

Preparation ,characterization and thermodynamic study of som transition metal complexes with new azo azomethen Ligand

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Abstract

The study include preparation of tetradentate azo azomethen ligand type (N₂O₂).This ligand preparation from condensation reaction between salicylaldehyde derivative containing azo group and o-phenylen diamine compound. This ligand has been identified by the many spectral methods such as floual transform Infrared (FTIR), Ultra violet – visible (Uv – vis.), elemental analysis and melting point measurement. Tetra chelate complexes of above ligand with Cu(II), Ni(II) and Co(II) were prepared. The (matel : ligand) (M:L) molar ratio measured by molar ratio method, and the result ratio was (1:1) for all complexes. These complexes were characterized by above spectral method in addition to atomic absorption spectra, molar conductivity measurement and magnetic susceptibility. The FTIR spectral data showed deprotonated ligand and coordenated with matel ion. The Uv-vis. and magnetic susceptibility results showed the proposed geometrical shapes were squar planner configuration for all complexes Fig.3 From the physical properties and calculation of thermodenamics parameter explanation this reaction was exothermic and spontaneous.

الخلاصة

تم في بحثنا هذا تحضير ليكاند أزو أزوميثين غير متمائل رباعي السن من نوع (N₂O₂). حضر الليكاند من تفاعل التكثيف بين مشتق السلسلديهايد المحتوي على مجموعة الأزو ومركب الأورثو فنلين ثنائي الأمين. لقد تم تشخيص الليكاند المحضر بواسطة الطرق الطيفية كطيف الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية والتحليل العنصري الدقيق (C.H.N) وقياس درجة الانصهار. كما تم تحضير سلسلة من المعقدات لهذه الليكاندات مع بعض أيونات الفلزات الانتقالية، وهي النحاس(II) والنيكل(II) والكوبلت(II). تم تحديد نسبة الفلز: ليكاند لهذه المعقدات بواسطة طريقة النسب المولية. وشخصت هذه المعقدات باستخدام الطرق الطيفية المذكورة في أعلاه فضلاً على قياس طيف الامتصاص الذري وقياسات التوصيلة المولارية والحساسية المغناطيسية. أظهرت نتائج طيف الأشعة تحت الحمراء فقدان بروتوني لليكاند عند تناسق هذه الليكاندات مع الفلزات المدروسة كما تنبأت نتائج الأشعة فوق البنفسجية – المرئية بالشكل الهندسي المتوقع وبينت أنها تتخذ الشكل المربع المستوي للمعقدات المحضرة جميعها. كذلك عززت نتائج قياسات الحساسية المغناطيسية الشكل المقترح للمعقدات المحضرة. وبينت قياسات التوصيلة الكهربائية أن المعقدات المحضرة غير أيونية وهذا يدعم الشكل المقترح في أعلاه. وأيضاً بينت نتائج حساب الدوال الترموديناميكية (ΔH , ΔS , ΔG) أن تفاعل التعقيد باعث للحرارة ويحصل بصورة تلقائية.

Introduction

Azo azomethen ligand and its complexes containing deferent metal ion such as Ni, Cu and Co studied widely were used in many fields such as ionic selective⁽¹⁻³⁾, liquid crystal^(4,5) and biological system^(6,7). Azo azomethen ligands contain azo group(-N=N-) and azomethen group (-C=N-) prepare by two procedure in the first (method A) involve shiff base preparation from condensation reaction between carbonyl group and amine compound and was added diazonium salt, prepared in the usual way⁽⁸⁾. The second procedure (method B) starting of diazonium salt preparation and was added condensation product. In this research have been prepared of of azo azomethen complexes and investigated using different chemical techniques. Because of the good thermal stability of this complexes have been thermodenamics study of complexes to found thermodenamics parameter (ΔH , ΔS , ΔG).

Experimental

Chemicals

All chemicals used in this work imported from (BDH, Aldrich and Merk) , including aniline, 4-Methoxyaniline , O-phenyldiamine , ET-OH salicylaldehyde , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and DMSO

Preparation of Ligand (azo azomethen compound).

Azo azomethen was prepared by two steps.

preparation of azo salicylaldehyde compounds.

a. preparation 5-(phenyl azo)-2-hydroxy benzylaldehyde (R1).

This compound was prepared by adding ethanolic solution (0.01 mol, 1.22gm) salicylaldehyde in basic medeia to diazonium chlorideprepared from diazonation reaction reactionto aniline at 0°C (as shown in schem1).

b. preparation5-(4-methoxyphenyl azo)-2-hydroxy benzylaldehyde (R2).

This compound was prepared by adding ethanolic solution (0.01 mol, 1.22gm) salicylaldehyde in basic medeia to diazonium chlorideprepared from diazonation reaction reaction to 4-methoxy aniline at 0°C (as shown in schem 1).

preparation of ligand (L).

Ligand was prepared by reflux(2h) to mixture ethanolic solution from (0.001 mol, o.226gm) (R1), (0.001mol, 0.24gm) (R2) and (0.001mol, 0.108gm) O-phenylen diamineand adding 2 drops glacial acitic acid(as shown in schem1).

preparation of complexes.

Complexes ion of above ligand have been preparation by reflux (30 min.) to mixture of ethanolic solution from matel salts ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and ligand at (1:1) ratio (Fig.3). Physical properties and elemental analysis to azo azomethen ligand and it's complexes as shown in table 1.

Thermodenamics parameter measurements.

Thermodenamics parameter have been calculate by using of the following equation.

$$\text{Log} \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

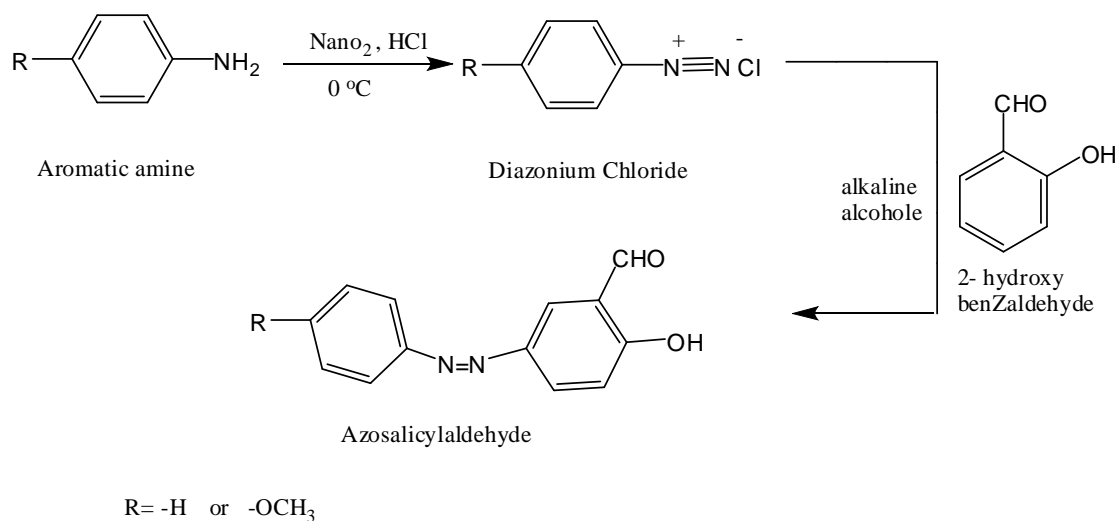
$$\Delta G = -RT \ln K_{eq}$$

$$\Delta G = \Delta H - T\Delta S$$

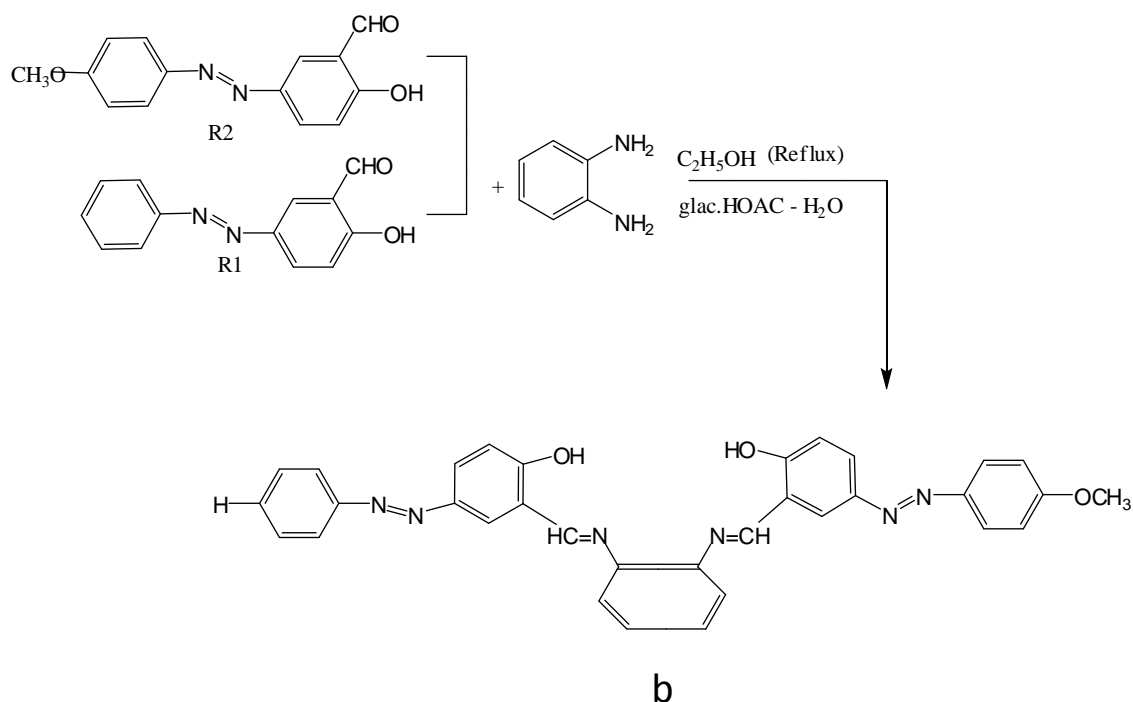
The data show in table 2.

Table -1- physical properties and elemental analysis of ligand and it's complexes.

Compound	color	M.P °C	Yield %	Molecular formula (M.Wt)	Cal. (Exp.) %			
					C%	H%	N%	M%
L	Dark orange	238-240		(C ₃₃ H ₂₆ N ₆ O ₃)	71.48 (72.32)	4.69 (4.61)	15.16 (15.12)	
CuL2	Brown	341-343	77	[(C ₃₃ H ₂₄ N ₆ O ₃)Cu]	64.33 (56.05)	3.89 (3.85)	13.64 (13.59)	10.32 (9.95)
NiL2	Red	336-338	74	[(C ₃₃ H ₂₄ N ₆ O ₃)Ni]	64.84 (65.45)	3.92 (3.90)	13.75 (13.71)	9.61 (9.12)
CoL2	Dark brown	320-322	72	[(C ₃₃ H ₂₄ N ₆ O ₃)Co]	64.81 (65.32)	3.92 (3.89)	13.74 (13.68)	9.64 (9.21)



a



Schem-1- (a). preparation of azo salicylaldehyde , (b). preparation of ligand (L).

Result and discussion.

The azo azomethen ligand has been prepared by two type of reaction, the first one include coupling reaction to prepared azo compound, and the second condensation reaction to prepared Schiff base compound. The final product is azo azomethen compound. Complexes of above ligand have been synthesized. Ligand and its complexes identified by FTIR, UV-Visible, magnetic susceptibility, atomic absorption and conductance measurements.

Infrared spectra of the ligand and its complexes.

The infrared spectral data of the ligand and its complexes with all ions under the study are in agreement with the expected range (see in Fig.1). A band in the range (3430-3450) cm^{-1} is due to $\nu(\text{OH})$ vibration heterocyclic⁽⁹⁾. Shifting and change location in this band compared with the free ligand because coordinate metal ion with ligand and deprotonation of this ligand⁽¹⁰⁾. A weak band at (2920 and 2960) cm^{-1} due to $\nu(\text{C-H})$ ⁽⁹⁾ aromatic and aliphatic respectively, and no change in this band in the spectra of complexes. A band at 1620 cm^{-1} is due to $\nu(\text{C=N})$ ⁽¹¹⁾ vibration. Shifting of this band to lower frequency compared with free ligand at 1605 cm^{-1} suggesting coordination of metal ion through nitrogen atom of azo methen group. A very weak band at 1480 cm^{-1} due to $(-\text{N=N}-)$ ⁽¹²⁾ bridge and no change in this band in the spectrum of the complexes. New bands which are not present in the spectrum of free ligand at 480 cm^{-1} and 650 cm^{-1} are attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibration respectively^(13,14).

Electronic spectra and magnatic moment.

Azo azomethen ligand (L).

The electronic spectra of the azo azomethen and it's complexes show in Fig.2. Two band absorption band at 247nm (40486Cm⁻¹) due explanation in the spectrum of the free ligand⁽¹⁵⁾, the to $\pi \longrightarrow \pi^*$ and the other band at 324nm (30864Cm⁻¹) due to ($n \longrightarrow \pi^*$).

Copper (II) complexes.

The electronic spectra of the Cu(II) complex showed two absorption band at (620 and 660)nm (16129 and 15151)Cm⁻¹ corresponding to ($^2B_{1g} \longrightarrow ^2E_g$) and ($^2B_{1g} \longrightarrow ^2A_{1g}$)⁽¹⁶⁾, transition with asquar planner complex. The magnatic moment value of this complex was found to be 1.67 B.M, which can be anormal value for squar planner low spin Cu(II) complex⁽¹⁷⁾.

Nickle (II) complexes.

The electronic spectra of the Cu(II) complex showed two absorption band at (390 and 460)nm (25641 and 21739)Cm⁻¹ corresponding to ($^1A_{1g(F)} \longrightarrow ^1A_{2g}$) and ($^1A_{1g(F)} \longrightarrow ^1B_{1g}$)⁽¹⁸⁾, transition with asquar planner complex. The magnatic moment value of this complex was found to be dimagnatic, which can be anormal value for squar planner low spin Ni(II) complex⁽¹⁹⁾.

Cobalte (II) complexes.

The electronic spectra of the Cu(II) complex showed two absorption band at (540 and 580)nm (18000 and 17500)Cm⁻¹ corresponding to ($^2A_{1g} \longrightarrow ^2T_{1g}$) and ($^2A_{1g} \longrightarrow ^2E_g$)⁽²⁰⁾, transition with asquar planner complex. The magnatic moment value of this complex was found to be 3.58 B.M, which can be anormal value for squar planner low spin of Co(II) complex⁽²¹⁾. The magnatic moment value and electronic spectral data listed in table 2.

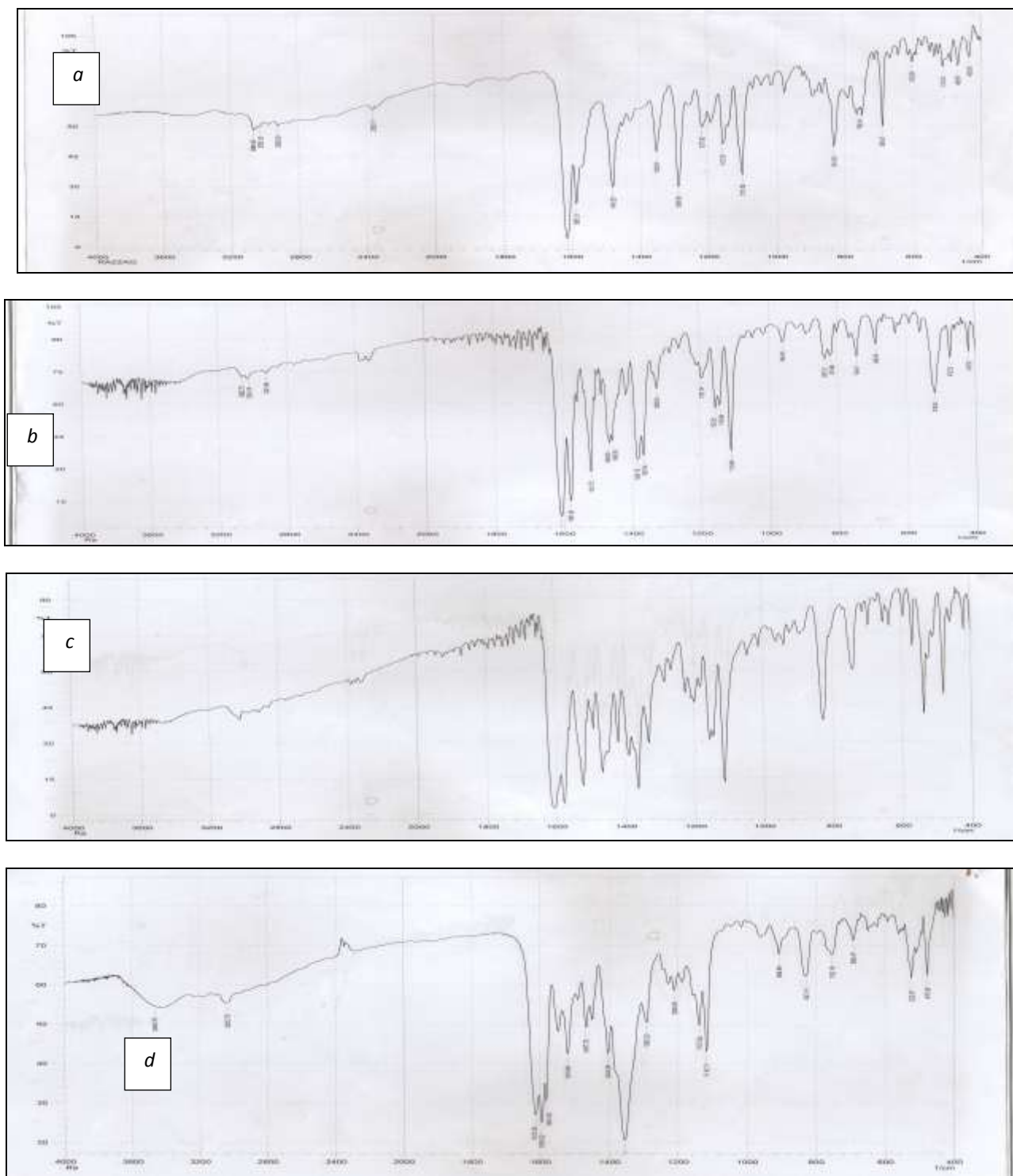


Fig.1: FTIR spectra; (a) free ligand , (b)Cu(II) complexe ,(c)Ni(II)complexe , (d)Co(II) complexes

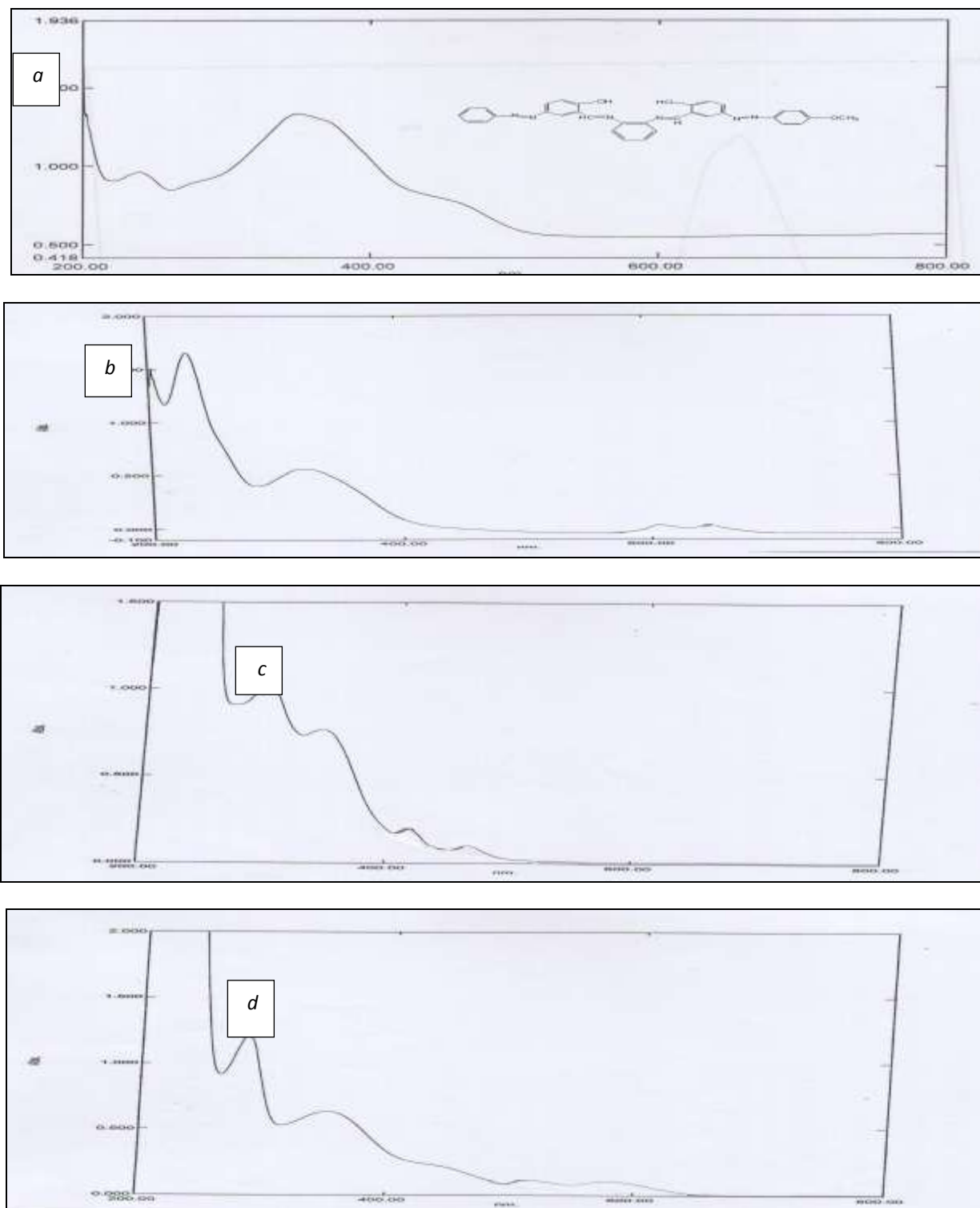


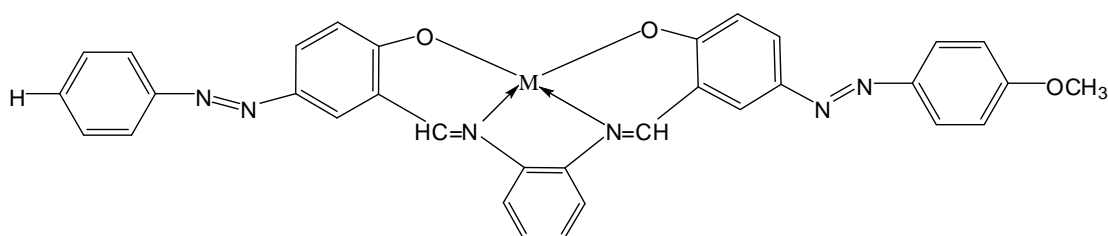
Fig.2: the absorption spectra; (a) free ligand , (b)Cu(II) complexe ,(c)Ni(II)complexe , (d)Co(II) complexe

Molar conductance measurements.

The molar conductance value in DMSO solvent ($4.86, 5.62$ and $5.75 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$) of the (Cu, Ni and Co) complexes respectively, indicated that the complexes under study is non electrolytic nature⁽²²⁾. The obtained value suggest that no anions present out side the coordination sphere. The data show in table 2.

Table-2- Electronic spectra, magnatic moment , thermodenamics and proposed structure of complexes ion.

complexes	Absorption <i>bands(cm-1)</i>	μ_{eff} <i>(B.M)</i>	Proposed structure	Thermodenamics parameter			
				T/K	ΔG <i>KJ.mol⁻¹K⁻¹</i>	ΔH <i>KJ.mol⁻¹K⁻¹</i>	ΔS <i>KJ.mol⁻¹K⁻¹</i>
CuL ₂	16129 15151	1.67	S.P	283.15	-9.09	-60.47	-0.18
				293.15	-8.64		-0.17
NiL ₂	25641 21739	0.00	S.P	283.15	-11.60	-89.52	-0.27
				293.15	-10.30		-0.27
CoL ₂	18000 17500	3.58	S.P	283.15			
				293.15			



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

Fig.3- proposed structure of complexes

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