

Synthesis and Identification of Iron (III) complex with methyl Benzothiazolyazo Bromo Salcylic acid

Abaas N. Al-Sharify and Jassem . M . A-Al-Hassien
Department of Chemistry , College of Science , University of Babylon , Iraq .

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Abstract

Iron (III) complex with 5-[2-(6-methyl benzothiazoly) azo] -3- bromosalcylic acid was prepared and characterized by using element analysis (C.H.N.O) and spectral techniques such as IR , UV. VIS. , Flame Atomic Absorption , and mole ratio study . Other physical parameters , for the complex , such as the effective magnetic moment (μ_{eff}) and the molar conductivity in solution also have been determined .

The spectroscopic studies of the reaction of Iron (III) and the ligand in their ethanolic solutions led to the formation of 1:2 (metal : ligand) molar ration . The physical and spectral studies of the solid complex indicated octahedral coordination via N and O atoms of the azo , hydroxyl and N in thiazoly ring . The complex has a paramagnetic properties and ionic features .

	-3- [(-6) -2] - 5
(IR)	(C.H.N.O.)	
	(FAA)	(UV.VIS)
(μ_{eff})		
		: (1:2)

Introduction

Thiazoly azo compounds form typical octahedral complexes with transition metals via coordination through nitrogen atom of the thiazole ring , nitrogen atom of the azo group and other donor atoms or groups which

are ortho to the azo group , the complex formed has a chelating rings , these rings greatly enhances the stability of the metal-dye bonds , as well as the stability of the organic molecule itself ^(1,2) . The linkages may be also stabilized by resonance

involving the entire groups ; indeed there is some possibility that the azo double bond is involved ⁽³⁾ . Thiazole derivatives are well known as biologically important compounds ^(4,5) , in other side salicylates play important role in medicine because of their biological effects ⁽⁶⁻⁸⁾ . There is a correlation between their biological activity (antiinflammatory , antibacterial , analgesic – antipyretic and fungicidal) and eventual prediction of drug action ⁽⁹⁻¹¹⁾ . For these reasons researchers have been made this studies of complex formation between these ligands and various metals . In analytical chemistry because of the high selectivity and the high molecular weight of these reagents , researchers can easily use these ligands in analytical chemistry to detect and evaluate the traces of the metal atom ^(12,13) . Iron (III) forms a variety of cationic , neutral and anionic complexes with different ligands . Ammines of Iron (III) are unstable and dissociate in water , chelating ligands such as 2,2'- bipyridin and phenanthrolin produce more stable complexes ⁽¹⁴⁾ .Magnetically Iron (III) , like manganese (II) , is high spin in nearly all of its complexes except those with the strongest ligands⁽¹⁵⁾ . In the high spin complexes , the magnetic momenta are always very close to the spin – only value of 5.9 BM , on other hand the low – spin complexes values of nearly 2.3 BM being obtained ⁽¹⁵⁾ . Iron (III) complexes exhibit the high – spin / low-spin crossover (spin equilibria) where these complexes are exist in two distinct species ,the high-spin electronic configuration of (6A_1) ($t_{2g}^3 e_g^2$) and the low-spin of (2T_2) ($t_{2g}^5 e_g^0$) .

Experimental

Physical measurements

IR spectra of the ligand and the complex are recorded using the apparatus FTIR-8400S Shimadzu

instrument (KBr pellet technique) in the region 500-4000 cm^{-1}

UV. VIS. spectra are obtained using a UV-1650 PC Shimadzu spectrophotometer with a quartz cell for 10^{-3} M solution complex in DMSO.

The elemental analysis were established by using a EURO EA Element Analyzer and Shimadzu AA 160 Atomic Absorption Flame Emission Spectrometer .

The magnetic susceptibility measurements were carried out by using a magnetic susceptibility balance MSB-MKI .

The molar conductivity for the solutions was measured by using a conductivity potentiometer INOLAB 740 for 10^{-3} M solution complex in DMSO at 25°C .

Ionization constants of the OH group for the ligand were determined potentiometrically according to the method given by Serjeant⁽¹⁷⁾ , and the potentiometric apparatus has been described previously ⁽¹⁸⁾ , by which titrations were performed at a constant temperature (25°C) using a digital PHM 62 potentiometer .

Materials

The complex and the ligand are air-sensitive and were handled under a dry atmosphere using dry-box techniques .

The water used was distilled . The Iron (III) ion solutions were prepared from ferric chloride salt . Aqueous solutions were made 0.001 M . The ligand used was prepared during this investigation . All the reagents were of analar R-grade and they were obtained from Fluka and BDH . Sodium nitrate was used for the preparation of the background electrolyte and stock solutions .

Preparation the reagent (MBABSA) :

The reagent methyl benzothiazolyl azo bromo salicylic acid (MBABSA) was prepared by the method described previously^(19,20,21) .

Dark yellow crystals of the ligand were obtained after the evaporation of the solvent, is characterized by C.H.N.O., IR, and UV. VIS. techniques. IR spectra reveal N = N stretching at 1440 cm^{-1} . Elemental and UV. VIS. spectral data are also in good agreement with the expected structure.

Preparation of the complex

The Iron (III) complex was prepared by taking two equivalents of the ligand (3.94g, 0.01 mole) with two equivalents of the ferric chloride (2.69g, 0.01 mole) in dry ethanol. Initially, the ligand was first dissolved in ethanol, where the colour of the solution was yellow. To this solution, ethanolic solution of ferric chloride was added. The change in colour was observed from yellow to purple-red, the whole solution was then kept under reflux for 4h ($70 - 80^\circ\text{C}$). Slow evaporation of this solvent led to the formation of a dark purple-red coloured powder. Scheme 1 gives a

systematic procedure of the preparation of ferric complex, the structure of which was confirmed by mole-ratio method to insure the formation of 1:2 (metal : ligand) complex.

Analytical data for the complex are as follows: Molecular formula of $\text{Fe C}_{30}\text{H}_{18}\text{ N}_6\text{ O}_6\text{ S}_2\text{ Br}_2$, calculated (found):

C = 42.9 (42.5), H = 2.1 (1.9), N = 10.0 (9.9), O = 11.4 (11.2) S = 7.6 (7.3), Fe = 6.7 (6.3). The analytical data show confirming the formation of the complex with mentioned molecular formula.

Results and Discussion

IR studies

The important peaks of the IR spectra of the ligand and the complex are summarized in Table 1. The modifying and shifting in the peaks and their intensities confirming the formation of the complex.

Table 1 : Important IR spectral frequencies for the ligand and the complex

Assignmet	Ligand	Complex
$\nu(\text{O} - \text{H})$	3100s	3400 s
$\nu(\text{C} - \text{O})$	1675 s	1610 s
$\nu(\text{C} - \text{N})$	1605 m	1501 w
$\nu(\text{N} = \text{N})$	1440 s	1400 m
$\nu(\text{Fe} - \text{O})$	-	Under 400
$\nu(\text{Fe} - \text{N})$	-	Under 400

Optical Studies

The electronic spectra of the ferric complex and of the ligand recorded in ethanol solvent are shown in figures 1 and 2, including a charge transfer bands at 410 nm and 510 nm of the ligand and the complex respectively, hence there is a 90 nm as a red shift, confirming a new compound was obtained.

Magnetic Properties

The effective magnetic moment (μ_{eff}) of the ferric complex lie in the

range (1.3 – 2.0) BM⁽¹⁵⁾. In this study, the complex of ferric ion with methyl thiazolyl azo bromo salicylic acid gave 1.6 BM, this result confirms that the complex has a paramagnetic properties.

Molar Conductivity

The molar conductivity in ethanolic solution of ferric complex was $55\text{ S}\cdot\text{mol}^{-1}\text{ cm}^2$, this indicates that the coordination core is ionic and confirms the structure of the complex.

Ionization Constants

The ligand has two acidic groups (COOH and OH), hence, it has two ionization constants, K_{a1} , and K_{a2} , the first one belongs to the COOH group and its dissociation constant was 6.9. The second belongs to the OH group and its dissociation constant was 10.3, these results insure that the ligand can coordinate with metal ion at pH above 10 (alkali media). This study agrees with the published date⁽²²⁾.

Conclusions

From the above data, the following conclusions may be drawn:

1. The simple method, which was used to prepare the azo dye ligand, leads to prepare many types of these ligands.
2. The strong coordination bonds, which was formed in such complexes, and the stability chelating rings, which was established, encouraged the investigators to study these coordination compounds.
3. The high molecular weight of these complexes made up them with high sensitivity towards metal ions and to use them as an analytical reagents.
4. The ligand ability towards transition metal ions was improved

because of the suitable arrangement of the donor groups forming five-membered chelate rings of high stability.

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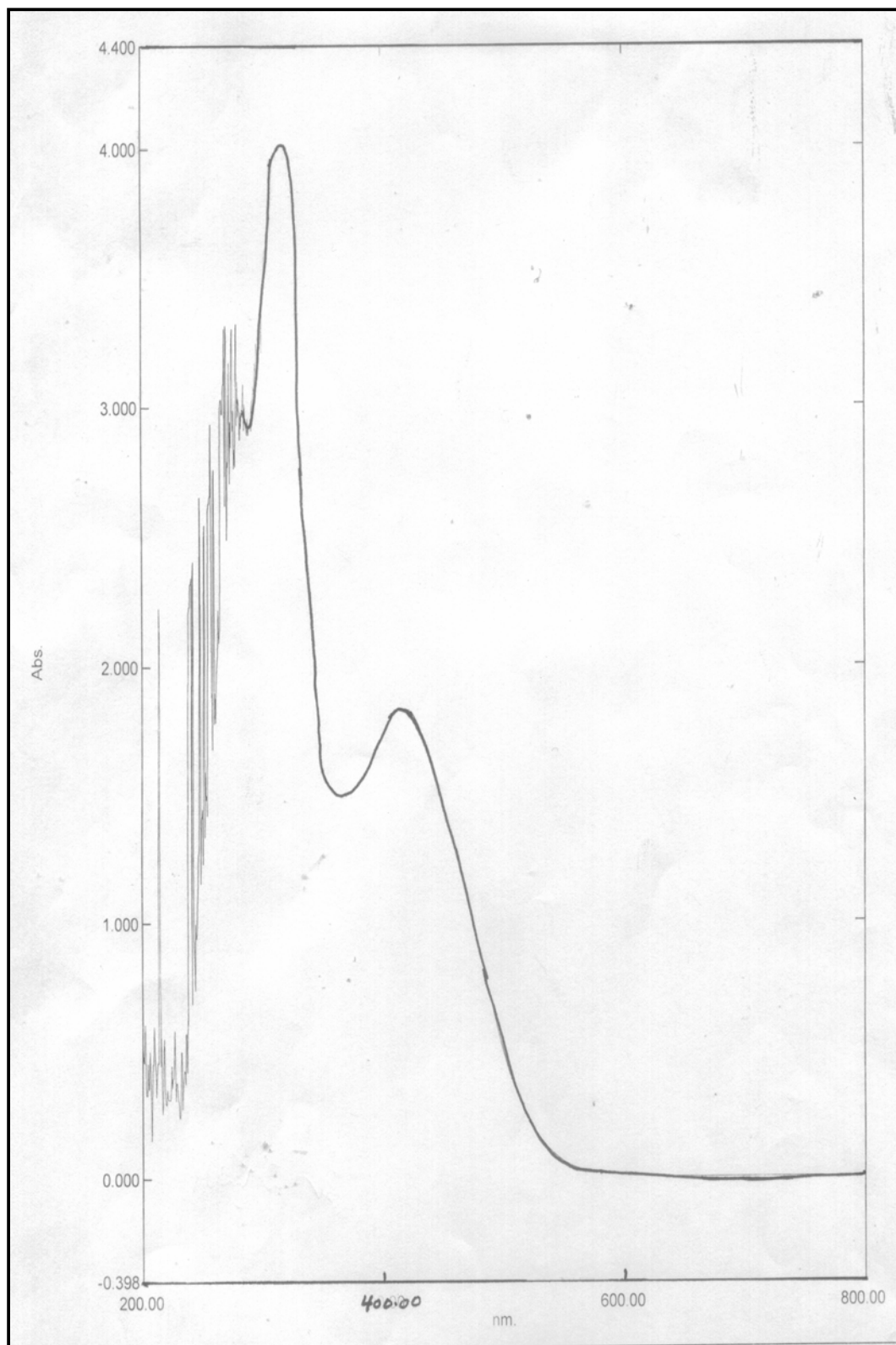
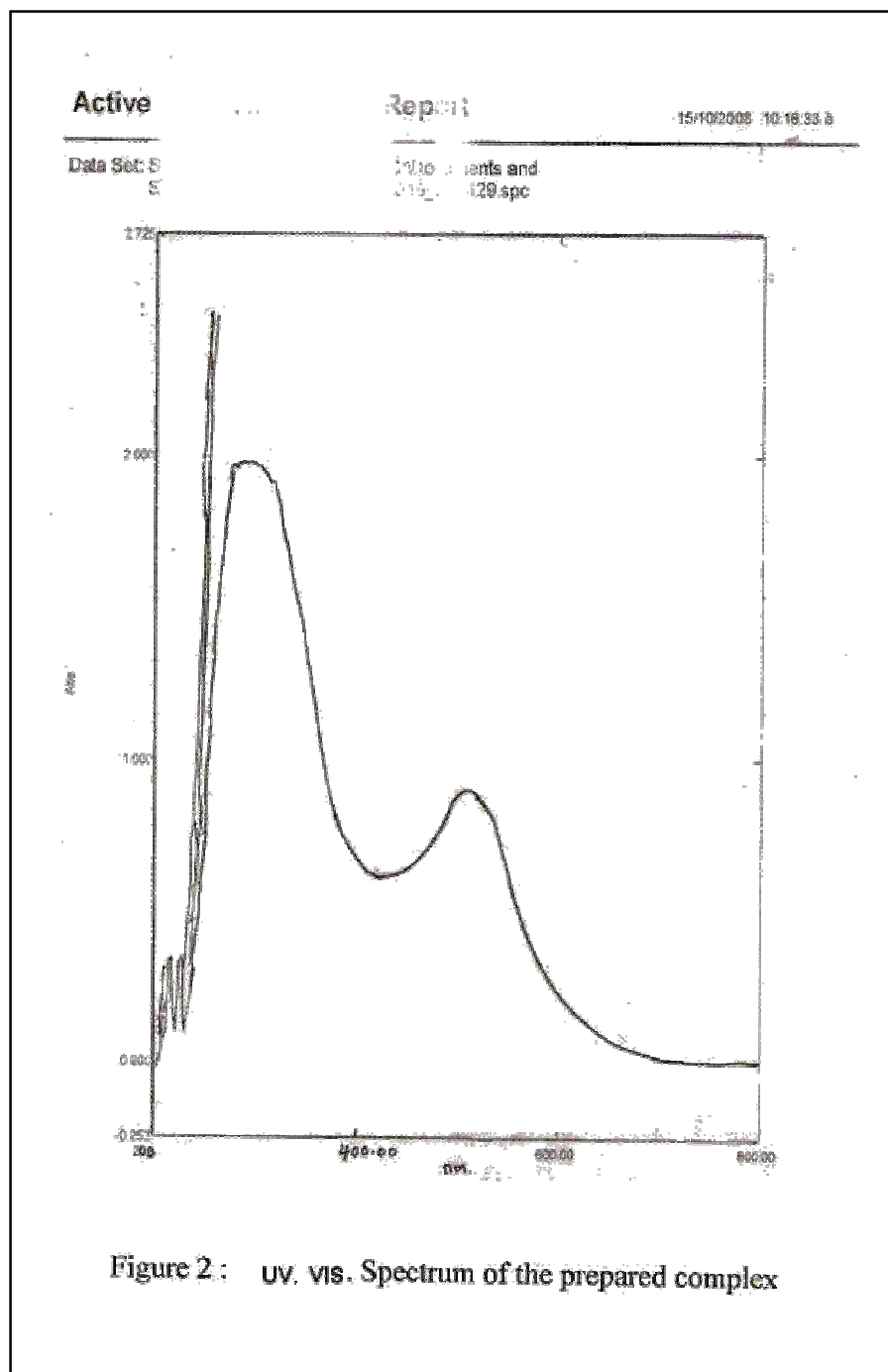


Figure 1 : UV. VIS. Spectrum of the ligand



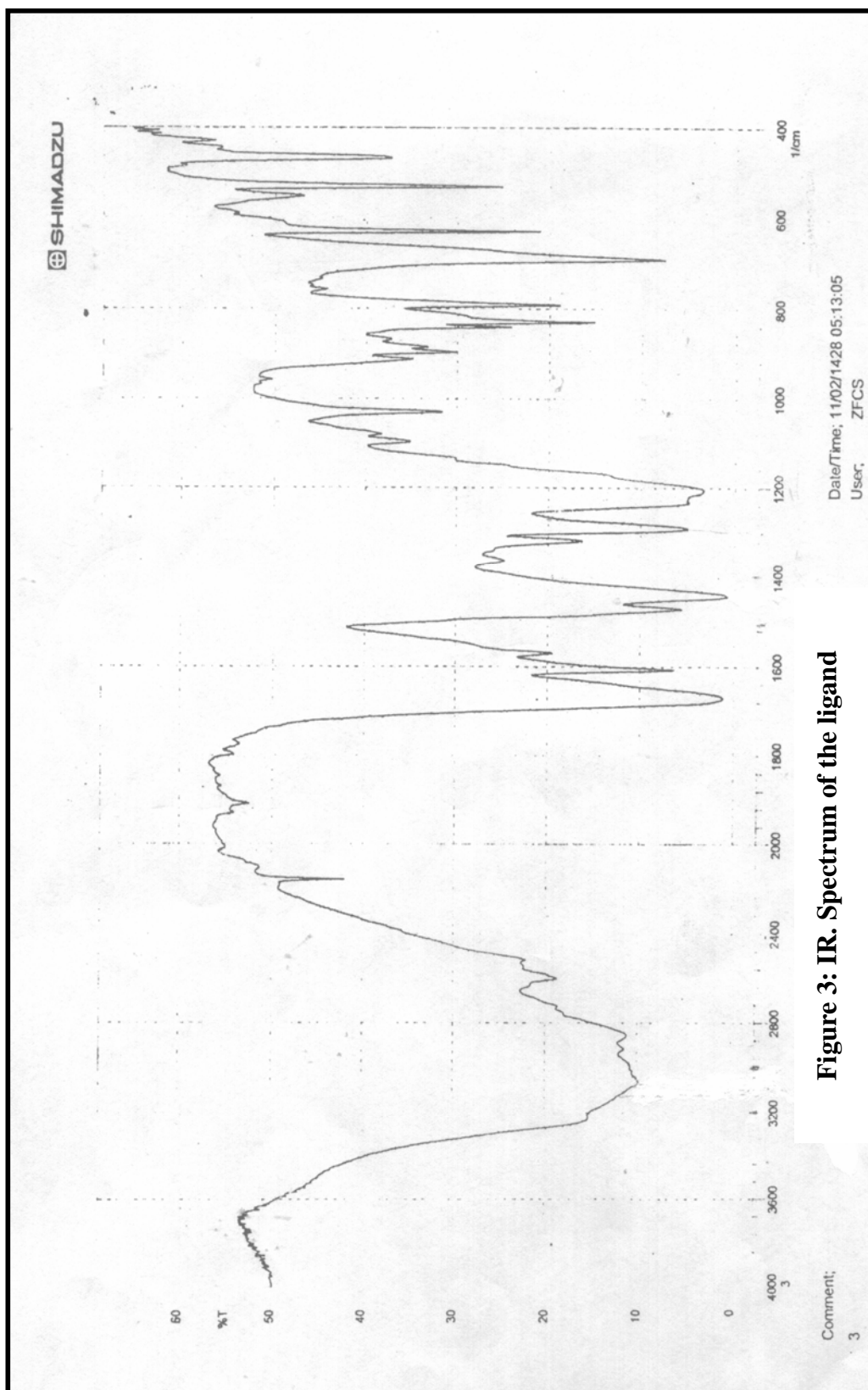


Figure 3: IR. Spectrum of the ligand

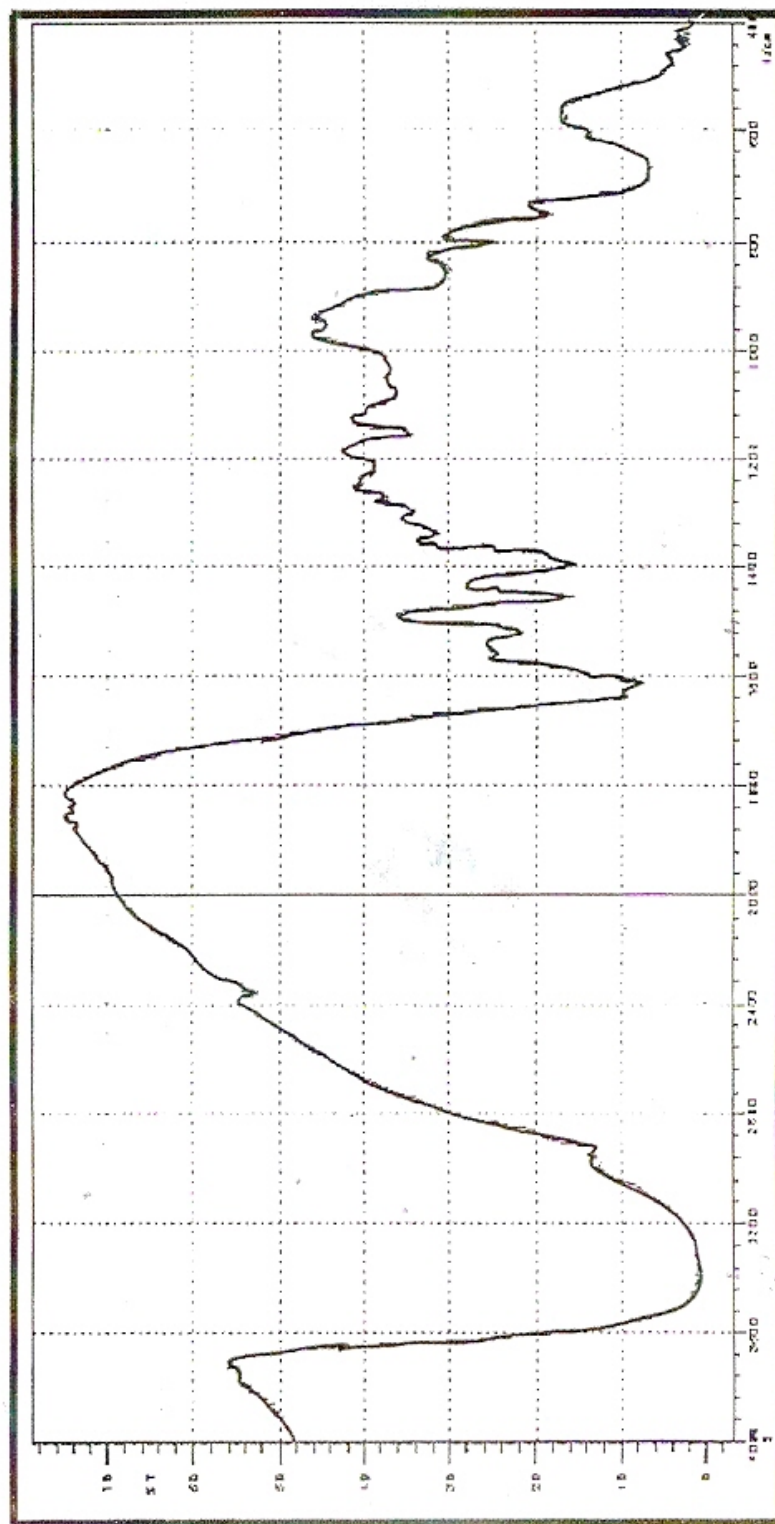


Figure 4 :IR Spectrum of the prepared complex

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