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Synthesis and Spectral Studies of Mn(II) and Cu(II) Complexes with 4,5 - dihydroxy - 3- (phpnyl azo) -2,7- disulfonic acid disodium naphthalene salt

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Abstract

The ligand , 4,5 - dihydroxy - 3- (phpnyl azo) -2,7- disulfonic acid disodium naphthalene salt (HPASASN) was synthesized (by the reaction between aniline and chromotropic acid disodium salt and characterized . Its ionization constants pk$_a$s were determined. Synthesis and spectroscopic investigation of its complexes with Mn(II) and Cu(II) in aqueous solutions complexes revealed the sole formation of the (1:2) (metal : ligand) complexes . Spectral and magnetic studies of the isolated Mn(II) and Cu(II) complexes indicate octahedral and tetrahedral coordination via the N atom of the azo group and the O atom of the hydroxyl group for these complexes sequentially . The molar conductivity of the complexes was determind in an alcoholic solutions .

الخلاصة

تم تحضير وتشخيص الليكاند 5,4 - ثنائي هيدروكسي - 3 - (فنيل ازو) -7,2- ثنائي حامض السلفونيك ثنائي صوديوم ملح النفثالين (بواسطة تفاعل الاثلين مع ملح حامض الكروموتروبيك ثنائي الصوديوم ، تم تعيين ثوبت التأين (pk$_a$s) لهذا الليكاند ، تم تحضير وتشخيص معقدات هذا الليكاند مع Mn(II) وCu(II) طيفياً وأظهرت هذه الدراسة ان التركيب الوحيد لهذه المعقدات هو (2:1) (فلز : ليكاند) بينت الدراسات المغناطيسية والطيفية لهذه المعقدات ان الشكل الهندسي لها هو ثماني السطوح وان التناسق كان عبر ذرة نيتروجين مجموعة الآزو وذرة اوكسجين مجموعة الهيدروكسيل ، عينت التوصيلية المولارية لهذه المعقدات في محاليلها الكحولية وبينت ان هذه المعقدات لها خواص آيونية .

Introduction

Homocyclic azo compounds form typical octahedral complexes with transition metals via coordination through N atom of the azo group and a strongly electron donating atom in the ortho position next to the azo group (1 ,2) .On other side heterocyclic azo reagents have been used as a photometric reagents in analytical chemisty (3-5) . Othors used as a drugs such as cadmium complex with 4-(2-pyridyl azo)-resorcinol which is used as an anti-tumour drug (6) . Also the reagent prontosil used as antibacterial drug (7) . The azo compounds widely used as a reagents in analytical analysis because of their easely preparation , higher stability and good sensitivity towarde some transition metal ions to form chelat complexes (8-10) . So these reagents use as inhibitors for many metal ions in human body (11) . The coordination of these compounds with metal ions depends upon the nature of the metal , its valence , the number of donor atoms within the ligand , the type of the forming chelating rings and the pH of reaction medium (12) . Their ability to coordinate increased if the ligand contains heterocycle with N or / and O atoms localized on sutable place to coordinate with the metal ion (13) . The azo compound which have an acidic groups such as OH^-, SO_3H^- , gives complexes with some metal ions depending on the value of pH of rection medium , calcium and magnesium complexes obtained at pH (9-10) (14) , while Zr^{2+} , Hf^{2+} , Th^{2+} and U^{2+} complexes obtained at pH(2-3) (15) , These ligands are soluble in water because of the existence of the acidic groups OH^- and SO_3H^-, so they have ability to absorb by fiber in aqueous solutions such as orange (II) pigment which is used in cloths dyeing (16,17) .

Experimental

- ❖ All the reagents used were of analar R-grade .
- ❖ $NaNO_3$ was used for the preparation of the background electrolyte and stock solutions .
- ❖ Water was doubly distilled stored in glass stoppered flasks.
- ❖ Electronic spectra were recorded on UV-1650Pc Shimadzu.
- ❖ IR analysis was carried out by FTIR-84005 Shimadzu Spectrophotometer .
- ❖ The pH measnrements were mad using in 0Lab740pH meter .
- ❖ The magnetic susceptibility measurements were made on MSB auto magnetic susceptibility balance .
- ❖ All these analyses were done at Chemistry Department Laboratory / Babylon University except the magnetic susceptibility which done at Al-Nahrain University Laboratories .

Preparation of the Ligand

4,5 - dihydroxy - 3- (phpnyl azo) -2,7- disulfonic acid disodium naphthalene salt (HPASASN) was prepared as it was described previously (18) by coupling diazotized aniline with chromotropic acid disodium salt in an ethanolic solution at 25-30°c . Its m.p. > 230°c It was identified by FTIR and Uv.-Visb. Spectroscopy , its color is red with molar extinction coefficient (ε) 0.5 × 10^3 L. mol^{-1} cm^{-1} at a maximum wavelength 540nm .

Preparation of the complex

[Mn (HPASASN $)_2$ (H_2O $)_2$] complex was prepared as follows : $MnCl_2$ (0.553g , 0.004mol) in distilled water (10 cm^3) was added with stirring to (HPASASN) ligand (3.733g , 0.004mol) in distilled water (10 cm^3) . To this mixture a 10% solution of NaOH (10 cm^3) was added . Soon a violet percipiate appeared . The precipitate was removed by filtration , washed with small aliquots of ethanol and dried over silica gel in a vacuum dessicator (yield 65%) . The complex do not have sharp melting point , it was above 350°c . [CuL_2] complex was prepared as follow : $CuCl_2$ (0.538 , 0.004 mol) was dissolved in distilled water (10 cm^3) and added with stirring to PASHN ligand (3.733g , 0.004 mol) dissolved in distilled water (10 cm^3) . To this mixture a 10% solution of NaOH (5 cm^3) was added . The mixture was heated to 60°c for 30 minutes a blue-violete color appeared , The solid complex collected and dried over silica gel in a vacuum dessicator (yield 70%) , The complex do not have sharp melting point it was above 300°c .

Determination of the acid dissociation constants of the ligand[19,20] :

The acid dissociation constants of the ligand were determind by using potentiometric method in distilled water at 25°c . The ionic strength of the mixture was adjusted with $NaNO_3$ (0.1M) . The results compared with pKa Values for similar ligands as shown in table (1) . The proton dissociation constants scheme of PASHN (H_2L) were found to be

$$H_2L \xrightleftharpoons{pKa_1} HL^- \xrightleftharpoons{pKa_2} L^=$$

pKa_1 (OH) far of N=N group
pKa_2 (OH) near to the N=N group

Determination of Molar Conductivity [23]

The molar conductivity was measured for the ligand and the complexes solutions (10^{-3}M) at 25°c in aqueous solution . The conductivities were 4.463 ms/cm , 3.16 ms/cm and 0.5ms/cm for the ligand , Mn(II) complex and Cu(II) complex sequentially

Determination of Magnetic Properties of the Complex[24]

The magnetic properties were measured for the complex according to Gouy method , The effective magnetic momentum (μ_{eff}) in 25^0c for Mn(II) complex was 6.1 BM , and for Cu(II) complex was 1.8 BM .

Identification of the Complex

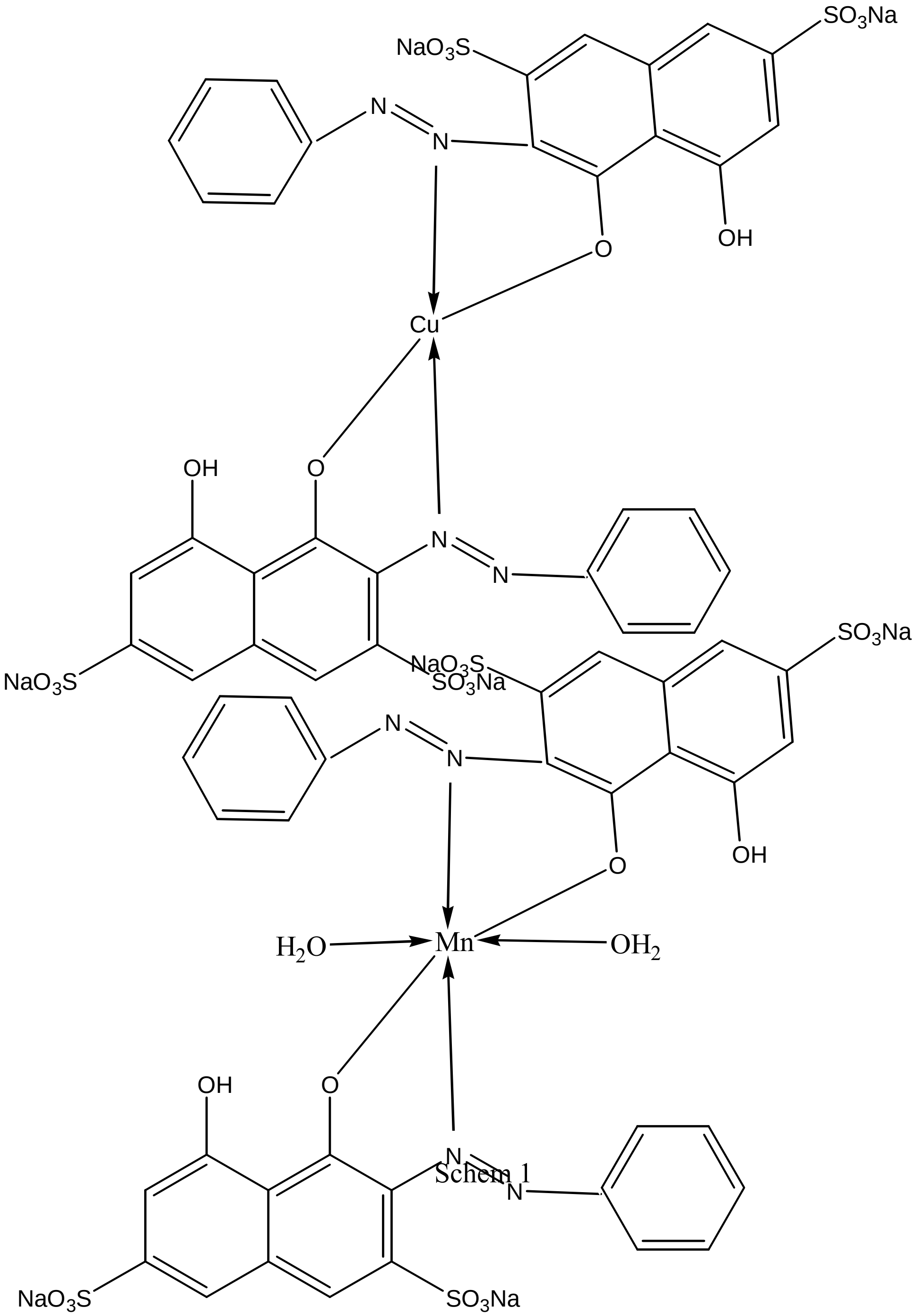
Two techniques were used to identify the ligand and the complex . The first was Uv.-Visb. Technique by which the electronic absorption spectra for the aqueous solution of the ligand and the complexes (10^{-3}M) were recorded . By comparing λ_{max} for these compounds we can detect the formation of these complexes . Figures 1,2 show the electronic spetra for the ligand and the complexes . The other technique was IR spectra , which were recorded for the solid ligand and solid complex with the range (400-4000) cm^{-1} with K Br disc , IR data were listed in table 2 . Figures (3-5) show the IR spectra for the ligand and complexes .

Determination of the Complex Composition by Applying Continous Variation Method [25]

The composition of the complexes was determind by jobs method which is indicated that the metal : ligand ratio was 1:2 for the two complexes .

Results and Discussion

The important vibrational bands of the azo dye 4,5 - dihydroxy - 3- (phpnyl azo) -2,7- disulfonic acid disodium naphthalene salt and its Mn(II) , Cu(II) complexes in the regions (3600-3200)cm^{-1} and (1700-1000)cm^{-1} are recorded in table 2 . The N=N stretching frequency in the free ligand is observed at 1500cm^{-1} . The shift of this band towards a lower frequency in the metal complexes suggests that coordination has taken place through the nitrogen atome of the azo group (26) . The C-O stretching mode of the naphthol is usually found around (1240-1280)cm^{-1} . The shift of phenolic C-O stretching towards higher frequencies in the metal complex suggest Mn-O bond formation (27,28) . Therefore , it is believed that chelation of the metal ion in its azo dye complex occurs through N and O atoms (Schem 1) .


SO$_3$Na
NaO$_3$S
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SO$_3$Na
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OH
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H$_2$O
Mn
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Schem 1
N
NaO$_3$S
SO$_3$Na

Schem1

Table 1 : Compartion of pKa values for the prepared ligand with similar ligands

Ligands	pKa_1	pKa_2	Ref.
HPASASN	9.7	11.7	This work
6-MeBTANA	6.2	9.2	10
B-BTANA	5.8	7.0	21
BTANA	-----------	8.5	22

Table 2 : IR Data for the ligand and Complexes (cm^{-1})

Compound	$V(N=N)$	$V(C-O)$	$V(C-N)$
HPASASN	1500	1240	1050
[Mn (HPASASN) $_2$ $(H_2O)_2$]	1450	1406	958
[Cu (HPASASN) $_2$]	1496	1201	1047

Electronic spectra of the reagent and its complexes shows two bands , the first at 511nm , 535nm and 576nm the second at 302nm , 312nm and 310nm for the ligand , Mn(II) and Cu(II) complexes respectively . The ground state electronic configuration here is $(t_2g)^3$ $(e_g)^2$. For any possible excited state , such as $(t_2g)^2$ $(e_g)^3$. There are no spin-allowed transitions , they are symmetry forbidden and a high-spin octahedral d^5 complex will only show extermely weak d-d transition bands in the visible area . These results agreed with the literature (29) . The references show that the effective magnetic moments μ_{eff} lies in the range (5.92-6.5)BM of the manganes (II) complexes , therefore , they classifys a high-spin complexes , but it lies in the range (1.75-2.2)BM for the copper (II) complexes , therefore they classifys a low-spin complexes (30,31) . The pka values are 9.7 and 11.7 for the ligand . The high basicity of the ligand may be ascribed to the sulfonyl groups and hydroxyl group attached to the naphthol group . The former value belongs to the farthest OH group of azo group , the second value for the nearest OH group of azo group , this interpretation is true because of the inter molecular hydrogen bonding between the hydrogen atom of OH group and the lone pair of electrons localizes on N atom of azo group . Molar conductivity data show that Mn^{2+} and Cu^{2+} complexes have no electrolyt feature due to the zero complex charge .

Several equilibrium models were tried but there were only with $[MnL_2(H_2O)_2]$ and $[CuL_2]$ models that convergence was achieved . The ratio of Mn(II) and Cu(II) to the ligand under investigation was MnL_2 . All these stadies of the isolated complexes indicate octahedral (sp^3d^2) , and tetrahedral (sp^3) via the N atom of the azo group and the O atom of the hydroxyl group for these complexes sequentially .

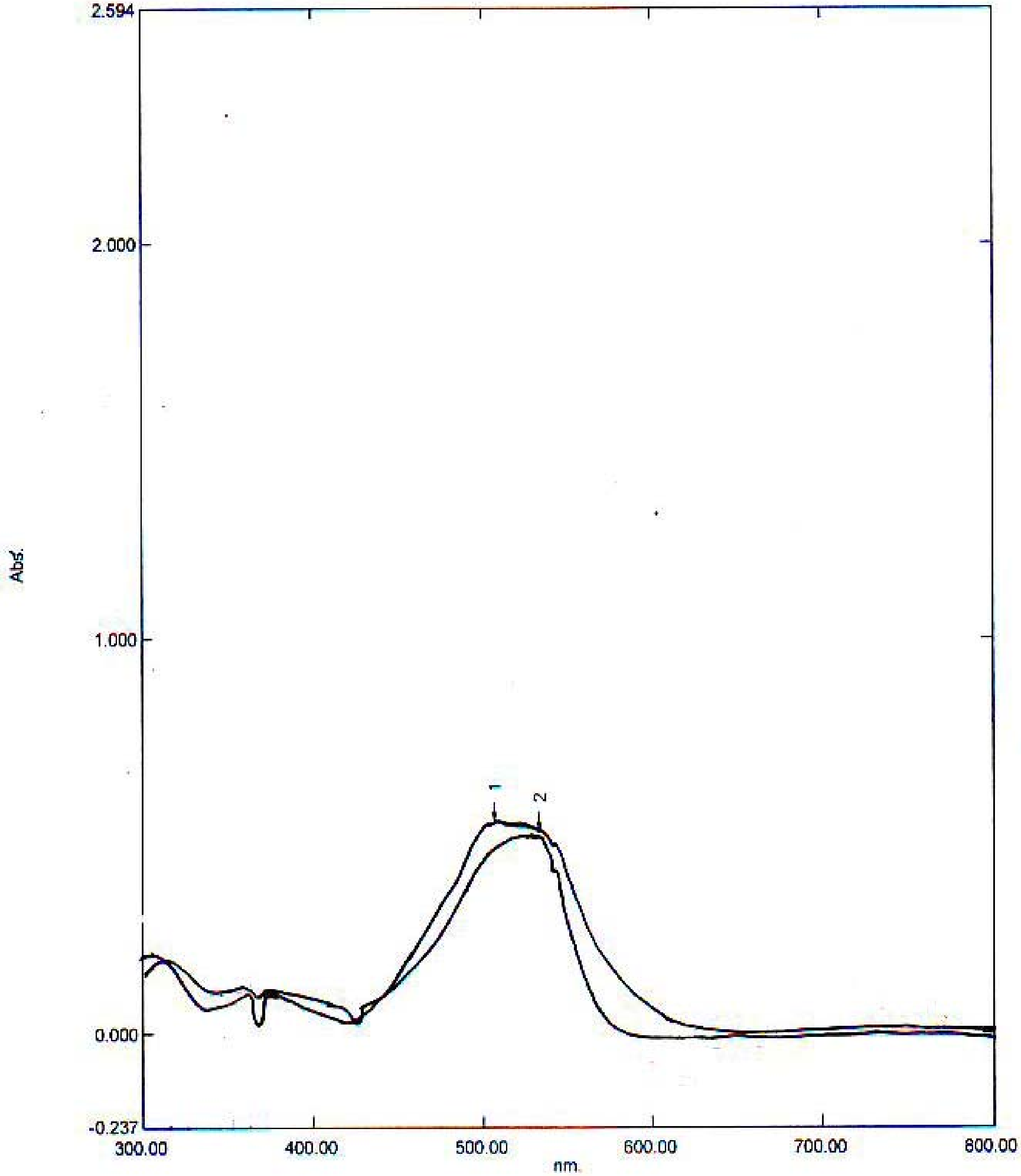


Figure 1: The Electronic Spectra for the Ligand (1) and Mn (II) Complex (2)

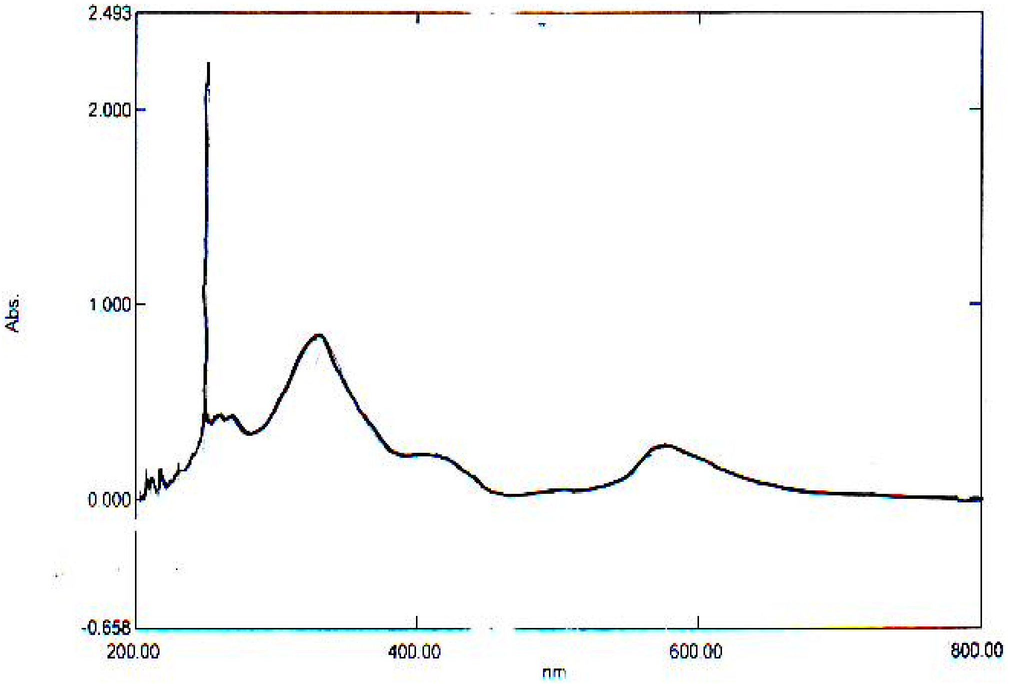
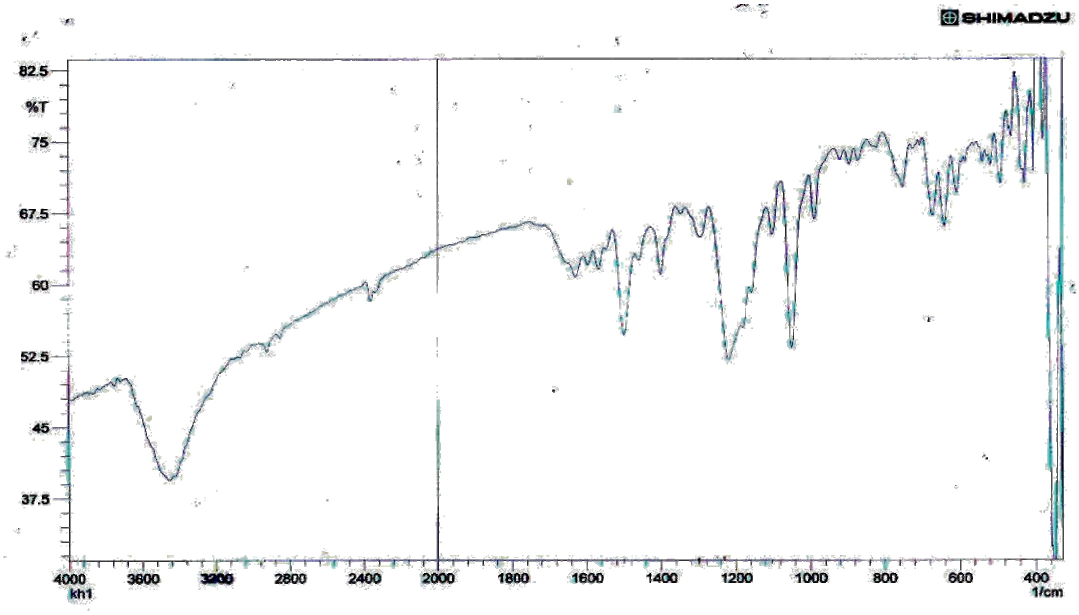
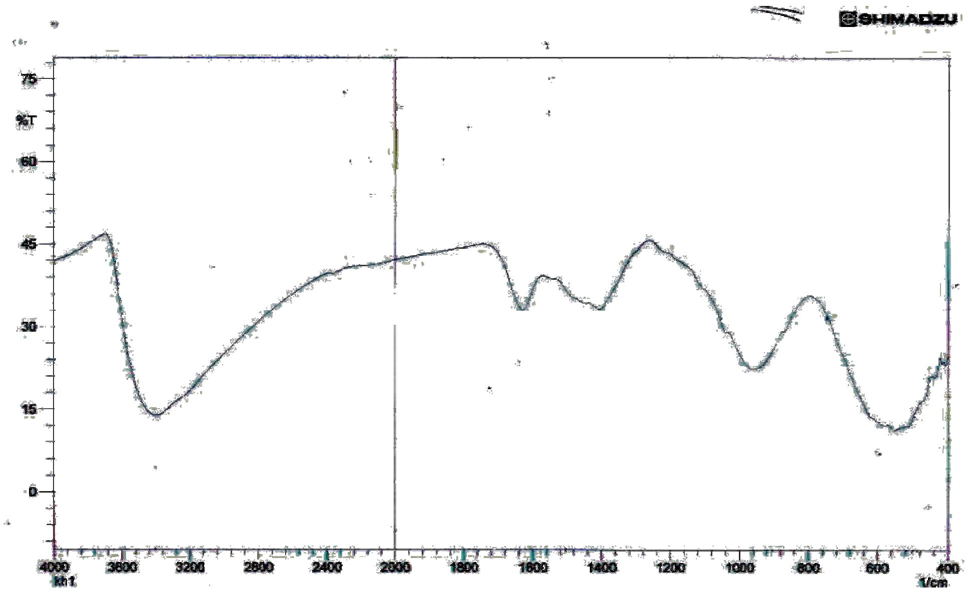


Figure 2: The Electronic Spectra for Cu(II) Complex



Figur 3 : IR Spectra for the Ligand



Figur 4 : IR Spectra for the Mn(II) Copmlex

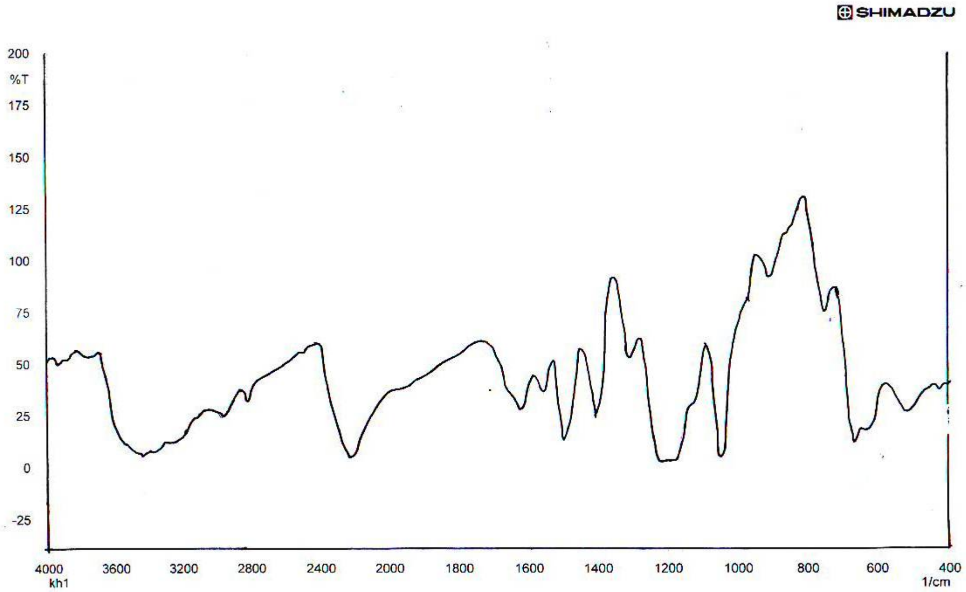


Figure 5: IR Spectra for the Cu(II) Complex

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