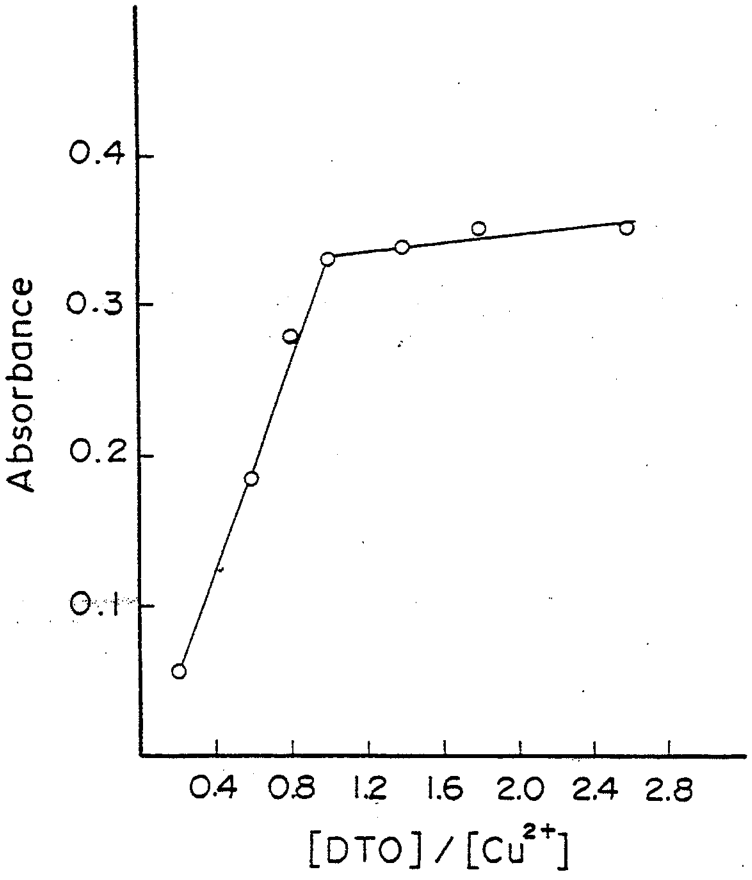


Fig. 8. Molar ratio plot of the Cu^{II}-dto complex

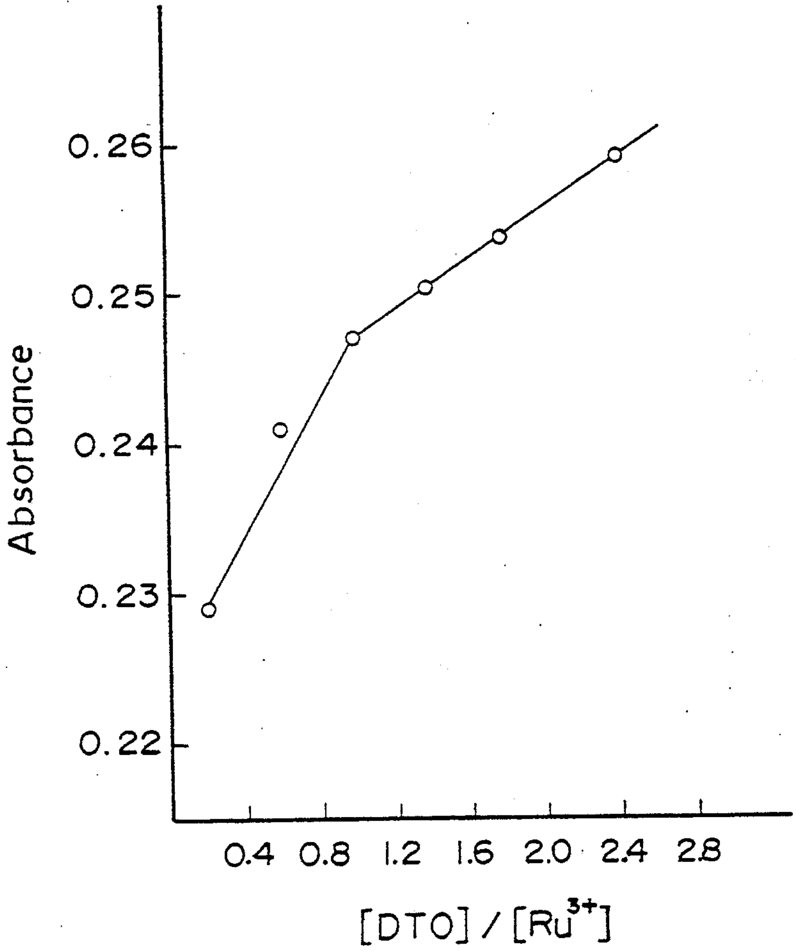


Fig. 9. Molar ratio plot of the Ru^{III}-dto complex

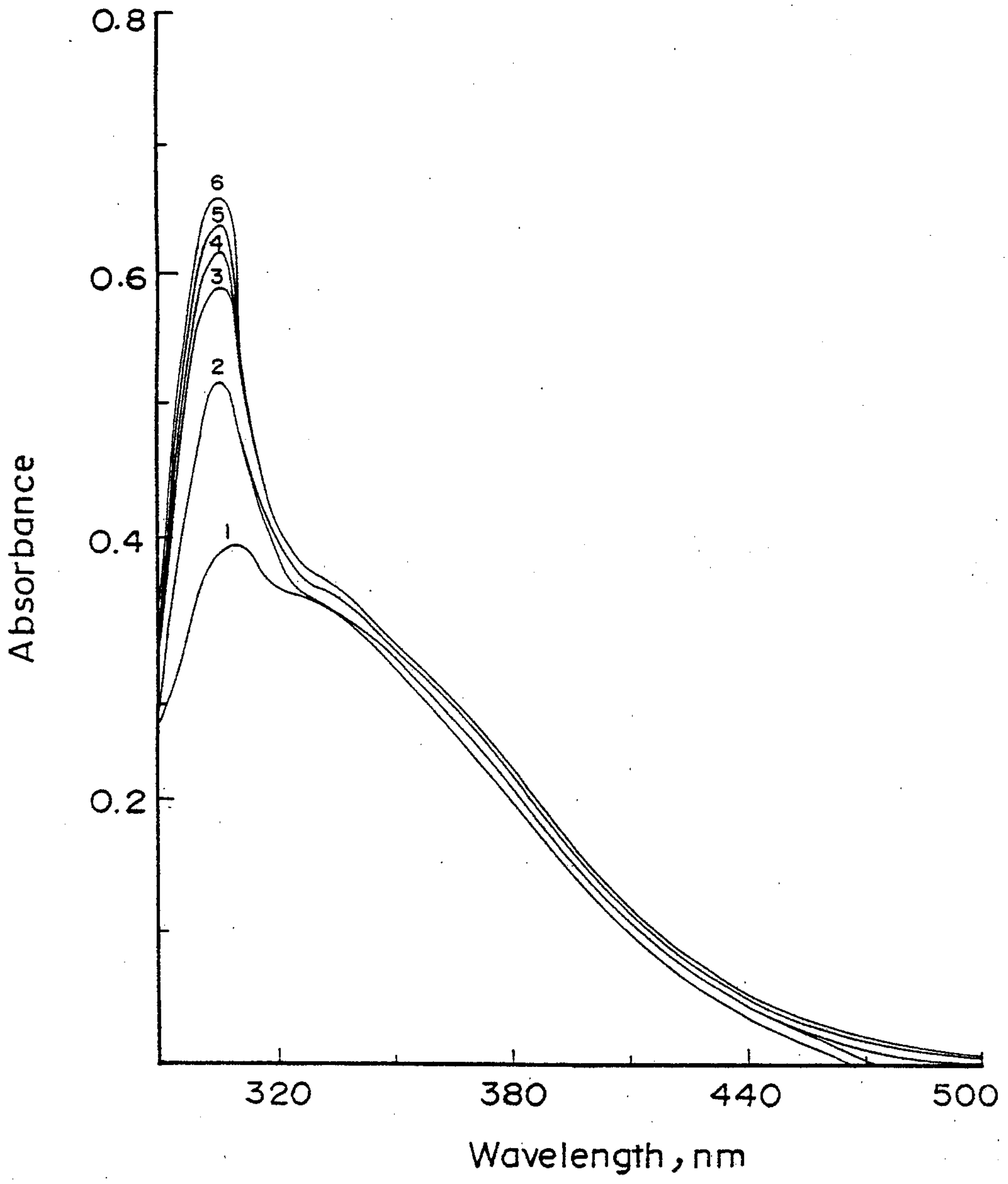


Fig. 10. Absorption spectra of the Cu-dto-acac complex solutions

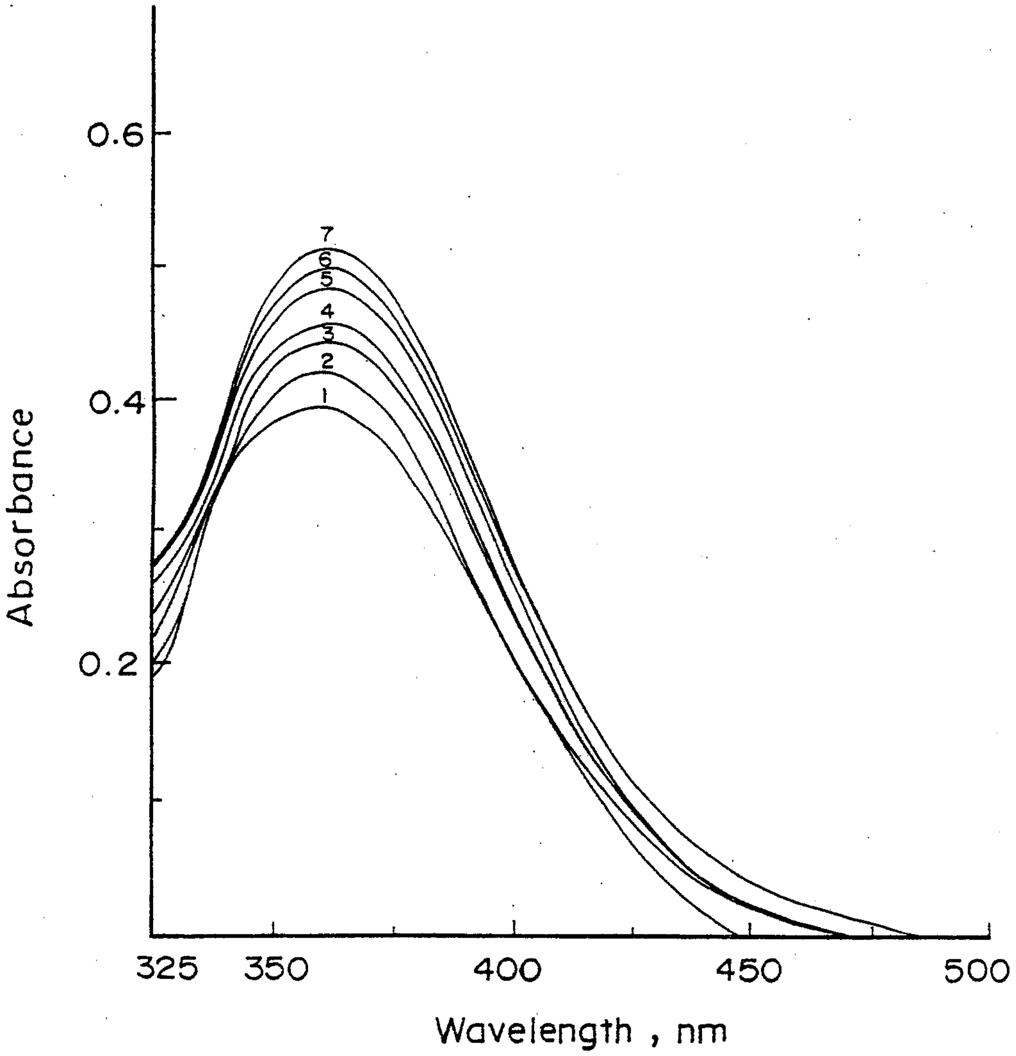


Fig. 11. Absorption spectra of the Cu-dto-8-HQ complex solutions

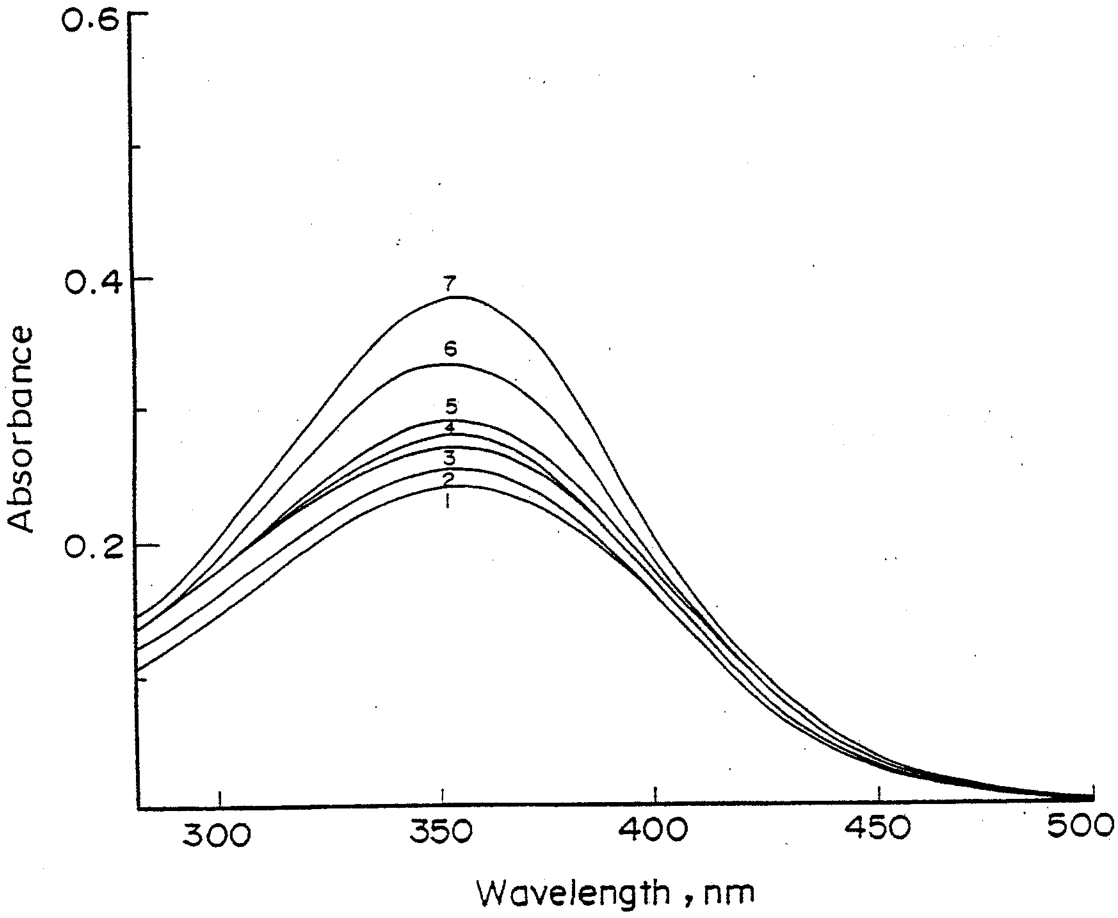


Fig. 12. Absorption spectra of the Cu-dto-taa complex solutions

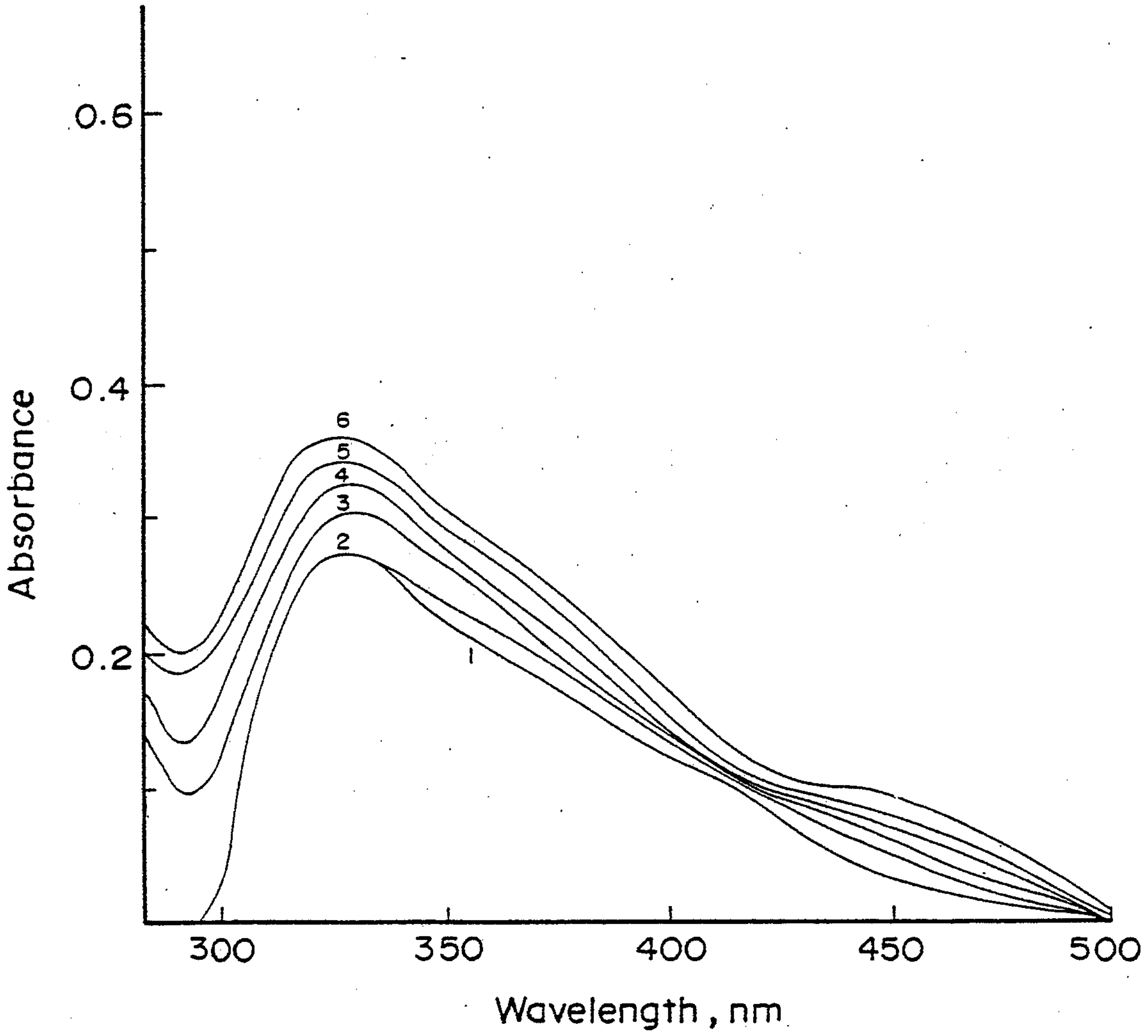


Fig. 13. Absorption spectra of the Cu-dto-o-phen complex solutions

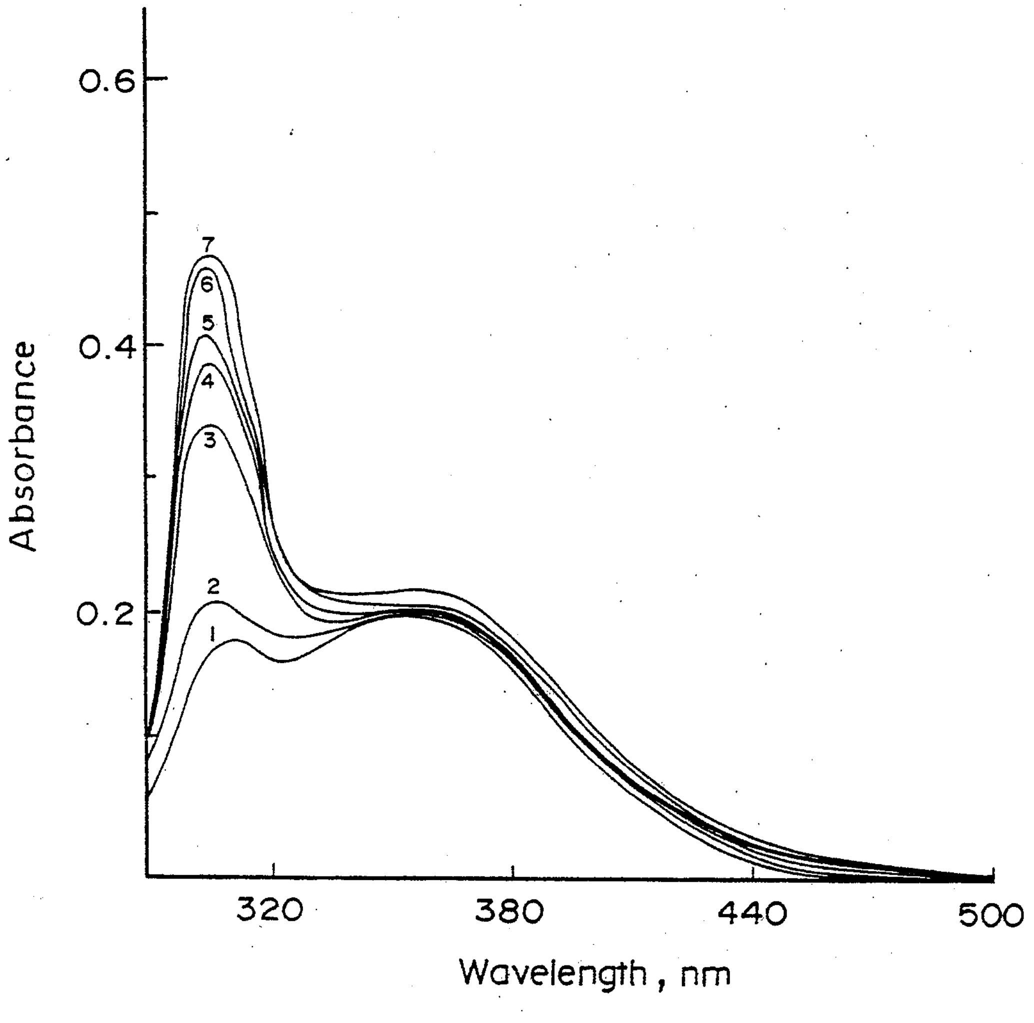


Fig. 14. Absorption spectra of the Cu-dto-bipy complex solutions

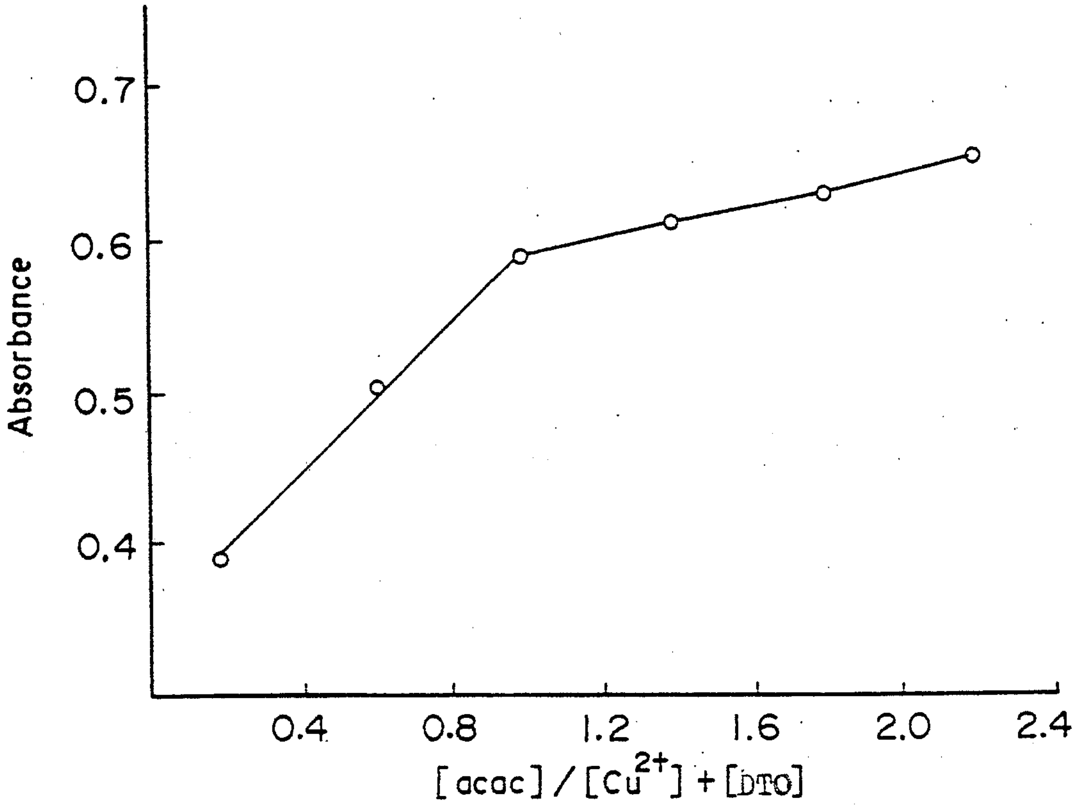


Fig. 15. Molar ratio of the Cu-dto-acac complex

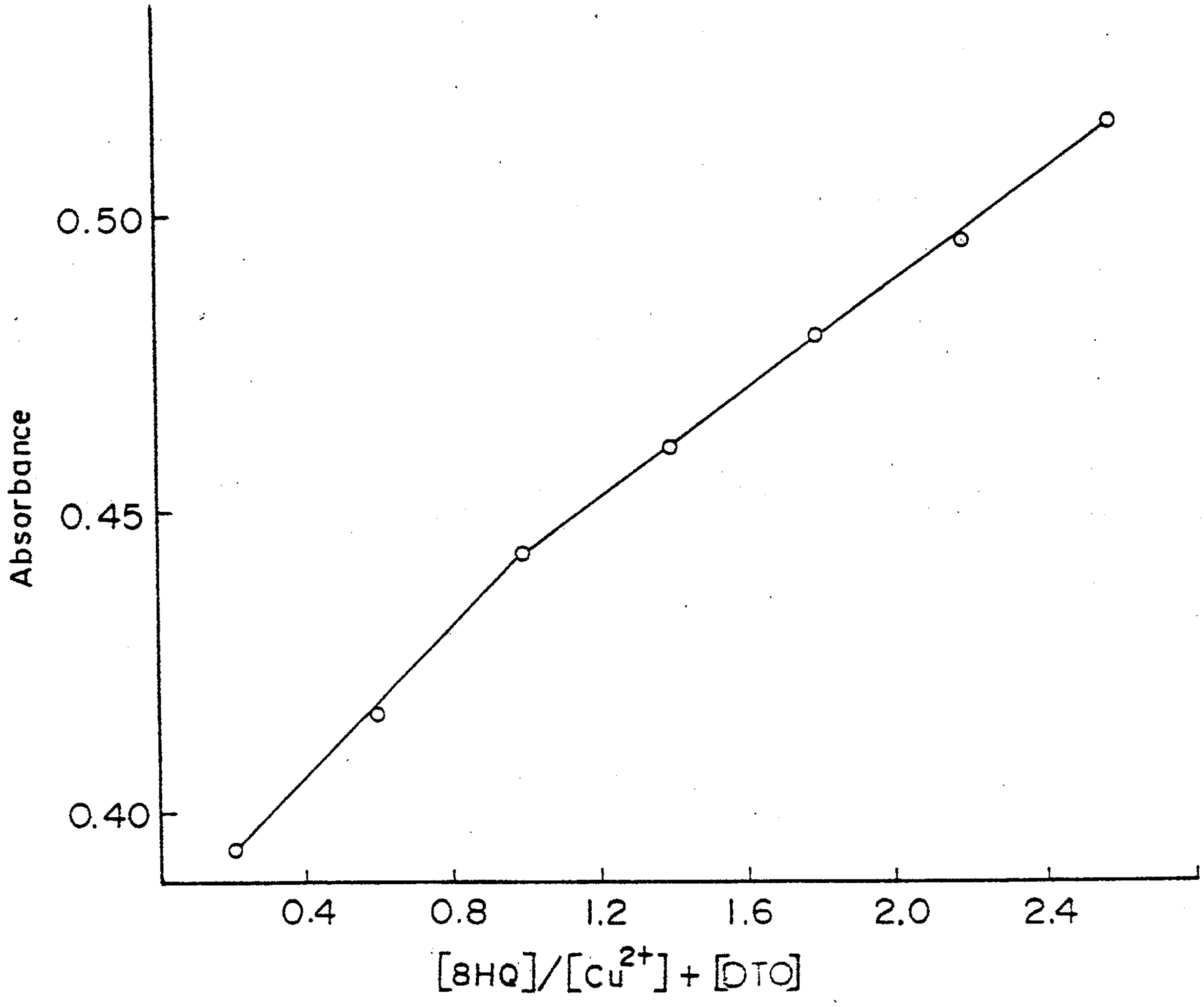


Fig.16. Molar ratio of the Cu-dto-8-HQ complex

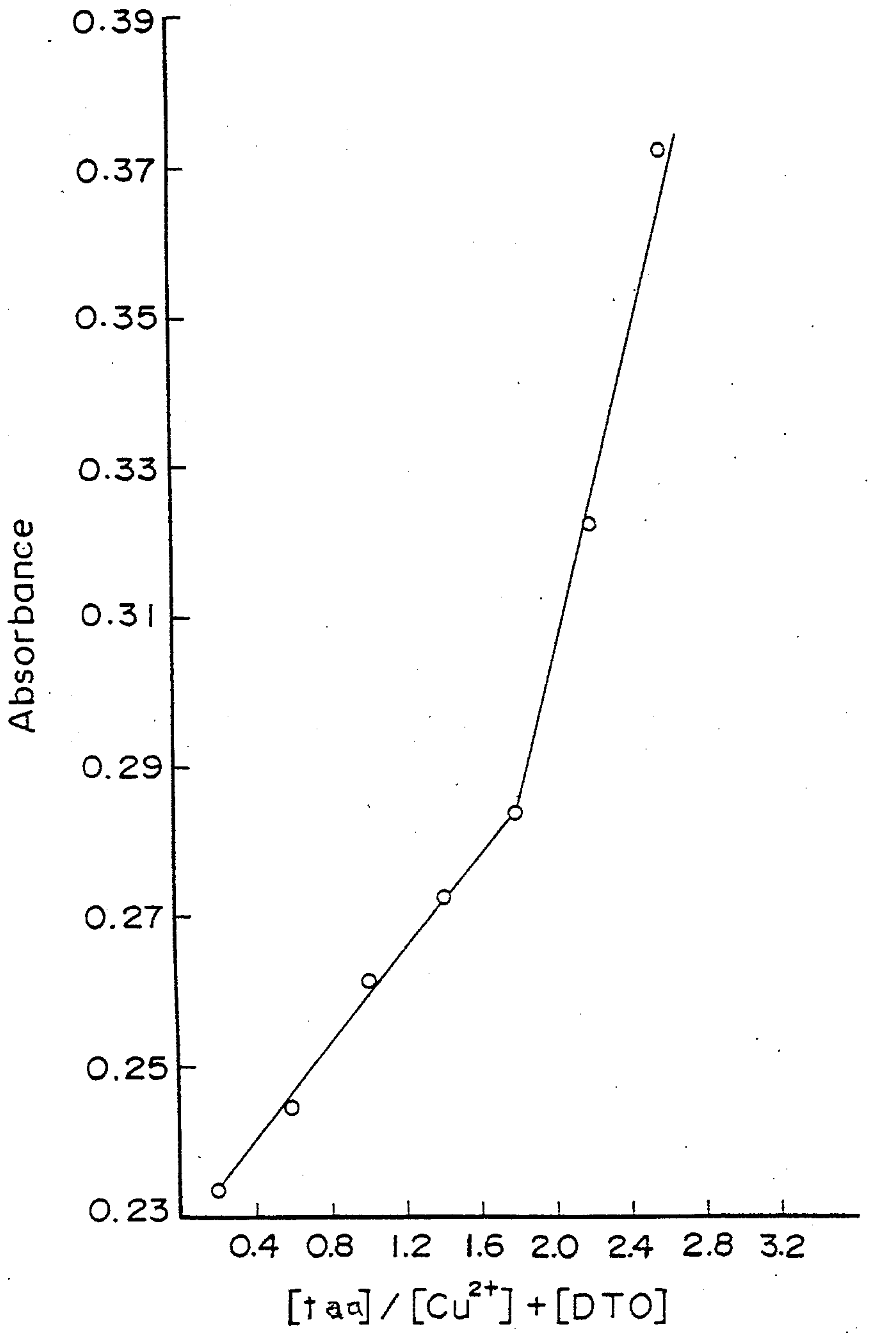


Fig. 17. Molar ratio of the Cu-dto-taa complex

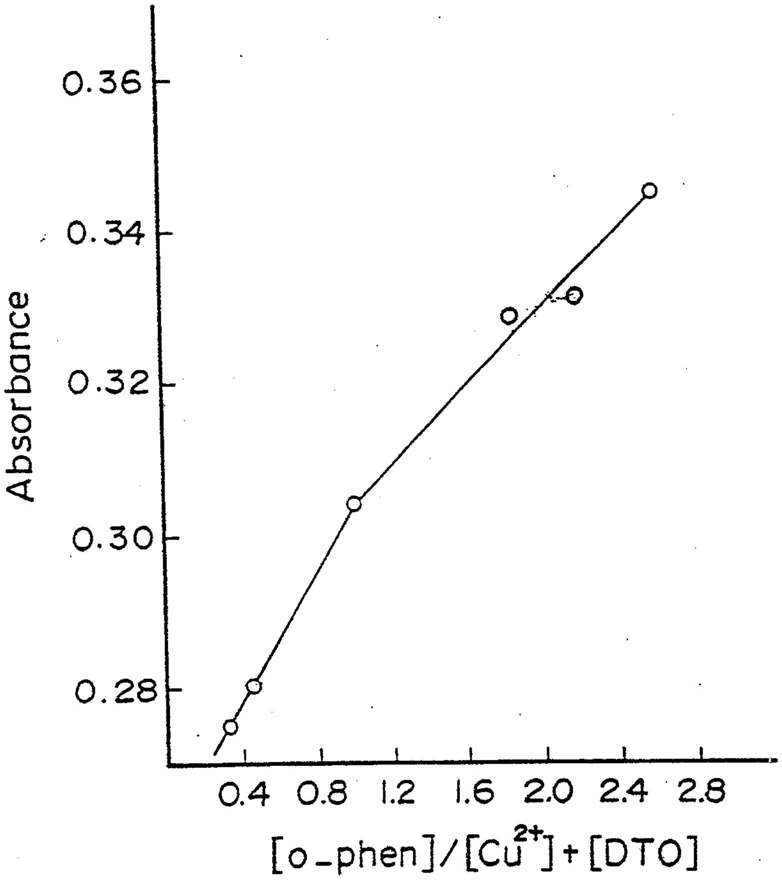


Fig.18. Molar ratio of the Cu-dto-o-phen complex

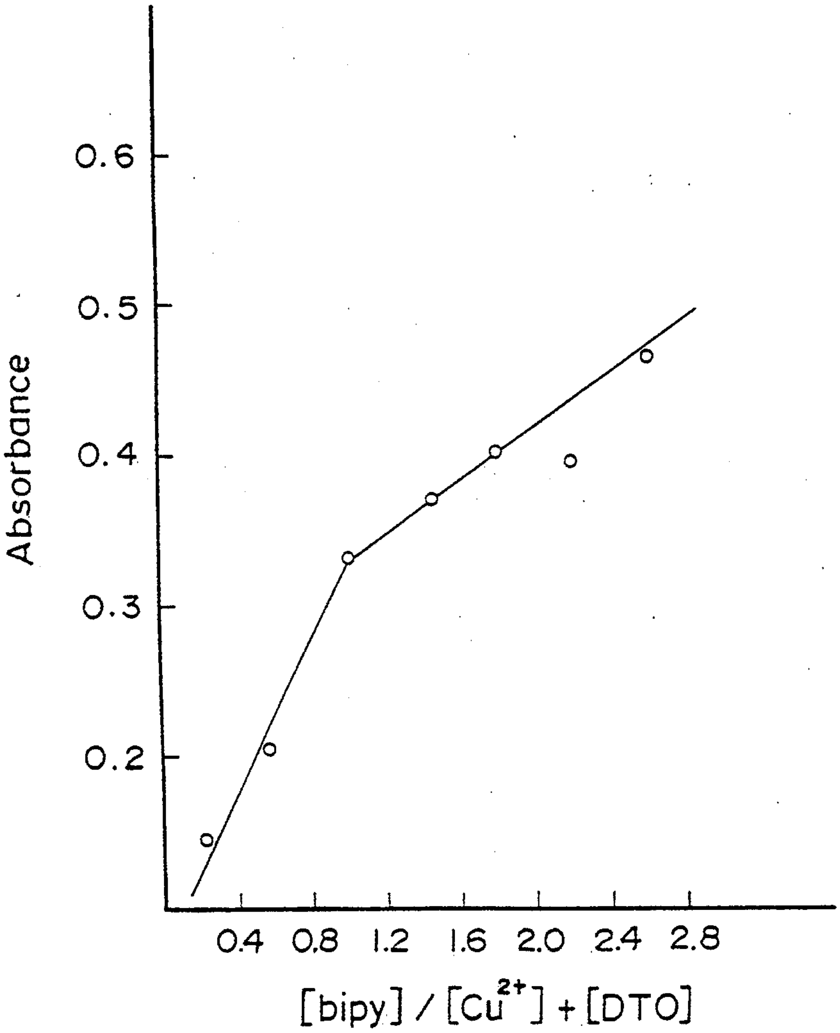


Fig.19. Molar ratio of the Cu-dto-bipy complex

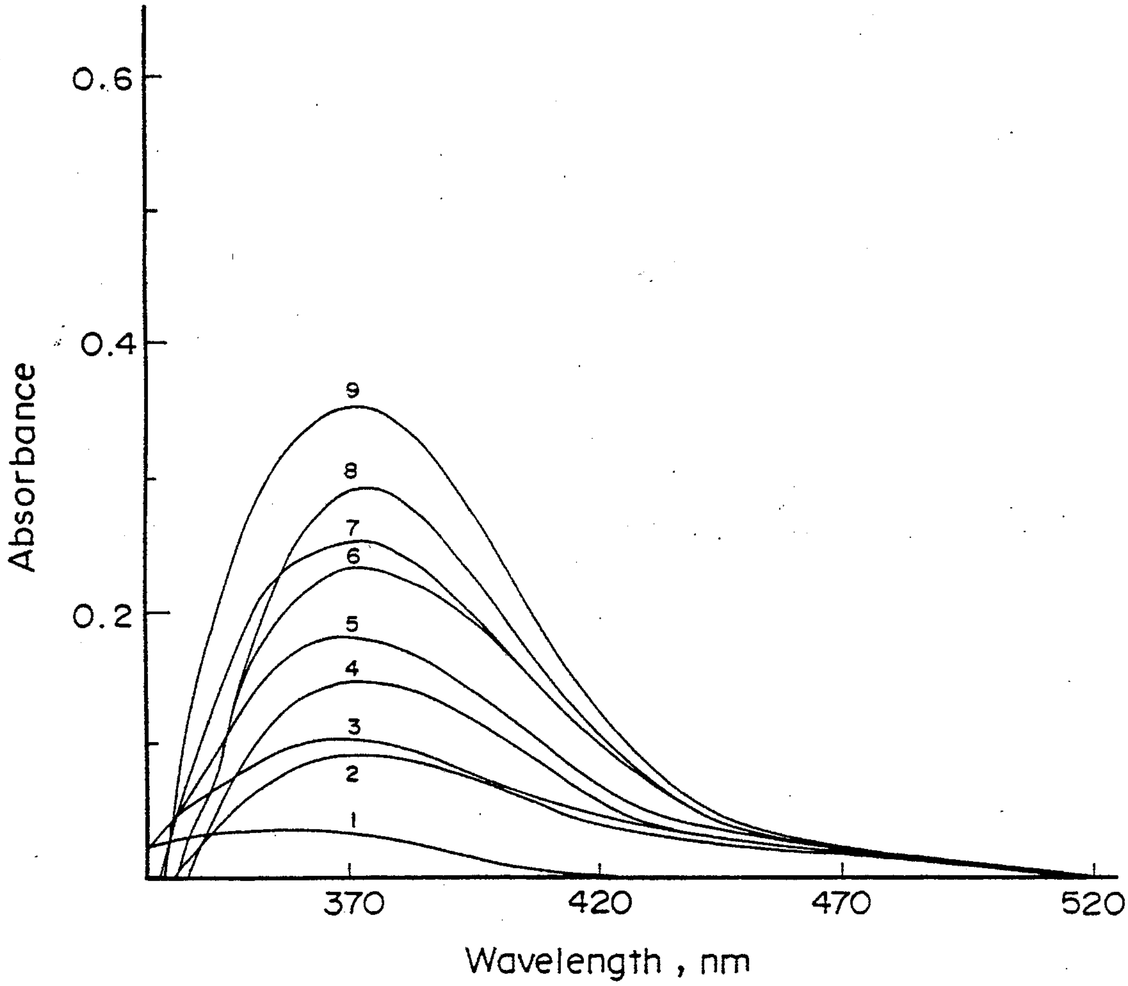


Fig. 20. Absorption spectra of the Cu^{II}-dto-complex solutions (continuous variation method).

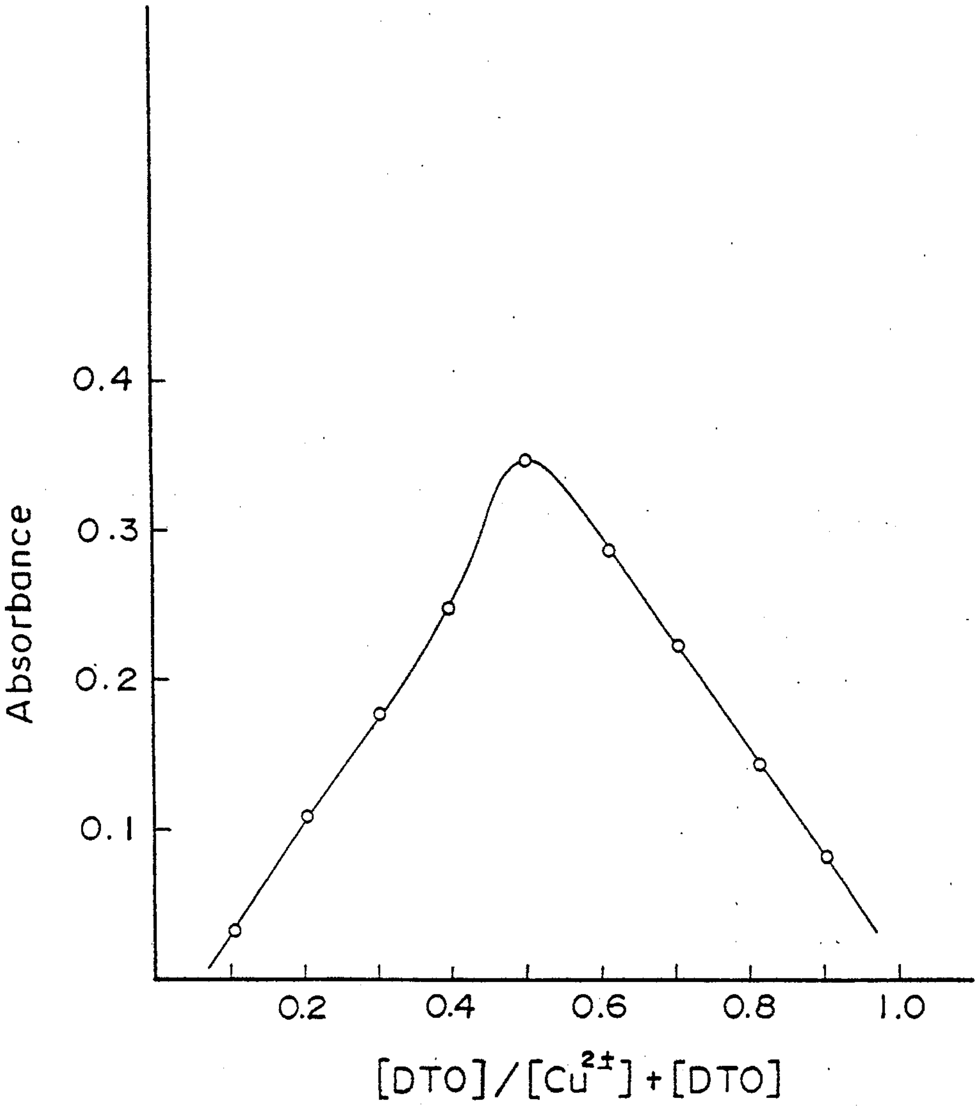


Fig. 21. Job's plot for the Cu-dto complex

CHAPTER IV

Characterization of the Isolated Binary Dithiooxamide complexes of Co(II), Ni (II) , Cu (II) , Ru (III) and Their Mixed Ligand Adducts

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Characterization of the Isolated Binary Dithiooxamide complexes of Co(II), Ni (II) , Cu (II) , Ru (III) and Their Mixed Ligand Adducts

This chapter represents the results obtained on characterizing the different synthesized binany Co (II) , Ni (II) , Cu (II) and Ru (II) complexes with dithiooxamide as well as the mixed ligand complexes of these metal ions, dto as primary ligand and acetate, o-phylenediamine, 8-hydrexyquinoline, salicylic acid, acetyl acetone, 2, 2-bipynidyl or thioacetamide as secondary ligands. Characterization of the solid complexes have been accomplished using several tools including: elemental analysis, TGA ,uv-visible and infrared spectroscopy as well as molar conductivity measurements for the complexes that dissolve in alcohol or dimethyformamide (DMF). Reflectance spectra were measured for the complexes which are sparingly soluble in the common organic solvents.

It is to be noted that, trials were made to prepare mixed ligand complexes of each of the above mentioned metal ions with dto as primary ligand and all of the secondary ligands used, but some gave unsatisfactory elemental analyses. Only those gave good results in the elemental analysis are considered in this thesis.

Elemental Analysis and Conductivity Data

Co (II) Complexes.

The Synthesized binary and mixed ligand complexes of Co (1l) are reported in Table 14, together with their elemental analysis and molar conductivity data. Two binary Co (II) complexes with dto were prepared, the first $H_3O[Co (dto)_3]$. $2 H_2O$, was obtained from neutral solutions by applying the first method of preparation as given in the experimental part (chapter II). This complex contains three mono-ionized dto ligands. The second binary complex, although it contains acetate groups coordinated to the Co (II) ion, is prepared from acid medium, using Co (II)-acetate and a medium of HCl and acetic acid as mentioned in the experimental part. This complex contains two nonionized dto molecules and two acetate groups coordinated to the Co (II) ions. The complex is sparingly soluble in the common organic solvents and in water and seems to be polymeric with the formula unit as given in Table 14 .

Only three mixed ligand complexes of Co (II) with dto and o-phen, 8-HQ or taa as secondary ligand gave satisfactory elemental analysis, all prepared from acid medium. The Co (II) ions in all the binary and mixed ligand complexes is hexacoordinated, as substantiated from spectroscopic data given herein after, which means that the acetate group acts in these complexes as a mono-dentate ligand. Conductivity data are consistent with 1:1 electrolyte for the binary $H_3O\ [Co(dto)_3]\ 2H_2O$ complex and 1:2 electrolyte for the mixed ligand complex containing 8-HQ as secondary ligand. The value of molor conductivity of 10^{-3} M ethanolic solution of the former is 62.5 $Ohm^{-1}\ cm^2\ mol^{-1}$ and that for the latter complex is 118.7 $Ohm^{-1}\ cm^2\ mol^{-1}$.

These values are in agreement with thereported range for 1:1 and 1:2 electrolytes in ethanol (96).

Ni (II) complexes

The obtained binary and mixed ligand Ni (II) complexes are shown in Table 15. Several complex species prepared from neutral and acid media gave reasonable elemental analysis data which reflects a high affinity of dto ligands towards the Ni (II) ions. The when prepared from neutral solutions and using $NiCl_2\ .\ 6H_2O$. This precursor was used to prepare mixed ligand complexes with acac, 8-HQ , sal , and taa as secondary ligands. The mixed ligand complexes are obtained by substitution of one dto ligand with a bidentate ligand or two monodentate ligands in the case of using thioacetamide (taa) as secondary ligand, where in all cases the Ni (II) ions are tetracoordinated.

On the other hand, upon using Ni (II) acetate in the acid medium, an acetate bridged complex having the formula $[Ni_2\ (dto)_2\ (CH_3COO)_2]$ was obtained in which the Ni (II) ions are still tetracoordinated as would be explained latter. The mixed ligand complexes obtained from acid medium in contrast to those obtained from neutral or slightly alkaline media, are cationic and contain a neutral dto molecule coordinated to the Ni (II) ions. The molar conductivity of acetylacetonate mixed ligand complex equals 86.2 Ohm^{-1} cm^{2} mol^{-1} for a DMF solution of 10^{-3} M concentration.

This value is consistent with 1:1 electrolyte, since the reasonable range for 1:1 electrolytes in DMF solutions as reported by Greary (96) is 65-90 Ohm^{-1} cm^{2} mol^{-1}. The other mixed ligand complex obtained from acid medium, i.e that containing o-phen as the secondary ligand is dinuclear Ni(II) complex contains a bridging neutral dto ligand and two terminal o-phen ligands. This complex is , unfortunately, sparingly soluble in all the common organic solvents and therefore its molar conductivity could not be measured.

Cu(II) Complexes

The prepared binary and mixed ligand Cu (II) complexes are reported in Table 16. Both the two experimental procedures used in this thesis resulted in the formation of Cu (II) complexes containing either dto alone, i.e. binary complexes or dto together with the secondary ligand in the mixed ligand complexes. The binary complex obtained from slightly alkaline medium is dinuclear and seems to be bridged by two Cl^{-} ions. Also, that obtained from acid medium using Cu (II) acetate is a dinuclear one and most likely has two acetate bridges which is quite familiar especially with Cu (II) ions (95) . Both the two complexes are insoluble in common organic solvents and seems to be polymeric with the two terminal dto ligands (monoionic) are involved in coordination to Cu(II) ions in a long chain.

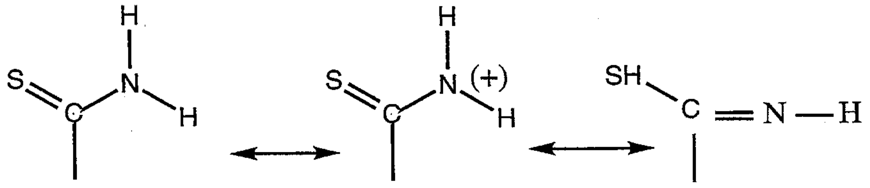
On the other hand, the two synthetic routes afforded mixed ligand complexes involving dto coordinated together with another ligand to the Cu (II) ion. In neutral or slightly alkaline media, the dto ligand is coordinated in its mono-anionic form while the neutral dto molecule is coordinated to the Cu (II) ion in the mixed ligand complex formed in the acid medium i.e $[Cu_2 (dto) (bipy) Cl_2] Cl_2$. Unfortunately all the Cu (II) complexes are sparingly souble in the common organic solvents and therefore their molar conducts could not be determined. Their behaviour comes in harmony with the expected polymeric nature of these complexes.

Ru (III) complexes

The synthesized binary and mixed ligand complexes of Ru (III) are reported in Table 17. The binary complex is soluble in DMF and the value of its molar conductivity is 82.5 $Ohm^{-1} cm^2 mol^{-1}$ which corresponds to 1:1 electrolyte in this DMF since the reasonable range(96) for 1:1 electrolyte in this solvent is reported to be 65-90 $Ohm^{-1} cm^2 mol^{-1}$. The complex was prepared in methanol and the expected solvolysis of $RuCl_3$ in this solvent tends to render the medium acidic and consequently the neutral dto molecules are coordinated to the Ru (III) ion. The same was found on using 8-hydroxyquinoline as secondary ligand and the preparation was in methanol. On using salicylic acid as secondary ligand and due to the high acidity of the reactants, 1:1 dilute amonia was added dropwise until precipitation started. In this case the obtained mixed ligand complex was found to contain two monovalent dto and one salicylate ligands (cf Table 17). The molar conductivity of this complex is 31.5 Ohm^{-1} cm^2mol^{-1} in DMF which is much lower than the value of 1:1 electroyte in DMF, i.e this complex is neutral and its DMF solution is nonelectrolyte. The acetate complex, prepared in acid medium, is dinuclear and contain two acetate bridges which satisfy the coordination requirements of the metal ion , i.e six-coordination. In this complex also the neutral dto molecules are coordinated to the metal ion.

The mixed ligand Ru (III) complexes, prepared from acid medium, all contain the neutral dto molecules coordinated to the metal ion. It could be concluded, therefore, that cationic complexes are formed on using acetylacetone and bipridyl as secondary ligands in this medium (cf. Table 17). The molar conductance values of 10^{-3} M DMF solutions of these two complexes are 75.4 and 112.6 Ohm^{-1} cm^2mol^{-1} (Table 17) indicating that the former is 1:1 electrolyte and the latter is 1:2 electrolytes. (96)

One can therefore conclude that the complexes formed in neutral or slightly alkaline media contain in general, monovalent dto ligands coordinated to the metal ions. On the other hand, in the complexes prepared from acid medium, neutral dto molecules are coordinated to the metal ion . This behaviour is general and looks reasonable since in acidic solutions, the thioamide function occurs in the neutral mode and can only coordinate to metal ions through the thione sulfur atoms (34). This can be understood from the following schematic representation of the most important resonance forms of the thioamide functionality:



(I) (II) (III)

In view of these resonating forms, the most probable mode to be exerted by the dto molecules in acid media is the thione (I) and neutral dto molecules are expected to be coordirated to the metal ions in such media. On the contrary, in neutral or alkaline media the thiol mode (III) is that favorable as the dto moleeule will lose proton from the SH group providing a monoanionic ligand to be coordinated to the metal ion in such media as could be seen from the complex species reported in Tables 14-17.

Table 14: Microchemical analysis data of the binary and mixed ligand CoII) complexes.

No	Compound	% Found (Calculated)					$\wedge_m^{(a)}$
		C	H	N	S	Co	
1	**$H_3O[Co(dto)_3]2H_2O$**	**18.81(15.33)**	**4.22(4.07)**	**17.87(17.88)**	**41.32(40.85)**	**12.53(12.49)**	62.5
2	**$[Co(dto)_2(CH_3COO)_2]$**	**22.86(23.02)**	**2.06(2.87)**	**13.82(13.43)**	**31.25(30.70)**	**14.50(14.12)**	Insol.
3	**$[Co(dto)(o\text{-}phen)(CH_3COO)_2]H_2O$**	**33.75(34.05)**	**5.10(4.49)**	**13.62(13.24)**	**15.73(15.13)**	**14.50(13.92)**	17.6
4	**$[Co(dto)(Taa)_2(CH_3COO)_2]$**	**20.80(21.24)**	**3.68(3.54)**	**9.33(9.91)**	**12.04(11.33)**	**11.75(10.42)**	22.4
5	**$[Co(8.HQ)(dto)_2](CH_3COO)$**	**36.22(35.79)**	**2.70(2.78)**	**13.59(13.91)**	**25.70(25.45)**	**12.10(11.67)**	118.7

(a) Ohm^{-1} cm^2 mol^{-1}, measured in ethanol.

Table 15: Microchemical analysis data of the binary and mixed ligand Ni(II) complexes.

No.	Compound	% Found (Calculated)					$\Lambda_m^{(a)}$
		C	H	N	S	Ni	
6	[Ni(dto)$_2$]2H$_2$O	**13.82(14.30)**	**2.78(2.93)**	**16.80(16.80)**	**37.76(38.23)**	**17.60(17.61)**	18.6
7	[Ni$_2$(dto)$_2$(CH$_3$COO)$_2$]	**19.86(20.27)**	**2.62(2.53)**	**12.25(11.82)**	**27.46(27.04)**	**25.30(24.79)**	**Insoluble**
8	[Ni(dto)(8HQ)]	**40.76(41.07)**	**3.25(3.44)**	**12.92(13.06)**	**20.44(19.89)**	**18.62(18.24)**	13.7
9	[Ni(dto)(sal)]	**34.53(34.31)**	**2.52(2.54)**	**9.12(8.89)**	**20.25(20.33)**	**18.82(18.62)**	**Insoluble**
10	[Ni(dto)$_2$(Taa)]H$_2$O	**18.27(18.49)**	**4.10(3.88)**	**18.24(17.97)**	**39.68(40.05)**	**15.02(15.06)**	28.5
11	Ni(dto)$_2$(bipy)]1.5H$_2$O	**34.76(35.10)**	**3.82(4.00)**	**17.55(17.54)**	**26.86(26.71)**	**11.87(12.25)**	**Insoluble**
12	[Ni$_2$(dto)(o-phen)$_2$]Cl$_4$	**28.77(28.20)**	**3.15(3.39)**	**14.43(14.14)**	**10.82(10.76)**	**20.35(19.75)**	**Insoluble**
13	[Ni(dto)(acac)]Cl$_2$H$_2$O	**23.82(24.05)**	**4.21(4.33)**	**7.96(8.02)**	**17.65(18.33)**	**17.10(16.80)**	86.2

(a) Ohm^{-1} cm^2 mol^{-1}, measured in DMF.

Table 16: Microchemical analysis data of the binary and mixed ligand Cu(II) complexes.

No	Compound	% Found (Calculated)					$\wedge_m^{(a)}$
		C	H	N	S	Cu	
14	$[Cu_2(dto)_2Cl_2]2H_2O$	**10.72(10.53)**	**2.50(2.65)**	**12.64(12.28)**	**27.61(28.06)**	28.42(27.84)	**Insoluble**
15	$[Cu(dto)\ (sal)]\ 2H_2O$	**29.87(30.26)**	**3.57(3.38)**	**8.21(7.84)**	**18.25(17.92)**	**17.34(17.78)**	**Insoluble**
16	$[Cu(dto)(acac)]2H_2O$	**26.82(26.44)**	**3.25(3.48)**	**8.50(8.80)**	**9.68(10.06)**	**20.23(19.96)**	**Insoluble**
17	$[Cu(dto)_2(o\text{-}phen)]4H_2O$	**25.41(24.94)**	**4.77(4.60)**	**17.26(17.44)**	**26.66(26.58)**	**12.78(13.18)**	**Insoluble**
18	$[Cu(dto)(8\text{-}HQ)]Cl\ H_2O$	**34.72(34.57)**	**2.84(2.63)**	**10.68(11.00)**	**17.11(16.74)**	**16.22(16.61)**	**Insoluble**
19	$[Cu_2(dto)_2(CH_3COO)_2]$	**15.22(14.90)**	**2.80(2.48)**	**11.86(11.59)**	**26.72(26.50)**	**29.49(26.29)**	**Insoluble**
20	$[Cu_2(dto)(bipy)Cl_2]Cl_2$	**31.42(30.82)**	**2.41(2.20)**	**10.88(10.28)**	**12.35(11.74)**	**22.85(23.30)**	**Insoluble**

(a) $Ohm^{-1}\ cm^2\ mol^{-1}$

Table 17: Microchemical analysis data of the binary and mixed ligand Ru(III) complexes.

No	Compound	% Found (Calculated)				$\Lambda_m^{(a)}$
		C	H	N	S	
21	[Ru (dto)$_2$Cl.H$_2$O]3H$_2$O	11.25(10.72)	2.10(1.78)	12.84(12.50)	27.92(28.59)	82.5
22	[Ru(dto)(8HQ)$_2$]Cl	43.51(44.07)	2.28(2.57)	10.62(10.28)	12.27(11.65)	68.7
23	[Ru(dto)$_2$sal]2H$_2$O	26.42(25.80)	2.30(2.15)	11.45(10.94)	24.82(25.02)	31.5
24	[Ru$_2$(dto)$_2$(CH$_3$COO)$_2$Cl$_4$]	10.65(10.62)	2.35(2.06)	8.87(8.26)	18.75(18.90)	insol.
25	[Ru(dto)(acac)$_2$]Cl	32.27(31.75)	3.83(4.00)	6.46(6.17)	15.02(14.11)	75.4
26	Ru$_2$(dto)$_2$(bipy)Cl$_4$]Cl$_2$.2H$_2$O	20.66(19.83)	2.53(2.36)	10.22(9.91)	15.51(15.11)	112.6

(a) in Ohm^{-1} cm^2 mol^{-1}, measured in DMF.

Infrared Spectra:

Infrared spectroscopy has became a very helpful tool in the study of molecular structure especially for complex compounds. In such cases, the spectrum of the ligand is usually compared with that of the complex compound in order to achieve an idea about the groups involved in complex formation as well as the influence of the electric field of the central metal ion in the charge distribution within the ligand. An insight in type of the bond formed between the ligand and the central metal ion can be gained from a careful investigation of the spectrum of the complex especially in comparison to that of the free ligand. To have a conclusive idea about the structure of the metal complexes, it seems necessary to make an assignment for the IR bands corresponding to the active groups in the ligand (dithiooxamide).

On the other hand, with respect to the mixed ligand complexes, the coordination of the secondary ligand can be verified from the IR spectra of the complexes. In this case and due to the expected large number of IR bands displayed by the two ligands and due to the possible mixing of some bands that are either similar or very near in frequency, it is important to identify at least the characteristic bands of the secondary ligands in addition to those of the primary one in order to support the other methods used for characterizing the mixed ligand complexes.

The important IR spectral bands of dithiooxamide and its Co (II) , Ni (II) , Cu (II) and Ru (III) complexes together with their tentative assignment, in addition to the bands that could be recognised for the secondary ligands are given in Tables 18-21. The corresponding spectra are shown in Figures 22-30.

The group of bands appearing in the range 3293 to 3137 cm^{-1}in the IR spectrum of dto have been assigned to the stretching vibration of the terminal NH_2 groups of the free dithiooxamide molecule (νNH_2) (97) . The strong band appearing at 1585 cm^{-1} in the spectrum of the free dto is due to the bending mode of the NH_2 group of the molecule, i,e δNH_2. Another strong band appears at 1480 cm^{-1} in the spectrum of the free dto. This band is assignable to the stretching vibration of the CN bond of the dto molecule, i.e νcn. The strong band found at 1200 cm^{-1} in the IR spectrum of the free dto is due to the stretching vibration of the C-C bond which is influenced, to some extent, by the neighbouring $\nu C\text{-}N$ frequency, i.e it is best ascribed to $\nu C\text{-}C + \nu CN$.

The position of this band, keeps in mind the already observed conjugation over the carbon - carbon bond (98) . The quite strong band occurring at 836 cm^{-1} in the spectrum of the free dto is assigned to $\nu C{=}S$ and indicate that the free ligand favors the cis thioamide form. This band together with the medium band due to πNH appearing at 703 cm^{-1} in the IR spectrum of the free ligand are indicative of a high

$\nu C{=}S$ double bond character. A rather stronge band appears in the spectrum of the free dto at 628 cm -1 which corresponds to the δ NCS vibration mode.

In the IR spectra of the complexes, significant changes could be observed as a result of the coordination of dto to the metal ions. The νNH_2 band appears, in most cases, as a broad and intense band with several submaxima on the low and high frequency sides of the main band. This behavior can be explained on the basis that the NH_2 groups are involved in strong intermolecular associations, mainly hydrogen bending with the available counter ions. Therefore, the NH_2 groups acquire some ammonium-type character. Moreover, the presence of overtones and combinations and their effect on the νNH_2 fundamentals explain such a broad profile absorbed for these bands. It should be noted here that no clear distinction between the intramolecular NH...N and intermolecular NH+...X- modes could be observed. As Nakamoto et al (99) pointed out, the position of νNH in a NH...X system depends not only on the effective strength of the association, but also on the charge and nature of X and on the Electro configuration around the nitrogen atom. These factors makes it rather complicated to compare our results with other similar but not identical systems. At first sight the low νNH_2 positions in the spectra of the present compounds seem to indicate extremely strong hydrogen bonding when compared with the free νNH_2 at about 3500 cm^{-1} . But due to the ammonium character of the bands it is better to take the νNH band at about 3200 cm^{-1} as a reference. In this case the frequency shift is not so large and we can state that the interactions are not of the strong type.

For the binary Co (II) complex, the νNH_2 band appears as a broad one and it shifts to lower frequency (at 3230 cm^{-1}) relative to the free dto. This behaviour is in agreement with the above discussion and indicates an ammonium type nature of the band. This together with the results of elemental analysis and conductivity data which suggest the coordination of three mono-ionised dto molecules reveal the formation of the complex by coordination of the ligands in their thiol form (III) as mentioned before. On the other hand, the acetate complex displayed an additional band at 1604 cm^{-1} (cf. Table 18) due to the νCOO of the coordinated acetate anions. The position of this band is indicative of the coordinate of the acetates as unidentate ligands (100,101) . The position of νCOO band in all the Co (II) mixed ligand complexes is in the range of monodentate acetate groups (cf. Table 18) .

Furthermore, the two strong bands appearing at 1585 cm^{-1} and 1430 cm^{-1} in the spectra of the free dto were found to possess marked shifts in the spectra of the complexes. The former band which has been assigned to δNH_2 shifts to lower frequencies whereas the latter which is due to νCN was found to shift towards higher frequencies. This behaviour can be explained as follows: on forming complexes, the positively charged metal ion stabilizes the negative charge on the sulfur atom, which occurs in the ionized thiol form of dto, and thus increases the double bond character of the CN bond, which is expressed as a rise in the frequency. This will, in turn, decrease the electron density on the nitrogen atom of the amine group resulting in an increase in its ammonium character and lowers its δNH_2 frequency. The νC-C band was found to locate, in most cases, at lower frequencies relative to its position for the free dto. As earlier stated the two thioamide moieties possess a conjugation over the C-C bond in the free ligand. Such a conjugation is lowered in the complexed ligand and one, therefore, would expect νCC to be situated at a lower frequency than in the free ligand. The band appearing, in the spectra of some mixed ligand complexes, in the region of 1200 - 1300 cm^{-1} is probably due to strong coupling of νCN with other vibrations in the region, especially the δNH vibration or other vibrations from the secondary ligands.

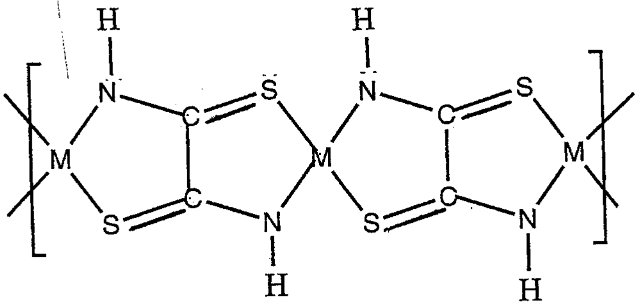
The νC=S band occurring at 836 cm^{-1} in the spectra of the free ligand was found to appear at a lower frequency in the binary Co (II) complex and at higher frequencies in the mixed ligand complexes. Such changes are reasonable because in the binary complex, the coordination of the sulfur atom decreases the bond order of the $C = S$ group while in the mixed ligand complexes, one would expect that the coordination of secondary ligand will increase the electron density on the metal ion which is not, of course, favorable and hence the metal ion tends to avoid accumulation of the negative charge by back donation to the available π*-orbitals on the sulfur atom leading to the observed increase in the double bond charaeter of the νC = S in the mixed ligand complexes.

It should be noted that due to the complications airsed from the presence of dto, acetate and the secondary ligands 8HQ, o-phen or taa all together in the same compound it is very difficult to recognize unambigously the bands of the secondary ligands, especially in the νCN region . In this region all the secondary ligands display strong bands which are expected to be involved in a strong coupling with the strong bands of dto especially νCN and δNN besides these complications the bands, in the high frequency region, that can be displayed by some secondary ligands, such as bipy are not metal sensitive since they originate in the heteroaromatic rings of the ligands.

The IR spectral features of the binary and mixed ligand Ni (II) complexes are assembled in Table 19. It is erident that the νNH_2 band exhibits a similar behaviour as mentioned before where it appears as a broad medium band centered in the range 3230 - 3250 cm^{-1} . The position and broadness of this band keeps in mind the involvement of the NH_2 groups of dto, in its Ni(II) complexes, in association via H-bonding with the counter ions or water molecules and also its ammonium character. A similar behaviour is also observed for the Cu(II) complexes.

The binary Ni(II) complex is neutral (cf. Table 15) and seems to be monomer formed by coordination of two monoionized dto ligands, this compound displays IR spectral features similar to those obtained for the Co (II) complex with dto, i.e the ligand in both acts as S,S donor from its thiole mode. However the mixed ligand Ni(11) complexes containing acetate, acetylacetone, 8-heydroxyquinoline, salicylate, thioacetamide or bipyridyl as secondary ligands, which are prepared from or slightly alkaline solutions, show differences in the spectral characteristics of dto relative to the binary complex.

On the other hand, the binary and mixed ligand complexes of Cu(II) showed similar changes of the spectral fundamentals of the dto relative to the Co (II) complexes as well as the binary Ni(II) - dto complexes. Such changes are in favor of the formation of polymeric Ni(II) complexes, which are prepared from neutral or slightly alkaline media, and / or at least dinuclear Cu (II) complexes. The most important differences in the IR spectra which indicate the polymeric or dinuclear nature of the complexes can be summarized as follows : (a) The band arising in the range 3270-3255 cm^{-1} as a shoulder of the main νNH_2 band around 3230cm^{-1}; (b) The most intense band in the range 1490-1370 cm^{-1} having predominantly νCN character ; (c) The conjugation over the carbon - carbon bond, which has been already observed for the free ligand (dto), remains in the planar polymeric complexes and a band with high νCC character can be observed in the range 1106 to 1270 cm^{-1} in the spectra of the complexes ; and (d) The νCS band is located in the spectra of those complexes at relatively high position in the range 875-860 cm^{-1} . All these changes were taken to indicate a planner polymeric structure for the complexes (3,14,33,97) . Such a polymeric structure exhibits the *cis* thioamide group which can be represented schematically for these complexes as follows:



This S-*cis* position has only been observed for cyclic organic molecules and complexes with cyclic structures (102,103) . The fundamentals for this *cis*-thioamide group will be different from the typical bands generally observed for the *trans* thioamide groups (97) .

S-cis S-trans

In addition to the above mentioned differences in the IR spectral features, another evidence for the polymeric, or dinuclear, complexes could be attained for those containing acetate groups where two bands near 1660 cm^{-1} and 1540 cm^{-1} are displayed. The former is due to νas (C = O) of the acetate and the latter is due to the νs (OCO) . The position of these two bands together with their frequency difference are in agreement with bridging carboxylate groups (104.105). Again, bands of the secondary ligands can be observed in the region 1500-600 cm^{-1}, but unfortunately due to the strong coupling with the reighbouring bands of dto, they can not be used for diagnostic purposes.

It should be noted that many of the copper (II) complexes have bridging chloride, acetate or dto in the formation of polymeric or dinuclear species. This, in turn, reflects the greater ability of Cu(II) to form such compounds with the possibility of metal-metal bonding (106). The IR spectra of Ru (III) complexes exhibit some similarities with those of the Co (II) complexes especially in the high frequency region. This behaviour reveals that the Ru(III) complexes are formed by coordination of the dto and other secondary ligands in the same way as the Co(II) complexes. Such similarities can be summarized as follows : (a) the νNH_2 band shifts to lower frequencies with a broad profile with several submaxima and a broad shoulder in the high frequency side, (b) the δNH_2 band was found to locate at lower frequency in the spectra of the Ru (III) complexes relative to its position in the free dto, while the νCN band was found to appear at higher frequencies. The shifts in these two bands came in agreement with the increased double bond character of the CN bond as a result of stabilization of the negative charge on the sulfur atoms upon coordination to the positively charged Ru (III) ions, and the appearance of the νCS band at lower frequencies in the spectrum of the binary Ru (III) complex relative to its position in the free dto and rises back to higher frequencies in the spectra of the mixed ligand complexes. A behaviour which comes in harmony with the previous□ explained changes in the CS group bond order in the binary and mixed ligand complexes.

Combination of the above discussed IR spectra with the results of element analysis provides the following important conclusions:

(i) The planar dithiooxamide molecule acts as bidentate ligand capable for coordination to the metal ions as S,S or S,N donor. The NH_2 groups of the ligand have an ammonium-type character due to either intramolecular or intermolecular associations.

(ii) The way by which this flexidentate ligand form complexes with metal ions depends on the reaction conditions, especially on the pH of the solutions. In neutral or slightly alkaline media, it works as monobasic bidentate ligand while in acid solutions it coordinates to the metal ions as neutral bidentate ligand.

(iii) Both the binary and mixed ligand Co (II) complexes are hexa-coordinate and the acetate groups in these complexes are all monodentately coordinated to the metal ions.

(iv) The infrared spectral features of most of the Ni (II) and Cu(II) complexes are in favour of polymeric structures. In the polymeric complexes dto neutral molecules, acetate or chloride ions act as bridges between two Ni (II) or Cu (II) ions in the complex. The determined metal contents are in good agreement with short chain polymers as compared with the literature results (20, 33, 98) on related but not identical work.

(v) Binary and mixed ligand Ru (111) complexes are all six - coordinate. The acetate groups in these complexes are bridging and some complexes have bridges of the dto molecules, i,e most of the Ru (111) complexes are polymeric and therefore they are sparingly soluble in the most common organic solvents.

(vi) Several types of complex species are formed including neutral and cationic complexes mainly on the reaction conditions as mentioned before.

Electronic Spectra

The electronic spectra of the binary M (II) – dto (where M = Co, Ni, Cu) and Ru (III) – dto complexes as well as their mixed ligand complexes have been recorded in ethanol or DMF solutions for the soluble complexes . Reflectance spectra were recorded as nujol mull, for the insoluble complexes . The spectra were recorded in the visible region mainly because the intra-ligand bands which were expected in the uv region are less important for structural determination purpose.

The obtained spectral characteristics (mainly ν_{max} in cm^{-1}) are given in Tables 22-25, and representative spectra are shown in Figures 31- 37 .

Cobalt(II) complexes display a broad multiple band in the visible region . This band comprise two or three maxima, the first two maxima occur in the range 25,700 – 19,200 cm^{-1} (cf. Fig. 31) and are associated with charge transfer transitions in views of their broadness and relatively high molar absorption coefficient. These bands are therefore due to LMCT, mainly S → M CT. Based on energy and relative intensity consideration (107) these two maxima are desirable to two types, namely σ S → M and π S → M Charge transfer (107, 108). The CT band of relatively higher energy is due to σ S→ M and that of relatively lower energy is assignable to πS → M charge transfer.

The third maximum occurring in the range 16,100 – 15,400 cm^{-1} is of low intensity and can be assigned to a d - d transition. This band is usually found in octahedral Co (II) complexes and corresponds to the transition $^{4}T_{1g} \rightarrow {}^{4}T_{1g}$ (P) (106).

The binary and mixed ligand Ni (11) complexes displayed either a broad band at 17,800-17,100 cm^{-1} associated with a well - defined shoulder at shorter wavelengths (18.800-17.800 cm^{-1}) as represented by Fig. 32 , or a single band with a maximum in the range 18,400-17.500 cm^{-1} (cf. Fig. 33). The composite band has, in general, high molar absorptivity and hence it represents the charge transfer transitions π S $\rightarrow$ Ni and $\rightarrow \sigma$ S Ni as explained before. On the other hand, the single band appearing in the spectra of some complexes is characterized by low molar extinction coefficient and as reported by lever (107), the square planar Ni (11) complexes can display a single d-d band in the range 16.000-19.500 cm^{-1} with low intensity. Therefore, this single band is due to the transition $^{3}A_{2g} \rightarrow {}^{3}A_{2g}$ (P) of the square planar Ni (II) complexes. It should be noted that this band is expected to be hidden under the intense CT bands appeared in some complexes, and the CT bands of those displaying this single d-d band, appear at shorter wavelengths. Copper (II) complexes comprise also one or two bands in the visible region, at longer wavelengths, in the range 23,200 - 16,200 cm^{-1} [representative reflectance spectra are shown in Figs. 34,35. The longer wavelength band is due to a d-d transition and its position is typical for distorted octahedral Cu (II) complexes (107), Since it was reported that the majority of six - coordinate Cu (II) complexes have a tetragonally distorted structure, where such complexes give rise to one absorption band near 16.000 cm^{-1} (107.109). Accordingly, a tetragonal distorted structure can be suggested for the present Cu (II) complexes. The shorter wavelength visible band appeared in the spectra of the complexes are due to charge transfer transitions.

The visible spectra of Ru (III) complexes are characterized by either a very broad band or a composite one with two maxima (cf. Figs. 36.37). The very broad band centered at about 22,200 cm^{-1}, is due to charge transfer transition and can include more than one type of charge transfer, since it has been pointed out that Ru (III) complexes possess both ligand to metal (110) and metal to ligand CT in this region. The former type is that occurring from either $\sigma\ \pi S \rightarrow \pi M$ and the latter type of charge transfer transition is due to $t_{2}g$ (M) $\rightarrow \pi^{*}$ (L). On the other hand, the two maximum appearing in the composite band displayed by some Ru (III) complexes (ct. Fig 38) can be attributed to the same types of charge transfer to the same types of charge transfer transitions.

Furthermore, some Ru (III) complexes displayed lower intensity bands or shoulders at rather lower energy, in the range 18,500 – 17,500 cm^{-1}. This band occurs in the range of d-d spectra of Ru (III). The ground state of Ru (III) is $^{2}T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^{2}A_{2g}$ and $^{2}T_{1g}$ which arise from

$T_{2g}{}^4$ eg^1 configuration (113). Consequently, one may assign the band appearing at 18,500 – 17,500 cm^{-1} to the $^2T_2g \rightarrow {}^2A_2g$ transition, but in the present complexes having the soft Lewis base donor S atoms and in view of the relatively high intensity of the band ([$\in$ in the order of 1.800 cm^2 mol^{-1}]) this band is best ascribed to a charge transfer transition (mainly π S → Ru (III) CT).

Based on the results of elemental analysis and conductivity data, as well as the foregoing discussion of the IR and electronic spectroscopy of the different complexes, the following conclusions could be drawn :

(a) Co (II), Cu (II) and Ru (III) ions form six coordinate complexes both as binary or in the mixed ligand complexes.

(b) The binary and mixed ligand Ni (II) complexes are all four-coordinate and possess a square planar geometry.

(c) The mixed ligand complexes of Co (II), Ni (II) and Cu (II) are formed by substitution of one dto ligand by either two monodentate ligands (acetate or thioacetamide) or one bidentate ligand.

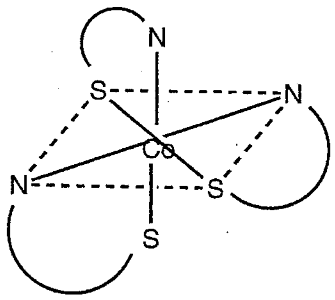
(d) Ru (III) mixed ligand complexes are formed by substitution of the coordinated chloride in the binary complex and in some mixed ligand complexes by substitution of two chlorides and one dto ligand.

(e) The dithiooxamide molecule is a flexibidentate ligand capable for coordination to metal ion as either as neutral S, S or mono-anionic S, N donor.

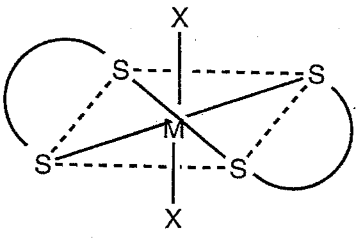
(f) Two types of complex species are mainly formed, namely neutral and catonic complexes are monomeric and some others are polymeric. The latter complexes are most likely low polymers, i. e of relatively short chain.

The results of the chemical analysis, conductivity measurement, IR and electronic spectroscopy suggest the following structures for the binary and mixed-ligand complexes :

(i) Monomeric complexes

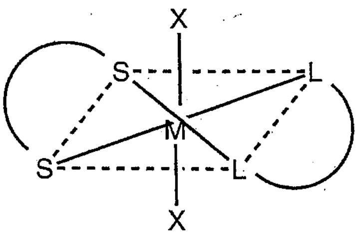


S⌒N = monovalent
dto ligand



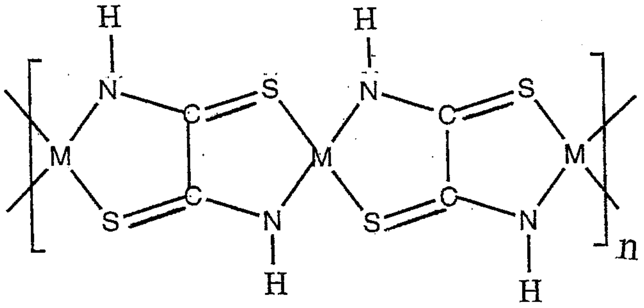
M = Co (II) or Ru (III)
X = Cl- or monodentate

S⌒S = neutral dto ligand



M = Co (II) or Ru (III)
L = bidentate secondary ligand (or monodentate ligands)

(ii) dto bridged complexes



M = Ni (II) or Cu (II) ;
n = 2 for dinuclear complexes

Table 18. Relevant IR Frequencies (in cm^{-1}) of dto and its binary and mixed ligand Co (II) complexes

Free dto	**compound**					**assignment**
	1	2	3	4	5	
3293 (m)						ν NH_2
3211 (m)	3230(b)	3244(b)	3238(b)	3228 b	3240 b	ν NH
3137 (m)						ν NH
		1660(w)	1604(w)	1656(w)	1612(w)	ν OCO(acetate)
1586 (s)	1548	1511(s)	1510(s)	1520	1526	δ NH_2
1430 (s)	1380	1382	1385(w)	1390	1394	νCN
		1340	1340(w)	1345		
1200 (s)	1110	1100 (m)	1278(w)	1270	1268	ν C-C
		1064	1096(w)			
836 (s)	826	863(s)	863(s)	845	852	νCS
703 (s)	705	703	708	702	703	πNH
628 (s)	680	834	630	635	635	δ NCS

b = broad, m = medium, s = strong, w = weak, sh = shoulder

Table 19. Relevant IR Frequencies (in cm^{-1}) of dto and its binary and mixed ligand Ni (II) complexes

Free dto	compound								assignment
	6	7	8	9	10	11	12	13	
3293(m) 3211(m) 3137(m)	3230b	3265sh 3247(m)	3260sh 3239(m)	3255sh 3240	3260sh 3238	3264sh 3248(m)	3240	3230	ν NH_2 ν NH ν NH
		1700(m) 1600(m)							ν OCO (acetate)
1586(s)	1565	1510(s)	1570(s)	1520	1530	1513(m)	1510	1515	δNH_2
1430(s)	1380	1370(w) 1347(w)	1400 1340	1420 1280	1380 1310	1447(w) 1312(w)	1420 1315	1390 1320	ν CN
1200(s)	1220	1106(s) 1016(s)	1270(m) 1200(w) 1052(s)	1170	1230 1076	1106(w) 1020(m)	1160 1050	1180 1100 1030	νCC + bands of secondary ligands
836(s)	825	871(s) 836(s)	829(s)	860	864	875(s)	870	856	ν cs
703(s)	715	774(s)	778(s) 659(s)	760	767	777(s) 736(w)	714	770	πNH+bands of secondary ligands
628(s)	612	615	592(s)	618	620	593	593	600	δNCS

b = broad, m = medium, s = strong, w = weak

Table 20. Relevant IR Frequencies (in cm^{-1}) of dto and its binary and mixed ligand Cu (II) complexes

Free dto	**compound**							**assignment**
	14	15	16	17	18	19	20	
3293(m) 3211(m) 3137(m)	32406	3230	3233(m)	3235	3234(m)	3230(m)	3338(s)	ν NH_2 ν NH ν NH
1586(s)	1570	1702 1568	1578(s) 1511(s)	1570(s)	1580 1558(s)	1600(s) 1567(m)		ν OCO+ bands of secondary ligands + δNH_2
1430(s)	1440	1438	1377(m)	1400(m)	1497(s) 1466(s) 1377(s) 1321(s)	1430 1320	1473(m) 1444(s) 1317(s)	ν CN+ bands of secondary ligands
1200(s)	1255	1265	1274(s)	1278(m)	1260	1281(m)	1158(s)	ν CC
836(s)	850	862	870(s)	867(s)	869(s) 820	869(s)	866	ν CC
703(s)	780 720	785	784(s) 730	796(m)	782(s) 741(s)	789(m)	776(s) 730(s)	πNH

b = broad, m = medium, s = strong, w = weak, sh= shoulder

Table 21. Relevant IR Frequencies (in cm^{-1})

of dto and its binary and mixed ligand Ru (III) complexes

Free dto	Compound						Assignment
	21	22	23	24	25	26	
3293(m)							ν NH_2
3211(m)	3240	3235	3230	3243	3230	3240	ν NH
3137(m)		319(b)		3120(b)		3131(b)	ν NH
1586(s)	1615	1609(m)	1610	1608)m)	1618(m)	1620(m)	δNH_2
1430(s)	1440	1442(sh)	1436	1431(s)	1448(m)	1444(m) 1403(s)	ν CC+ bands of secondary ligands
1200(s)	1215 1058	1223(w) 1057(w)	1220 1070	1214 1062	1210 1048	1212(m) 1033(w)	νCC+ bands of secondary ligands
836(s)	826	822(w)	830	827	857(w)	825	ν CC
628(s)	610	593(m)	597	615(m)	588	590(m)	δNCS

b = broad, m = medium, s = strong, w = weak, sh= shoulder

Table 22. Electronic spectral data of the Co (II) complexes

No.	complex	ν_{max},cm^{-1}	ε_{max}^{a}	assignment
1.	Co (II) – dto	25,000 20,000 15,900	4,3000 3,200 900	CT CT d-d
2.	Co (II) – dto-Ac	25,600 20,800 16,100	b b b	CT CT d-d
3.	Co (II) – dto-o-phen	25,000 20,000 15,400	7,400 5,300 890	CT CT d-d
4.	Co (II) – dto-taa	25,700 19,200	6,400 4,200	CT CT
5.	Co (II) – dto – 8HQ	25,300 19,800	6,700 5,100	CT CT

a) cm^{2} mol^{-1}; b) = reflectance

Table 23. Electronic spectral data of the Ni (II) complexes

No.	complex	ν_{max}, cm^{-1}	ε_{max} ^{a}	assignment
6.	Ni (II) -dto	17,700	110	d -d
7.	Ni (II) –dto- ac	17,800 sh 17,400	b	CT
8.	Ni (II) –dto-acac	18,600 sh 17,800	12,500 10,000	CT
9.	Ni (II) –dto-8HQ	17,500	800	d –d
10.	Ni (II) –dto-Sal	18,400	b	d –d
11.	Ni (II) –dto-taa	18,800 sh 17,100	8,500 6,700	CT
12.	Ni (II) –dto-bipy	18,200	b	d –d
13.	Ni (II) –dto-ophen	17,600	b	d -d

a) cm^2 mol^{-1}; b) = reflectance

Table 24. Electronic spectral data of the Cu (II) complexes

No.	complex	ν_{max},cm^{-1}	ε_{max}^{a}	assignment
14.	Cu (II) -dto	16,200	b	d -d
15.	Cu(II) – dto - sal	23,200 18,200	b b	CT d –d
16.	Cu(II) – dto – acac	21,900 18,200	b b	CT d –d
17.	Cu(II) – dto –ophen	16,400	b	d –d
18.	Cu(II) – dto –8HQ	19,800 16,300	b b	CT d –d
19.	Cu(II) – dto – Acetate	20,000	b	CT
20.	Cu (II) – dto-bipy	19,900	b	CT

a) cm^{2} mol^{-1} ; b) = reflectance

Table 25. Electronic spectral data of the Ru (III) complexes

No.	complex	ν_{max},cm^{-1}	ε_{max}^{a}	assignment
21.	Ru (III)-(dto) 8HQ	26,300 17,500	0.800 1,900	Intraligand CT
22.	Ru (III) – dto	27,000 22,700	11,200 7,600	Intraligand CT
23.	Ru (III) – dto –sal	23,200	6,200	CT
24.	Ru (III) – dto – ac	22,800	8,500	CT
25.	Ru (III) – dto – acac	22,200	b	CT
26.	Ru (III) – dto – bipy	20,400 18,500	4,000 1,800	CT CT

a) cm^2 mol^{-1} ; b) = reflectance

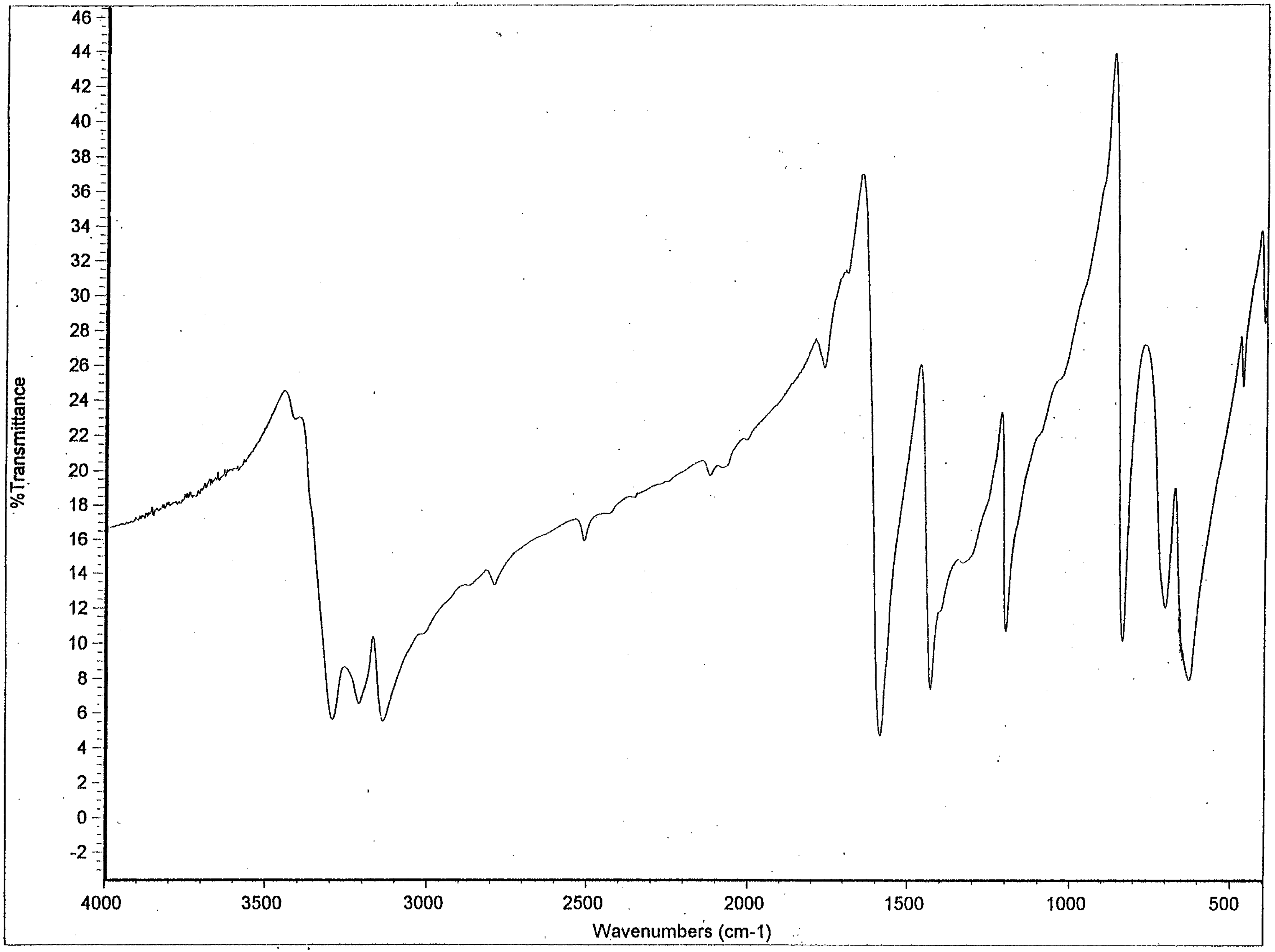


Fig. 22. IR spectrum of the free dto

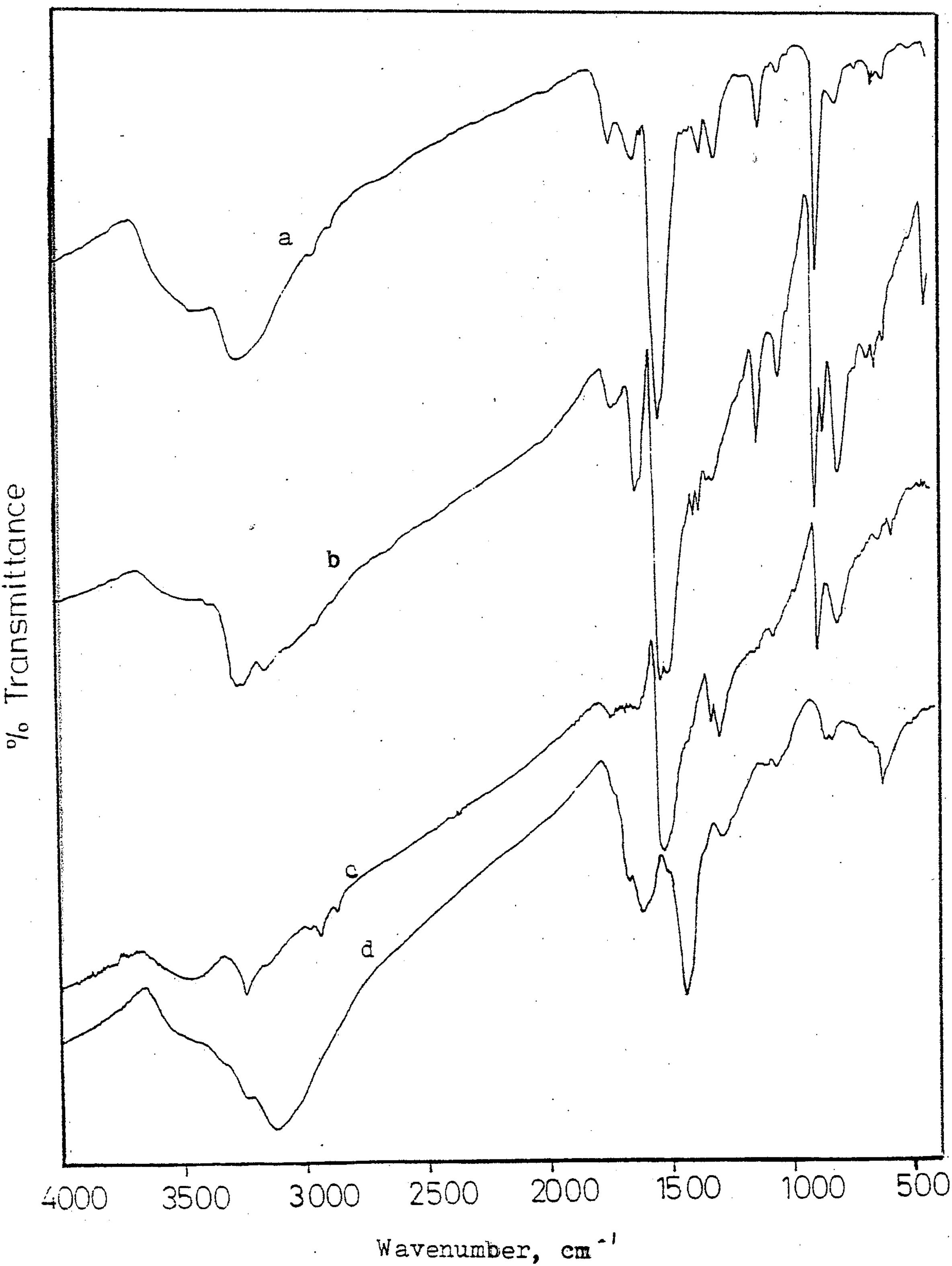


Fig. 23. **IR spectra of the binary metal complexes, a) Co^{II}, b) Ni^{II}, c) Cu^{II} and d) Ru^{III}**

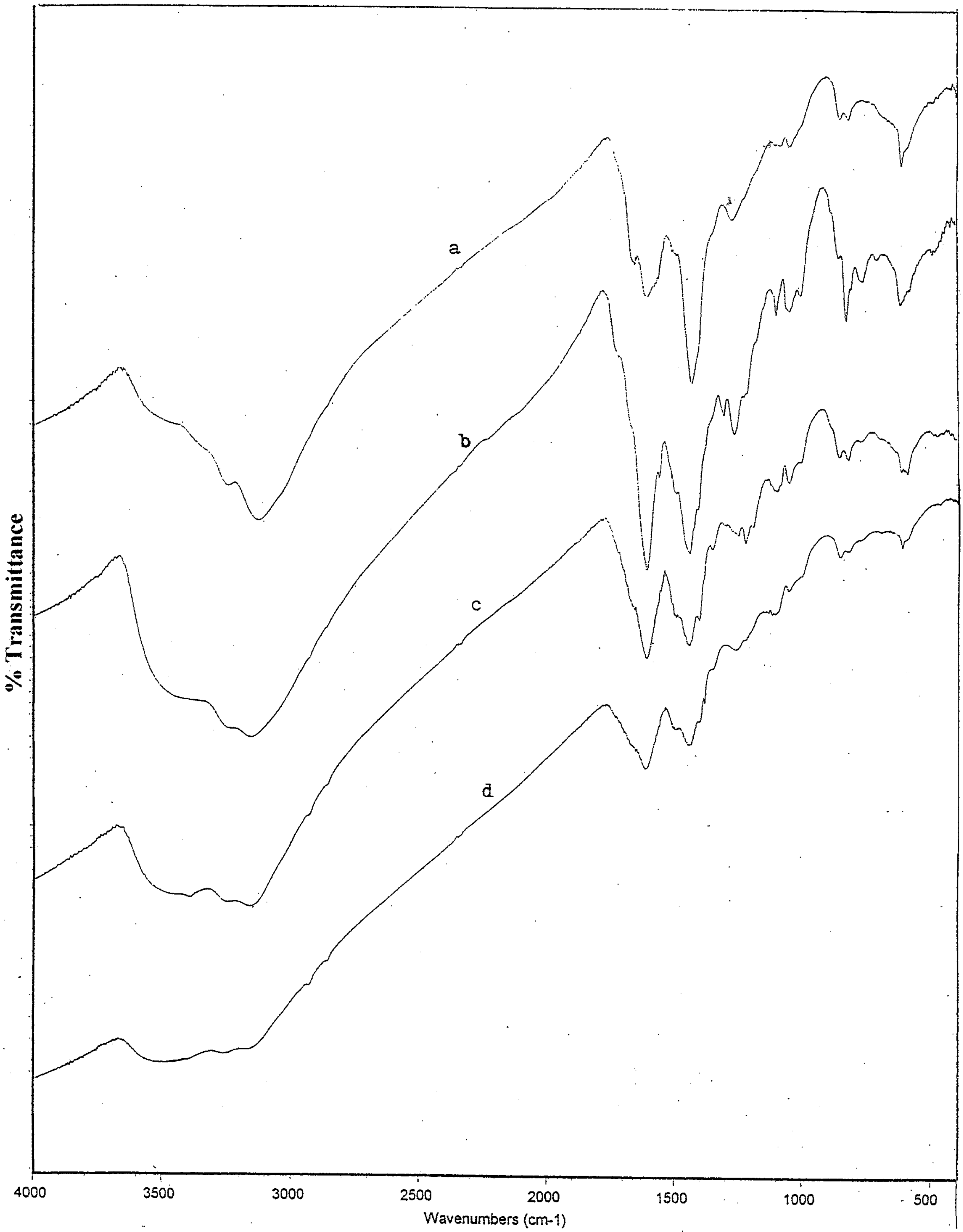


Fig. 24. IR spectra of the mixed ligand Co^{II} complexes : a) dto + acetate, b) dto + o-phen, c) dto + taa, and d) dto + 8HQ

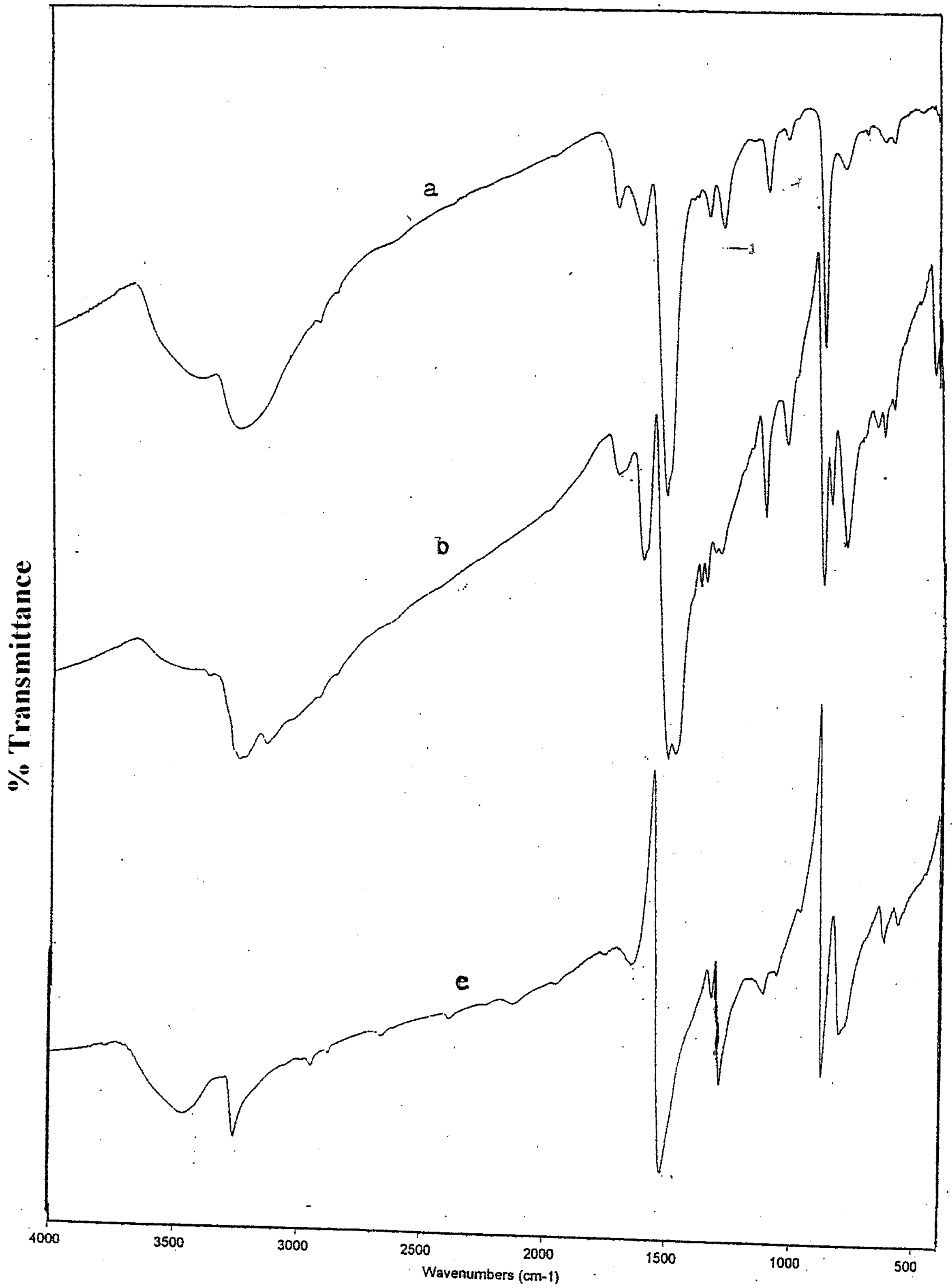


Fig. 25. IR spectra of the mixed ligand Ni^{II} complexes : a) dto + acetate, b) dto + acac, and c) dto + 8HQ

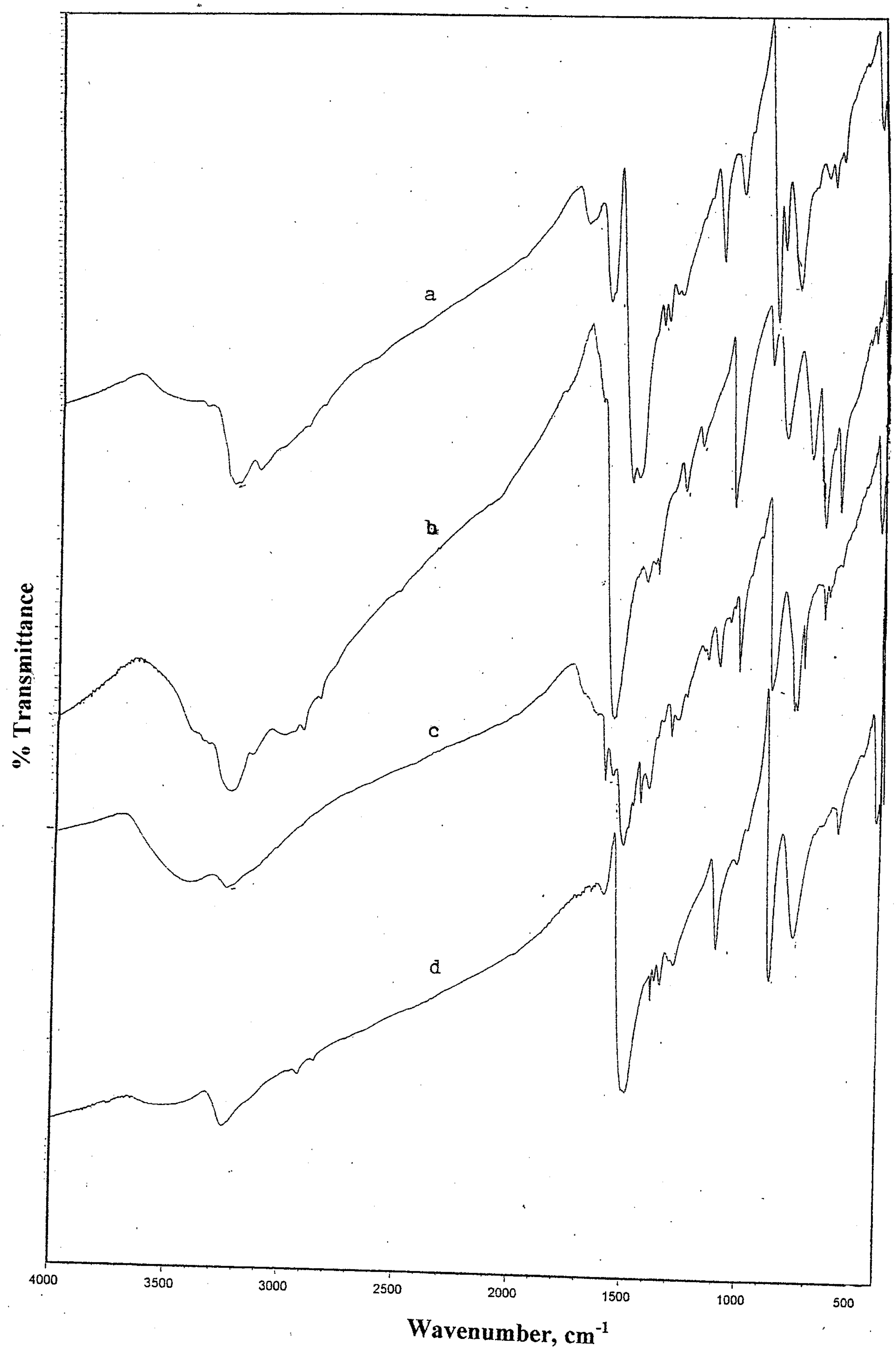


Fig. 26. IR spectra of the mixed ligand Ni^{II} complexes : a) dto + sal, b) dto + taa, c) dto + bipy, and d) dto + o-phen

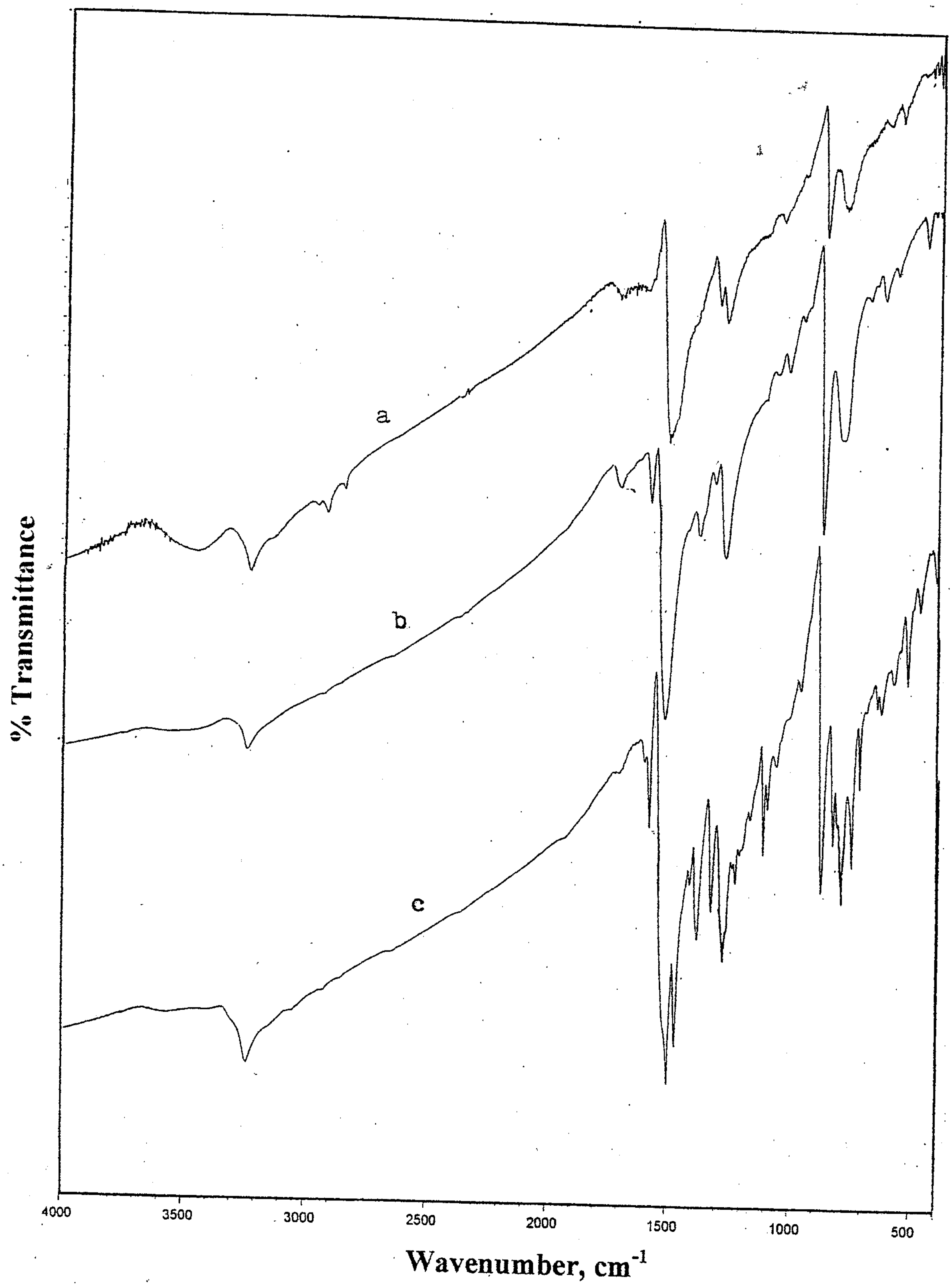


Fig. 27. IR spectra of the mixed ligand Cu^{II} complexes : a) dto + acetate, b) dto + acac, and c) dto + 8HQ

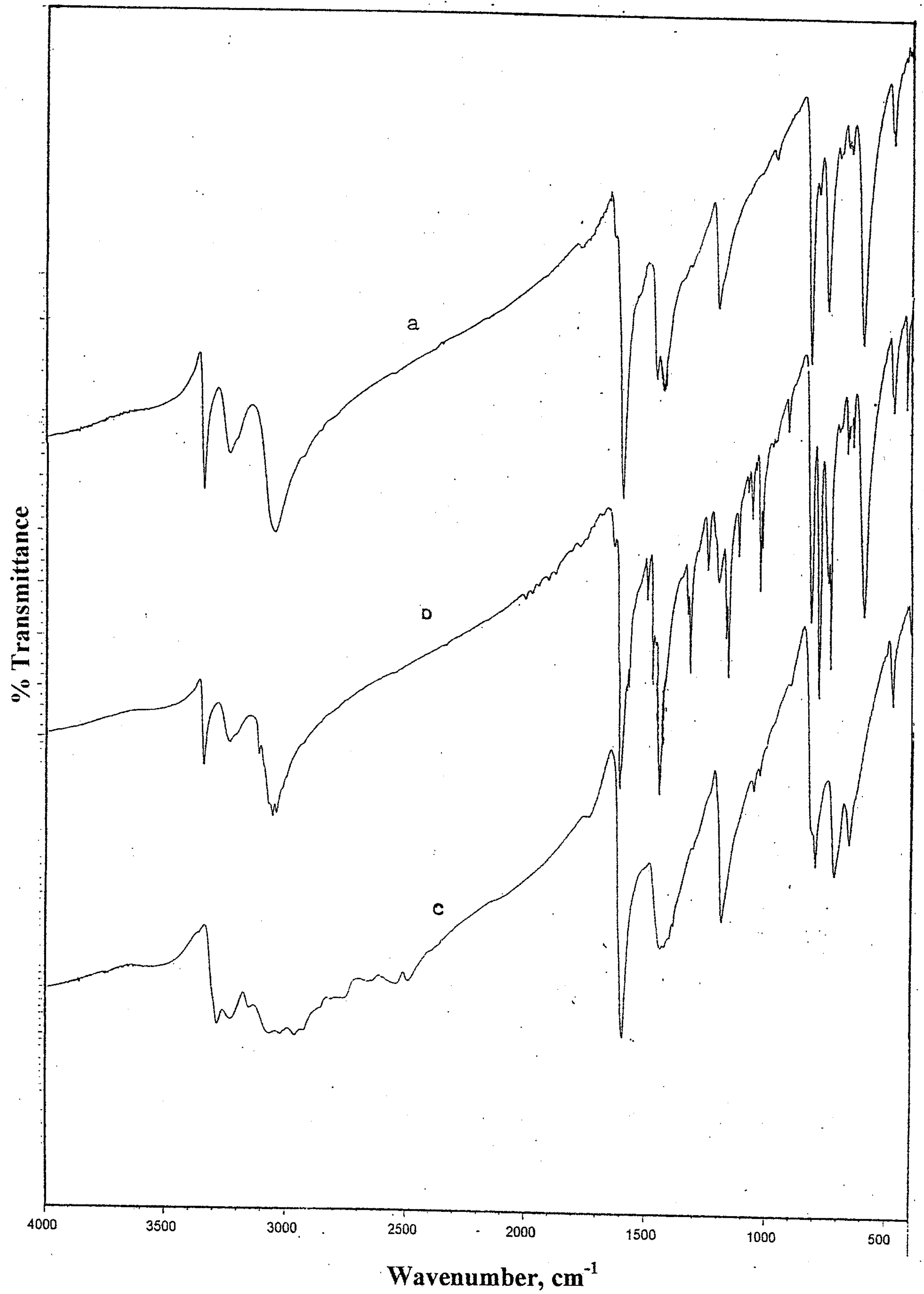


Fig. 28. IR spectra of the mixed ligand Cu^{II} complexes : a) dto + sal , b) dto + bipy, and c) dto + o-phen

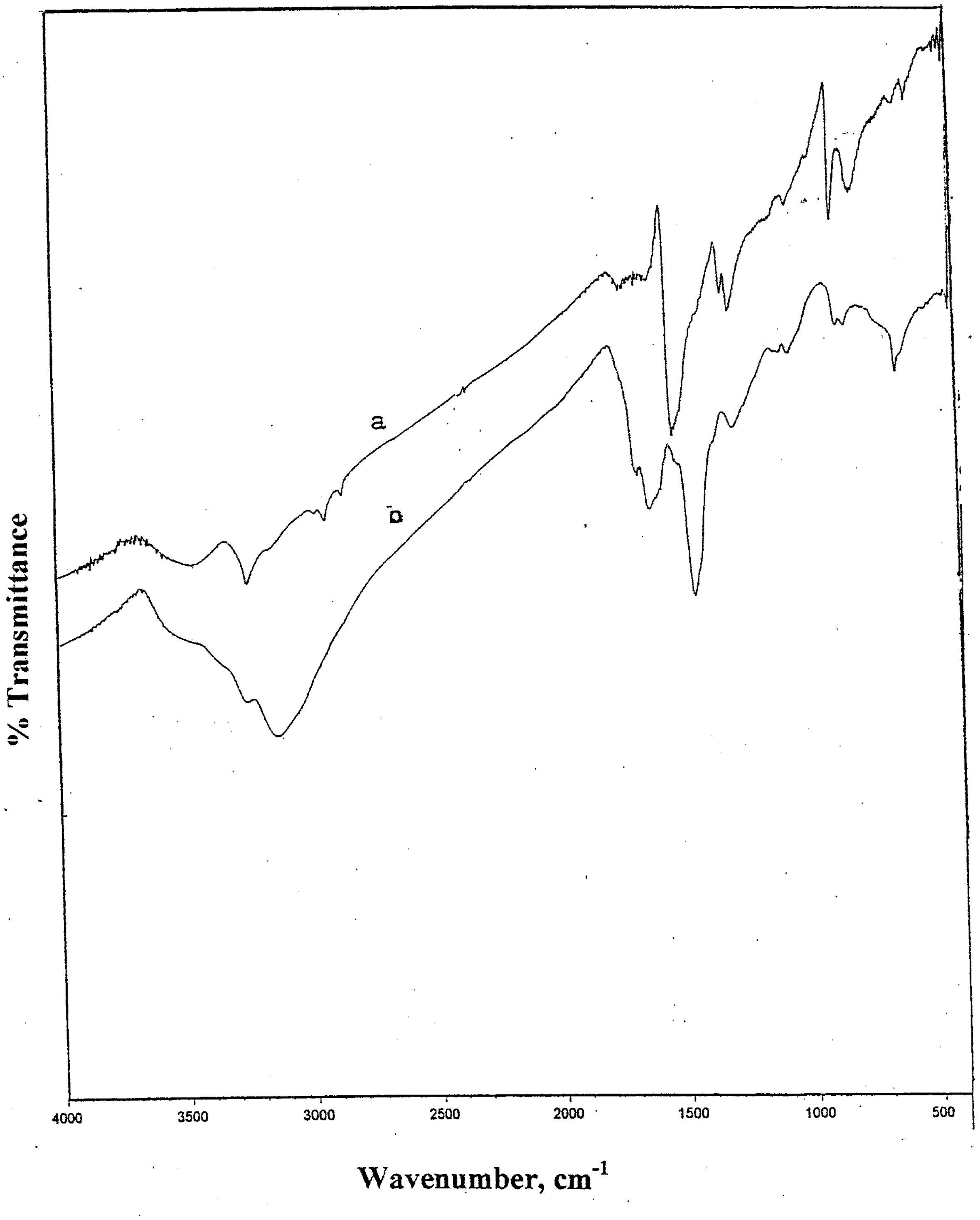


Fig. 29. IR spectra of the mixed ligand Ru^{III} complexes : a) dto + 8HQ, and b) dto + acetate

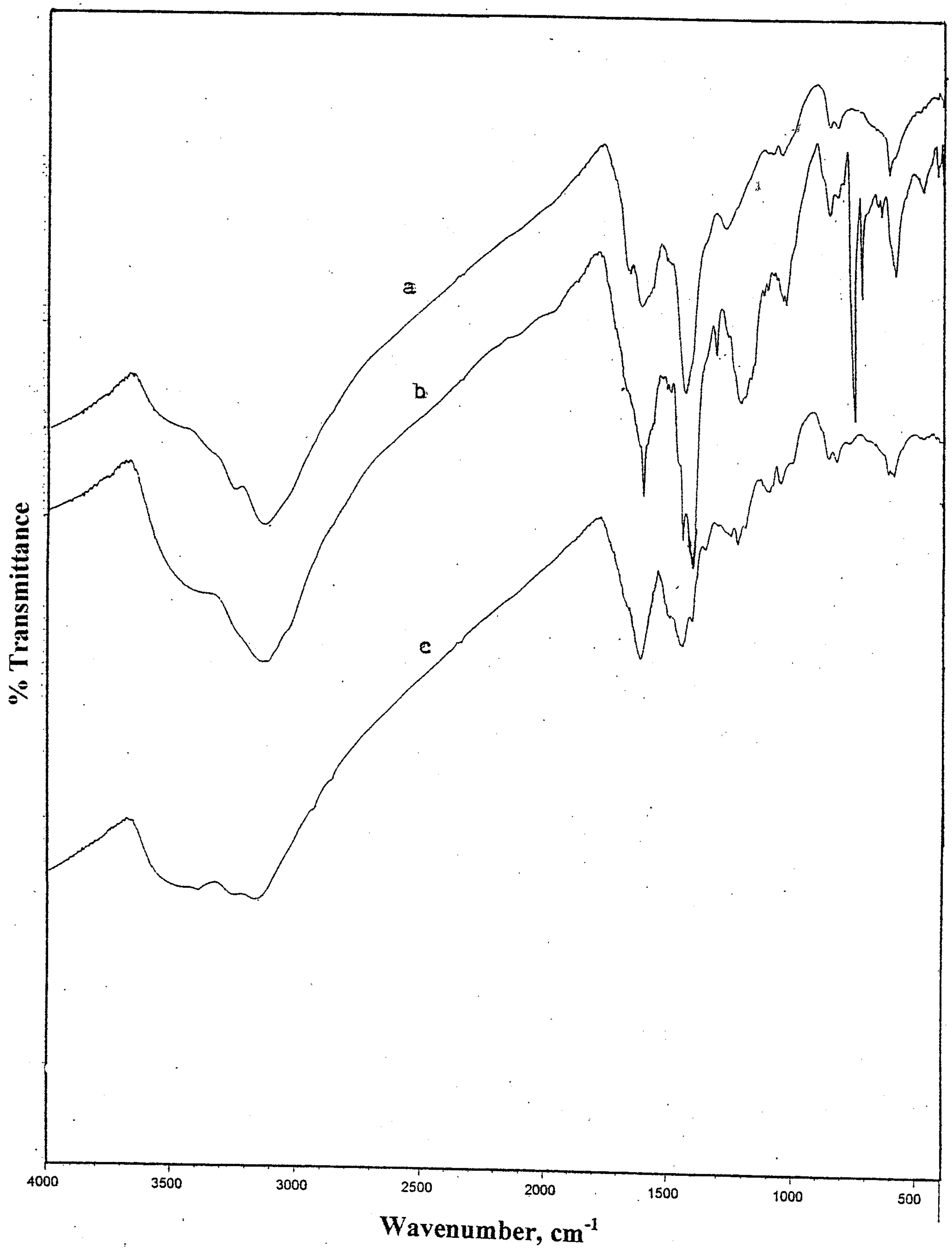


Fig. 30. IR spectra of the mixed ligand Ru^{III} complexes : a) dto + sal, b) dto + acac, and c) dto + bipy

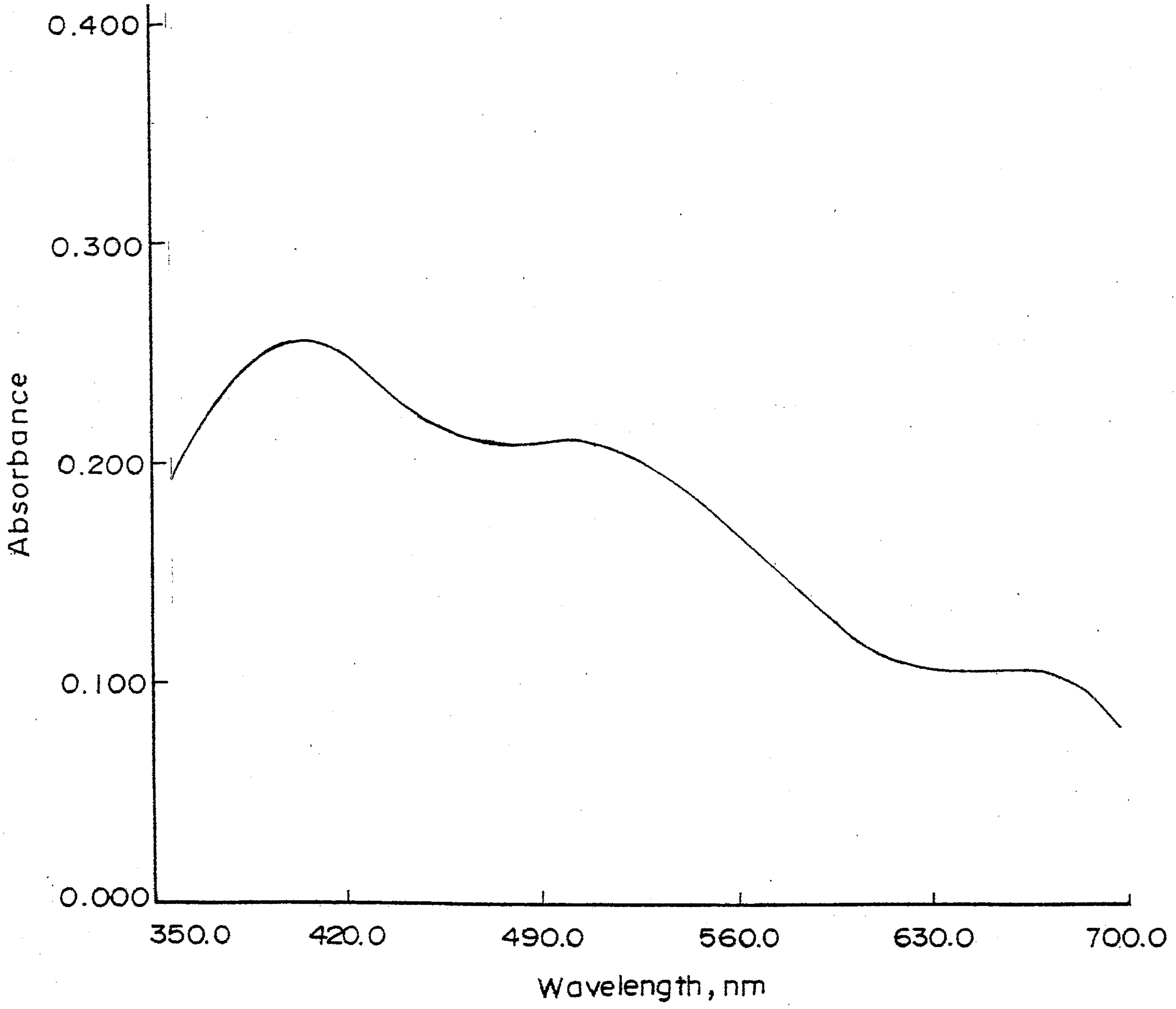


Fig.31. Electronic spectra of Co^{II} complexes

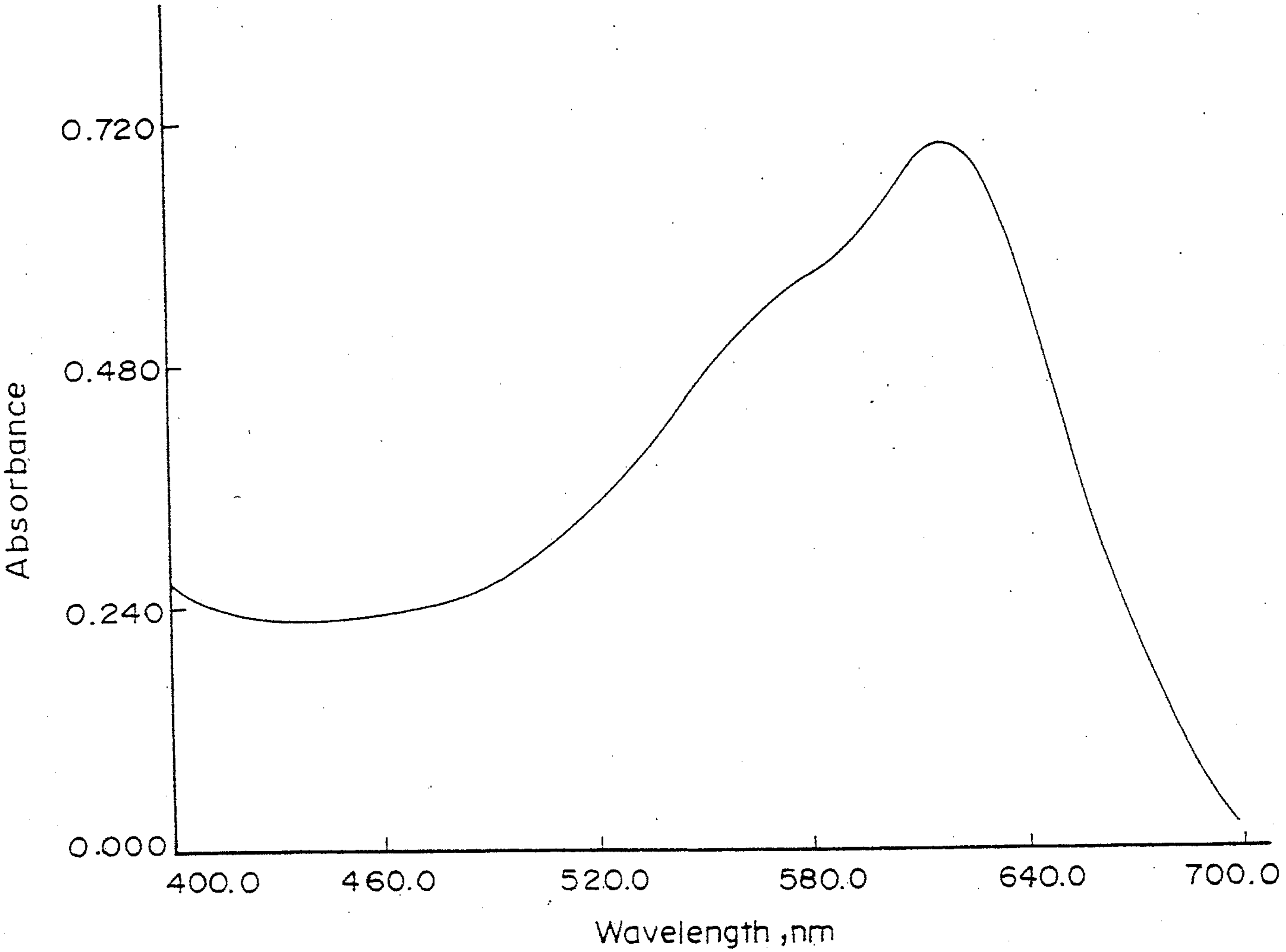


Fig. 32. Electronic spectra of Ni^{II} + dto + acetate

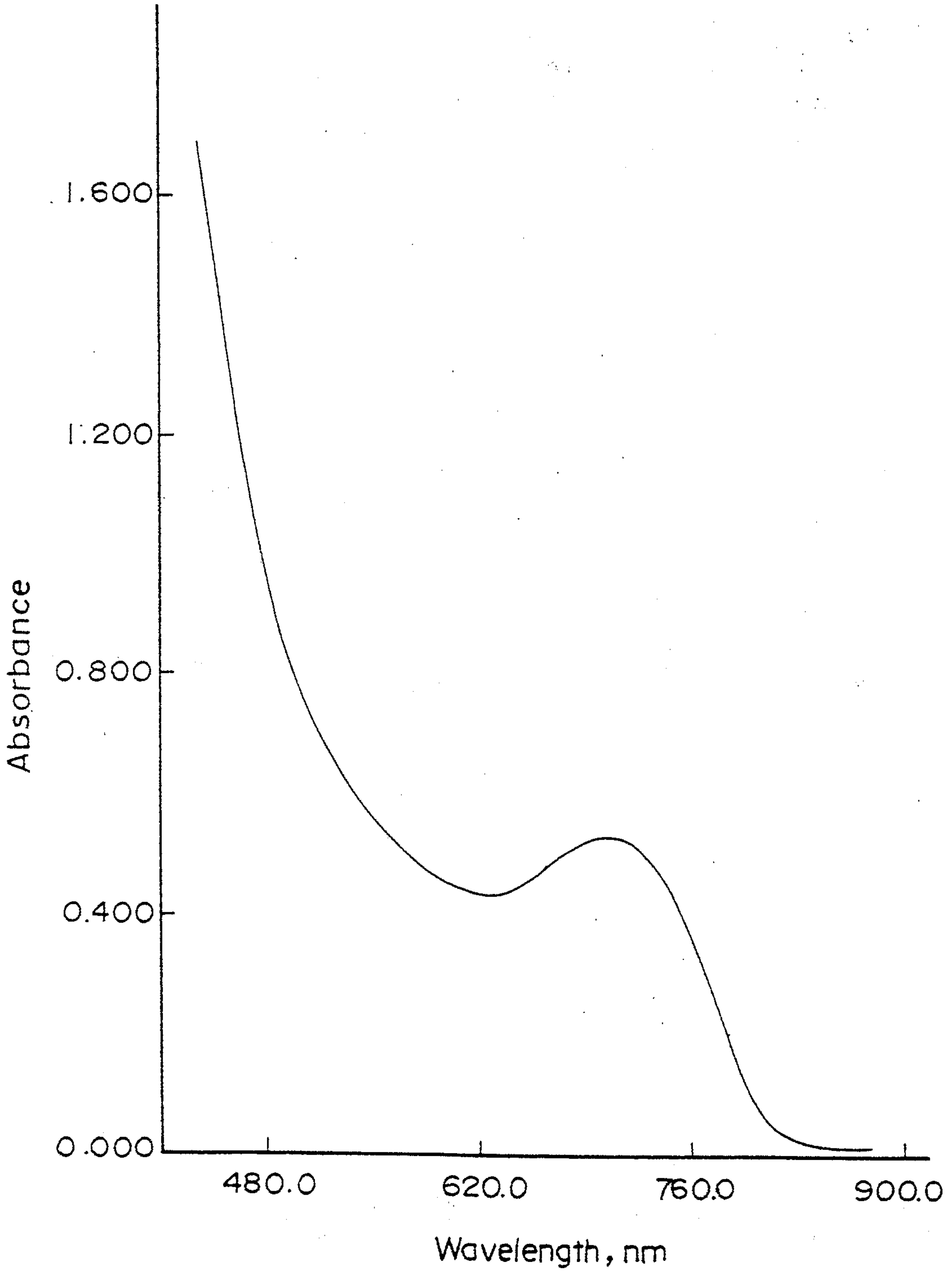


Fig. 33. Electronic spectra of Ni^{II} + dto + acetate

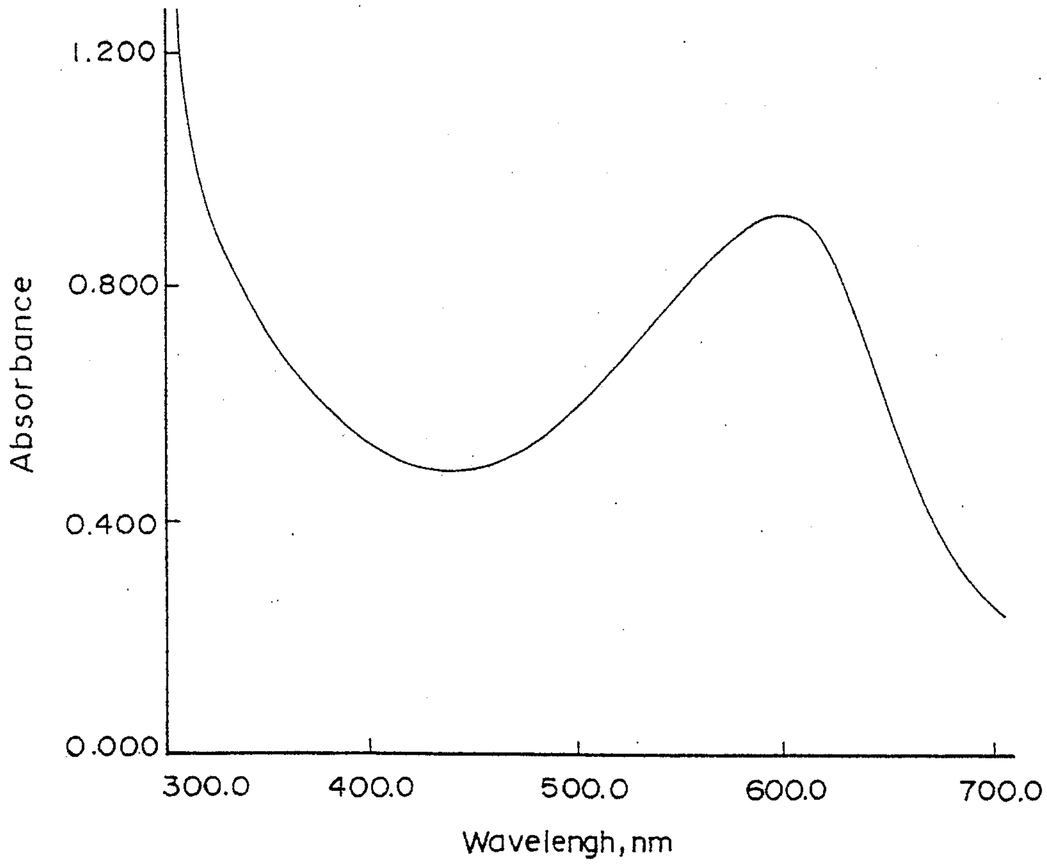


Fig. 34. Electronic spectra of mixed ligand Cu^{II} + dto + o-phen complex

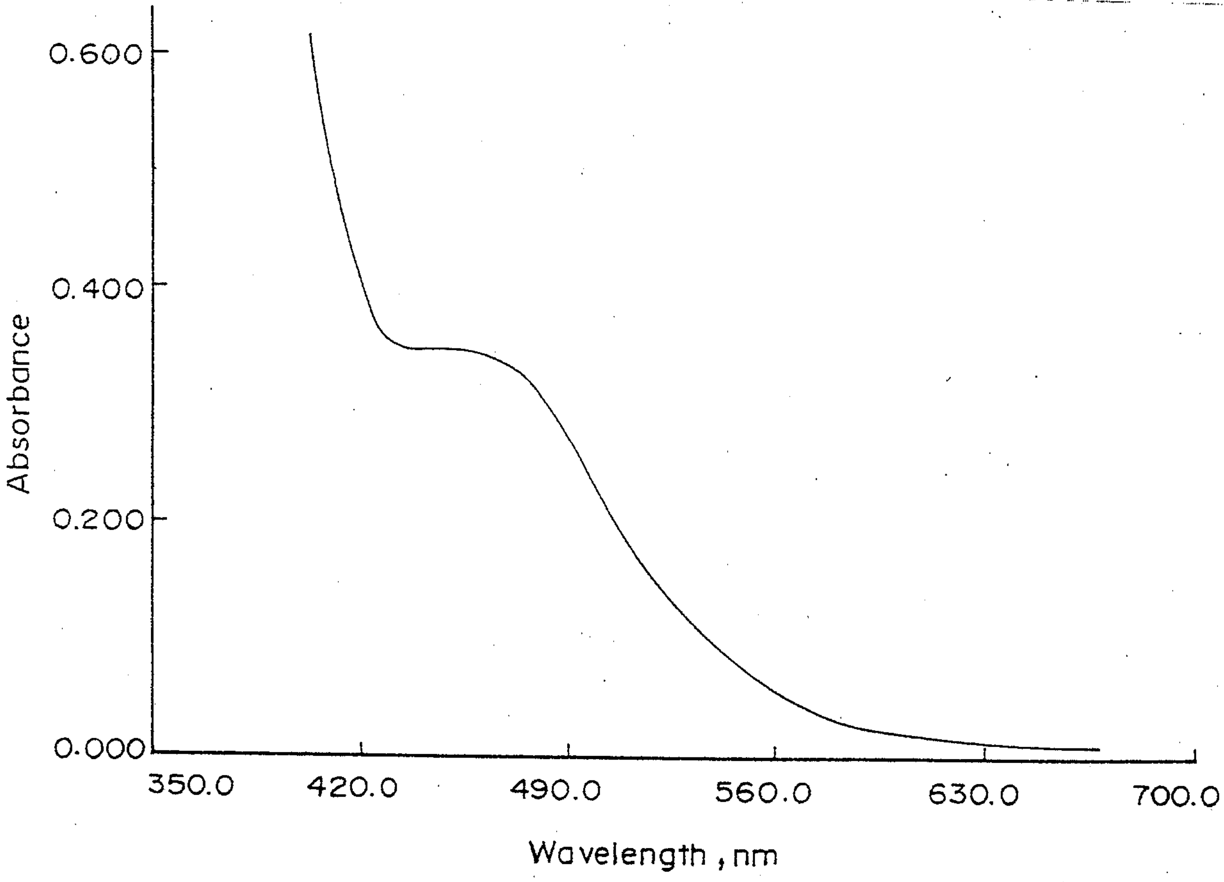


Fig. 35. Electronic spectra of mixed ligand Cu^{II} + dto + o-phen complex

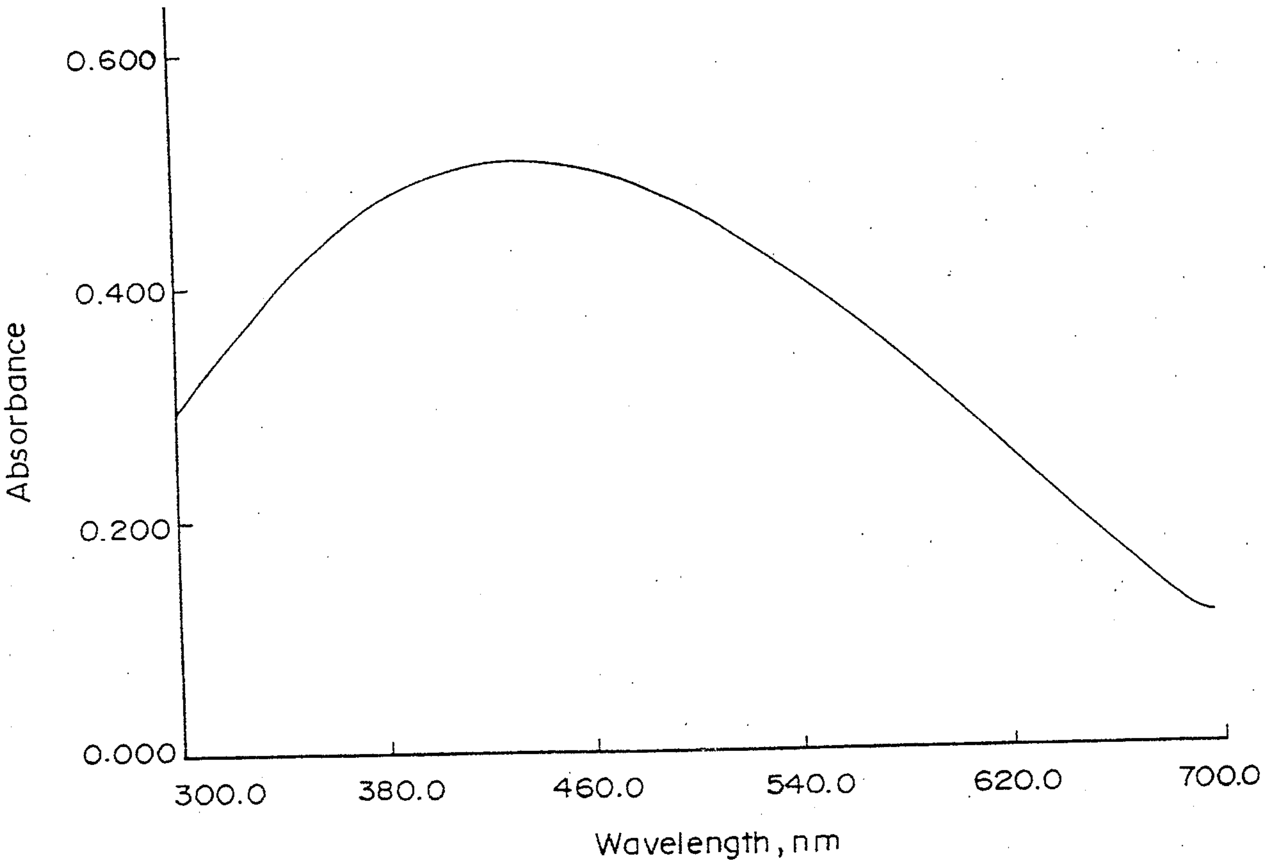


Fig. 36. Electronic spectra of mixed ligand Ru^{III} + dto + 8-HQ complex

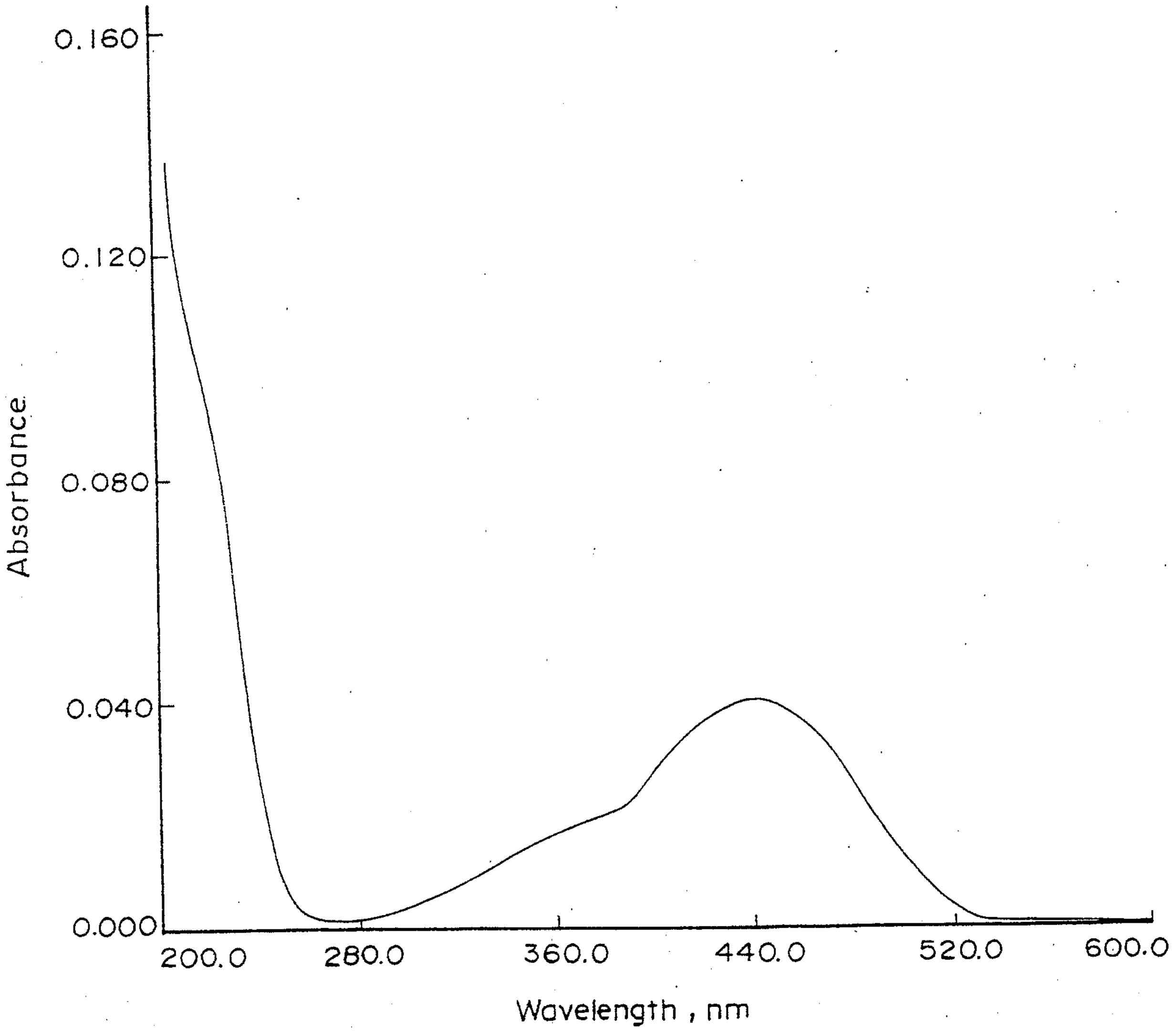


Fig. 37. Electronic spectra of mixed ligand Ru^{III} + dto + 8-HQ complex

CHAPTER V

Thermal analysis of the complexes

CHAPTER V

Thermal analysis of the complexes

Thermal analysis plays an important role in studying the structure and properties of the metal complexes. The extent of reaction on fractional conversion term, f (α), is given by:

$$\alpha = (X_i - X)/(X_i - X_f)$$

and the fraction remaining is given by:

$$(1- \alpha) = (X - X_f)\ (X_i - X_f)$$

Where X is the measured value for the extensive variable (mass, enthalpy, volume, etc.); X_I and X_f are, respectively, its initial and final values at the beginning and at the end of the reaction of interest. This is applied when only a part of the experimental data range is being analyzed or several different experiments are being compared. The equations and methods are developed in terms of α. However, one may substitute for α, values for the measured change in the extensive variable, X, without any loss of general applicability.

The most general differential equation commonly used to describe the reaction rate is:

$$\alpha / dt = f(\alpha)\ k\ (T) \qquad (1)$$

Where the rate of change of α is expressed as a product of separable functions for α and temperature. The term, f (α), can be fitted occasionally by the equation:

$$F\ (\alpha) = (1- \alpha)^2 \qquad (2)$$

A fit of the temperature dependent expression, k(T), by the Arrhenius equation is almost attempted:

$$k\ (T) = A\ exp.\ (-E/RT) \qquad (3)$$

The differential method is fully developed to apply any set of experiments with differing temperature programs. The constancy of E/R with α and temperature is tested. If E/R is constant, the correct value for the pre-exponential factor A is determined, and then the applicability of equation (2) is tested .

The equation (1) may be written differentially:

$$\frac{d\alpha}{\alpha dT}=\frac{d\ln\alpha}{dT}=\frac{A}{q}\frac{(1-\alpha)^n}{\alpha}\exp\left(-\frac{E}{RT}\right) \qquad (4)$$

Where q = dT/ dt is the linear heating rate of the substance by °C/ min or °C/ sec. The approximate solution of this equation is given by Horowitz and Metzger(113), the value of the decomposed substance fraction. α_m, at the moment of maximum development of reaction (with $T=T_m$) being determined from the relation(114):

$$(1-\alpha_m) = n^{1/1-n} \qquad (5)$$

The experiment was constructed at different initial concentrations. c_1 and c_2 ,their rates are $-d\,c_1 / dt = k\,c_1^n$ and $-d\,c_2 / dt = k\,c_2^n$ so:

$$n = (\ln(-d\,c_1/dt) - \ln(-d\,c_2/dt) / (\ln c_1 - \ln c_2) \qquad (6)$$

Simply, the order of reaction, n, is calculated.

The differential method is applied for a single isothermal experiment in the form:

$$Ln\,d\alpha/dt = n\ln(1-\alpha) + \ln k(T) \qquad (7)$$

The plot of ln dα /dt, as a function of ln (1- α), ln k (T) is obtained from the intercept at α equals zero. If the plot is linear, then its slope is equal to the reaction order, n. The change in the order during the reaction is observed directly from changes in the slope of the plot. The " initial rate ", v_o , is obtained from this method so that if initial rates are obtained from several experiments performed at different initial concentrations, c_o , then one may write:

$$\ln v_o = n_o \ln c_o + constant \qquad (8)$$

The " order as a function of initial data " , n_o , may be compared with n , the " order as function of time " . The two orders may differ in cases for which the reaction kinetics is complex, i.e. where intermediates and products affect the form of the rate equation and value of n. Thus ,this distinction between the two orders can be useful in establishing reaction mechanism.

For non- isothermal experiments:

$$d\alpha/dt = f(\alpha)\,A\,exp.\,(-E/RT) \qquad (9)$$

One obtains, upon taking logarithms, for a value of α, α_i

$$ln\ (d\alpha / dt)_i = ln\,f(\alpha_i)A\text{-}E/RT_i \qquad (10)$$

where the subscript i refers to the value of the variable at α_i .

The plot of ln dα /dt , as 1/T values at the same degree of conversion from a series of experiments at differing constant heating rates would result in a straight line with a slope of –E/R and an intercept of lnAf(α_i) These values at α_i are obtained from the slope and the intercept of the latter equation (115,116).

$$T_i\,ln\ (d\,\alpha/dt)_i = T_i\,lnA\,f\,(\alpha) - E/R \qquad (11)$$

It is more common to perform thermal analysis experiments at a constant heating rate. In general, as α increase, the T and 1/T points will be skewed to higher temperatures especially at faster heating rates. The slopes of [ln t(α)- n ln (1- α)] curves are equal to the reaction order, n.

When a reaction occurs, the DTA curves show the changes in heat content controlled by recording some peaks. For a reaction at a rate varying with temperature, i.e., possesses an E_a, the position of the peak varies with the heating rate(117, 118).

The temperature distribution in the DTA specimen holders obeys the general heat flow equation:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c}\nabla^2 T = \frac{1}{\rho c}\frac{dq}{dt} \qquad (12)$$

where:

T	Is the absolute temperature in Kelvin.
t	Is the time in sec.
K	Is the thermal conductivity.
ρ	Is the density.
c	Is the specific heat.
dp/dt	Is the rate of heat generation due to a chemical reaction per unit volume of the sample.

No heat effects occur in the reference sample, so the temperature distribution in the reference is given by:

$$\frac{\partial T}{\partial t}=\frac{k}{\rho c}\nabla^2 T \Leftrightarrow OR \Rightarrow \frac{dT/dt}{\partial t}=\frac{k}{\rho c}\nabla^2 T \qquad (13)$$

If the sample is assumed to be a cylinder of radius (a) and of infinite length with a temperature of the outside is given by $T = T_o + \phi t$, is a constant rate of the temperature rise and T is the initial temperature. The temperature, T_r,at the center of reference sample is given by integrated equation (13) with proper limits:

$$T_r = T_o + \phi t - (\phi \rho c a^2 / 4k) \qquad (14)$$

In equation (12), the rate of heat generation is function of temperature in the active sample, i.e., the temperature outside the holder rises at a linear rate. So, the solution of this equation expressing the temperature at the center of the sample will be of the form:

$$T_s = T_h + \phi t - f(dq/dt) \qquad (15)$$

Where f (dq/dt) is a function of the reaction rate.

The differential temperature (θ), is the difference in temperature between the centers of both the sample and the reference where:

$$\theta = f\left(\frac{dq}{dt}\right)_{sample} - \left(\frac{\Phi \rho c \alpha^2}{4k}\right)_{reference} \qquad (16)$$

And
$$\frac{d\phi =}{dt} f\left(\frac{dq}{dt}\right)\frac{d^2 q}{dt^2} \qquad (17)$$

From equation (17) is maximum, dϕ /dt is zero. Since the rate of heat absorption to the rate of reaction, equation (17) states that the peak differential deflection occurs when the reaction rate is a maximum. This is true only when the heating rate of the reference is constant.

Most reaction of the type solid – solid can be described by an equation:

$$\frac{dx}{dt} = A(1-x)^n e^{-E/RT} \qquad (18)$$

Where:

dx/dt	Is the rate of reaction.
x	Is the fraction reacted.
n	Is the empirical order of reaction.
T	Is the Kelvin temperature.

If the temperature rises during the reaction, the rate dx/dt will rise to a maximum value then returns to zero as it exhausted. The maximum rate occurs when (dx/dt) is zero.

$$\frac{d}{dt}\left(\frac{dx}{dt}\right)=\frac{dx}{dt}\left(\frac{E\phi}{RT^2}\right)-An(1-x)^{n-1}e^{-E/RT} \qquad (19)$$

If the temperature rises at a constant rate ϕ and occurs at T_m:

$$\left(\left(\frac{E_\phi}{RT_m^2}\right)-An(1-x)_m^{n-1}e^{-E/RT_m}\right) \qquad (20)$$

T_m is the sample temperature at which the peak DTA deflection occurs. Equation (18) can be integrated assuming a constant heating rate to obtain the extent of reaction as a function of temperature as follows:

$$\frac{1}{n-1}\left(\frac{1}{(1-x)^{x-1}}-1\right)=\frac{ART^2}{E_\phi}e^{-E/RT}\left(1-\frac{2RT}{E}\right) \qquad (21)$$

Combination between equations (20) and (21), where the obtained equation is applicable for n not equal to zero or unity:

$$\frac{1}{n-1}\left(\frac{1}{(1-x)_m^{n-1}}\right)=\frac{1}{n}\frac{1}{n(1-x)_m^{n-1}}\left(1-\frac{2RT_m}{E}\right) \qquad (22)$$

$$n(1-x)_m^{n-1}=1+(n-1)\frac{2RT_m}{E} \qquad (23)$$

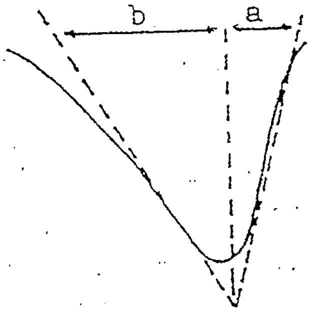
This equation does not contain the heating rate except as T_m varies with heating rate. The product $n(1-x)_m^{n-1}$ is not only independent of ϕ, but is very nearly equal to unity. Substituting this value in equation (20) and differentiating neglecting small quantities:

$$\therefore \frac{d\left(\ln\frac{\phi}{T_m^2}\right)}{d\left(\frac{1}{T}\right)} = -\frac{E}{R} \qquad (24)$$

The activation energy for a simple decomposition reaction can be determined by making DTA runs at a number of heating rates.

From equation (23), the amount of the undecomposed reaction at the peak temperature will decrease as the exponent, n, is decreased. This implies that the corresponding DTA peak will become more asymmetric as n is decreased. It should be possible to express the degree of asymmetry in terms of n, providing that the peak shape is independent of heating rate and the values of the kinetic constant.

For a quantitative picture for the peak shape, the shape index "S" is defined (119) as the absolute value of the ratio of the slopes of the tangents to the curve at the inflection points:



$$S = \frac{\left(\frac{d^2x}{dt^2}\right)^1}{\left(\frac{d^2x}{dt^2}\right)^2} \qquad (25)$$

Subscripts 1 and 2 refer to the value of these quantities at the inflection points. From equation (19) and (25), the shape index is a function only of the reaction order, n:

$$S = \frac{(3-\alpha)[\beta-(3-\alpha)](1-x)_1}{(3+\alpha)[\beta-(3+\beta)](1-x)_2}\left(\frac{T_2}{T_1}\right)^4 \qquad (26)$$

$$\alpha = \sqrt{9-4\left(2-\frac{1}{n}\right)\left(1-\frac{2RT}{E}\right)} \qquad (27a)$$

$$\beta = 2\left(2-\frac{1}{n}\right) \qquad (27b)$$

The ratio T_2/T_1 is slightly greater than unity (= 1.08). The order of the reaction process (first – order, second – order,….. etc.) can be determined from the symmetry of the DTA curve. The asymmetry of the peak is simply a/b and the reaction order (119) is calculated as follows:

$$S = 0.63n^2 \qquad (28)$$

and $$n = 1.26(a/b)^{1/2} \qquad (29)$$

The values of collision factor, Z, can be obtained in case of Horowitz Metzger (114) by making use of the relation:

$$Z = \frac{\Delta E_a}{RT_m}\beta \exp\left(\frac{\Delta E_a}{RT_m^2}\right) \qquad (30)$$

Also. The entropies of activation (ΔS^*) can be obtained from the relation:

$$Z = \frac{kT_m}{h}\exp\left(\frac{\Delta S^*}{R}\right) \qquad (31)$$

Where, R represents molar gas constant, β is rate of heating (KS^{-1}), k is the Boltzmann constant and h is the Planck's constant(120).

In what follows, thermal analysis of a selected number of the isolated binary and mixed ligand complexes is described.

The TGA data of the octahedral H_3O $[Co)dto)_3]_2H_2O$ complex are represented in Figure (38). Four characteristic peaks at (47.4), (204.6), (265.2), and (523.4)°c are observed, all of them are of exothermic behavior. The mechanism of the effect of temperature on the complex is represented in the following scheme:

$$\begin{tikzcd}
{[Co(dto)_3]3H_2O} \arrow[r, "47.4^\circ C"] & {[Co(dto)_3]2H_2O} \arrow[d, "204.6^\circ C"', "\begin{array}{l} calced.96.18 \\ Found.96.42\% \end{array}"] \\
{Co(dto)+C_2N_2H_4} & {[Co(dto)_2]} \arrow[l, "265.2^0 C"', "\begin{array}{l} Caled\ .,63.19\% \\ Found\ ,62.96\% \end{array}"]
\end{tikzcd}$$

Finally the complex is subjected to heating up to (523.4)$^\circ C$ giving CoO as a final product (% calcd 15.8; % found 15.57).

Following the data for the prepared Ni (II) complexes, eight samples have been studied from the thermal analysis viewpoint. Most of these complexes gave numerous peaks indicative of successive and stepwise mechanistic decomposition steps.

The $[Ni(dto)_2]2H_2O$ complex gave five peaks at (100) , (144.7) , (199.5) , (242.8) and (336.5)$^\circ C$ (cf. Figure 39) . The assignment of these peaks can be given according to the following proposed mechanism:

$$\begin{tikzcd}
{[Ni(dto)_2]2H_2O} \arrow[r, "100^\circ C"] & {[Ni(dto)_2]H_2O} \arrow[d, "144.7^\circ C"] \\
{Ni(C_2N_2H_4S_2)} \arrow[d] & {[Ni(dto)_2]} \arrow[l, "242.8^\circ C"'] \\
{} \arrow[r, "336.5^\circ C"] & NiS
\end{tikzcd}$$

It is apparent that the geometry of the complex persists as square planar, independent of temperature up to (242.8)$^\circ C$. This, in turn, reflects the higher thermal stability of the complex as a result of its polymeric nature as pointed out in the previous chapter.

On the other hand the square planar complex, $[Ni(dto)(acac)]H_2O$, showed only two TG peaks at (121.4) and (336.3)$^\circ C$ as clear from figure (40).

The first peak is assignable to the removal of the H_2O molecule existing in the outer sphere. The second one is due to the dissociation of both dto and acetylacetonate moieties with the formation of NiS as the final product. This final product suggests that the ac.ac, moiety dissociates at first, following by the dissociation of the dto moiety.

The thermogram of the square planar $[Ni(dto)(8-HQ)]$complex, shown in Fig. (41), displays four peaks at (168), (292), (329.5) and

(463.7)°C, the first peaks corresponds to the dissociation of (8-HQ) ligand with removal of CH_2CHCN fragment. The second peak can be assigned to the beginning of dissociation of the dto ligand with removal of S and NH species. The third peak corresponds to the dissociation of the rest of 8-HQ ligand.

The fourth step is assigned to the removal of the rest of dto ligand with the formation of Ni S as a final product. Such a trend of dissociation can be considered as good example for the coordination combination between dto and 8-HQ to the Ni (II) ions. Also, a similar behaviour was observed for the thermal decomposition of the mixed ligand complex containing thioacetamide as a secondary ligand (cf.Fig.42), where three decomposition steps at (100), (330) and (500)°C are observed. The final product was Ni S.

On the other hand, the square planar $[Ni(dto)(Sal)]$ complex gave three TG peak at (123.5), (332.7) and (500)°C (Fig. 43). The first peaks corresponds to the starting dissociation of the salicylate ligand while the second step is assigned to the dissociation of both dto and the rest of the salicylate ligands. The third one is due to dissociation of the rest of the dto ligand with the formation of NiO+2S the final product.

The $[Cu(dto)(8HQ)]Cl.H_2O$ complex gave five peaks at (60.6), (176), (305.8), (376.5) and (419.7)°C (Fig. 44). The structure of this complex was suggested to be square planar where both dithiooxamide and 8-quinolinolate ligands act as bidentate ones coordinating to the Cu(II) ion. The first peak is due to the loss of water molecule while the second one corresponds to the loss of the chloride with starting dissociation of (8-HQ) ligand, where a fragment of dihydropyridine ($CONH_3$) is being lost. The third peak is probably due to the complete removal of the (8-HQ) ligand with the beginning decomposition of the dto ligand .

Such an approach is related to the competitive complexing ability of both ligands. The fourth peak is due to dissociation of the residual species and formation of CuS as final product.

The $[Cu(dto)_2(o-Phen)]4H_2O$ complex (Fig.45) gave five peaks at (136.27), (193.96), (225.69), (284.82) and (453.57)°C. The first peak is due to removal of the four water molecules, while the second assigned to the beginning of dissociation of o-phenylenediamine ligand .

The third peak is due to the dissociation of dto ligand with removal of HCNS molecule. The fourth peak is due to further decomposition of the dto ligand with formation of $Cu_2(SCN)_2$. The last peak probably assigned for the dissociation of $CuSCN$ species with the formation of metallic Cu as final product.

The complex $[Cu(dto)Sal]2H_2O$ gave three thermogravimetric peaks at (207.6), (239.9) and (428.3)°C (Fig. 46). The first one corresponds to the removal of the two water molecules, while the second peak is due to the dissociation of the salicylate ligand with starting dissociation of the dto ligand. The third peak, however, is due to a further decomposition with the formation of CuO as final product.

The octahedral $[Ru(dto)_2Cl.H_2o]3H_2O$ complex gave five TG peaks at (53.05) , (280.93) , (366.03) , (429.49) and (490)°C (Fig. 47) . The first peak assigned to the removal of three water molecules and the second step is the removal of chloride with dissociation of one dto. The third peak assigned to complete dissociation for the second dto molecule leering RuS_2, the last peak .

The $[Ru(dTO)(8-HQ)_2]Cl$ complex which is of conducting property showed four TG steps with peaks at (110) , (224.6) , (389.1) and (500) °C (Fig. 48) . The first peak is assignable to the removal of the chloride while the second one is due to the dissociation of 8-HQ ligands . The third peak is assigned to the decomposition of the dto ligand with the formation of RuS as final product. The final product suggests that the decomposition of dto results in the formation of reducing species that are able to reduce the trivalent Ru to the divalent state in the formed RuS. Similar trend could be observed from the thermal analysis of the complex $[Ru(dto)_2 sal]2H_2O$ (Fig. 49). Five decomposition steps were observed ending with the formation of metallic ruthenium which indicates the formation of reducing species during the dissociation of the complex.

Kinetics of thermal decomposition of the complexes

The aforementioned thermal analysis data reveal the occurrence of an exothermic peak in the temperature range 47.4 – 224.6 C that can be assigned to the dehydation of the complexes (121,122).

The energies of activation (Ea) of the solid-solid formation reactions have been determined from the therograms using the method of Rilogan et al (119). Ea was determined from the stop of the lincs (Figs 50-61). The reactions are nearly first order as indicated in Table (29) . The orders were estimated by the peak assymmetry method(123). Values of the kinetic parameters of the decomposition of the complexes are recorded in Table (29).

The data relate to the following general observations and conclusions:

1- It is evident that both the polymeric and other complexes have a uniform decomposition pattern. In all complexes dehydration being the first step, whenevr they containing water molecules, loss of the side chain of the ligand being the second step and the loss of the ligand fragments are the third or later steps with the ultimate products being the metal oxide, sulphide or metallic residue as in the case of ruthenium.

2- All the complexes for all the peaks are nearly of first order decomposition kinetics.

3- All the entropy values are negative and are approximately of the same magnitude. The negative values of Δs indicated that the activated complex has a more ordered structure than the reactants(124), and further the low values of Z indicate the slow nature of the reaction (125). In general, there is a direct relation between Ea and Z. The values of Ea and Z decrease in the order Ru > Ni.

4- All the ΔH values are negative and they are affected by the geometry of the complex, meanwhile they are related to the basicity of the secondary ligand.

Table 26. Thermogravimetric analysis data of the binary and mixed ligand Co(II) and Ni(II) complexes

complex	Temp.°C	%Calcd	%Found	Change
$H_3O[Co(dto)_3]2H_2O$	47.41	96.18	96.42	Loss of H_2O
	204.62	63.19	62.96	Loss of dto+2 H_2O
	265.20	25.80	24.51	Loss of dto+$C_2N_2H_4$
	523.37	15.88	15.57	Residue CoO
$[Ni(dto)_2]$ $2H_2O$	144.5	82.37	83.74	Loss of 2 H_2O
	242.8	60.68	62.29	Loss of C_2N_2S
	336.5	22.35	23.92	Residue NiS
[Ni(dto) (acac)] H_2O	121.42	93.5	95.20	Loss of H_2O
	336.33	32.77	35.36	Loss of acac + dto
				Residue NiS
[Ni(dto) (8HQ)]	168.01	83.50	48.34	Loss of C_3H_3N
	292.05	68.90	70.49	Loss of (S + NH)
	329.55	40.60	42.12	Loss of C_6H_3O
	463.68	28.19	29.66	Residue NiS
$[Ni(dto)_2$ (taa)] H_2O	100	95.16	95.89	loss of H_2O
	330	39.46	40.48	loss of taa + dto+ NH_2+NH
[Ni(dto) (sal)]	123.54	96.05	97.00	Loss of ½ H_2O
	332.67	36.12	35.88	Loss of $C_7H_5O_3$+ $C_2N_2H_3$
	500	44.10	44.44	Residue NiO + 2S

Table 27. Thermogravimetric analysis data of the complexes mixed ligand Cu(II)

complex	Temp.°C	%Calcd	%Found	Change
[Cu(dto)(8HQ)]Cl.H_2O	60.62	95.27	95.82	Loss of H_2O
	176.01	95.75	67.49	Loss of Cl
	305.81	40.04	41.39	dto+C_2NH_3
	376.49	36.89	36.09	NH+NH_2+all 8HQ
	479.76	33.47	33.84	Loss dto
				Residue CuS+S
[Cu(dto)$_2$ (o-phen)]4H_2O	136.27	86.08	86.75	Loss of 4H_2O
	193.96	65.22	63.17	Loss of $C_6H_8N_2$
	225.69	53.82	53.98	Loss of NHCS
	284.82	46.90	46.37	(dto)
	453.57	12.26	8.77	Residue CuSCN
				Residue Cu
[Cu(dto) (sal)]2H_2O	207.62	50.45	49.52	Loss of 2H_2O
	239.35	40.35	40.02	Loss of salicylate
	428.03	18.27	17.31	+NH_3+NCS
				Residue CuO

Table 28. Thermogravimetric analysis data of the binary and mixed ligand Ru(III) complexes

complex	Temp.°C	%Calcd	%Found	Change
$[Ru(dto)_2Cl.H_2O]3H_2O$	53.05	95.98	96.7	Loss of H_2O
	280.93	53.34	55.03	Loss of $2H_2O+Cl+C_2H_4N_2S_2$
	366.01	43.53	43.53	Loss of NCS
	429.49	39.0	38.41	Residue RuCS
	490	22.5	23.56	Residue Ru
$[Ru(dto)(8HQ)_2]Cl$	110	93.48	95.10	Loss of Cl
	224.65	50.3	50.27	Loss of $8HQ+C_6H_5$
	389.07	43.35	44.21	Loss of C_3H_3
	500	24.43	25.5	Residue RuS
$[Ru(dto)_2(Sal)]2H_2O$	66.45	93.1	94.28	Loss of $2H_2O$
	268.38	49.3	48.25	Loss of $C_2N_2H_3S$
	350	28.8	28.24	Loss of the
	419	24.2	23.62	second dto
	448.66	92.80	22.41	Residue Ru_2O_3

Table 29. Thermdynamic parameters of the thermal decomosition of the complexes

complex	**Step**	**n**	**E_a**	**β**	**$Zx10^3$**	**ΔS^*X10^3**	**Temp k**	**ΔH**
$H_3O[Co(dto)_3]2H_2O$	1st	1.071	73.64	2.13	0.0391	-275.6	477.6	-131.67
	2nd	1.30	161.49	2.47	0.089	-269.9	538.2	-145.27
	3rd	0.7971	705.50	1.49	0.159	-268.4	796.37	-213.7
$[Ni(dto)_2]2H_2O$	1st	1.15	114.47	2.26	0.074	-269.4	420.4	-113.28
	2nd	1.20	170.85	2.33	0.100	-267.8	473.8	-126.9
	3rd	0.890	320.08	1.75	0.110	-269.0	606.5	-163.1
$[Ni(dto)(acac)]\ H_2O$	1st	0.84	264.00	1.62	0.084	-277.4	609.3	-165.3

$Z, S^{-1}; \Delta S^*, k] . K^{-1}\ mol^{-1}$

Table 29. continued

[Ni(dto)(8HQ)]	1st	1.19	38.65	2.33	0.024	-278.9	447.0	-123.3
	2nd	0.99	235.4	1.99	0.049	-275.1	565.0	-155.46
	3rd	1.16	122.3	2.27	0.055	-274.7	602.5	-165.5
[Ni(dto)$_2$(taa)]H$_2$O	1st	0.60	739.4	0.70	0.018	-283.9	617.1	-175.2
[Ni(dto) (Sal)]	1st	0.80	285.0	1.50	0.084	-271.3	605.6	-164.3
[Cu(dto) (8-HQ)]Cl.H$_2$O	1st	1.03	133.6	2.06	0.073	-270.7	333.6	-122.7
	2nd	1.20	243.0	2.34	0.140	-265.3	449.1	-129.4
	3rd	1.17	184.7	2.30	0.066	-272.7	578.8	-153.1
	4th	1.29	165.4	2.45	0.078	-272.1	649.5	-168.5
	5th	0.96	200.1	1.92	0.055	--272.5	692.7	-231.9
[Cu(dto)$_2$ (O-phen)]4H$_2$O	1st	0.97	116.2	1.95	0.053	-273.8	409.3	-140.5
	2nd	0.95	286.1	1.97	0.155	-265.3	466.9	-155.4
	3rd	1.03	101.7	2.05	0.050	-274.0	498.7	-163.7
	4th	1.26	301.4	2.41	0.136	-262.5	557.8	-141.7
	5th	1.13	283.2	1.66	0.096	-270.1	725.6	-157.6
[Cu(dto)(Sal)].2H$_2$O	1st	1.26	200.8	2.41	0.107	-268.5	480.6	-146.3
	2nd	0.94	258.7	1.62	0.080	-272.7	512.3	-178.1
	3rd	0.88	262.2	1.82	0.082	-272.3	701.3	-190.7
[Ru(dto) $_2$H$_2$Ocl]^3	1st	0.803	46.33	1.51	0.017	-282.7	489.0	-138.29
	2nd	0.796	1207.2	1.49	0.308	-261.8	702.4	-183.91
[Ru(dto)(8HQ) $_2$]Cl	1st	1.668	55.96	2.80	0.037	-276.3	497.6	-137.5
	2nd	0.796	433.0	1.49	0.117	-269.3	662.0	-178.3
	3rd	0.63	1155.5	0.825	0.163	-267.0	699.5	-186.7
[Ru(dto) $_2$ Sal]2H$_2$O	1st	1.469	78.87	2638	0.046	-275.4	541.3	-149.1
	2nd	0.975	480.18	1.951	0.172	-266.0	653.8	-173.9
	3rd	1.064	474.3	2.122	0.174	-266.4	692.8	-184.5

Z, S^{-1}; ΔS*, k] . K^{-1} mol^{-1}

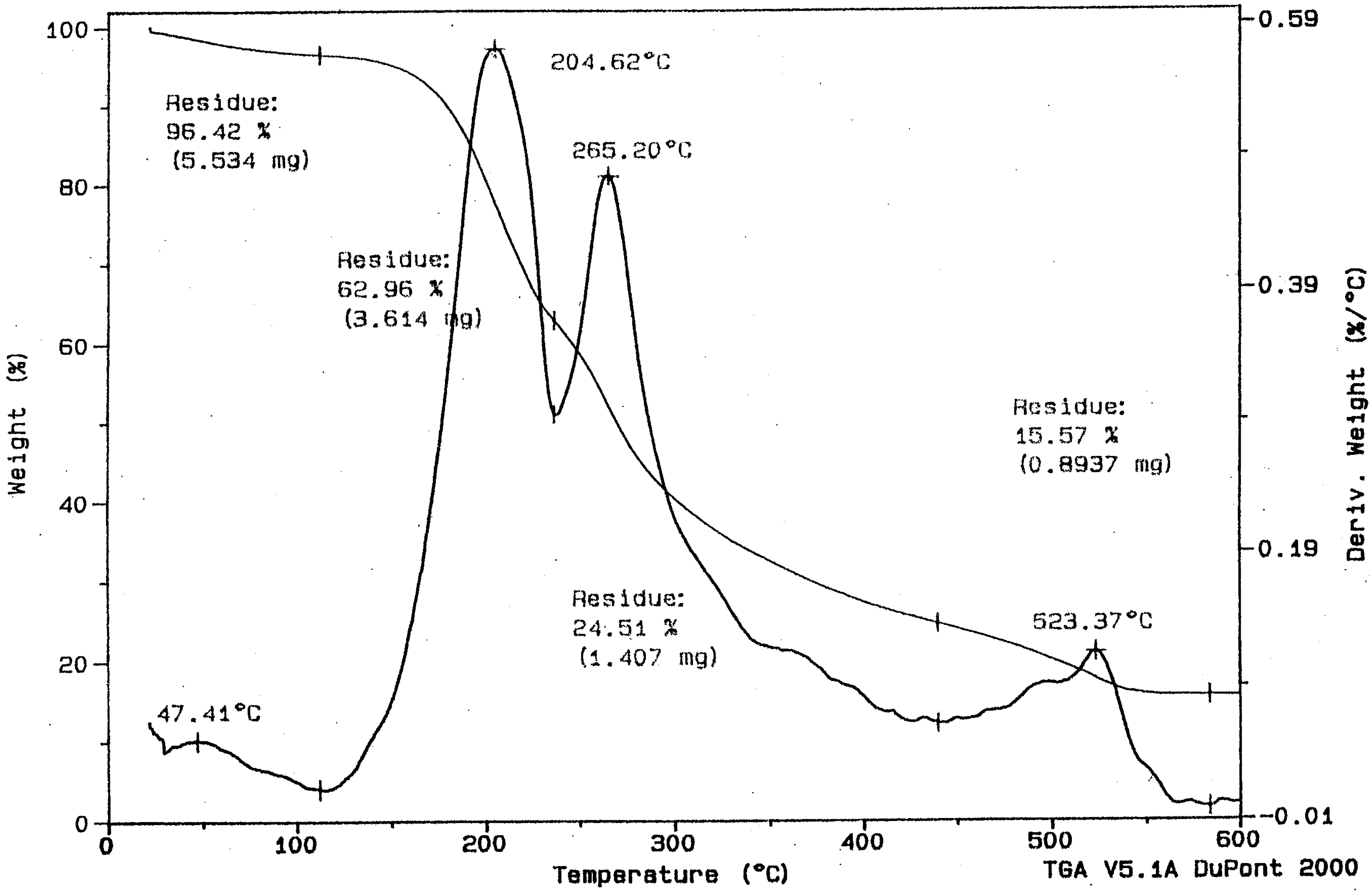


Fig. 38. TG curve of the binary Co^{II} complex

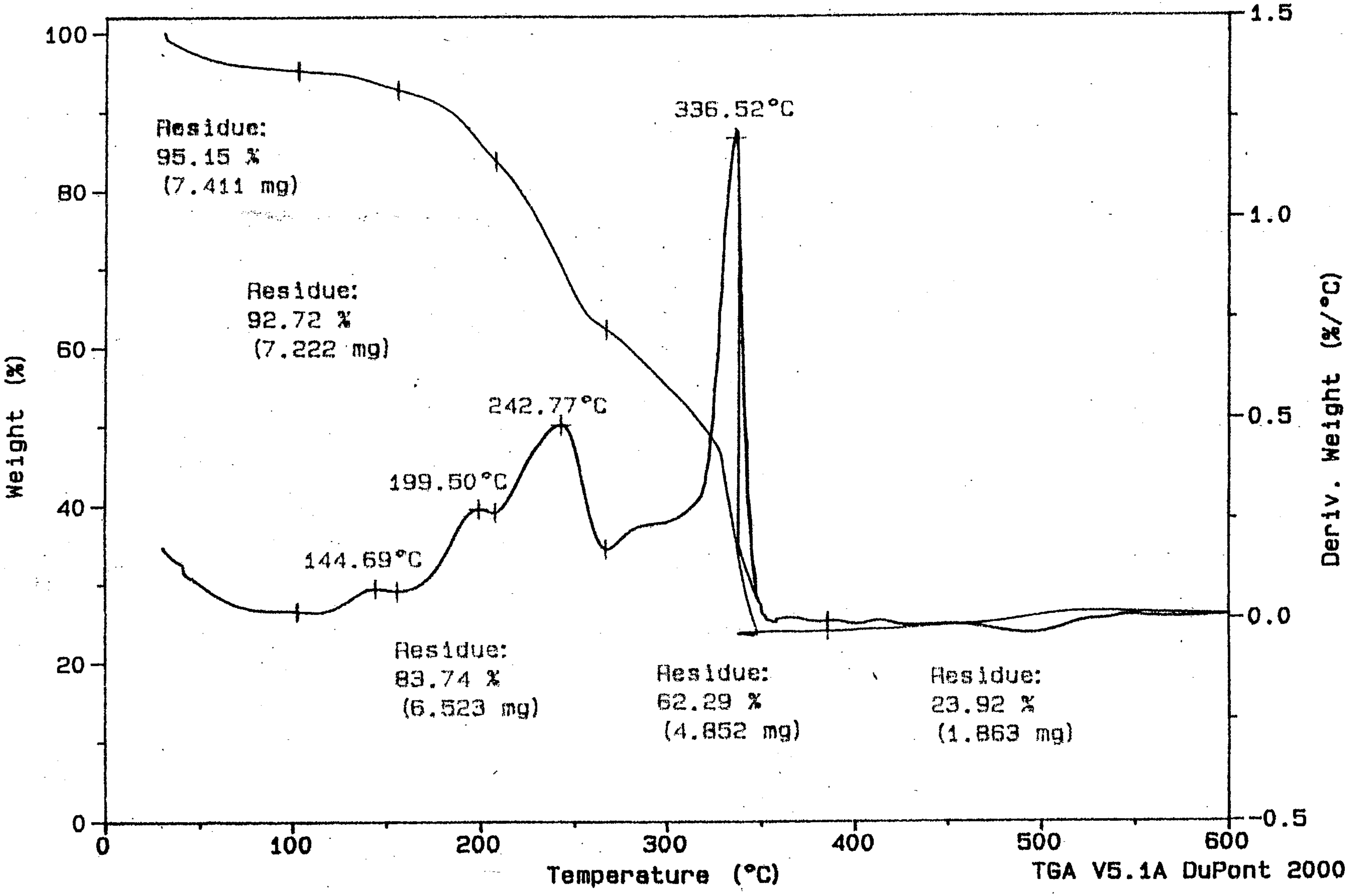


Fig.39. TG curve of the binary Ni^{II} complex

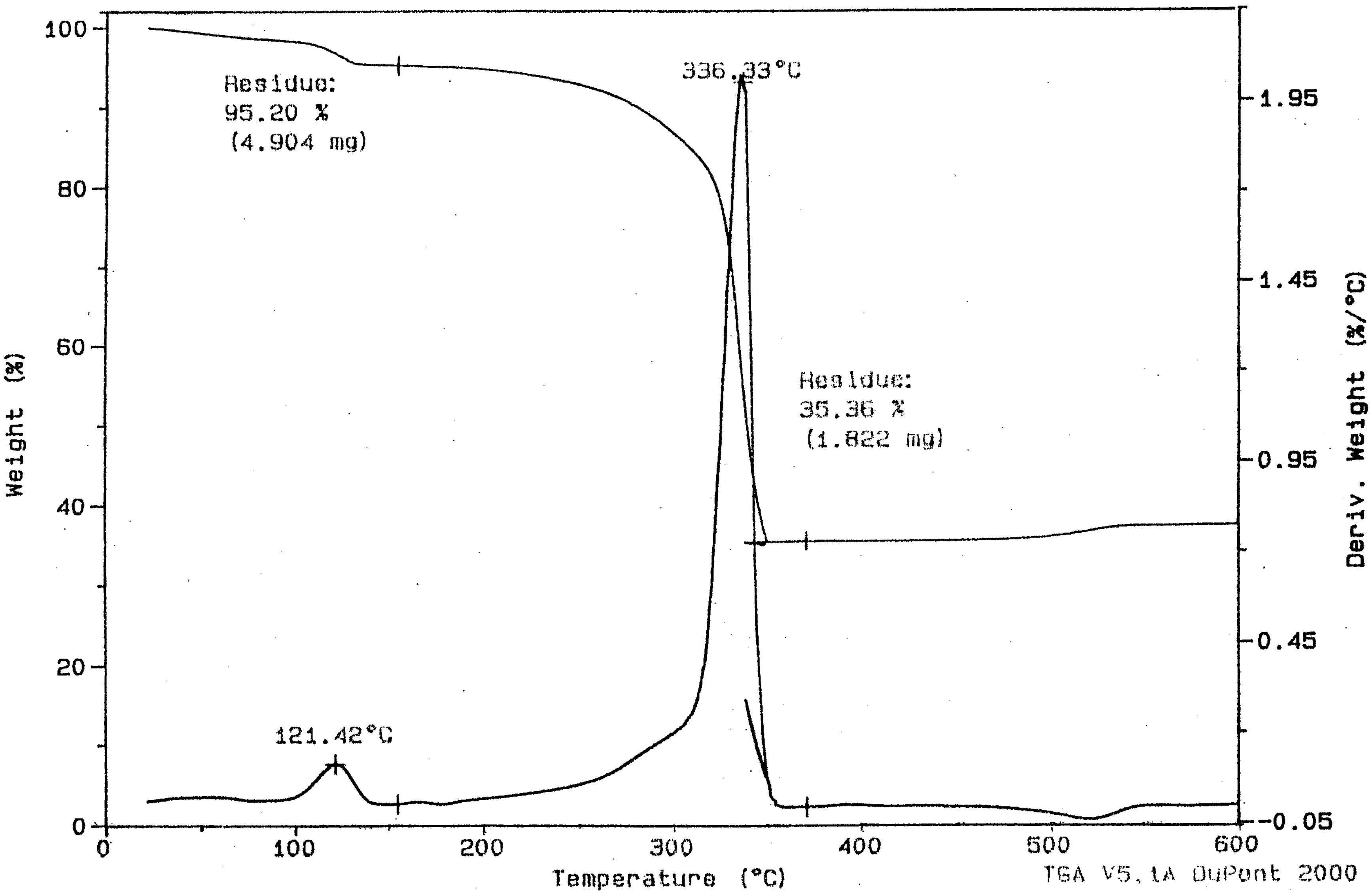


Fig. 40. TG curve of Ni^{II} + dto + acac complex

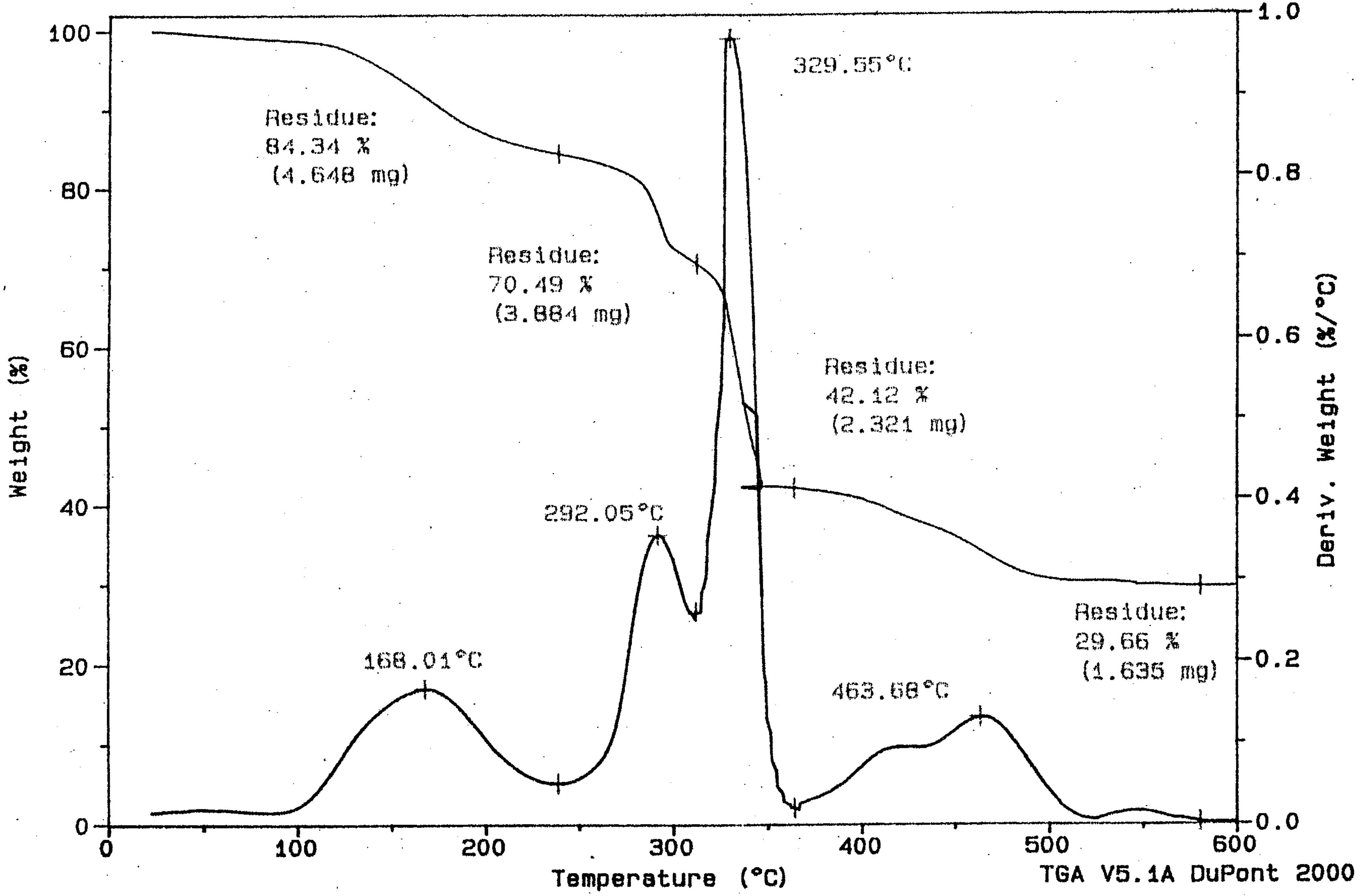


Fig. 41. TG curve of Ni^{II} + dto + 8-HQ complex

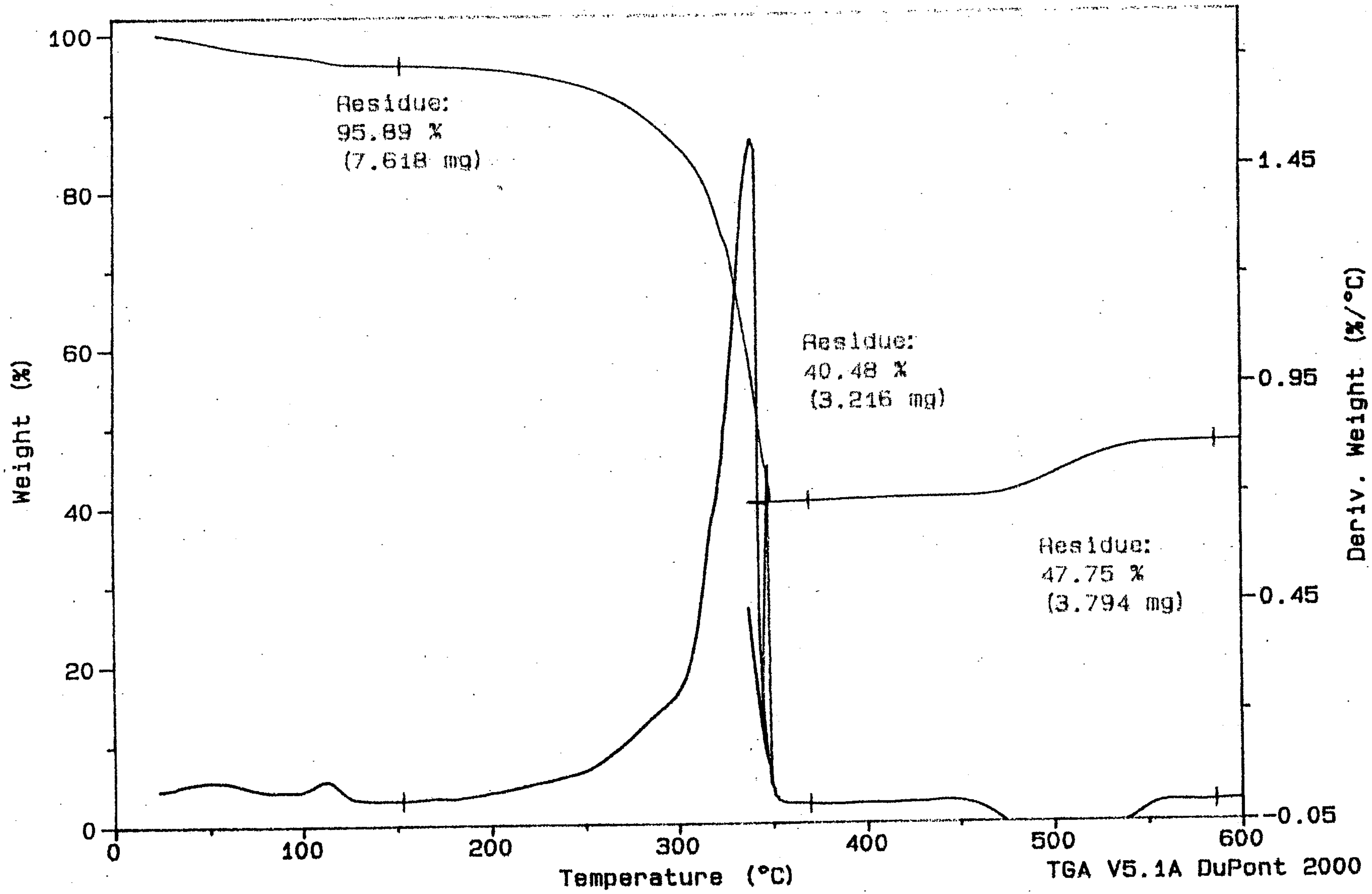


Fig.42. TG curve of Ni^{II} + dto + taa complex

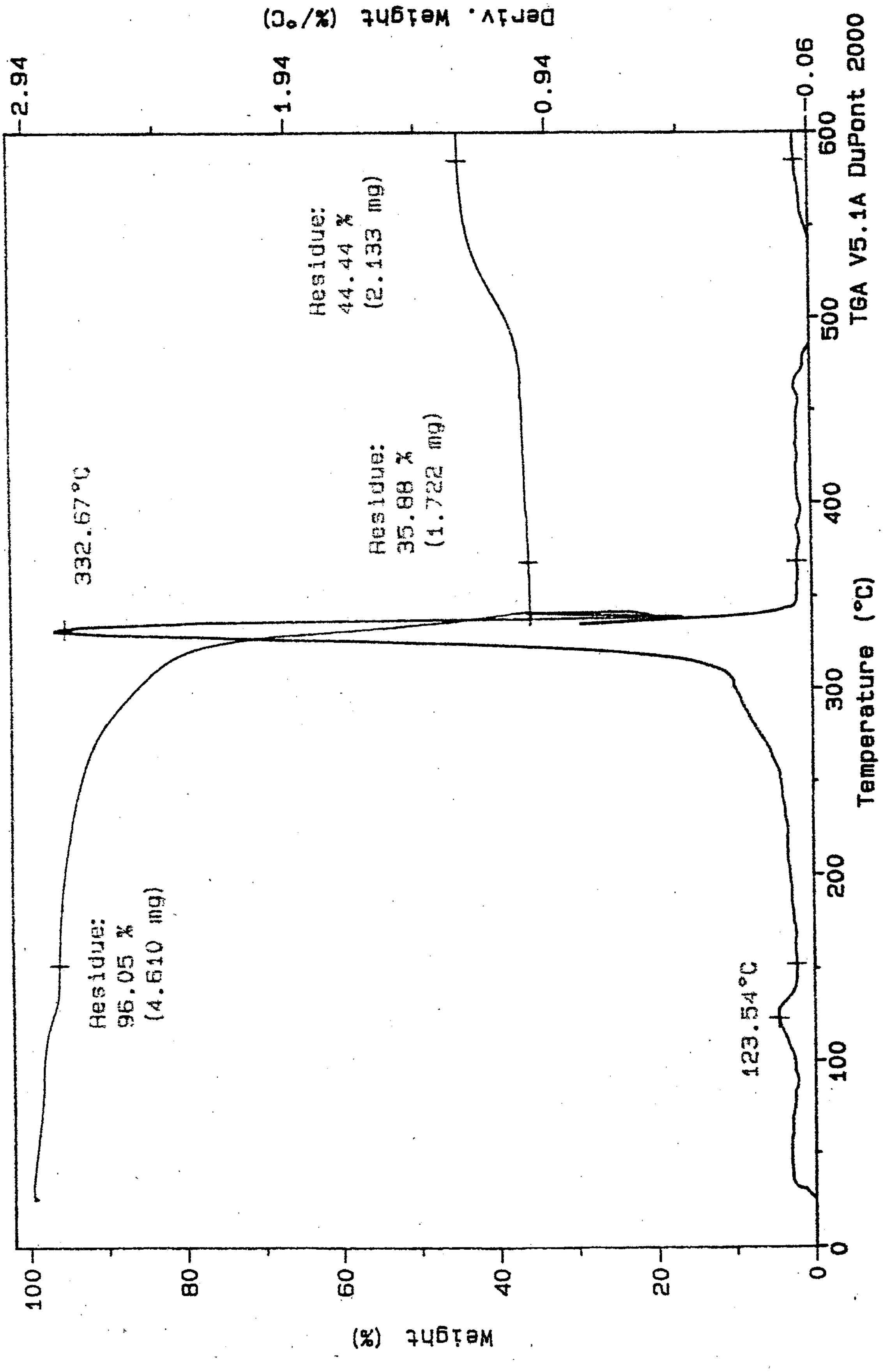


Fig. 43. TG curve of Ni^{II} + dto + sal complex

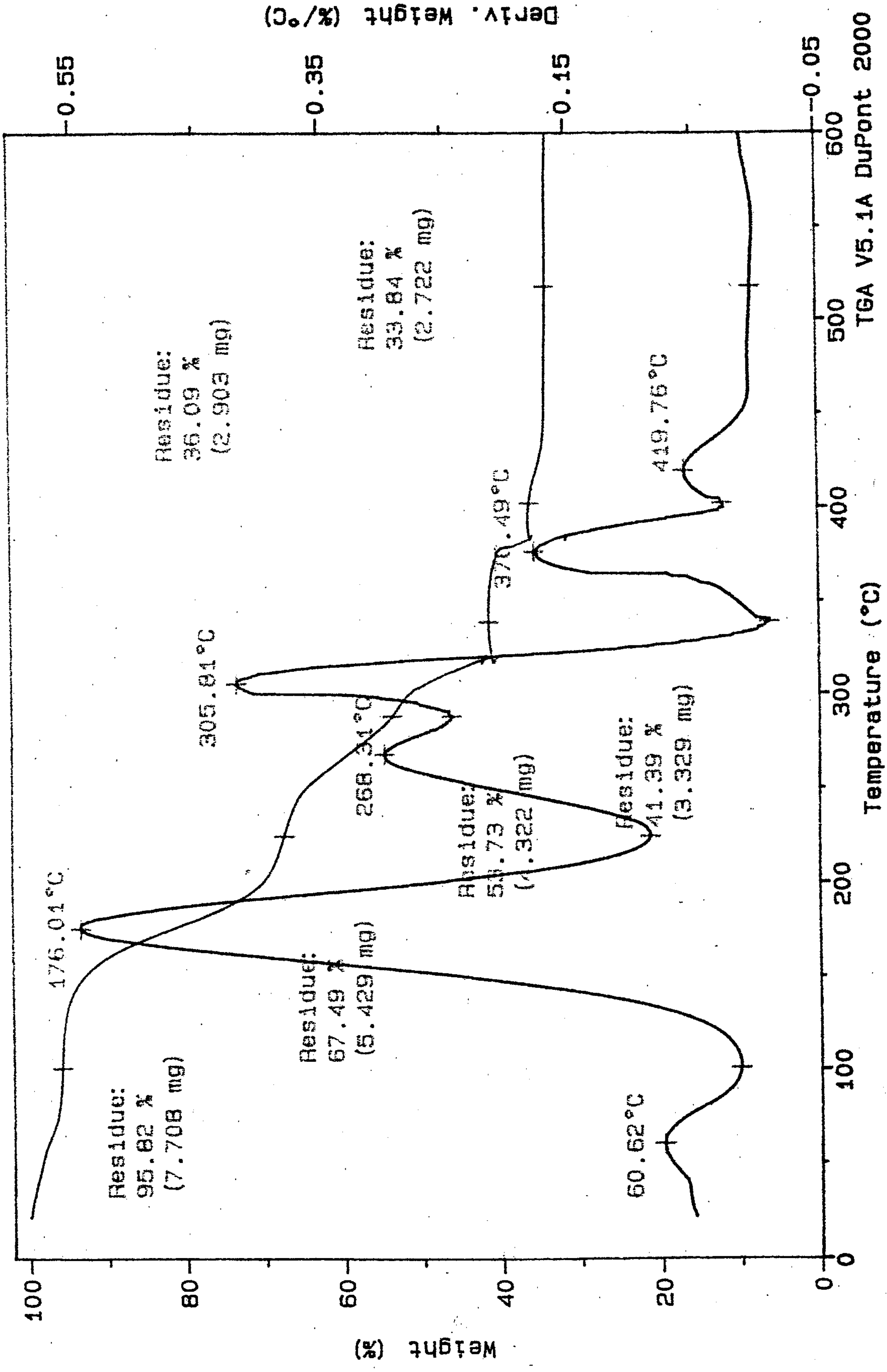


Fig. 44. TG curve of Cu^{II} + dto + 8-HQ complex

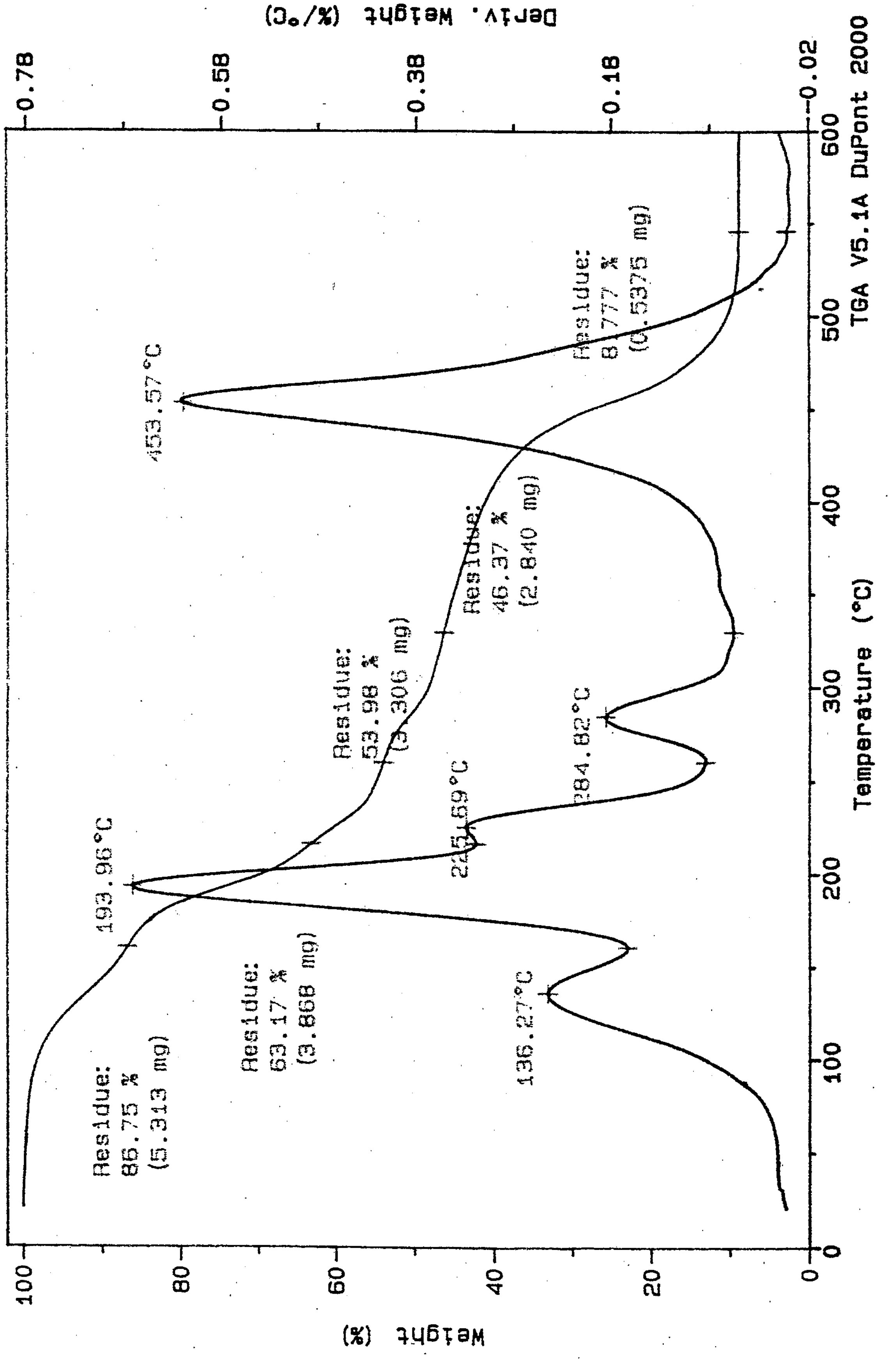


Fig. 45. TG curve of Cu^{II} + dto + o-phen complex

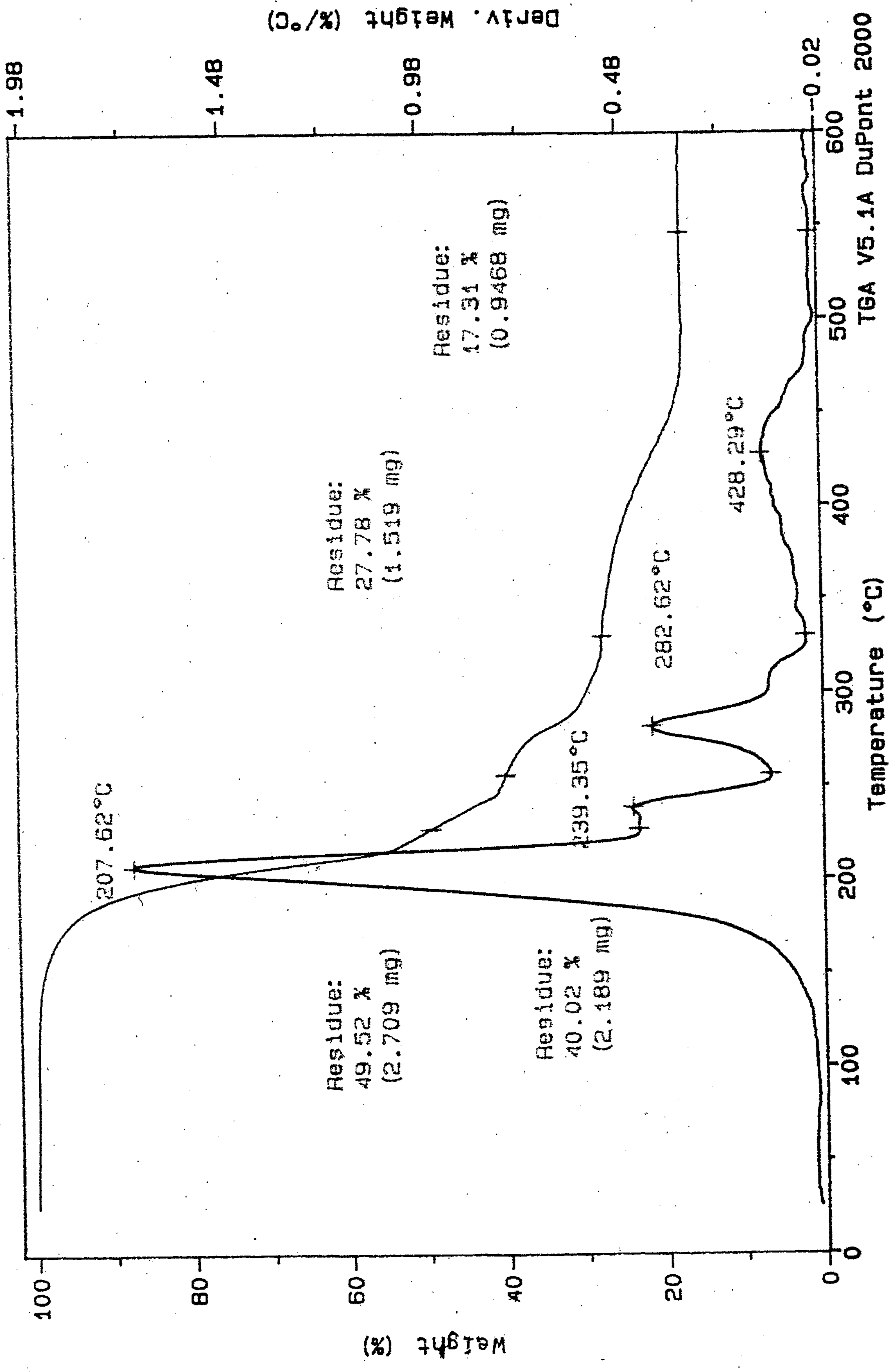


Fig. 46. TG curve of Cu^{II} + dto + sal complex

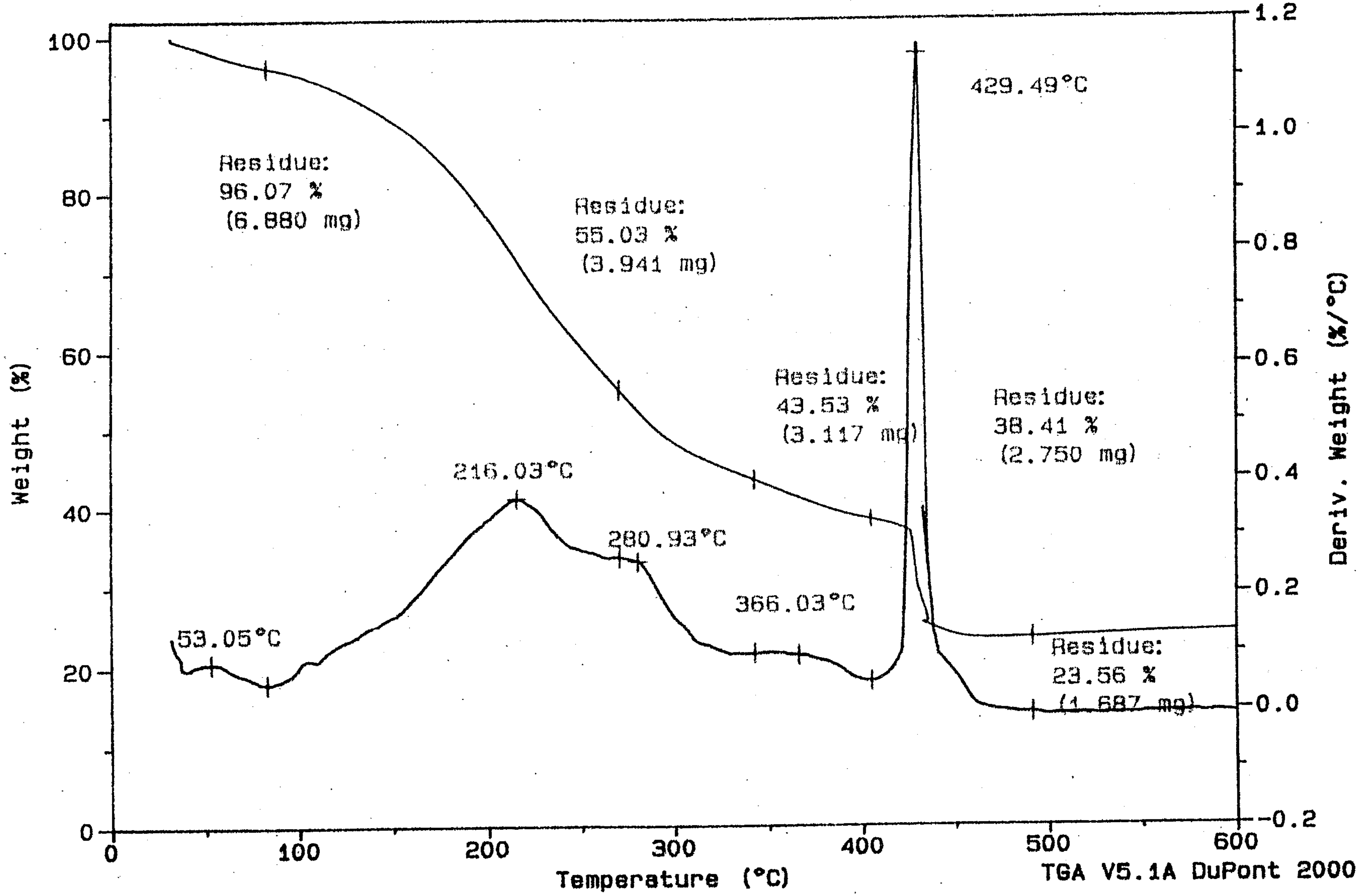


Fig. 47. TG curve of the binary Ru^{III} complex

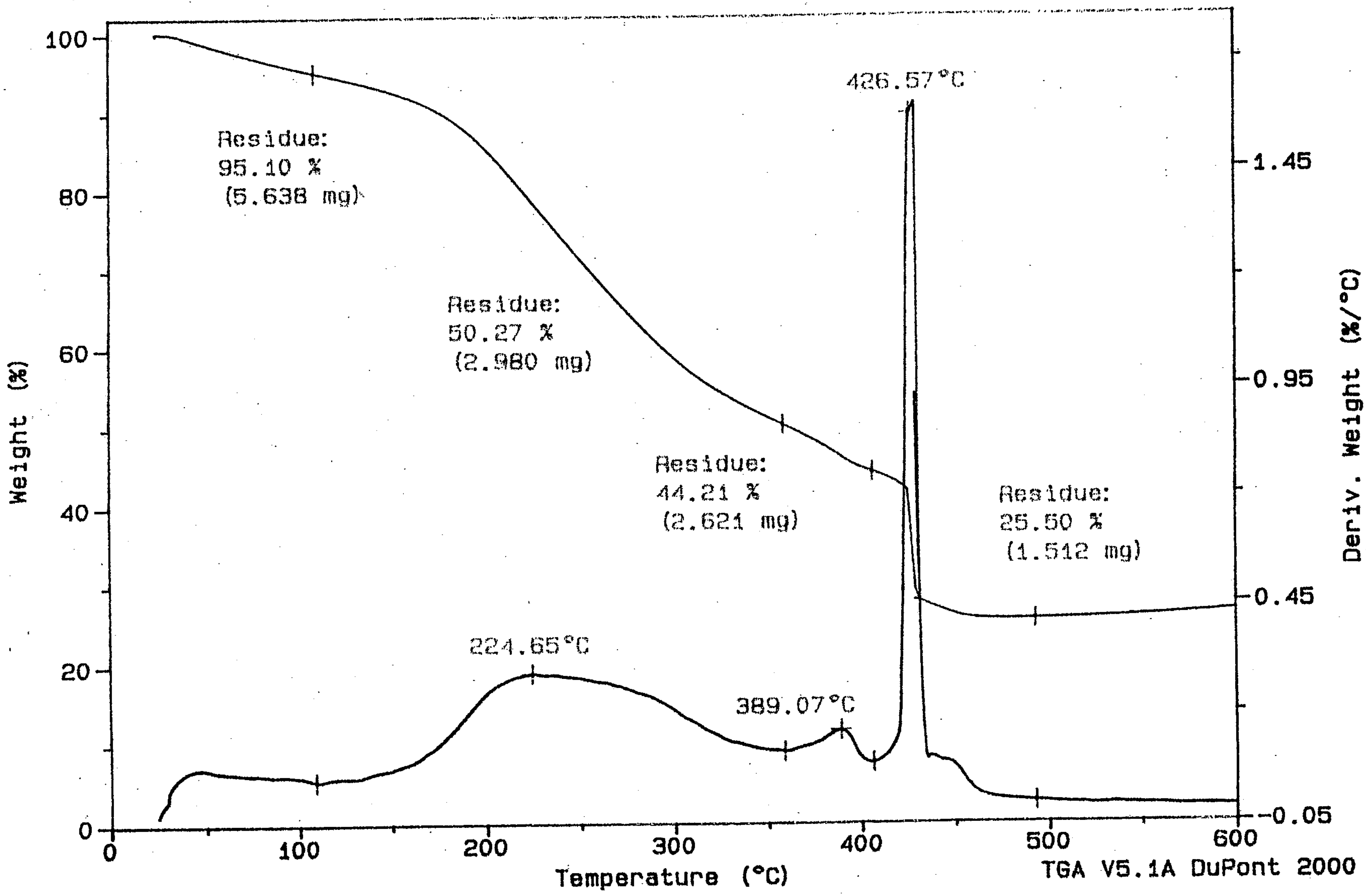


Fig. 48. TG curve of Ru^{III} + dto + 8-HQ complex

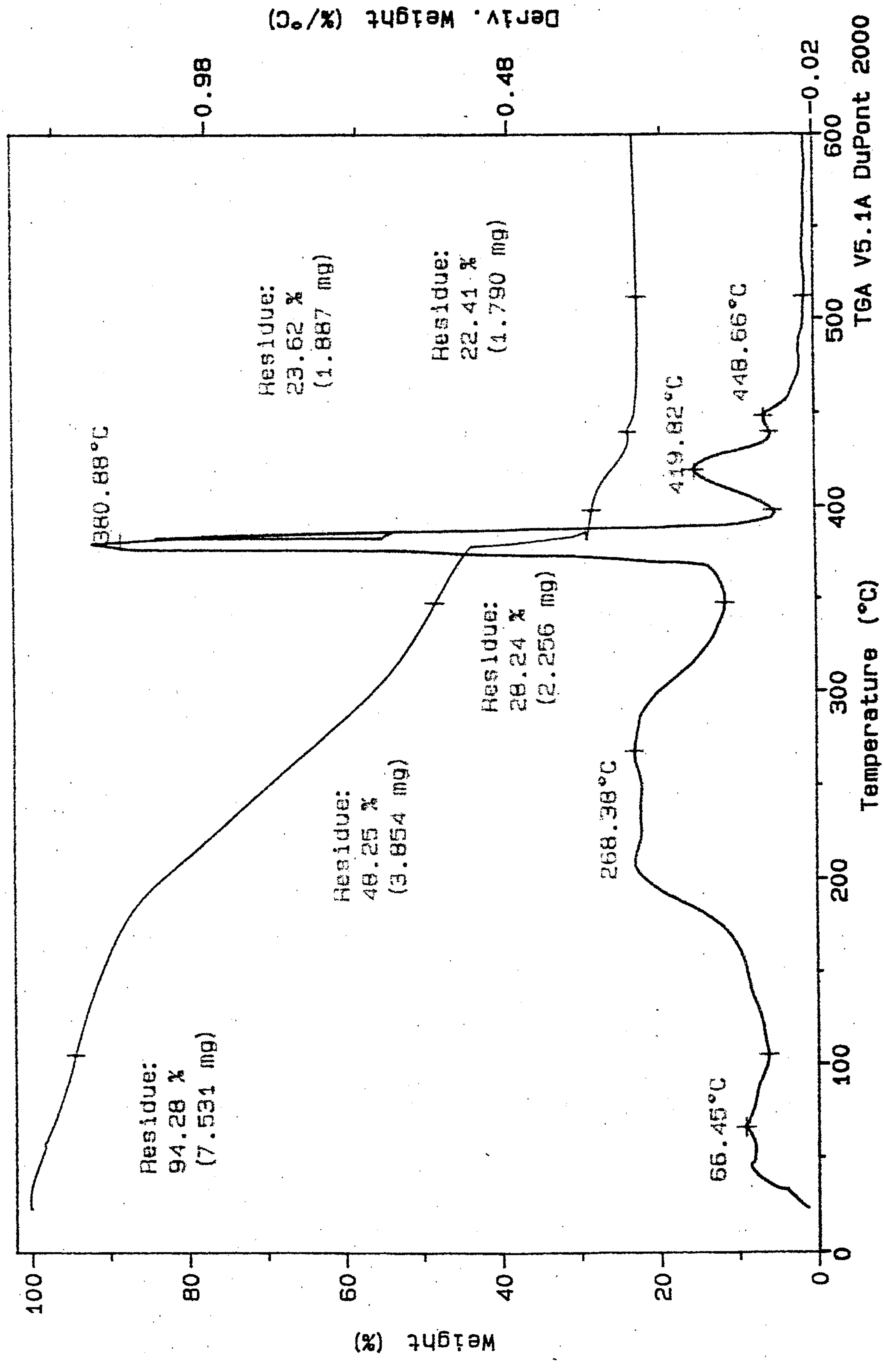


Fig. 49. TG curve of Ru^{III} + dto + sal complex

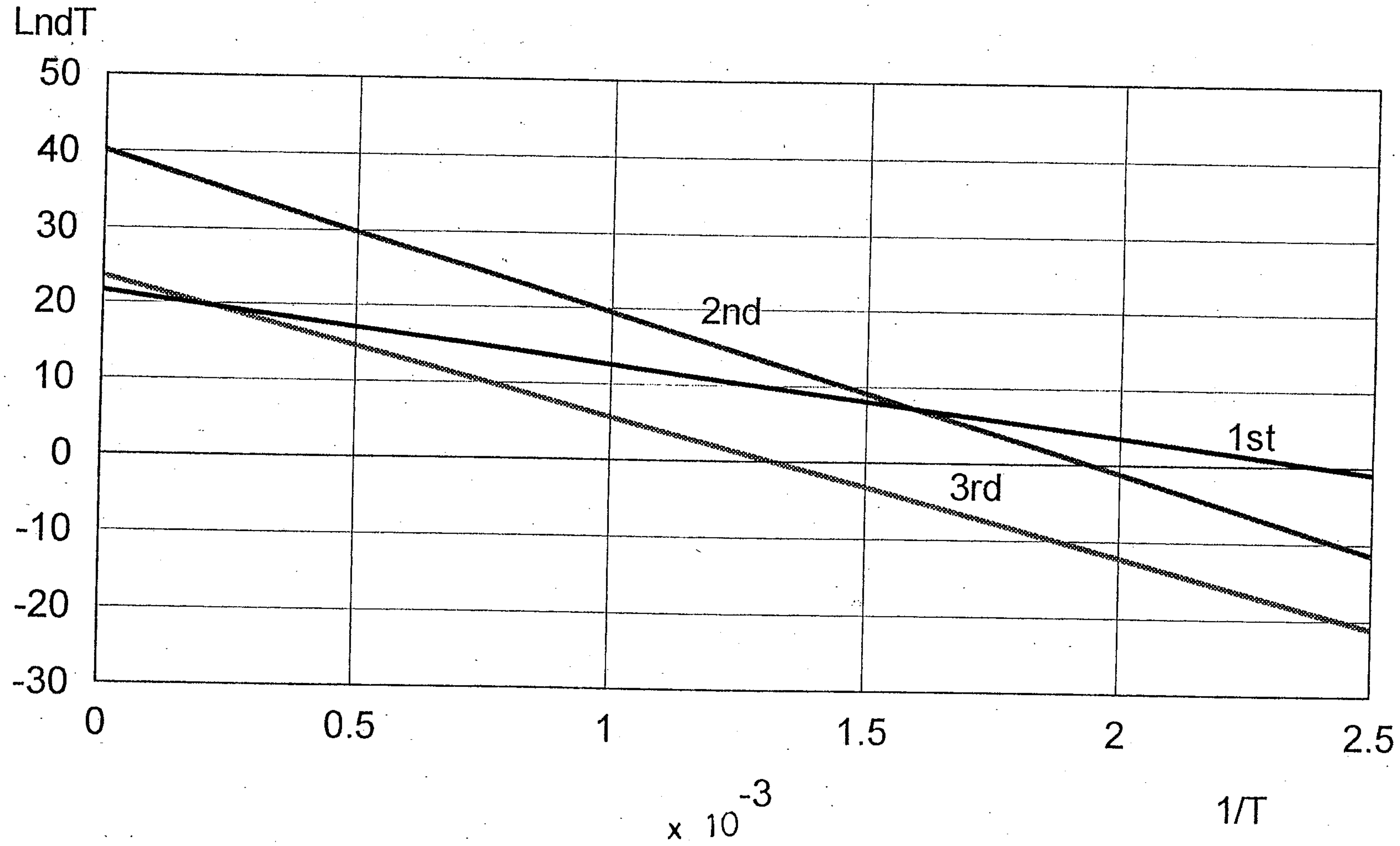


Fig. 50. Plot of *lndT* versus *1/T* of the binary Co^{II} complex

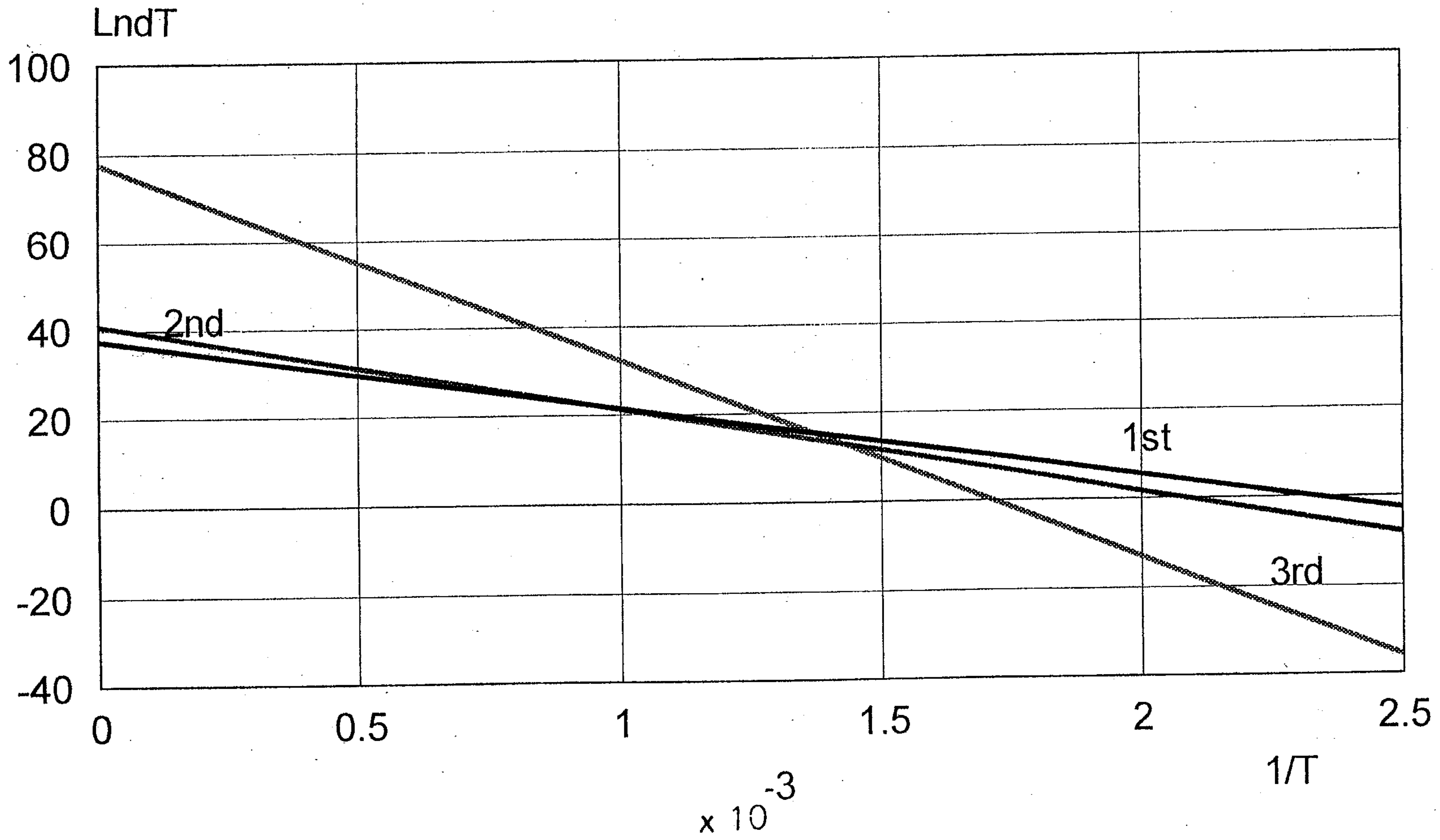


Fig.51. Plot of *lndT* versus *1/T* of the binary Ni^{II} complex

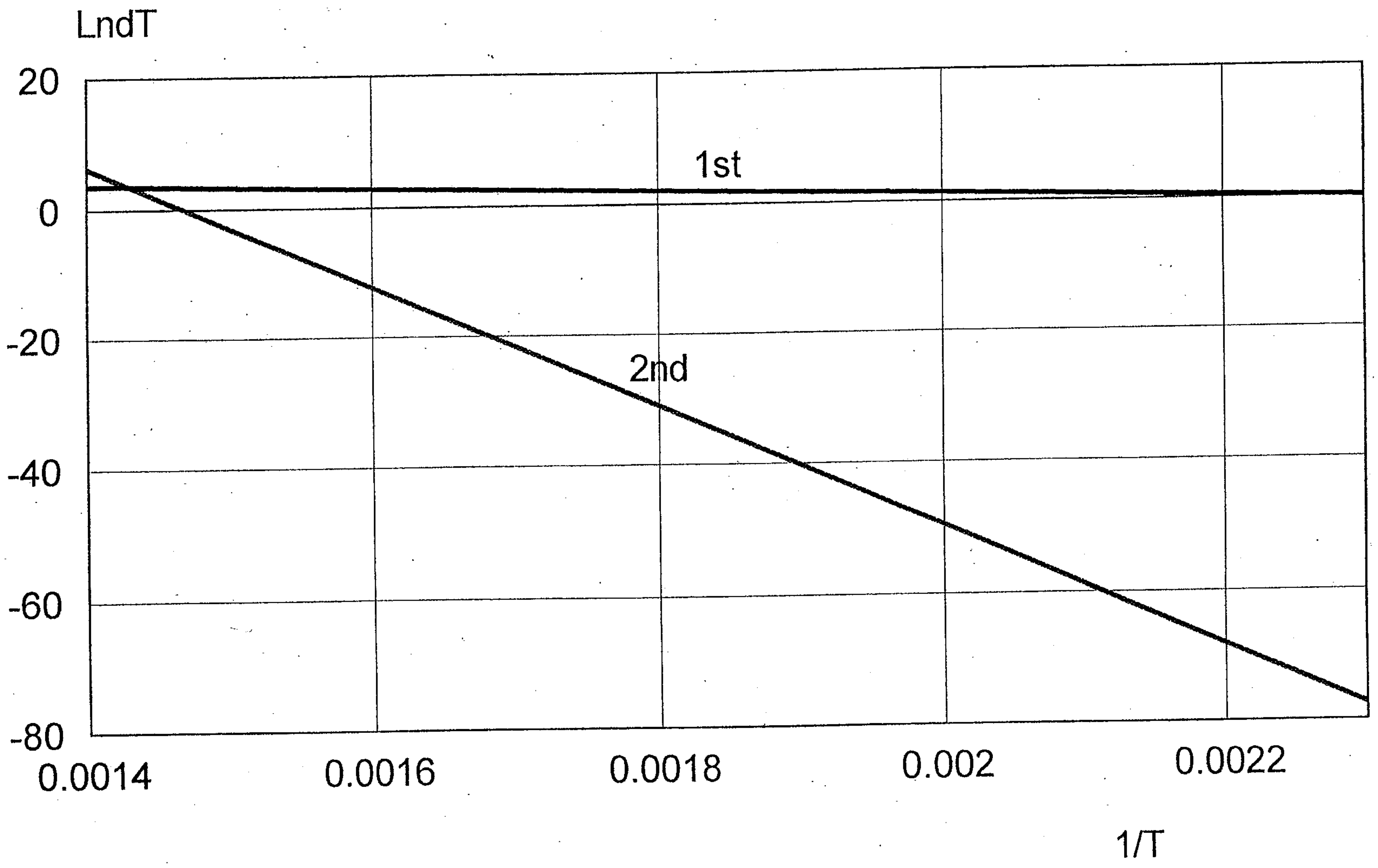


Fig. 52. Plot of *lndT* versus *1/T* of Ni^{II} + dto + acac complex

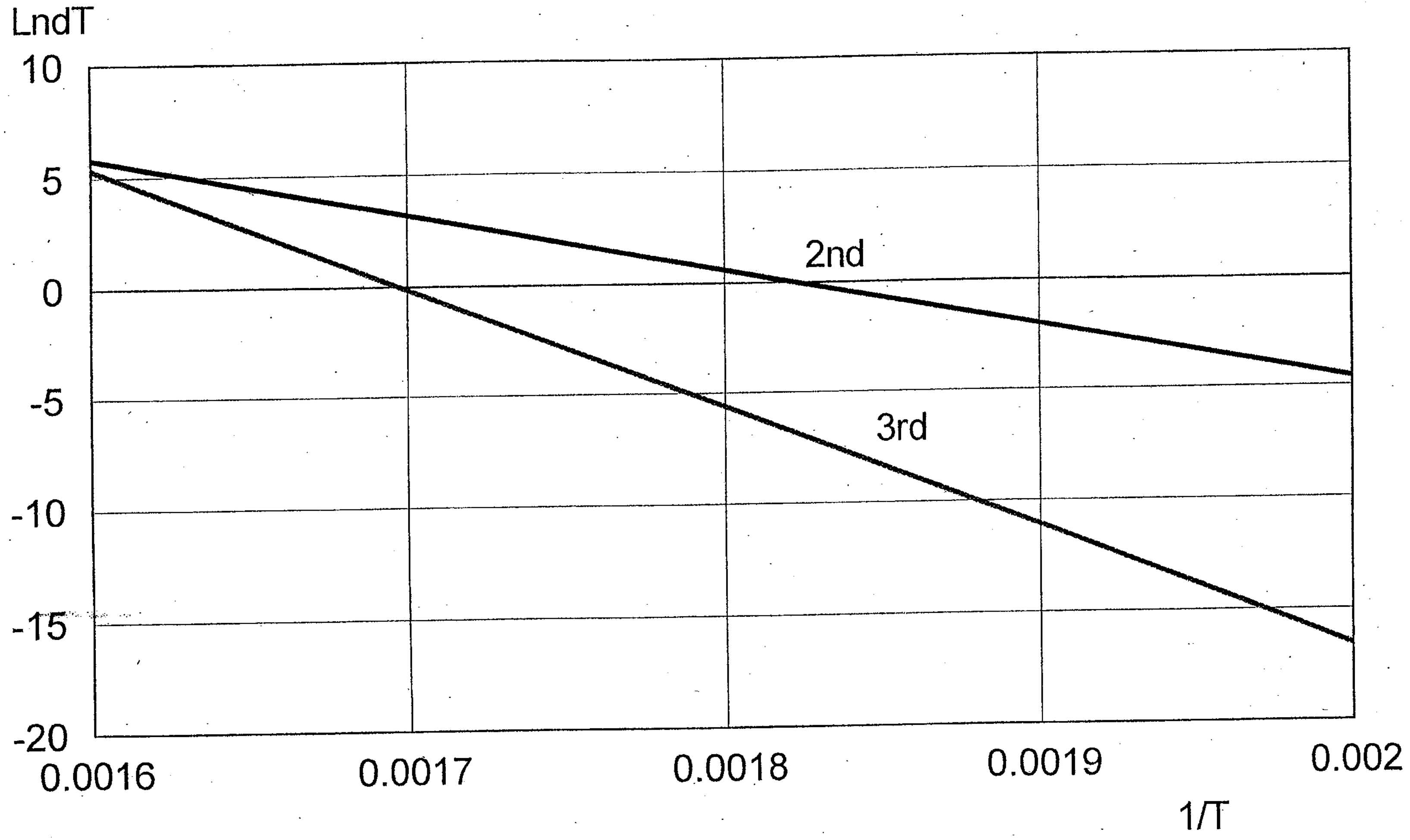


Fig. 53. Plot of *lndT* versus *1/T* of Ni^{II} + dto + 8-HQ complex

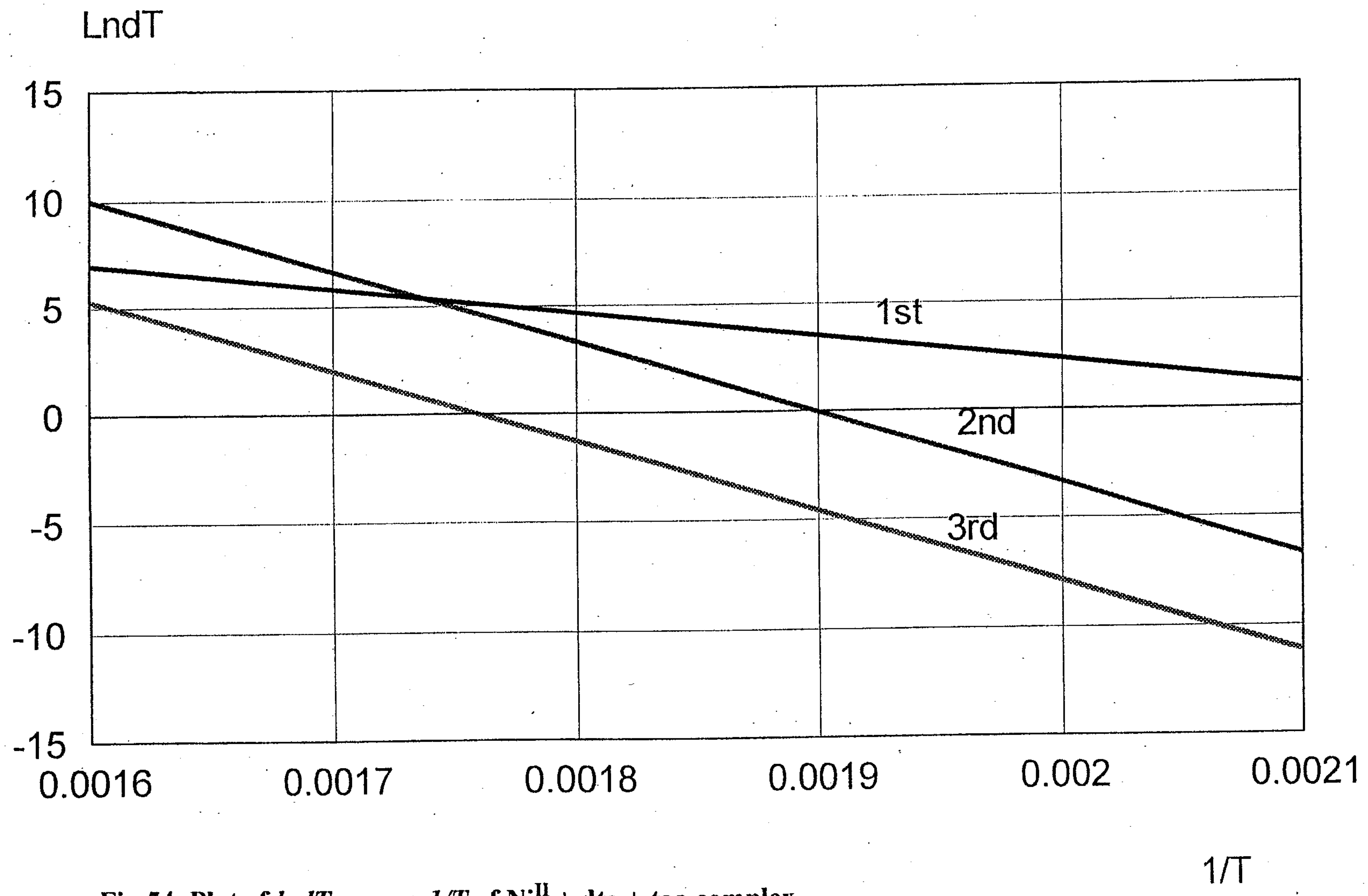


Fig.54. Plot of *lndT* versus *1/T* of Ni^{II} + dto + taa complex

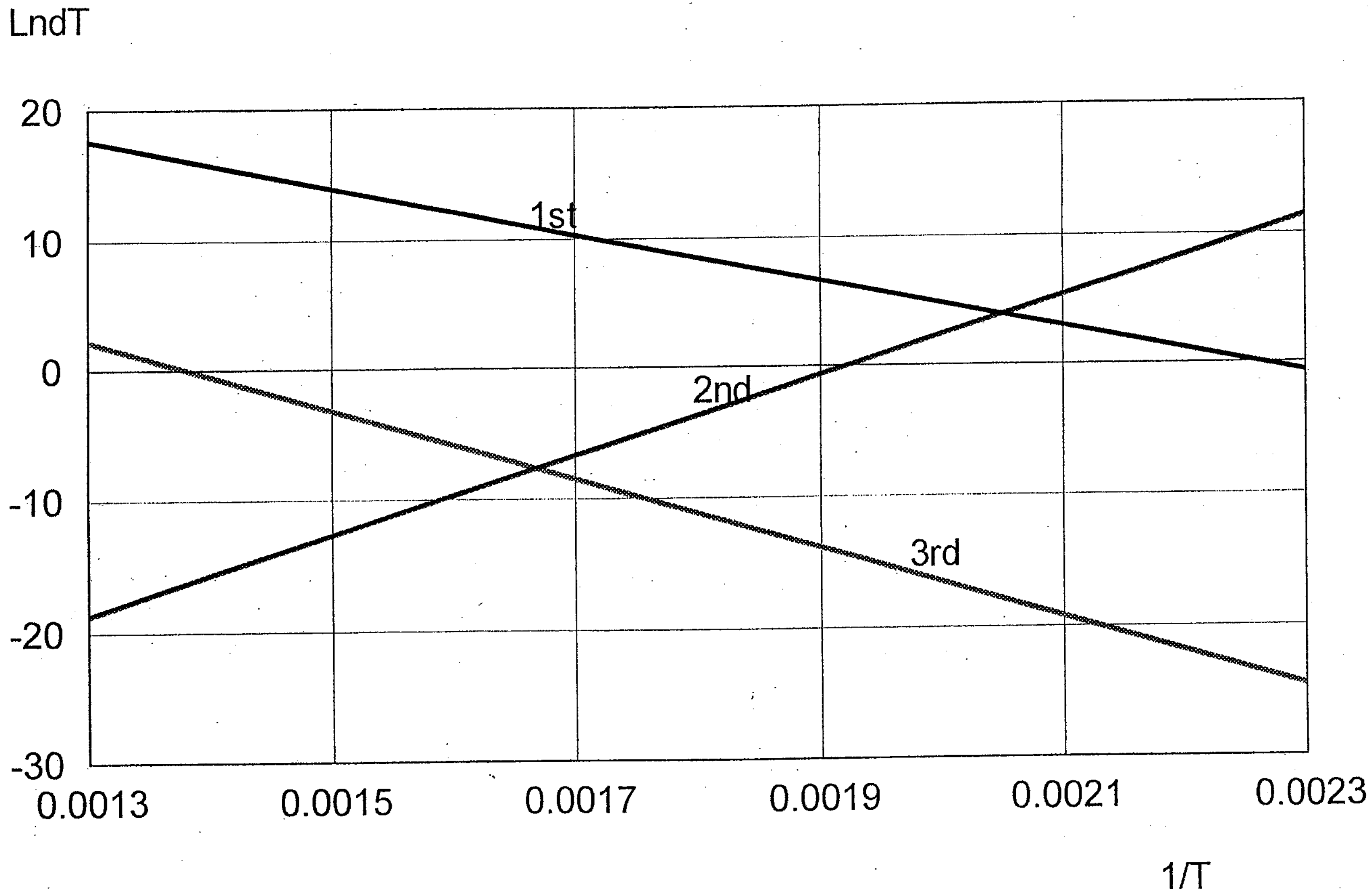


Fig. 55. Plot of *lndT* versus *1/T* of Ni^{II} + dto + sal complex

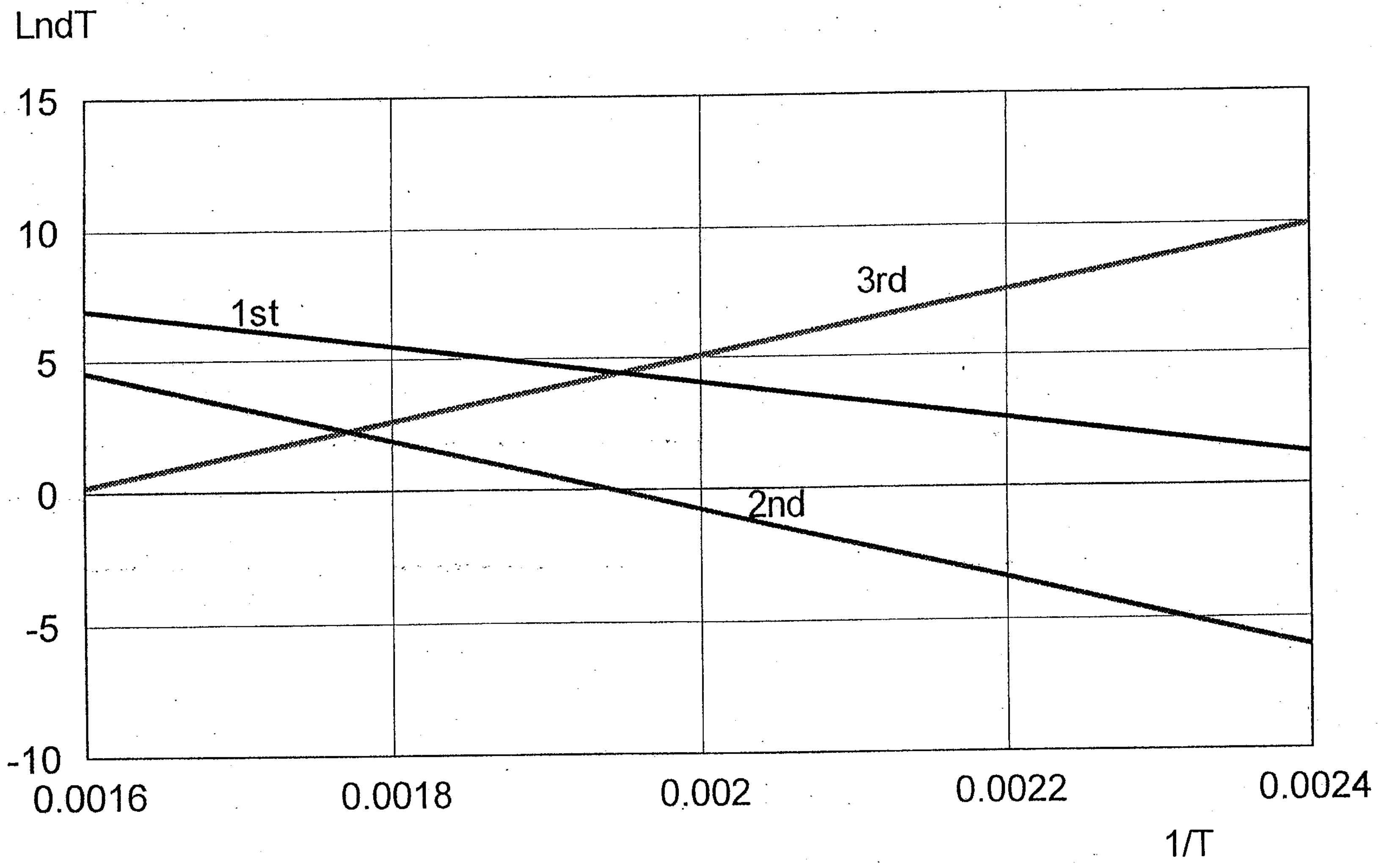


Fig. 56. Plot of *lndT* versus *1/T* of Cu^{II} + dto + 8-HQ complex

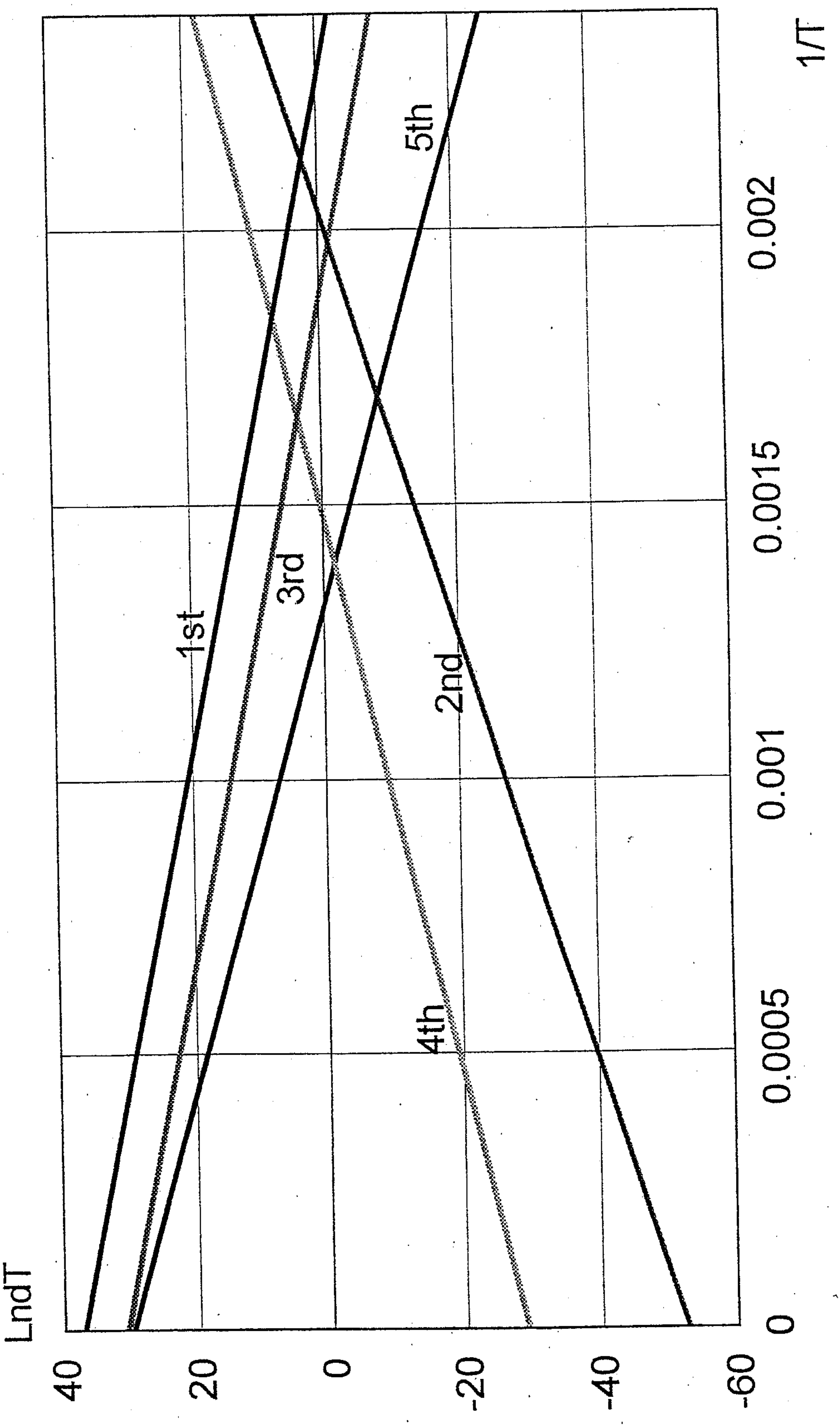


Fig. 57. Plot of *lndT* versus *1/T* of Cu^{II} + dto + o-phen complex

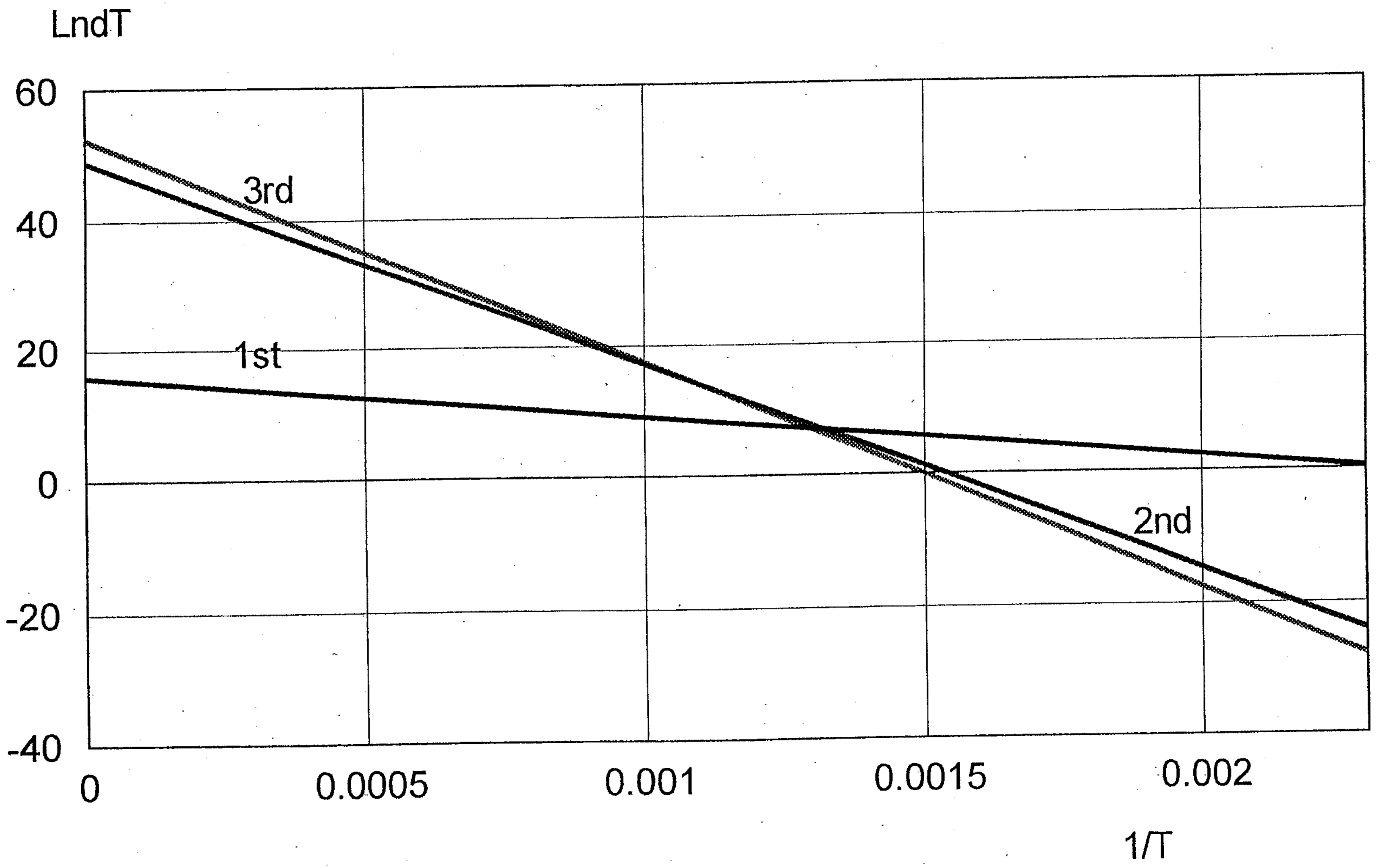


Fig. 58. Plot of *lndT* versus *1/T* of Cu^{II} + dto + sal complex

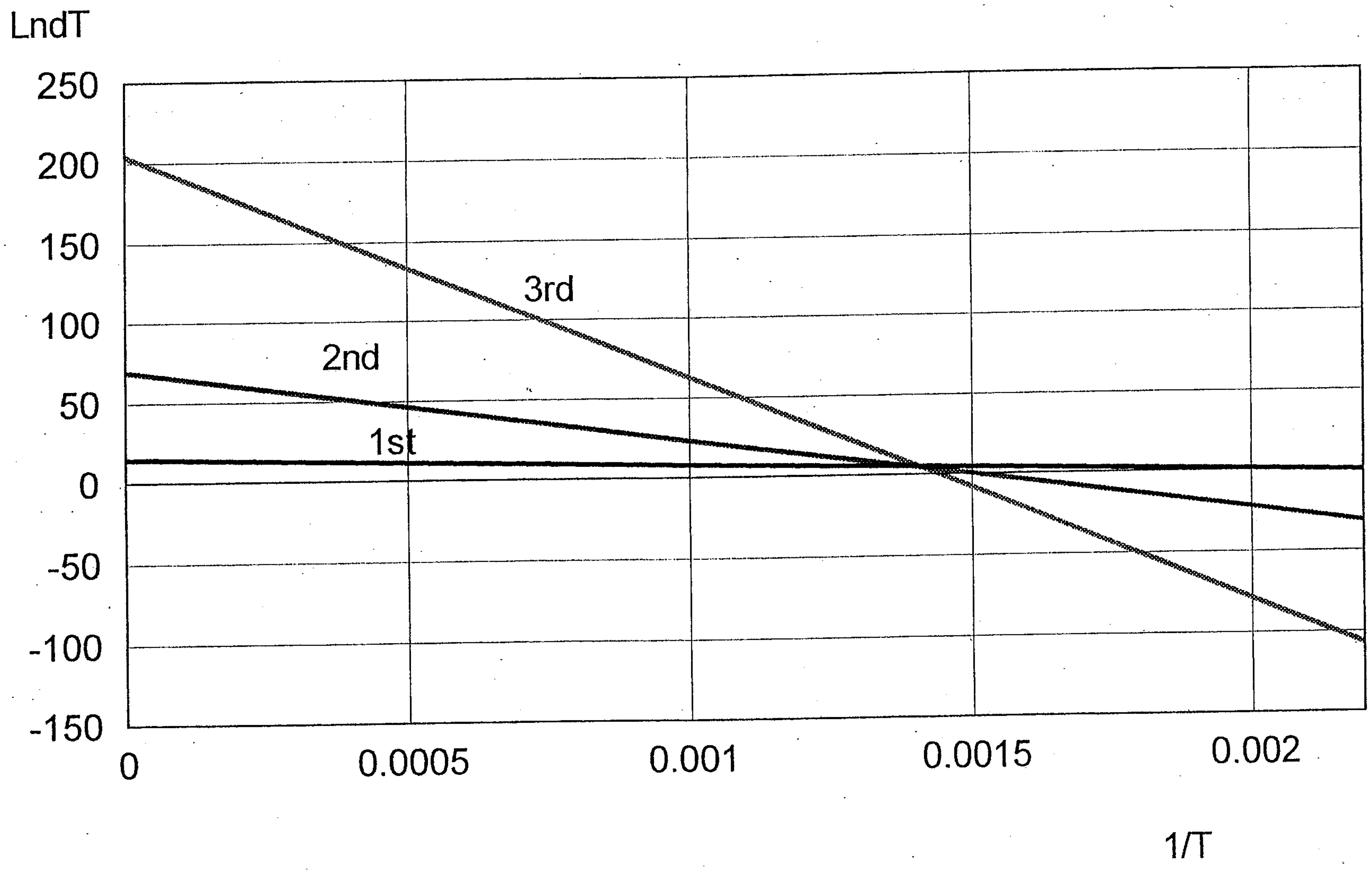


Fig. 59. Plot of *lndT* versus *1/T* of the binary Ru^{III} complex

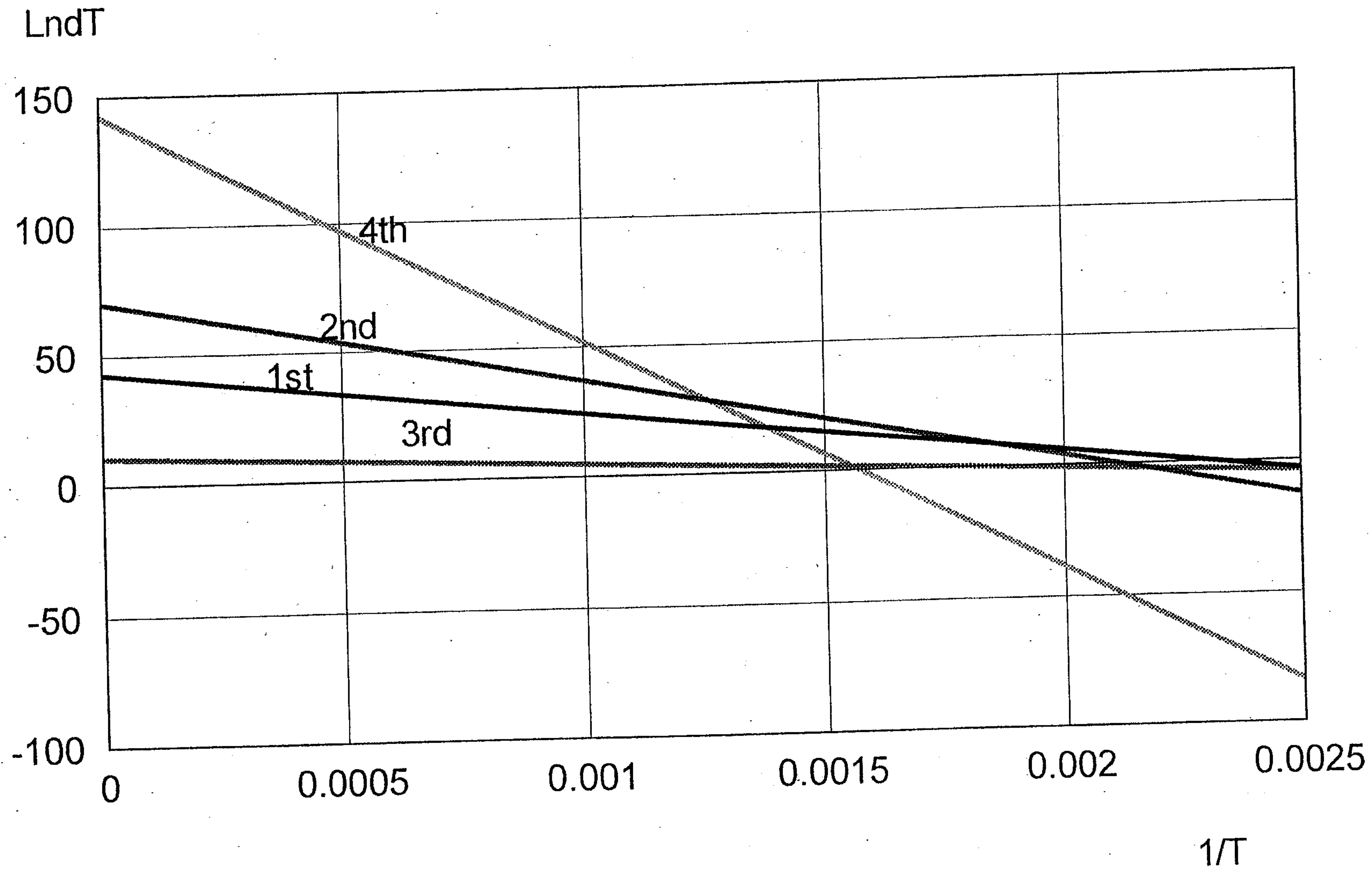


Fig. 60. Plot of *lndT* versus *1/T* of Ru^{III} + dto + 8-HQ complex

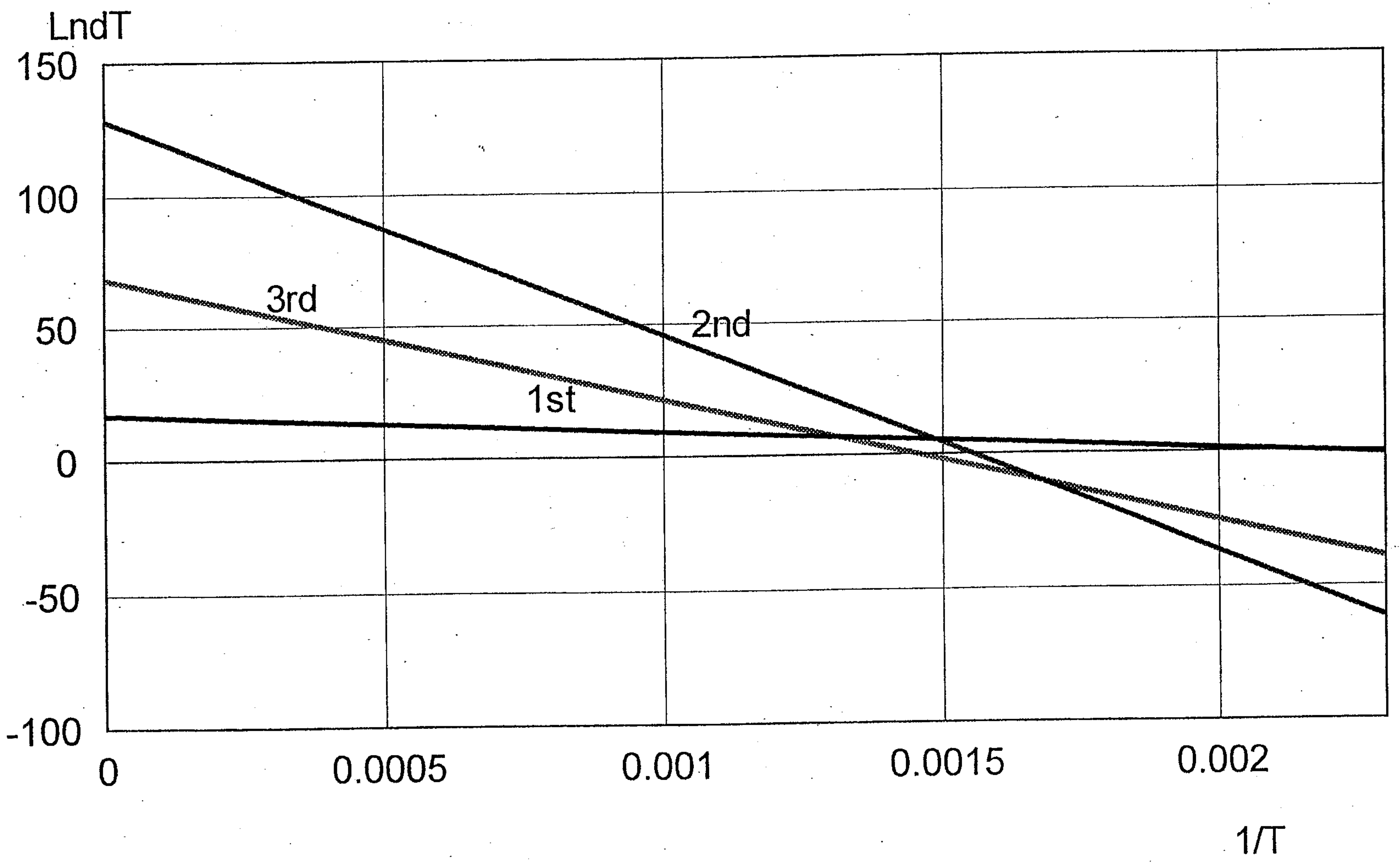


Fig. 61. Plot of *lndT* versus *1/T* of Ru^{III} + dto + sal complex

SUMMARY

SUMMARY

The general scope of this thesis is to present a systematic study on the transition metal complexes with dithiooxamide and their mixed ligand complexes formed by using a variety of secondary ligands with the intention to investigate the possibility of formation of the complexes in solution and to check their stability. It is also intended to isolate the complexes in the solid form to understand the mode of bonding between the ligand and the metal ions and also to investigate their thermal decomposition. The metal ions used are Co (II), Cu (II) and Ru (III).

In what follows, a brief description of the different chapters included in the present thesis is given.

1 - The **first chapter** reports a general literature survey on the metal complexes of dithiooxamide as well as other related N, S donor ligands. A survey on the biological and industrial importance of the metal ions used in this thesis is also given.

2 - In the **second chapter**, the experimental details for the spectrophotometric study of complex formation of solution and the methods used for determining the steroichiometry and formation constants are described. The methods used for preparation of the solid complexes as well as the methods of determination of the metal ion content in these complexes are

reported in this chapter. The various equipments used for different measurements are also given.

3 - **Chapter III** is dealing with the study of the binary and mixed ligand Co (II), Ni (II), Cu (II) and Ru (III) complexes formed in solution. The study involves spectrophotomertic determination of the stoichiometry of the complexes using the molar ratio and continuous variation methods as well as evaluation of the apparent formation constants of the complexes formed in solution. The results obtained were discussed in relation to the nature of the metal ion and also to the basic character of the secondary ligand.

4 - **Chapter IV** reports the synthesis and characterization of the solid complexes of Co (II), Ni (II), Cu (II) and Ru (III) with dithiooxamide as the primary ligand and a number of secondary ligands. The secondary ligands used are 8 – hydroxyquinoline, acetylacetone, o- phenylenediamine, salicylic acid and thio-acetamide. Characterization of the isolated solid complexes has been accomplished using several tools in including elemental analysis, conductivity measurements, infrared and electronic spectroscopy. The studies given in this chapter revealed the following con clusions:

(I) The NH_2 groups of dithiooxamide have an ammonium type character due to intermoleeular or intramolecular association.

(II) The dto molecule acts as bidentate ligand capable of coordination to the metal ions as S,S or S,N donor.

(III) The dto molecule behaves as ambidentate ligand forming a variety of complex species depending upon the pH of the medium. The complexes formed are either monomeric or polymeric depending on both the nature of the metal ion and the medium in which the complexes were prepared.

(IV) The binary and mixed ligand Ni (II) complexes are all four coordinate and assume a square planar geometry. The Co (II) and Ru (III) complexes are hexa-coordinate assuming octahedral stereochemical configuration while Cu (II) complexes were found to be of either square planar or tetragonally distorted octahedral environment.

5 - **Chapter V** includes the results of the thermogravimetric analysis of a selected number of the isolated solid complexes. The study provides an investigation of the way by which thermal decomposition of the complexes takes place where it was found that the final product of the decomposition could be either the metal sulfide or oxide depending on the nature of the secondary ligand. The kinetics of dissociation of the complexes have been studied and the thermodynamic parameters were determined and discussed.

Finally, the thesis was ended with a list of the references used.

REFERENCES

REFERENCES

1- F. Feigl and V. Anger, "Spot Tests In Inorganic Analysis" 6th Edn, Elsevier, London, (1972).

2- R.N. Hurd, G. De La Mater, G.C Mc Elheny and J. P. Mc dermott, " Advances In The Chemistry Of Coordination Compounds" S. Kirschner Ed., Macmillan, New York 1961, P.30.

3- G.Y.Ye ,Y.Nakano , G.R Frauenhoff, D.R Whitcomb, F . Takusagawa and D. H . Busch, Inorg. Chem , **30** , 1603 (1991).

4- P .Ray, J Xavier ,J. Ind Chem. Soc. **38**. 535, (1961)

5- K. Lieber Meister and G.Z Hagelloch, Z. Naturforsch **5B**, 79 (1950).

6- D.A. Ostlie, U.S Patent 3481759 , 1969 ; Chem. Abst. **71** ,72 167 (1969)

7- W. J. Stratton and D.H. Busch, J. Am. Chem. Soc. **82** ,4834 (1960)

8- L. Menabus, G.C. pellacani and G. Peyronel, Inorg. Nucl. Chem. Lett. **10** , 187 (1974).

9- A, Pignedoli and G. Peyronel, Gazz Chim. Ital,**43,** 546(1963).

10- H.O Desseyn , W.A. Jacob and M. A. Herman, spectrochim Acta, **25 A**, 1685 (1969)

11- G . Peyronel, A. C. fabretti and G. C. Pellacani , J. Inorg. Nucl. Chem. **35**, 973 (1973)

12- G.C. Pellacani and G.Peyronel, Ionrg. Nucl .Chem .Lett **8**, 299 (1972) ; A.C. Fabretti, G.C. Pellacani and G. Peyronel, Gaazz. Chim. ltal **103** , 397 (1973)

13- N.O. Desseyn , B. J. Vander Vaken and M. A. Herman, Appl. Spectorsc . **32** , 101 (1978).

14- H. Hofmans, H .O. Desseyn and M.A. Herman , Spectrochim. Acta **38** A , 1307 (1982) .

15- M. R. Grecn, N, Jubran, B. E. Bursten and D. H. Busch, Inorg. Chem. **26**, 2336 (1987).

16- H. Hofmans, H.O. Desseyn , R.A. Dommisse, P.V Nuffel and A.T.H lenstra , Transition Met. Chem. **9**, 213 (1984) .

17- L. Antolini, A.C. Fabretti, G. Franchini , L. Menabue G.C. pellacani, H. O. Desseyn, R. Dommisse and H. C. Hofmans J. Chem Soc Dalton Trans , 1921 (1984).

18- H. Hofmans , H.O Desseyn J. Shamir and R. Dommisse , Inorg. Chim. Acta **45** L227 (1981) .

19- A. Pignedoli and G. Peyronel, Acta Crystallogr **B33** 1439 (1977).

20- R. N Hurd ,G. De la Mater, G.C. Mc El heny and L.V. Peiffer, J. Am. chem . Soc . **82** , 4454 , (1960)

21- C . R . Kanekar and A.T. Casey , J. Inorg . Nucl Chem. **31** , 3105 (1969)

22- J. E. Sarneski , H. L. Surrenant, F. kmolen and C.N. Reilley , Anal Chem. **47** , 23216 (1975)

23- B. Slootmaekers , S .P. Perlepes and H. O. Desseyn spectorchim. Acta **45** , 1211(1989)

24- H. Hofmans and H . O. Desseyn, Thermochim. Acta **85** 67 (1985)

25- B . Slootmaekers , S. P. Perlepes and H. O. Desseyn, Spectroc. Int. J. **4,** 265(1985)

26- H. Hofmans and H.O. Desseyn, Bull Soc. Chim. Belg. **95** 83(1986)

27- P. Geboes E.L. Esmans and H.O. Desseyn Thermochim. Acta **124,** 17 (1988).

28- P. Geboes and H.O. Desseyn, Spectorchim. Acta **44,** 963 (1986)

29- G. Peyronel G.C. Pellacani G. Benetti and G. Pollacei J. Chem. Soc. Dalton Trans. 867 (1973)

30- R .L. Martin and A. F. Masters, Inorg .Chem. **14**, 884 (1975)

31- G.C. Pellacani G. Peyronel G. Pollocci and R. coronati , J. Inorg. Nucl chem. **38,** 1619 (1976)

32- G.C Pellacan, G peyronel T . Feltri and Menabue, spectrochim. Acta **32A** ,285 (1976)

33- A. Ray and D.N. Sathyarayana, Ind. J. chem. **15 A**, 591 (1977) .

34- S.H.J. De Beukelcer and H.O. Desseyn spectrochim. Acta **51 A** , 1617(1995)

35- B. Slootmaeker, E. Manessi – Zoupa, S.P. Perlepes and H.O. Desseyn, Spectrochim Acta **52A** , 1255 (1996)

36- B . Slootmaekers , A.C. Fabretti, H.O. Desseyn and S.P. Perlepes, Spectrochim. Acta **52 A** , 1275 (1996)

37- B. Slootmaekers A.C. Fabretti , H. O. Desseyn, R. Vochten and S.P. Perlepes, Spectrochim. Acta **52** A, 1883 (1996)

38- M. A. El–Gahami, Synth. React. Inorg. Met – Org. Chem. **21** , 623 (1991)

39- O.V. Mikailov and V.K. Polovnyak, Ind. J. Chem. **31A,** 54 (1992)

40- Z. Semekal , F. Brezina Z. Sindelar, R. klicka and M. Nadrorink, Transition Met. Chem. **21**, 49 (1996)

41- S.O. Akapo, Anal Chim. Acta **34**, 35 (1997)

42- M.C. Aversa, P. Bonaccorsi, D.W Brucea , F. Caruso, P.Giannetto, S. lanza and S. Morrone , Inorg. Chim. Acta **256** , 235 (1997)

43- P.J. Werkman, A. Schasfoort R.H . Wicringa and A.J. Schouten, Thin Solid Films **323** , 243 (1998) .

44- S. K. Sengupta O.P. Pandey and G. K . Pandey, Ind. J. Chem. **37A** , 644(1998)

45- B . Slootmaekers, R. Kauleers , J. Janssens and H.O. Desseyn, Thermochim Acta **311** , 141(1998) .

46- M.A. Abou Taleb, L. Labib and M.F. Iskander, Polyhedron 13 3015 (1194)

47- P. Kopel , F. Brezina, Z. Travnicek, Z. Sindelar, J. Lasovsky and J. Marek, Polyhedron **14**, 199 (1995)

48- .L Long, D.X Zeng X .Q. Xin and B.S. Kang, Synth. Rect. Inorg. Met- Org. Chem. **26**, 723 (1996)

49- G.Rosace , G. Guffrida, M Saitta G.Guglielmo , S Campagna and S. Lanza , Inorg. Chem. **35**, 6816 (1196)

50- K. R. Barnard , A. G. wedd and E.R. Tick, Inorg. Chem. **29** , 891(1990)

51- H.T. Dicek and M. Form, Angew Chem. Int. Ed . Engl. **14**, 250 (1975)

52- H.T. Dieck and M.Form , Z Anorg Allg. Chem. **515**,19 (1984).

53- T. Kitson , Echic Chem., **22**, 43 (1985)

54- N. E, Dixon .C Gazzala, R. L . Blakeley and B. Zerner, Science, **191** , 114 (1976)

55- B . Macias . J. J. Criado , M . V Vialla , M. R. Iglesias and M. Castillo, Polyhedron, **12** , 501 (1993)

56- S.J. Lippared , Pure Appl .Chem., **59** , 739 (1987)

57- M. Castillo, J.J. Criado , B. Macias and M. V. Vaquero , Inorg. Chim. Acta **124**, 127 (1986)

58- B . Macias, M. V.Villa and R. Rodriguez – Gallego , Transition Met. Chem., **20**, 347 (1995)

59- J. J. Criado .J.M Salas and M. Medard, Inorg. Chim. Acta, **174**, 67(1990)

60- A.S.A. Zidan , A.A El-Said and A. A. M. Aly, Synth. React. Inorg. Met. Org.Chem. , **22**,1355 (1992)

61- M. J. Kendrick, M. T. May, M. J. Plishka and K .D., Robinson, Metals in Biological System Ellis Horwood , New York (1992)

62- M.G. Kanatzidis, Inorg. Chim. Acta **168**, 101 (1990)

63- P.A. Lindahi , N. Kojima, R. P. Hausinger, J .A . Fox . B. K Teo, C.T. Walsh and W.H. Orme- Johnson , J. Am. Chem. Soc. 106 3062

64- S. J .Lippard , Prog. Inorg. Chem. **11** , 23 4 (1970)

65- K.D. Karlin and J. Zubieta, in "Copper Coordinate Chemistry Biomedical and Inorganic Perspective" , Adenie press, Albany , NY (1983)

66- E. L. Ulrich and J. L. Markley , Coord. Chem. Rev. **27** , 109 (1978)

67- P.M. Collman ,H.C Freeman , J. M Guss , M Murata,V.A Norro, J. A. M Ramshar and M. P. Venkatapa , Nature **272** , 319 (1978).

68- D. Davis and R.S. Drago, C.K., Inorg . J. Chem. 27 ,4759, (1988)

69- C.M., Che , W.H Leung. and C.K. J. Poon. . J. Chem. Soc. Chem. Commun, 173 (1987).

70- C.M. Che and V.W. Yam, J. Amer .Chem. Soc. **109**-1262, (1978).

71- A. M. El-Hendawy and M.S. El-Shahawi, polyhedron **8**, 2813 (1989).

72- B. Meunier Bull Soc. Chim. Belg. **4**, 57 (1986)

73- Y. Uemorri, H. Myakawa and E. kyuno, Inorg. Chem. **27**, 377 (1988)

74- L. Marko, J. Organomet. Chem. , **305**, 333(1986)

75- Y. Uemori , H. Miyakawa and E. Jyuno, Inorg. Chem. 27 377 (1988)

76- G. Gross and J.P. laruent, Inorg. Chim. Acta **105**, 63 (1995).

77- M. M. Taqui Khan, Ch. Sreelatha , Mirzza S.A. Kamachand Raia and Abdi S.H., Inorg. Chim. Acta **154**, 103 (1988)

78- M.M. Taqui Kan, Kan N.H. Kureshy R. I. and Borcicha A.AB ., Inorg. Chim. Acta **174** , 175 (1990)

79- M.M.Taui Khan, S.A. Mizra Z.A. Shaikh Sreelatha Ch., Panl P., Shukla R. S., srinivea D., Prakas Rao, Abdi S.H., Bhatt S. D. and Ramachandraiah G., Polyhedron **11** , 1821 (1992)

80- A. M. El – Hendawy, Polyhedron **9**, 2309 (1990)

81- D.D. Agarwal, Jain R., Charkavorty A. And Restogi R., Polyhedron **11**, 463 , (1992)

82- R. A. Sheldon, and J. K. Kochi, " Metal Catalysed Oxidation of Organic Compounds Academic Press New York (1981) .

83- G. Balavoine, Eskenzi F. Meunier and Riviere H., Tetrahedron Lett 25 3187(1984).

84- A. M. El–Hendawy, A.Kureshy and Shahab M., Polyhedron, **11**, 523 (1992).

85- A. Clearfied, Progr Inorg. Chem. **47** , 371 (1998)

86- C. Bellitto, F. Federic, A. Altomare, R . Rizzi an S. A. Ibrahim , Inorg. Chem. **39** , 1803 (2000).

87- H. Hofmans, H. O. Desseyn and M. A. Herman, Spectrochim. Acta **38 A** , 1213 (1982).

88- J. C. Miller and T.M. Brody, J. Pharamcal Exp. Ther. **121**, 43 (1957).

89- J.H. Yoe and A. L. Jones Ind. Eng. Chem. Anal **16** , 111 (1944).

90- P. Job , Ann. Chim. **6** , 97 (1935).

91- H. Irving And R.J. P.William, J. Chem. Soc. 3192 (1953) .

92- A. A. Grinerg and K. B. Yastimerski Bull. Acad. Sci. USSR, Div. Chem. Sci. 329 (1952).

93- S. A. Ibrahim, Polyhedron **11** , 1349 (1992)

94- S. A. Ibrahim, M. R. Mahmoud, M. B. Saleh and I.T.Ahmed, Trans. Met. Chem. (London)**14**, 494 (1994

95- F. A. Cotton and G. Wilkenso, " Advanced Inorganic Chemistry" Wiley New York (1972) .

96- W. J. Geary, Coord. Chem. Rev. 7, 81 (1971).

97- D. Merink and B. Kedzzia , Bull Acad. Polonaise XXVII - , 305 (1979)

98- H.O. Desseyn A. J. Arts and M.A. Herman, Spectorchim Acta **36A** , 59(19810

99- K. Nakamoto, M. Margoshes and R. E. Rundle, J. Am. Chem. Soc. **77** , 6480 (1955)

100- K. Nakamoto Infrared and Raman Spectra of Inorganic and Coordination Compounds 4th ed. John Wiley New York (1986)

101- G. B. deacon and R. J. Phillips Coord. Chem. Rev. **33,** 227 (1980)

102- H. O. Desseyn, W .Van Reil, L. Van Haverbeke and A. Goeminne Trans. Met. Chem. **5** , 88 (1980)

103- G. Schoeters and H.O. Desseyn, Trans. Met. Chem. **6** , 305 (1981)

104- S. A . Ibrahim , M. A. El- Gahami and A.M. Hammam, Chimica Scripta **29** , 229 (1989)

105- T. A. Stephenosn And G. Wilkinson J. Ionrg. Nucl. Chem. **29** . 2122 (1967).

106- J. E. Huheey Inorganic Chemistry Principles of Structures and Reactivity , Harper Row New Your 2nd ed (1978).

107- A. B. P. Lever " Inorganic Electronic Spectroscopy" Elsevier Amsterdam, 4th, ed. (1984)

108- C. K. Jorgensen Progr. Inorg. Chem. **12**, 101 (1970)

109- A. R. Amundsen, J. whelan and B. Bosnich, J. Am. C hem. Soc. **99** , 6730

110- I .T Ahmed , A. A Boraei And S.A. Ibrahim, Synth. React. Inorg. Met . Org. Chem. **27** , 169(1997)

111- G.M. Byruand and J.E. Fregusson , Aust J. Chem. **24** , 274 (1971)

112- F. Felix , J. E Fregusson , H. V. Golel and A. Luid, J. Am. Chem. Soc . **102** , 4096 (1980).

113- C. J. Ballhausen "Ligand Field Theory" Mc – Grow Hill , New Yor (1962).

114- H. H. Horwoitz and G. Metzger, Anal. Chem. **35**, 1464 (1963).

115- H.R. Ostwald and E. Dubler in H.G. Weidermann, Thermal Analysis, VCH, Switzerland, Vol. 2 (1972).

116- E.S. Freeman and B. Carrol, J. Phys. Chem. **62**, 394 (1958).

117- A.W. Coats and J. P. Redfern, Nature **20** , 68 (1964).

118- W. W. Wandlandt; "Thermal methods of analysis" Wiley, New York (1974).

119- G. O. Piloyan, I. D. Ryalochikov and O. S. Novikova, Nature **22**, 1229 (1966).

120- M.L. Dhar and O. Singh, J. Thermal. Anal. **37**, 259 (1991).

121- J. Garcia, M. C. Molla, J. Barras and E. Eseriva, Thermochim. Acta **106**, 155 (1986).

122- M. S. Masoud, S. S. Haggag, E. M. Soliman and M.E. El – Shabasy, J. Mater. Sci., **26**, 1109 (1991).

123- G. M. Bancroft and H. D. Gesser, J. Inorg. Nucl. Chem. **27**, 1537 (1965).

124- H. E. Kissinger, Anal. Chem. **29**, 1703 (1957).

125- J. Chacko and G. parmeswaran, J. Therm. Anal. **29**, 3 (1984).

126- S. S. Sawhney and A. K. Bandsal, Thermochim. Acta **66**, 347 (1983).

بسم الله الرحمن الرحيم

وزارة التعليم العالي
جامعة أم القرى
كلية العلوم التطبيقية

نموذج رقم (١٠)

إجازة أطروحة علمية في صيغتها النهائية بعد إجراء التعديلات

الاسم (رباعي) : سعيد محمد أحمد الأشقر .... كلية : العلوم التطبيقية . قسم : ...... الكيمياء
الأطروحة مقدمة لنيل درجة : الماجستير .... في تخصص : كيمياء غير عضوية
عنوان الأطروحة : ((تحضير ودراسة خصائص لبعض مترابطات ثنائي ثيوكاربامات ومتراكباته للعناصر الانتقالية .

الحمد لله رب العالمين والصلاة والسلام على أشرف الأنبياء والمرسلين وعلى آله وصحبه أجمعين وبعد :

فبناءً على توصية اللجنة المكونة لمناقشة الأطروحة المذكورة أعلاه والتي تمت مناقشتها بتاريخ ٢٠/١٠/١٤٢١هـ بقبولها بعد إجراء التعديلات المطلوبة، وحيث قد تم عمل اللازم ؛ فإن اللجنة توصي بإجازتها في صيغتها النهائية المرفقة للدرجة العلمية المذكورة أعلاه ...

والله الموفق ...

أعضاء اللجنة

المشرف	المناقش الداخلي	المناقش الخارجي
الاسم : أ.د/ سعيد أحمد إبراهيم	الاسم : د. محمد سعيد محفوظ القرشي	الاسم : د. محمد عبدالحكيم الج
التوقيع :	التوقيع :	التوقيع : ....

يعتمد

رئيس قسم

الاسم : أ.د. [illegible] سعيد الحبشي

التوقيع : ....

- يوضع هذا النموذج أمام الصفحة المقابلة لصفحة عنوان الأطروحة في كل نسخة من الرسالة .

جامعة أم القرى
كلية العلوم التطبيقية
قسم الكيمياء

تحضير ودراسة خصائص بعض متراكبات ثنائي ثيوأوكساميد مختلطة الليجندات للعناصر الانتقالية

رسالة مقدمة من

سوسن محمد أحمد الأشقر

بكالوريوس في العلوم (كيمياء)

وذلك كجزء من متطلبات الحصول على درجة الماجستير
في العلوم ((كيمياء غير عضوية))

الإشـــراف

د. سوسن سعيد حجاج	أ.د. سعيد احمد إبراهيم
أستاذ مساعد الكيمياء غير العضوية	أستاذ الكيمياء غير العضوية
جامعة أم القرى–كلية العلوم التطبيقية	جامعة أم القرى–كلية العلوم التطبيقية
(قسم الطالبات) مكة المكرمة	مكة المكرمة

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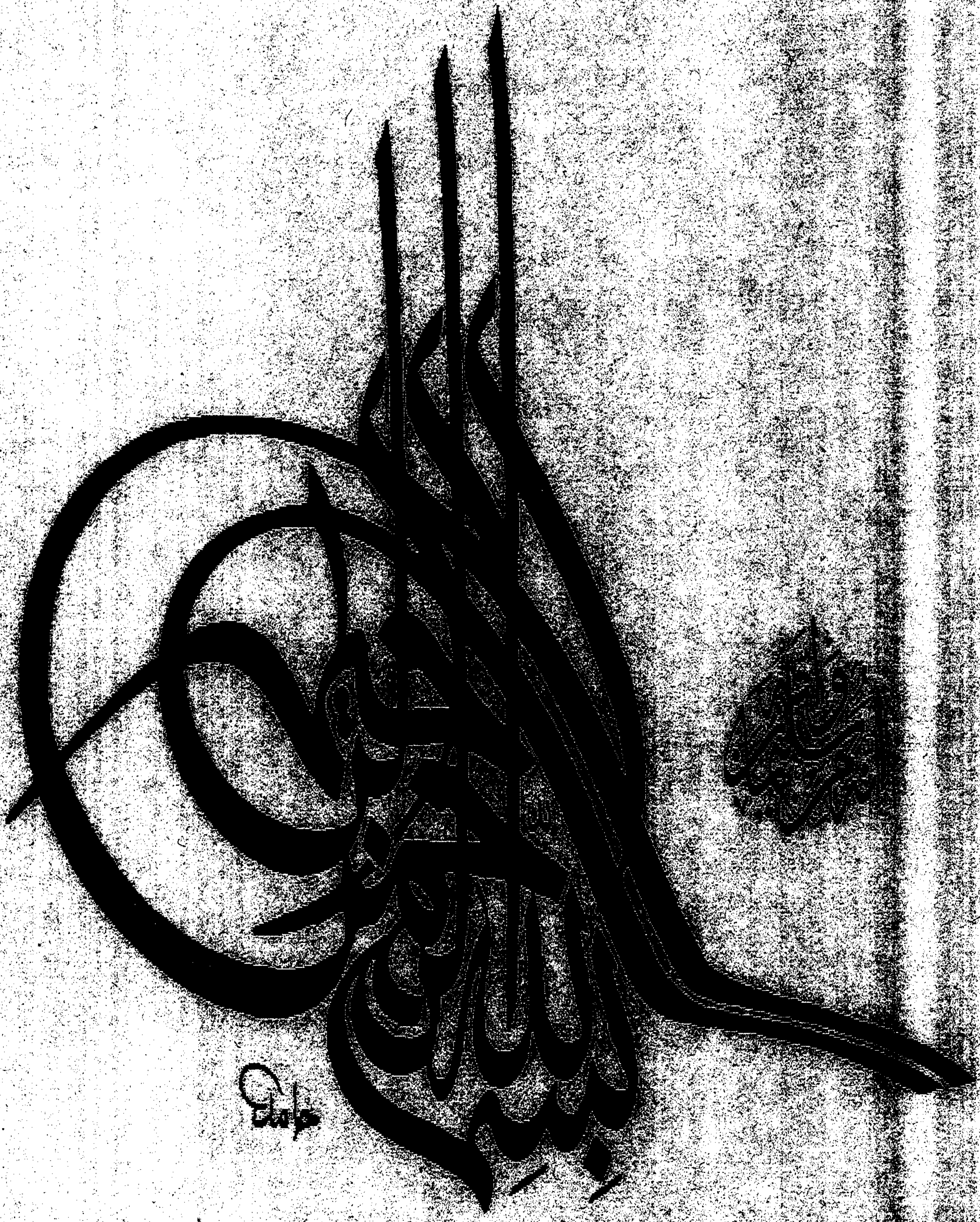

الملخص العربي

تتضمن الرسالة طرق التحضير والتعرف على خصائص المتراكبات مختلطة الليجندات لمركب ثنائي ثيوأوكساميد مع أيونات عناصر الكوبلت والنيكل والنحاس وكذلك أيونات الروثينيوم الثلاثية باستخدام عدد من الليجندات الثانوية مثل ٨ - هيدروكسي كينولين، أسيتيل أسيتون، أرثو - فينيلين ثنائي الأمين، حمص السليسليك وكذلك ثيوأسيتاميد.

واشتملت طرق التعرف على خصائص المتراكبات كل من التحاليل العنصرية وقياسات التوصيل الكهربي والقياسات الطيفية في منطقتي الأشعة فوق البنفسجية والمرئية وأيضاً في منطقة الأشعة تحت الحمراء.

والرسالة تحتوي على خمسة أبواب نوجز محتواها فيما يلي:

١ - يتضمن الباب الأول مسحاً مكتبياً عن الأبحاث المنشورة والخاصة بمتراكبات ثنائي ثيوأوكساميد والليجندات القريبة منها وكذلك للأبحاث المنشورة عن الأهمية البيولوجية والصناعية للأيونات الفلزية المستخدمة في هذه الرسالة.

٢ -يشمل الباب الثاني الجزء التجريبي من الرسالة والذي يتضمن طرق تحضير المتراكبات الأولية والمتراكبات مختلطة الليجندات وكذلك طرق تقدير المحتوى الفلزي في المتراكبات كما يتضمن كذلك سرداً للأجهزة المستخدمة في الدراسات المختلفة التي أجريت للتعرف على خصائص المتراكبات.

٣ - يقدم الباب الثالث نتائج دراسة تكوين المتراكبات في المحلول وتتضمن الدراسة تقدير النسب التركيبية للمتراكبات باستخدام الطرق الطيفية كما تتضمن تعيين ثوابت تكوين هذه المتراكبات وقد استخدمت لهذا الغرض طريقتان هما النسبة الجزيئية والتغير المستمر. وقد نوقشت النتائج في ضوء طبيعة كل من الأيون الفلزي والليجند الثانوي.

٤ -يحتوي الباب الرابع على نتائج دراسة خصائص المتراكبات الأولية ومختلطة الليجندات التي تم فصلها في الحالة الصلبة وقد أمكن من هذه الدراسة استنتاج مايلي:

أ - جزئ ثنائي ثيوأوكساميد يعمل كليجند ثنائي العطاء ويستطيع الترابط مع الأيون الفلزي إما عن طريق ذرتي كبريت أو ذرة كبريت وذرة نيتروجين.

ب - مجموعتا الأمين في جزئ الليجند لهما خواص أمونيومية كنتيجة للترابط الهيدروجيني داجل الجزئ والارتباط البيني مع أيونونات الكلوريد أو الخلات.

ج - يعتمد نوع المتراكب المتكون على الوسط الذي تم فيه التحضير وخاصة الرقم الهيدروجيني للوسط حيث تبين أن المتراكبات المتكونة تكون أحادية أو متجمعة.

د - تكون متراكبات النيكل الثنائي رباعية التناسق سواءً الأولية أو مختلطة الليجندات وتأخذ الشكل البنائي المربع المستوى.

هـ - متراكبات الكوبلت الثنائي والروثينيوم الثلاثي سداسية التناسق ولها الشكل الهرمي ثماني الأوجه أما متراكبات النحاس الثنائي فتتكون على صورتي المربع المستوي والهرم ثماني الأوجه المشوه.

٥ - يتضمن الباب الخامس نتائج التحليل الحراري الوزني للمتراكبات الصلبة من حيث كيفية تحللها حرارياً والتعرف على الخطوات التي يتم بها التفكك حراريا كما يشتمل هذا الباب على دراسة حركية التفكك الحراري للمتراكبات وتعيين الثوابت الديناميكية الحرارية لعملية التفكك.

وقد ذيلت الرسالة بقائمة المراجع التي تم الاستعانة بها في الدراسات المختلفة التي تضمنتها هذه الرسالة.

والله ولي التوفيق،،

تمت بحمد الله.