ANALYTICAL CHEMISTRY OF THE SEPARATION OF SOME METAL IONS WITH BENZIMIDAZOLE FROM MIXED SOLUTIONS

A DISSERTATION IN PARTIAL FULFILMENT
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Declaration Certificate

This is to certify that the thesis bearing the tittle '**Analytical chemistry of the separation of some metal ions with benzimidazole from mixed solutions**' submitted by Rozina Begum contains experiments and other related work exclusively carried out by the candidate herself under our supervision. The work has been done mostly in the Laboratories of the Department of Chemistry, Dhaka University. Thermal analysis data have been collected at the Laboratory of the HBRI, Dhaka. The candidate has fulfilled all the terms and conditions of the requirements of M. Phil thesis. In addition she has already published a paper on her work.

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SUMMARY

With a view to develop an analytical method for the separation and determination of certain metal ions using benzimidazole, various synthetic solutions of metal ions mixture were prepared and treated with benzimidazole. For effective separation and determination an appropriate masking agent such as EDTA or hydroxylamine hydrochloride was employed. It has been observed that the Ag^{+} can be quantitatively separated and estimated by benzimidazole in the presence of various metal ions such as Mn^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+} etc except the presence of Co^{2+}. In the presence of Co(II) ion , Ag is deposited like a mirror rather than being separated as a Ag-benzimidazole complex evidently due to the reduction process.

Prior to the application of benzimidazole as an analytical reagent, the composition and properties of metal complexes with benzimidazole have been investigated in the present work. The benzimidazole complexes of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Hg(I) and Hg(II) were also prepared and characterized by chemical analysis, thermal analysis, magnetic susceptibility measurement, IR and uv spectrophotometric techniques.

The composition of Cu(II), Zn(II), Ag(I) and Hg(II) complexes of benzimidazole were studied by both Job's continuous variation method and mole ratio method using precipitation technique. The metal to ligand ratio for Cu(II), Zn(II) and Ag(I) were found to be as 1:2 and 1:1 for Hg(II).

Based on the analytical data, thermal properties and stoichiometry of the complexes the empirical formula of the complexes are designated as

1. $Co(C_7H_6N_2)_2Cl_2.6H_2O$
2. $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$
3. $Ni(C_7H_6N_2)Cl_2.2H_2O$
4. $Cu(C_7H_6N_2)_2Cl_2.2H_2O$
5. $Zn(C_7H_6N_2)_2SO_4.2H_2O$
6. $Ag(C_7H_6N_2)_2NO_3$
7. $Hg(C_7H_6N_2)Cl_2.2H_2O$
8. $Hg(C_7H_6N_2)Cl.2H_2O$
9. $Hg(C_7H_6N_2)NO_3.2H_2O$

It has been suggested from the infrared studies of the complexes that the metal ligand bonding occurred through the unsaturated nitrogen atom of the imidazole ring of benzimidazole.

Magnetic susceptibility measurements indicates that Co(II), Ni(II) and Cu(II) complexes are paramagnetic and Zn(II), Ag(I), Hg(II) and Hg(I) complex are diamagnetic as expected. The magnetic moment values suggested that the complexes of Co(II) and Cu(II) have distorted tetrahedral structure as expected and Ni(II) complex has octahedral structure.

The deprotonation of benzimidazole in presence of metal ions still remains controversial and needs complete structural determinations for conclusive results.

CONTENTS

CHAPTER-1

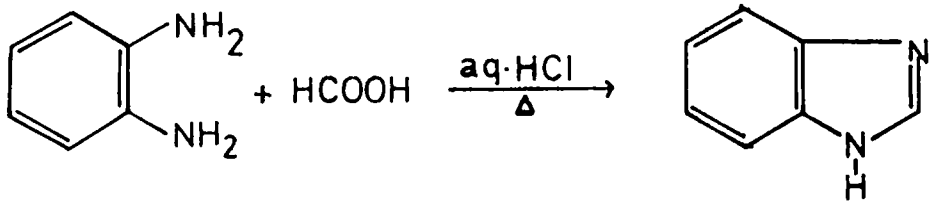
INTRODUCTION

INTRODUCTION

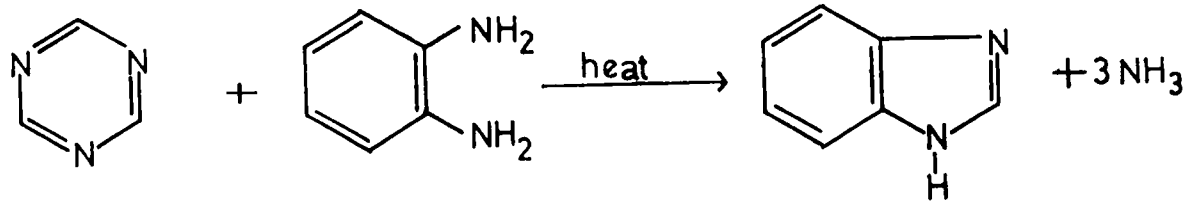
1.1 Benzimidazole as a ligand for complexing metal ions

Benzimidazole is chemically known as 1,3-benzodiazole or benzoglyoxaline. Benzimidazole is a heterocyclic compound in which a benzene ring is fused to the 4,5 position of imidazole. It is a member of important group of substances, which are of great practical applications in a wide variety of fields[1].

A number of methods have been devised for the synthesis of benzimidazole in which the Phillips synthesis[2] is the most widely applicable method. In this method o-arylenediamines and monocarboxylic acids are used. In general the carboxylic acid is heated with the diamine in aqueous hydrochloric acid.



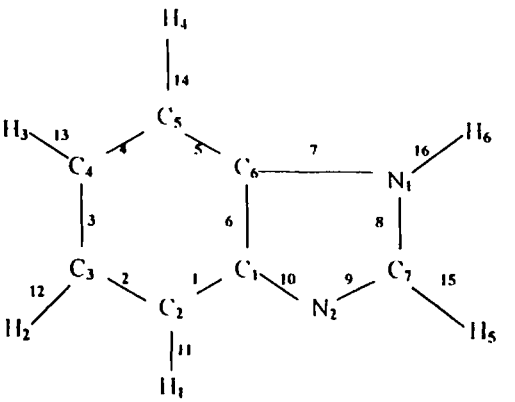
Benzimidazole can be obtained[3] by allowing o-phenylenediamine to react with *S*-triazine at temperatures just over the melting point of the diamine. The reactions of this type generally proceed in good yield (100% yield).



Benzimidazole is a light brown crystalline solid, which melts at 170°C. The decomposition temperature of benzimidazole is 405°C[4]. Benzimidazole is soluble in methanol, ethanol, acetone and hot water, sparingly soluble in ether and insoluble in benzene.

The crystal and molecular structure of benzimidazole was determined by Edixhoven *et al*[5]. The detailed molecular and crystal data of benzimidazole are summarized in Table 1 and Table 2 respectively.

Table 1. Molecular structure of benzimidazole[5]



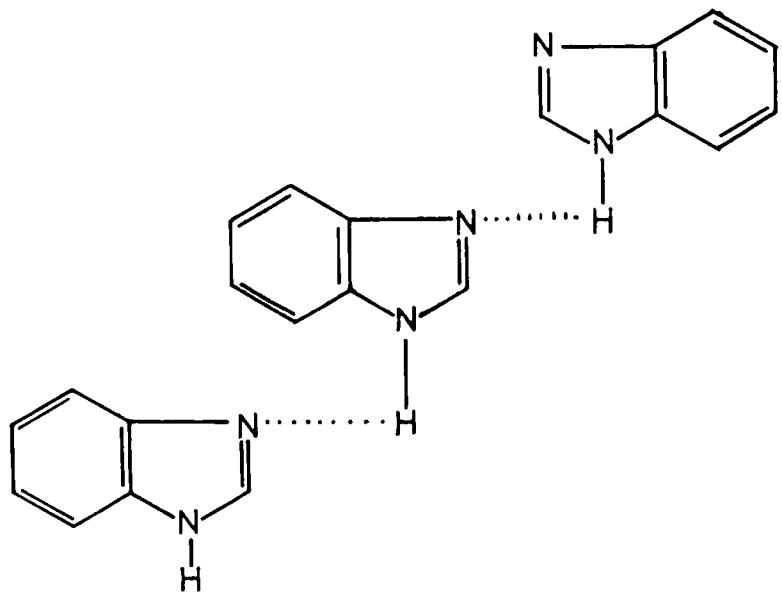
Bond distance(Å)		
1=1.389(4)	7=1.372(4)	13=1.07(4)
2=1.386(4)	8=1.346(4)	14=0.98(4)
3=1.401(5)	9=1.311(5)	15=1.03(4)
4=1.378(5)	10=1.395(3)	16=0.90(4)
5=1.401(4)	11=0.94(4)	
6=1.392(4)	12=1.02(4)	

Angles(°)			
1,2=117.8(3)	5,7=131.9(3)	1,11=117(2)	5,14=123(2)
1,6=120.6(3)	6,7=105.8(2)	2,11=126(2)	7,16=126(2)
1,10=130.0(2)	6,10=109.5(2)	2,12=117(2)	8,16=127(2)
2,3=120.9(3)	7,18=106.6(3)	3,12=122(2)	8,15=121(2)
3,4=122.3(3)	8,9=114.0(3)	3,13=111(3)	9,15=125(2)
4,5=116.1(3)	9,10=104.2(2)	4,13=125(3)	
4,6=122.4(3)	1,11=117(2)	4,14=121(2)	

Table 2. Crystal data of benzimidazole

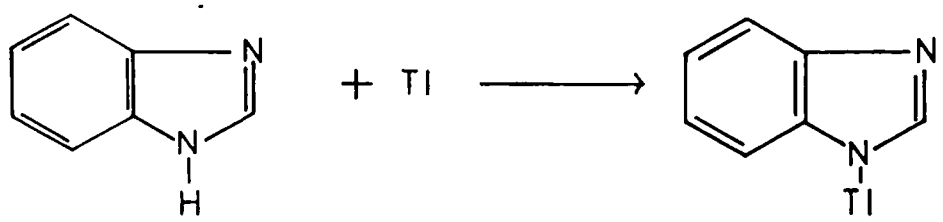
Compound	Crystal type	a(Å)	b(Å)	c(Å)	Z	Space group	R	Reference
Benzimidazole	Monoclinic	6.940	13.498	6.808	4	$p2_1nb$	0.04	5

In the crystalline structure each benzimidazole molecule is connected to two neighbors, generated by a two-fold screw axis along the x-axis, via a hydrogen bond of 2.00(4) Å from H_6 to N_2[6].



Escande and Galigne[7] also studied the crystal structure of benzimidazole. They made tow independent determination of benzimidazole crystal structure which arc compared by half-normal probability plot analysis. This study shows good agreement between the refined parameters and no systematic errors.

Benzimidazole forms coordination complexes with different metal ions. It coordinates with metal ions either through the nitrogen of position-3 that is unsaturated nitrogen or through position-1 by the replacement of hydrogen. Lee studied the interaction between imidazoles and Thallium(I) chloride[8]. Thallium(I) chloride reacts with benzimidazole and produces polymeric TlLCl (where, L= benzimidazole). In TlLCl, L is coordinated to Tl through the N-1 position and the reaction can be represented as



In most cases the coordination of benzimidazole with transition metal ions occur through the nitrogen of position-3. The charge distributions on nitrogen atoms N-1 and N-3 (Table-3)[9] calculated by the semiempirical Pariser-Parr-Pople SCF method and the CNDO/2 method explained the reactivities of benzimidazole at the position-3.

Table 3[9]. Calculation of charge distribution

	CNDO/2		CNDO/S	
Position of N	σ+π	π	σ+π	π
N1	5.1282	1.6726	5.0977	1.7226
N2	5.2250	1.2110	5.2369	1.2106

The magnitude of the charge at position-3 is apparently more than N-1 for both methods. Thomas *et al.*[10] have assumed that the unsaturated nitrogen is the most active site of the substituted benzimidazole based on the study of formation constants. Freiser's spectroscopic study[11] on the chelates of the derivatives of benzimidazole substantiated this assumption.

Resonance energy for benzimidazole was estimated by a semiempirical SCF-MO procedure[9]. The values of 129.3 kJ/m for benzimidazole, 87.6 kJ/m for pyridine and 83.8 kJ/m for benzene. Benzimidazole thus has relatively high resonance energy and this is reflected in the good thermal stability of polymers containing the benzimidazole moiety.

Benzimidazole and its derivatives is sufficiently acidic. The acidity is reflected in the ability to form metallic compounds[12]. From hydrolysis constants a pK_a value of 12.57 have been estimated for benzimidazole and a value of 14.2 for imidazole. From electrometric titration[13] a pK_a value of 12.3 for benzimidazole was found. Remick[14] reported that the acidic properties of benzimidazoles like those of the imidazoles seem to be due to the stabilization of the ions by resonance. Thermodynamic pK_a values (in acetonitrile) have been obtained spectrophotometrically for 2-substituted derivatives[12]. It has been demonstrated that there is a correlation of pK_a values with the magnitude of the electrostatic energy of interaction of the electron pair of the nitrogen atom being protonated, with the π system[15].

Benzimidazole is weakly basic, being somewhat less basic than the imidazole. Annulation of a benzo ring reduces the basicity of the pyridine-like nitrogen and results in a pK_a~5.5 for benzimidazole and pK_a~7.0 for imidazole[16].

Nakajima and Pullman[17] studied the basicity and ionization potential of benzimidazole with other heterocycles containing more than one N-atom. They reported that the first ionization potential of benzimidazole and other heterocycles containing two N-atoms is due to the electrons of the free double bonds of the nitrogen. The n-ionization potentials of nitrogen heterocycles were calculated[18] and the ionization potential is linearly correlated with the basicity (pK_a values) of the compounds in the series of imidazoles and benzimidazole.

Kambe *et al.*[19] have investigated the melting behavior of benzimidazole and 2-phenylbenzimidazole by differential scanning calorimetry and described the structure of the molecules. By comparison with polyphenyls it appears that benzimidazole has higher values of Tm and it is suggested that hydrogen bonding in the benzimidazole is a factor in a relative lowering of entropy of melting (Δs) values[19].

Khovratovich and Borisevich[20] have carried out systematic studies of the infrared spectra of benzimidazole. They suggested that a band at 3484 cm^{-1} might be assigned to the N-H stretching vibration, which reflected an intramolecular H bond increases the NH band intensity.

Rabiger and Joullie[21] studied the ultraviolet spectra of benzimidazole and its derivatives. It is evident that the absorption pattern of benzimidazole resembles that of a substituted benzene derivative, the short and long wavelength absorption bands correspond to transitions in the imidazole and aryl rings, respectively.

Proton magnetic resonance spectra (^{1}H NMR) and ^{13}C NMR spectra of benzimidazole, benzoxazole and N-methylbenzimidazole were studied by Benassi *et al*[22]. Proton chemical shifts have been used to obtain estimates of the electron distribution in benzimidazole[23].

^{14}N NMR spectra of benzimidazole, imidazole and 1-methylbenzimidazole have been measured by the direct method[24]. The ^{14}N NMR spectra showed a linear relationship between chemical shifts and SCF-(Pariser-parr-pople) MO π-charge densities.

Minkin *et al.*[25] calculated the dipole moment of benzimidazole by the equation, $\mu = 0.127\times10^{-18}[(P_\alpha-P_c)T]0.5$ where μ = dipole moment, P_α = electron polarization at infinite dilution and P_e = electron polarization. The μ of benzimidazole in benzene and dioxane is 3.93D and 4.08D respectively.

1.2 Importance of benzimidazole

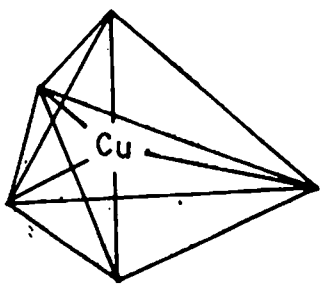
The benzimidazole moiety is present in a great variety of pharmaceutical compounds with anthelmintic action and other applications[26]. The compound may act biologically by competitive inhibition in nucleic acid synthesis[27].
Benzimidazole exhibit peculiar spectroscopic, redox and acid-base properties, which make them suitable substrates for the generation of laser radiation[28]. Other applications of benzimidazole include their use as solar filters[29], as inhibitors of copper corrosion in alloys[30] and as ligands in coordination

chemistry[31]. It has been utilized for separation of certain metal ions in the field of analytical chemistry.

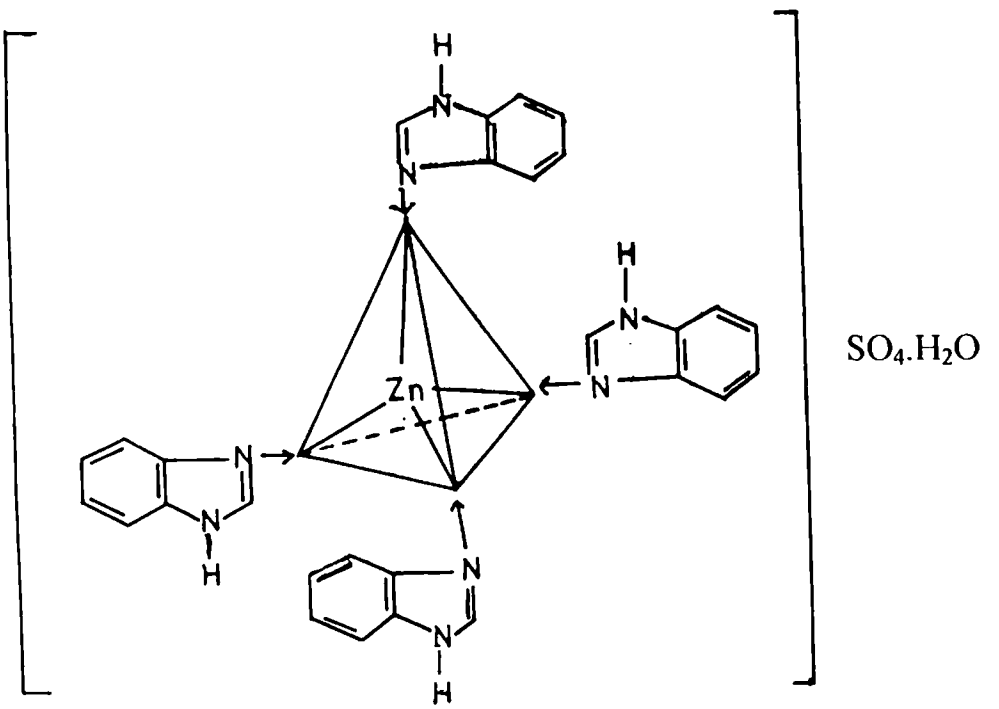
1.3 Metal complexes of benzimidazole and its related derivatives

A number of molecular complexes containing benzimidazole and its derivatives have been reported in the literature. Artemenko *et al.*[32] studied the complexing behavior of Ag(I) with benzimidizole, 2-methyl benzimidazole and 2-hydroxymethyl benzimidazole. In methanolic solution Ag(I) forms complexes of the type L_2AgNO_3. The IR spectra indicate that the ligands are presumably bound via the N-atom of position-3. The complexes have greater antibacterial action.

Preparation and spectral studies of the complexes of Cu(I), Cu(II) and Ag(I) with bulky chelating ligand 1,6-Bis (2-benzimidazolyl)-2,5-dithiahexane (L) was reported by birker *et al*[33]. They prepared the stable complexes of the type MLX (M = Cu(I) or Ag(I); L = 1,6-Bis(2-benzimidazolyl)-2,5 dithiahexane and X = ClO_4^- or NO_3^-) and $CuL(ClO_4^-)$. The Cu(I) and Ag(I) complexes are diamagnetic and $Cu^{II}L$ compounds are entirely consistent with trigonal-bipyramidal coordination as shown below



Gosh and Mishra[34] have prepared the complexes of Zn(II), Cd(II), Hg(II) and Hg(I) with benzimidazole and 2-methyl benzimidazole and characterized by electrical conductivity and IR spectral data. They prepared the complexes of the type $M(BZH)_2X_2$ (M = Cd(II) and Hg(II); BZH = benzimidazole and X = Cl^-, Br^- and NCS^-), $[Zn(LH)_4]SO_4$ and [Hg(Bz)Cl]. From electrical conductance value of the complexes (Λ_m = 20-35 ohm^{-1} mol^{-1} cm^2) it shows that anions are coordinated to metal atom. The insolubility of the complex [Hg(BZ)Cl] indicates its polymeric nature. The molar electrical conductance value of $[Zn(LH)_4]SO_4.H_2O$ in DMF (Λ_m=122 ohm^{-1} mol^{-1} cm^2) indicates the ionic nature of sulphate group in DMF solution. From stoichiometry and IR spectral studies four coordinated tetrahedral structure is suggested for Cd^{2+}, Zn^{2+} and Hg^{2+} complexes, since tetrahedral structure is more preferable geometry for these metal ions.



Tetrahedral structure of $[Zn(C_7H_6N_2)_4]SO_4.H_2O$

The preparation, spectral and magnetic properties were reported by Elbeck *et al.*[35] for complex of Co(II), Ni(II) and Cu(II) with 2-methyl imidazole (MIZ). These complexes have been compared with those of 2-methylpyridine. The complexes $M(MIZ)_2X_2$ (X = Cl^-, Br^-or I^-) have tetrahedral structure whereas $Ni(MIZ)_2Cl_2$ has a polymeric octahedral structure.

The differences between the complexes of 2-methylimidazole and 2-methyl pyridine discussed in terms of steric hindrance and basicity of the two ligands (For 2-methylimidazole $pK_a = 7.8$ and for 2-methyl pyridine $pK_a = 5.9$).

Crane and Rachel[36] studied the Co(II), Ni(II), Cu(II) and Zn(II) complexes of bidentate ligand 2-(2′-hydroxy-3′-methylphenyl)-benzimidazole (HL). They reported that the complexation has been shown to yield a series of mononuclear complexes of general formula $ML_2.2CH_3OH$ (M = Co, Ni, Cu, Zn). The complexes were sparingly soluble in water and all common organic solvents except DMF and DMSO. From IR spectral studies the complexes probably exist predominantly as distorted tetrahedral structure. These were confirmed by their magnetic properties.

Studies of some Nickel(II) complexes of nitrogen heterocyclic ligand of the type $NiLX_2$ (L = pyridine, quinoline or benzimidazole; X = Cl^- or Br-) and NiL_2X_2 have been reported by Goodgame *et al*[37]. The complexes have distorted octahedral structure and in the complexes $NiLCl_2$ one nitrogen atom and four chloride ions surround each nickel ion. The magnetic and spectral studies indicate that benzimidazole is very similar to pyridine as a ligand and suggested that it acts as a bridging ligand and coordinates through its pyridine

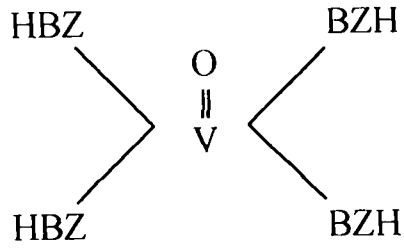
like nitrogen atom and also shows covalent character in the metal-ligand bonding in these complexes.

Goodgame and Cotton[38] prepared and characterized the complexes of benzimidazole of Co(II) such as $Co(BZD)_2$, $[Co(HBZD)_4]ClO_4$, $Co(HBZD)_2X_2$ (in which X = Cl^-, Br^-, I^- or NO_3^-). Skraup *et al.*[39] have reported the preparation of bis-benzimidazole Co(II) with the suggestion of its use in quantitative separation of Co(II).

Haider and Shahida[40] studied on the preparation, spectral and magnetic properties of complexes of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) with benzimidazole. These metal complexes of benzimidazole except Hg(II) was also studied by Haider *et al*[41]. The complexes were bis-ligated and have a molecule of water possibly as lattice water. They showed by the spectral studies that the metal ligand bonding occurred through unsaturated nitrogen atom of the ligand. From magnetic properties studied they suggested that all complexes were paramagnetic except Zn(II) complex. The latter was diamagnetic. The complexes were of tetrahedral in geometry.

Haider *et al.*[42] studied the benzimidazole complexes of some toxic metals such as Cd(II), Hg(II) and V(IV). They reported that benzimidazole acts as a monodentate ligand and metal is coordinated also through the unsaturated nitrogen atom of the ligand. From conductivity measurements they showed that except $[VO(C_7H_6N_2)H_2O]SO_4$, anions are coordinated to the metal atoms. Magnetic measurements indicate that Cd(II) and Hg(II) complexes are

diamagnetic and have tetrahedral structure on the other hand V(IV) complex is paramagnetic and has square pyramidal structure.



Square pyramidal structure of $VO(C_7H_6N_2)_4$

1.4 The background of the analytical use of benzimidazole

The following characteristics of the benzimidazole molecule allow it to be used in analytical chemistry.

1. The major property of a benzimidazole reagent applicable to inorganic analysis is its ability to form stable complexes with specific metal ions. This ability is essential for providing the equivalent quantities of the metal to be separated.

2. Benzimidazole is a brown crystalline solid and has a stoichiometric structure. It is highly soluble in alcohol so it is usually easy to provide a reagent concentration of 10^{-3} to 10^{-2} M that is quite sufficient for analytical purpose.

3. Benzimidazole shows quantitative stability of analytically important properties. Vardasco *et al.*[43] reported that the practical importance of many benzimidazole derivatives provide necessary means for the development of analytical methods for quantitative determinations of metals under suitable conditions.

4. The specificity of benzimidazole for some metal ions such as Ag^{+} in presence of many other cations in the EDTA solution make it an important reagent for adopting a complete separation.

5. Benzimidazole is quite stable to oxidizing[44] and reducing[45] agents. In analytical systems, a reducing reagent such as ascorbic acid is frequently used in analysis for masking. Benzimidazole can be easily used as reagent in such system without prejudice by masking reagents.

6. Benzimidazole form stable complexes with metal ions. El-Haty *et al.*[46] have studied on the complex formation between the metal ions such as Cu(II) and Ni(II) with benzimidazole and calculated their stability constant shown in Table-4. The high stability of metal complexes with this reagent is suitable for quantitative bonding of metals, which can open the way for developing methods for the determination of metals.

Table 4. Stability constants for the metal-(benzimidazole) binary complexes[46]

Metal	Ligand	Stability constant	
		$\log \beta_1$	$\log \beta_2$
Cu(II)	$C_7H_6N_2$	4.10 ±0.03	7.71±0.08
Ni(II)	$C_7H_6N_2$	3.88 ±0.07	7.15±0.01

7. Benzimidazole can coordinate metal ions with the participation of the nitrogen atoms in position-3 of imidazole ring. The participation of the atoms of the heterocycle in complex formation is an important factor for analytical chemistry.

8. Benzimidazole reacts with a number of cations and anions to form insoluble salts which are useful in quantitative and qualitative analysis of these ions. Feigle and Gleich[47] have investigated the formation of salts with benzimidazole. These salts are indicated in Table 5.

Table 5

Cation	Formula of salt
Mercury (I)	$C_7H_5N_2HgCl$
Copper	$4C_{14}H_{10}N_4Cu.NH_3.H_2O$
Zinc	$4C_{14}H_{10}N_4Zn.NH_3.H_2O$

1.5 Plan and purpose of the present work

The transition metals are most important in various fields of applications. To recovery or to obtain a pure substance, it is often necessary to separate some of these from a mixture. Biological activity of benzimidazole and its derivatives has been reported in the literature. Previously some works done in this laboratory[40-42] on benzimidazole have been mentioned. The analytical application of benzimidazole such as separation of some metal ions from mixed solutions has not been explored so far. In the present investigation benzimidazole has been used as a new reagent for the separation, extraction and determination of transition metals. The composition and properties of such complexes have also been investigated in the present work.

The benzimidazole complex of transition metals particularly that of silver is important from the point of view of analytical chemistry. The complex has greater antibacterial action[32]. Thus the imidazole nucleus and their derivatives are known to play extremely crucial parts in the structures and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions. The prevention of corrosion of metal surfaces by depositing a film of the metal-imidazole derivative complexes is of industrial and other preventive applications.

In the present investigations, it was also considered necessary to make a systematic study of the benzimidazole-metal ion interaction in aqueous or aqueous-alcoholic medium leading to the formation of some definite complexes.

The research was undertaken in order to achieve the under mentioned interests.

1. Preparation of benzimidazole complexes of some transition metals to study the ligand-metal ion interaction.

2. Studies on the composition of some complexes by the continuous variation method and mole ratio method to determine the metal / ligand ratio in the complexes.

3. Determination of metal contents in the complexes and study of thermal properties with a view to determine their molecular composition and stability.

4. Investigation of the methods of metal-ligand coordination as well as melting point, solubility, magnetic moment and energetics of the ligand molecule.

5. Studies of the spectral properties of the complexes as an aid to elucidate the micro structural features of the complexes.

6. Investigation of the benzimidazole molecule as a separator of metal ions from a mixture of metal ions in presence of the masking agent.

7. Quantum chemical study of the complexation of imidazole with transition metal ions.

CHAPTER-2

EXPERIMENTAL

EXPERIMENTAL

2 Synthesis of Some Metal Complexes of Benzimidazole

2.1 Materials and methods

In general, all synthetic works were carried out using standard techniques with some modifications as and when needed. The solvents and reagents used in the synthetic and analytical work were of laboratory grade quality supplied by the well-known foreign manufacturing companies.

2.2 Preparation of the Complexes

2.2.1 Preparation of dichloro bis (benzimidazole) cobalt (II) hexahydrate, $Co(C_7H_6N_2)_2Cl_2.6H_2O$

Ethanolic solution of $CoCl_2.6H_2O$ (3m mol, 0.7137g in 15ml) was added slowly to an ethanolic solution of $C_7H_6N_2$ (6m mol, 0.7088g in 10ml). The solution was allowed to stand for crystallization of the product. After 5 days a royal blue insoluble precipitate was obtained. The product was separated by filtration of the liquid part, washed with absolute alcohol and dried in desiccator.

Yield: 0.6530g (59.47% with respect to metal ion).
Melting point: 280°C.

2.2.2 Preparation of dinitro bis(benzimidazole) Co(II) dihydrate, $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$

The benzimidazole complex of $Co(NO_3)_2.6H_2O$ was prepared by treating methanolic solution of $Co(NO_3)_2.6H_2O$ (4.9m mole, 1.45g in10ml) and benzimidazole (9.5m mole, 1.13g in 10ml). The $Co(NO_3)_2.6H_2O$ solution was added to benzimidazole solution with constant stirring. The mixed solutions were heated slowly. A violet colored precipitate was separated, the product was isolated from the liquid by filtration, washed with methanol and dried in a desiccator over silica gel.

Yield: 0.431g (19% with respect to metal ion)
Melting point: Above 300°C.

2.2.3 Preparation of dichloro mono(benzimidazole) Ni(II) dihydrate, $Ni(C_7H_6N_2)Cl_2.2H_2O$

2.3750g (0.1 mole) of $NiCl_2.6H_2O$ and 1.1751g (0.1 mole) of benzimidazole were each dissolved in 10ml of ethanol separately. The two prepared solutions were mixed and slowly evaporated to dryness. The yellow crystals were obtained. The product was thoroughly washed with ethanol and dried at 120°C.

Yield: 1.6165g (57% with respect to metal ion)
Melting point: Above 300°C.

2.2.4 Preparation of dichloro bis(benzimidazole) Cu(II) dihydrate $Cu(C_7H_6N_2)_2Cl_2.2H_2O$

0.8501g (6m mole) $CuCl_2.2H_2O$ and 1.4100g (12m mole) benzimidazole were dissolved in 30ml and 20ml ethanol respectively. The two solutions were then mixed in a beaker with continuous stirring. Then olive green precipitates were formed within five minutes. The solution was allowed to stand for one hour. The liquid part was filtered and the solid product was washed with water and ethanol and dried in desiccator.

Yield: 1.8265g (59% with respect to metal ion)
Melting point: Above 300°C.

2.2.5 Preparation of bis(benzimidazole) Zn(II) sulphate dihydrate, $Zn(C_7H_6N_2)_2SO_4.2H_2O$

0.5740g (2m mole) of $ZnSO_4.7H_2O$ and 0.4691g (04 mole) of benzimidazole were dissolved in 20ml of aqueous ethanol (1:1 ratio) respectively. The two solutions were mixed together slowly with continuous stirring. A white colored precipitate was obtained which was allowed to stand for 30 minutes. The product was then collected by filtration, washed with distilled water and ethanol and dried in a desiccator.

Yield: 0.4750g (59.82% with respect to metal ion)
Melting point: Above 287°C.

2.2.6 Preparation of bis(benzimidazole) Ag(I) chloride, $Ag(C_7H_6N_2)_2NO_3$

An ethanolic solution of $AgNO_3$ (6.34m mole, 0.5390g in 50ml) was added slowly into an ethanolic solution of benzimidazole (12.68m mole, 0.7500g in 20ml) with constant stirring. The solid product formed was separated by filtration of the mother liquors. The solid product was washed several times with distilled water followed by ethanol and dried over silica gel in a desiccator.

Yield: 1.0090g (78.33% with respect to metal ion)
Melting point: Above 263°C.

2.2.7 Preparation of dichloro(benzimidazole) mercury(II) dihydrate, $Hg(C_7H_6N_2)Cl_2.2H_2O$

The benzimidazole complex of Hg(II) chloride was prepared by adding a methanolic solution of mercuric chloride (1.8100g, 6m mole) slowly to methanolic solution of benzimidazole (0.7860g, 6m mole) with constant stirring. White precipitate formed was produced immediately on mixing. The solid product was isolated, washed with methanol and dried over silica gel.

Yield: 1.8100g (69% with respect to metal ion)
Melting point: Above 300°C.

2.2.8 Preparation of mono chloro benzimidazole mercury(I) dihydrate, $Hg(C_7H_6N_2)Cl.2H_2O$

The compound was prepared following the method of Mishra[34]. About 0.7001g of $Hg(C_7H_6N_2)Cl_2.2H_2O$ was suspended in 50ml aqueous ethanol (1:4 ratio) and refluxed for about 1 hr. Then it was filtered while hot and the clear filtrate was then evaporated down to 30ml and was left for crystallization. After 3 days a cream colored insoluble crystal was obtained. The product was filtered and washed with absolute alcohol and dried in a desiccator.

Yield: 0.3476g (52% with respect to metal ion)
Melting point: 230°C.

2.2.9 Preparation of benzimidazole mercury(I) nitrate dihydrate, $Hg(C_7H_6N_2)NO_3.2H_2O$

1.3440g $Hg_2(NO_3)_2.2H_2O$ dissolved in 40ml water. Then solution was mixed with 20ml ethanolic solution of benzimidazole (0.2771g, 2.3m mole) and refluxed for 2 hours. The light brown precipitate was formed which was collected by filtration of the liquid part and the solid was dried in desiccator.

Yield: 0.3510g (39.82% with respect to metal ion)
Melting point: 320°C.

2.3 Characterization of the complexes

2.3.1 Determination of the composition of some complexes

The compositions of Cu(II), Ag(I), Zn(II) and Hg(II) complexes were studied by both Job's continuous variation method and mole ratio method using precipitation as the key factor.

Job's continuous variation method

Job's continuous variation method[48] has been frequently used for the study of complexes in isomolar solutions. In this method the solution properties that are the linear functions of the concentrations of the species involved such as refractive index[49], heat of mixing[50], density[51], dielectric constant[52], light absorption[53] and ion exchange[54] etc are used.

In Job's method, the sum of the total analytical concentration of the complexing agent 'L' and the metal ion 'M' is kept constant in each mixture of a series of solutions and their ratio is varied. If it is assumed that only one complex ML_n is formed then a Job's curve with a maximum or a minimum may be obtained by plotting any one physical property n of the system which is a linear function of the concentration of the complex against solution composition and n may be evaluated from the curve.

Khorasani[55] applied Job's method to a heterogeneous system in which a solid phase is in equilibrium with the solution phase, and studied the precipitation

reaction between silver ion and chloride, bromide, iodide, thiocyanate, chromate and phosphate ions

Considering the precipitation reaction of the type

$$M^{n+} + yL \rightleftharpoons [ML_y]^{n+}$$

So that,

$$K = \frac{[ML_y]^{n+}}{[M^{n+}]\,[L]^y} \qquad (1)$$

and considering c_1, c_2 and c_3 = the concentration of M, L and $[ML_y]^{n+}$ respectively, the mixtures of L and M are prepared by mixing solutions of a mol/dm^3 in the ratio x:(1-x) by volume, thus keeping the total concentration constant. Then

$$c_1 = a\,(1-x) - c_3 \qquad (2)$$

$$c_2 = ax - yc_3 \qquad (3)$$

$$c_1 c_2^{\,y} = kc_3 \qquad (4)$$

where, a = initial concentration of each solution

x = volume of metal ion M^{n+} solution in the mixture

y = number of ligand molecule coordinated with each metal ion

k = equilibrium constant of the reaction

The condition for a maximum or a minimum in the plot of c_3 against x is that $dc_3/dx = o$

Differentiating equations (2), (3) and (4) with respect to x, one gets

$$\frac{dc_1}{dx} = -a - \frac{dc_3}{dx} \quad (5)$$

$$dc_2/dx = a - y dc_3/dx \quad (6)$$

$$c_2^y dc_1/dx + y c_1 c_2^{(y-1)} dc_2/dx = k\, dc_3/dx \quad (7)$$

When, $dc_3/dx = 0$, then

$$dc_1/dx = -a \quad (8)$$

$$dc_2/dx = a \quad (9)$$

and $$c_2^y dc_1/dx + y c_1 c_2^{(y-1)} dc_2/dx = 0 \quad (10)$$

From equation (8), (9) and (10), one gets

$$-ac_2^y + ayc_1c_2^{(y-1)} = 0$$

$$\text{or, } y = \frac{ac_2^y}{ac_1c_2^{(y-1)}} = c_2/c_1 \quad (11)$$

Plotting the value of c_1 and c_2 from equation (2) and (3) in equation (11) and imposing the restriction of concentration of $[ML_y]^{n+}$ at the time of mixing, the value of 'y' is evaluated from the equation.

$$y = \frac{ax}{x(1-x)} = x/1-x \quad (12)$$

Therefore, by determining the value of x for which c_3 is a maximum, y can be calculated[56].

In the mole ratio method the concentration of metal ion is kept constant and the concentration of the ligand is increased stepwise. In the plot of absorbance or amount of precipitate versus moles of reagent added, the interception of the curves obtained by extrapolation of the linear segments give the ratio

$$\frac{\text{moles of reagent}}{\text{moles of metal}}$$

Procedure

In Job's method, a set of nine centrifuge tubes was washed, dried and weighed to constant weight. Exactly 1.0 to 9.0 cm^3 of the metal ion solution were transferred into 9 separate centrifuge tubes. Equimolar benzimidazole solutions were added in the reverse order of the metal ion solutions of the tube. On mixing the solution precipitation occurred immediately. Then the tubes were centrifused, allowed to settle for half an hour. With the help of an elongated tip dropper, the mother liquor was removed carefully. The tubes with precipitate were heated in an oven at about 110°C until constant weight was obtained.

In the mole ratio method a constant volume of metal ion solution i,e. 2 cm^3 of the metal ion solution were transferred to each centrifuge tube and the benzimidazole solution in the order of 1, 2, 3, 4, 5, 6, 7, 8, 9 cm^3 were added. The precipitates formed in the different tubes were treated and weighed as in the previous method.

The results are shown in Tables 2.1 to 2.8 and the corresponding plots are shown in Figs. 2.1 to 2.8.

Table 2.1. Composition determination of Benzimidazole-Copper(II) complex by Job's continuous variation method

Concentration of $C_7H_6N_2$ solution = 3.2×10^{-2}

Concentration of Cu(II) solution = 3.2×10^{-2} M

Serial No.	Mole fraction of the metal ion	Corresponding weight of the complex (g)
1	0.900	0.0085
2	0.800	0.0168
3	0.700	0.0230
4	0.600	0.0218
5	0.500	0.0202
6	0.400	0.0130
7	0.300	0.0110
8	0.200	0.0070
9	0.100	0.0011

Table 2.2. Composition determination of Benzimidazole-Copper(II) complex by mole ratio method.

Concentration of $C_7H_6N_2$ solution = 3.2×10^{-2} M

Concentration of Cu(II) solution = 3.2×10^{-2} M

Serial No.	Mole ratio L/M	Corresponding weight of the complex (g)
1	0.45	0.0051
2	0.85	0.0110
3	1.40	0.0175
4	1.87	0.0200
5	2.34	0.0230
6	2.75	0.0250
7	3.33	0.0230
8	3.82	0.0245
9	4.05	0.0231

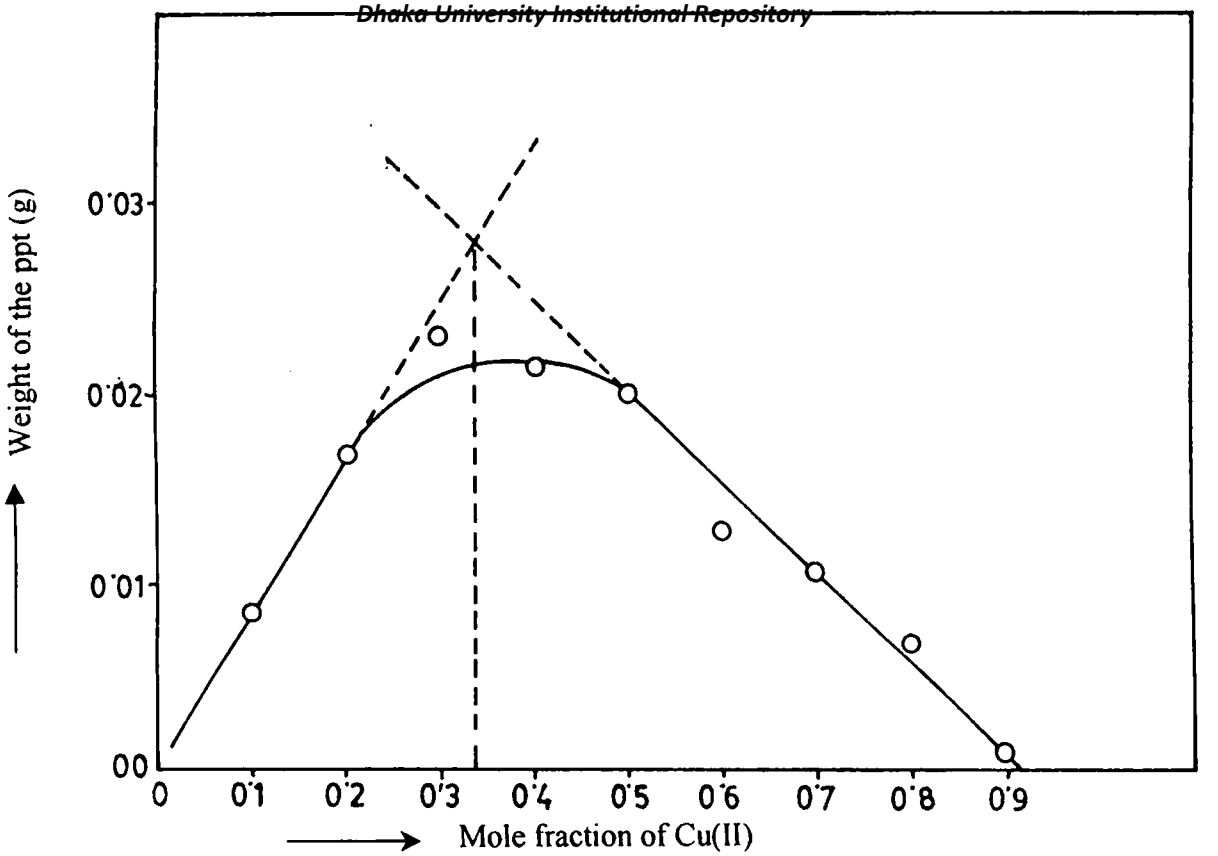


Fig. 2.1 Continous variation of benzimidazole and copper concentrations keeping a constant total concentration of 3.2×10^{-2} M

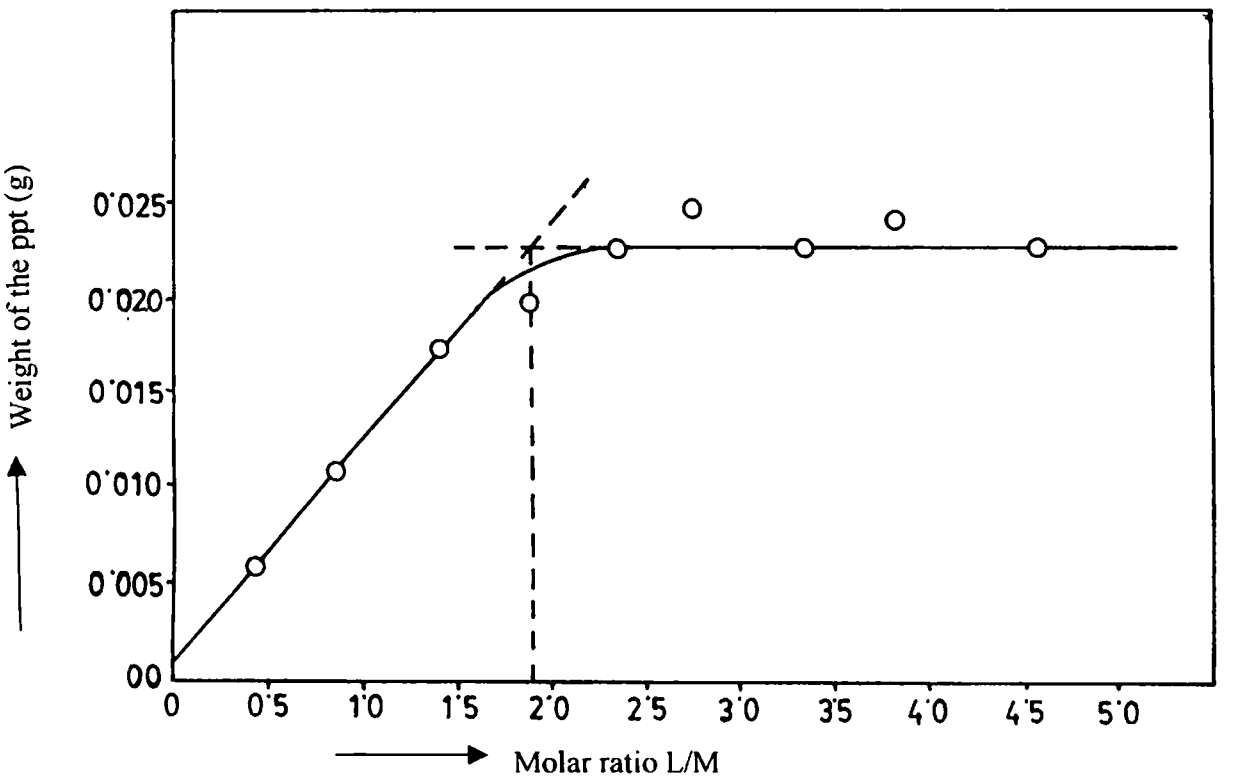


Fig. 2.2 Variation of benzimidazole concentration with Cu(II) Concentration held at 3.2×10^{-2} M

Table 2.3. Composition determination of Benzimidazole-Zinc(II) complex by Job's continuous variation method

Concentration of $C_7H_6N_2$ solution = 3×10^{-2} M

Concentration of Zn(II) solution = 3×10^{-2} M

Serial No.	Mole fraction of the metal ion	Corresponding weight of the complex (g)
1	0.900	0.0125
2	0.800	0.0231
3	0.700	0.0310
4	0.600	0.0294
5	0.500	0.0283
6	0.400	0.0230
7	0.300	0.0205
8	0.200	0.0110
9	0.100	0.0055

Table 2.4. Composition determination of Benzimidazole-Zinc(II) complex by mole ratio method

Concentration of $C_7H_6N_2$ solution = 3×10^{-2} M

Concentration of Zn(II) solution = 3×10^{-2} M

Serial No.	Mole ratio L/M	Corresponding weight of the complex (g)
1	0.49	0.0009
2	0.99	0.0140
3	1.49	0.0195
4	1.99	0.0240
5	2.49	0.0255
6	2.99	0.0270
7	3.49	0.0255
8	3.99	0.0240
9	4.49	0.0255

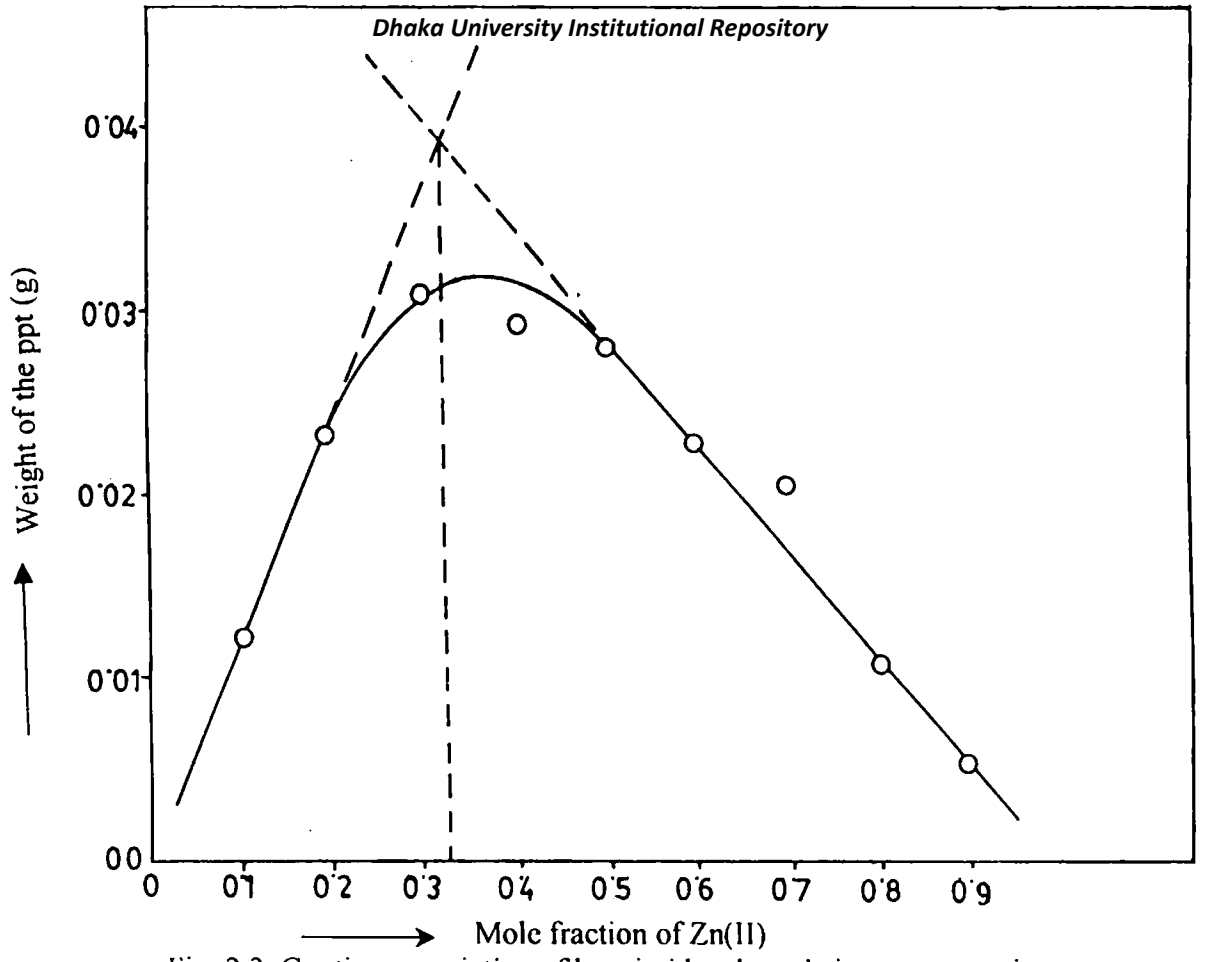


Fig. 2.3 Continous variation of benzimidazole and zinc concentrations. Keeping a constant total concentration of 3×10^{-2} M

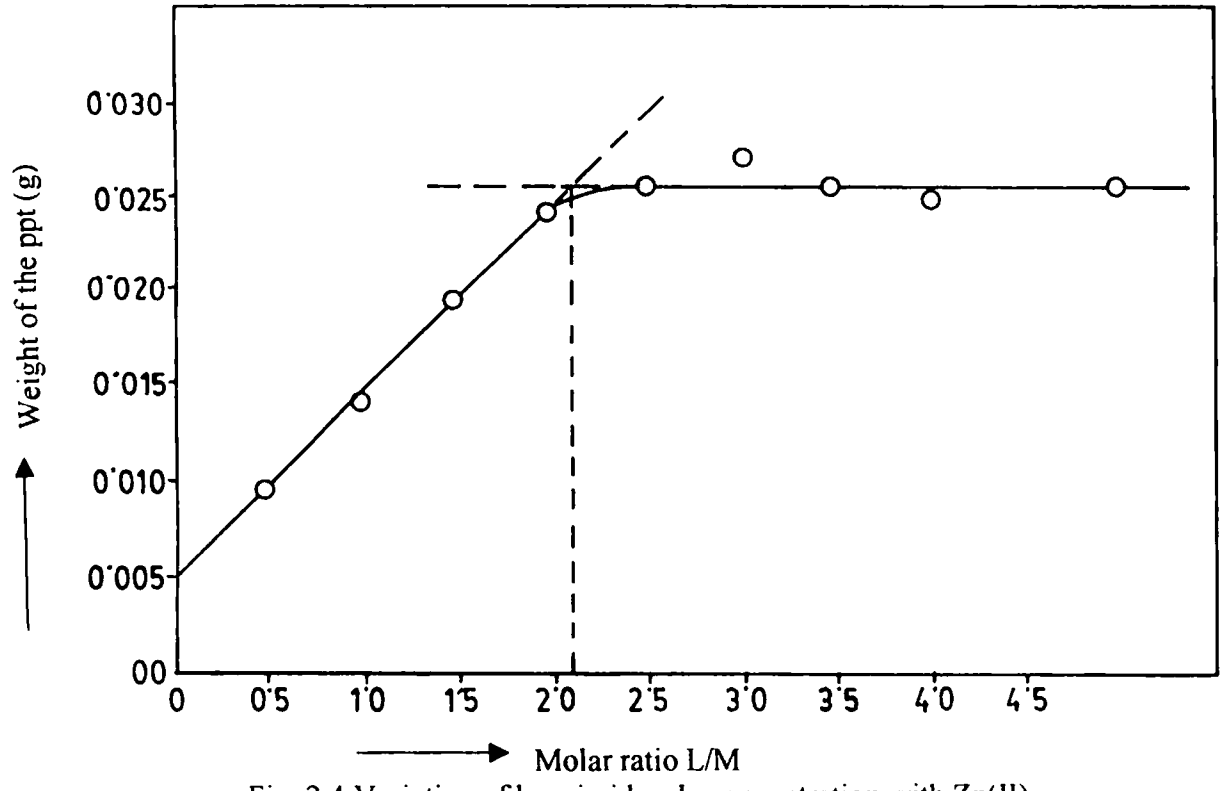


Fig. 2.4 Variation of benzimidazole concentration with Zn(II) Concentration held at 3×10^{-2} M

Table 2.5. Composition determination of Benzimidazole-Silver(I) complex by Job's continuous variation method

Concentration of $C_7H_6N_2$ solution = 2.94×10^{-2} M

Concentration of Ag(I) solution = 2.94×10^{-2} M

Serial No.	Mole fraction of the metal ion	Corresponding weight of the complex (g)
1	0.900	0.001
2	0.800	0.0105
3	0.700	0.0170
4	0.600	0.0222
5	0.500	0.0304
6	0.400	0.0333
7	0.300	0.0306
8	0.200	0.0290
9	0.100	0.0057

Table 2.6. Composition determination of Benzimidazole-Silver (I) complex by mole ratio method

Concentration of $C_7H_6N_2$ solution = 2.94×10^{-2} M

Concentration of Ag(I) solution = 2.94×10^{-2} M

Serial No.	Mole ratio L/M	Corresponding weight of the complex (g)
1	0.51	0.0065
2	1.03	0.0120
3	1.54	0.0176
4	2.06	0.0196
5	2.58	0.0196
6	3.09	0.0179
7	3.61	0.0194
8	4.13	0.0181
9	4.64	0.196

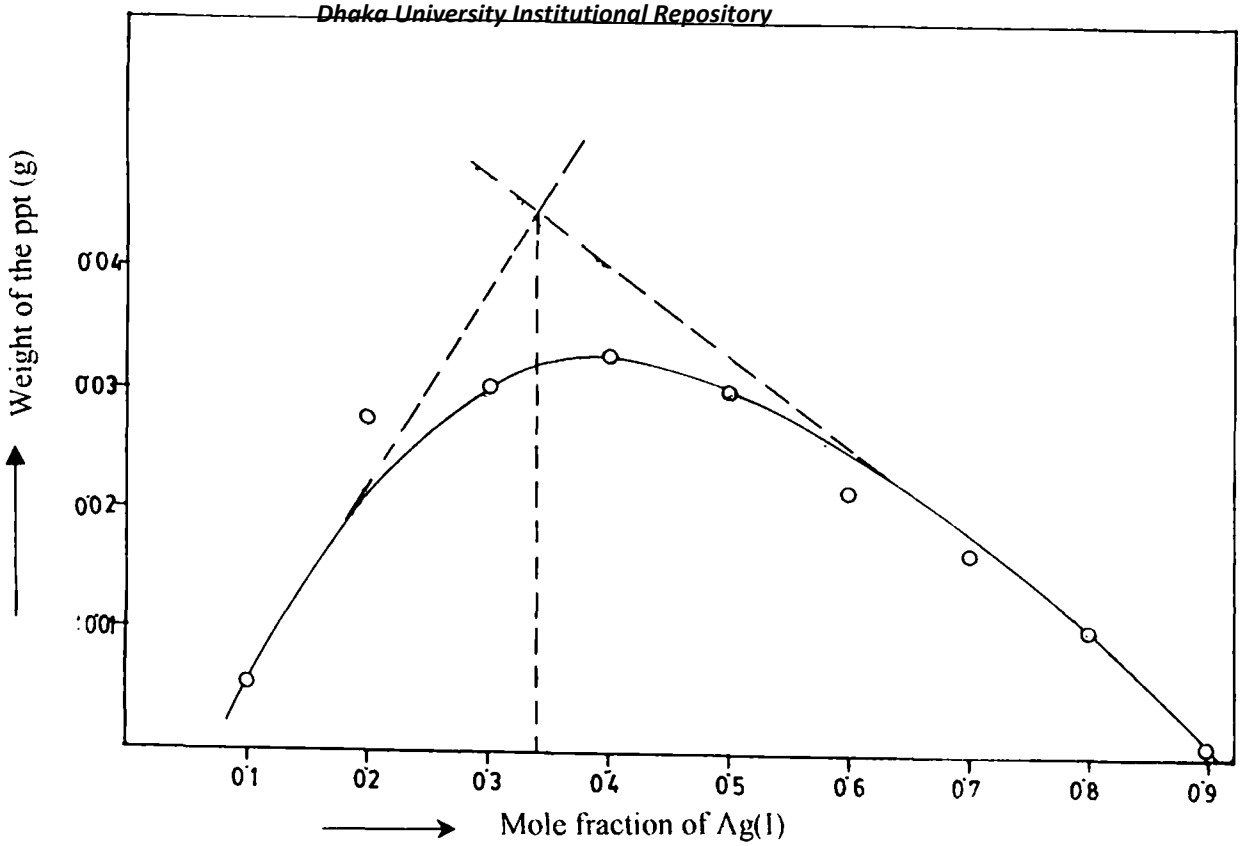


Fig. 2.5 Continous variation of benzimidazole and silver concentrations keeping a constant total concentration of 2.94×10^{-2} M

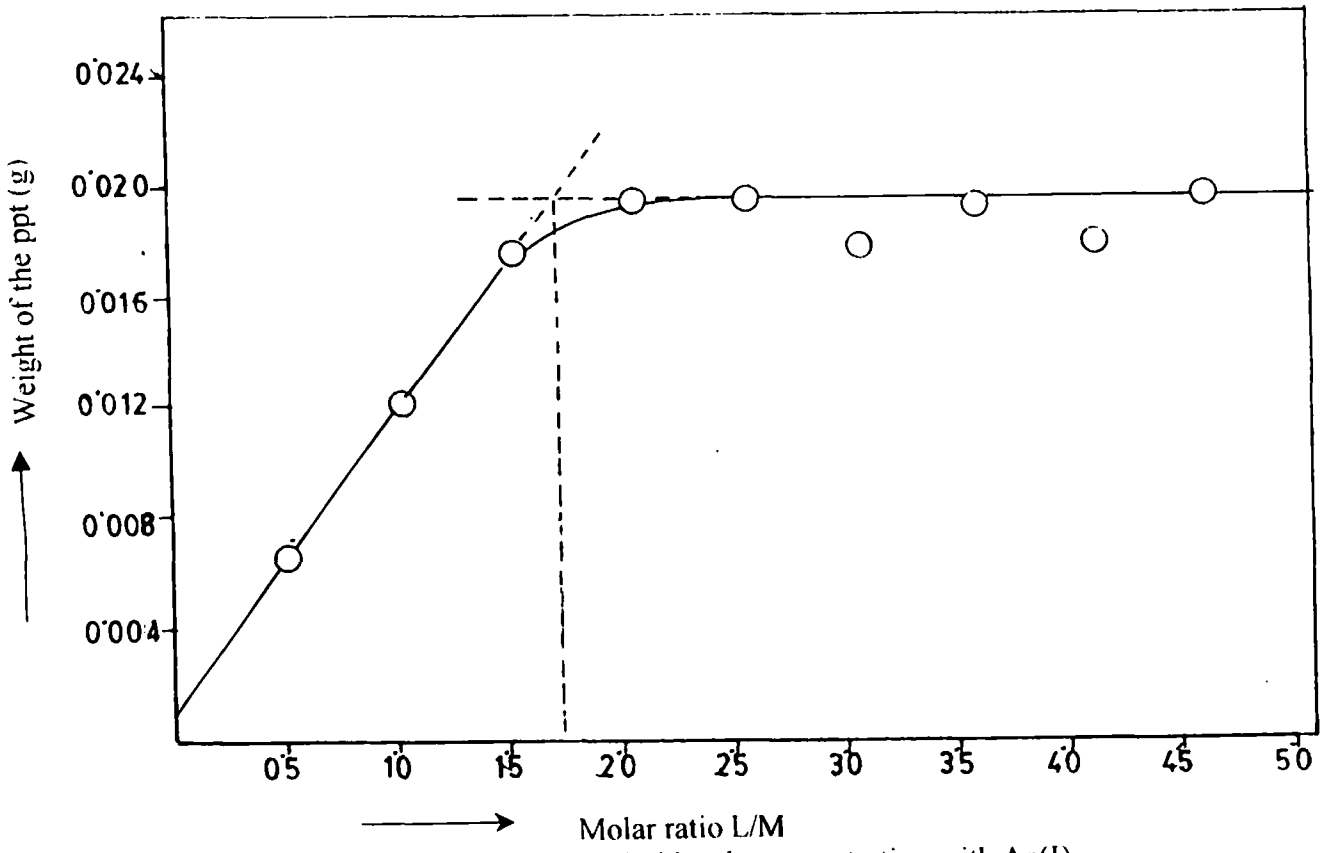


Fig. 2.6 Variation of benzimidazole concentration with Ag(I) Concentration held at 2.94×10^{-2} M

Table 2.7. Composition determination of Benzimidazole-Mercury(II) complex by Job's continuous variation method

Concentration of $C_7H_6N_2$ solution = 1.33×10^{-2} M

Concentration of Hg(II) solution = 1.33×10^{-2} M

Serial No.	Mole fraction of the metal ion	Corresponding weight of the complex (g)
1	0.900	0.0080
2	0.800	0.0194
3	0.700	0.0250
4	0.600	0.0290
5	0.500	0.0325
6	0.400	0.0292
7	0.300	0.0188
8	0.200	0.0114
9	0.100	0.0062

Table 2.8. Composition determination of Benzimidazole-Mercury(II) complex by mole ratio method

Concentration of $C_7H_6N_2$ solution = 1.33×10^{-2} M

Concentration of Hg(II) solution = 1.33×10^{-2} M

Serial No.	Mole ratio L/M	Corresponding weight of the complex (g)
1	0.40	0.0095
2	0.85	0.0183
3	1.48	0.0210
4	1.80	0.0210
5	2.50	0.0211
6	2.95	0.0220
7	3.45	0.0282
8	3.95	0.0210
9	4.70	0.0221

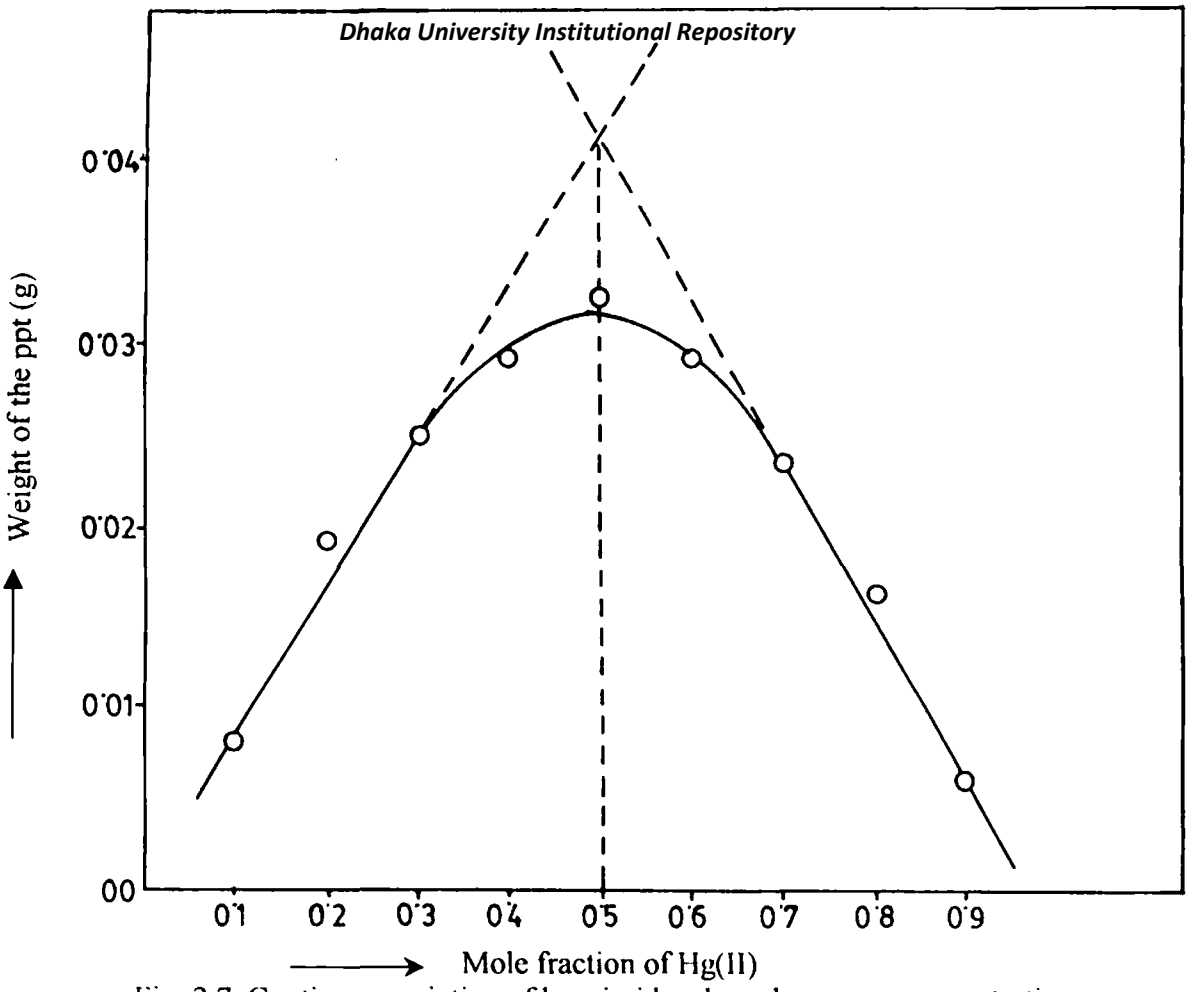


Fig. 2.7 Continous variation of benzimidazole and mercury concentrations keeping a constant total concentration of 1.33×10^{-2} M

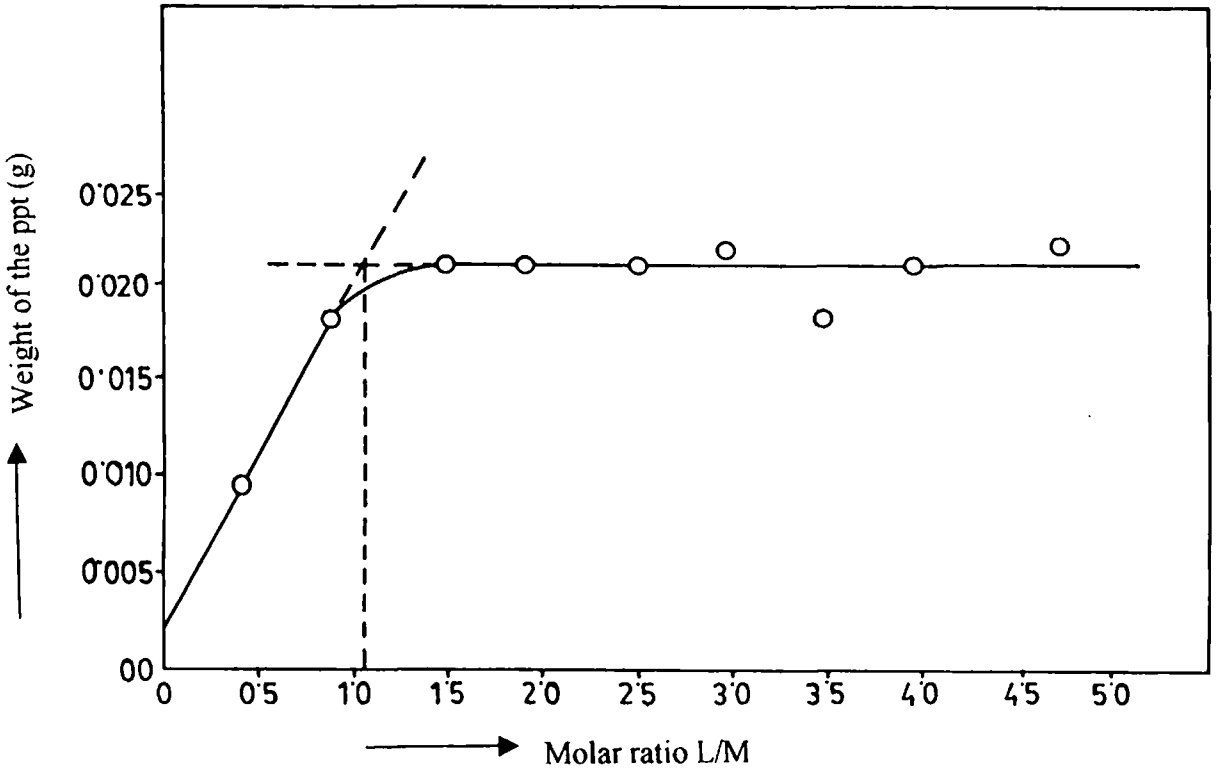


Fig. 2.8 Variation of benzimidazole concentration with Hg(II) Concentration held at 1.33×10^{-2} M

2.3.2 Solubility of the complexes

The solubility of the complexes was investigated quantitatively in the usual manner in different solvents at room temperature, which are shown in Table 2.9. In each observation the solvent and the solid products (about 0.0003g) were taken in 5ml of the solvents and solubility was noted in a qualitative manner by visual observation.

Table 2.9. Visual solubility of the solid products

Code names of the compounds	Soluble	Insoluble
A	CH_3OH, Conc. HCl, HNO_3, CH_2Cl_2, NH_4OH	H_2O, C_2H_5OH, CH_3COCH_3, $CHCl_3$, CCl_4, C_6H_6, NaOH
B	Conc HCl, HNO_3, sparingly in DMF & DMSO	CH_3OH, C_2H_5OH, CH_3COCH_3
C	DMSO, CH_3OH, Conc HCl, HNO_3, sparingly in C_2H_5OH	H_2O, $CHCl_3$, CCl_4, C_6H_6, NaOH
D	H_2O, CH_3OH, $CHCl_3$, Conc. HNO_3, DMSO	C_2H_5OH, ether, CH_3COCH_3, CCl_4, C_6H_6
E	DMSO, DMF, Conc HCl, HNO_3, and H_2SO_4	H_2O, CH_3OH, C_2H_5OH, CCl_4, CH_2Cl_2, NaOH, NH_4OH
F	DMSO, DMF, Conc H_2SO_4, sparingly in hot H_2O, CH_3COCH_3 and CH_2Cl_2	CH_3OH, H_2O, C_2H_5OH, CCl_4, C_6H_6, $C_6H_5NO_2$, Conc. HCl, NaOH, NH_4OH
G	DMSO, DMF, Conc. HNO_3, sparingly in CH_3COCH_3	CH_3OH, H_2O, C_2H_5OH, $CHCl_3$, CH_2Cl_2, NaOH, NH_4OH, Conc. HCl
H	Conc. HNO_3, HCl, DMSO, sparingly in CH_3COCH_3.	CH_3OH, H_2O, C_2H_5OH, NH_4OH
I	Conc. HNO_3, HCl	CH_3OH, H_2O, C_2H_5OH, CH_3COCH_3, DMF, DMSO, H_4OH

2.3.3 Estimation of the metal contents

The metal contents of all the prepared complexes except silver complex were determined by complexometric method. The silver was determined by volumetric method. Priors to metal estimation the stock solution of the metal complexes were prepared by digesting the complex with concentrated nitric acid to bring the metal ion into solution.

Preparation of the stock solution

Exactly weighed amounts of approximately 0.2-0.3g of complex and 3-4ml of concentrated nitric acid were taken in the porcelain crucibles and was heated on a hot plates until the volume was down to 1ml. The solution was cooled at room temperature and transferred into a 100ml volumetric flask and made to the mark with distilled water.

2.3.3.1 Complexometric determination of Cobalt (II), Nickel (II), Copper(II), Zinc (II) and Mercury (II)

The stock solution for cobalt, nickel, copper, zinc and mercury complexes were prepared as described in the previous section. The metal contents of these solutions were determined complexometrically as described in Vogel[57] for cobalt, nickel, copper, zinc and mercury. The results are given in Table 2.10.

2.3.3.2 Determination of Silver (I)

The determination of silver content in the complex $[Ag(C_7H_6N_2)_2]NO_3$ was made by the volumetric method[58]. Prior to determination the organic part of the complex was destroyed by digestion with nitric acid in a Parr bomb using Teflon vessel which is described below.

Exactly 0.2000g of the complex was taken in the Teflon cup of the Parr bomb and 2-3ml of concentrated nitric acid was added to it. The cup with the sample was heated for about four hours in the oven at 110-120°C. The bomb was cooled at room temperature, the solution was transferred into a 100ml volumetric flask and distilled water was added to it up to the mark.

The results and the empirical formula of the complexes based on this analysis are given in Table 2.10.

Table 2.10. Elemental data of the benzimidazole complexes

Code names of the compounds	Metals	% Metal		Empirical formula of the complexes
		Found	Calculated	
A	Co(II)	12.07	12.42	$Co(C_7H_6N_2)_2Cl_2.6H_2O$
B	Co(II)	13.11	12.94	$Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$
C	Ni(II)	20.18	20.68	$Ni(C_7H_6N_2)Cl_2.2H_2O$
D	Cu(II)	15.35	15.60	$Cu(C_7H_6N_2)_2Cl_2.2H_2O$
E	Zn(II)	14.83	15.04	$Zn(C_7H_6N_2)_2SO_4.2H_2O$
F	Ag(I)	25.15	26.55	$Ag(C_7H_6N_2)_2NO_3$
G	Hg(II)	46.11	47.10	$Hg(C_7H_6N_2)Cl_2.2H_2O$
H	Hg(I)	50.02	51.39	$Hg(C_7H_6N_2)Cl.2H_2O$
I	Hg(I)	47.67	48.12	$Hg(C_7H_6N_2)NO_3.2H_2O$

2.3.4 Thermal analysis

Thermograms of the complexes were obtained by RIGAKU thermal analysis station TAS 100 with basic TG unit Thermoflex TG 8110 from HBRI laboratory, Dhaka. The changes of weight of the sample were recorded directly by means of singly X-Y recorder. The linear heating rate controlled by the temperature programmer panel was 10°C/minute.

Thermogravimetry (TG) provides the analyst with a quantitatively measurement of any mass change associated with a chemical reaction. It can directly record the loss in weight of a sample with temperature due to dehydration or decomposition. It gives an idea about bond strength and nature of bonding of various constituent parts. Weight loss at lower temperature is generally due to removal of purely lattice components or weakly bonded components, such removal of components are usually endothermic. Study of differential thermal analysis (DTA) of a substance shows the nature of chemical changes occurring during decomposition process i,e. whether it is exothermic or endothermic. The energy changes associated with those processes may also be obtained from thermal analysis.

Thermogravimetric analysis gives some important information about the complex compound, such as thermal stability, the composition of complex, number of lattice water or the amount of metal present in the complex. From differential thermal analysis we can also get some information such as decompositions, fusion, phase changes and purity of the complex.

DTA used in the qualitative analysis of complex materials and TGA used in the study of the recommended drying temperatures of gravimetric precipitates.

The results of thermogravimetric analysis and DTA always affected by the weight of sample, particle size, heating rates, furnace atmosphere, geometry of sample holders and the mode of preparation of a sample. For a better thermogravimetric results a sample with small weight and small uniform particle size are essential.

The thermograms of the samples are shown in Fig 2.9-2.17 and the results of thermal analysis of the samples are summarized in Table 2.11

Table 2.11. Thermal behavior of metal benzimidazolates

Compound	Steps involved	Temp. range °C	Observed loss in wt (%)	Calcd. Loss in wt (%)	Remarks
$Co(C_7H_6N_2)_2Cl_2.6H_2O$	I	225	6.75	7.59	Two molecules of water appear to be lost.
	II	345	31.08	30.26	Six molecules of water along with one Cl^- appear to be lost.
	III	590	86.48	87.57	All volatile components including organic parts are lost. The end product is possibly CoO or Co_3O_4.
$Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$	I	325	17.23		Expulsion of two molecules of H_2O and some unidentified decomposition products.
	II	390	86.53	87.05	All volatile components such as organic parts, NO_3, and H_2O are removed, the end product possibly CoO or Co_3O_4.
$Ni(C_7H_6N_2)Cl_2.2H_2O$	I	65	11.53	12.68	Two molecules of water appear to be lost.
	II	305	19.0	-	Two molecules of H_2O and some fragments of the ligand are lost.
	III	480	78.0	79.31	All volatile product lost with decomposition. The residue is NiO.
$Cu(C_7H_6N_2)_2Cl_2.2H_2O$	I	210	8.36	8.84	Two molecules of water are lost.
	II	210-490	83.95	84.36	All volatile products are lost. The residue is CuO.
$Zn(C_7H_6N_2)_2SO_4.2H_2O$	I	600	86.0	84.9	All components are lost with decomposition. The residue is ZnO.
$Ag(C_7H_6N_2)_2NO_3$	I	210	5.55	-	Destruction of some fragments of the ligand.
	II	270	34.0	29.07	
	III	500	75.9	73.4	All volatile components including organic parts are lost. The end product is Ag_2O.
$Hg(C_7H_6N_2)Cl.2H_2O$	I	185	8.11	9.22	One molecule of water is lost.
	II	185-275	100	-	The entire volatile portion is evaporated.
$Hg(C_7H_6N_2)Cl_2.2H_2O$	I	183	9.26	8.45	Two molecules of water are lost.
	II	183-430	100	-	The product undergoes decomposition and is volatile including Hg.
$Hg(C_7H_6N_2)NO_3.2H_2O$	I	275	8.57	8.46	Two molecules of water are lost.
	II	325	51.42	51.87	The entire component is removed along with the conformation of the corresponding HgO.
	III	580	100	-	Mercury is vaporized.

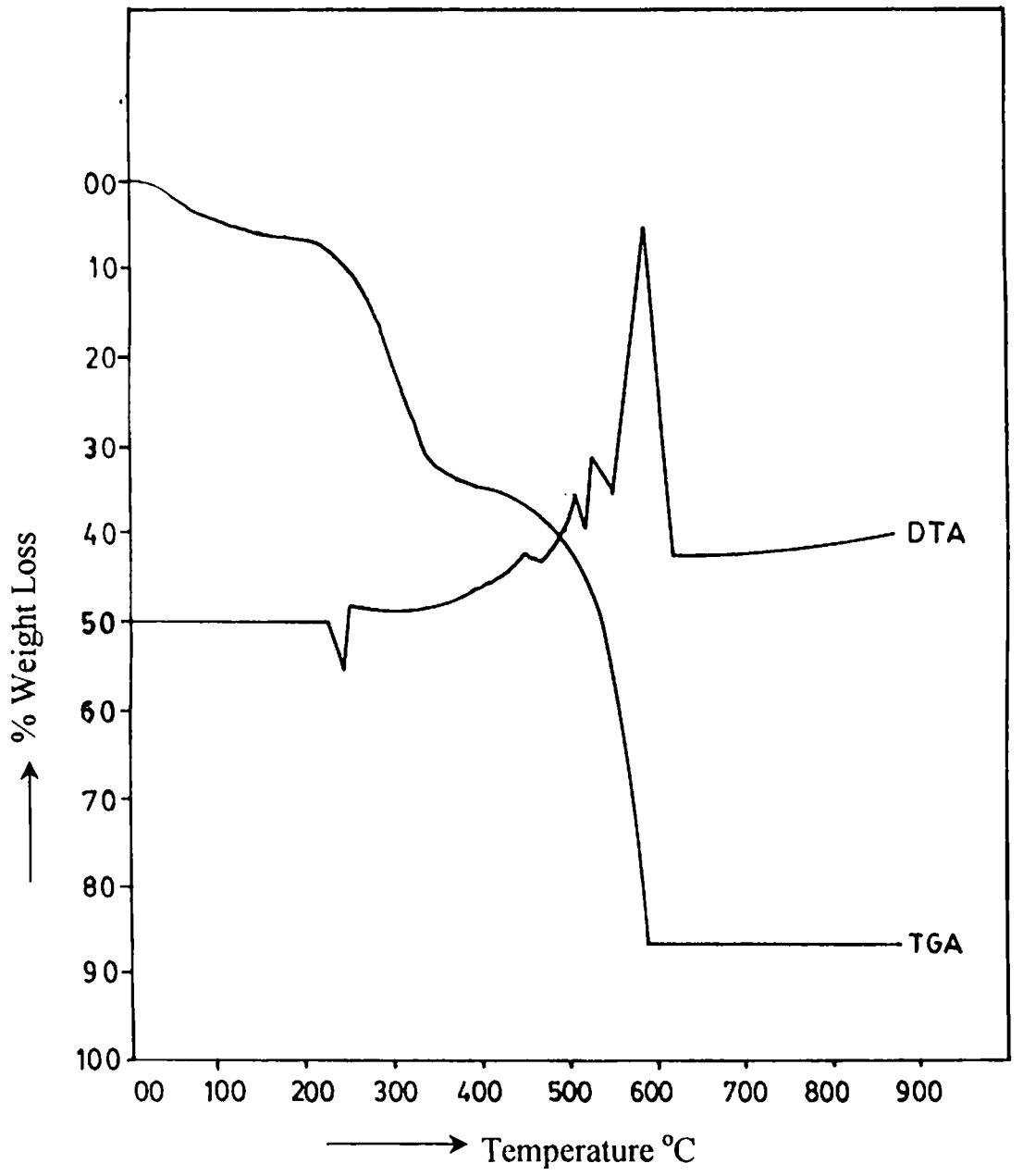


Fig. 2.9 TGA and DTA curve of $Co(C_7H_6N_2)_2Cl_2.6H_2O$

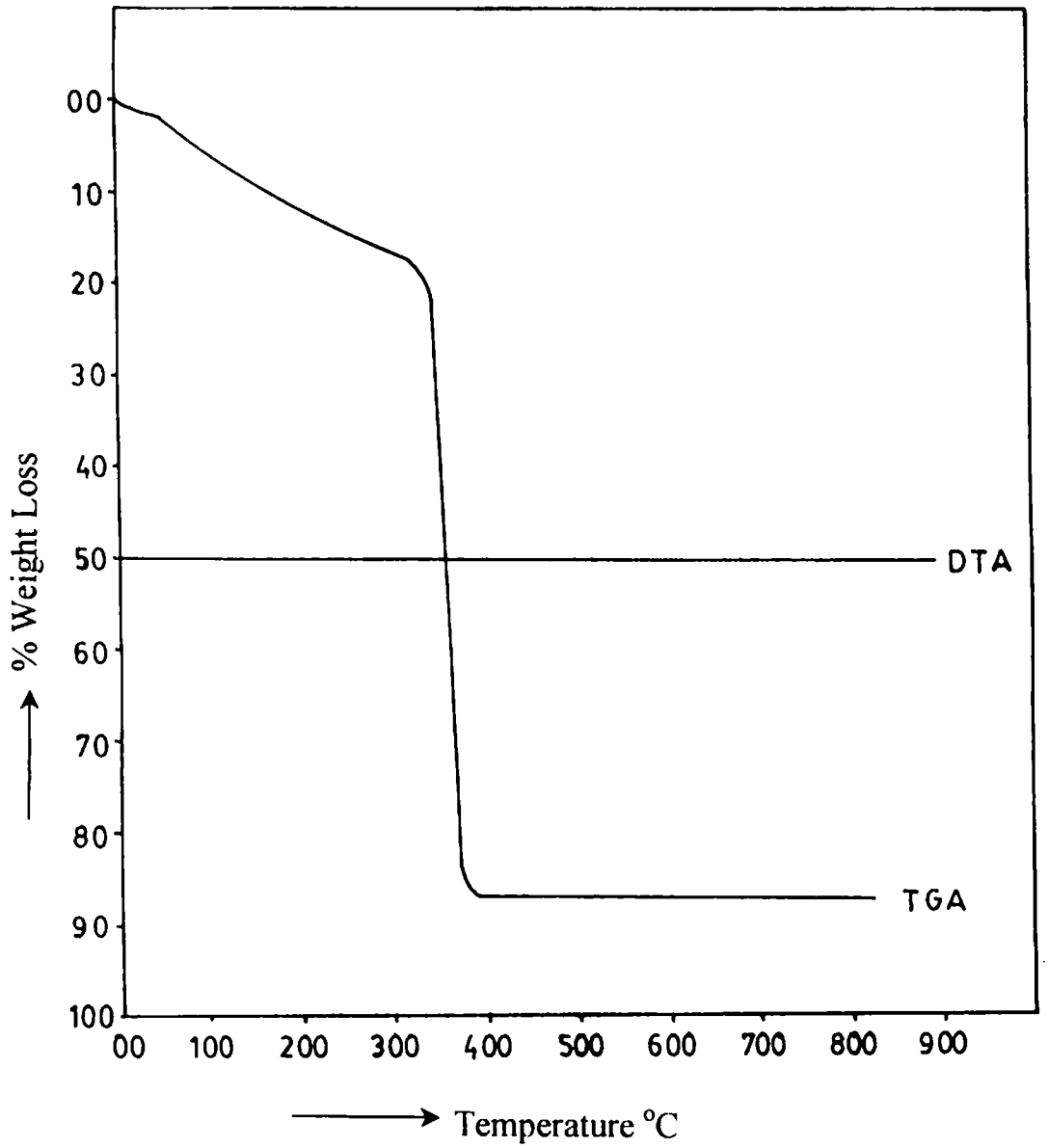


Fig. 2.10 TGA and DTA curve of $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$

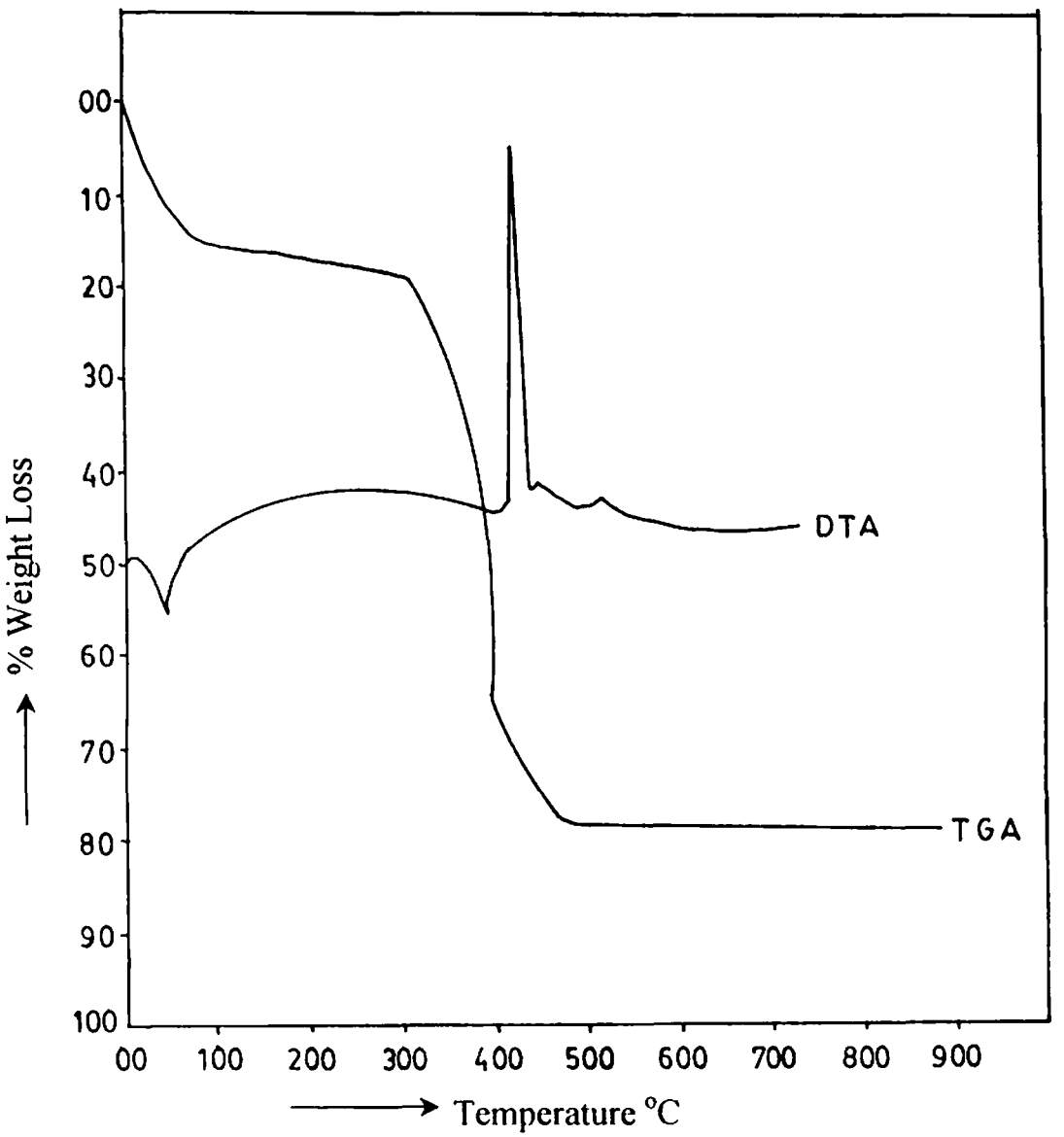


Fig. 2.11 TGA and DTA curve of $Ni(C_7H_6N_2)Cl_2.2H_2O$

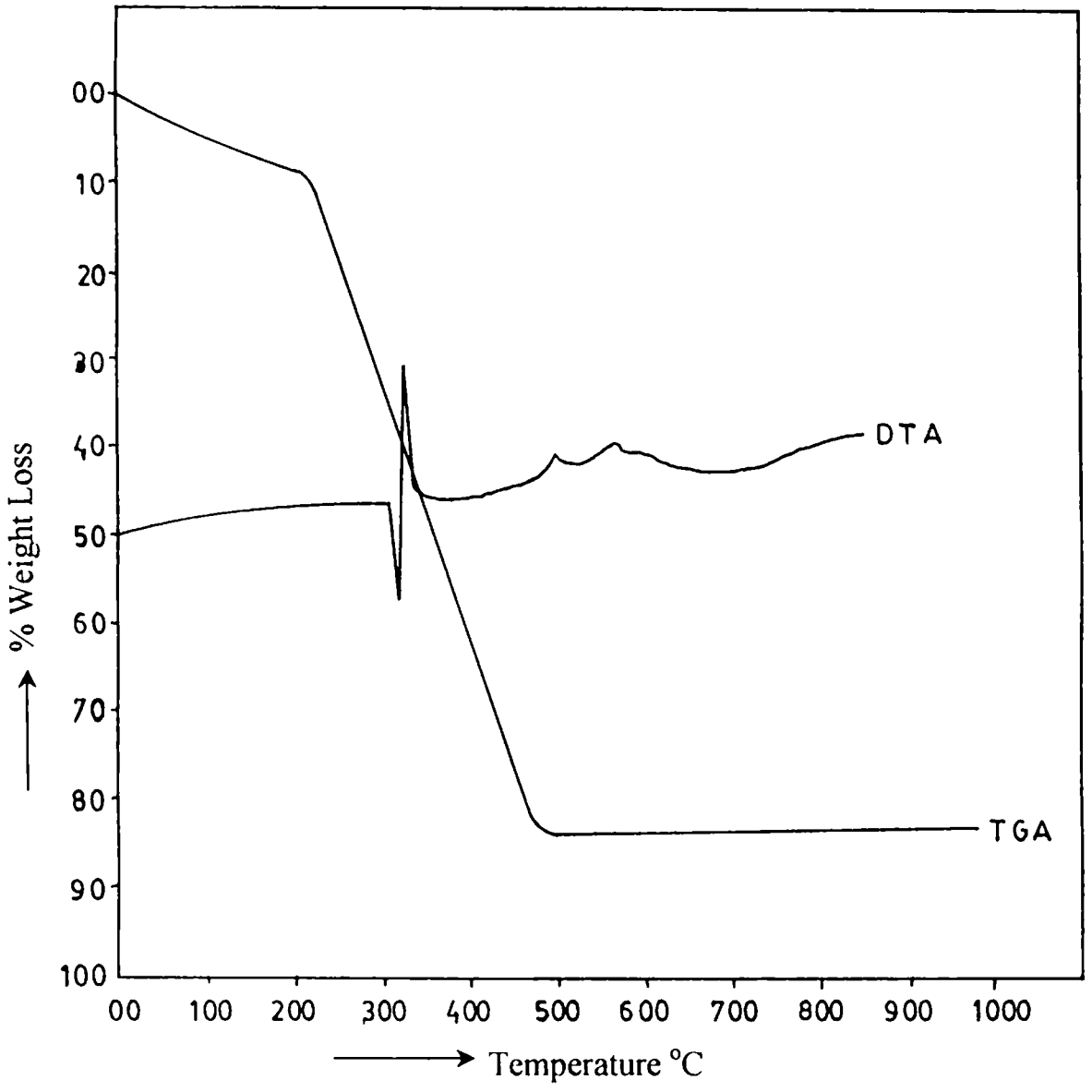


Fig. 2.12 TGA and DTA curve of $Cu(C_7H_6N_2)_2Cl_2.2H_2O$

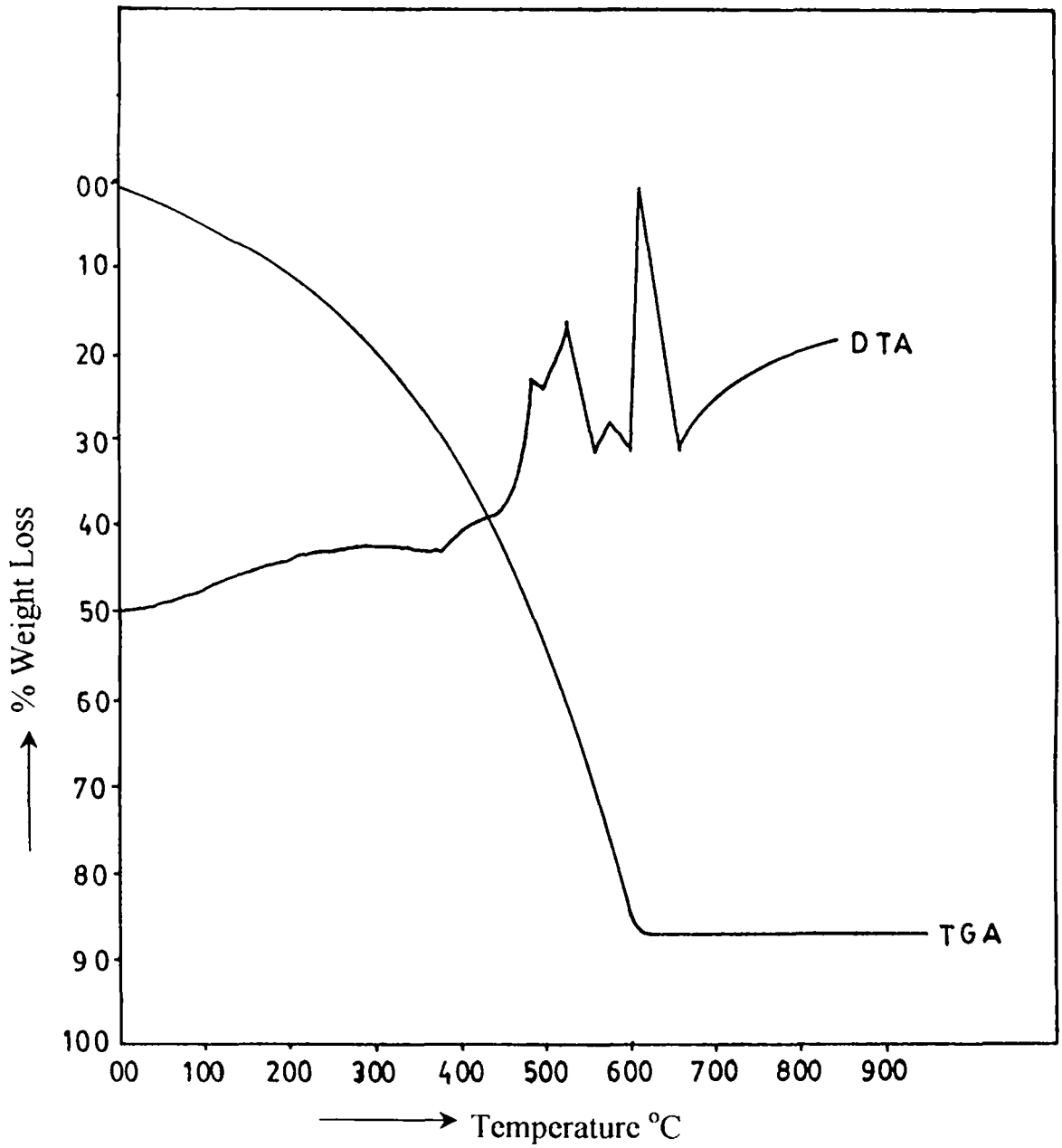


Fig. 2.13 TGA and DTA curve of $Zn(C_7H_6N_2)_2SO_4.H_2O$

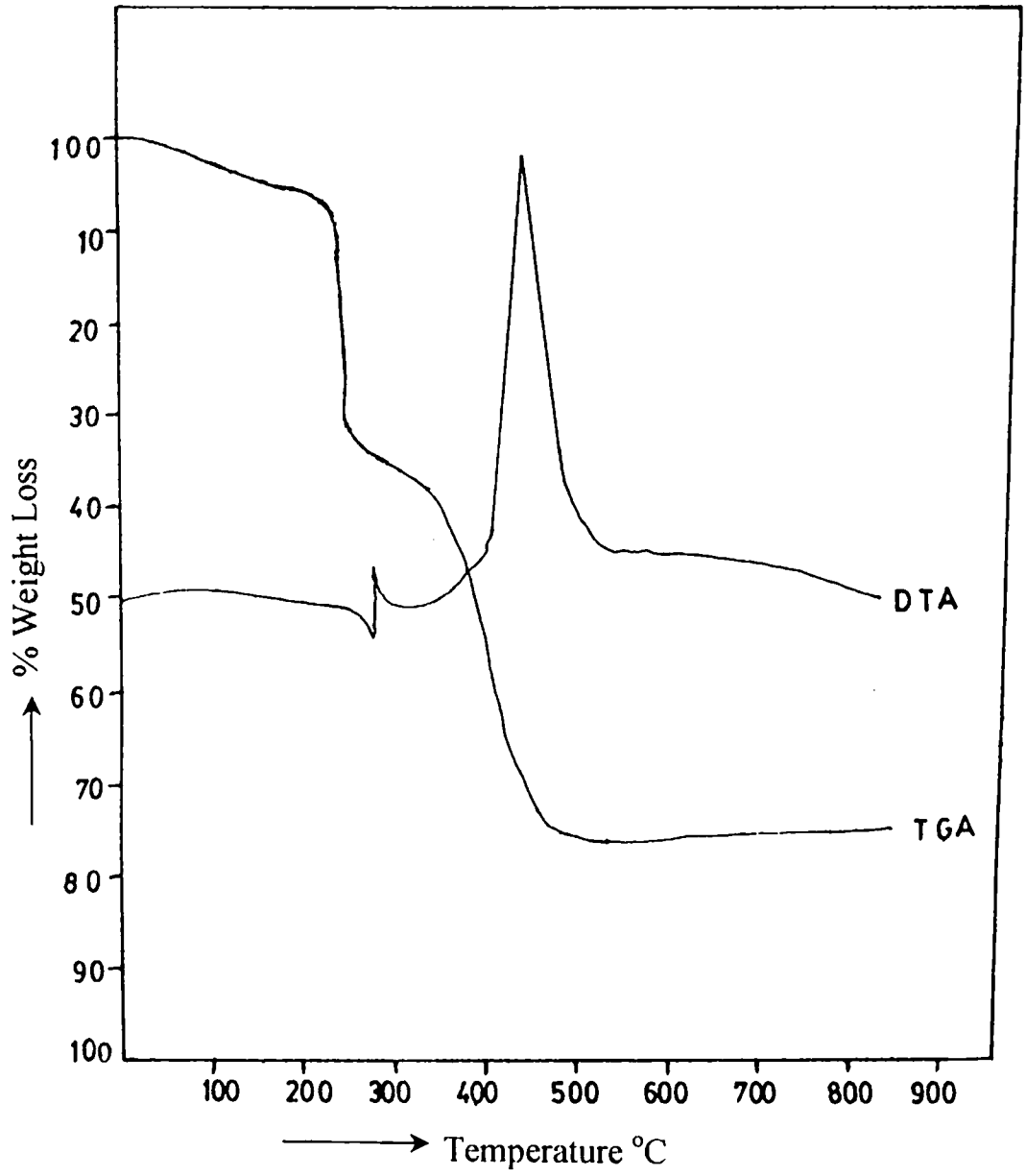


Fig. 2.14 TGA and DTA curve of $Ag(C_7H_6N_2)_2NO_3$

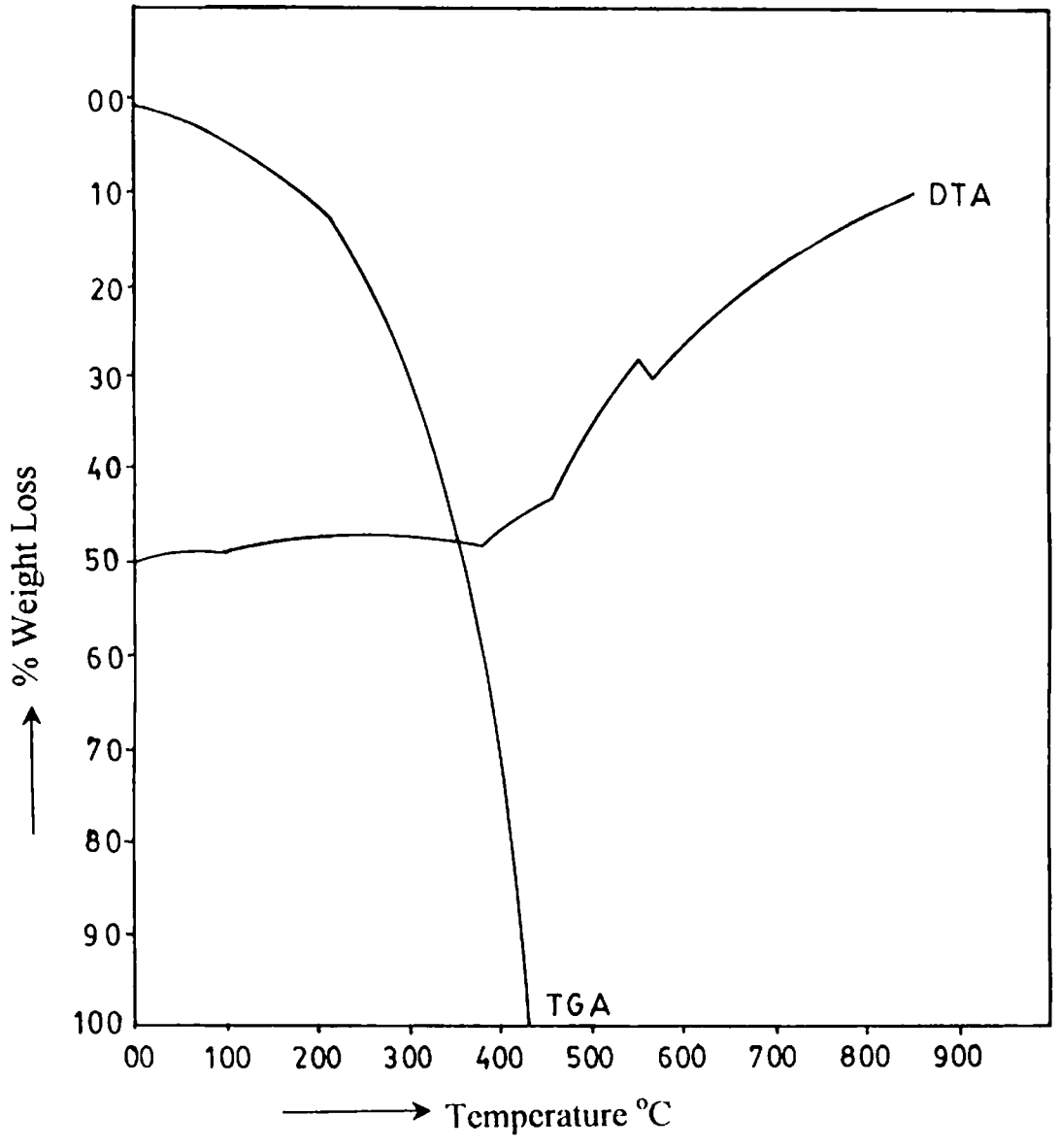


Fig. 2.15 TGA and DTA curve of $Hg(C_7H_6N_2)Cl_2.2H_2O$

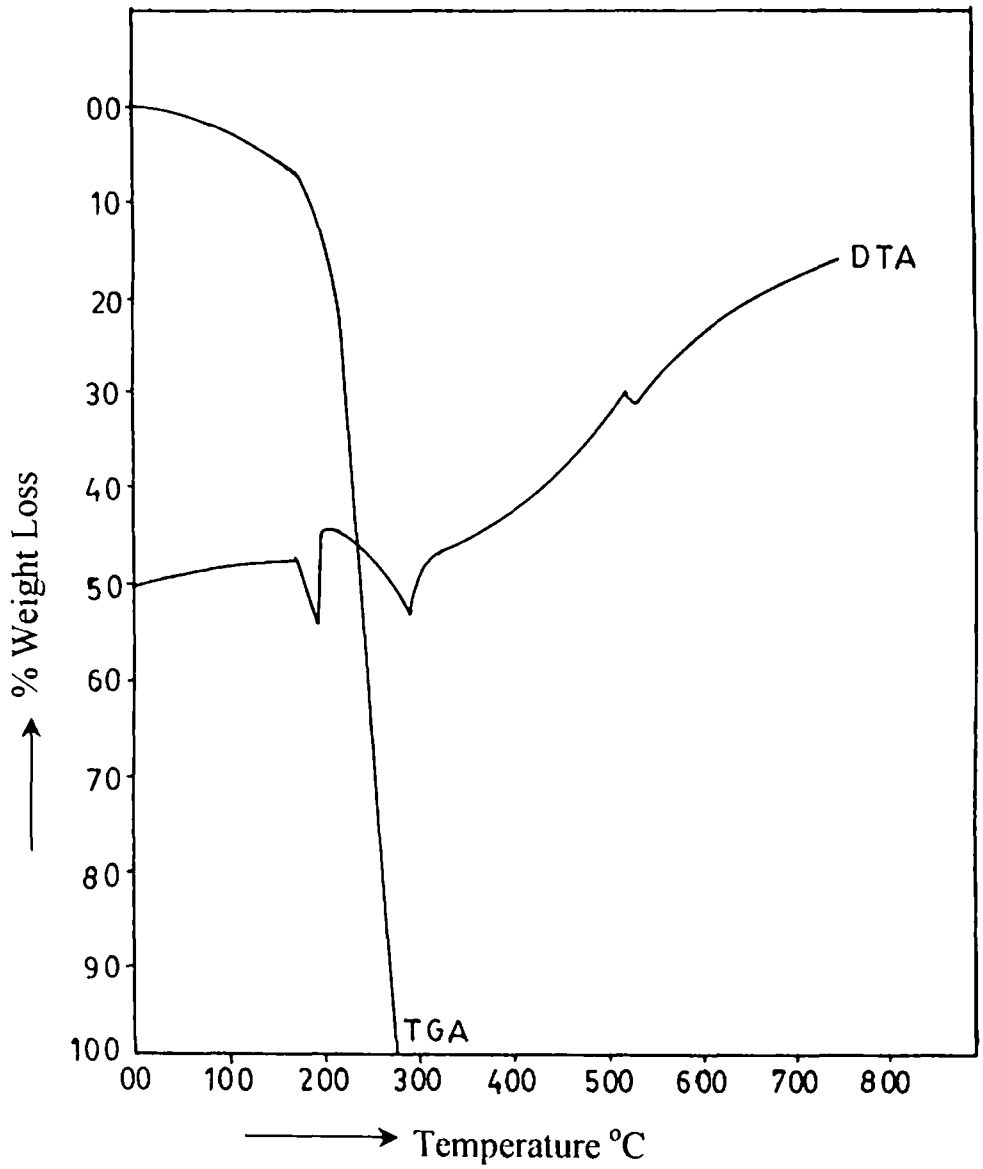


Fig. 2.16 TGA curve of $Hg(C_7H_6N_2)Cl.2H_2O$

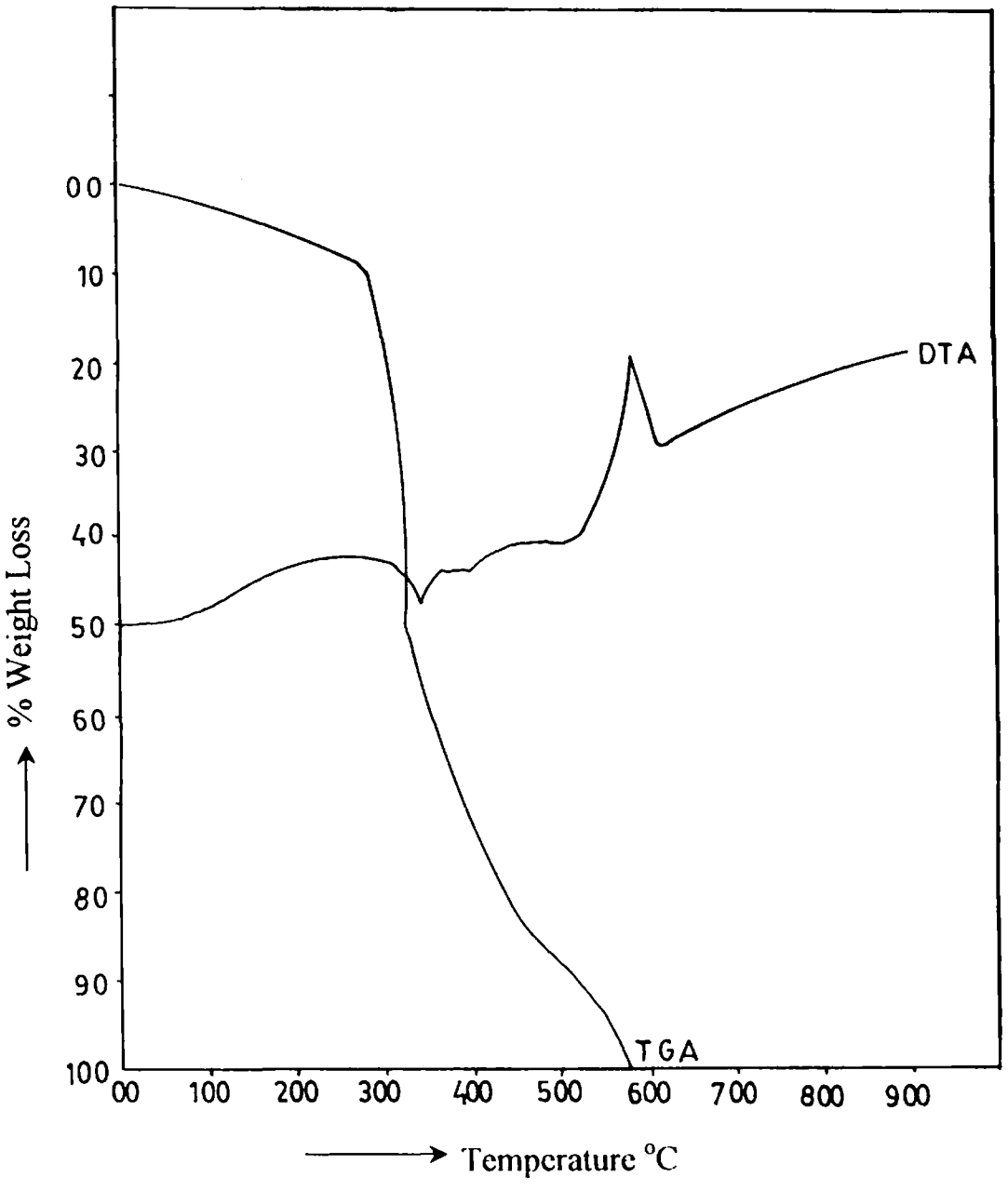


Fig. 2.17 TGA and curve DTA of $Hg(C_7H_6N_2)NO_3.2H_2O$

2.3.5 Infrared spectrum

A complex molecule has an infrared spectrum exhibiting a large number of normal vibrations[59]. Normal modes are divided into two classes

1. The skeletal vibrations, which involve the whole or large part of the molecular framework.
2. The characteristic group vibration, which involve only a small portion of the molecule.

Skeletal frequency usually fall in the range 1400-700 cm^{-1} and arise from linear to branched chain structure. Group frequencies are usually almost independent of the structure of the molecule as a whole, and with a few exception falls in the region well above and below that of the skeletal modes. It can be used to reveal the presence or absence of the group in the molecule and this is frequently of tremendous help in characterizing the molecular structure.

Infrared spectral investigation provides for microscopic information on the nature of the bonds between the metal ions and the ligand of the complex compounds. Infrared spectrum analysis of a complex are not conclusive study but is complementary to other technique used for structural characterization of chemical bonds.

From the ir study valuable information are obtained regarding the structure of the complexes and the hydrated nature of the compound can be identified. The previous aspects of complex formation may also be characterized with the help of this technique.

Infrared spectroscopy has been used specifically for a number of problems in benzimidazole chemistry, particularly in relation to the phenomenon of hydrogen bonding[60-61].

Infrared spectra of the complexes during the present work were recorded with a Shimadzu Infrared spectrophotometer of Japan, Model IR-470. The working range of the instrument is 4000-400 cm^{-1}. The recording were carried out by using KBr pellets.

The infrared spectra of benzimidazole and its metal complexes are given in Fig 2.18 to 2.27 and absorption bands are listed with relative intensities and band assignments in the Tables 2.12 - 2.21.

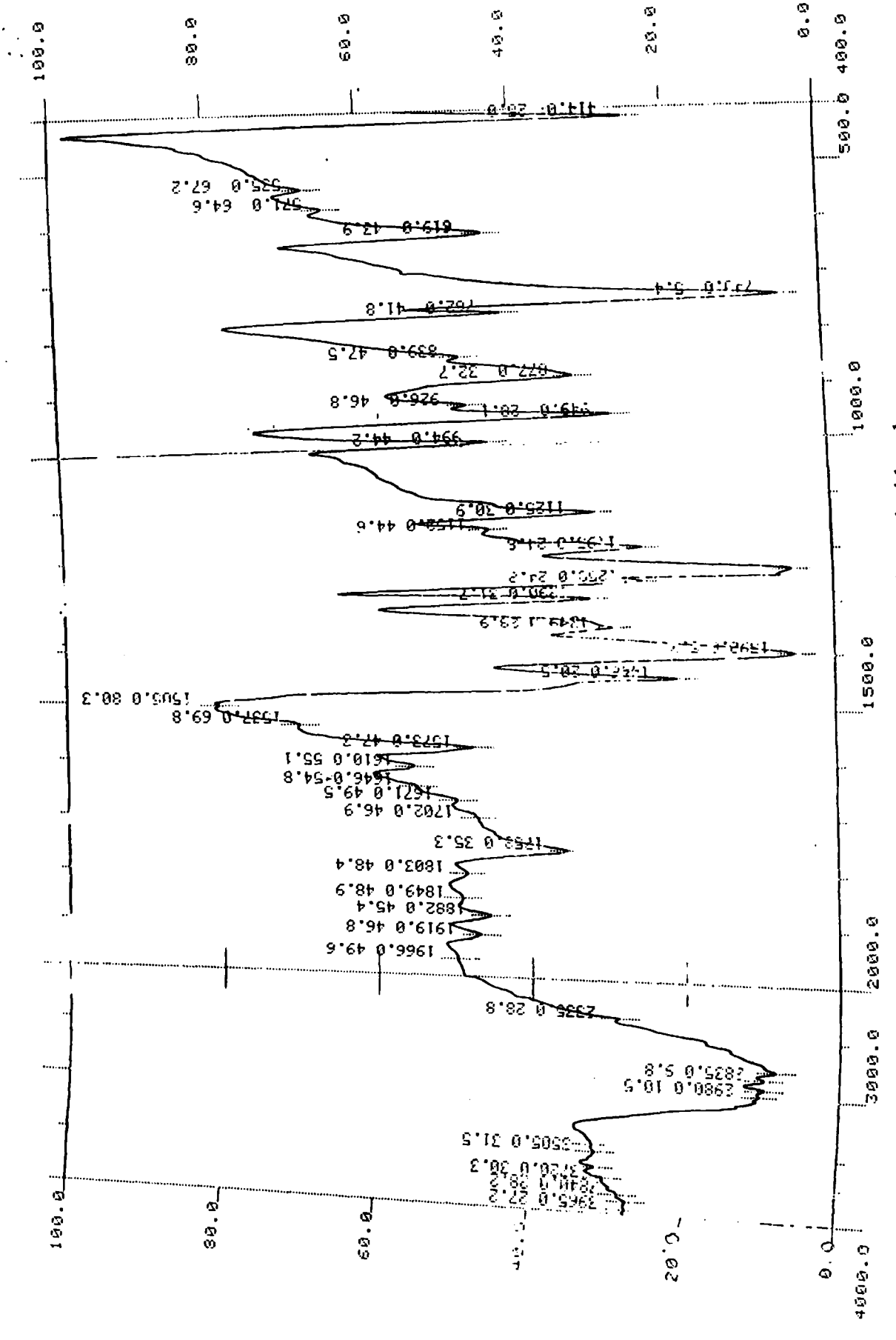


Fig. 2.18 IR spectrum of benzimidazole

Table 2.12. IR spectral data for the ligand (benzimidazole)

Wave No. Cm^{-1}	Relative intensity	Band assignment	Previous report[62]	
			Wave No. cm^{-1}	Relative intensity
3450	b	O-H or N-H stretching		
3100		C-H stretching in	3110	s
3040	s	aromatic	3060	s
2835		system	2800	s
1610	b		1622	w
1573	s	C=N stretching	1590	s
1505	w	C=C stretching	1497	w
1446	s	N-H deformation vibration	1459	s
1398	sh		1392	sh
1349	m		1347	w
1290	s	C-N stretching	1274	s
1250	s		1247	vs
1195	s		1203	s
1125	s	C-H bending in plane	1135	s
994	s	C-C-N stretching	1004	s
949	s		958	m
926	m		933	w
877	sh		882	sh
839	w		847	vw
762	s		769	s
749	vs	C-H bending out of plane	745	s
619	m		616	w
517	w		577	w
535	w		540	w

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium, sh = shoulder.

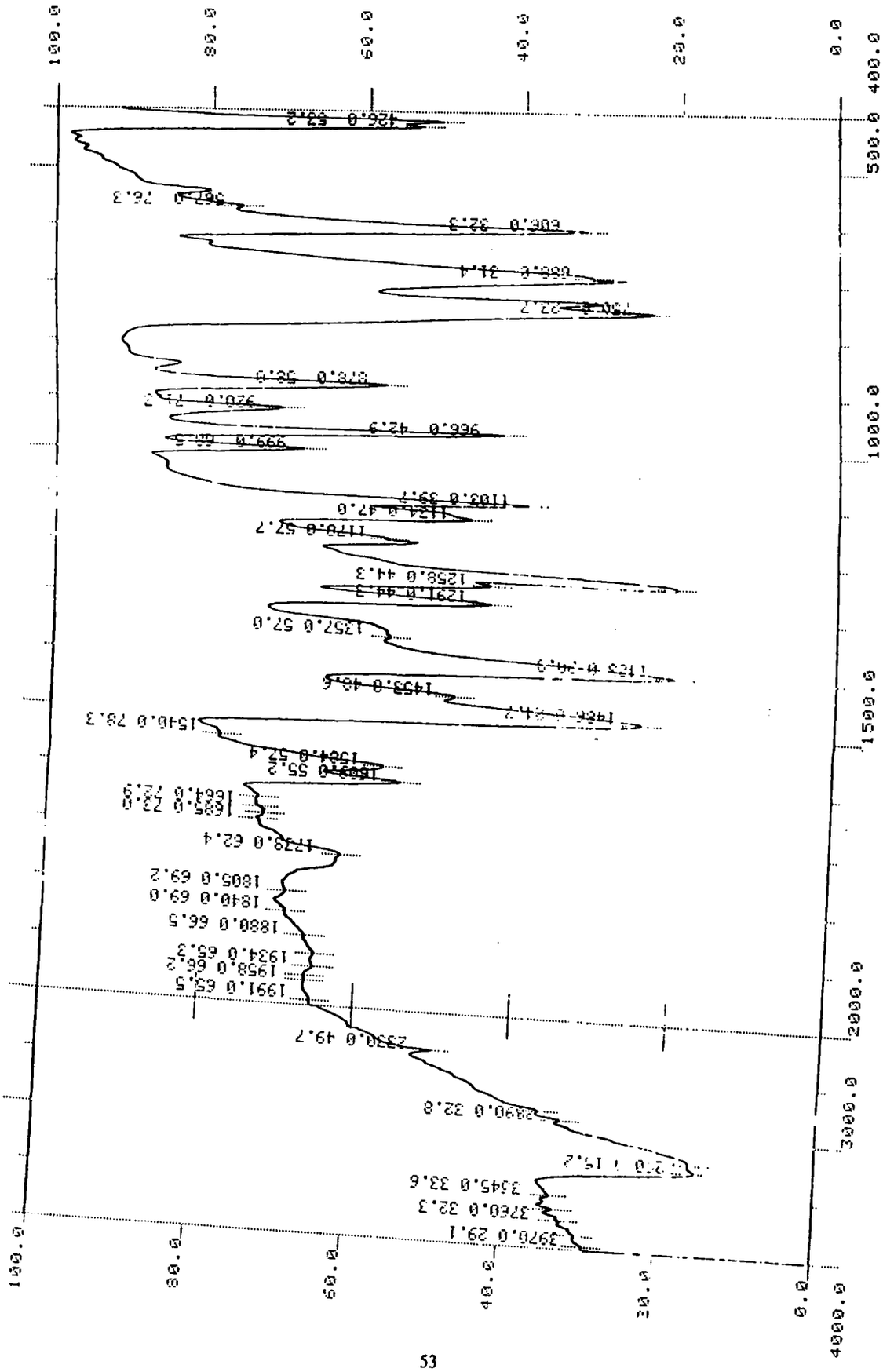


Fig. 2.19 IR spectrum of $Co(C_7H_6N_2)_2Cl_2.6H_2O$

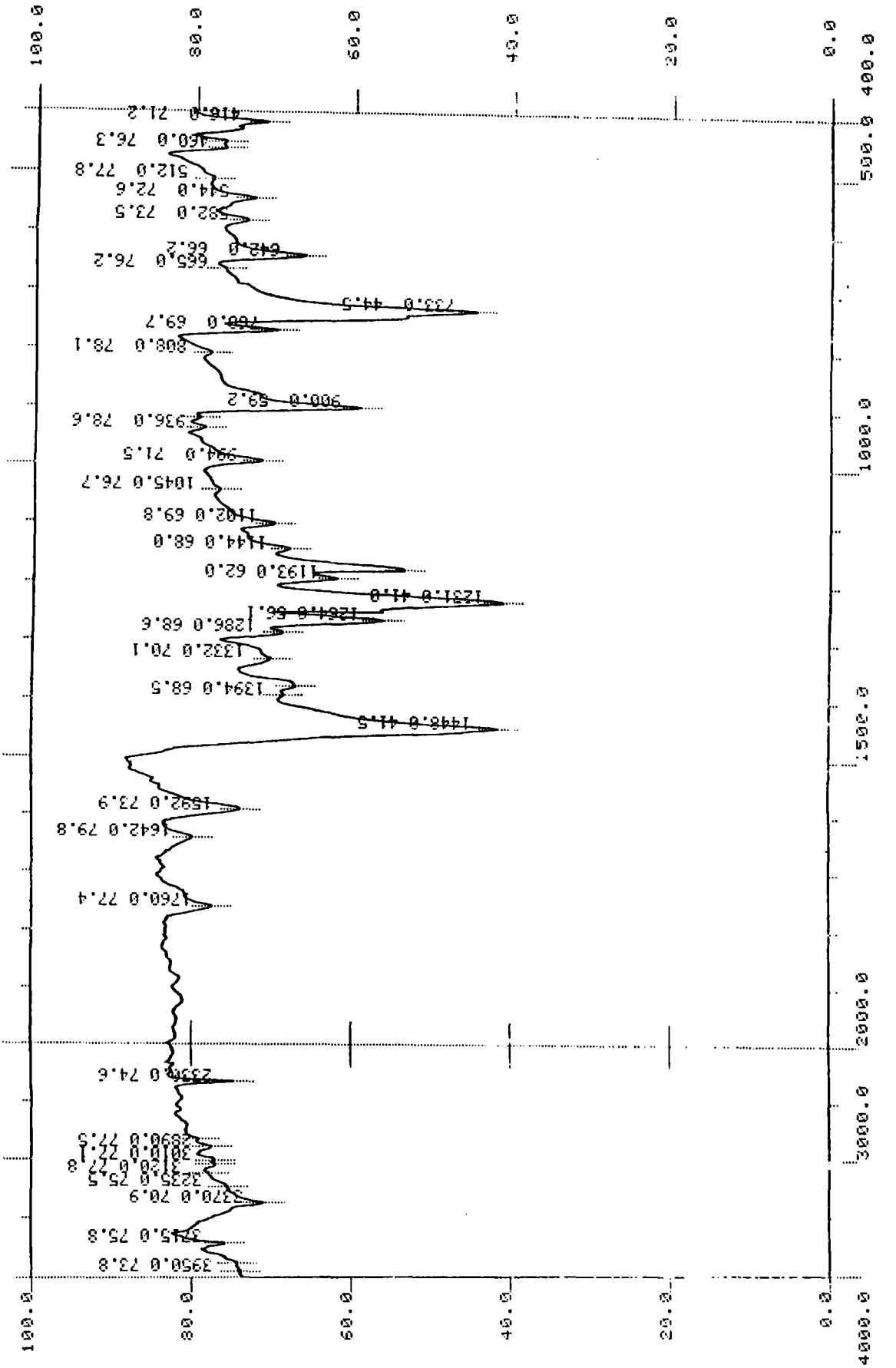


Fig. 2.20 IR spectrum of $Co(C_7H_6N_2)_2NO_3.2H_2O$

Table 2.13. IR spectral data for the $Co(C_7H_6N_2)_2Cl_2.6H_2O$

Wave No. cm^{-1}	Relative intensity	Band assignment
3290	b	OH or N-H stretching
2890	m	C-H stretching in aromatic system
1609	s	O-H bending of water
1584	s	C=N stretching in aromatic nuclei
1486	s	N-H deformation vibration
1453	s	CH_2 stretching
1403	vs	
1291 1258	s s	C-N stretching
1178	m	O-H bending of water
1134	m	C-H bending (in plane)
999 966	s	C-C-N stretching
878	s	
750	vs	C-H bending (out of plane)
426	s	Co-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

Table 2.14. IR spectral data for the $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3370	s	O-H or N-H stretching
3120 3010 2890	m	C-H stretching in aromatic system
1642	b	O-H bending of water
1592	m	C=N stretching in aromatic nuclei
1448	vs	N-H deformation vibration
1264	m	C-N stretching
1231	s	
1193	m	O-H bending of water
1102	m	C-H bending in plane
994	m	C-C-N stretching
900	s	
733	vs	C-H bending (out of plane)
416	s	Co-N stretching

Vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

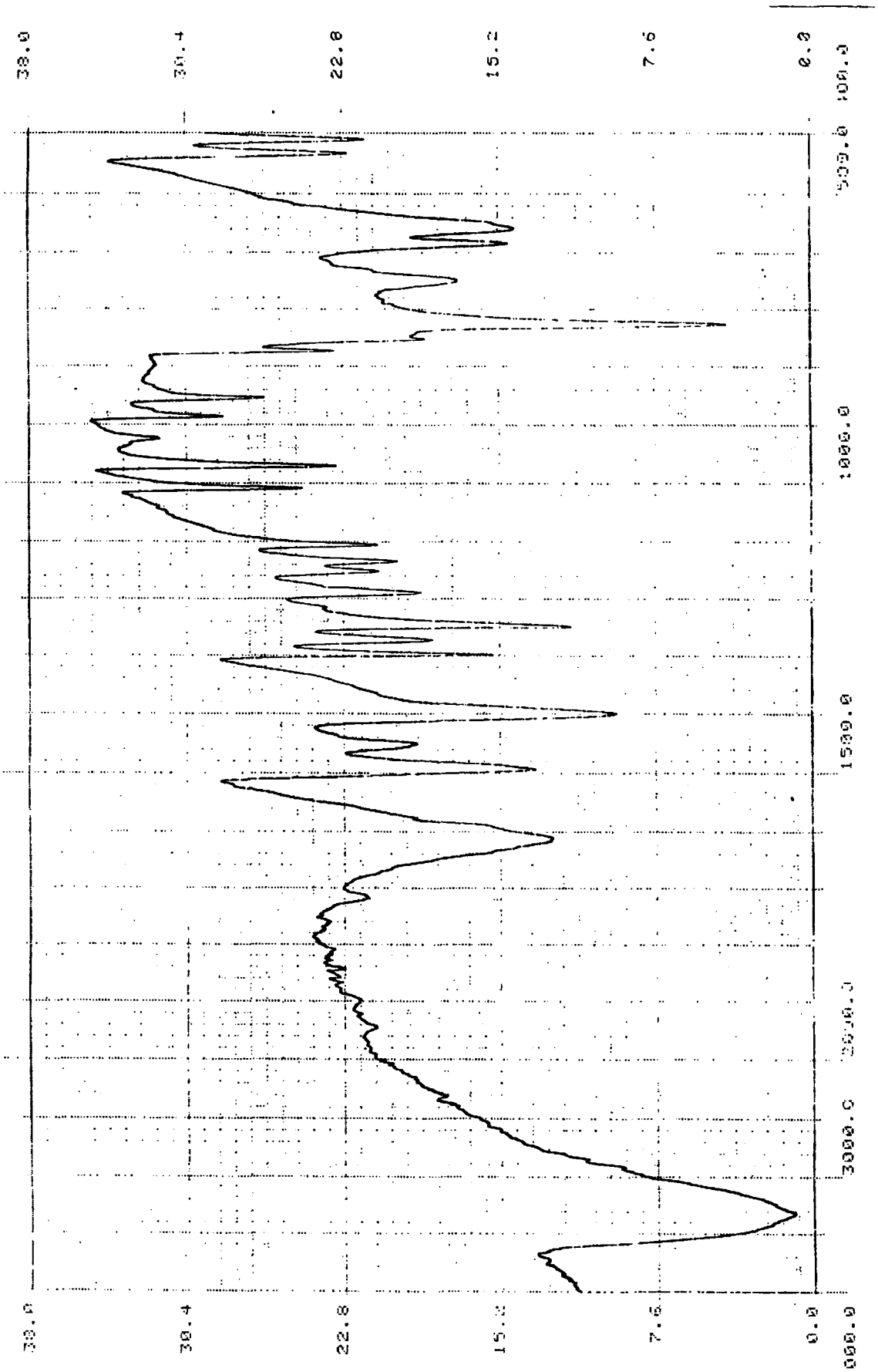


Fig. 2.21 IR spectrum of $Ni(C_7H_6N_2)Cl_2.2H_2O$

Table 2.15. IR spectral data of $Ni(C_7H_6N_2)Cl_2.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3330	b	O-H or N-H stretching
2995	w	C-H stretching in aromatic system
1610	b	O-H bending of water
1580	m	C=N stretching in aromatic nuclei
1495	s	N-H deformation vibration
1450	s	CH_2 stretching
1400	vs	
1300 1250	s	C-N stretching
1190	s	O-H bending of water
1105 1110	m	C-H bending in plane
970	s	C-C-N stretching
885 855	s	
727	vs	C-H bending (out of plane)
455	s	Ni-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

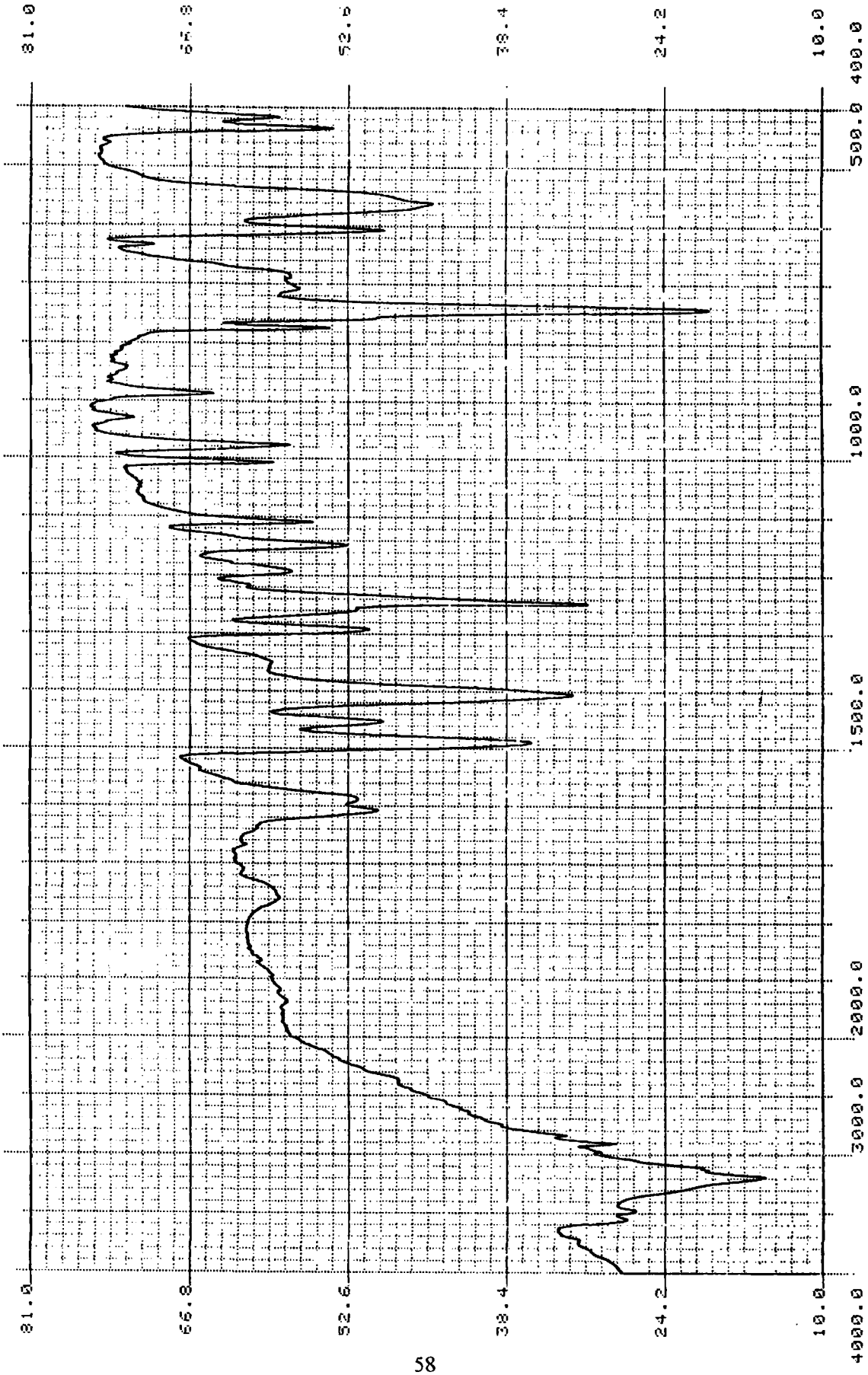


Fig. 2.22 IR spectrum of $Cu(C_7H_6N_2)_2Cl_2.2H_2O$

Table 2.16. IR spectral data for $Cu(C_7H_6N_2)_2Cl_2.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3480	b	O-H or N-H stretching
3200	s	N-H stretching
2980	m	C-H stretching in aromatic system
1640	m	O-H bending of water
1590	b	C=N stretching
1495	s	N-H deformation vibration
1450	m	CH_2 stretching
1410	s	
1295 1250	m s	
1195	m	O-H bending of water
1148 1110 1010	m	C-H bending in plane
978	S	C-C-N stretching
740	vs	C-H bending (out of plane)
435	s	Cu-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

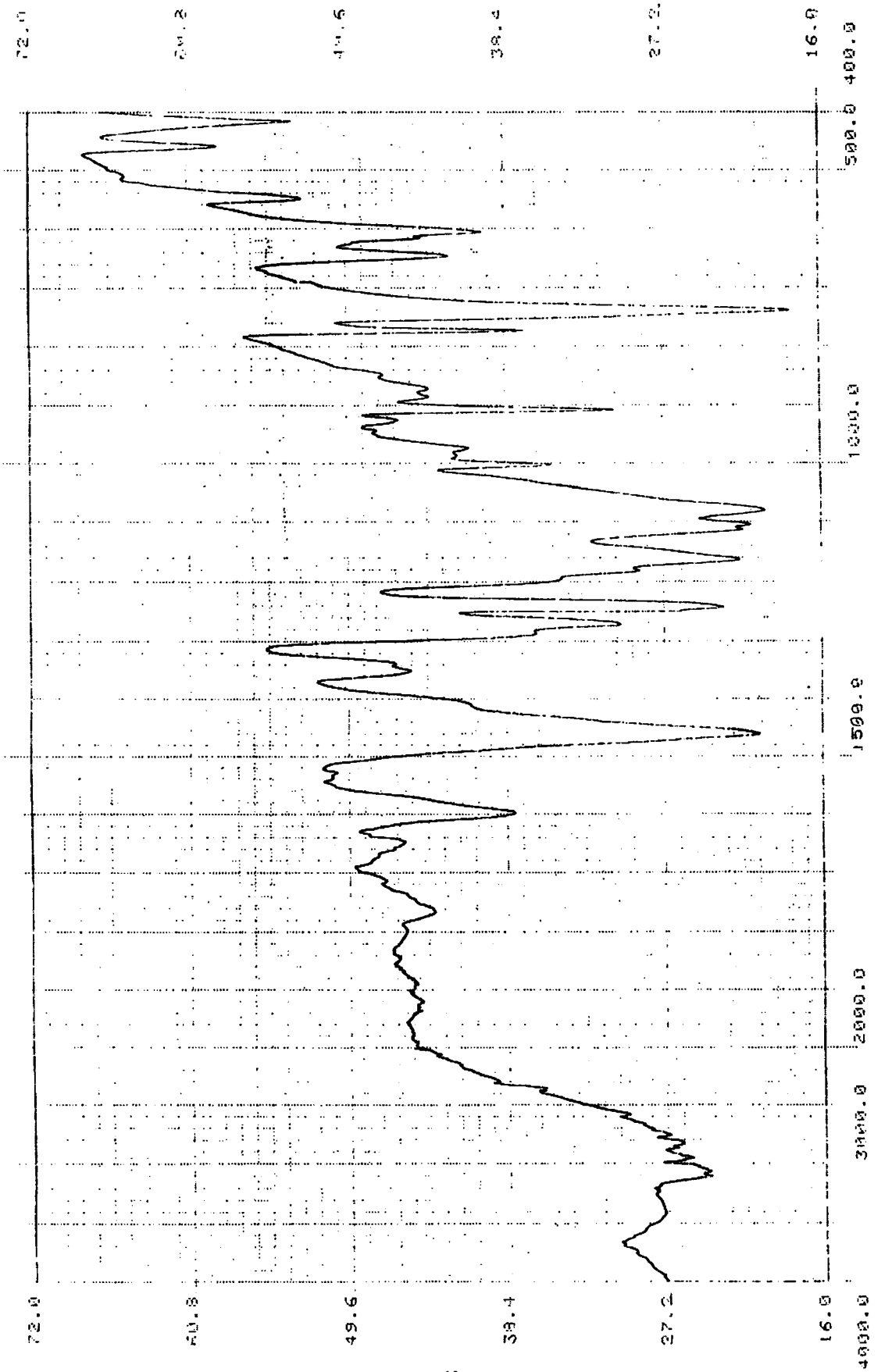


Fig. 2.23 IR spectrum of $Zn(C_7H_6N_2)_2SO_4.2H_2O$

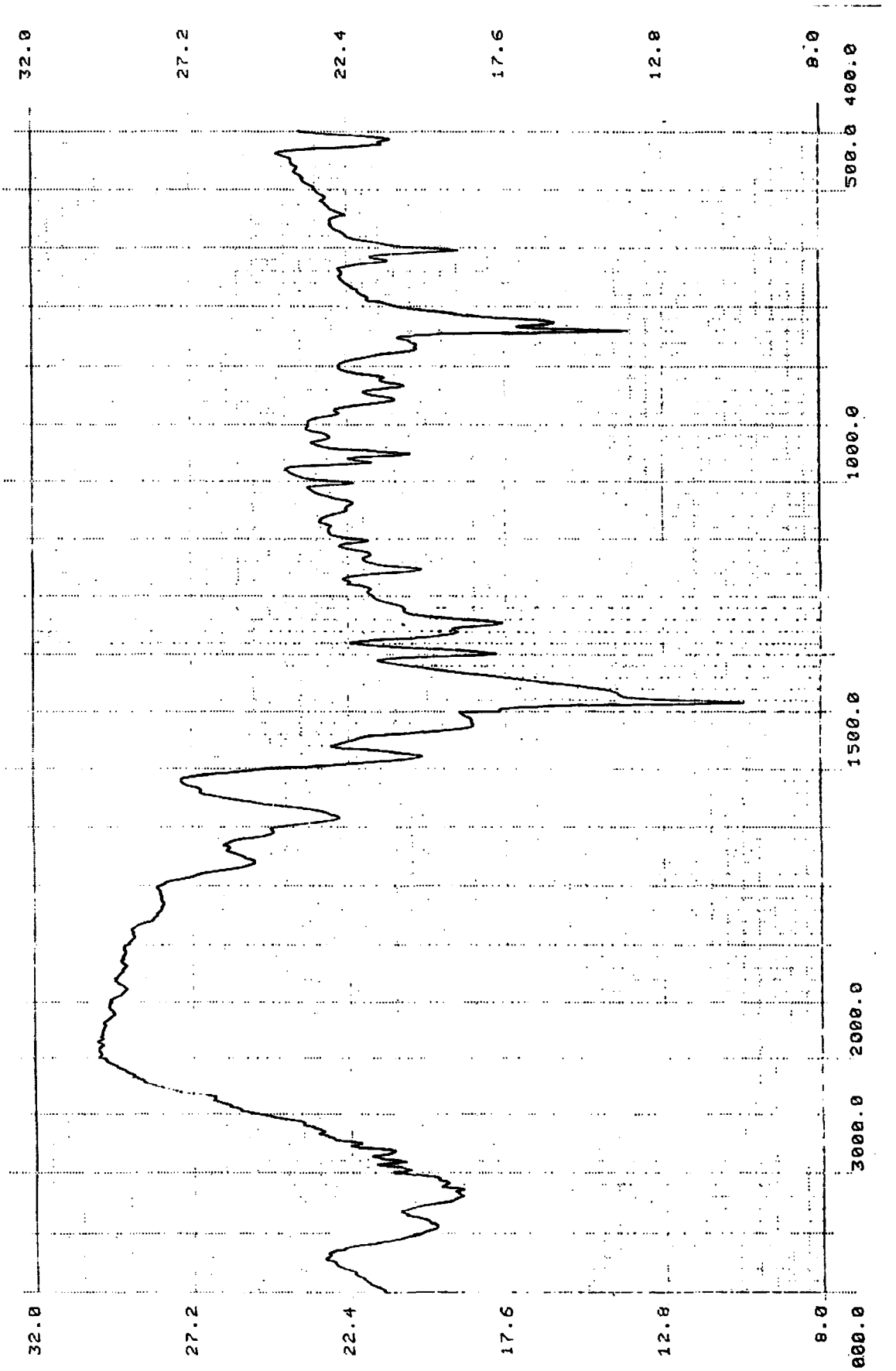


Fig. 2.24 IR spectrum of $Ag(C_7H_6N_2)_2NO_3$

Table 2.17. IR spectral data of $Zn(C_7H_6N_2)_2SO_4.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3500	b	O-H or N-H stretching
3060	m	C-H stretching in aromatic system
1645	b	O-H bending of water
1598	s	C=N stretching
1530	w	C=C stretching
1460	vs	N-H deformation vibration
1350 1270	m s	C-N stretching
1185	m	O-H bending of water
1242 1145	s	S=O stretching
1080 1003	m s	C-H bending in plane
910	s	
740	vs	C-H bending out of plane
460	s	Zn-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

Table 2.18. IR spectral data of $Ag(C_7H_6N_2)_2NO_3$

Wave No cm^{-1}	Relative intensity	Band assignment
3450	b	O-H or N-H stretching
3140	m	C-H stretching in aromatic system
1610	s	C=N stretching
1585	s	C=C stretching in aromatic nuclei
1480	s	N-H deformation vibration
1385	vs	
1300	s	C-N stretching
1245	s	
1005	m	C-H bending in plane
740	vs	C-H bending out of plane
423	s	Ag-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

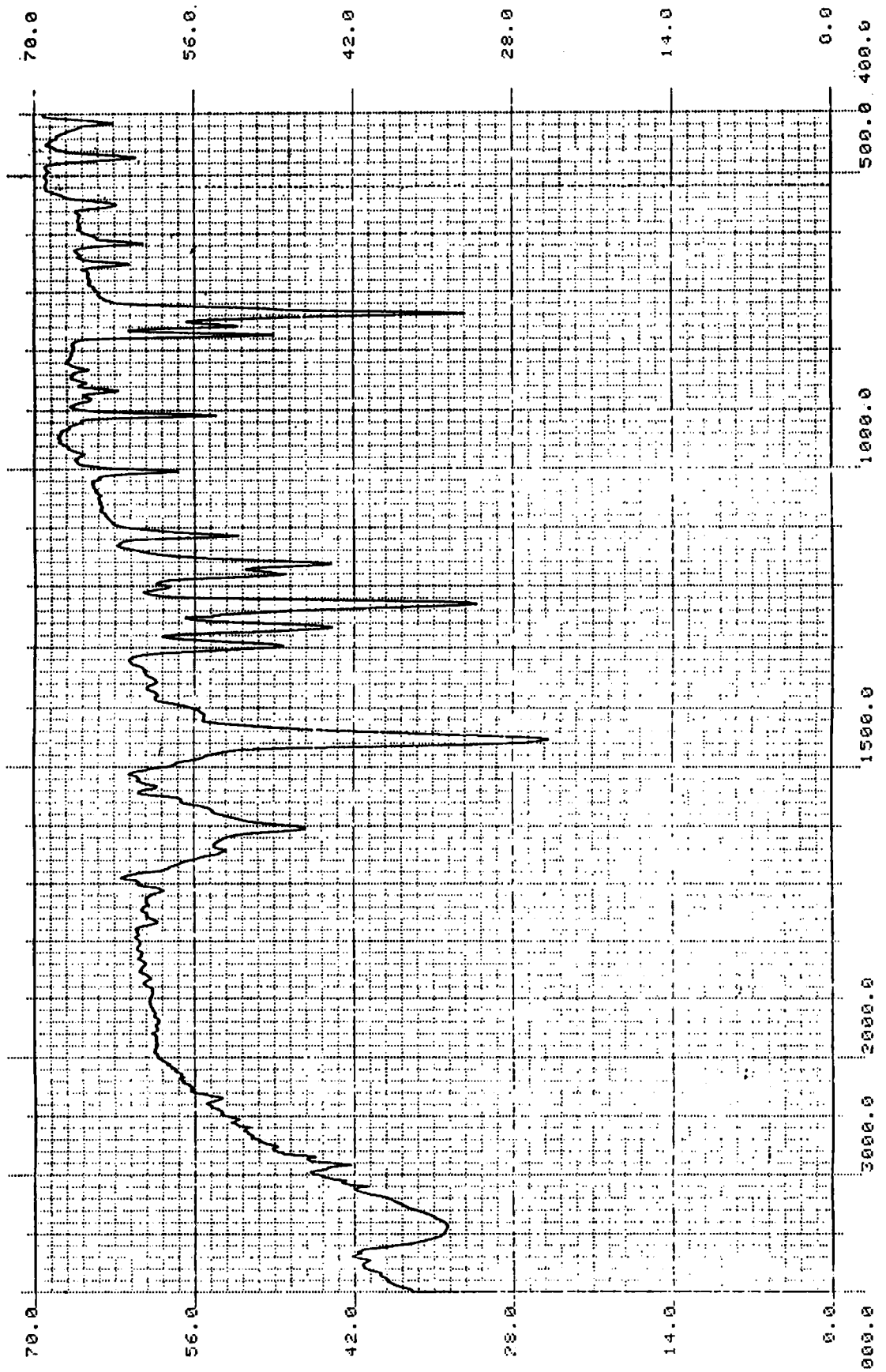


Fig. 2.25 IR spectrum of $Hg(C_7H_6N_2)Cl_2.2H_2O$

Table 2.19. IR spectral data of $Hg(C_7H_6N_2)Cl_2.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3450	b	O-H or N-H stretching
3100 3045 2920	m	C-H stretching in aromatic system
1643	b	O-H bending of water
1605	s	C=N stretching
1538	m	C=C stretching in aromatic nuclei
1453	vs	N-H deformation vibration
1380	m	
1297 1265	s	C-N stretching
1230	m	
1200	m	
1180	m	O-H bending of water
1115 1005	s	C-H bending in plane
9010	s	
757	vs	C-H bending out of plane
470	s	Hg-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

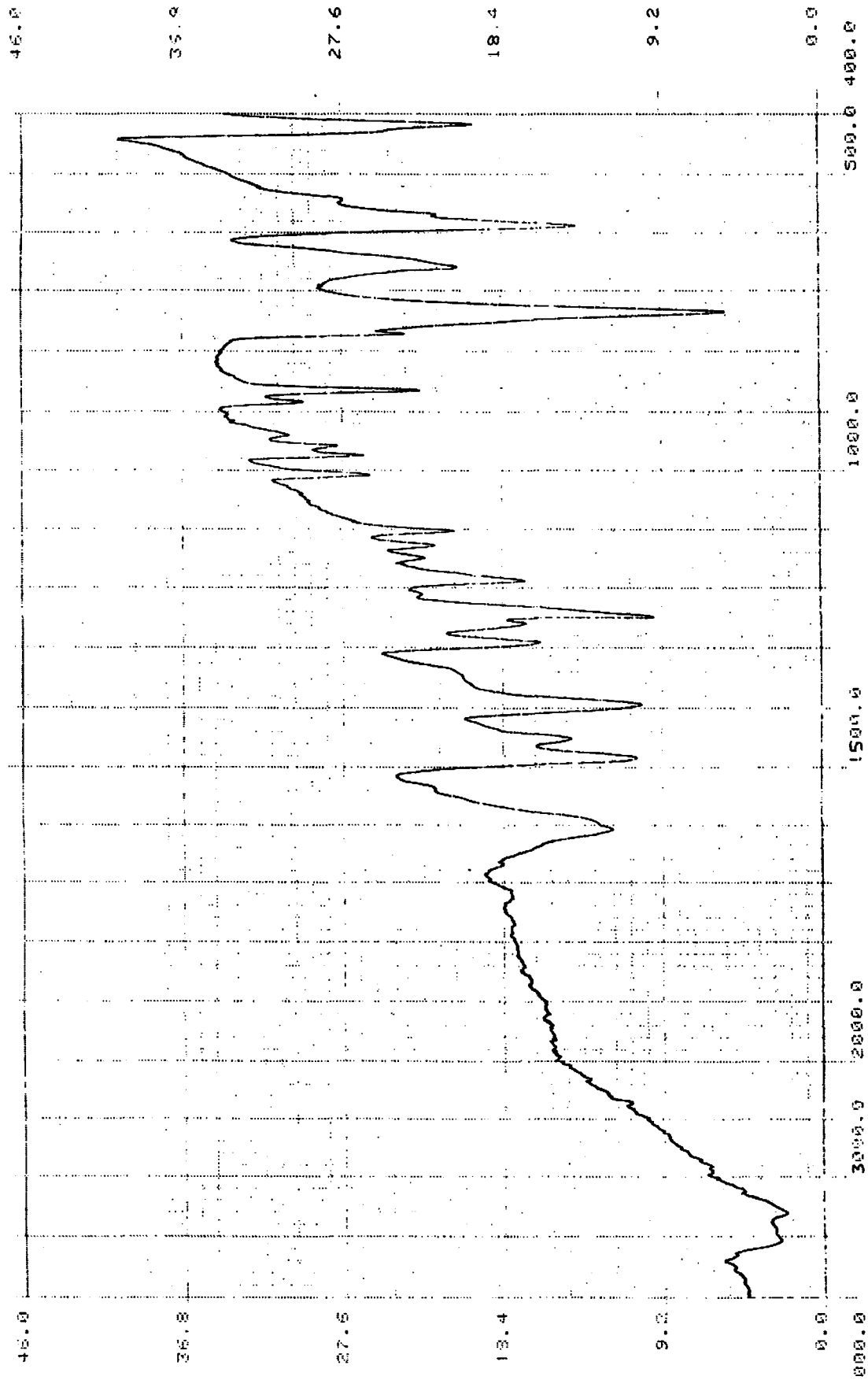


Fig. 2.26 IR spectrum of $Hg(C_7H_6N_2)Cl.2H_2O$

Table 2.20. IR spectral data of $Hg(C_7H_6N_2)Cl.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3540	b	O-H stretching
3310	m	N-H stretching
3010	w	C-H stretching in aromatic system
1610	b	O-H bending of water
1595	m	C=N stretching
1535	m	C=C stretching in aromatic nuclei
1485	s	N-H deformation vibration
1450	m	CH_2 stretching
1395	s	
1290 1250	m s	C-N stretching
1193	m	O-H bending of water
1105 1010	m	C-H bending in plane
975	m	C-C-N stretching
865	s	
735	vs	C-H bending out of plane
425	m	Hg-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

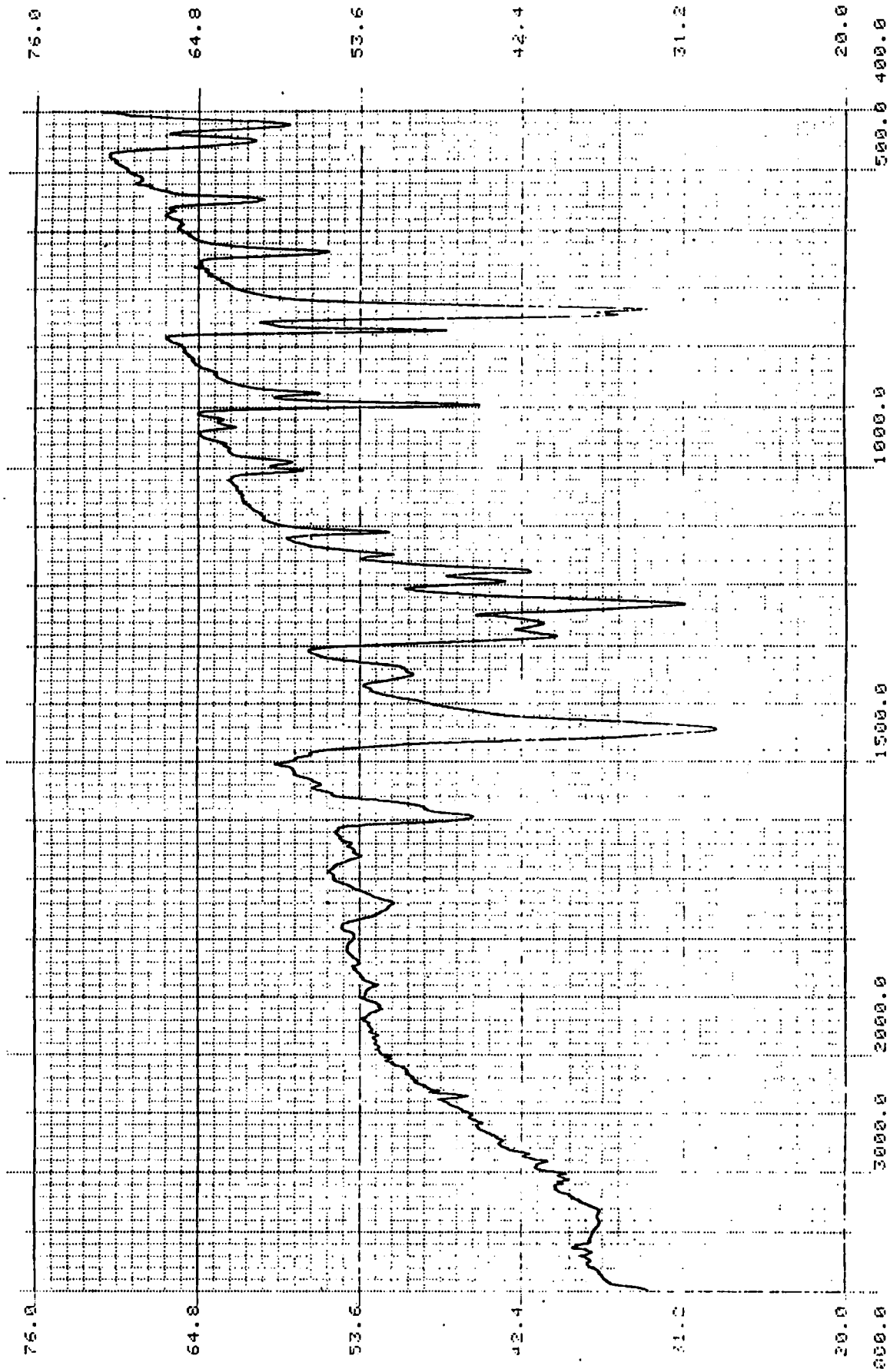


Fig. 2.27 IR spectrum of $Hg(C_7H_6N_2)NO_3.2H_2O$

Table 2.21. IR spectral data of $Hg(C_7H_6N_2)NO_3.2H_2O$

Wave No cm^{-1}	Relative intensity	Band assignment
3320	b	O-H or N-H stretching
3095 3060 3020	m	C-H stretching in aromatic system
1640	b	O-H stretching of water
1595	s	C=N stretching
1540	m	C=C stretching
1445	s	N-H deformation vibration
1285 1262	m	C-N stretching
1232	s	
1195	s	O-H bending of water
1110 1005	s	C-H bending in plane
898	s	
750 738	vs	C-H bending out of plane
450	s	Hg-N stretching

vs = very strong, v = very, w = weak, b = broad, s = strong, m = medium

2.3.6 Electronic spectrum

The electronic absorption spectra were carried out in Nujol mulls with Shimadzu uv-visible spectrophotometer, model UV-160, in the wavelength in the range of 200-800 nm.

Ultraviolet spectra of complex compounds can give at least qualitative knowledge of their electronic properties. Energy absorbed in the UV region produces changes in the electronic energy of the molecule resulting from the transitions of electrons. The transitions consist of the excitation of electron from a filled molecular orbital (usually non-bonding p or bonding π orbital) to next higher energy orbital (an antibonding π or σ orbital)[63]. Consequently the electronic spectra will indicate absorption of energy. The different possible origin for the electronic absorption spectra of complexes are[64]

(i) Spectra associated principally with the ligand.

(ii) Spectra involving electronic transitions between the metal and the ligands, charge-transfer spectra.

(iii) Spectra associated principally with the metal, influenced by the presence of the ligands, d-d transition.

(iv) Spectra associated with the counter ion.

Therefore, the particular spectra associated any one c-compound is dependent upon the energy of d-orbitals, their degeneracy and the number of electron distributed in the orbitals. If the spectrum of the molecule is not mere superposition of the spectra of the ligand, an electronic interaction is indicated. In the UV region the absorption bands of the complexes occur due to the d-d, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. Relatively weak absorption band in the

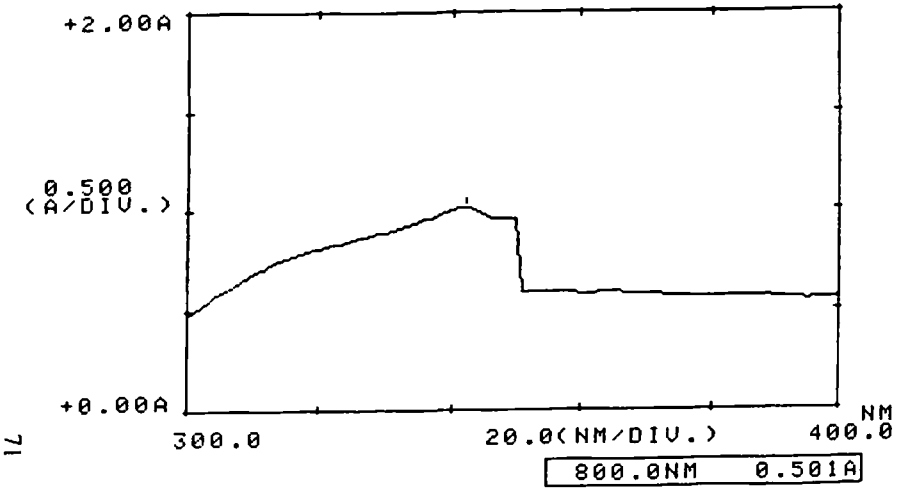
region 300-370 nm usually indicates $n \rightarrow \pi^*$ transition and the bands to high intensity (242-279) nm[65] in associated with the $\pi \rightarrow \pi^*$ transition.

The visible and ultraviolet spectroscopy is a simple but powerful tool for the interpretation of the chemical bonding and structure of the complex compound. It may be used to analyse ions, compounds or mixtures and to follow reaction paths and rates.

The spectra of benzimidazole and its metal complexes are shown in Figs. 2.28-2.37 and the data for various transitions in the uv region are given in Table 2.22.

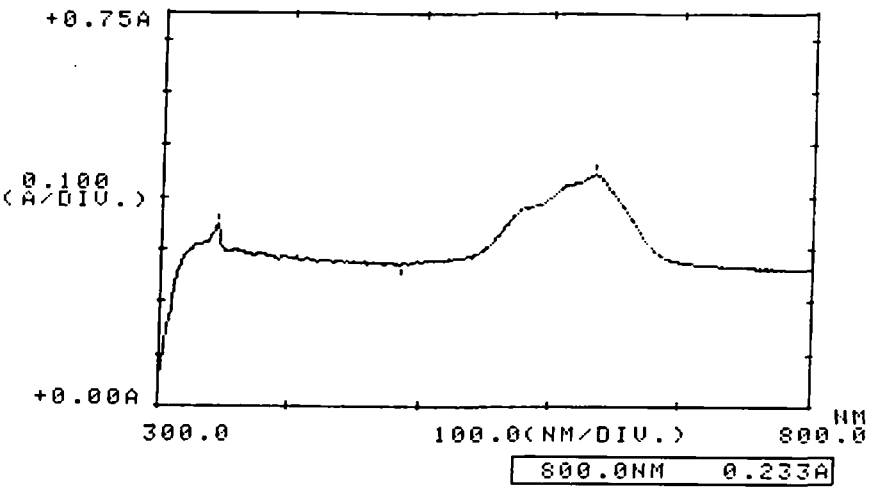
Table 2.22. Electronic spectral data for benzimidazole and its metal complexes

Compounds	Absorption bands λ_{max} in nm		
	Charge transfer d-d	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$C_7H_6N_2$	Not observed	342	Not observed
$Co(C_7H_6N_2)_2Cl_2.6H_2O$	633	343	,,
$Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$	592	326	,,
$Ni(C_7H_6N_2)Cl_2.2H_2O$	461	340.5	,,
$Cu(C_7H_6N_2)_2Cl_2.2H_2O$	387	342	,,
$Zn(C_7H_6N_2)_2SO_4.2H_2O$	Not observed	343	,,
$Ag(C_7H_6N_2)_2NO_3$	,,	342.5	,,
$Hg(C_7H_6N_2)Cl_2.2H_2O$	,,	343	,,
$Hg(C_7H_6N_2)Cl.2H_2O$	,,	342.5	,,
$Hg(C_7H_6N_2)NO_3.2H_2O$	,,	320.7	,,



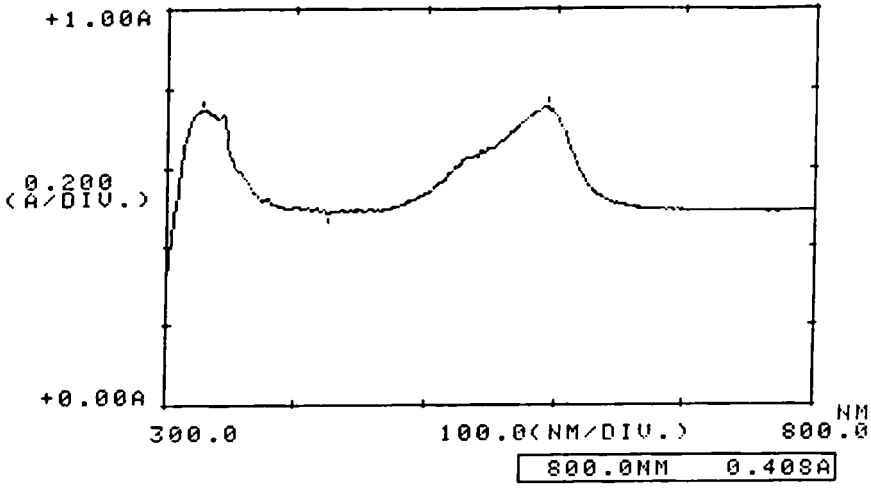
-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
342.0	1.017		

Fig. 2.28 uv spectrum of benzimidazole



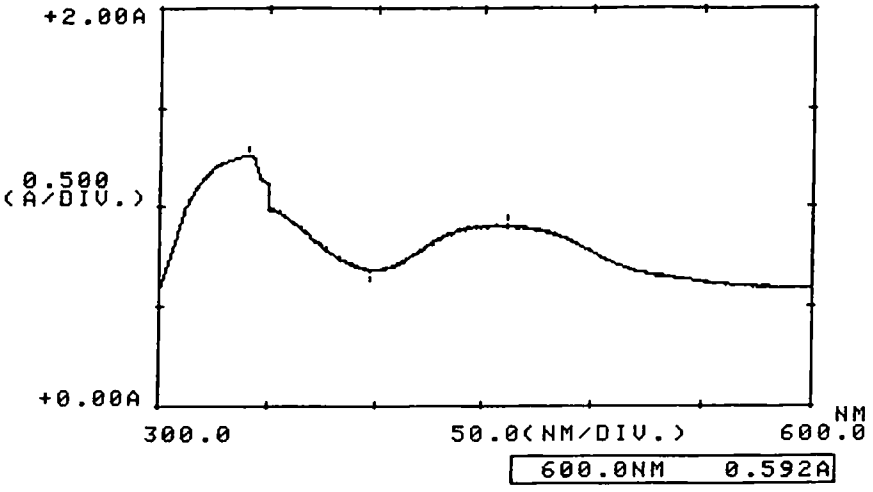
-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
633.0	0.444	484.0	0.271
343.0	0.345		

Fig. 2.29 uv spectrum of $Co(C_7H_6N_2)_2Cl_2.6H_2O$



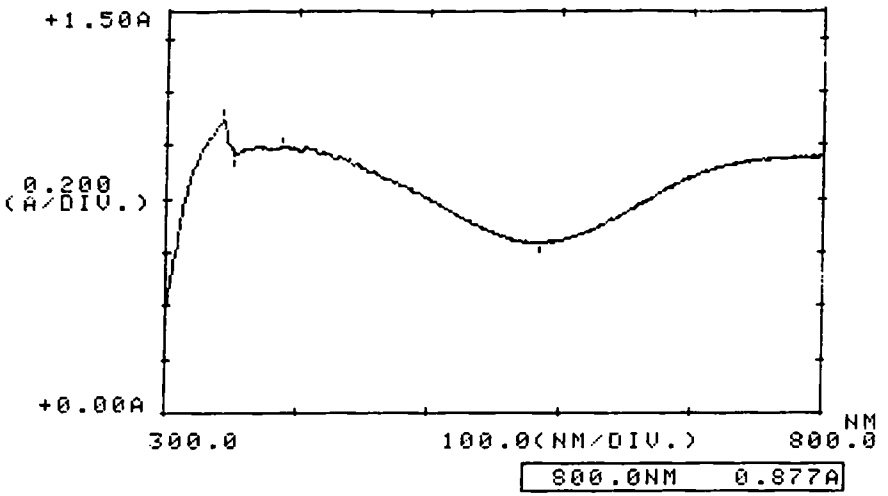
-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
592.0	0.754	425.0	0.486
326.0	0.750		

Fig. 2.30 uv spectrum of $Co(C_7H_6N_2)_2NO_3.2H_2O$



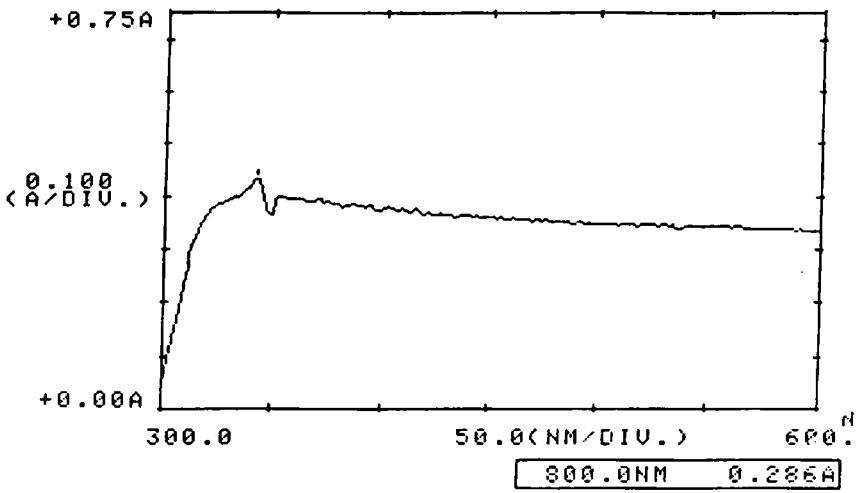
-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
461.0	0.910	397.5	0.680
340.5	1.260		

Fig. 2.31 uv spectrum of $Ni(C_7H_6N_2)Cl_2.2H_2O$



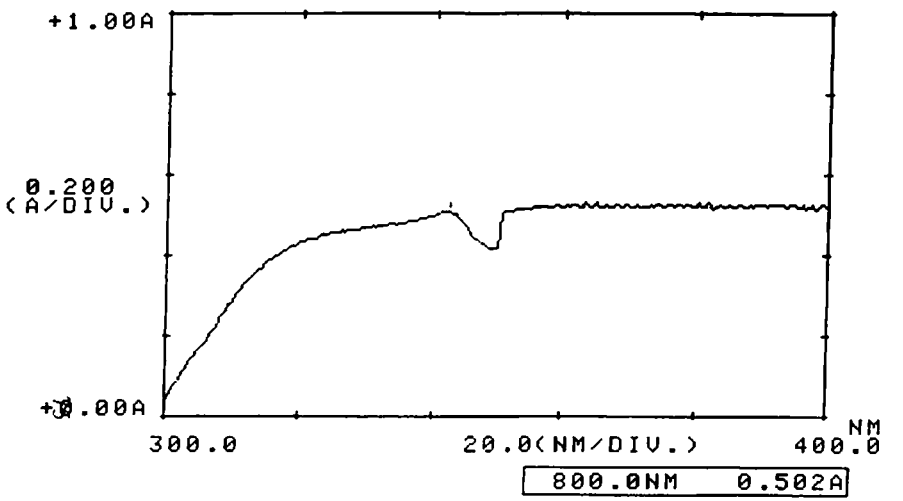
-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
387.0	0.998	584.0	0.634
342.0	1.094	351.0	0.960

Fig. 2.32 uv spectrum of $Cu(C_7H_6N_2)_2Cl_2.2H_2O$



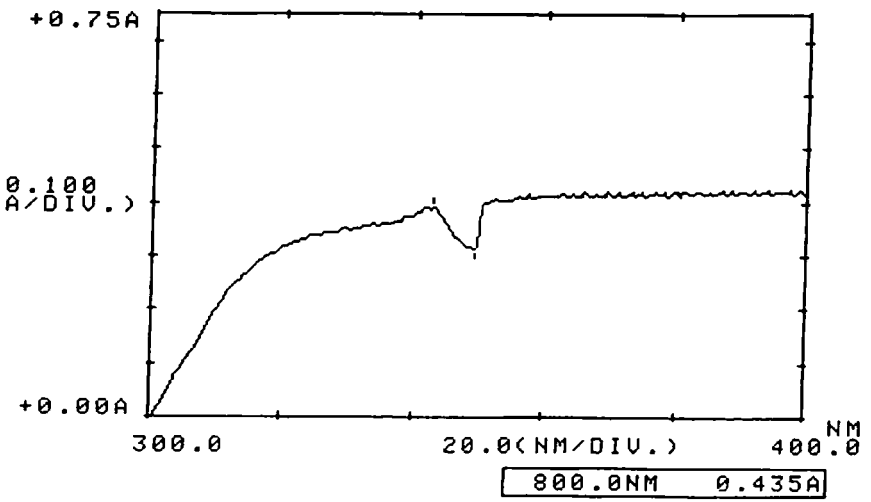
-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
343.0	0.435		

Fig. 2.33 uv spectrum of $Zn(C_7H_6N_2)_2SO_4.2H_2O$



λ	ABS	λ	ABS
342.5	0.509		

Fig. 2.34 uv spectrum of $Ag(C_7H_6N_2)_2NO_3$



-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
343.0	0.389	349.5	0.313

Fig. 2.35 uv spectrum of $Hg(C_7H_6N_2)Cl_2.2H_2O$

2.3.7 Magnetic susceptibility

The general purpose of the magnetic susceptibility measurements were done in the present study to determine the magnetic moment of a compound which gives information about the number of unpaired electrons, oxidation number and finally, an overall view of the electronic configuration of the complex and possible geometrical patterns.

The magnetic susceptibility of the prepared complexes in the solid state was measured using Curie-Cheneveau Magnetic balance, which was locally constructed, in this laboratory. The standard substance (Mohr's salt) of known magnetic susceptibility (X_o) was used and the following relationship was used for the calculation of X_o value.

$$X_g = \frac{m_0(\theta_1-\theta_0)}{m(\theta_2-\theta_0)} X_0$$

where,

X_g = magnetic susceptibility of the substance under study

X_o = magnetic susceptibility of the standard substance

m_o = mass of the standard substance

m = mass of the substance under study

θ_1 = deflection due to the substance under study

θ_2 = deflection due to standard substance and

θ_o = deflection due to empty container

In the present work all the weights and magnetic susceptibility values are expressed in C.G.S units. In terms of Bohr magneton, susceptibility can be expressed as

$$M_\mu = [3RTX_\mu]^{1/2} = 2.83[X_\mu T]^{1/2} \text{ Bohr magneton}$$

where, M_μ = Magnetic moment of the molecule

T = Temperature in $^\circ K = (t+273)^\circ C$

X_μ = magnetic susceptibility × molecular weight

$= X_g \times M$

Therefore, $M_\mu = 2.83[X_g MT]^{1/2}$ Bohr magneton and

$$X_o = \frac{9500\times10^{-6}}{T+1}$$

where T is the absolute temperature.

To calculate the number of unpaired electrons per molecule by using spin quantum number s, we have relation

$$M_\mu = g[s(s+1)]^{1/2} = 2[s(s+1)]^{1/2}$$

where, g = Lande splitting factor = 2

s = spin quantum number which is equal to half of the number of unpaired electrons in the molecule or ion.

Procedure

Thin pyrcx glass tubes were used as sample holder in the measurements of deflections. At first a clean dry weighed tube was packed uniformly with finely powdered Mohr's salt upto a marked length. It was then weighed and hung by a very fine thread from the torsion arm of the balance. After the system had attained the rest position, the magnet was rotated very slowly away from the tubc. A telescope directed at a mirror scale arrangement followed the deflection of the torsion arm. The reading of the scale were noted at the points of maximum deflection to both the right and the left sides. The tube was emptied, washed, dried and filled up to the previously marked length with the sample, which is to be investigated. The sample with the tube was then weighed and the deflection was noted as before. Again the tube was washed, dried and the deflection due to empty tube was noted. The magnetic susceptibility was then calculated by using the equation described above. The values of magnetic susceptibility and magnetic moment of the complexes has been given in the Table 2.23.

Calculation as an example

The calculation of the magnetic moment of $Co(C_7H_6N_2)_2Cl_2.6H_2O$ complex is given below

$T = (273+29)K$

$m_o = 0.0807g$

$m = 0.2018g$

$0_1 = 0.10$

$0_2 = 8.15$
$\theta_o = 0$
$M = 474.176$

Now,

$$X_g = \frac{m_0(\theta_1-\theta_0)}{m(0_2-\theta_0)} X_0 \text{ C.G.S}$$

$$= \frac{0.0807\times0.1}{0.2018\times8.15} \times \frac{9500\times10^{-6}}{303}$$

$$= 0.15382\times10^{-6} \text{ C.G.S}$$

Therefore magnetic moment is calculated on the basis of the assumption that the empirical formula represent the molecular composition.

$$M_\mu = 2.83[0.15382\times10^{-6}\times474.176\times302]^{1/2}$$
$$= 4.20 \text{ B.M}$$

Table 2.23. Magnetic susceptibility and magnetic moment of the complexes

Sample	Magnetic susceptibility in C.G.S unit	Magnetic moment in B.M
$Co(C_7H_6N_2)_2Cl_2.6H_2O$	0.15382×10^{-6}	4.20
$Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$	0.15568×10^{-6}	4.14
$Ni(C_7H_6N_2)Cl_2.2H_2O$	0.13299×10^{-6}	3.02
$Cu(C_7H_6N_2)_2Cl_2.2H_2O$	3.29232×10^{-6}	1.80
$Zn(C_7H_6N_2)_2SO_4.2H_2O$	0	0
$Ag(C_7H_6N_2)_2NO_3$	0	0
$Hg(C_7H_6N_2)Cl_2.2H_2O$	0	0
$Hg(C_7H_6N_2)Cl.2H_2O$	0	0
$Hg(C_7H_6N_2)NO_3.2H_2O$	0	0

2.4 Benzimidazole as an analytical reagent in presence of masking agent

Masking may be defined as the process in a reaction system in which a substance, without physical separation of it or its insoluble, colored or gaseous reaction products is prevented by the addition or presence of certain chemical substances that does not enter a particular reaction. These substances are termed masking agents. The masking agents should form a more stable complex with the interfering ion, and a less stable complex with the ion to be determined, than does the reagent itself. In the field of the complex stabilities, it is possible to calculate the necessary concentration of the masking reagent and the maximum permissible amount for the correct results. On the basis of the complex forming properties of the individual ions, it can be decided to a first approximation as to what types of compounds may come into consideration in course of the reactions. For instance, the effects masking agents can be particularly applied with advantage in the field of analytical chemistry.

Benzimidazole form complexes with many transition metal ions. The selectivity of the reagent may be improved by the use of masking agents. The interferences can often be masked, thus eliminating separations, which are time consuming and a possible source of error.

In the present investigation the methods were investigated for the application of benzimidazole in the separation or determination of certain metal ion from mixed solutions by using masking agents. Particular mention may be made in connection with the formation of silver benzimidazole complex as precipitate

in presence of many metal ions if Na_2EDTA is used during the precipitation reactions.

Procedure

A series of solutions of several metal ions was prepared in which the metal ion concentrations were fixed at 0.05M. Then equal volumes (10 ml) of the prepared Cu^{2+}, Ni^{2+} and Ag^{+} ion solution was mixed in a beaker and adding a known excess of a standard EDTA solution for masking. After stirring 45ml 0.05M benzimidazole solution was added slowly with constant stirring. A white colored silver-benzimidazole complex was formed which was separated by sucktion filtration and dried in a desiccator and its constant weight was determined. By using the filtrate the excess EDTA was subsequently titrated with standard $ZnSO_4$ solution to measure the total quantity of the combined Cu and Ni content.

Next Cu^{2+} and Ni^{2+} ion solution was taken as previously described and Cu^{2+} ion was masked with hydroxylamine hydrochloride ($HONH_2HCl$) solution. Then Ni^{2+} ion was determined by back titration[66].

For the mixtures of the pairs of Mn^{2+}-Ag^{+}, Cu^{2+}-Ag^{+}, Ni^{2+}-Ag^{+}, Fe^{3+}-Ag^{+} ions the procedures were followed as previously described.

This process could not be applied for Co^{2+}-Ag^{+} ion mixture, because the silver was deposited in the beaker like a mirror due to the presence of Co^{2+}ion which undergo oxidation in presence of air and benzimidazole reagent. The results are shown in Table 2.24.

Table 2.24. Separation of Ag(I) with benzimidazole

Mixture of metal Ions	Determination of metal ion		Amount of Ag^{+}-benzimidazole complex in (g)
	Observed metal ion in (g)	Calc. Metal ion in (g)	
Ag^{+}	-	-	0.4024
Mn^{2+}+Ag^{+}	17.9700	19.13	0.4017
Ni^{2+}+ Ag^{+}	18.7033	20.18	0.4015
Cu^{2+}+ Ag^{+}	24.8266	26.28	0.4012
$Fe3^{+}$+ Ag^{+}	11.4360	13.84	0.4022
Ni^{2+}+Cu^{2+}+Ag^{+}	20.02	22.95	0.4013
Ni^{2+}+ Cu^{2+}	Ni^{2+}=16.8939	20.18	-
Co^{2+} + Ag^{+}	$Co^{2+}\rightarrow Co^{3+}$	-	Ag mirror

2.5 Quantum chemical study of the complexation of imidazole

The *AB initio* quantum chemical study of 1:1 complex of divalent transition metal ions, M^{2+} (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) with the uncharged imidazole (HIm) and imidazole anion (Im), a similar compound of benzimidazole have been carried out.

In this study the DEC 5000/25 workstation at the Department of Chemistry, University of Dhaka was used to perform the calculations. All the calculations were performed based on the LCAO-MO-SCF method with the 3-21G basis set[73].

The computational details are in the published paper, enclosed at the end of the thesis.

CHAPTER-3

DISCUSSION OF THE RESULTS

DISCUSSION OF THE RESULTS

The resonance energy of benzimidazole, pyridine and benzene are 129.3 kj/m, 87.6 kj/m and 83.8 kj/m respectively[9]. The comparable higher resonance energy suggests that it will have more propensities towards complexation. This higher resonance of benzimidazole arises from the wider delocalization of electron over greater number of atoms compared to pyridine or benzene. This effect increases nucleophilic attack towards metal ions.

The present study deals with the preparation and characterization of benzimidazole complexes of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Hg(I) and Hg(II) and also deals with the investigation of masking effect of benzimidazole in the field of analytical chemistry. Various physico-chemical techniques have been used for the characterization of metal-benzimidazole compounds and results obtained give an idea about the structural aspects of these complexes.

3.1 Preparation of the complexes

The preparations of these complexes were carried out in alcoholic or aqueous alcoholic medium by adopting simple and straightforward method. Benzimidazole forms complexes with Cu(II), Zn(II), Ag(I) and Hg(II) instantly and also forms complexes with other metals ions in presence of masking agents.

Silver is unstable in light and air. The complexation of the metal with benzimidazole is able to increase the stability of the silver compound since silver benzimidazole compound is not affected in presence of light.

3.2 Melting point

Most of the complexes synthesized in the present work melt at near or above 300°C. The compound $Hg(C_7H_6N_2)Cl$ melt at relatively low temperature (230°C). The low melting point suggests that the compound is possibly molecular complex. High melting point of the complexes indicates the ionic nature of the complexes possibly it might have formed some polymeric framework.

3.3 Solubility of the complexes

The complexes studied in the present work arc soluble in dimethyl sulfoxide (DMSO) except $Hg(C_7H_6N_2)NO_3.2H_2O$, DMSO is a strong ionic solvent and it may be surmised that the complexes are ionic in nature. All the products synthesized are insoluble in water except $Hg(C_7H_6N_2)_2Cl_2.2H_2O$. However, $Hg(C_7H_6N_2)NO_3.2H_2O$ is insoluble in all common organic and inorganic solvents but soluble in concentrated acids (HNO_3, HCl etc) due to reactions.

3.4 Stoichiometry of the complexes

By the application of the Job's continuous variation and mole ratio methods the compositions of Cu(II), Zn(II), Ag(I) and Hg(II) benzimidazolates were determined. The results of these methods have been given in Table 2.1 to Table 2.8 and Fig. 2.1-2.8.

In the copper complex the Job's plot in Fig. 2.1 showed a maximum at 0.33 mole fraction of the metal, which indicates 1:2 metal to ligand ratio. This is also supported by mole ratio method (Fig. 2.2) where metal to ligand ratio is 1:2 i,e the empirical formula of the complex is $Cu(C_7H_6N_2)_2Cl_2$.

For zinc complex the maximum in the Job's plot in Fig 2.3 was found at 0.33 mole fraction of the metal. This is indicative of the formation of complex in 1:2 ratio. From the mole ratio method (Fig 2.4) the molar ratio of metal:ligand is also found at 1:2 which is mutually related to the Job's method. It is confirmed that the empirical formula of the complex is $[Zn(C_7H_6N_2)_2]SO_4$.

The Job's plot of silver complex in Fig 2.5 showed a maximum of 0.34 mole fraction of the metal ion. This corresponds to the 1:2 metal to ligand ratio i,e. the empirical formula of the complex is $[Ag(C_7H_6N_2)_2]NO_3$. The mole ratio plot in Fig 2.6 also showed that the silver ion formed complex with benzimidazole in the ratio 1:2.

In the case of mercury complex, the Job's plot in Fig 2.7 showed a maximum at 0.5 mole fraction of the metal ion, which agrees with the 1:1 metal to ligand ratio. This result attributed to the composition of the complex as

$Hg(C_7H_6N_2)Cl_2$. From the mole ratio plot in Fig 2.8 it is also clear that mercury forms complex with benzimidazole in the ratio 1:1.

3.5 Elemental analysis

The metal contents of the complexes were determined by the conventional methods in the present investigation. The procedures have been discussed in the section 2.3.3 (chapter-2). The results are shown in Table 2.10. Based on the analytical data, thermal properties and stoichiometry of the complexes the empirical formula of the compounds are designated as follows

1. $Co(C_7H_6N_2)_2Cl_2.6H_2O$
2. $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$
3. $Ni(C_7H_6N_2)Cl_2.2H_2O$
4. $Cu(C_7H_6N_2)_2Cl_2.2H_2O$
5. $Zn(C_7H_6N_2)_2SO_4.2H_2O$
6. $Ag(C_7H_6N_2)_2NO_3$
7. $Hg(C_7H_6N_2)Cl_2.2H_2O$
8. $Hg(C_7H_6N_2)Cl.2H_2O$
9. $Hg(C_7H_6N_2)NO_3.2H_2O$

3.6 Thermal Analysis

3.6.1 Thermal analysis of $Co(C_7H_6N_2)_2Cl_2.6H_2O$

The TGA and DTA curves of the complex $Co(C_7H_6N_2)_2Cl_2$ are shown in Fig 2.9. There is gradual weight losses of 6.75% at 225°C which indicate the removal of two molecules of water (Calc. weight loss 7.59%). In the second stage there is another gradual weight loss of about 31.08% at 345°C which may correspond to the removal of further four molecules of water and one chloride as HCl (Calc. weight loss 30.47%). In the third stage within the temperature range of 345-590°C a gradual weight loss is also found which may be due to the removal of six molecules of water along with two chloride as HCl and two benzimidazole molecules (Observed weight loss is 86.48% and Calc. weight loss is 87.57%). The residue remained constant from 590°C to 800°C and corresponds to the conversion of CoO or Co_3O_4. The DTA curve showed a sharp exothermic peak at 590°C. The weight of the residue is 13.52% and calc. wt for CoO 15.79% and for Co_3O_4 16.92%.

The TGA and DTA curves showed that the complex $Co(C_7H_6N_2)_2Cl_2.6H_2O$ prepared by precipitation methods has a different temperature of decomposition. It follows that the method of formation of the sample should be standardized.

3.6.2 Thermal analysis of $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$

From the TGA and DTA curves of the complex $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$ are shown in Fig 2.10. A gradual decrease in the weight of the sample is

noted. At 325°C the loss in weight is 17.23% which does not correspond to removal of any particular component of the complex. It may be possibly due to the loss of two molecules of water along with some fragments of the ligand. At 390°C a steep weight loss is 86.53% may be due to the removal of two water molecules along with two nitrate ions and two benzimidazole molecules (Calc. weight loss is 87.05%). The weight loss of the residue remained constant up to the conformation of CoO or Co_3O_4. Observed wt loss 13.47%, Calculated for CoO 16.45% and for Co_3O_4 17.62%.

3.6.3 Thermal analysis of $Ni(C_7H_6N_2)Cl_2.2H_2O$

The TGA and DTA curves of the complex $Ni(C_7H_6N_2)Cl_2.2H_2O$ are shown in Fig 2.11. The loss of weight of 11.53% at 65°C which may be attributed to the removal of two water molecules (calc. weight loss is 12.68%). From 65°C to 305° C, a gradual weight loss of 19.0% is observed which don't correspond to the removal of any particular fraction of the complex. In the next stages there is a rapid weight loss of 78.0% at 480°C which may be due to the removal of two molecules of water, two chloride ions as 2HCl along with benzimidazole molecule (Calc weight loss is 79.67%). There is no further decrease in the weight and the residue corresponds to the formation of NiO. The expected weight loss for the formation of NiO is 22% (Calc weight loss is 26.35%). At 50°C an endothermic peak and at 425°C a strong exothermic peak are observed in the DTA curve.

TGA and DTA have showed that the temperatures of the dehydration depend on the nature of both metal and ligand.

3.6.4 Thermal analysis of $Cu(C_7H_6N_2)_2Cl_2.2H_2O$

The TGA and DTA curve of the complex $Cu(C_7H_6N_2)_2Cl_2.2H_2O$ are shown in Fig 2.12. There is about 8.36% loss in weight at 210°C, which may be attributed to the removal of two molecules of water (Calc. Wt loss 8.84%). The second sharp weight loss was observed from 210°C to about 490°C. At this range the entire component is removed along with the conversion of the corresponding metal oxide (Observed weight loss 83.95% and Calc weight loss is 84.36%). The DTA curve showed both exothermic and endothermic peaks at this region. The types of chemical changes involved in this region are not clear. The residue 16.05% is in agreement with the formation of Cu_2O (Calc 16.36%) as the end product.

3.6.5 Thermal analysis of $Zn(C_7H_6N_2)_2SO_4.2H_2O$

The TGA and DTA curve of the complex $Zn(C_7H_6N_2)_2SO_4.2H_2O$ are shown in Fig 2.13. There is a gradual weight loss upto 600°C. The decomposition of the complex corresponds to the intense exo-effects as observed by the DTA curve (Observed weight loss 86%, Calc. weight loss is 84.9%). The DTA curve showed a strong exothermic peak at 610°C. This may be due to the removal of all components with the formation of corresponding oxide. The weight loss for the formation of ZnO was found 14.0% and calculated weight loss is 18.76%. The greater loss indicates some amounts of ZnO may also be lost.

The TGA curve of the hydrates does not indicate of loss of H_2O molecule. This may be due to firm retention due to strong bonding of H_2O in the molecular structure of $[Zn(C_7H_6N_2)_2SO_4.2H_2O]$.

3.6.6 Thermal analysis of $Ag(C_7H_6N_2)_2NO_3$

The TGA and DTA curves of the complex $[Ag(C_7H_6N_2)_2]NO_3$ are shown in Fig 2.14. A gradual decrease in the weight of the sample is noticed. At 210°C the loss in weight is around 5.55% which does not correspond to removal of any particular part of the molecule of the complex. It may be due to the destruction of some fragments of the ligand. At 270°C the weight loss is 34% corresponds to the removal of one benzimidazole molecule (Calc. weight loss is 29.07%). The 75.9% weight loss at 500°C is due to the complete decomposition of benzimidazole and nitrate parts of the molecule (Calc. weight loss 73.4%). The DTA curve showed a sharp exothermic peak at 445°C. The residue remained constant from 500°C to 600°C and corresponds to the conversion to Ag_2O. The expected weight loss for the formation of Ag_2O is 28.54% and the observed weight loss is 24.1%. The greater loss appears to be due to the sublimation of Ag_2O. The formatted of Ag_2O was proved by chemical analysis of the residue using Volhard's method[58].

3.6.7 Thermal analysis of $Hg(C_7H_6N_2)Cl_2.2H_2O$

The TGA and DTA curves of the complex $Hg(C_7H_6N_2)Cl_2.2H_2O$ are shown in Fig 2.15. The TGA data indicate the complete removal of water at 183°C at

the first stages of TGA curve upon heating of the hydrates of this complex (Observed weight loss 9.26%, calcd. weight loss 8.45%). Further heating of the complexes leads to the decomposition at 400°C and all the components are removed. Around 430°C the compound is completely volatilized. The interpretation of the thermogram is rather difficult due to the volatile nature of the compound.

The possibility of removing water before the start of decomposition of anhydrous compounds permitted preparation of anhydrous compounds $Hg(C_7H_6N_2)Cl_2$.

3.6.8 Thermal analysis of $Hg(C_7H_6N_2)Cl.2H_2O$

From the TGA and DTA curves of the complex $Hg(C_7H_6N_2)Cl.2H_2O$ which are shown in Fig 2.16. A gradual weight loss of about 8.11% at 185°C is found which may be due to the removal of the two water molecules (Calc. weight loss 9.22%). Within the temperature range 185°C-275°C a sharp and rapid weight loss is found and no residue is left. This may be due to the removal of all the components. The DTA curve showed two endothermic peaks at 195°C and 310°C.

The thermogram is apparently very simple but the interpretation is rather difficult. The fact that there is no residue in the decomposition products of the original compound. The complex is completely volatilized.

3.6.9 Thermal analysis of $Hg(C_7H_6N_2)NO_3.2H_2O$

The TGA curve of the complex $Hg(C_7H_6N_2)NO_3.2H_2O$ is shown in Fig 2.17 the two molecules of water are completely removed at 275°C. Observed weight loss 8.57%, Calc. weight loss 8.64%. In the next stages it sharply undergoes decomposition and at 325°C a decrease in the weight is found correspond to 51.42% which may be due to the removal of all components with the formation of corresponding metal oxide, HgO (Calc. weight loss 51.87%). Above this temperature of 570°C there is no residue left because Hg is vaporized. This is also supported by DTA curve, because a strong exothermic peak is observed at 580°C.

The formation of anhydrous compound by the removal of water molecule made it possible for the preparation of a compound $Hg(C_7H_6N_2)NO_3$.

3.7 Infrared spectrum

In the ir spectral study the spectra of the complexes are compared with that of the ligand. The patterns of the spectra are more or less similar to one another and seem to have undergone considerable shifts when complexed with metal.

3.7.1 IR spectrum of the ligand ($C_7H_6N_2$)

The ir spectrum of benzimidazole (Fig 2.18) compared with a previous report[62] in Table 2.12. Comparison of the spectra shows that these are similar to one another in the range of band assignments.

It was reported[67] that the N-H stretching vibration of imidazole appears as a sharp peak in the range of 3480-3300 cm^{-1}. In the spectrum of benzimidazole a peak with broad base appear at 3450 cm^{-1} which is assigned to the N-H stretching vibration. Broadening of the peak possibly indicate the presence of moisture in KBr or benzimidazole. The C=N stretching appear at 1573 cm^{-1} with a strong intensity which is very close to the comparative records. The bands at 1195-1125 cm^{-1} are assigned to C-H bending in plane and a very strong band at 749 cm^{-1} is attributed to C-H bending out of plane.

3.7.2 IR spectrum of $Co(C_7H_6N_2)_2Cl_2.6H_2O$

The ir spectrum of $Co(C_7H_6N_2)_2Cl_2.6H_2O$ (Fig 2.19 and Table 2.13) shows a broad peak at 3290 cm^{-1} is due to the OH or N-H stretching vibration. In the free ligand the N-H stretching vibration was observed at 3450 cm^{-1}. Underhill *et al.*[67] have reported that N-H stretching frequency is shifted to the lower wave number due to coordination of the ligand with metal ion. The medium peak observed at 2890 cm^{-1} is assigned to C-H stretching vibration of aromatic ring. A strong peak at 1609 cm^{-1} arise either from C=C skeletal vibration or from unbound water[68] or both. A medium absorption peak at 1178 cm^{-1} also indicates the presence of water in the complex. The C=N stretching vibration occurs at 1584 cm^{-1} with strong intensity but in the free ligand it is observed at 1573 cm^{-1}. This shifting to higher frequencies by 11 cm^{-1} indicates that imidazole ring tertiary nitrogen is involved in bonding[69]. A strong peak found at 1486 cm^{-1}, which is due to the N-H deformation vibration. The C-H bending vibration (in plane) is observed at 1134 cm^{-1} and the C-H bending vibration (out of plane) with very strong intensity is observed at 750 cm^{-1}. In the

spectrum of the complex a new strong band appears at 426 cm^{-1} which is absent in the spectrum of the ligand. This is indication of Co-N stretching vibration.

3.7.3 IR spectrum of $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$

The ir spectrum of $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$ (Fig 2.20 and Table 2.14) shows a strong peak at 3370 cm^{-1}. This is due to O-H and N-H stretching vibration. The lower frequency of the N-H stretching vibration is indicates of the co-ordination of the ligand with metal ion. The medium peaks observed at 3010 cm^{-1} and 2890 cm^{-1} are assigned to the aromatic C-H stretching vibration. The O-H bending vibration of water molecule is observed at 1642 cm^{-1} with a broad intensity, which indicates the presence of unbound lattice water in the complex. Another medium peak at 1193 cm^{-1} also indicates the presence of water in the complex. A very strong peak at 1448 cm^{-1} is assigned to the N-H deformation vibration. A medium peak at 1592 cm^{-1} and 1264 cm^{-1} is due to the C=N and C-N stretching vibration respectively. The C-H bending vibration (in plane) occurs at 1102 cm^{-1}. A very strong peak observed at 733 cm^{-1} is assigned due to the C-H bending vibration (out of plane). In the spectrum of the complex a new strong peak appears at 416 cm^{-1} which is absent in the spectrum of the ligand and the presence of this new peak obviously indicates Co-N stretching vibration.

3.7.4 IR spectrum of $Ni(C_7H_6N_2)Cl_2.2H_2O$

In the ir spectrum of $Ni(C_7H_6N_2)Cl_2.2H_2O$ (Fig 2.21 and Table 2.15) a broad band at 3330 cm^{-1} is due to O-H or N-H stretching vibration and this occurs at lower frequency than the N-H stretching vibration of free ligand due to the coordination of the ligand to metal ion. The aromatic C-H stretching vibration is found at 2995 cm^{-1}. The broad band at 1610 cm^{-1} is observed due to the unbound water in the complex. A strong absorption peak at 1190 cm^{-1} also indicates the presence of water in the complex. The C=N stretching vibration occurs at 1580 cm^{-1} as a medium peak. A strong peak found at 1495 cm^{-1}, which is due to the N-H deformation vibration. The two strong peaks at 1300 cm^{-1} and 1250 cm^{-1} are assigned to C-N stretching vibration. The C-H bending vibration (in plane) is observed with strong intensity at 1105 cm^{-1} and 1010 cm^{-1} and a very strong peak due to C-H bending vibration (out of plane) occurs at 727 cm^{-1}. A sharp peak at 970 cm^{-1} is assigned to C-C-N stretching vibration. A strong peak at 455 cm^{-1} is due to Ni-N stretching vibration.

On the basis of the above observation it may be concluded that the coordination of ligand to metal ion occurred through the unsaturated nitrogen atom of the ligand.

3.7.5 IR spectrum of $Cu(C_7H_6N_2)_2Cl_2.2H_2O$

From the ir spectral data of $Cu(C_7H_6N_2)_2Cl_2.2H_2O$ (Fig 2.22 and Table 2.16) a broad peak at 3480 cm^{-1} is observed which is due to the O-H stretching vibration and a strong peak at 3200 cm^{-1} due to N-H stretching vibration. The

N-H stretching vibration is shifted to lower frequency due to the co-ordination of the ligand with metal ion. At 2980 cm^{-1} a medium peak may be assigned due to aromatic C-H stretching vibration. The O-H bending vibration of unbound crystal water is observed at 1640 cm^{-1} with medium intensity. It is also proved by the presence of a medium peak at 1195 cm^{-1}. The peak at 1495 cm^{-1} and 1250 cm^{-1} with strong intensity are attributed to N-H deformation vibration and C-N stretching vibration respectively. The broad peak at 1590 cm^{-1} is assigned to the C=N stretching vibration. The C-H bending vibration (in plan) occurs at 1110 cm^{-1} and 1010 cm^{-1}. A very strong peak at 740 cm^{-1} is assigned due to the C-H bending vibration (out of plane). The presence of a new strong band at 480 cm^{-1} is assigned due to the Cu-N stretching vibration. The comparative analysis of the ligand and complex on the basis of the data in Tables 2.12 and 2.16 suggest metal co-ordination occurred through the unsaturated nitrogen atom.

3.7.6 IR spectrum of $Zn(C_7H_6N_2)_2SO_4.2H_2O$

The ir spectrum of $Zn(C_7H_6N_2)_2SO_4.2H_2O$ (Fig 2.23 and Table 1.17) shows a broad peak at 3500 cm^{-1} which is due to the O-H or N-H stretching vibration. A very strong peak due to the N-H stretching vibration is observed at 1460 cm^{-1}. A medium peak at 3060 cm^{-1} is assigned due to the aromatic C-H stretching vibration. A broad band at 1645 cm^{-1} and a medium band at 1185 cm^{-1} are attributed to O-H bending vibration of unbound crystal water in the complex. At 1598 cm^{-1} a strong peak is due to C=N stretching vibration. The C-N stretching vibrations are found at 1350 cm^{-1} and 1270 cm^{-1}. The two strong peaks observed at 1242 and 1145 cm^{-1} are assigned due to S=O

stretching vibration for free SO_4^{-2} ion. The C-H bending vibrations (in plane) occur at 1080 cm^{-1} and 1003 cm^{-1} and a very strong peak due to C-H bending vibration (out of plane) is observed at 740 cm^{-1}. A new strong peak at 460 cm^{-1} is assigned due to Zn-N stretching vibration because the peak is absent in the ir spectrum of the ligand.

3.7.7 IR spectrum of $Ag(C_7H_6N_2)_2NO_3$

The N-H stretching vibration of imidazole appears as a sharp peak in the range 3480-3300 cm^{-1}[67]. The ir spectrum of $Ag(C_7H_6N_2)_2NO_3$, (Fig 2.24 and Table 2.18) shows a broad peak at 3450 cm^{-1}. This is assigned due to the stretching vibration of -OH or >NH group. But the absence of a strong peak at 1150 cm^{-1}, indicate the absence of water molecule constituent in the complex.

The medium peak observed at 3140 cm^{-1} is assigned due to the aromatic C-H stretching vibration. The C=C stretching vibration of aromatic ring occurs at 1610 cm^{-1}. The C=C stretching and N-H deformation vibrations are found at 1585 cm^{-1} and 1480 cm^{-1} respectively. The absorption band at 1300 cm^{-1} with strong intensity is assigned to C-N stretching vibration. A strong peak due to C-H bending (out of plane) is observed at 740 cm^{-1}. In the ligand there is only one peak at 414 cm^{-1} whereas in the Ag-complex there are two strong peaks at 414 and 423 cm^{-1} respectively. The new band is indicative of Ag-N stretching vibration. The presence of N-H stretching vibration indicates that co-ordination occurs through unsaturated nitrogen atom of the ligand.

3.7.8 IR spectrum of $Hg(C_7H_6N_2)Cl_2.2H_2O$

The ir spectrum of $Hg(C_7H_6N_2)Cl_2.2H_2O$ (Fig 2.25 and Table 2.19) shows a broad peak at 3450 cm^{-1} which is due to the O-H or N-H stretching vibration. A very strong peak at 1453 cm^{-1} is due to the N-H deformation vibration. The combination of bands noted is characteristic of a secondary amide presence in the complex. The three medium peaks at 3100, 3045 and 2920 cm^{-1} indicate C-H stretching vibration for aromatic system. The C=N stretching vibration occurs at 1605 cm^{-1}. The O-H bending vibration is observed at 1643 cm^{-1} with a broad intensity, which indicates the presence of unbound lattice water in the complex. It is confirmed by the presence of O-H bending vibration at 1180 cm^{-1}. Two strong peaks at 1297 and 1265 cm^{-1} are indicative of a C-N stretching vibration. The peaks at 1115 and 1005 cm^{-1} with strong intensity are attributed to C-H bending vibration (in plane) and a very strong peak at 757 cm^{-1} due to the C-H bending vibration (out of plane). A strong peak at 470 cm^{-1} is assigned to the Hg-N stretching vibration because the peak was absent in the ir spectrum of the ligand (benzimidazole).

3.7.9 IR spectrum of $Hg(C_7H_6N_2)Cl.2H_2O$

From the ir spectral data of $Hg(C_7H_6N_2)Cl_2.2H_2O$ (Fig 2.26 and Table 2.20) a broad peak at 3540 cm^{-1} is observed, broadened owing to the O-H stretching vibration and a medium peak at 3310 cm^{-1} indicate N-H stretching vibration. The shifting of N-H stretching vibration from the N-H stretching vibration of the free ligand to lower frequency due to the co-ordination of the ligand to the metal ion through unsaturated nitrogen atom.

The C-H stretching vibration for aromatic system occurs at 3010 cm^{-1}. A medium peak at 1595 cm^{-1} is due to C=N stretching vibration. The C=C stretching vibration is observed at 1535 cm^{-1}. A broad band at 1610 cm^{-1} and a medium band at 1193 cm^{-1} are due to the O-H bending vibration of unbound crystal water. A strong peak at 1250 cm^{-1} is assigned to the C-N stretching vibration. The C-H bending vibration (in plane) occurs at 1010 cm^{-1} and a very strong peak at 735 cm^{-1} due to the C-H bending vibration (out of plane). The presence of two medium peaks at 425 cm^{-1} and 414 cm^{-1} are assigned to Hg-N stretching vibration because in the ir spectrum of free ligand there was only one peak at 414 cm^{-1}. So the new band at 425 cm^{-1} is the indication of Hg-N stretching vibration.

3.7.10 IR spectrum of $Hg(C_7H_6N_2)NO_3.2H_2O$

The ir spectrum of $Hg(C_7H_6N_2)NO_3.2H_2O$ (Fig 2.27 and Table 2.21) shows a broad peak at 3320 cm^{-1}. This is assigned to the stretching vibration of -OH or >NH group. But the presence of a strong peak at 1195 cm^{-1}, indicates the presence of water molecule constituent in the complex. The three medium peaks at 3095, 3060 and 3020 cm^{-1} indicate C-H stretching vibration for aromatic system. The C=N stretching vibration occurs at 1595 cm^{-1} with strong intensity. A broad band at 1640 cm^{-1} is due to the O-H bending vibration of unbound lattice water in the complex. A strong peak at 1445 cm^{-1} and a medium peak at 1540 cm^{-1} are attributed to N-H deformation vibration and C=C stretching vibration respectively. The two medium peaks at 1285 and 1262 cm^{-1} are observed to the C-N stretching vibration. The C-H bending vibration (in plane) occurs at 1110 cm^{-1} and 1005 cm^{-1} with strong intensity

and a very strong peak at 738 cm^{-1} indicative of a C-H bending vibration (out of plane). The presence of a new strong peak at 450 cm^{-1} is assigned due to the Hg-N stretching vibration.

3.8 Electronic spectrum

In the present investigation comparison of λ_{max} value of the ligand with corresponding λ_{max} values of the complexes indicate difference in the absorption regions. This difference is due to the site through which the ligand is bonded with the metal[70].

From the electronic spectrum (section 2.3.6) it is observed that the free ligand has one absorption band at 342 nm in the ultraviolet region usually indicative of $n \rightarrow \pi^*$ transition which is due to non-bonding electrons on the nitrogen atom.

The Co(II) complexes, $Co(C_7H_6N_2)_2Cl_2.6H_2O$ and $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$ shows absorption bands in the visible region at 633 nm and 592 nm respectively due to $d \rightarrow d^*$ transition. The bands are assumed to be charge transfer band. The compounds also shows an absorption band at 343 nm and 326 nm respectively due to $n \rightarrow \pi^*$ transition. The spectrum changes from one compound to another suggesting that the energy levels of the cobalt ion are affected by the anions, which must therefore be at least weakly coordinated.

The Ni(II) complex, $Ni(C_7H_6N_2)Cl_2.2H_2O$ shows absorption band at 461 nm which is attributed to $d \rightarrow d^*$ transition. It also gives one absorption band at 340 nm due to $n \rightarrow \pi^*$ transition.

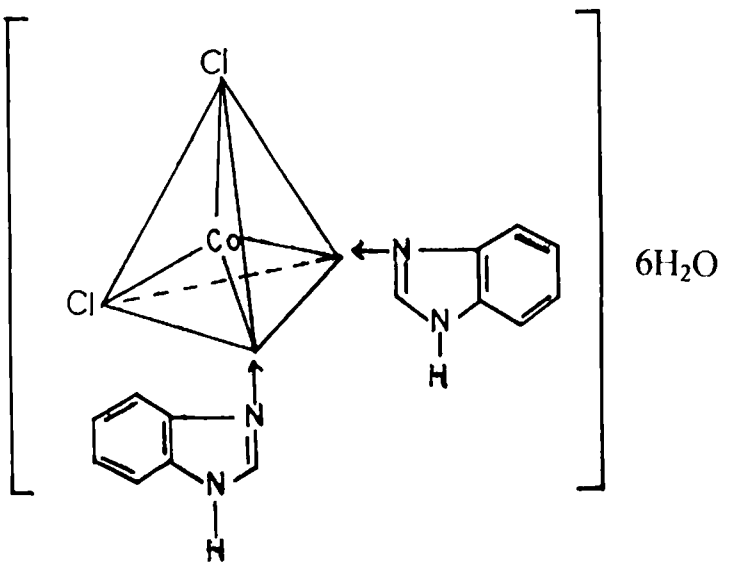
The Cu(II)-benzimidazole complex shows absorption bands at 387 nm due to $d \rightarrow d^*$ transition. This compound shows one absorption band at 342 nm due to $n \rightarrow \pi^*$ transition.

The complexes of Zn(II), Ag(I), Hg(II) and Hg(I) with benzimidazole showed only one absorption band at approximately 343 nm and the complex $Hg(C_7H_6N_2)NO_3.2H_2O$ shows one absorption band at 320.7 nm due to $n \rightarrow \pi^*$ transition. No transition occurs in the visible region because Zn^{2+}, Ag^+, Hg^{2+} and Hg^+ ions contain d^{10} electronic system. There are no possible changes in metal-ligand bonding, because of small shifting of the spectral position of complexes as compared to the ligand positions.

3.9 Magnetic susceptibility

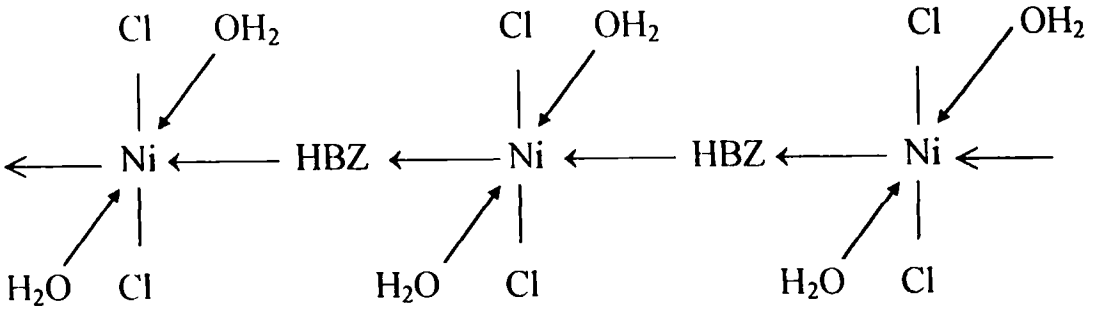
The magnetic moment of the complexes $Co(C_7H_6N_2)_2Cl_2.6H_2O$ (blue) and $Co(C_7H_6N_2)_2(NO_3)_2.2H_2O$ (violet) are 4.20 B.M. and 4.14 B.M. respectively, on the basis of the empirical formula. The values indicate that the cobalt ion in both the complex molecules have three unpaired electrons and exist in +2 oxidation state. The differences in color and magnetic moment (~0.06 B.M.) in between the compounds due to the variation in the Cl^- and NO_3^- ions is a natural consequence of the fact that anions in these complexes contribute

relatively little to the total ligand field. The results suggest that the complexes belongs to distorted tetrahedral geometry and paramagnetic in nature.



Distorted tetrahedral structure of $[Co(C_7H_6N_2)_2Cl_2]6H_2O$

From the magnetic moment values (3.02 B.M.) of the complex $Ni(C_7H_6N_2)Cl_2.2H_2O$, the nickel ion in the complex molecule contains two unpaired electrons and exist in +2 oxidation state. Depending on the nature and strength of ligand, Ni^{2+}ions can adopt a number of geometry[71] and the magnetic moment values indicate a polymeric octahedral structure for this complex and this is paramagnetic.



Polymeric octahedral structure of $Ni(C_7H_6N_2)Cl_2.2H_2O$

The magnetic moment of the Cu(II) complex, $Cu(C_7H_6N_2)_2Cl_2.2H_2O$ is 1.80 B.M. The complex is paramagnetic in nature. The value indicates the presence of one unpaired electron and exists in +2 oxidation state[72]. Cu^{2+} is a d^9 ion, therefore there are two geometry depending upon the distribution of the nine electrons. The distorted tetrahedral arrangements of the Cu(II) complexes of 2-methylimidazole similar to benzimidazole have been suggested from electronic spectrum[35].

The results from magnetic susceptibility value suggest that the complexes of Zn(II), Ag(I), Hg(II) and Hg(I) have zero magnetic moments i,e. diamagnetic. These are in agreement with the expected from the theoretical point of view since the Zn(II), Ag(I), Hg(II) and Hg(I) ions have d^{10} electronic system.

3.10 Benzimidazole as an analytical reagent in presence of masking agent

The development of procedure for the separation and determination of metal ions using benzimidazole may be a new and interesting area of analytical chemistry. Systematic studies on the use of benzimidazole for the purpose have been carried out. Masking agent such as EDTA or hydroxylamine hydrochloride have been used for effective separation.

From the Table 2.24 (section 2.4) it has been shown that Ag(I) forms complex with benzimidazole immediately and can be separated easily from several interfering elements such as Al^{3+}, Ni^{2+}, Cu^{2+}, Fe^{3+} etc in the presence of EDTA. However, the separation of Ag(I) from Co(II), using benzimidazole was not possible even in the presence of EDTA. In this case metallic silver was deposited on the walls of the glass container. This may be due to the oxidation of Co(II)-EDTA complex to Co(III)-EDTA complex in presence of benzimidazole. During this process Ag(I) is reduced to metallic silver. Further investigation may produce a procedure for the separation of Ag(I) from Co(II). From the test of Ag(I) and Mn(II) with benzimidazole it was observed that the condition for the reaction of Mn(II) is different from that of Ag(I). No interference was observed from Mn(II) during the separation of Ag(I). The separation of Ag(I) was effectively carried out and was comparable as in the case of individual ion experiments. The above observation suggests that benzimidazole can be used for the determination of Ag(I) in presence of several other metal ions with a satisfactory degree of separation.

In this study, it was expected that the behavior of Cu(II) towards benzimidazole would be similar to Ag(I) since they belong to the same family.

With the hope of developing an analytical procedure for the separation and determination of copper, Cu(II), benzimidazole and hydroxylamine hydrochloride were mixed in different combinations. However none of those combinations were successful for effective separation of copper ion.

In future analysis for selecting the reagent for any specific metal ion would provide more simplified procedure of separation from interfering substances. The analytical application of the reagent capable of co-ordinating a metal ion from mixed solutions by using masking agents looks very promising.

3.11 Quantum chemical study of the complexation of imidazole

The *AB initio* calculations were done for isolated system where the effect of anion and solvent molecules were not considered although the complexing in aqueous media is much concerned with small differences between the interaction of the cation with water and with the ligand, and between the hydration of resulting species.

The optimised $\angle Zn^{2+}N_1C_2$ angle was found to be 124^0 and for the other metal ion, it was assumed to form the M^{2+}.(HIm) complex having $\angle M^{2+}N_1C_2$ angle of 124^0. The binding energies (ΔE) for the M^{2+}.(HIm) and M^{2+}.(Im) complexes along with their M^{2+}....N distances are presented in Tables 1 and 2, respectively.

Table 1. Interaction of metal ions with uncharged imidazole

M^{2+}	Binding energy (kcal/mole)	M^{2+}-N distance (Angstrom)
Fe^{2+}	-182.41	1.95
Co^{2+}	-185.34	1.90
Ni^{2+}	-173.39	1.80
Cu^{2+}	-169.19	1.85
Zn^{2+}	-174.37	1.88

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Table 2. Interaction of metal ions with imidazole anion.

M^{2+}	Binding energy (kcal/mole)	M^{2+}-N distance (Angstrom)
Fe^{2+}	-389.76	1.85
Co^{2+}	-393.36	1.80
Ni^{2+}	-383.11	1.75
Cu^{2+}	-379.56	1.80
Zn^{2+}	-387.37	1.75

The charge distribution of atoms of HIm and Im obtained from the Mulliken population analysis[74] is presented in Table 3.

Table 3. Charge distribution of uncharged imidazole and imidazole anion

	Atom	Uncharged Imidazole	Imidazole anion
1	N	-0.637	-0.732
2	C	-0.063	-0.113
3	C	-0.068	-0.737
6	N	-0.915	-0.737
7	C	0.404	0.227

The binding energy of each metal ion with imidazole anion was found to be double than that with the uncharged imidazole. Comparision of the binding energy shows an order of the stability of the complex of $Co^{2+}>Fe^{2+}>Zn^{2+}>Ni^{2+}>Cu^{2+}$.

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AB INITIO QUANTUM CHEMICAL STUDY OF THE COMPLEXATION OF SOME DIVALENT TRANSITION METAL IONS WITH IMIDAZOLE

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ABSTRACT

Ab initio quantum chemical calculations were performed on the comlexation of divalent transition metal ions (Fe^{2+}, Co^{2+} Ni^{2+}, Cu^{2+} and Zn^{2+}) with the uncharged imidazole and imidazole anion in the gas phase. The binding energy of each metal ion with imidazole anion was found to be double than that with the uncharged imidazole. Comparison of the binding energy shows an order of the stability of the complex of. $Co^{2+} > Fe^{2+} > Zn^{2+} > Ni^{2+} > Cu^{2+}$.

INTRODUCTION

The imidazole nucleus and their derivatives such as benzimidazole are known to play an important role in the structures and functionality of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions. In vitamin B_{12} and several of its derivative, one of the five nitrogen atoms coordinated to Co(II) comes from dimethylbenzimidazole[1]. Many investigations[2-8] were carried out to study the spectral and magnetic properties of the metal (Fe, Co, Ni, Cu, Zn, Pb etc) complexes containing imidazole and substituted imidazole ligands. A few of those studies were focussed to find out which of the two nitrogen atoms in the imidazole and substituted imidazole is the active site for coordination. Thomas *et al.*[8] have assumed that the unsaturated nitrogen is the most active site of the substituted benzimidazole based on the study of formation constants. Freiser's spectroscopic study[9] on the chalets of the derivatives of benzimidazole substantiated this assumption. On the basis of the x-ray result, Lundberg[10] has suggested that the interaction of Zn(II) ion with the uncharged imidazole molecule is of the same order of strength as that with the anion, i.e., the coordination may take place either through the unsaturated nitrogen of uncharged imidazole or at any of the two nitrogens of the imidazole anion.

In this paper, *ab initio* quantum chemical study of 1:1 complexes of divalent transition metal ions, M^{2+}. (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) with the uncharged imidazole (HIm) and imidazole anion (Im) have been reported.

METHOD AND COMPUTATIONAL DETAILS

M^{2+}-HIm (uncharged imidazole) complex : Zn(II) was placed at various positions around the N_1 atom of uncharged imidazole molecule varying geometrical parameter 118° $\leq \angle Zn^{2+} N_1C_2 \geq \angle$ 128° (Fig. 1) having all of the atoms of Zn(II)-HIm in one plane.

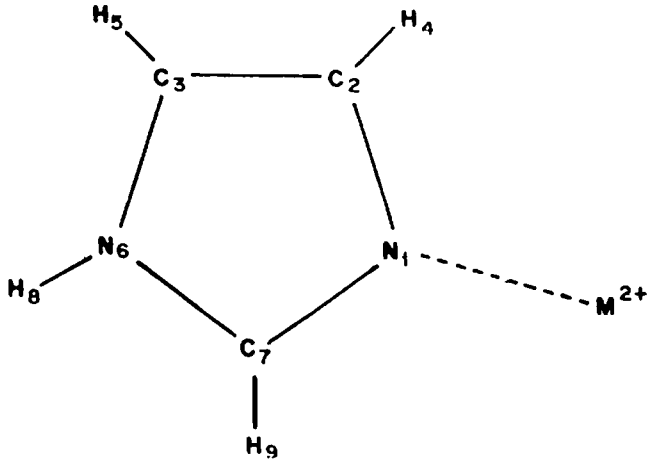

Fig. 1. M^{2+} complex formation with uncharged imidazole nucleus.

Thus the $\angle Zn^{2+}N_1C_2$ angle was optimised. Then the $M^{2+} \ldots N_1$ internuclear distance was varied from 1.7Å to 2.0Å keeping the $\angle Zn^{2+}N_1C_2$ angle at the previously optimised value. The imidazole molecule's geometry was kept fixed throughout the calculations at the experimental value[11].

M^{2+}–Im (imidazole anion) complex : The hydrogen (H_8) attached to the N_6 atom was excluded and the geometry of the resulting imidazole anion was assumed to be the same as that of the uncharged imidazole. The metal ion M^{2+} was placed near the N_6 atom having $\angle M^{2+}N_6C_3$ angle of 122°, because the $\angle H_8N_6C_3$ angle in HIm was 122°. Then the calculations were done by varying the $M^{2+} \ldots N_6$ distance from 1.7Å to 2.0Å.

All the calculations were performed based on the LCAO-MO-SCF method with the 3-21G basis set[12]. The DEC 5000/25 Workstation at the Department of Chemistry, University of Dhaka was used to perform the calculations. The binding energies, ΔE shown in Tables 1 and 2 were calculated as the difference in the total energy of the complex and the sum of the total energies of its components.

$$\Delta E = E_{complex} - E_{ligand} - E_{metal\ ion}$$

where, $E_{complex}$ is the total energy of the M^{2+}. (HIm) or M^{2+}. (Im) complex. Total energy of the ligand (E_{ligand}) and the metal ion ($E_{metal\ ion}$) were obtained by performing the SCF calculation for the isolated HIm or Im and M^{2+}, respectively.

RESULTS AND DISCUSSION

The optimised $\angle Zn^{2+}N_1C_2$ angle was found to be 124° and for the other metal ion, it was assumed to form the M^{2+}. (HIm) complex having $\angle M^{2+}N_1C_2$ angle of 124°. The binding energies (ΔE) for the M^{2+}. (HIm) and M^{2+}. (Im) complexes along with their M^{2+} ... N distances are presented in Tables 1 and 2, respectively. Among the five transition

TABLE 1.

INTERACTION OF METAL IONS WITH UNCHARGED IMIDAZOLE.

M^{2+}	Binding energy (kcal/mole)	M^{2+} – N distance (Angstrom)
Fe^{2+}	– 182.41	1.95
Co^{2+}	– 185.34	1.90
Ni^{2+}	– 173.39	1.80
Cu^{2+}	– 169.19	1.85
Zn^{2+}	– 174.37	1.88

TABLE 2.

INTERACTION OF METAL IONS WITH IMIDAZOLE ANION.

M^{2+}	Binding energy (kcal/mole)	M^{2+} – N distance (Angstrom)
Fe^{2+}	– 389.76	1.85
Co^{2+}	– 393.36	1.80
Ni^{2+}	– 383.11	1.75
Cu^{2+}	– 379.56	1.80
Zn^{2+}	– 387.37	1.75

metal ions studied here, Co^{2+} forms the most stable complex having the binding energy of –185.04 kcal/mol at a Co^{2+} . . . N distance of 1.9Å, comparatively Cu^{2+}. (HIm) complex is the least stable by 16.15 kcal/mol. For M^{2+}. (HIm) and M^{2+}. (Im) complexes of each metal ion the binding energy follow exactly the same trend in going from Fe^{2+} to Zn^{2+} as reflected in Fig. 2. The most important feature of the plot of binding energy *vs* number of *d*-electrons (Fig. 2) is that the graph closely resembles part of the double humped plot for most of the physical properties against the number of *d*-electrons.

The charge distribution of atoms of HIm and Im obtained from the Mulliken population analysis[13] is presented in Table 3. Although the negative charge of N_6 is higher than that of N_1 in HIm, the N_1 atom is the most favourable coordination site because of the presence of positive hydrogen at N_6 thus nullifying the negativity of N_6. In Im, the negative net charge is equally distributed on the two nitrogens of the imidazole

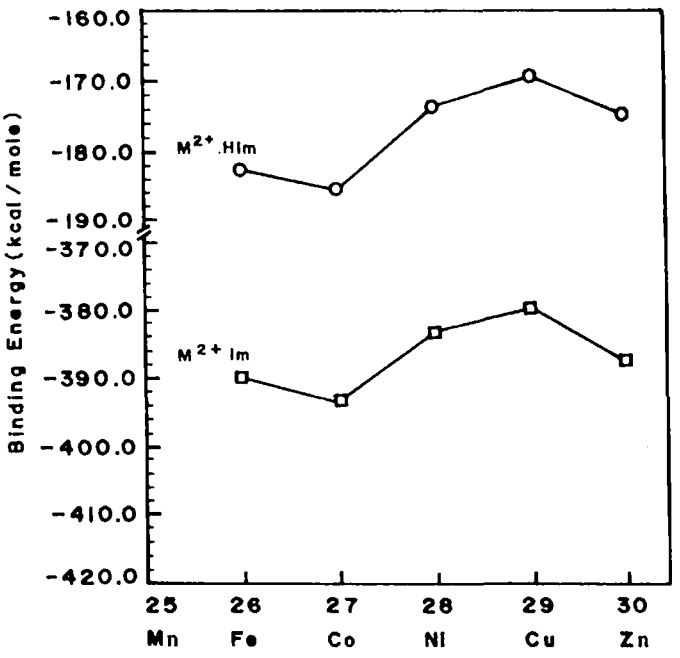

Fig. 2. Binding energies of M^{2+} metal ions with uncharged imidazole (HIm) and with (Im) anion.

TABLE 3.

CHARGE DISTRIBUTION OF UNCHARGED IMIDAZOLE AND IMIDAZOLE ANION.

	Atom	Uncharged imidazole	Imidazole anion
1	N	− 0.637	− 0.732
2	C	− 0.063	− 0.113
3	C	− 0.068	− 0.737
6	N	− 0.915	− 0.737
7	C	0.404	0.227

ring. Thus both nitrogen atoms are equally favourable for coordination, agree well with the assumption of Lundberg[10]. The binding energy of each metal ion with the Im is 2.2 times higher than that of the HIm, and this result, however, does not agree with the prediction of the result from x-ray crystallography[10]. Formation of the M^{2+}. (Im) complex will largely depend on the ionisation of HIm to Im in the solution. If the ionisation of HIm occurs readily then the M^{2+}. (Im) will be the predominant species largely.

CONCLUSION

It is well established that the *ab initio* quantum chemical method is a powerful tool to study the complexation of metals ions with the various ligands. This paper clearly indicates the possible binding site of the ligand and also the possible species to be formed because of complexation. The *ab initio* calculations were done for isolated system where the effect of anion and solvent molecules were not considered although the complexing in aqueous media is much concerned with small differences between the interaction of the cation with water and with the ligand, and between the hydration of resulting species.

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