

Synthesis, Characterization and Thermal Studies of Schiff Bases Derived from 2,4-Dihydroxy benzaldehyde and their Complexes with Co(II), Ni (II), Cu(II)

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Abstract: The synthesis characterization of new imine prepared via condensation of 2,4-Dihydroxy benzaldehyde with 3,3'-diaminobenzidine. The structure of imine was characterized by elemental analysis FTIR, ¹H-NMR, UV-Vis, mass spectroscopic and TG/DSC. The results show an agreement with the proposed structure. Was used to synthesize the complexes of type [M₂(L)] [M= Co (II), Ni (II), Cu(II)] and their complexes were characterized by methods of spectral analysis FTIR, UV-Vis, mass spectroscopic, molar conductivity, thermal analysis was carried out using the DSC knowing if these complexes contain water molecules that are consistent with the central atom and also study some thermodynamic functions of prepared compounds and was included evaluation of magnetic properties of prepared complexes. The results showed that the complexes of Co(II), and Cu(II) have paramagnetic properties and Shape would be tetrahedral, while the complex of Ni(II) have diamagnetic properties. So square planar with four nitrogen and four oxygen atoms from the Schiff base ligand.

Keywords: Schiff base, 2,4-Dihydroxy benzaldehyde, Cobalt, Complexes

1. Introduction

In recent years, interest in the design, synthesis and coordination chemistry of polydentate chelating ligands capable of forming stable complexes with metal ions has resulted in the study of a large number of new chelating agents. Schiff bases are the ligands which give these opportunities and for this reason have attracted the attention of researchers for many decades [1,2]. These compounds are widely spread due to several characteristics, including the high degree of complexity of the complex. There are many attempts to increase the solubility and stability of these complexes, especially when used as symmetric factors and asymmetric [3,4]. It was also used in nanotechnology applications asymmetric catalysis as well [5].

Some complexions were used as second-line nonlinear optics (NLO) because they provide additional flexibility when compared with organic chromophores through the presence of metals (color, magnetism, polarization, oxidation behavior, thermal stability, brilliance, etc.) [6-9]. They are very useful for applications in electrical devices because they have the properties of liquid crystal light emitting [10, 11].

2. Experimental

2.1 Materials and Instrumentation

The 2,4-Dihydroxy benzaldehyde and 3,3'-diaminobenzidine used for the preparation of the Schiff base were obtained from the Sigma Aldrich. The metal salts, MCl₂.xH₂O [M=Co, Ni, x=6; Cu, x=2] was purchased from British Drug House. All the organic solvents from Fisher Chemical. All solvents and chemicals were used without further purification.

Infrared (IR) spectra were recorded on a FTIR-84005-SHIMADZU by using KBr pellets. The ¹H-NMR spectra were obtained on Bruker-400HZ. the spectra have been recorded in DMSO, at room temperature. UV-Vis spectra were obtained in DMF on uv-win5, using 10mm quartz cells. Mass spectra were recorded on 5975C-Agilent Technologies and EI technology at electronic power of 70eV. Magnetic properties were measured using a device called the Auto magnetic susceptibility Balance. Using glass tubes with a diameter of 0.324 cm. The transition temperatures of the prepared complexes were measured using a DSC-60 device, with a temperature range starting at room temperature to 350 °C at heating rate of 10 °C/min.

2.2 Synthesis of Schiff base ligand

The ligand 4,4',4'' (E,1'E,1''E) ([1,1'biphenyl] 3,3',4,4' Tetrayltetrakis (azanylylidene)) tetrakis (methanylylidene)) tetrakis (benzene 1,3-diol) prepared from 2,4-Dihydroxybenzaldehyde (0.552g, 4mmol) dissolved in 5ml of methanol and drops of glacial acetic acid were added to this solution, then added dropwise from 3,3'-diaminobenzidine (0.214g, 1mmol) in 15ml Methanol solution. The contents were refluxed (3h) where the formation of an orange deposit during the interaction and followed by interaction using (TLC). Interaction is an inert atmosphere of Argon gas.

Schiff base ligand (C₄₀H₃₀N₄O₈): yield: 75%, color: orange, M.P.: 303°C

2.3 Synthesis of the Metal complexes

The complexes of Schiff base ligand were prepared by the addition of Schiff base ligand (1mmol) was dissolved in (2:4:4 ml) of [DMF:EtOH:MeOH] respectively to metal salt

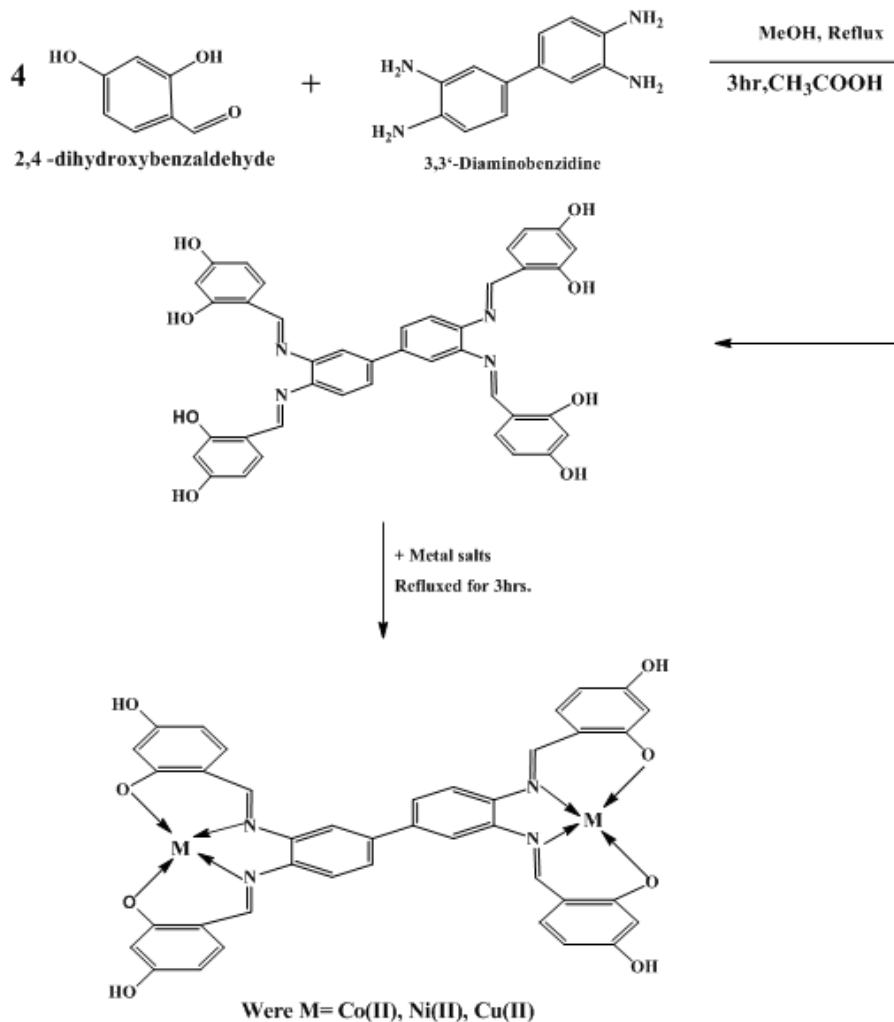
(2mmol) $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$ dissolved in methanol (5ml). The resulting mixtures were boiled under reflux for 3h and under an inert atmosphere of the Argon gas (Ar), then leave the product to dry and then wash the residue with the ether to get the required complex. Scheme 1 illustrate the preparation of the Schiff base ligand and complexes Co(II), Ni(II), Cu(II).

$[\text{Co}_2(\text{C}_{40}\text{H}_{26}\text{N}_4\text{O}_8)]$: yield: 78.6%, color: Black crystals, M.P.: $>300^\circ\text{C}$

$[\text{Ni}_2(\text{C}_{40}\text{H}_{26}\text{N}_4\text{O}_8)]$: yield: 78%, color: Red powder, M.P.: $>300^\circ\text{C}$

$[\text{Cu}_2(\text{C}_{40}\text{H}_{26}\text{N}_4\text{O}_8)]$: yield: 80%, color: Dark brown crystals, M.P.: $>300^\circ\text{C}$

Schem1



2.4 FT-IR spectra

The prominent bands observed in the IR spectra of the Schiff base ligand (L) and its complexes are listed in Table 1 and fig.1a-d. In order to study the binding mode of Schiff base ligand to the metal ions in complexes the IR spectrum of the free ligand compared with the spectra of the corresponding complexes. The infrared spectrum of the Schiff base ligand showed absorption band at 1614cm^{-1} assigned to the $(\text{C}=\text{N})$ stretching vibrations [12,13], indicating the formation of the Schiff base linkage. In all the complexes, this band is shifted to lower frequencies in the range ($1601\text{--}1606\text{ cm}^{-1}$) upon complexation with the metal Centre [14].

New vibrations at ($420\text{--}498\text{cm}^{-1}$) and ($500\text{--}549\text{cm}^{-1}$) which are not present in the free Schiff base are attributed to the existence of $\nu(\text{M-O})$ [15] and $\nu(\text{M-N})$. Its packages weaken the hydroxide group, underscoring their association which appearing in the region 3053cm^{-1} in the ligand disappears in the complexes.

Table 1: Molar Conductance and Infrared spectroscopic data of the Schiff base ligand and its binuclear metal complexes

Compound	$\nu_{\text{C-H}}$ (Ar.)	$\nu_{\text{C-H}}$ Alph.	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$ (Ar.)	Other	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
L	3053	2937	1614	1520	$\nu_{\text{O-H}}$ 3345	----	----
$[\text{Co}_2(\text{L})]$		2930	1602	1548	----	549	498
$[\text{Ni}_2(\text{L})]$		2900	1606	1548	----	525	420
$[\text{Cu}_2(\text{L})]$		2948	1601	1549	----	500	412

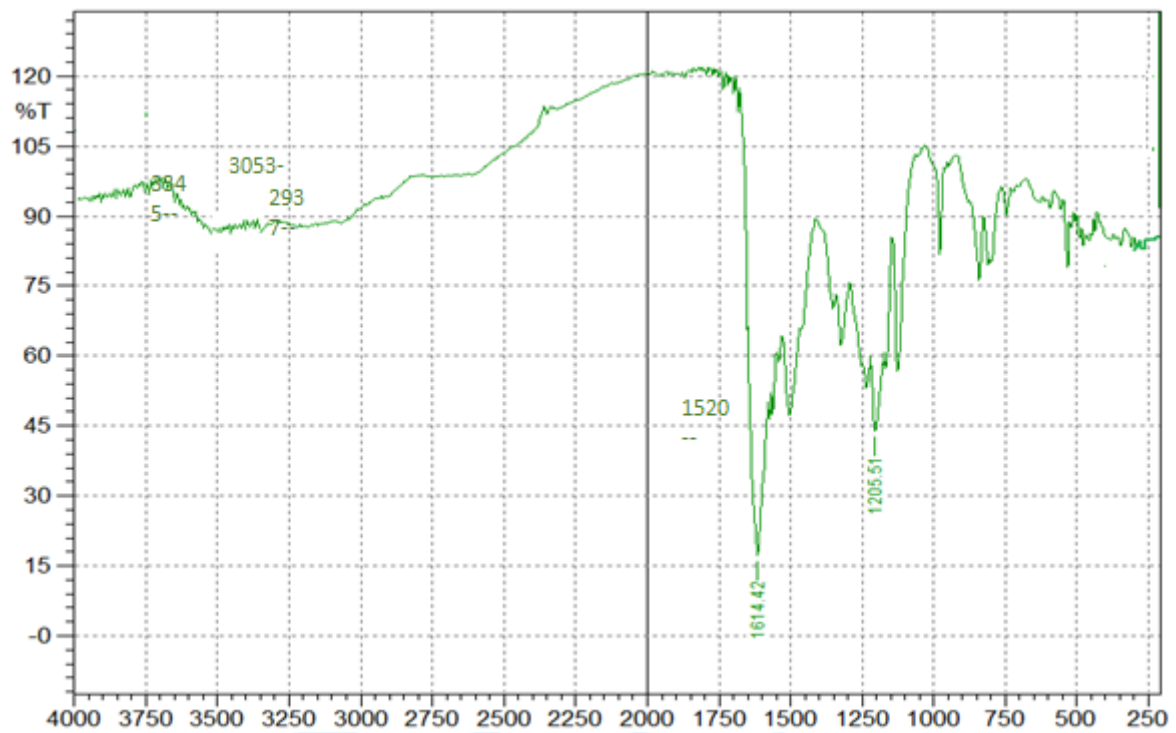


Figure 1 (a): IR spectrum of L

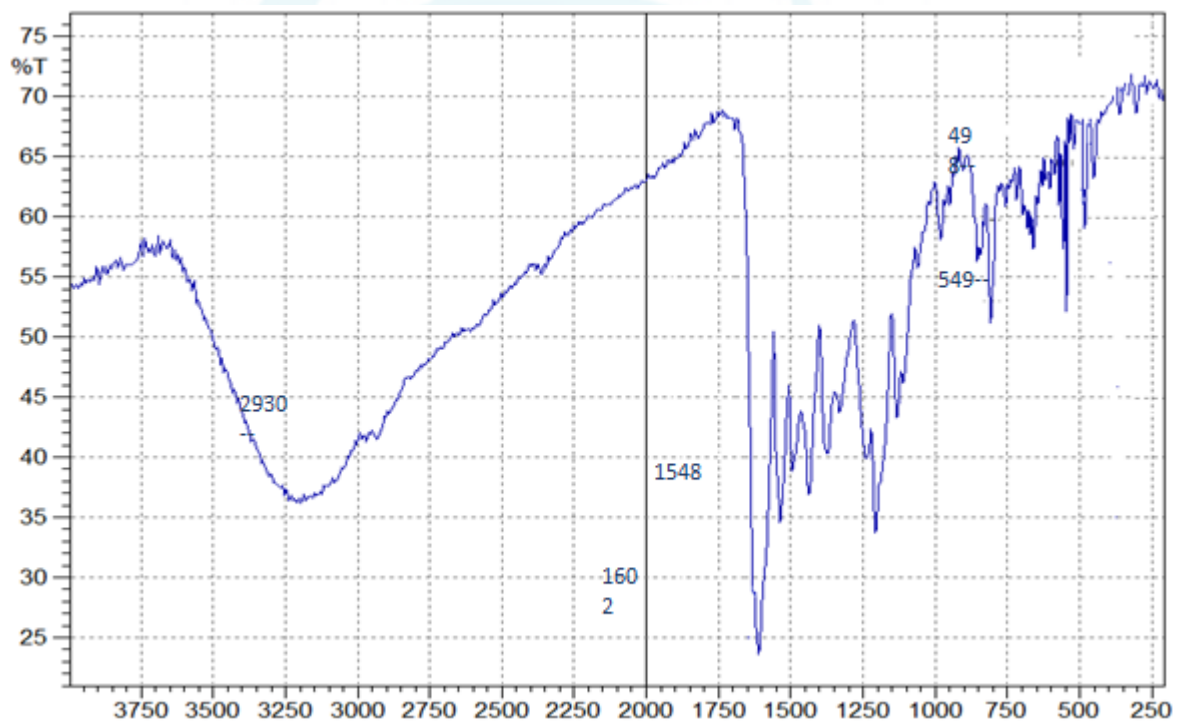
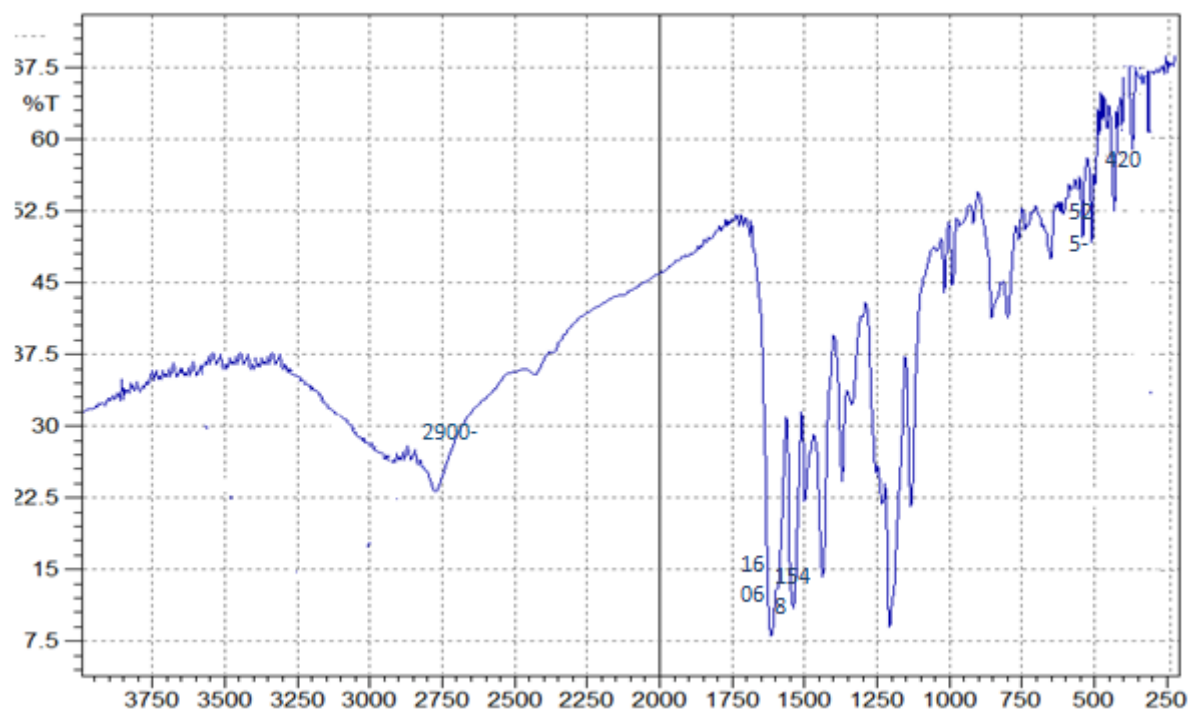
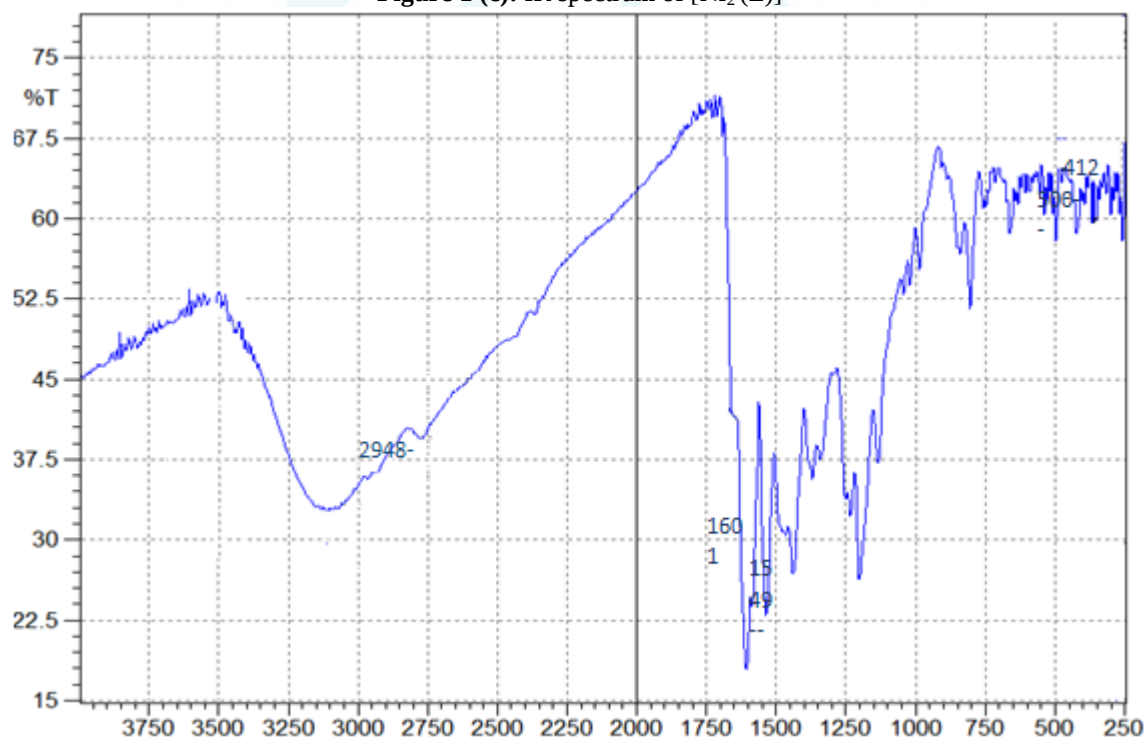


Figure 1(b): IR spectrum of [Co₂(L)]

Figure 1 (c): IR spectrum of $[\text{Ni}_2(\text{L})]$ Figure 1 (d): IR spectrum of $[\text{Cu}_2(\text{L})]$

Electronic spectra

Electronic absorption spectra are summarized the date of complexed and ligand in the table 2. The electronic spectra of the Schiff base ligand and their complexes have been measured in DMF solution between 200-800 nm at room temperature. In the spectra of the Schiff base ligand, the absorption band observed at 304nm were assigned to $\pi-\pi^*$ transition and the band at 380 nm were assigned due to $n-\pi^*$ transition associated with the azomethine chromophore ($\text{C}=\text{N}$)[16], Fig2a.

The spectra of the prepared complexion showed absorption bands ranging from 452-425nm due to the transmission of

the M-L type between the metal and ligand and weak bands ranging (600-540nm) to the d-d transitions in the visible spectrum, Which confirms complex[17,18], fig.2b-d.

Table 2: Electronic spectra of Schiff base ligand and metal complexes

Compound	$\pi^*-\pi$ nm	$\pi^*-\pi$ nm	M-L Nm	d-d nm
L	304	380	-----	-----
$[\text{Co}_2(\text{L})]$	306	390	435	555,585
$[\text{Ni}_2(\text{L})]$	305	391	452	550,590,660
$[\text{Cu}_2(\text{L})]$	298	-----	425	540,570

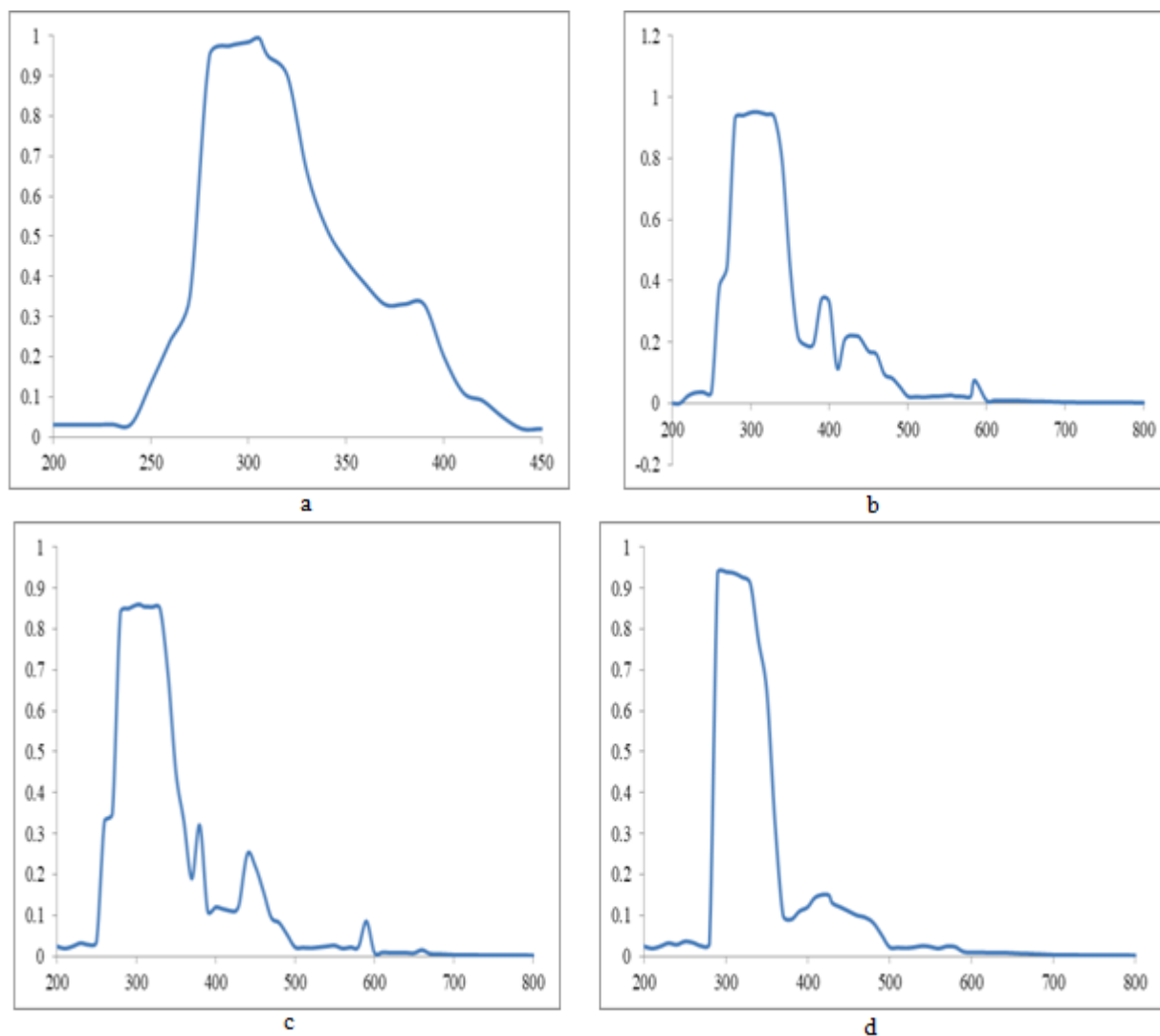


Figure 2: Electronic spectra of L and its Co(II), Ni(II), Cu(II) complex (a–d)

¹H-NMR

¹HNMR spectral studies of synthesized ligand indicated signal at 10.2 ppm to the proton group (-C=N-) and Signal and 13.4ppm due to proton hydroxyl group (-OH) [19,20] fig.3

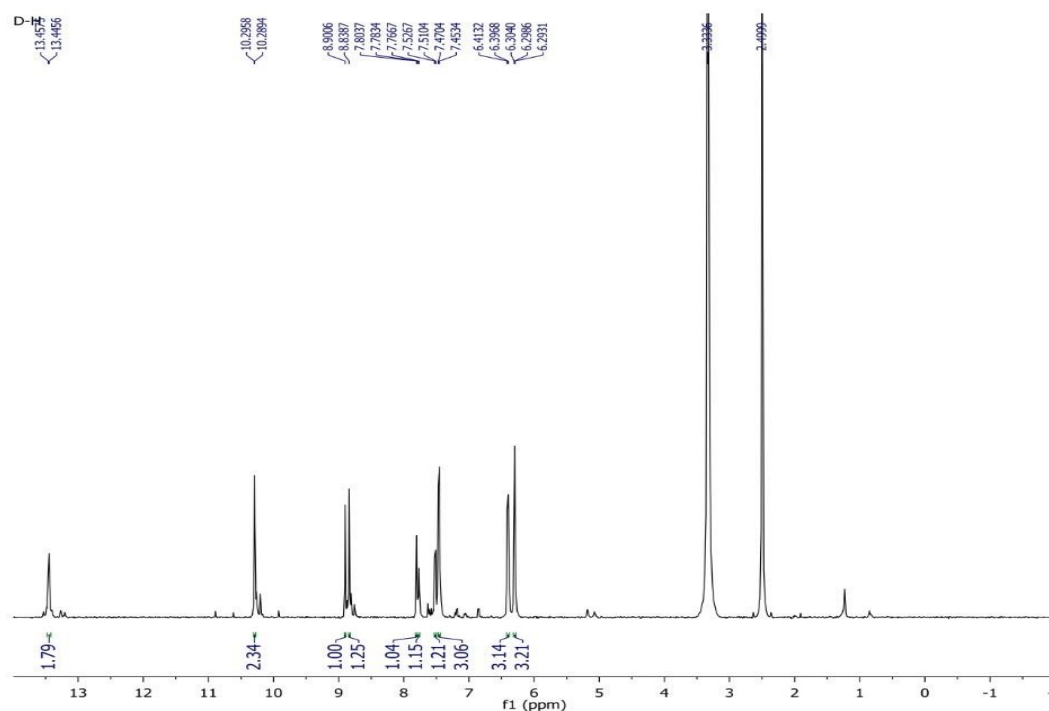


Figure 3: ^1H NMR spectra of Schiff base L

Mass Spectroscopy

The mass of Schiff base ligand and Ni (II) complex exhibit molecular ion peak at m/z at (695.4, 809.3) fig.4a, band peak of ion base at m/z at (105.0, 73.2) respectively.

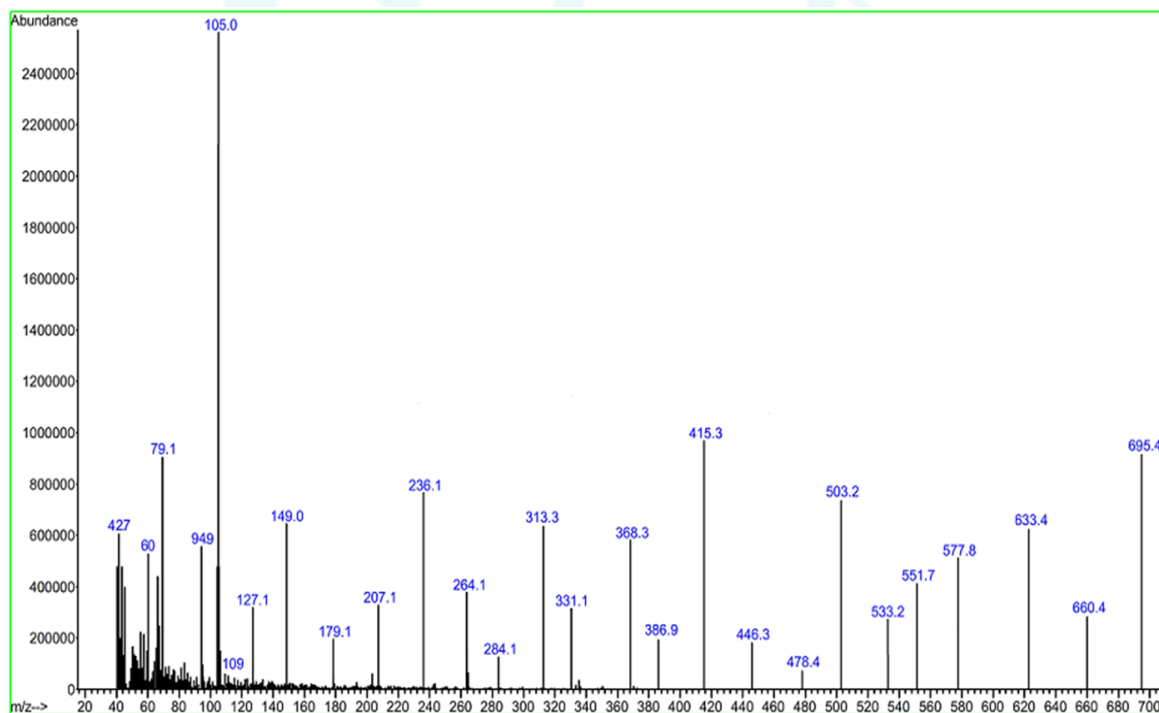


Figure 4(a): Mass spectra of Schiff base ligand

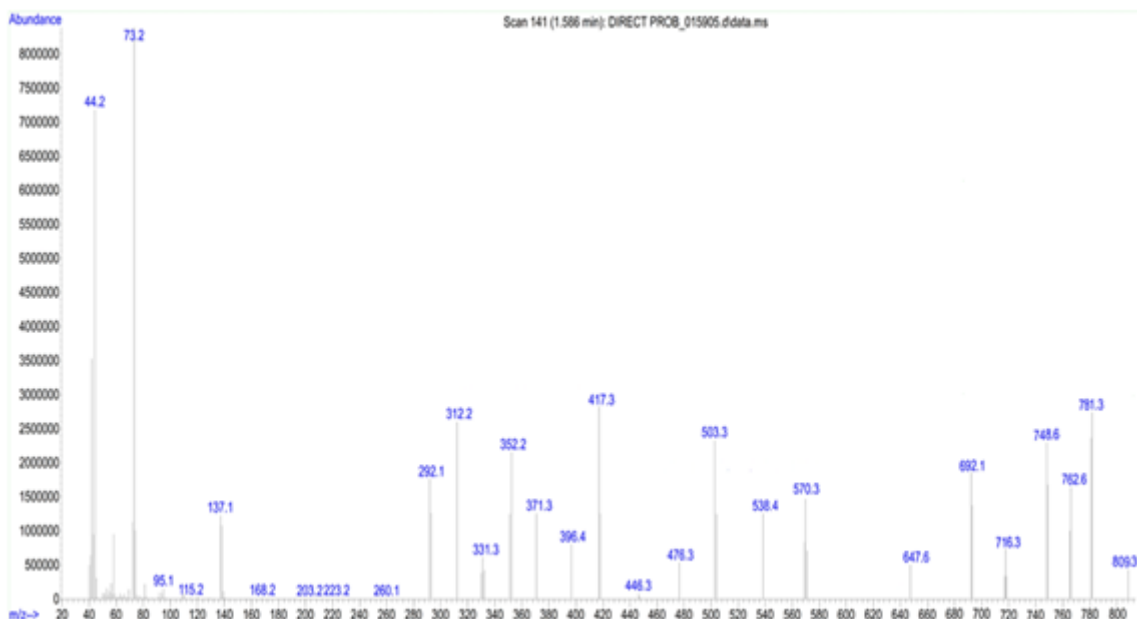


Figure 4 (b): Mass spectra of Ni (II) complex

Molar Electrical conductivity

Molecular conductivity of Co (II), Ni (II) and Cu (II) ions was measured with ligands at a concentration of 10^{-3} M meted dissolved in DMF, each separately at the tested temperature and was used by the DMF as a reference. The results in the table 3 where conductivity values show that the complexes behave in the behavior of neutral (non-electrolytic) compounds of the lack of any ionic due properties, because chloride ions do not exist outside the coordinate all as the ion's counter ion.

Table3: Electrical conductivity and molar conductivity of prepared complexes

Formula of complex	Cell Constant A(cm ⁻¹)	Electrical Conductivity Ohm ⁻¹	Molar conductivity Ohm-1 .cm-1/mol
[Co ₂ (C ₄₀ H ₂₆ N ₄ O ₈)]	1.1	14.5×10^{-6}	15.95
[Ni ₂ (C ₄₀ H ₂₆ N ₄ O ₈)]	1.1	14.2×10^{-6}	15.62
[Cu ₂ (C ₄₀ H ₂₆ N ₄ O ₈)]	1.1	20.1×10^{-6}	22.11

Magnetic properties

The results showed of magnetic properties of prepared complexes that the complexes of Cobalt (II) and Copper (II) have paramagnetic properties and shape would be tetrahedral [21-24], while the complex of Nickel (II) have diamagnetic properties so a square planar will be its shape [25]. As in the table4. The effective magnetic moment(μ_{eff}) of the complex was calculated according to the following equations:-

$$X_m = X_g \cdot M.\text{wt} \quad \dots \dots \dots 1$$

$$X_A = X_m + D \quad \dots \dots \dots 2$$

$$\mu_{\text{eff}} = 2.828 \sqrt{X_A \cdot T} \text{ B.M} \quad \dots \dots \dots 3$$

Table 4: Results of magnetic measurements and hybridization of prepared complexes

Formula of complex	Mass magnetic susceptibility $X_g \cdot 10^{-6}$	Molar magnetic susceptibility $X_m \cdot 10^{-6}$	Correc. factor $D \cdot 10^{-6}$	Atomic magnetic susceptibility $X_A \cdot 10^{-6}$	Effective magnetic moment μ_{eff} (B.M.)	Hybridization
[Co ₂ (C ₄₀ H ₂₆ N ₄ O ₈)]	4.819	3064.86	362.1-	2702.76	2.538	SP ³
[Ni ₂ (C ₄₀ H ₂₆ N ₄ O ₈)]	0.903	574.71	359.6-	215.11	0.716	dsp ²
[Cu ₂ (C ₄₀ H ₂₆ N ₄ O ₈)]	2.805	1784.35	371.5-	1412.85	1.835	SP ³

TG/DSC

The temperature gradients for the transitions in the prepared vehicles show in fig.5a –c were different transitions, ranging from on peak to several peaks most of which indicate the presence of residues of the solvent and the other of the ligand fusibility and the prepared complex or the beginning of their disintegration. On the other hand, some dynamic functions (entropy, free energy and activation energy) were calculated based on the mathematical relations of the coats-Redfern equation [26,27], which were used to calculate the dynamic

functions of the prepared compounds Table5. There is difference in the prepared compounds due to the size of the metal, the nature of the bond and the appropriate vacuum regulation. The change in enthalpy ΔH , change in entropy ΔS and the change in free energy ΔG were calculated from the equations following

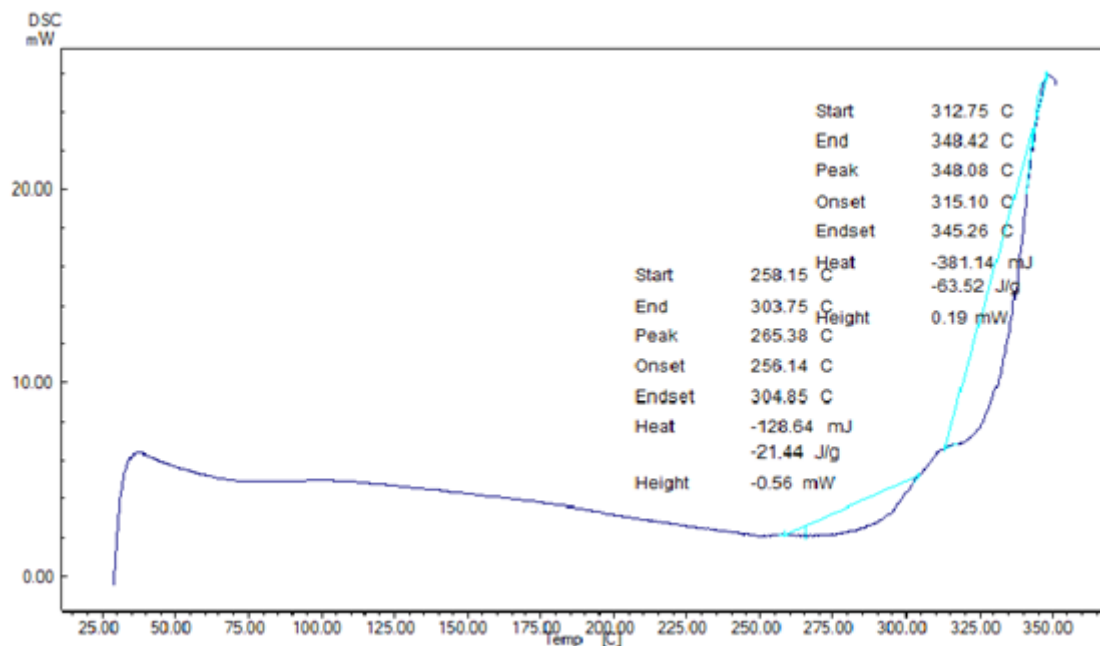
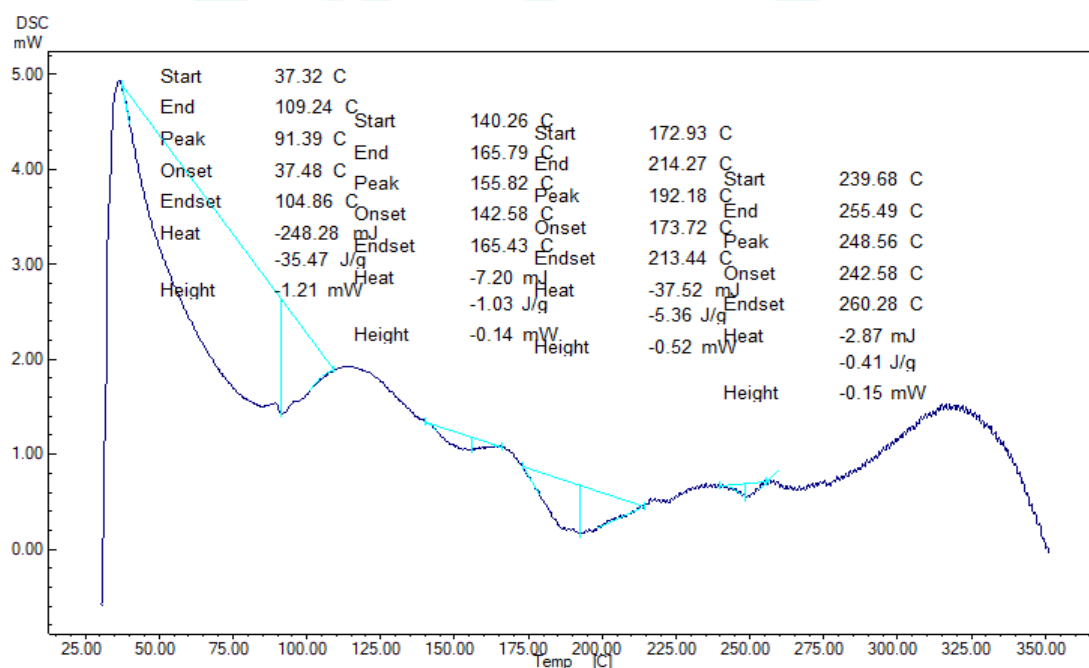
$$\Delta H = E - RT \quad \dots \dots \dots 4$$

$$\Delta S = R \ln \left(\frac{A_h}{K_B T_s} \right) \quad \dots \dots \dots 5$$

$$G = \Delta H - T \Delta S \quad \dots \dots \dots 6$$

Table 5: Some thermodynamic functions of prepared compounds

Formula of complex	E KJ/mole	ΔH KJ/mole	ΔS KJ/mole	ΔG KJ/mole
$C_{40}H_{30}N_4O_8$	19.067	14.595	-0.278	164.159
$[Co_2(C_{40}H_{26}N_4O_8)]$	7.911	4.045	-0.276	132.385
$[Ni_2(C_{40}H_{26}N_4O_8)]$	118.798	114.342	-0.277	262.278

**Figure 5(a):** DSC curve of Schiff base ligand**Figure 5(b):** DSC curve of Co(II) complex

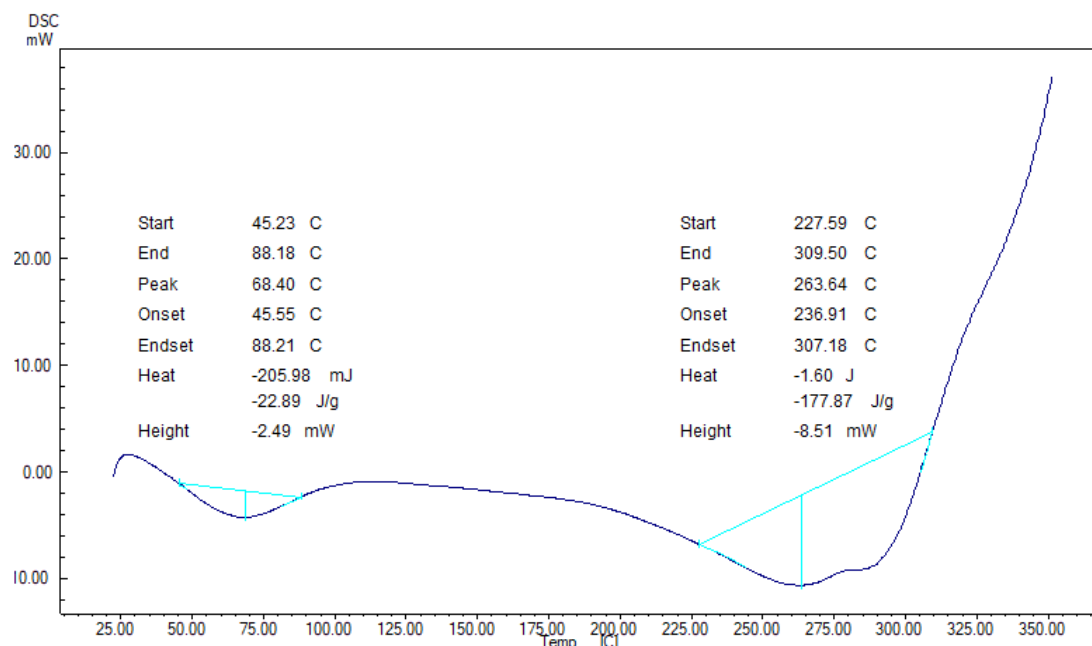


Figure 5(c): DSC curve of Ni (II) complex

3. Conclusion

The newly synthesized binucleating ligand was used to prepare Co (II), Ni(II) and Cu(II) complexes. The data obtained from these studies were in good agreement with the proposed structure and composition of the ligand and the metal complexes. Through various diagnostic methods such as IR UV-Visible and ¹H-NMR and mass spectrometry, the synthetic formulas of the prepared compounds were suggested. The preparation rules were considered to be multiple chelating ligands and through measurements of magnetic sensitivity and electric conductivity The Cobalt (II) and Copper (II) complex took the tetrahedral geometry and Take Nickel (II) complex the geometry square shape. The study of thermal analysis using the DSC if these complexes not contain water molecules that are consistent with the central atom and also study some thermodynamic functions of prepared compounds.

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