Some new transition metal complexes of bis (2-methyl furfuraldene)-4,4`-methylene bis (cyclohexylamine) ligand

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Abstract

New Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) Schiff base complexes which have the molar ratio 2:1 metal to ligand of the general formula $[M_2(L) X_4]$ (where L=bis(2-methyl furfuraldene)-4-4`-methylene bis(cyclo-hexylamine) ) were prepared by the reaction of the metal salts with the ligand of Schiff base derived from the condensation of 2:1 molar ratio of 2-acetyl furan and 4-4`-methylene bis (cyclohexylamine). The complexes were characterized by elemental analysis using atomic absorption spectrophotometer ,molar conductance measurements, infrared, electronic spectra,and magnetic susceptibility measurement. These studies revealed binuclear omplexes. The metal(II) ion in these complexes have four coordination sites giving the most expected tetrahedral structure and square planar for Cu(II)ion.

Key words : Schiff base ,transition metal ,binuclear complexes .

Introduction:

Schiff base ligand bonding through azomethine-N and furane-O- atoms to the central metal ion formed important class of biologically active ligands[1] and played an essential role in agriculture, pharmaceutical and industrial chemistry [2].Schiff base are generally important due to synthetic flexibility,selectivity and sensitivity towards certain transition and non-transtion metal atoms[3]. The majority of Schiff base that give stable complexes usually act as multidentate N-N and N-O donors with formation of mononuclear and polynuclear complexes [4].In addition to their interesting ligational properties,both Schiff bases and their complexes have important biological, industrial applications and they proven antitumour and numerous activities [5-7].

The aim of the present research is the synthesis and characterization of new iron(II),cobalt(II),nickel(II),copper(II)and zinc(II) coordination complexes with new Schiff base ligand derived from 2-acetyl furan and 4,4`-methylene bis (cyclohexylamine).

Materials and methods :

All the chemicals were of reagent grade used as supplied without further purification . The elemental contents were determined using spectral method by atomic absorption spectrophotometer type Pye Unicam SP9 atomic absorption spectrophotometer (Phillips) Table -1. The molar conductance measurement was carried out in DMF (10^{-3} M) at 25C° using conductivity meter model PCM3-Jenway. Infrared spectra of the ligand and its complexes were recorded on FourierTransform FT-IR spectrophotometer , Tensor 27C°.Brucker 2003 using KBr discs at the range 400-4000 cm^{-1}.The electronic spectra were studied by using Shemadzu C° UV-Vis Recording UV-160 spectrophotometer for 10^{-3}M

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solution of compounds in DMF at 25 C^o,using 1cm quartz cell . Magnetic susceptibility measurements were made by the Faraday method at 25 C^o using Brucker MB6 apparatus . Melting points or decomposition temperatures were measured on an Electrothermal 9300 melting point apparatus and were uncorrected.

Preparation of the compounds :

1- **Perpetration of ligand** :[8]

Asolution of 4,4`-methylenebis(cyclohexylamine) (0.01 mol,2.10 g) in absolute ethanol $15cm^3$ was added dropwise to the ethanol $15cm^3$ solution of 2-acetylfuran (0.02 mol,2.20g) with stirring and the mixture was heated under reflux for 7 hrs . The solution was concentrated to half of its initial volume and cooled to room temperature and on further cooling in ice bath, the precipitate was separated by filtration , wash with cold ethanol and dried in vacuum.

2- Perpetration of complexes :

All complexes were prepared by the same general procedure as follows :

To a solution of the metal salt (0.02 mol)in absolute ethanol 15 cm^3 a hot solution of the ligand (0.01 mol ,3.94g) in absolute ethanol 15 cm^3 was added . The reaction mixture was heated to the boiling point of ethanol under reflux for 3-4 hrs with occasional shaking and on cooling colourd solid complexes were filtered off, washed several times with cold ethanol and dried in vacuum

Result and Discussion :

Analytical and physical data Table -1 support the formation of transition metal complexes for which the reactions occure in 2:1 metal to ligand ratio. The following equation represents the formation of these complexes:

$$\mathbf{2MCl_2.nH_2O + L \longrightarrow [M_2LCl_4] + nH_2O}$$

M=Fe(II),Co(II),Ni(II),Cu(II) and Zn(II).
L= represent the Schiff base ligand .
n=0,2,4,6

The prepared complexes are all solids and stable in air at room temperature . They are insoluble in water, moderately soluble in methanol and ethanol but soluble in dimethylformamide and dimethyl sulphoxide .

The molar conductance values are too low account for any dissociation of the complexes in DMF , indicating the non - electrolytic nature of the complexes [9,10] the elemental contents were determined by atomic absorption spectrophotometer Table (1). The infra red spectra of the free ligand showed a strong band at 1635 cm^{-1} assignable to ʊC═N of the azomethine.The observation of this band confirms the formation of azomethine linkage.On complex formation ʊC═N band shifted to lower frequency region by about 33-59 cm^{-1} indicating coordination through nitrogen atoms of both azomethine groups [7,11,12] . Another important band which appeared at 1290 cm^{-1} due to VC-O-C (furan ring) stretching vibration . Also a negative shift of 16-25 cm^{-1} was observed in the furan ring vibration suggesting coordination of the metal atom through the oxygen atom of two furan rings [13] . In addition to these changes , new band in the ir region at 457 - 472

and 519-592 cm^{-1} (not observed in the spectra of the free ligand) were assigned to the stretching modes of M-

N and M-O bands respectively [14,15]. For the chloro complexes the ν(M-Cl) band could not be observed since its located below the limits of our infrared spectrophotometer .

The ligands are characterized by two absorption bands in the UV region . A high intensity band appeared at 34965 cm^{-1} is attributed to $\pi \rightarrow \pi^*$ transition of furan ring and a second band with lower intensity appeared at 2890cm-1 is attributed to $n \rightarrow \pi^*$ transition of azomethine group .Both bands showed a lower shift on coordination with a metal ion . These observation represent a further Indication for the coordination of the ligand to the metal ions [13,16]. The electronic spectra (Table -3) Fe(II) complex exhibited absorption band at 31847 cm^{-1} which belongs to charge transfer and another band at 26316 cm^{-1} which is caused by the electronic transition $^5E(D)$ $^5T_2(D)$ [17-18].The magnetic moment value of 5.5 BM supports a tetrahedral of the type high spin around Fe(II) ion [19].The electronic spectrum of Co(II) complex showed only υ_3 band in the visible region at 14620 cm^{-1} of $^4A_2(F)$ $^4T_1(P)$ transition . The other two bands υ_1 and υ_2 due to $^4A_2(F)$ $^4T_2(F)$ and $^4A_2(F)$ $^4T_1(F)$ transitions were absent since υ_2 falls below the limit of our instrument and the position of υ_1 is in the near infrared region , below 5000 cm^{-1} indicating tetrahedral geometry around Co(II) ion . The mangnetic measurement of Co(II) complex exhibited magnetic moment value of 4.7 BM which is within the tetrahedral environment.[18,20,21]. The electronic spectra of the Ni(II) complex showed a band at 13774 cm^{-1} region due to $^3T_1(F)$ $^3T_1(P)$ υ_3 . This result is in a good agreement with the expected tetrahedral geometry for this complex since the other band $^3T_1(F)$ $^3T_2(F)$ υ_1 and $^3T_1(F)$ $^3A_2(F)\upsilon_2$ usually is located bellow the instrumental limit .The magnetic moment value 3.6 BM for the complex confirmed the presence of two unpaired electrons and tetrahedral environment it [16,18,22] .The electronic spectra of Cu(II) complex showed abroad band at 15152 cm^{-1} which may be assigned duo to the combination of transition ^2B_1g ^2B_2g υ_1, ^2B_1g ^2A_1g υ_2 and ^2B_1g $^2Eg\upsilon_3$ in square planar field .Another high intensity band at 33784cm^{-1} is due to charge transfer transition [23-25] . The magnetic moment value of this complex is 1.49BM which is lower than 1.73 BM due to anti-ferromagnetic interaction between two Cu ions ,which comfirmed the binuclear nature of the complex [23].The Zn(II) due to their diamagnetic properties and no d-d transition only a strong charge transfer band around 36764 cm^{-1} and based on stoichiometry of this complex ,it was four coordinated ,which could be tetrahedral geometry is the more preferred stereo chemistry for Zn (II)[26].

Conclusion

New Schiff base ligand(L) bis (2-methyl furfuraldene)-4,4´- methylene bis (cyclohexyl amine)with its dineclear metal complexes of the type $[M_2(L)Cl_4]$ have been synthesized. The structure of the ligand and its complexes were determined by several methods such as FT-IR,UV-Vis, elemental contents ,molar conductivities and magnetic susceptibility .The Schif base is neutral tetradentate coordinated through both azomethine nitrogen atoms and oxygen furan ring are used as ligand for dinuclear metal complexes and according to the above measurements the Fe(II),CO(II), Ni(II), and Zn(II) complexes have tetrahedral geometry while Cu(II) complexes have square planar geometries around the central ions.Fig-1 and fig-2.

Table (1):analytical data and some physical properties of the ligand and its complexes.

Compound	**Colour**	**Yield"%**	**Melting point(C^o)**	**Λ_M(DMF) (Ohm^{-1} mol^{-1} cm^2)**	**M% Calculated (Found)**
L	Beige	72	150-152	———	
$[Fe_2(L)Cl_4]$	Brown	87	136-138	13.05	12.11 (11.9)
$[Co_2(L)Cl_4]$	Dark olive	78	170d*	11.78	———
$[Ni_2(L)Cl_4]$	Olive	80	140d*	16.04	9.84(9.05)
$[Cu_2(L)Cl_4]$	Gray	74	189d *	11.79	9.81(8.81)
$[Zn_2(L)Cl_4]$	Dark beige	83	252d*	19.79	9.30(8.92)

d*=decomposition temperature

Table(2):Characteristic infrared band (cm^{-1}) of the free ligand and its complexes.

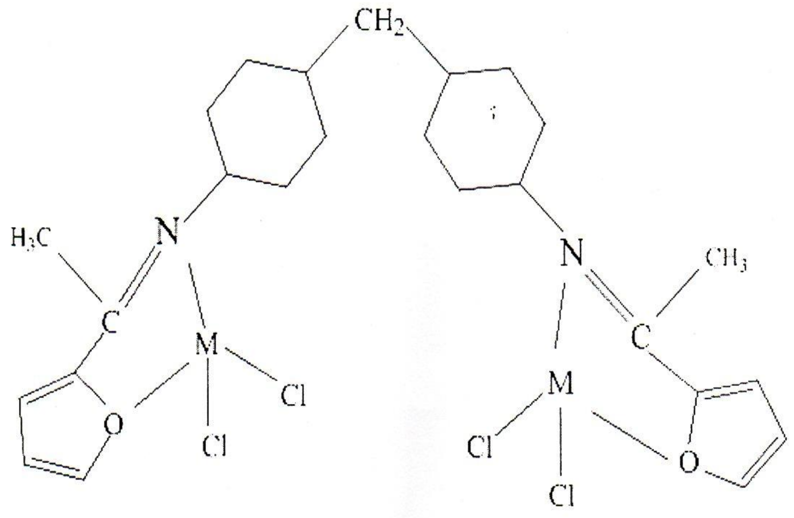
Compound	**ƲC=N**	**ƲC-O-C (Furan)**	**ƲM-N**	**ƲM-O**
L	1635	1290	——	———
$[Fe_2(L)Cl_4]$	1602	1274	472	592
$[Co_2(L)Cl_4]$	1579	1288	457	555
$[Ni_2(L)Cl_4]$	1578	1268	472	519
$[Cu_2(L)Cl_4]$	1588	1265	472	592
$[Zn_2(L)Cl_4]$	1585	1271	472	561

Table (3): The electronic spectra and magnaetic moment of the ligand and its complexes .

Compound	Absorption region(cm^{-1})	Possible assignment	μeff(BM)
L	28902 34965	$\rightarrow \pi^{*} n$ $\pi \rightarrow \pi^{*}$	————
[$Fe_2(L)Cl_4$]	26316 31847	$^{5}E(D) \rightarrow {}^{5}T_2(D)$ C.T*	5.55
[$Co_2(L)Cl_4$]	14620 27624	$^{4}A_2(F) \rightarrow {}^{4}T_1(P)$ C.T	4.70
[$Ni_2(L)Cl_4$]	13774 37313	$^{3}T_1(F) \rightarrow {}^{3}T_1(P)$	3.64
[$Cu_2(L)Cl_4$]	15152 33784	$^{2}B_1g \rightarrow {}^{2}B_2g$ $^{2}B_1b \rightarrow {}^{2}A_1g$ $^{2}B_1g \rightarrow {}^{2}Eg$ C.T	1.49
[$Zn_2(L)Cl_4$]	36764	C.T	Dia**

*CT=charge transfer

**Dia=Diamagnetic



M=Fe(II) ,Co(II),Ni(II),Zn(II)

Fig.1: Proposed structure of the prepared complexes

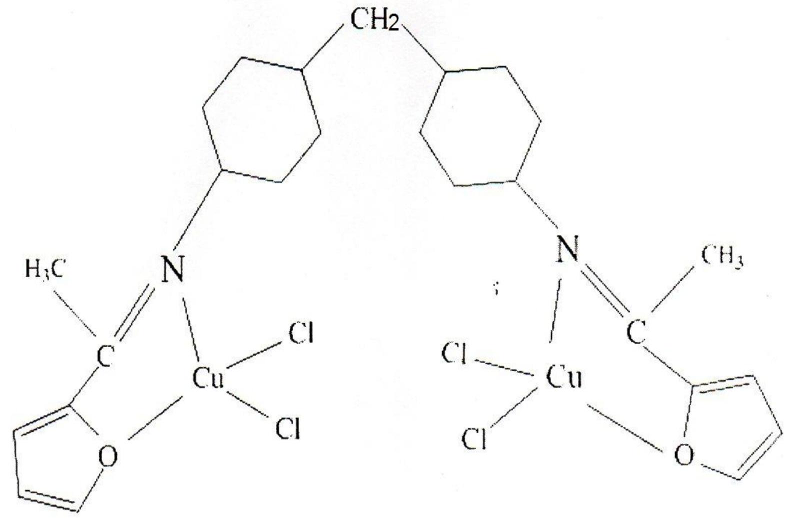


Fig.2: Proposed structure of the Cu(II) complex.

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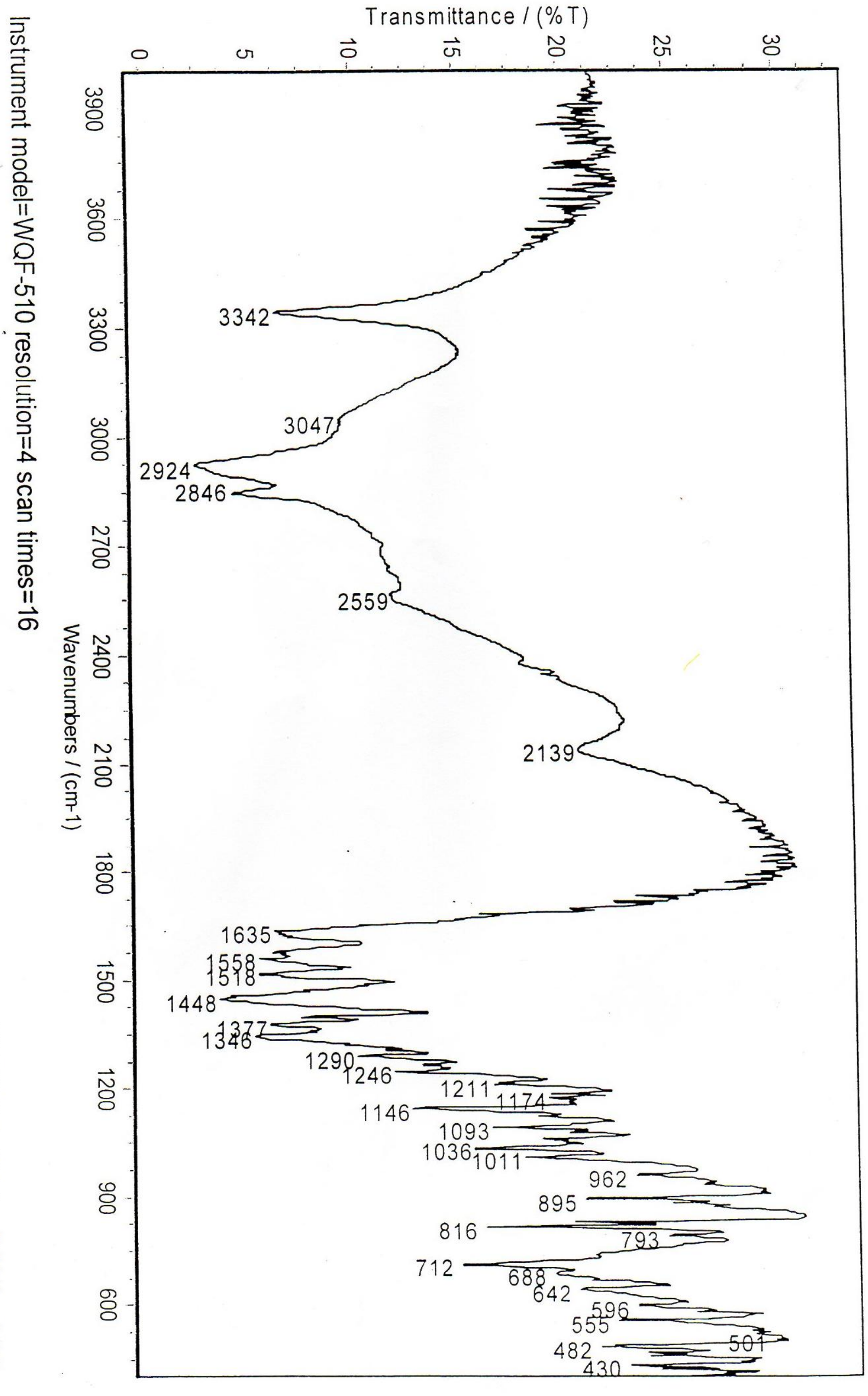

Fig-3:The infrared of of the ligand (L)

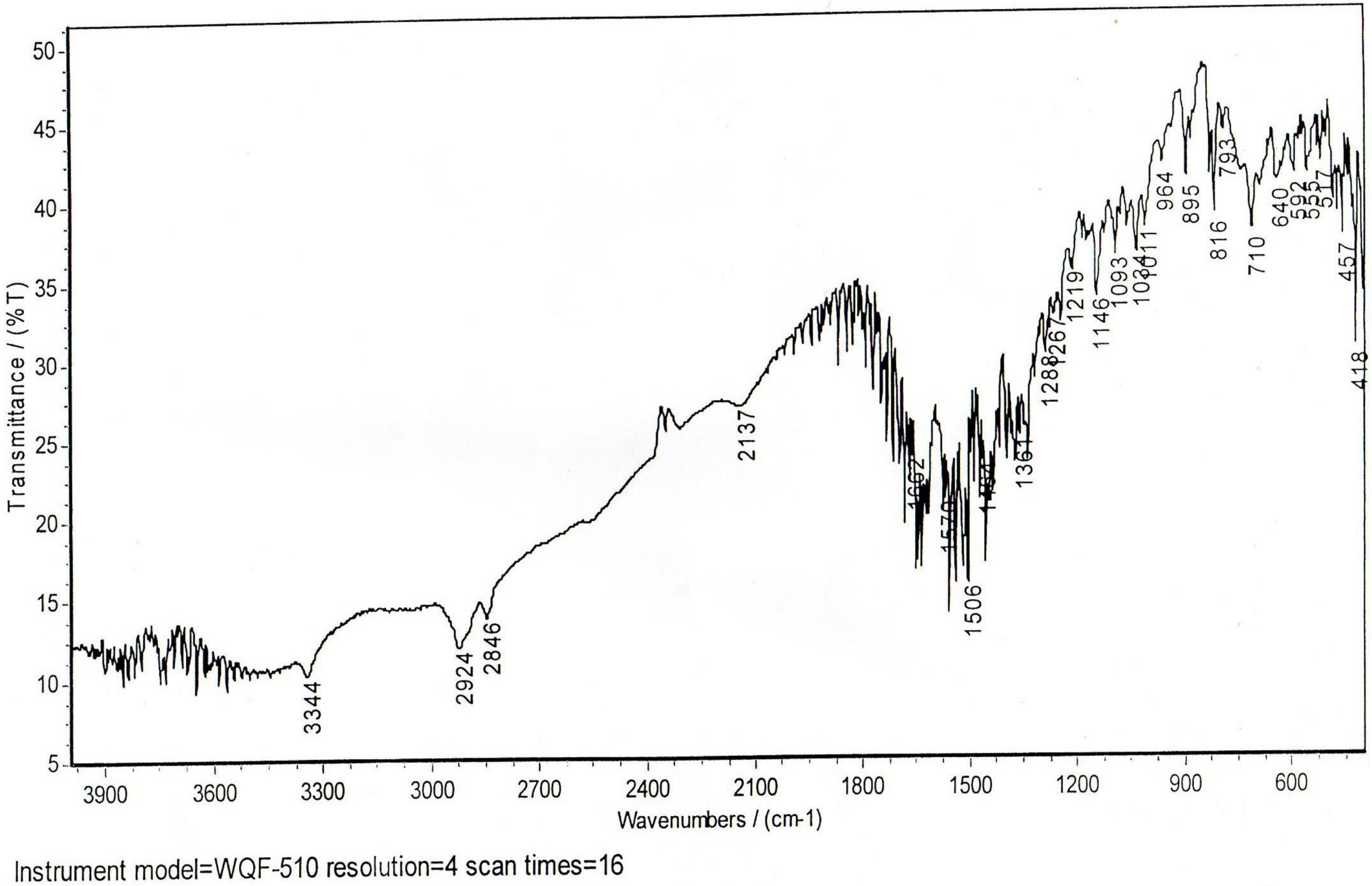

Fig-4:The infrared of the complex$[Co_2(L)Cl_4]$

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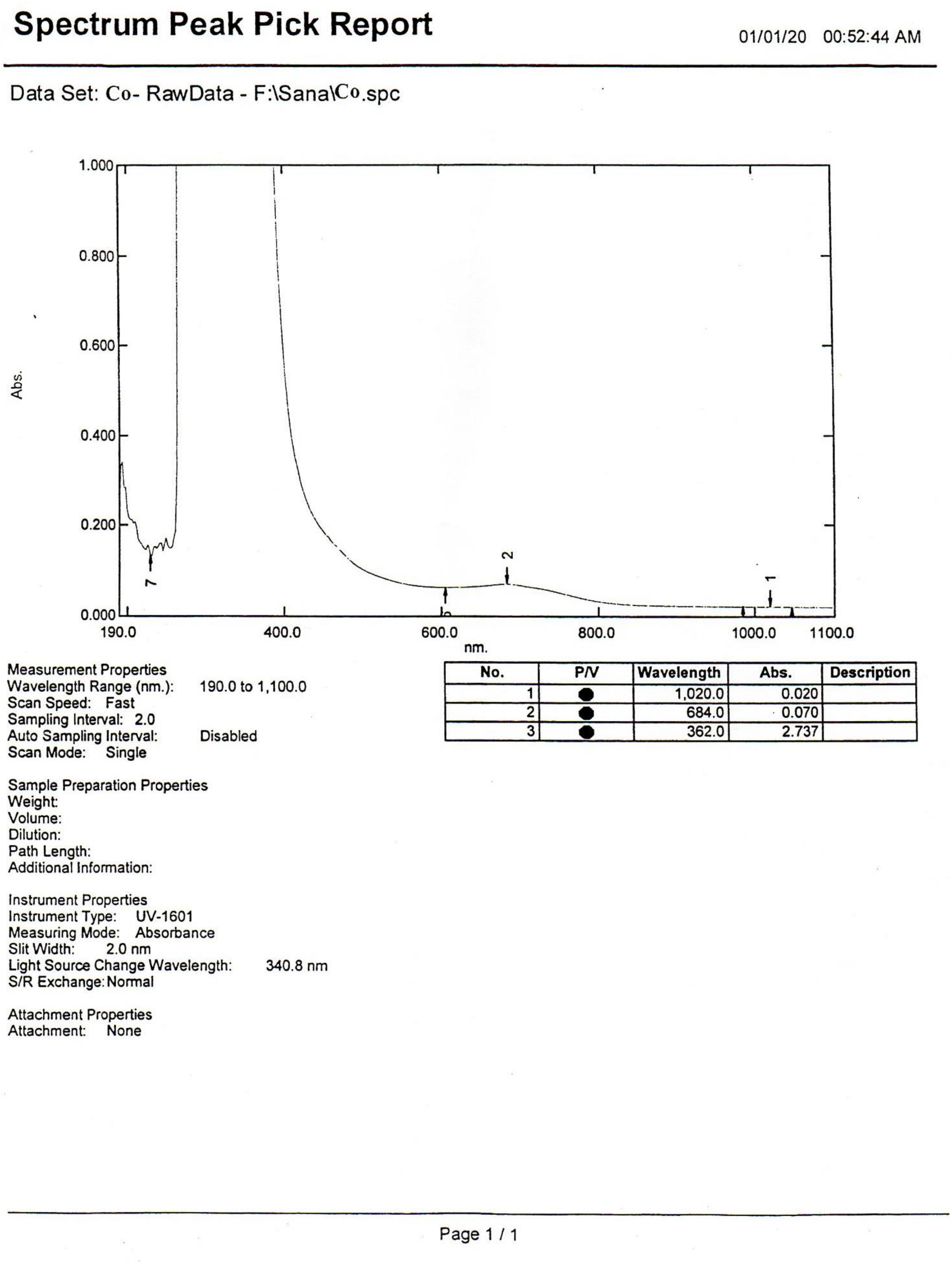

Spectrum Peak Pick Report 01/01/20 00:52:44 AM

Data Set: Co- RawData - F:\Sana\Co.spc

Measurement Properties
Wavelength Range (nm.): 190.0 to 1,100.0
Scan Speed: Fast
Sampling Interval: 2.0
Auto Sampling Interval: Disabled
Scan Mode: Single

No.	P/V	Wavelength	Abs.	Description
1	●	1,020.0	0.020	
2	●	684.0	0.070	
3	●	362.0	2.737	

Sample Preparation Properties
Weight:
Volume:
Dilution:
Path Length:
Additional Information:

Instrument Properties
Instrument Type: UV-1601
Measuring Mode: Absorbance
Slit Width: 2.0 nm
Light Source Change Wavelength: 340.8 nm
S/R Exchange: Normal

Attachment Properties
Attachment: None

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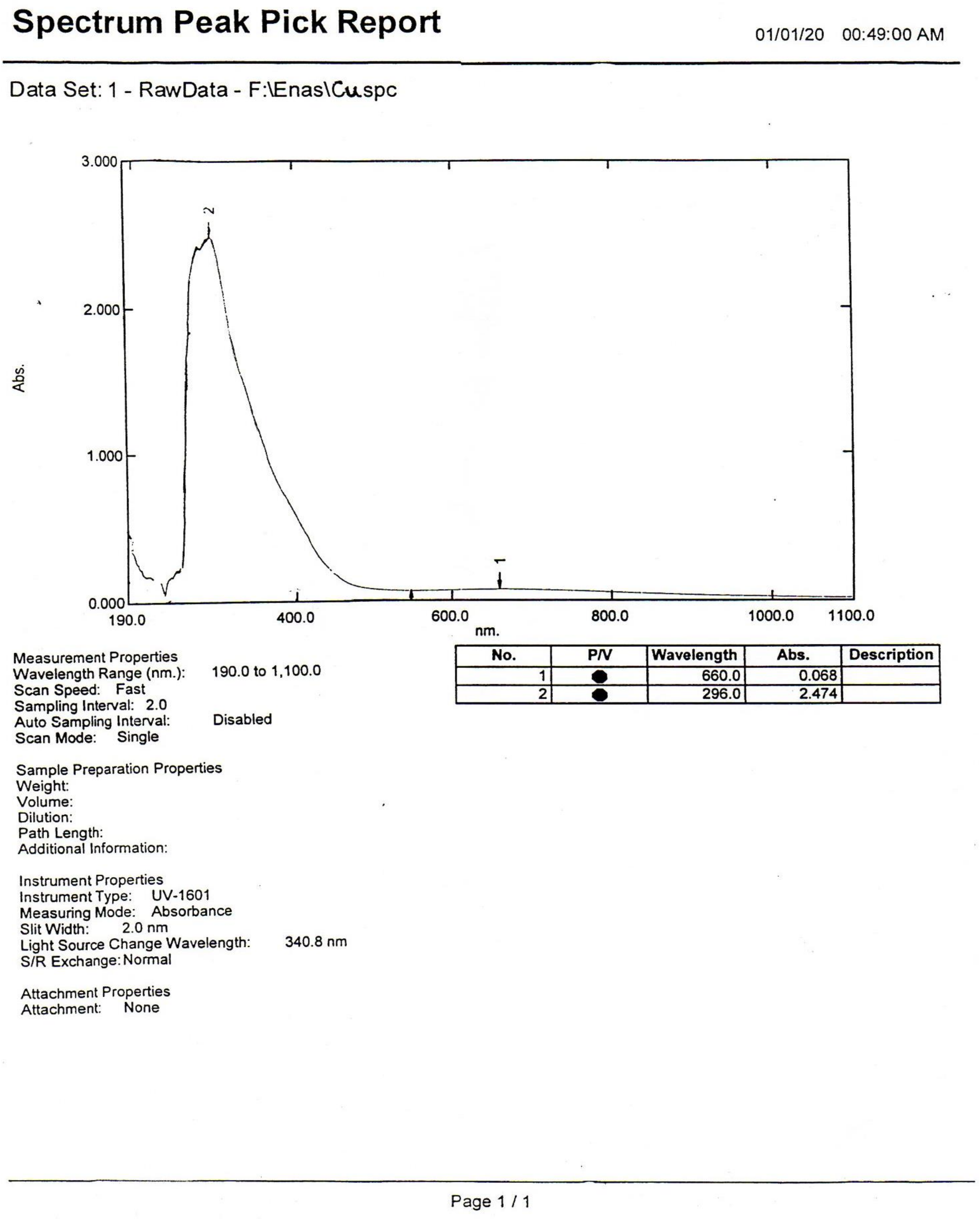
Fig-5: Electronic spectrum for the complex $[Co_2(L)Cl_4]$



Spectrum Peak Pick Report

01/01/20 00:49:00 AM

Data Set: 1 - RawData - F:\Enas\Cu.spc

No.	P/V	Wavelength	Abs.	Description
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2	●	296.0	2.474	

Measurement Properties
Wavelength Range (nm.): 190.0 to 1,100.0
Scan Speed: Fast
Sampling Interval: 2.0
Auto Sampling Interval: Disabled
Scan Mode: Single

Sample Preparation Properties
Weight:
Volume:
Dilution:
Path Length:
Additional Information:

Instrument Properties
Instrument Type: UV-1601
Measuring Mode: Absorbance
Slit Width: 2.0 nm
Light Source Change Wavelength: 340.8 nm
S/R Exchange: Normal

Attachment Properties
Attachment: None

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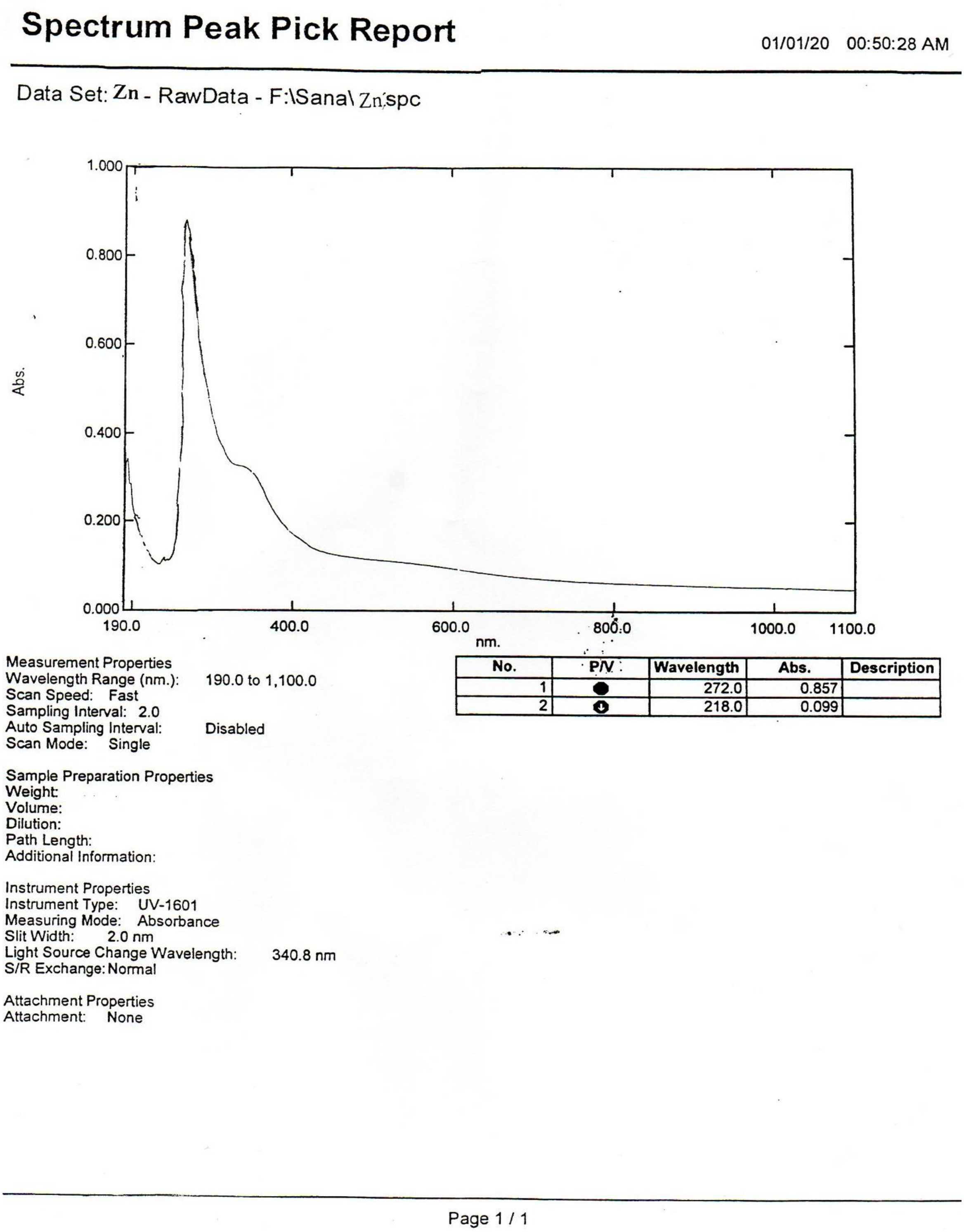
Fig-6:Electronic spectrum for the complex[$Cu_2(L)Cl_4$]



Spectrum Peak Pick Report 01/01/20 00:50:28 AM

Data Set: Zn - RawData - F:\Sana\ Zn.spc

No.	P/V	Wavelength	Abs.	Description
1	●	272.0	0.857	
2	⊙	218.0	0.099	

Measurement Properties
Wavelength Range (nm.): 190.0 to 1,100.0
Scan Speed: Fast
Sampling Interval: 2.0
Auto Sampling Interval: Disabled
Scan Mode: Single

Sample Preparation Properties
Weight:
Volume:
Dilution:
Path Length:
Additional Information:

Instrument Properties
Instrument Type: UV-1601
Measuring Mode: Absorbance
Slit Width: 2.0 nm
Light Source Change Wavelength: 340.8 nm
S/R Exchange: Normal

Attachment Properties
Attachment: None

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Fig-7:Electronic spectrum for the complex[$Zn_2(L)Cl_4$]

بعض معقدات العناصر الانتقالية الجديدة لليكاند بس (2-مثيل فورفورالدين) -`4,4 - مثيلين بس(سايكلوهكسيل امين)

رنا عبد المالك سليمان ال قبع * ***ماهر عبد الرزاق محمد الطائي*** **

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الخلاصة:

يتضمن البحث تحضير عدد من المعقدات الجديدة الحاوية على ايونات الحديد والكوبلت والنيكل والنحاس والخارصين الثنائية الموجبة مع ليكاند من نوع قواعد شيف بس (2-مثيل فوفورالدين)`4-4 -مثيلين بس (سايكلوهكسيل امين)المشتق من تفاعل2- استيل فيوران و`4-4 -مثيلين بس (سايكلو هكسيل امين) وبنسبة مولية 2 :1 تكونت المعقدات بنسبة 2 :1 من الملح الفلزي والليكاند وهي تمتلك الصيغة العامة $[M_2(L)Cl_4]$(حيث تمثلL ليكاند قاعدة شيف، M تمثل ((Zn(II), Cu(II), Ni(II), Co(II), Fe(II)) . تم تشخيص المعقدات الناتجة بألتحليل الدقيق للعناصر بواسطة طيف الامتصاص الذري وقياسات التوصيل المولاري واطياف الاشعة تحت الحمراء والاطياف الالكترونية والقياسات المغناطيسية0وقد اتضح من هذه الدراسات بأن المعقدات ثنائية النوى تكون فيها الايونات الفلزية في هذه المعقدات رباعية التناسق لتعطي بنية رباعي السطوح وبنية المربع المستوي لايون النحاس الثنائي الموجب الاكثر احتمالا .