SYNTHESIS AND STRUCTURAL STUDIES ON SOME TRANSITION METAL COMPLEXES DERIVED FROM SUBSTITUTED SYMMETRIC TRIAZINES

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DEDICATED TO

MY MOTHER, FATHER
SISTERS AND BROTHERS

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ABSTRACT

Co(II), Ni(II), Cu(II) and Zn(II) complexes of herbicidally active AZIPROTRYN (AZP) and Hydrazinoethanol derivative of atrazine (HEATZ) have been synthesized from methanolic media at pH ≈ 6. They have been characterized on the basis of analytical, thermal, conductance, IR spectral and electronic spectral studies. The studies show that the complexes are stable to atmospheric conditions and are electrolytes. The metal to ligand ratios are 1:2 and 1:1, respectively, for AZP and HEATZ. IR studies show that AZP is a neutral NN donor while HEATZ is a monobasic ONN donor with characteristic alkoxide bridging. Azido nitrogen and ring nitrogen centres in AZP and alkoxide oxygen, hydrazinonitrogen and ring nitrogens in HEATZ have been identified as binding centres. In HEATZ alkoxide bridging is a notable feature due to which the complexes achieve dinuclearity. Tetrahedral geometry for Co(II), Ni(II) and Zn(II) complexes and square planar geometry for Cu(II) complex of

AZP have been proposed. Based on electronic spectral studies, Co(II), Ni(II), Cu(II) complexes with the composition $[M_2L_2(H_2O)_4]Cl_2$ (L = HEATZ) have been adjudged octahedral.

Thermochromism has been observed with cobalt (II) complex of HEATZ. It is pink in colour at room temperature, but changes to green through a transient blue colour as it is heated to 220°C.

Preliminary antimicrobial studies on *E. coli* and *S. aureus* have been done using AZP, ATZ, HEATZ, metal salts, complexes and related compounds.

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ABBREVIATIONS AND SYMBOLS

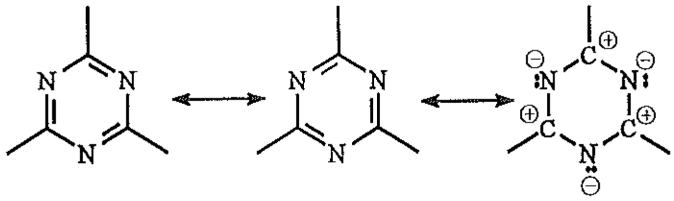
ATZ	2-chloro-4-ethylamino-6-isopropylamino-S-triazine (ATRAZINE)
AZP	2-methylthio-4-azido-6-isopropylamino-s-triazine (Aziprotryn)
DMG	Dimethyl glyoxime
EDTA	Ethylenediamine tetra acetic acid
HEATZ	2-hydrazinoethanol derivative of Atrazine
IR	Infrared
M.pt	Melting point
mmol	milimole
nm	Nanometer
Oh	Octahedral
ppm	Parts per million
Td	Tetrahedral
TLC	Thin layer chromatography
ν_a	Asymmetric stretch
ν_s	Symmetric stretch

I. INTRODUCTION

Metal complexes of physiologically active heterocyclic ligands have promising applications in view of enhanced liposolubilities and modified electron distributions. Improved antimicrobial, insecticidal, insect growth regulating, plant growth regulating, weedicidal, herbicidal, etc; activities of metal complexes have been documented in literature [1-5].

Several five and six membered N heterocyclic ligands containing 1, 2 or 3 hetero atoms have been investigated for metal binding abilities. Symmetric triazine (1,3,5-triazine) (I) (Fig. 1) belongs to class of six membered heterocyclics containing three azomethine nitrogen centres. Chloro, methoxy, methylthio, alkylamino substituted 1,3,5-triazine like; Atrazine, Simazine, Prometone, Prometryn, Aziprotryn have gained world wide recognition in view of their established, outstanding herbicidal properties [6-9]. Compounds containing azomethine centers have played significant role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals . Interest on such complexes has been very known due to the role they play in providing synthetic models for the metal containing sites in metalloproteins and enzymes [10,11].

A wide variety of ligands containing azomethine centers which vary in denticity, flexibility, nature of donor atoms and electronic properties have been studied. Due to the electronegativity difference between nitrogen and carbon, the π electrons in the ring of symmetrical triazines are localized in the vicinity of nitrogen atoms. A polar mesomeric form (II), that bears additional pair of unshared electrons on each nitrogen is likely to result in potential metal binding characteristics [12].



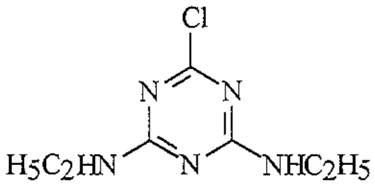
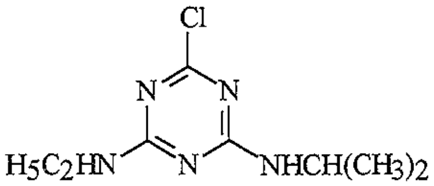
(I) (II)

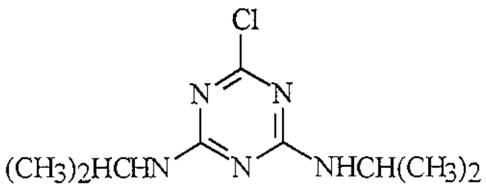
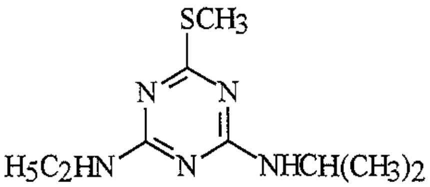
Fig 1. Resonance structures of S-triazine

S- triazine; as such, has not received attention of coordination chemists, probably due to the hydrolytic instability and low base strength [13]. Studies on the dissociation constants, show that the substituents at positions 2, 4, 6 and particularly those at position 2 can alter the basicity of triazines (Table1). The basicity of 4,6-alkylamino-S-triazines is significantly affected by the electron donating ability of the substituent at position-2. For example the basicity of 2-chloro-4-ethylamino-6-isopropylamino-S-triazine (ATRAZINE) (pKa = 1.7) is considerably enhanced by replacing the Chloro group with methylthio (SCH_3) group in AMETRYN (pKa = 4.1).

Studies have also shown that increasing electron donating capacity of the substituent at position 2 and decreasing size and branching of N alkyl groups in the 4 and 6 positions have resulted in increasing the solubility [12]. The chlorine atom in 2- Chloro-4,6-bis(alkylamino)-S-triazines is replaced by a variety of nucleophiles (Table2) [12].

Table 1. Physical properties of some S-triazine herbicides

Structural and chemical denomination	Common name	Melting point (°C)	Solubility in water at 20 - 25^{0}C (ppm)	pKa 21^{0}C
 2-Chloro-4,6-bis(ethylamino) -S-triazine	Simazine	225 - 227	5	1.7
 2-Chloro-4-ethylamino-6-isopropy amino-S-triazine	Atrazine	175 - 177	33	1.7

Structural and chemical denomination	Common name	Melting point (°C)	Solubility in water at 20 - 25°C (ppm)	pKa 21°C
 2-Chloro-4,6-bis-isopropyl-amino-S-triazine	Propazine	212 - 214	8.6	1.7
 2-Methylthio-4-ethylamino-6-isopro amino-S-triazine	Ametryn	84 - 86	185	4.1

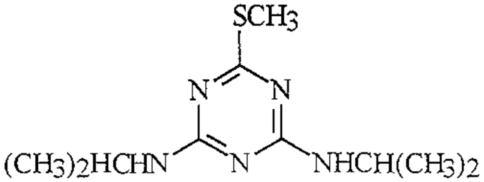
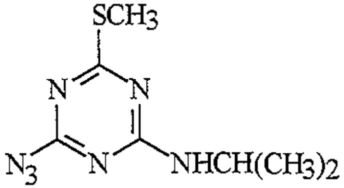
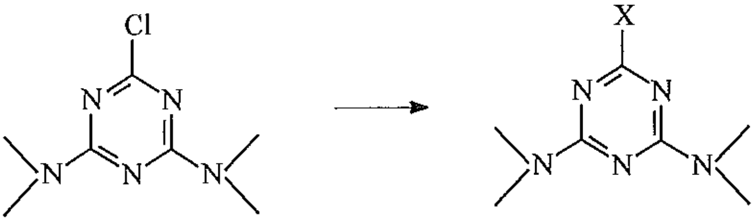
Structural and chemical denomination	Common name	Melting point (°C)	Solubility in water at 20 - 25^{0}C (ppm)	pKa 21^{0}C
 2-Methylthio-4,6-isopropylamino -S-triazine	Prometryn	118 - 120	48	4.1
 2-Methylthio-4azido-6-isopropylam -S-triazine	Azipotryn	90 - 95	50	4.0

Table 2. Nucleophilic reactions affecting the chlorine atom of 2-Chloro-4,6-bis(alkylamino)-s-triazine [12]



Attacking agent	Resultant substituent	References
H^+ or OH^-	-OH	[14a]
SH-	-SH	[14b]
$NH_2CSNH_2.HCl/NaOH$	-SH	[15]
Alkyl OH, OH^-	-O-alkyl	[14c]
NH_3, Alkyl-NH_2, $(alkyl)_2NH$	$-NH_2$,NH-alkyl,$N(alkyl)_2$	[16]
NH_2NH_2, NH_2NH-alkyl	$-NHNH_2$,-NHNH-alkyl	[14d]
KCN	-CN	[17]
NaN_3	$-N_3$	[18]

1.1 SECTION A

LITERATURE SURVEY

Studies on the interaction of metal ions with pesticides have shown that these compounds are widely used in agriculture and can form stable complex species with metal ions [19-20]. Metal ions, on the other hand, may affect remarkably the fate of pesticides, e.g., catalyze their decomposition [21] or inactivate them [22]. Cu(II) ion is known to be very active in influencing pesticide chemistry and biochemistry, due to its efficient binding ability [23]. The herbicidal properties of the s triazine were discovered in 1952 by a research group of J.R.Geigy Ltd., in Basel, Switzerland. The first patent applications were made in 1954 covering 2-Chloro-4,6-bis (alkylamino)-S-triazines [24], 2-methoxy and 2-methythio -4,6-bis (alkylamino)-S-triazines [25], and their influence on the growth of plants . The selective action of these compounds and their unique herbicidal properties compared with the existing classes of herbicides were first reported in 1955 [26, 27]. Major research efforts and worldwide field tests following their original discovery established the outstanding selective herbicidal properties of the -s-triazine. Atrazine, simazine, prometryn, and ametryn were the compounds that gained major recognition in agriculture. Among the numerous S-triazine derivatives investigated thereafter, only a limited number have reached the marketing stage.

Attempts to substitute the chlorine, methylthio, or methoxy groups with other substituents such as other halogen atoms or halogenated alkyl groups have resulted in compounds of no practical importance.

Only the azido derivatives, first synthesized by Degussa [28], are of any particular interest, especially the compounds of Ciba Ltd. An example of this group is 2-methylthio-4-azido-6-isopropyl amino-S-triazine, i.e., aziprotryn [29], in which both the methylthio and the azido group were introduced as substituents.

The growth of literature on synthesis and application of 2,4,6- substituted S-triazine since 1952 has no parallel development with respect to their coordination chemistry. In fact studies on metal binding abilities of simple or substituted S-triazine in general and chelating S-triazine in particular are relatively scanty. As the present investigation aims at the synthesis and structural studies on metal complexes of symmetric triazine, a brief survey of the existing literature is presented.

Metal Complexes of Symmetric Triazine

Literature survey reveals growing interest on synthesis, structural studies and applications of transition and non transition metal complexes of substituted symmetric triazine. Ca^{2+}, Sr^{2+}, Ba^{2+} complexes of trimercapto triazine; Pb^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} complexes of 2,4,6-tris (2-pyridyl) 1,3,5-S-triazine; Cu^{2+}, Fe^{2+} interaction with some triazine herbicides Pd^{2+} complex containing 4-amino 2,6-dimercapto 1,3,5-triazine have been reported.

It is worthwhile to synthesize metal complexes with some selected symmetrical triazine containing functional groups like $-NHNH_2$, $-COCH_3$, $-CONH_2$, $-N_3$ at positions 2,4,6- (adjacent to ring nitrogen atoms) to facilitate metal binding through efficient chelation. Some of the significant results from synthesis, physico-chemical and characterization studies on metal complexes have been summarized in Table 3.

Table 3. Literature on metal complexes of triazine

Substituted symmetric triazine	Metal ion(s)	Type (s) of study	Salient feature(s)	Reference
Atrazine, desisopropyl-atrazine, desethylatrazine, desethyldesisopropyl-atrazine and prometryn	Cu(II), Cd(II), Zn(II), and Pb(II)	Polarographic and Voltammetric Titrations.	pH range 2 to 8 proved suitable only for complexation with Cu(II)	[30]
Prometone, hydroxy-prometone, Propazine and Prometryn	Cu(II)	Potentiometric and Polarographic	The s-triazine pesticides form relatively stable complexes with Cu^{2+} ions. CuL_2 is the only complex species formed at PH ~ 6	[31]
Atrazine, Ametryn Promeryn and prometryn	Fe(III)	HPLC	Ferric perchlorate and sulfate greatly promote the photodegradation of atrazine and other triazine in moderately acidic aqueous solutions	[32]

Substituted symmetric triazine	Metal ion(s)	Type(s) of study	Salient feature(s)	Reference
Melamine	Cr(III)	Elemental analysis, IR, electronic spectra and electrical conductivity	Types of study showed the bidentate nature of melamine	[33]
2,4,6-tris(2'-pyridyl)-1,3,5-S-triazine	Cu(II)	Elemental analysis, IR, electronic spectra EPR spectra, X-ray and powder diffraction	Results indicate five coordinate geometry around the copper (II) ion, intermediate between trigonal bipyramid and square- pyramid structures	[34]
Atrazine, prometryn, terbutylazine, simazine	Pb(II), Cd(II)	Electronic spectra, rate constants	The s-triazine herbicides studied proved strong inhibitions of rape alcohol dehydrogenase(ADH)	[35]

Substituted symmetric triazine	Metal ion(s)	Type(s) of study	Salient feature(s)	Reference
2,4,6-trimercapto-triazine (TMT)	Ca(II), Sr(II), Sr(II)	X-ray technique	In Ca(II) and Sr(II), the structures consist of of alternating layers of hydrated metal cations and π- stacked TMT groups. Compound of Ba(II) forms as a polymeric molecule with covalent bonds between the Ba atoms and TMT ligands.	[36]
Thiopyridyl triazine derivatives	Pt(II)	X-ray and *in vitro* cytotoxic potency against human colon cancer cell line (HT-29)	The ligand 2,4,6-trithiopyridyl-1,3,5 triazine and its platinium complex were found to be 10 - 30 times more potent than cisplatin.	[37]

Substituted symmetric triazine	Metal ion(s)	Type(s) of study	Salient feature(s)	Reference
2,4,6-tris (2'-pyridyl)-S-triazine	Ru(III)	Spectrophotometric	The ruthenium- TPTZ complex can be extracted into nitrobenzene from aqueous Solutions containing perchloric acid; Beer's law is then obeyed in the range of 4-40 μg of ruthenium (III). Applications to synthetic mixtures and to plated brass are reported.	[38]
2,3,5,6-tetrakis-(2'-pyridyl) pyrazine and 2,4,6-tris-(2'- pyridyl)-1,3,5-triazine	Co(II)	Analytical studies, diffuse reflectance spectra, conductivity and magnetic moment	The conductivities of the complexes correspond to values expected for bi-uni electrolytes. The temperature dependence of their magnetism has shown that in some instances there exists a spin - state equilibrium	[39]

Substituted symmetric triazine	Metal ion(s)	Type(s) of study	Salient feature(s)	Reference
2,4,6-trimercapto triazine (TMT)	Cu(I)	X-ray and electronic spectra.	The complex $[(CuPPh_3)_6L_2]$ shows visible emission in the solid state and in fluid solution at room temperature.	[40]
2,4,6-tris (2'-pyridyl)-1,3,5-S-triazine.	Pb(II)	X-ray	The complexes depend upon the particular solid -state structures, involving, as they do, charge-transfer packing	[41]
1,3,5-s-triazine, and 2,4,6-tris (2'-pyridyl) - 1,3,5-S-triazine	Co(II)	Microanalyses, visible absorption spectra, and magnetic moment	The complexes are stable only in the solid state below room temperature and in the absence of moisture. There is some evidence for a strong interaction between H_2O and s-triazine in the Cl and NCS compounds.	[42]

1.2 SECTION B

GENERAL OBJECTIVES AND SCOPE OF THE PRESENT INVESTIGATION

GENERAL OBJECTIVE

- selection of suitable symmetrical-triazines.
- synthesis of metal complexes.
- structural studies on metal complexes.
- Investigations of the possible applications.

SCOPE OF THE PRESENT INVESTIGATION

From the literature survey, it has been noted that so far no significant attempts have been made to synthesize metal complexes of herbicidally active aziprotryn and derivatives of atrazine in which the Choro group is replaced by nucleophilic functions which can also promote chelation. Aziprotryn, with the azide ($-N_3$) group at the position adjacent to ring nitrogen can form a stable six- membered chelate with metal ions. The ligand is suitable even for solution studies leading to the evaluation of stability constants. 2-Chloro-4,6-alkylamino-S-triazine like atrazine, propazine, simazine, can be converted into 2-hydrazino and 2-hydrazinoethanol derivatives which can interact with transition metal ions as potential bi- or tridentate ligands. It is proposed to develop a new chelating s-triazine derivative by replacing the Chloro group in atrazine (2-Chloro-4-ethylamino-6-isopropylamino-S-triazine) with hydrazine or a substituted hydrazine functions. Synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes with aziprotryn and derivatized atrazine will be carried out. Conditions for isolation of pure metal complexes will be worked out. Structural studies of these complexes on the basis of analytical, conductance, IR spectra, electronic spectra and magnetic susceptibility have been proposed. Further, a preliminary screening of these complexes alongwith the ligands and related compounds against some gram positive and gram negative bacteria will be tried.

1.3 SECTION C

MATERIALS AND METHODS

All of the chemicals used are of analar grade. Solvents like methanol, ethanol, petroleum ether, 2-chloroethanol, chloroform and 1,4-Dioxane were used. These were purified by standard reported procedures [43]. During the synthesis of complexes a 5% (V/V) methanolic ammonia solution was used to adjust the pH. Pure samples of aziprotryn (AZP), and atrazine was obtained from Larodan Fine Chemicals AB, Sewden. Hydrazinoethanol derivative of ATZ was synthesized in our laboratory. Analar grade metal chlorides of Co(II), Ni(II), Cu(II) and Zn(II) were procured from Aldrich Chemicals. Hydrazine hydrate (80% solution, d = 1.03 kg/l) was a Riedel - de Hen sample and was used directly. Solvents were purified following reported procedures. Vibrational (IR) spectra were recorded on a Pye Unicam SP 2000 spectrophotometer, in 200- 4000 cm^{-1} range, using a potassium bromide disc as reference material. Electronic spectra were registered in the range 200 - 900 nm at room temperature using Beckman DU-65 spectrophotometer . Conductivities were measured in methanol using a Philip Harris conductometer. Melting points of ligands and complexes were determined on BOCK-MONOSCOP apparatus and are uncorrected. The purity of the ligands and complexes was tested by thin layer chromatography (TLC). The metal complexes have been analyzed for metal and chlorine. Cobalt(II) and zinc(II) were estimated complexometrically using EDTA. Nickel (II) and copper (II) were estimated gravimetrically as $Ni(DMG)_2$ and Cu (benzoin-α-Oxime) respectively. Chloride contents were analyzed as AgCl [44]. The alcoholic function of HEATZ was checked by xanthate and ceric ammonium nitrate test [45] .

II. METAL COMPLEXES OF AZP AND HEATZ

In this chapter synthesis and structural studies on metal complexes of 2-methylthio-4-azido -6-isopropylamino-s-Triazine (AZP) (section A) and Hydrazinoethanol derivative of 2-chloro-4-ethylamino-6-isopropylamino-s-Triazine (Atrazine) (HEATZ) (section B) will be presented. Aziprotryn and Atrazine are known compounds while HEATZ is synthesized from Atrazine. Section C presents prelimenary results of antimicrobial studies.

2.1 SECTION A

METAL COMPLEXES OF 2-METHYLTHIO-4-AZIDO-6-ISOPROPYL-AMINO-S-TRIAZINE (AZIPROTRYN)

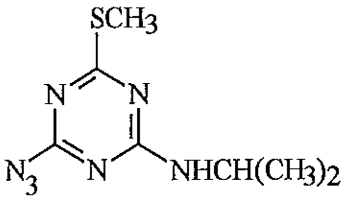


Fig 2. Structure of aziprotryn (AZP)

In this section Co(II), Ni(II), Cu(II) and Zn(II) complexes formed by 2-methylthio-4-azido-6-isopropylamino-S-triazine (aziprotryn) will be discussed. The ligand of interest is expected to behave as neutral bidentate system offering NN centres for metal binding interactions.

2.1.1 EXPERIMENTAL

Metal complexes of AZP were synthesized from non-aqueous media. The complexes were observed to form in methanol, ethanol, iso-propanol and n-butanol. The solubility of AZP showed notable increase in the presence of metal ions. The separation of complexes was increasingly facile with decreasing polarity of the solvent. The pH of the reaction medium affected the complex formation. pH range 5.0 - 6.0 gave better yields. This is probably because of the following pH dependent equilibrium.

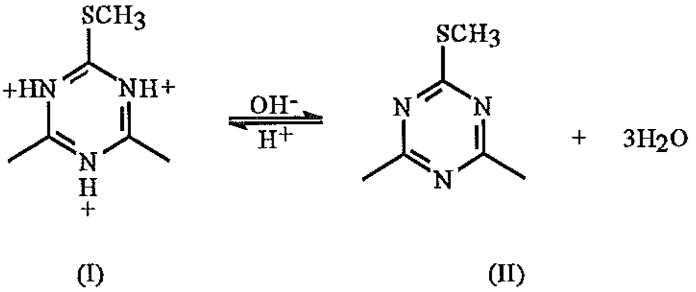


Fig 3. pH dependent equilibrium in AZP

The equilibrium is likely to shift to right at high pH (about 6), thus making the lone pair on any ring nitrogen available for metal binding interaction. Hence, the preferred structure in complex formation is (II).

Synthesis of Metal Complexes

The following general method was employed for the synthesis of metal complexes of aziprotryn.

To the methanolic solution (10 mL) of divalent metal chloride (0.22 mmol) 52.8 mg, Cobalt (II); 52.7 mg, Nickel(II); 37.8 mg, Copper(II); and 30.24 mg, Zinc (II)], methanolic solution (10 mL) of aziprotryn (0.44 mmol, 0.1 g) was added in small portions to obtain a clear solution. The pH of the reaction mixture was adjusted to 6 by adding 5% (V/V) methanolic ammonia solution.

The reaction mixture was then refluxed for 6 h on steam bath and was finally concentrated. The colored product obtained was filtered in hot condition and was washed successively with small amounts of methanol, and petroleum ether. It was dried in vacuum. The purity of the complexes was tested by TLC using different solvent mixtures. Yields of the compounds are given in Table 2.1a.

2.1.2 RESULTS AND DISCUSSION

All metal complexes except that of zinc are colored and are stable to air and moisture. They decompose at high temperatures (110 - 160^{0}C). They are soluble in common organic solvents like methanol, ethanol, chloroform, acetonitrile etc; but insoluble in water.

2.1.2.1 Elemental Analysis

Table 2.1a presents the analytical data of the complexes . The complexes have been analyzed for metal, chloride and aziprotryn percentages. Based on the percentage of metal chloride and aziprotryn the following formulations have been adjudged $Co(C_7H_{11}N_7S)_2Cl_2$, $Ni(C_7H_{11}N_7S)_2Cl_2$, $Cu(C_7H_{11}N_7S)_2Cl_2$ and $[Zn(C_7H_{11}N_7S)(H_2O)Cl]Cl$.

The data shows M: L: Cl is 1:2:2. The presence of two chlorides per metal ion is also indicative of the neutral form of the ligand in the complexes .

2.1.2.2 Conductance Studies

The conductance measurements of the complexes have been made using freshly prepared methanolic solutions (10^{-3}M). The molar conductance data is presented in (Table 2.1a). This shows that Co(II), Ni(II) and Cu(II) complexes are 1:2 electrolyte while Zn(II) complex is a 1:1 electrolyte. From conductance studies, it is concluded that the two chloride ions of Co(II), Ni(II) and Cu(II) complexes are present in the ionization sphere. That means the metal ion is bound to two AZP molecules in its coordination sphere. The data for Zn(II) complex, however suggested a 1:1 electrolyte behavior.

Table 2.1a Analytical data of the complexes of aziprotryn.

Complex with formula	Colour	M.P / dec.temp (°C)	Yield (%)	Calcd.(Found)% Chlorine	Calcd.(Found)% Metal	Λ_m (Ω^{-1} Cm^{2}mol^{-1})
Co(II) complex $[Co(AZP)_2]Cl_2$	Blue	150 - 160	50	(12.1) 12.23	(10.20) 10.16	152
Ni(II) complex $[Ni(AZP)_2]Cl_2$	Light green	110 - 120	55	(12.20) 12.24	(10.13) 10.10	143
Cu(II) complex $[Cu(AZP)_2]Cl_2$	Green	130 - 140	55	(12.03) 12.13	(10.83) 10.85	133
Zn(II) complex $[Zn(AZP)_2H_2OCl]Cl$	White	120 - 130	50	(12.51) 12.46	(11.39) 11.46	74

2.1.2.2. IR Spectra

Comparison of the ir spectra of AZP and its metal complexes reveals bidentate nature of the ligand. The data in (Table 2.1b) suggests that AZP is binding to the metal ions through a nitrogen of the N_3 group and an azomethine / ring nitrogen. From IR data, it may be deduced that AZP is behaving as a neutral NN donor. The following discussion will present the details.

Free AZP spectrum shows characteristic bands corresponding to $\nu_{N\text{-}H}$, $\nu_{a\,(NNN)}$, $\nu_{s\,(NNN)}$, $\nu_{(C=N)}$, $\nu_{(C\text{-}S)}$ vibrations besides several other bands assignable to C_3N_3 ring vibrations as documented in literature [47]. The strong, sharp band at 3290 cm^{-1} is due to $\nu_{(NH)}$, while intense band at 2110 cm^{-1} is assignable to $\nu_{a\,(NNN)}$ [46]. Another multiplet observed in 1610 - 1595 cm^{-1} is characteristic of three ring azomethines of S-triazine moiety. The bands appearing at 1650 - 1700 cm^{-1} may be due to $\nu_{(N=N)}$, and other ring vibration. A band of relatively less intensity at 1580 cm^{-1} may be due to $\delta_{(N\text{-}H)}$. Bands observed around 1400, 800, 730, 550 cm^{-1} are due to the C_3N_3 ring vibrations [47]. Bands due to $\nu_{s(NNN)}$, $\delta_{(NNN)}$ are located at 1375, and 670 cm^{-1} [46].

The characteristic features observed in the spectra of the complexes are

(I) an upward shift in $\nu_{a\,(NNN)}$ bands and a downward shift in $\nu_{s\,(NNN)}$ and $\delta_{(NNN)}$.

(II) splitting of $\nu_{(C=N)}$ band.

(III) appearance of non ligand band.

The participation of N_3 group in coordination is evidenced by an upward shift $\nu_{a\,(NNN)}$ and down ward shift $\nu_{s\,(NNN)}$ and $\delta_{(NNN)}$. These features are displayed by the spectra of Co(II), Ni(II), Cu(II), and Zn(II) complexes. The $\nu_{a\,(NNN)}$ in these complexes appears in the range of 2130 - 2200 cm^{-1} in comparison with that of free aziprotryn (2110 - 2160 cm^{-1}).

The intensity of $\nu_{a\,(NNN)}$ decreases in the order free AZP > Co(AZP) > Ni(AZP) > Zn (AZP) > Cu(AZP). This decreasing intensity order of $\nu_{a\,(NNN)}$ band may be attributed to increasing metal ligand interactions. The $\nu_{s\,(NNN)}$ shows a down ward shift in all the complexes. Besides, the low intensity band in the range of 670 cm^{-1} show a negative shift below 650 cm^{-1}. This features support coordination through the azido group [46]. Azido (N_3) group in AZP is represented as resonance hybrid of the following forms.

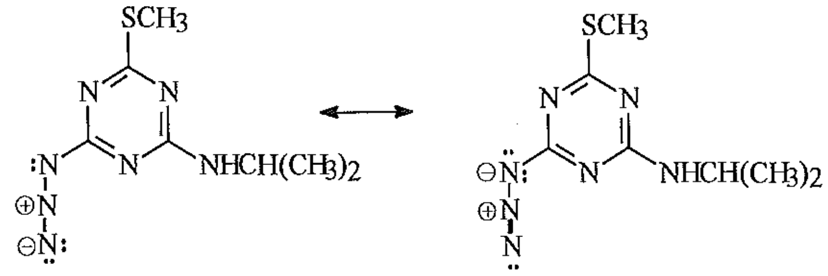


Fig 4. Resonance structure of AZP

Based on the availability of non bonding electron pair the chelate size (alongwith ring nitrogens as another binding centre), it is reasonable to conclude that the terminal nitrogen is the only possible binding centre. While ionic azide functions are symmetrical and linear the covalent azides are not expected to be so symmetric [48]. Further, when the terminal nitrogen is involved in bonding, the symmetry and the linearity are very much reduced.

The other interesting feature in the spectra of these complexes is the splitting of the multiple band assignable to $\nu_{(C=N)}$. In free aziprotryn the three azomethine (ring) functions do not have identical environments due to the presence of $S\text{-}CH_3$, N_3 and $NHCH(CH_3)_2$ groups. This could be the reason for the appearance of a triplet like structure corresponding to $\nu_{(C=N)}$ in free aziprotryn spectrum.

In the same region the expected bands for, $\nu_{(N=N)}$ and $\delta_{(NH)}$ are present. In the spectra of the complexes the $\nu_{(C=N)}$ shows a distinct division in to at least three structures well separated and located in the range of 1575 - 1640 cm^{-1}. This provides an unambiguous evidence to suggest that one of the azomethine nitrogens is involved in coordination while the others are free.

The spectra of the complexes show evidence for M-N vibrations which appear as bands of low intensity in the range of 430 - 560 cm^{-1} [49]. In case of Zn (II) complex presence of coordinated water is evidenced by non ligand bands at 900 - 910 cm^{-1} and 605 cm^{-1} which are characteristics of rocking and wagging modes [50].

Table 2.1b Characteristic infrared frequencies (cm^{-1}) of the complexes of aziprotryn.

Compound	$\nu_{(N\text{-}H)}$	$\nu_{a\,(NNN)}$	$\nu_{(C=N)}$	$\nu_{s\,(NNN)}$	$\delta_{(NNN)}$	New bands
Ligand	3290	2160	1610-1595	1375	670	———
Co(II) complex	3100-3600	2180	1600-1630	1360	625	450, 560
Ni(II) complex	3160-3500	2170	1615-1625	1370	660	430, 480, 490
Cu(II) complex	3320-3480	2170	1620-1650	1360	620	475
Zn(II) complex	3320-3580	2190	1610-1640	1370	650	900-910, 605, 490

2.1.2.3 Electronic Spectra

Assignments for various transitions are based on the supporting literature from standard references [51,52]. Aziprotryn is a white, crystalline compound and has no absorption characteristics in the visible region. The spectra of metal complexes show characteristic bands in the visible region, which can be assigned to various d-d transitions that are in support of the stereochemistry of the complexes.

Co(II) complex is blue in color and shows an intense absorption band at 18761 cm^{-1} with multiple structures at 15151 cm^{-1}, 14493 cm^{-1} and 13888 cm^{-1} . Such a band pattern is assignable to tetrahedral geometry [53]. The intense absorption band at 18761 cm^{-1} is assignable to the transition $^4A_2 \rightarrow {}^4T_1$ (P) of tetrahedral geometry while the multiple structures are due to spin forbidden transitions from $^4A_2$ state to several doublet states which attain notable intensity due to spin - orbit coupling. The other two expected transitions in the near infrared region $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1(F)$ are not recorded due to instrument limitations. Ni(II) complex is pale green in color and shows high intensity broad band located at 14388 cm^{-1} which can be assigned to $^3T_1(F) \rightarrow {}^3T_1$ (P) of tetrahedral geometry . Other two bands corresponding to $^3T_1(F) \rightarrow {}^3T_2(F)$, $^3T_1(F) \rightarrow {}^3A_2(F)$ transitions which are generally observed in the near infrared region could not be visualized due to instrument limitation.

The spectrum of Cu(II) complex is typical with a broad strong band in the region of 14492 to 12600 cm^{-1}. Which can be explained on the basis of square planar geometry shifting towards elongated octahedron due to two solvent molecules located at larger distances in solutions. This is a general observation with respect to several square planar complexes of Cu(II) which transform in to distorted octahedral geometry in solution [54,55] . In fact, in well resolved spectra such Cu(II) complexes show three band structures whose frequencies shift hypsochromically with increasing solvent interaction along the axial ends. The broad band observed in the present case can be assigned to a merger of the expected transitions $^2B_1 \rightarrow {}^2A_2$, $^2B_1 \rightarrow {}^2B_2$, $^2B_1 \rightarrow {}^2E$. Square planar geometry is proposed for Cu (II) complex.

Zn(II), being a d^{10} system is not expected to show any d-d transition. Based on the composition tetrahedral geometry is assigned.

Table 2.1.c Electronic spectral data of the complexes of aziprotryn.

Compound	**Electronic spectra bands** (ν_{max} cm^{-1})
Co(II) complex	18761, 15151, 14497, 13888
Ni(II) complex	14388
Cu(II) complex	14492 - 12600

CONCLUSION

On the basis of analytical, conductance and spectral data it is concluded that aziprotryn behaves as a neutral bidentate NN donor towards Co(II), Ni(II), Cu (II) and Zn (II), involving terminal nitrogen of azido group and one adjacent ring nitrogen in coordination. Tetrahedral geometry for Co(II), Ni(II) and Zn(II) complexes and square planar geometry for Cu(II) have been proposed. The proposed structure are given in Figure 6.

2.2 SECTION B

METAL COMPLEXES OF HEATZ

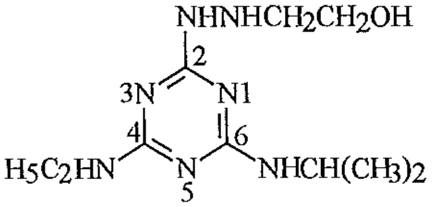
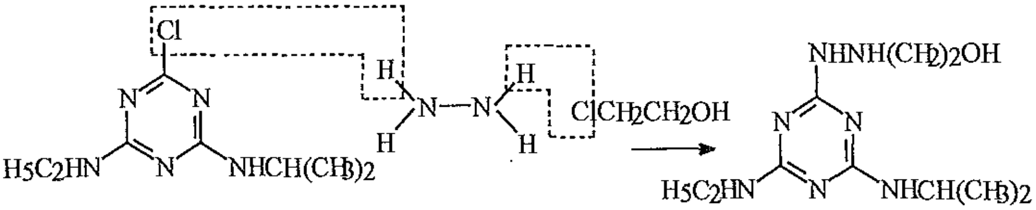


Fig 5. Structure of HEATZ

Atrazine (ATZ) indicated no coordination in the pH range 2 to 8. This might be explained by the relatively acid character of atrazine, demonstrated through low protonation constants for N1 and N3 atoms with pka = 1.7 [56]. The reason for this is obviously the vicinity of a Cl atom at the position 2. The possibility of binding a metal ion to an N5 atom, as well as to amino N atoms, is also very low because of the stearic factors.

In this section Co(II), Ni(II) and Cu(II) complexes of a new atrazine derivatives will be discussed. The



2.2.1 Experimental

Synthesis of Hydrazinoethanol Derivative of Atrazine (HEATZ)

In this synthesis 2-chloroethanol serves the purpose of a solvent and also of a reagent. Formation of hydrazinoethanol from hydrazine and chloroethanol is a known reaction, which in turn replaces chloride from atrazine [12].

To 0.5 g (2.32 mmol) of Atrazine, 2-chloroethanol (10 mL), and (0.14 mL, 2.32 mmol of hydrazine hydrate) were added and the mixture was refluxed on steam bath with continuous stirring for eight hours. The off white solid, separated during this time was filtered and washed with 2-chloroethanol. The product was dried under vacuo. It was recrystallized from methanol.

Yield: 77.6 %
Melting point / decomposition temperature: 160-162°C

Synthesis of Metal Complexes

The following general method was employed for the synthesis of metal complexes. To the methanolic solution (10 mL) of divalent metal chloride (0.19 mmol) 46.6 mg, Cobalt(II); 46.4 mg, Nickel(II); 33.4 mg, Copper(II)], 0.1 g (0.39 mmol) the methanolic suspension (10 mL) of HEATZ was added in small amounts to obtain a clear solution. The pH of the reaction mixture was adjusted to 6 by adding 5% (V/V) methanolic ammonia solution and then the mixture was refluxed for 6 h. Finally the reaction mixture was concentrated. The colored product was filtered in hot condition and was washed successively with small amounts of methanol and petroleum ether. It was dried in vacuum. The purity of each complex was tested by T.L.C. using different solvents. The Yields of the compounds are given in Table 2.2a

General Characteristics of the Compounds

HEATZ is soluble in water and most of the common polar solvents. Solubility in water is a characteristic feature. This is probably due to the hydrogen bonding caused by ethanol function. Increasing solubility associated with increasing electron donating capacity of the substituents at C-2, has been observed in some earlier studies [12]. The derivative gives qualitative tests for alcoholic function. Co(II), Ni(II) and Cu(II) complexes are brightly colored crystalline compounds and are stable to atmosphere condition. They do not melt but decompose. The decomposition temperatures are distinctly different from that of the free ligand. The complexes dissolve in water and most of the common organic solvents.

2.2.2 RESULTS AND DISCUSSION

2.2.2.1 Elemental Analysis of the Complexes

The analytical data of all the complexes is given in Table 2.2a. Metal and chloride analysis shows M:L:Cl ratio as 1:1:1 in all the complexes. Analysis also suggests the presence of two molecules of water per metal ion. Thus, the general composition of the complexes is given as $ML(H_2O)_2Cl$, where M = Co(II), Ni(II) and Cu(II).

2.2.2.2 Conductance Study

Conductance recorded in 10^{-3} M freshly prepared aqueous solutions (Table 2.2a) shows that all the complexes are 1:1 electrolytes and the chloride ion is present in the ionization sphere. The data also suggests that the ligand could be present as mononegative ion in these complexes, probably due to the deprotonation of alcoholic group during complex formation. Hence, the complexes may be formulated as $[ML(H_2O)_2]Cl$.

Table2.2a Analytical and conductance data of the complexes.

Complex with formula	Color	M.P / dec. temp (°C)	Yield (%)	Calcd.(Found)%		Λ_m
				Chlorine	Metal	(Ω^{-1} cm^2 mol^{-1})
Co(II) complex $[Co(II)(HEATZ)(H_2O)_2]Cl$	Pink	Changes its color from pink to blue at 200 and to green at 220.	36.7	(9.20) 9.21	(15.22) 15.28	71
Ni(II) complex $[Ni(II)(HEATZ)(H_2O)_2]Cl$	Light green	210 - 212	42.3	(9.18) 9.21	(15.27) 15.23	87
Cu(II) complex $[Cu(II)(HEATZ)(H_2O)_2]Cl$	Green	199 - 202	39.3	(9.60) 9.10	(16.74) 16.78	110

2.2.2.3 IR Spectral Study of HEATZ Complexes

The IR spectrum of free ligand shows a very broad, strong band in the region 3600- 2500cm^{-1} assignable to four types of $\nu_{(NH)}$ vibrations and one $\nu_{(OH)}$. All these functions are likely to involve inter as well as intra - molecular hydrogen bonding interactions, due to which the broad band structure has resulted. Another multiple band in the region 1650 - 1590 cm^{-1} is due to $\nu_{(C=N)}$ along with $\delta_{(OH, NH)}$ vibration. Other characteristics are the strong band at 1100 cm^{-1} and medium intensity band at 1000 cm^{-1} assignable to $\nu_{C\text{-}O}$ (alcoholic) and $\nu_{(N\text{-}N)}$ of hydrazine moiety [60 - 62]. The spectra of metal complexes show better resolutions, probably due to diminished hydrogen bonding and stereochemical changes accompanying metal - ligand interaction.

Notable features in the spectra of complexes in comparison with the free ligand spectrum are:

(I) Modifications of the broad band (3600 - 2500 cm^{-1}) into a relatively narrow band with components in the region 3500 - 2900 cm^{-1}. The absence of band structure in the region 2500 -2900 cm^{-1}, can be attributed to deprotonation of alcoholic group and its subsequent involvement in metal bonding. This derives further support from the absence of $\delta_{(OH)}$ and shifting $\nu_{(C\text{-}O)}$ alcoholic bands.

(II) Appearance of a relatively sharp strong band in the region 1610 - 1620 cm^{-1} in place of 1590 - 1650 cm^{-1} band of the free ligand. If the low frequency component is assumed to be due to $\delta_{(OH)}$, its absence in the spectra of complexes further supports the deprotonation. Down ward shift of band from 1650 → 1620 → 1610 cm^{-1} can be attributed to the involvement of one ring nitrogen in coordination. N1 or N3 may be involved in this process [57-59].

(III) Positive shifts in $\nu_{(C\text{-}O)}$ and $\nu_{(N\text{-}N)}$ are strong indications of the participations of the deprotanted alcoholic oxygen and hydrazino nitrogen in metal binding process. Particularly the shift in $\nu_{(C\text{-}O)}$ ($\Delta\nu_{C\text{-}O} = 40 - 45\ cm^{-1}$) is very large, which distinctly points towards bridging interaction of the alkoxide oxygen [60 - 62].

(IV) Appearance of new / non - ligand bands in the spectra of complexes assignable to rocking and wagging modes of coordinated water and M-N, M-O vibrations confirm the interaction between metal, ligand and water molecules [63]. From ir data It can be concluded that the ligand HEATZ behaves as a monobasic tridentate towards Co(II), Ni(II) and Cu(II), involving a ONN donor system in bonding process with characteristic alkoxide bridging. Consequently the complexes could be formulated as dinuclear compounds with the general formula $[M_2L_2(H_2O)_4]Cl_2$.

Table 2.2b Characteristic infrared frequencies (cm^{-1}) of the complexes.

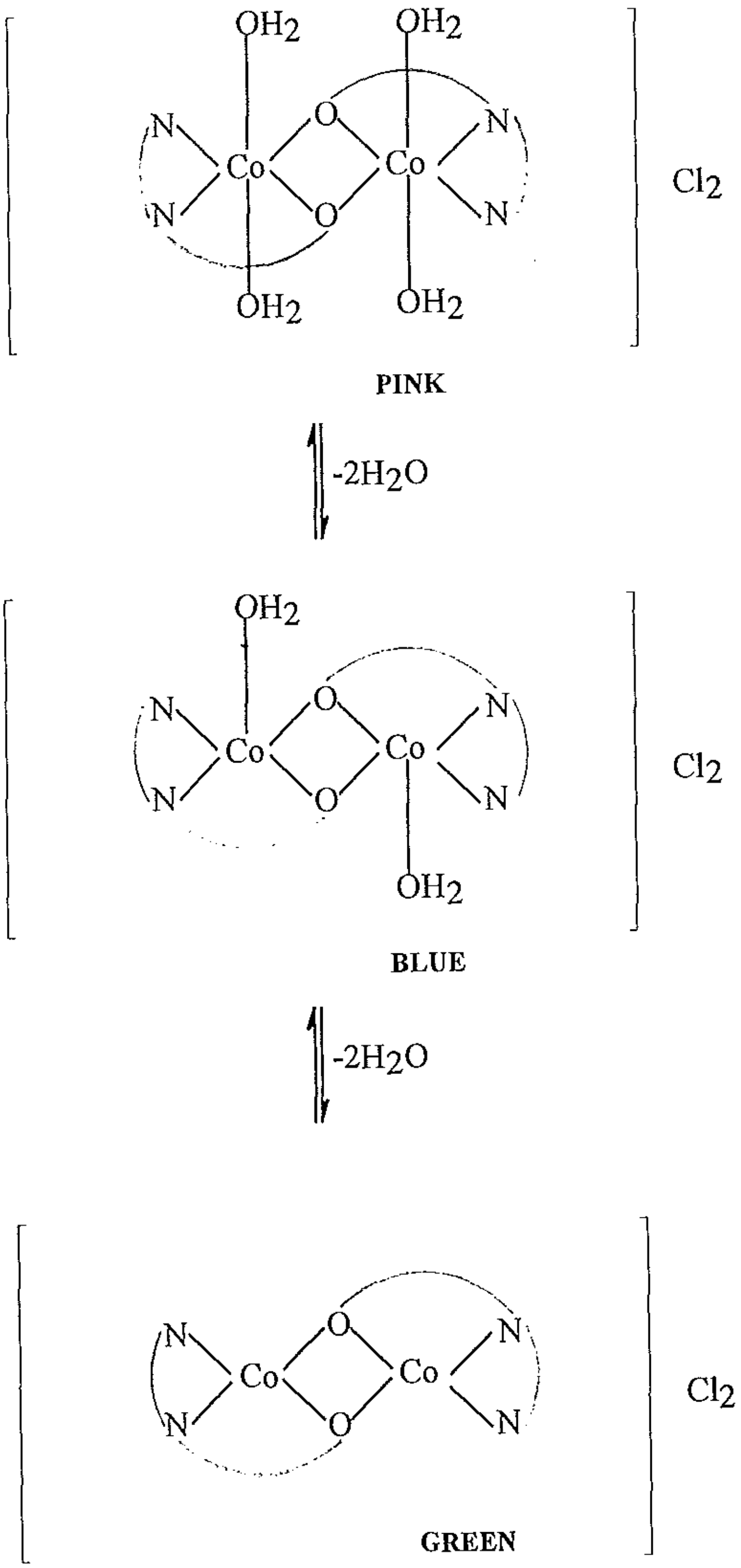
Compound	$\nu_{(NH)} + \nu_{(OH)}$	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(N-N)}$	New bands
Ligand	3600 - 2500	1650 - 1590	1100	1000	———
Co(II) complex	3500 - 3300	1620 - 1610	1140 - 1145	1010 - 1015	875, 920, 525, 485.
Ni(II) complex	3500 - 2900	1620	1140	1025	900, 970, 550,490.
Cu(II) complex	3500 - 3000	1610	1110 - 1140	1020	950, 920, 555, 495.

Table 2.2c Electronic spectral data of the complexes.

Compound	**Band position** (ν_{max}, cm^{-1})	**Assignment of transitions**
Co(II) complex	19092 - 20,000	$^4T_1(F)\rightarrow{}^4T_1(P)$
Ni(II) complex	11625	$^3A_2\rightarrow{}^3T_2$
	14124	$^3A_2\rightarrow{}^3T_1(F)$
	21739	$^3A_2\rightarrow{}^3T_1(P)$
Cu(II) complex	11780	$^2B_1\rightarrow{}^2A_2$
	12468	$^2B_1\rightarrow{}^2B_2$
	13158	$^2B_1\rightarrow{}^2E$

CONCLUSION

Based on analytical, conductance, thermal and spectral studies it is concluded that HEATZ behaves as monobasic tridentate NNO donor employing ring nitrogen, hydrazino nitogen and alkoxide oxygen (bridging) in bonding. Octahedral geometries have been proposed for the complexes (Fig 7). Thermochromism is an interesting feature observed with the Co(II) complex.



SCHEME 2. Deaquation of thermochromic $[Co_2L_2(H_2O)_4]Cl_2$

SECTION C

ANTIMICROBIAL STUDIES

Many physiologically active herbicides, have been studied for antimicrobial properties. Prometryn and cyanuric acid were studied for nucleic acid metabolism in *Escherichia coli* [64]. Atrazine, prometryn, and simazine have been screened against *Bacillus sustilis* [65]. When these physiologically active compounds are bound to metal ions, their properties may be enhanced or reduced depending on the binding sites, the electronic distribution and the availability or non availability of active functional groups which are responsible for the activity

As the ligands under investigation are well known herbicides, a preliminary comparative screening of these compounds, their metal complexes, metal salts and related compounds against *Escherichia coli* and *Staphylococus aureus* has been carried out following 'Agar Diffusion method'. The observations show that all these compounds don't have any significant effect on these microbes.

Perhaps these compounds may have selective inhibitions on other microbes. Further studies are needed to identify the organism on which these compounds can be active.

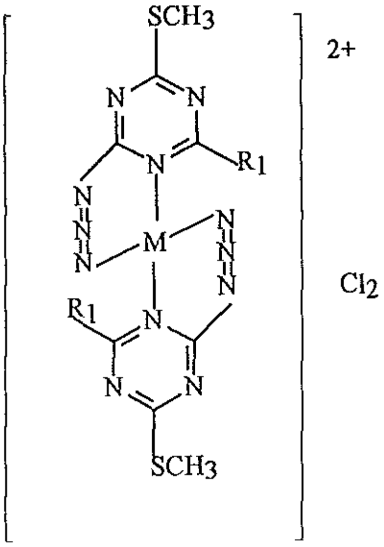


Fig 6. Metal complexes of AZP. $R_1 = NHCH(CH_3)_2$

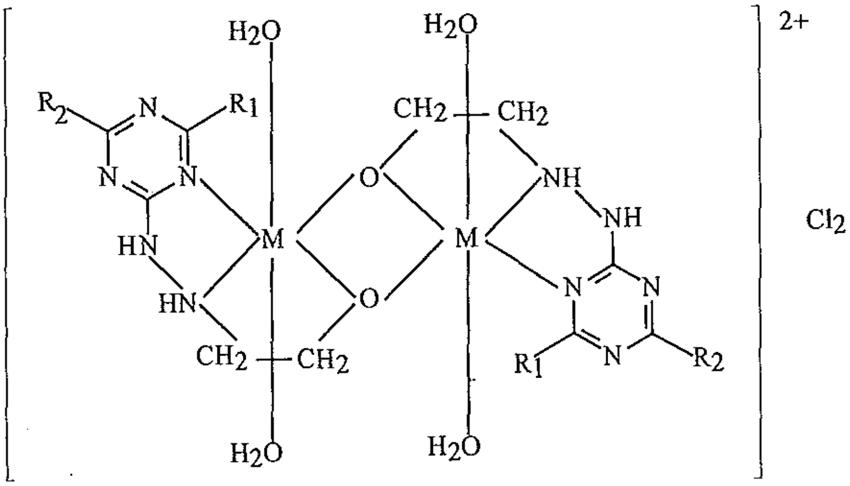


Fig 7. Metal complexes of HEATZ. $R_1 = NHC_2H_5$, $R_2 = NHCH(CH_3)_2$

M = Co(II), Ni(II), Cu(II)

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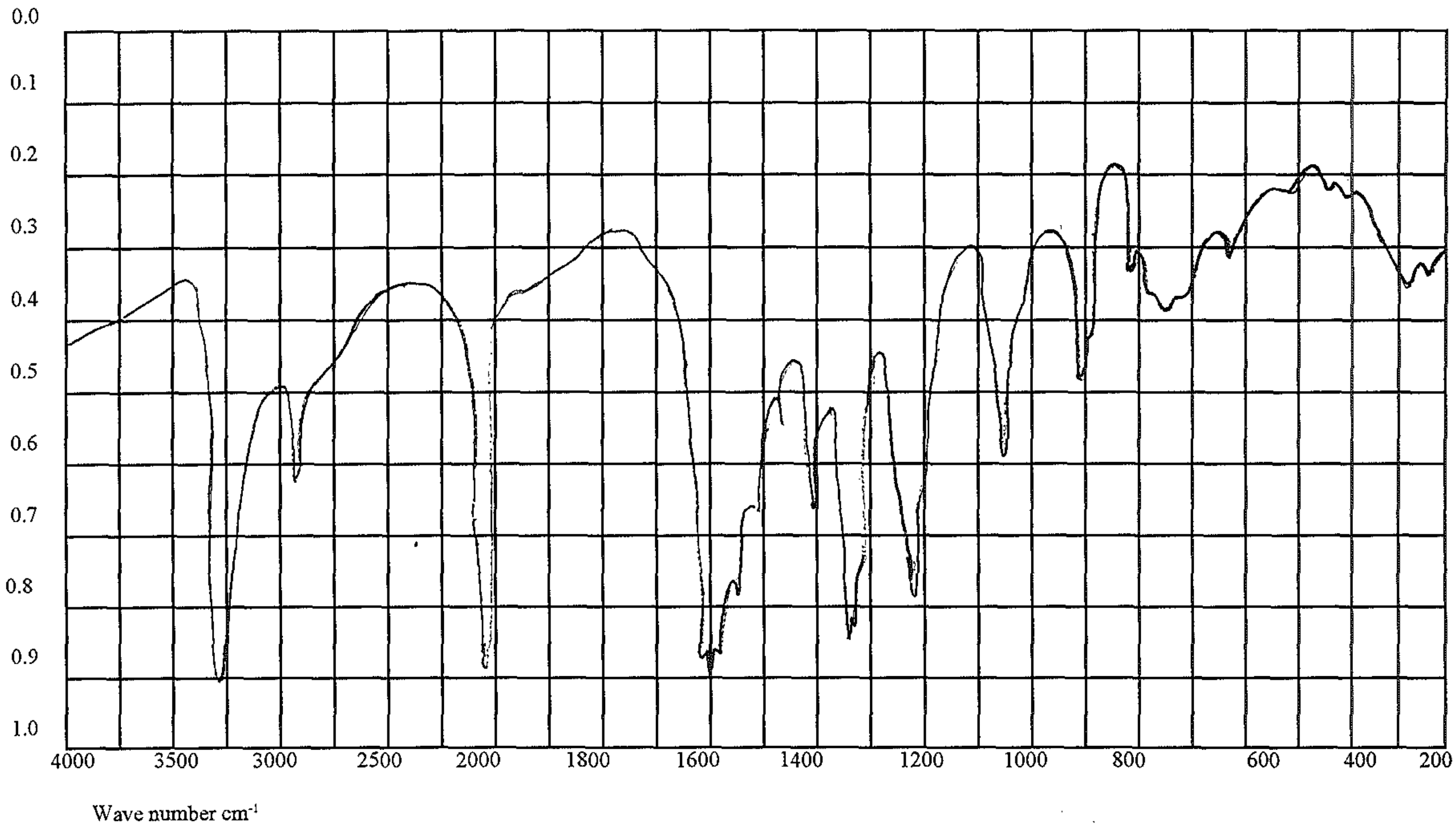
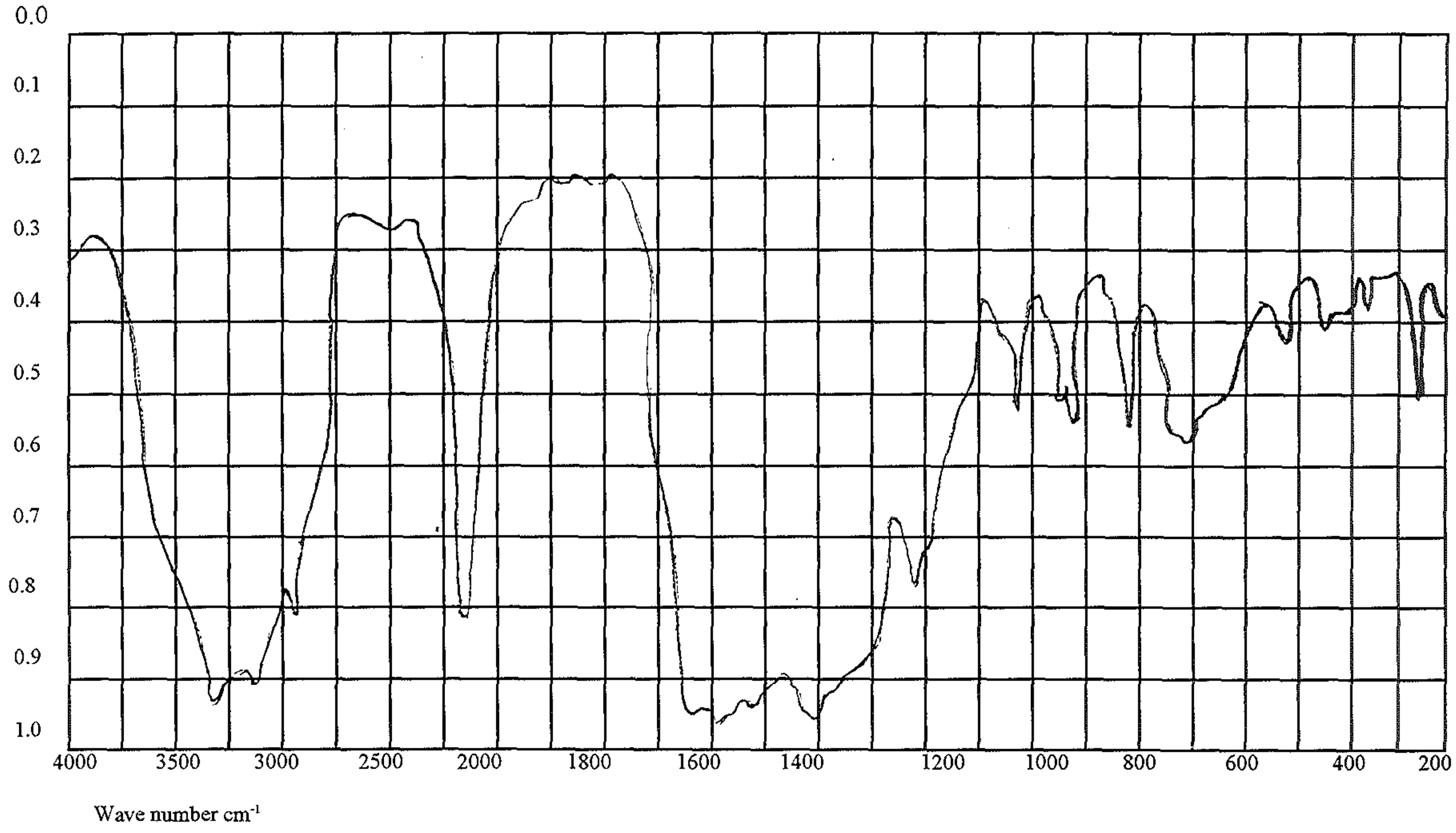
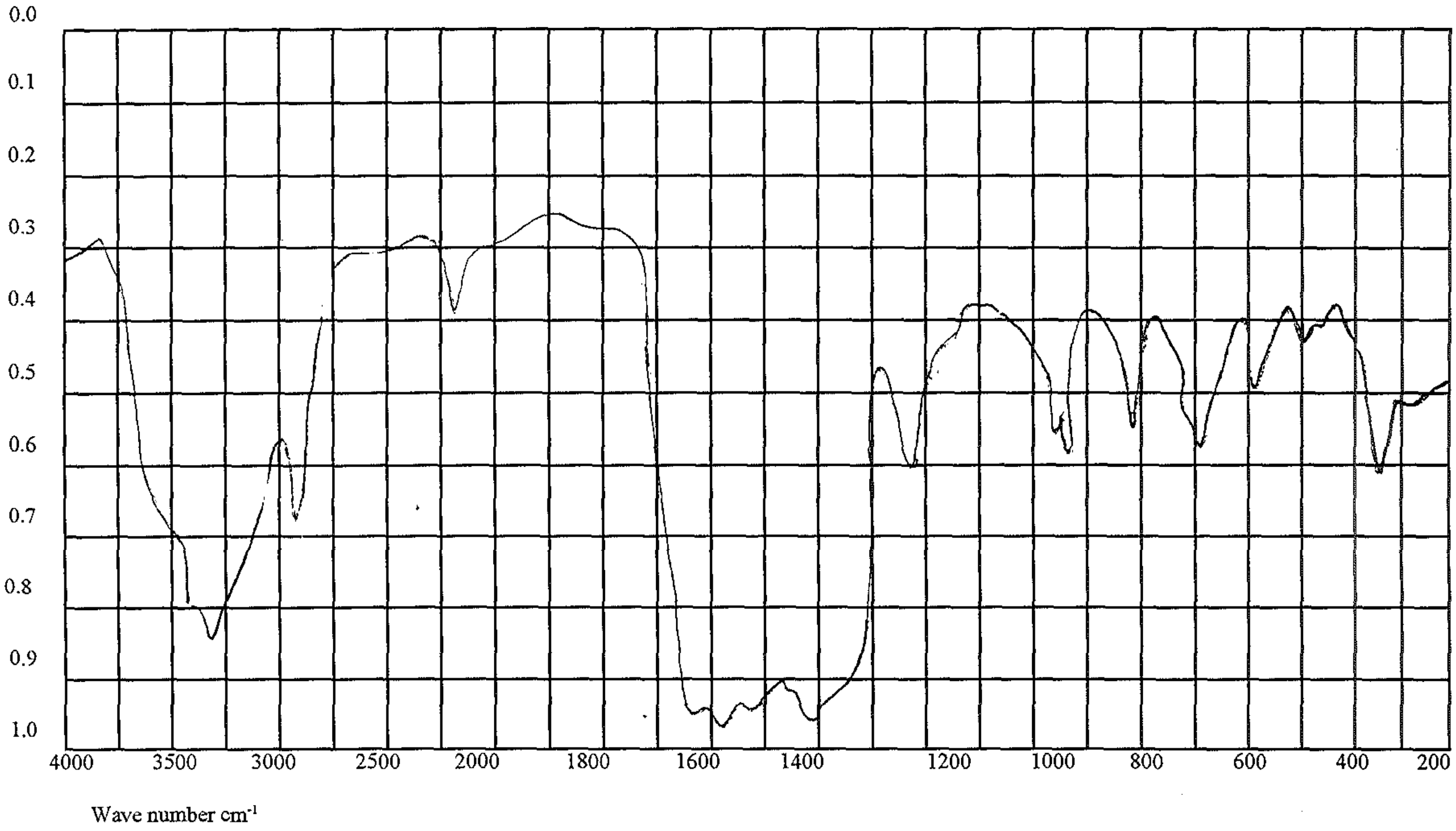


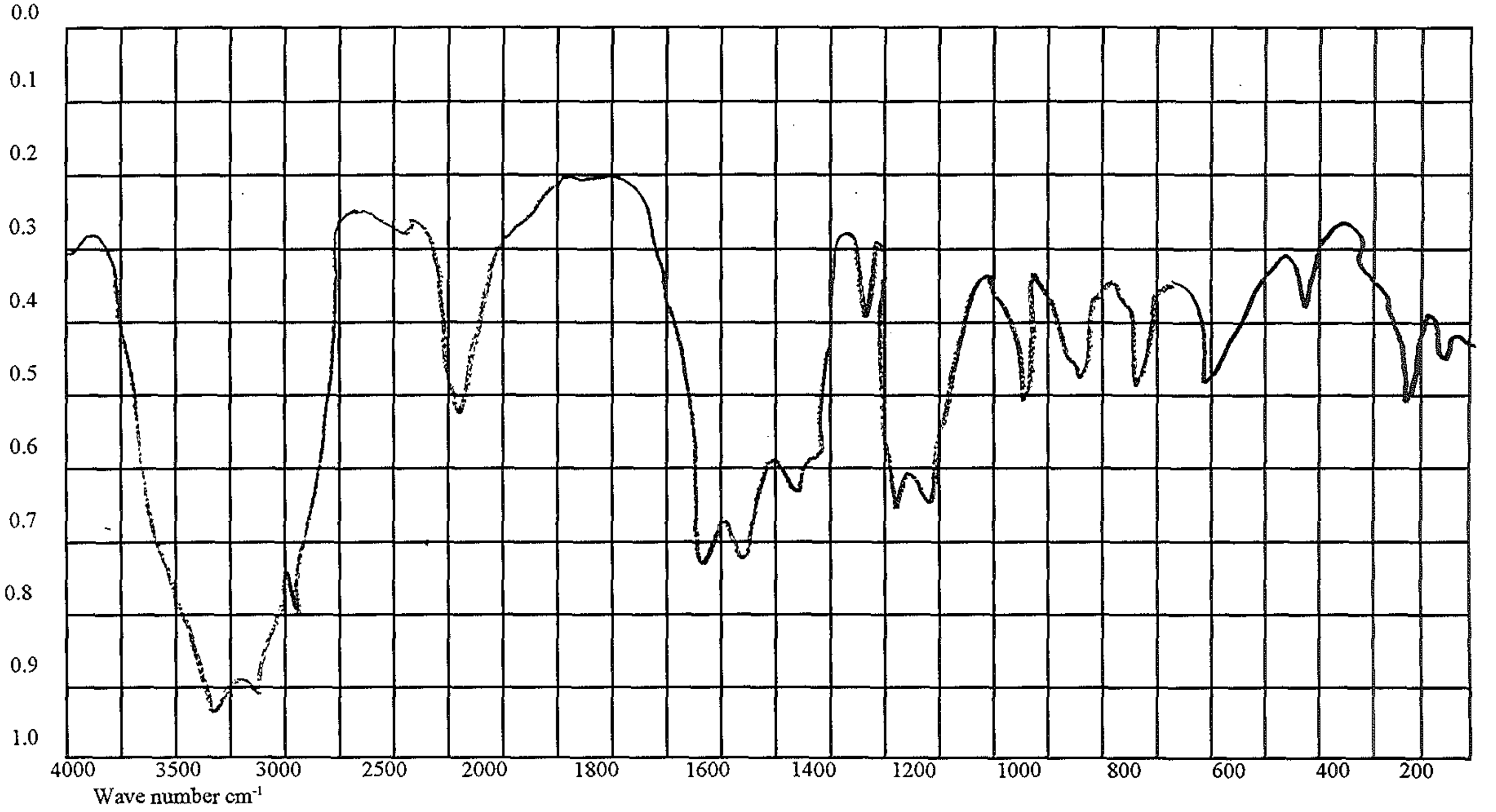
IR Spectrum of [AZP]



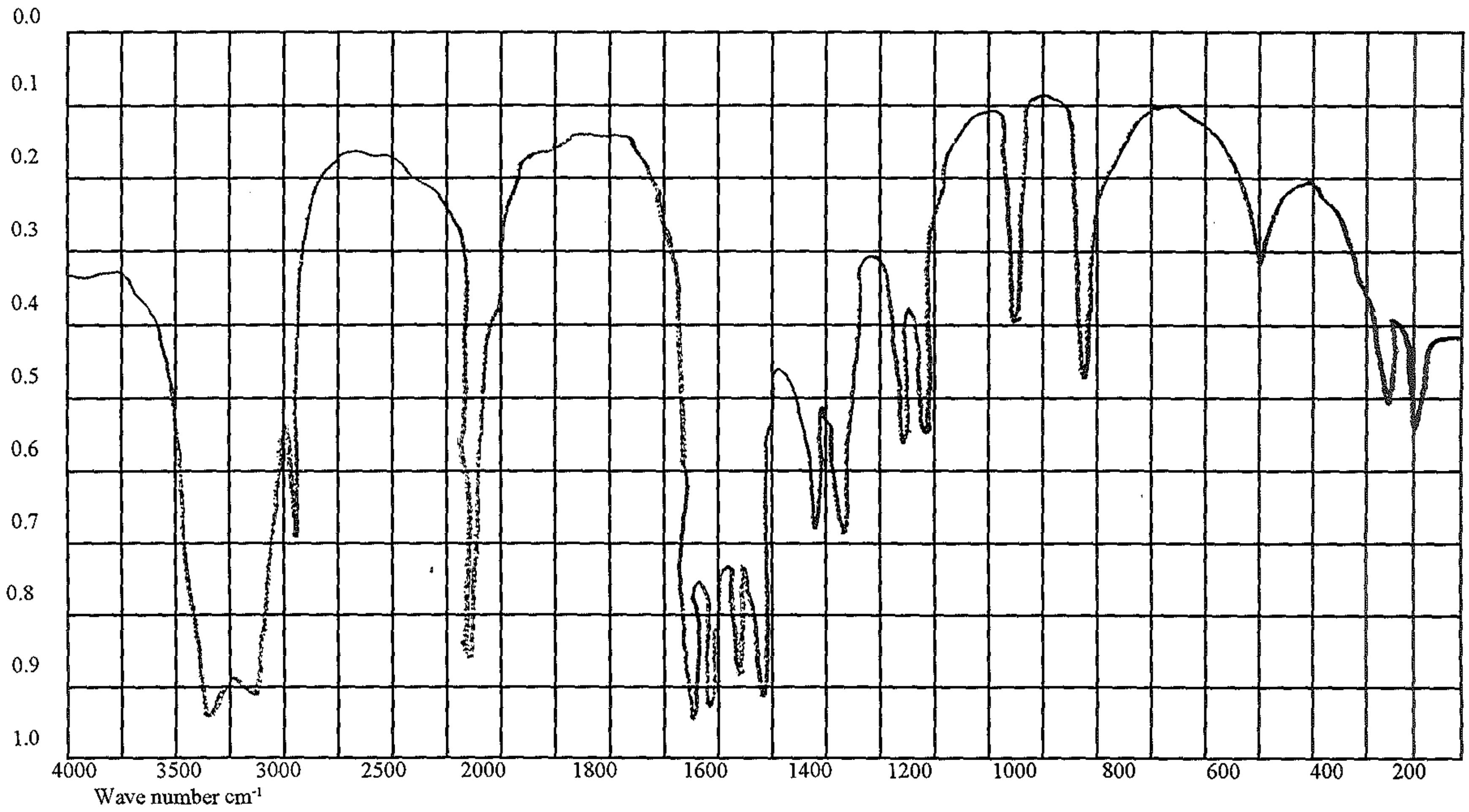
IR Spectrum of [Ni(AZP)$_2$]Cl$_2$



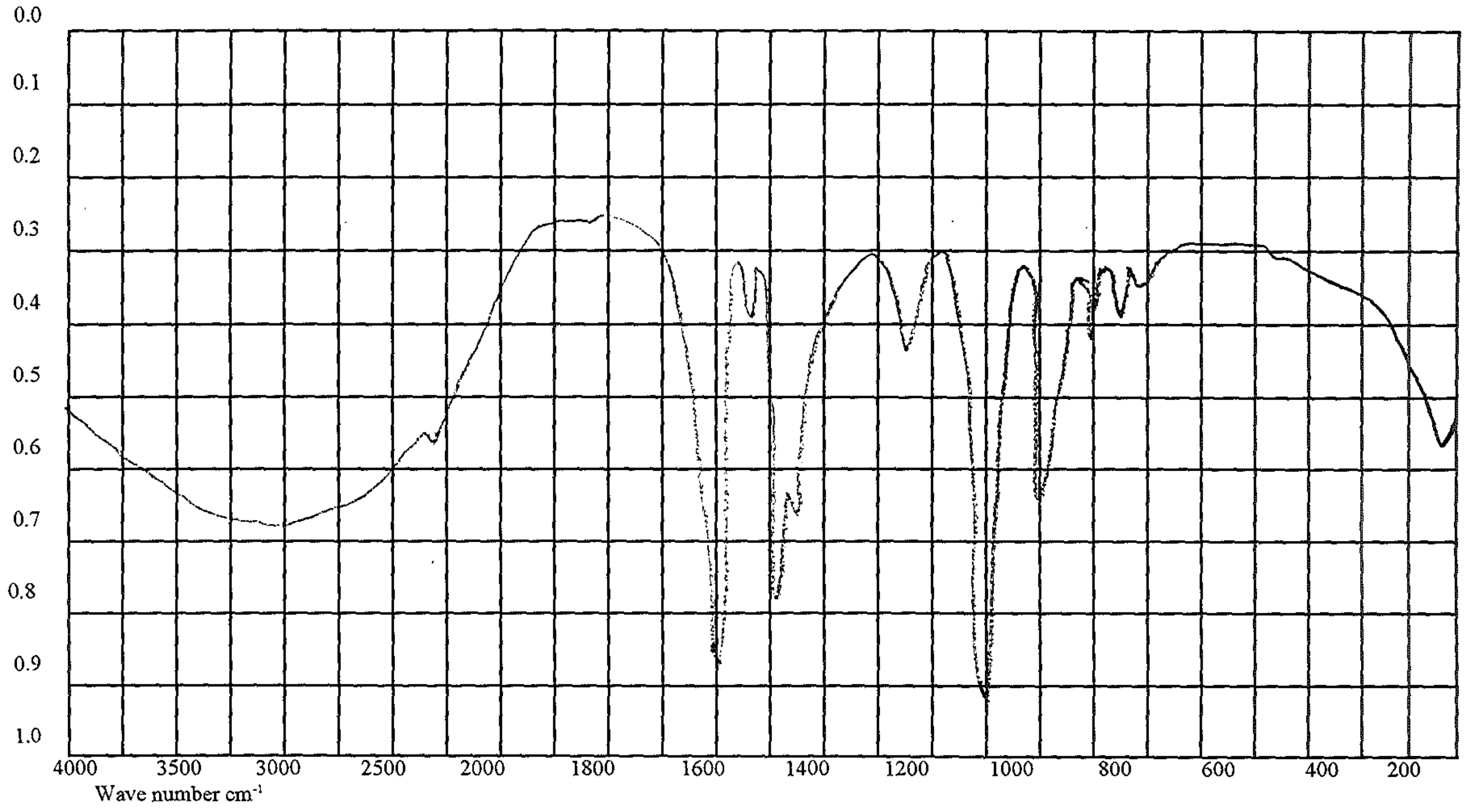
IR Spectrum of $[Cu(AZP)_2]Cl_2$



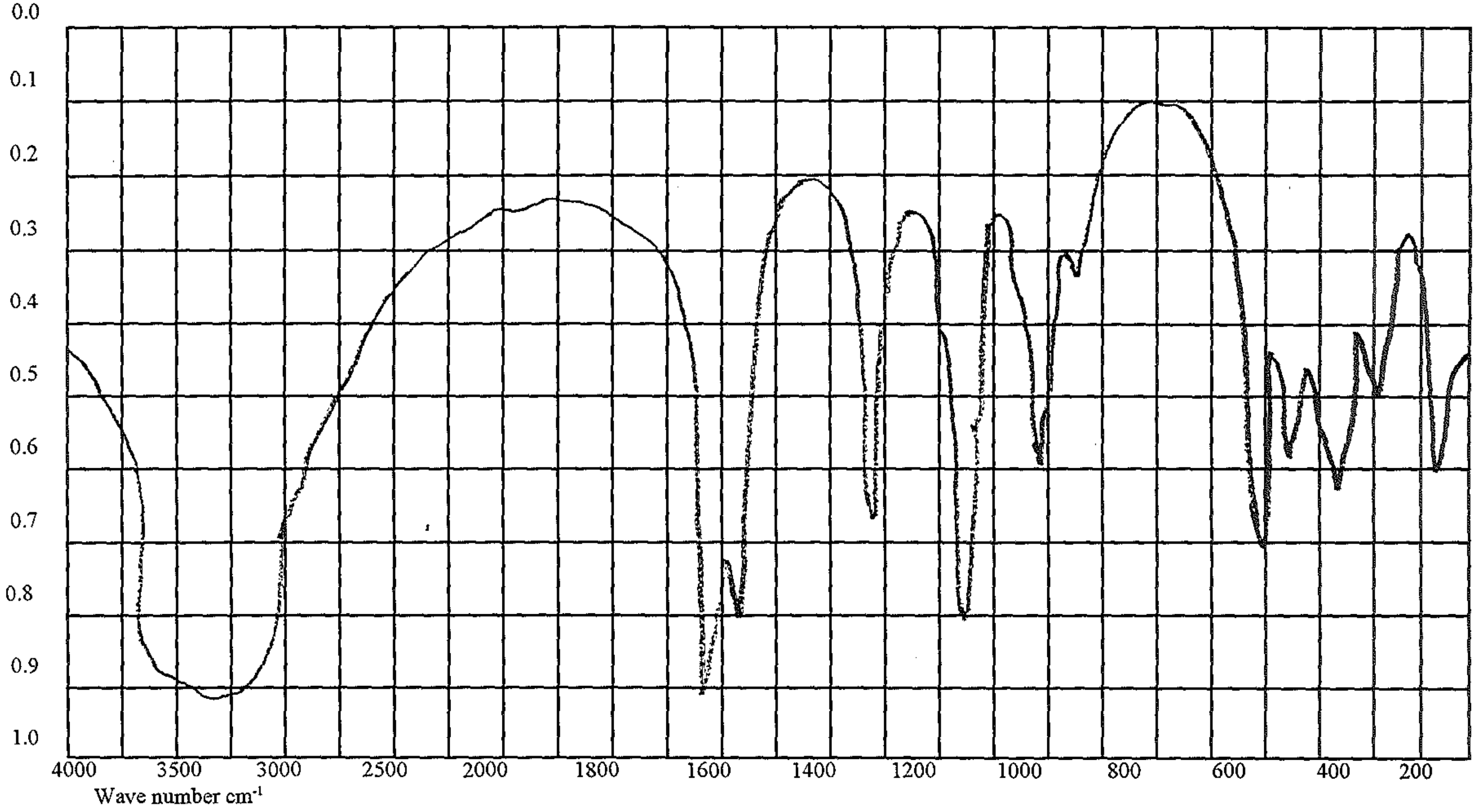
IR Spectrum of $[Zn(AZP)_2]Cl_2$



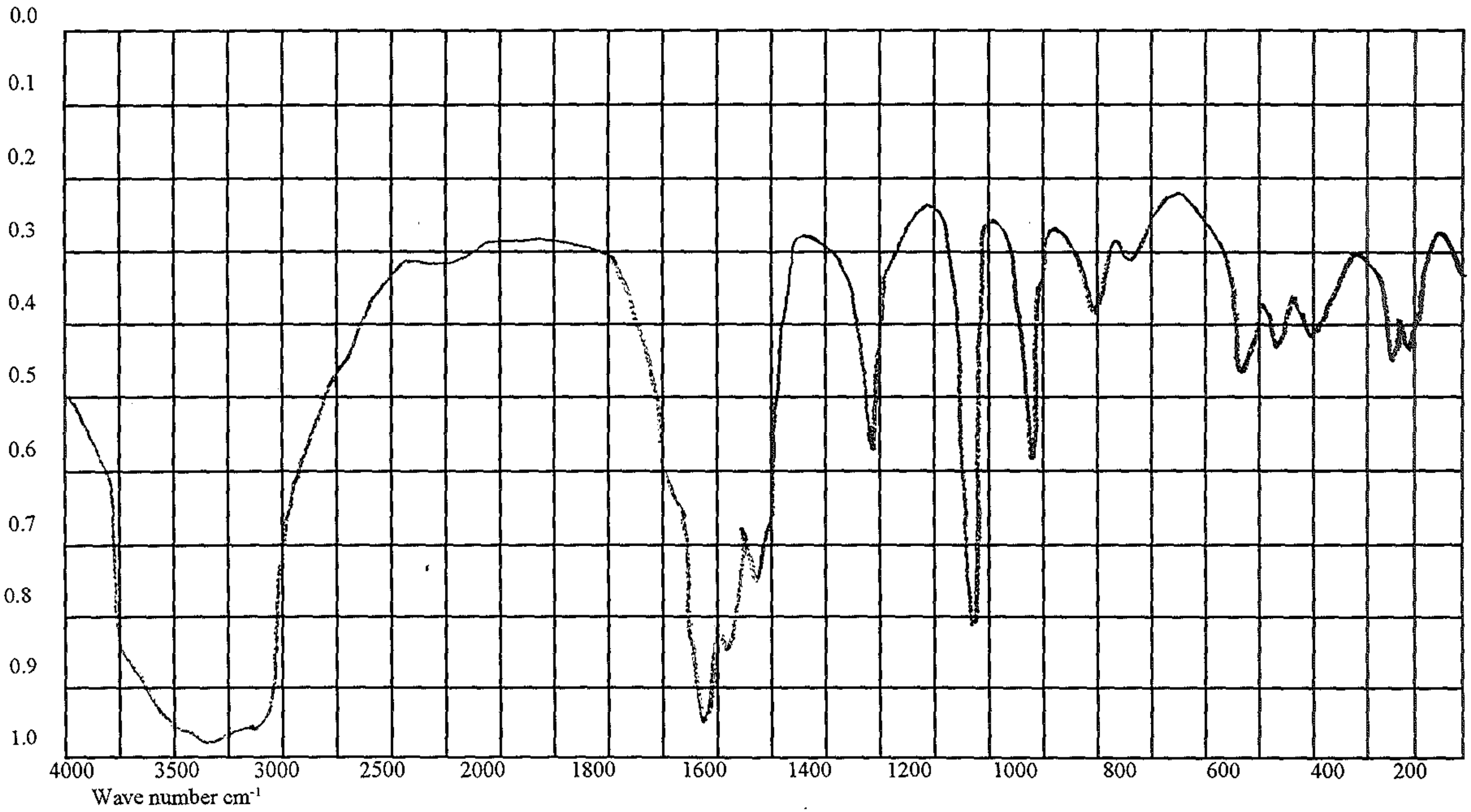
IR Spectrum of $[Co(AZP)_2]Cl_2$



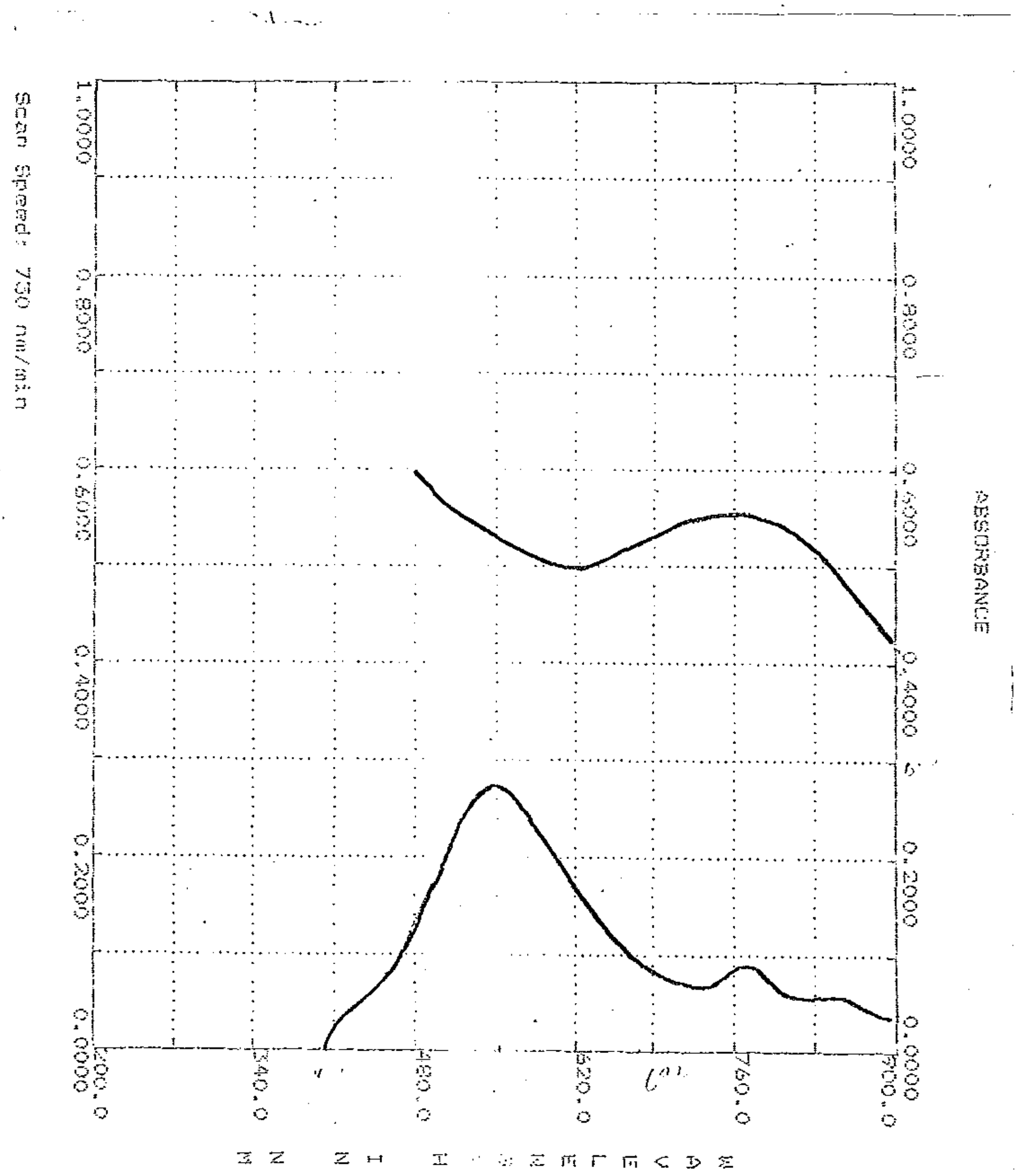
IR Spectrum of [HEATZ]



IR Spectrum of [Cu(HEATZ)(H_2O)$_2$] Cl

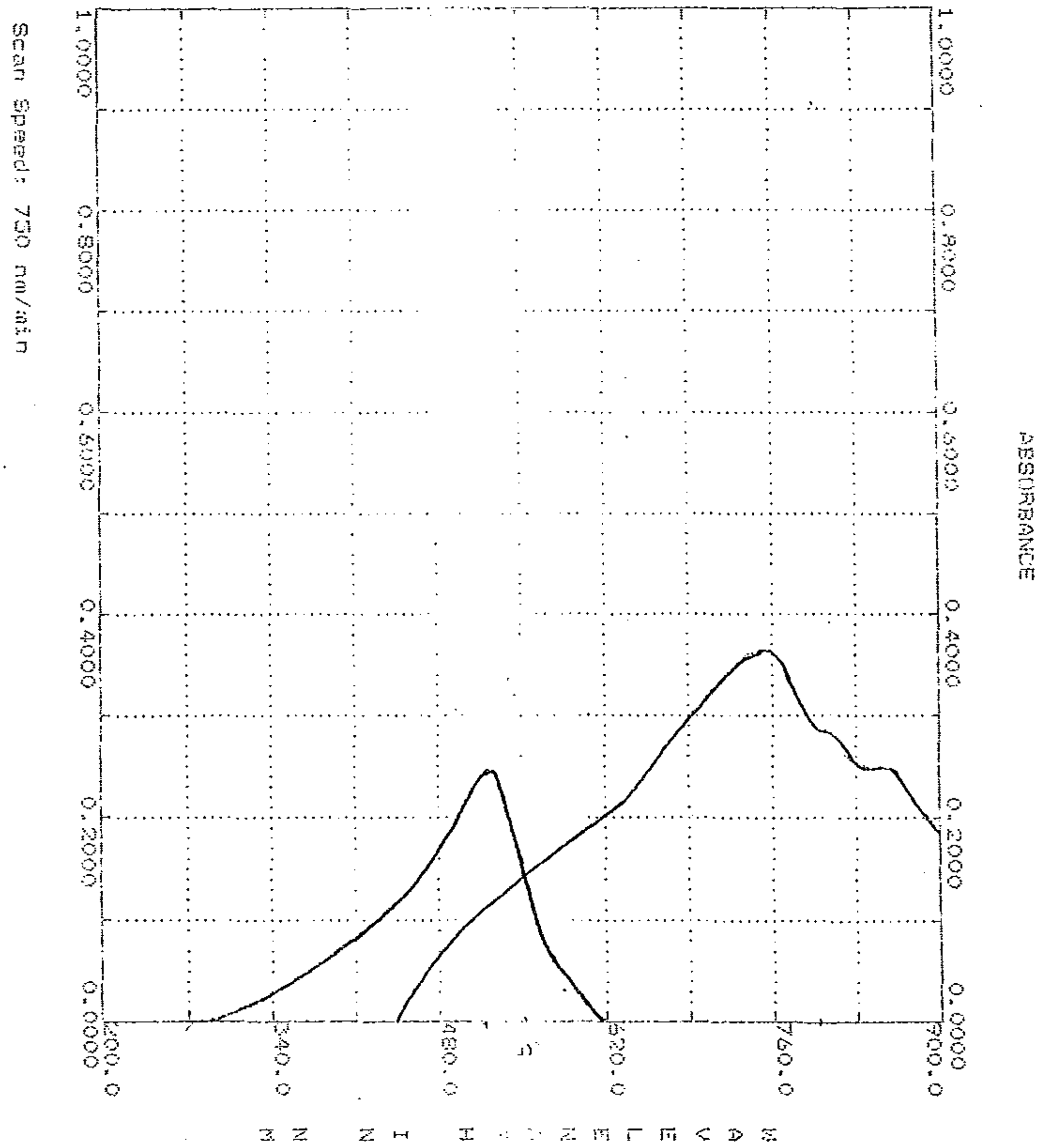


IR Spectrum of [Co(HEATZ)(H_2O)$_2$] Cl



(a) Electronic spectrum of $[Cu(AZP)_2]Cl_2$

(b) Electronic spectrum of $[Co(AZP)_2]Cl_2$



(a) Electronic spectrum of [Cu(HEATZ) $(H_2O)_2$]Cl

(b) Electronic spectrum of [Co(HEATZ) $(H_2O)_2$]Cl

DECLARATION

I, the undersigned, declare that this thesis is my original work and has not been presented for any degree in any other university and that all sources of material used for the thesis have been duly acknowledged.

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Signature:

This thesis has been submitted for examination with our approval as University Advisors.

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Signature:

Place and date of submission: School of Graduate Studies,
Addis Ababa University
June, 1999