

Spectroscopic and thermal properties studies of Schiff base and its metal complexes

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Abstract— The synthetic method of some transition metal complexes with selective Schiff base containing nitrogen and oxygen donor ligand derived from the condensation of 5-bromo-2-hydroxybenzaldehyde with N,N'-dimethylamino aniline have been developed, characterized and presented. The prepared complexes fall into the stoichiometric formulae of $[M(L)2.2H_2O]_nH_2O(A)$ [$M = Cu(II), Co(II), Mn(II)$] and $[Zn(L)2(OCH_3)_2](B)$, where two types of complexes were expected and described. The ligand and its metal complexes have been characterized by different physicochemical methods, elemental analysis, molar conductivity, (UV-vis, Mass, Infrared, 1H NMR spectra) and thermal analysis (TG and DTG) techniques. The optimized bond lengths, bond angles and calculated the quantum chemical parameters for the ligand (HL) are investigated. HOMO–LUMO energy gap, absolute Electronegativities, chemical potentials, and absolute hardness have been calculated. The IR data of the ligand suggested the existing of a monobasic bidentate binding involving azomethine nitrogen and O-atom of phenolic hydroxyl. ESR spectra show the simultaneous presence of a planar trans and a nearly planar cis isomers in the 1:2 ratio for all N,O complexes. TG curves reflect a lower thermal stability of complexes compared with Ligand due to the presence of water molecules in outside of the coordination sphere. The activation thermodynamic parameters, such as activation energy (E_a), enthalpy (ΔH^*), entropy (ΔS^*), and Gibbs free energy change of the decomposition (ΔG^*) are calculated using Coats–Redfern and Horowitz-Metzger methods.

Keywords — Schiff base, Transition metals, ESR, TG and DTG analysis, Thermodynamic parameters.

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1 INTRODUCTION

Efforts have been made to carry out detailed studies to synthesize and elucidate the structural and electronic properties of complexes with hydroxybenzlidene derivatives. hydroxybenzlidene derivatives are a good series of ligands capable of binding metal ions leading to metal complexes with increasing properties. The high stable potential of hydroxybenzlidene derivative complexes in different oxidation states increased the application of these compounds in a wide range. Ligands with potential oxygen and nitrogen donors, such as hydroxybenzlidene and its derivatives are quite interesting which have gained special attention, not only because of the structural chemistry and their importance in medical chemistry [1-3], but also because these materials are used as drugs and they are reported to possess a wide variety of biological activities against bacteria and fungi. They also have become a useful model for bioinorganic processes, which have many biochemical and pharmacological activities [4,5].

The Schiff base contain azomethine group ($HC=N$). They are used as substrates in the preparation of industrial and biologically active compounds via ring closure, cycloaddition and replacement reactions [6]. Schiff's base ligands are potentially capable of forming stable complexes with most transition metal ions which served as model compounds for biologically important species [7]. Schiff base having antipyrine moiety can coordinate to metal as neutral molecules or after deprotonation as anionic ligands and can adopt variety different coordination modes. The possibility of their being able to transmit electronic effects between a reduce unit and metal centre is suggested by the delocalization of the bonds in the antipyrine chain [8]. Antipyrine and their metal complexes have considerable interest because of their biological activities, such as antitumour, antiviral, anticancer, antifungal, antibacterial and antimalarial [9-12]. They also have been used as drugs and are reported to possess a wide variety of biological activities against bacteria, fungi and

certain type of tumors and also are useful model for bioinorganic processes.

In connection of widely applications for Schiff base ligands and their metal complexes, we have synthesized and characterized a new series of metal(II) complexes of Co(II), Cu(II), Zn(II), and Mn(II) with Schiff base ligand derived from 5-bromo-2-hydroxy benzaldehyde and *N,N*'-dimethylamino aniline. The synthesized compounds have been characterized on the basis of spectroscopic methods including IR, UV-vis, ¹H NMR, and mass spectroscopy as well as elemental analyses and molar conductance measurements. Thermogravimetric (TG/DTG) analyses of the ligand and its metal complexes were derived and discussed [13].

2 EXPERIMENTAL SECTION

2.1. Preparation of the ligand

Methanolic solutions of *p*-*N,N*-dimethyl amino aniline (0.01 mole) and (5-bromo-2-hydroxybenzaldehyde) (0.01 mole) were refluxed together for 4 hrs over a steam bath (Fig. 1). The excess solvent was removed by evaporation and the concentrated solution was cooled in an ice bath with stirring. The Schiff base which separated out as a colored powder is collected and dried in vacuum [7,14].

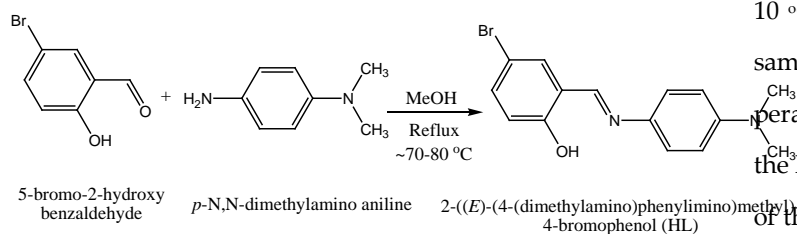


Fig. 1. Synthetic route of Schiff base ligand (HL).

2.2. Preparation of the metal complexes

All the chemicals used were of Aldrich Chemical Co. quality. All the complexes were prepared using a 1:2 (metal ions: ligand) molar ratio following a general method. Hot solutions of metal salts (Co(II), Cu(II), Mn(II) and Zn(II)) (1.0 mmole) in MeOH and solutions of the required amount of Schiff base (HL) (2.0 mmole) in MeOH were stirred at room temperature and then maintained at reflux temperature on water bath at ~70-80 °C for 2-3 hours. The

products were filtered, washed with MeOH and dried in a desiccator over anhydrous CaCl₂.

2.3. Analytical and physical measurements

Elemental microanalyses of the separated ligand and solid chelates for C, H and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. The ¹H-NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d₆ as the solvent and TMS as an internal reference. Infrared spectra were recorded as KBr pellets using a Pye Unicam SP 2000 spectrophotometer. Ultraviolet-visible (UV-vis) spectra of the compounds were recorded in solution using a Unicam SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), [Hg{Co(SCN)₄}], was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [15] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\text{eff}} = 2.84 [T\chi_M^{\text{cor.}}]^{1/2}$. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of 10 °C/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10 x 5 x 2.5 mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a KOH-H₂O₂ mixture. The halide content was then determined by titration with a standard Hg(NO₃)₂ solution using diphenylcarbazone indicator. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA. The molecular structures of the investigated compounds are optimized by HF method with 3-21G basis set. The molecules are built with Perkin Elmer ChemBio Draw and optimized using Perkin Elmer ChemBio 3D software. Quantum chemical parameters for the investigated molecules are calculated.

3 Results and discussion

3.1. Synthesis and characterization of the ligand

In the present investigations, the ligand (HL) was prepared by stirring an appropriate amount of 5-bromo-2-hydroxybenzaldehyde with the corresponding p-N,N'-dimethyl aniline in ethanol. Schiff base ligand (HL) is soluble in common organic solvents. The Schiff bases formed was characterized with respect to its composition by elemental and spectral analysis. Elemental analysis data of the ligand (HL) is given in Table 1 and IR spectra in Table 2. Elemental analysis data of the ligand (HL) show good agreement with theoretical data.

Table 1. Analytical data of HL and its metal complexes.

Compound ^a	Calc. (Exp.) %			
	C	H	N	M
HL	56.58 (56.60)	4.75 (4.71)	8.81 (8.80)	-
[Mn (L) ₂ (H ₂ O) ₂] ₂ H ₂ O (1)	47.19 (47.2)	4.19 (4.8)	7.34 (7.34)	7.20 (7.12)
[Co(L) ₂ (H ₂ O) ₂] ₅ H ₂ O (2)	43.85 (43.99)	3.90 (4.02)	6.82 (6.87)	7.18 (7.25)
[Cu (L) ₂] ₂ H ₂ O (3)	50.17 (50.30)	3.90 (4.18)	7.80 (7.81)	8.86 (8.72)
[Zn(L) ₂ (OCH ₃) ₂] (4)	50.30 (50.5)	4.45 (4.45)	7.34 (7.34)	8.57 (8.40)

^aThe analytical data agree satisfactory with the expected formulae represented as given in structure HL.

Table 2. IR spectra of HL and its metal complexes.

Comp. ^b	v(O-H)	v(C-O)	v(C=N)	v(M-O)	v(M-O)H ₂ O
HL	3443	1178	1611	-	-
(1)	3405	1122	1614	467	520
(2)	3414	1168	1613	450	629
(3)	3753	1163	1618	450	599

(4)	3439	1013	1627	560	513
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^b Numbers as given in Table 1.

The selected geometrical structure of the investigated ligand is calculated by optimizing their bond lengths and bond angles. The calculated molecular structure for HL is shown in Fig. 2. The selected geometric parameters are listed in Table 3. The C7-N9 bond with length 1.268 Å for ligand (HL) is a normal imine bond. The surfaces of frontier molecular orbital theory (FMOs) are shown in Fig. 2.

The HOMO-LUMO energy gap, ΔE, which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems (Fig. 3). The smaller is the value of ΔE, the more is the reactivity of the compound has [16-19]. The calculated quantum chemical parameters are given in Table 4. Additional parameters such as ΔE, absolute Electronegativities, χ, chemical potentials, Pi, absolute hardness, η, absolute softness, σ, global electrophilicity, ω [17-19], global softness, S, and additional electronic charge, ΔN_{max}, have been calculated according to the following equations [17-19]:

$$\Delta E = E_{LUMO} - E_{HOMO}, \quad (1)$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2}, \quad (2)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}, \quad (3)$$

$$\sigma = 1/\eta, \quad (4)$$

$$Pi = -\chi, \quad (5)$$

$$S = \frac{1}{2\eta}, \quad (6)$$

$$\omega = Pi^2 / 2\eta, \quad (7)$$

$$\Delta N_{max} = -Pi/\eta \quad (8)$$

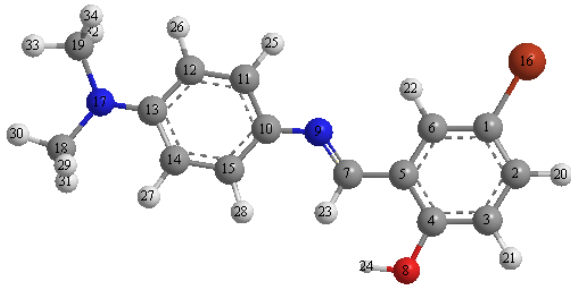
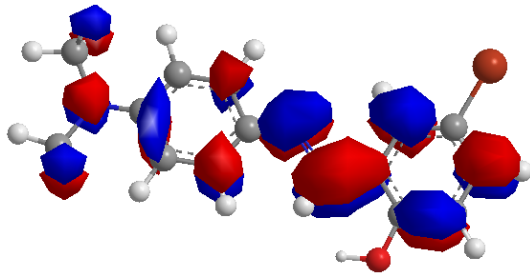
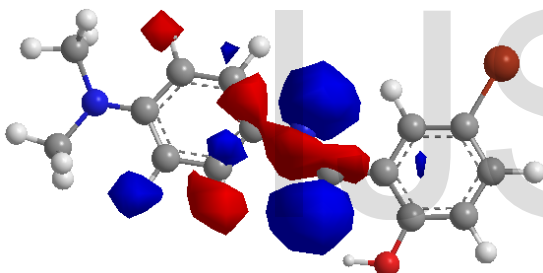


Fig. 2. The calculated molecular structures of the ligand (HL).



LUMO



HOMO

Fig. 3. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for HL.

Table 3. The selected geometric parameters for HL.

Bond lengths (Å)		Bond angles (°)	
C(19)-H(34)	1.114	H(29)-C(18)-N(17)	111.458
C(19)-H(33)	1.112	C(19)-N(17)-C(18)	120.551
C(19)-H(32)	1.114	C(19)-N(17)-C(13)	119.684
C(18)-H(31)	1.114	C(18)-N(17)-C(13)	119.765
C(18)-H(30)	1.112	H(27)-C(14)-C(15)	114.78
C(18)-H(29)	1.114	H(27)-C(14)-C(13)	121.828
C(15)-H(28)	1.102	C(15)-C(14)-C(13)	123.392
C(14)-H(27)	1.102	C(14)-C(13)-C(12)	114.85
C(12)-H(26)	1.102	C(14)-C(13)-N(17)	122.937
C(11)-H(25)	1.106	C(12)-C(13)-N(17)	122.88
O(8)-H(24)	0.968	H(26)-C(12)-C(13)	122.89
C(7)-H(23)	1.097	H(26)-C(12)-C(11)	114.869
C(6)-H(22)	1.103	C(13)-C(12)-C(11)	122.892
C(3)-H(21)	1.104	H(28)-C(15)-C(10)	122.049

C(2)-H(20)	1.103	H(28)-C(15)-C(14)	116.29
C(10)-C(15)	1.345	C(10)-C(15)-C(14)	121.661
C(14)-C(15)	1.344	H(25)-C(11)-C(12)	117.97
C(13)-C(14)	1.35	H(25)-C(11)-C(10)	119.818
C(12)-C(13)	1.35	C(12)-C(11)-C(10)	122.212
C(11)-C(12)	1.343	C(15)-C(10)-C(11)	115.66
C(10)-C(11)	1.346	C(15)-C(10)-N(9)	128.221
C(1)-C(6)	1.342	C(11)-C(10)-N(9)	116.119
C(5)-C(6)	1.35	C(10)-N(9)-C(7)	127.524
C(4)-C(5)	1.353	H(23)-C(7)-N(9)	117.085
C(3)-C(4)	1.346	H(23)-C(7)-C(5)	117.879
C(2)-C(3)	1.34	N(9)-C(7)-C(5)	125.036
C(1)-C(2)	1.339	H(22)-C(6)-C(1)	117.397
N(17)-C(19)	1.487	H(22)-C(6)-C(5)	120.833
N(17)-C(18)	1.487	Dihedral angles (°)	
C(13)-N(17)	1.282	C(5)-C(7)-N(9)-C(10)	179.965
C(1)-Br(16)	1.894	C(4)-C(5)-C(7)-N(9)	179.926
N(9)-C(10)	1.27	C(7)-N(9)-C(10)-C(11)	179.966
C(7)-N(9)	1.268	N(9)-C(10)-C(11)-C(12)	179.966
C(4)-O(8)	1.363	C(12)-C(13)-N(17)-C(18)	179.972
C(5)-C(7)	1.352	C(3)-C(4)-O(8)-H(24)	179.535
		C(13)-N(17)-C(19)-H(32)	62.551

Table 4. The calculated quantum chemical parameters of the investigated ligand (HL).

Parameter	
HOMO (a.u)	-0.2913
LUMO (a.u)	-0.1094
ΔE (a.u)	0.1819
χ (a.u)	0.2004
η (a.u)	0.0909
σ (a.u) ⁻¹	10.9945
Pi (a.u)	-0.2004
S (a.u) ⁻¹	5.4972
ω (a.u)	0.2207
ΔN_{\max}	2.2029

Synthesis and characterization of metal complexes

The complexes were synthesized by reacting ligand with the metal ions in 2: 1 L:M ratio in methanolic medium (Fig. 4). On the basis of elemental analysis, the complexes were found to have the composition, as given in Table 1. The molar conduct-

ance of the complexes in DMSO lies in the range of 0.7–12 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their non-electrolytic behavior [18,20].

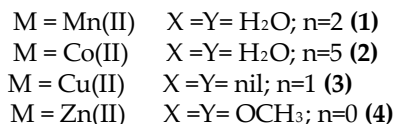
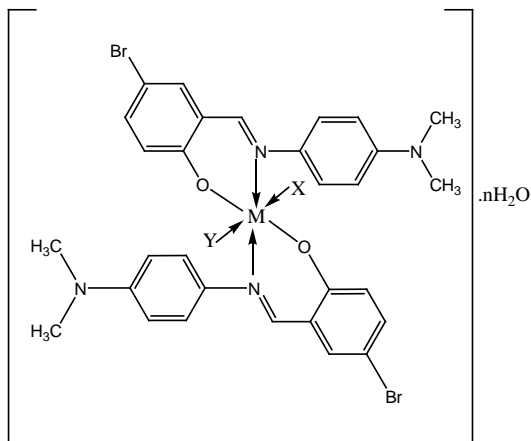
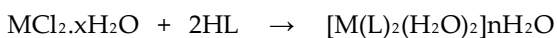


Fig. 4. The proposed structures of the complexes.

The complexes are stable in air and atmosphere. All the complexes are soluble in DMF and DMSO, but they are insoluble in some common organic solvents. The analytical data (Table 1) indicate that the metal to ligand ratio is (M:2L) $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]n\text{H}_2\text{O}$ as obtainable in the following reaction.



where L = ligand and M = Cu(II), n = 1; Co(II), n = 5H₂O; Mn(II), n = 2H₂O.

3.3. Conductivity measurements

Conductivity measurements have been used in structural elucidation of metal complexes (mode of coordination) within the limits of their solubility. The molar conductance of 10⁻¹M solutions of the complexes in DMSO is measured at room temperature. It is concluded from the results that M(II) chelates with HL ligand under investigation were found to have molar conductance values in the range from 0.7–12 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for 1:2 (M:L) complexes, indicating non-electrolytic nature of these compounds and there is no counter ion present outside the co-

ordination sphere of copper complexes [18,20,21]. This is in accordance with the fact that conductivity values for a non-electrolyte are below 50 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO solution [21]. Such a non-zero molar conductance value for each of the complex in the present study is most probably due to the strong donor capacity of DMSO, which may lead to the displacement of anionic ligand and change of electrolyte type [18,21].

3.4. Mass spectra of the ligand and Cu(II) complex

Mass spectrometry as a powerful structural characterization technique in coordination chemistry has been successfully used to confirm the molecular ion peaks of HL Schiff base and investigate its fragment species. The fragment pattern of mass spectrum believes an impression for the successive degradation of the target compound with the series of peaks corresponding to various fragments. Also, the peaks intensity gives an idea about the stability of fragments especially with the base peak. The recorded mass spectrum of HL Schiff base ligand reveals the molecular ion peak confirms strongly the condensation of o-vanillin with 4-methyl-1,2-phenylenediamine in 2:1 mol ratio and the proposed formula.

The mass spectrum of HL shows mass peaks at m/z 319,301,223,195,159,119, 77, and 55. The first mass peaks corresponds to the ligand, the second one proceeds by loss of OH and the third proceeds by loss of Br. The mass spectrum for the complex of HL with Cu(II) shows mass peaks at m/z 820,751,659,606,516,328,275,171,128,94 and 50.

3.5. ¹H NMR spectra

El-Sonbati et al. [7,14,22] investigated the ¹H NMR spectra of HL and complex (4) were recorded in DMSO-d₆. The ¹H NMR spectrum of aromatic protons (Ar-H) of HL the benzene rings appeared in the range of 6.78–7.80 ppm. The signal at 2.50 ppm is assigned to the methyl (CH₃) protons. HL showed a strong peak at 9.84 and 8.98 ppm for OH and C=N protons, respectively, of Schiff base ring. The signal due to OH proton disappears

in D₂O solution and this attributed to the strongly hydrogen bonded. The very weak and broad bands of protons were most probably resulted from intra H-bondings of OH protons with N atoms of azomethine group. The disappearance of the phenolic proton signal from the ¹H NMR spectrum of complex (4), support the proton displacement from the OH group through the metal ions. A comparison of the chemical shifts of the ligand with its complex such as Zn(II) complex indicate that the signal due to phenolic proton is absent in the complex spectrum. This can be attributed due to the deprotonation of the phenolic group and subsequently the replacement of the protons by metal. The azomethine proton signal is observed up-field at δ 8.89 ppm in case of Zn(II) complex. It supports the coordination of azomethine nitrogen to metal ion. Therefore, the ¹H NMR result supports the assigned geometry.

3.6. IR spectra

A detailed interpretation of IR bands of the ligand and the metal complexes is discussed. The IR spectra of the free ligand and metal complexes were carried out in the range of 4000-400 cm⁻¹ (Table 2). The IR spectrum of the ligand show a broad band between 3200 and 3450 cm⁻¹, which can be attributed to phenolic OH group. This band disappears in all complexes except Zn(II) complex (4) after complexation, due to crystal water in complexes, which can be attributed to involvement of phenolic OH in coordination. The involvement of deprotonated phenolic OH group in complexes is confirmed by the shift of ν (C-O) stretching band observed at 1178 cm⁻¹ in the free ligand to the lower frequency to the extend of 10-20 cm⁻¹ [7,14]. Also, coordination of the Schiff base to the metal ions through the nitrogen atom is expected to reduce electron density in the azomethine link and lower the ν (HC=N) absorption frequency. This band at 1611 cm⁻¹ in the free Schiff base ligand is shifted to a lower wave number side ($\Delta\nu \sim 2-14$ cm⁻¹) in all the complexes indicates the participation of the azomethine group in coordination to the metal ions through the lone pair of electrons on

the nitrogen. In the IR spectrum of all the complexes, IR band is observed between 450 and 560 cm⁻¹ which is attributed to the ν (M-N) stretching vibrations and the second band appeared between 514 and 630 cm⁻¹ which is assigned to the phenolic oxygen to metal atoms stretching vibrations ν (M-O) [7,14]. There are also two bands affected after complexation belonging to the benzene ν (C=C) stretching vibration at 1365 cm⁻¹, that clearly show that ligand coordinated to the metal ions from benzene's hydroxyl oxygen and nitrogen atom of azomethine groups [7,14].

3.7. Magnetic moments

The magnetic moment observed for Mn(II) complexes lies in the range 5.92 BM corresponding to five unpaired electrons. At room temperature Cu(II) complexes show magnetic moment in the range 1.94 BM corresponding to one unpaired electron [18].

3.8. Electronic spectra

3.8.1. UV-vis spectra and magnetic moments

The electronic absorption spectra of the Schiff base ligand and the metal complexes under investigation were recorded within the range 28560-12450 cm⁻¹. The data of electronic spectrum of HL Schiff base ligand was collected in DMF solvent with five absorption bands (A–D, F). The bands A & B located at 32460 and 29850 cm⁻¹ were assigned to transition motions of phenyl rings [23]. The transition band at 352 nm corresponded to $n \rightarrow \pi^*$ transition of azomethine group CH=N, while the bands C & D at 25310 and 28980 cm⁻¹ assigned to $n \rightarrow \pi^*$ transitions of donating atoms like oxygen and nitrogen which are overlapped with the intermolecular LCT from aromatic rings. The peaks within the transition motions of phenyl rings have been relatively unaffected in the spectra of the complexes; this is expected for the relatively unshared of aromatic ring in chelation. The band E within 28400 cm⁻¹ assigned to $n \rightarrow \pi^*$ transition due to involving molecular orbitals of the CH=N chromophore. In the spectra of the complexes, the bands of the azomethine chromophore bands (the bands of $n \rightarrow \pi^*$ transition) are shifted

to lower frequencies or lost, indicating that the imine nitrogen atom is involved in coordination to the metal ion.

In the present study, the temperature magnetic moment data of Cu(II) complex (3) show μ_{eff} . Value is 1.78 B.M. corresponding to one unpaired electron. $[\text{Cu}(\text{L})_2]$ show a broad band around 14320 cm^{-1} which may be due to the envelop of transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{2g}$ and $\rightarrow {}^2\text{E}_g$ suggesting a square planar geometry for the complex [24]. The cobalt complex has two bands, one at 23980 cm^{-1} and the other at 14970 cm^{-1} , which are assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions, respectively. Calculated 10Dq energy of the Co(II) complex is 1480 cm^{-1} and the Racah parameters in the order 0.690 of the free metal ion value suggesting considerable overlap in the metal -bond. From the position of the bands and the magnetic moment value of 4.78 BM, the geometry of the cobalt suggested the geometry of the complex as octahedral. The observed magnetic moment value of Mn(II) complex is found to be 5.35 B.M. which is low compared to the spin-only value for high-spin Mn(II) complexes. The low value can be attributed to the presence of Mn(II) species [24,25]. The weak spectral bands in Mn(II) complex at $17238, 21270$ and 24290 cm^{-1} are attributed to $6\text{A}_{1g} \rightarrow 4\text{T}_{1g}(\text{G}), 6\text{A}_{1g} \rightarrow 4\text{T}_{2g}(\text{G})$ and $6\text{A}_{2g} \rightarrow 4\text{E}_g$ transitions, respectively. They are in accordance with octahedral stereochemistry [26].

3.9. Thermogravimetric analyses

3.9.1. Thermogravimetric analysis of ligand (HL)

In the present investigation, the heating rates controlled at $10 \text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere and the weight loss measured from ambient temperature up to $\sim 1000 \text{ }^\circ\text{C}$. the data listed in Table 5. The weight losses for each chelate calculate within the corresponding temperature range.

The thermogravimetric curve of free ligand HL shows three decomposition steps within the temperature range $30\text{-}800 \text{ }^\circ\text{C}$. the first step of decomposition within the temperature range $27\text{-}294 \text{ }^\circ\text{C}$ corresponding to loss of HBr, $2\text{CH}_4, \text{NH}_3$ and C_2H_2 with

amass loss of 50.0 (calc. 49.0) the second step of decomposition within the temperature range $296\text{-}441 \text{ }^\circ\text{C}$ corresponding to loss of $\text{H}_2\text{O}, \text{C}_2\text{H}_2$ with amass loss of 14.1 (calc. 13.8). The third step of decomposition within the temperature range $441\text{-}769 \text{ }^\circ\text{C}$ corresponding to loss of $3\text{C}_2\text{H}_2, \text{NH}_3, \text{CH}_4$ with amass loss of 34.7 (calc. 34.9) the subsequent steps corresponding to removal of the organic part of the ligand leaving carbon residue [16].

3.9.2. Thermogravimetric analysis of complexes

The thermogravimetric curve of Mn(II) complex (1) shows four decomposition steps within the temperature range $40\text{-}800 \text{ }^\circ\text{C}$. The first step of decomposition within the temperature range $39\text{-}70 \text{ }^\circ\text{C}$ corresponding to loss of $2\text{H}_2\text{O}$ with amass loss of 4.71 (calc.4.73) the second step of decomposition within the temperature range $70\text{-}232 \text{ }^\circ\text{C}$ corresponding to loss of $2\text{H}_2\text{O}, 4\text{CH}_4$ with amass loss of 13.22 (calc. 13.14). The third step of decomposition within the temperature range $232\text{-}387 \text{ }^\circ\text{C}$ corresponding to loss of $\text{C}_2\text{H}_2, 2\text{NH}_3$ with amass loss of 8.0 (calc. 7.8). the fourth step of decomposition within the temperature range $388\text{-}770 \text{ }^\circ\text{C}$ corresponding to loss of $2\text{H}_2\text{O}, 10\text{C}_2\text{H}_2, \text{Br}_2, \text{N}_2$ with amass loss of 60.8 (calc. 61.2). The subsequent steps corresponding to removal of the organic part of the ligand leaving manganese oxide and Carbon residue.

Table 5. Thermal analyses data for HL and its metal complexes.

Comp. ^b	TG Temp. range ($^\circ\text{C}$)	DTG _{max} ($^\circ\text{C}$)	Stage	Mass loss %Found (Calc.)	Assignment	Metallic residue
HL	27-294	267	1 st	50.0 (49.0)	Loss of HBr, $2\text{CH}_4, \text{N}_2, \text{C}_2\text{H}_2$	Carbon atoms residue
	296-441	408	2 nd	14.1 (13.8)	Loss of $\text{H}_2\text{O}, \text{C}_2\text{H}_2$	
	441-769	602	3 rd	34.7 (34.9)	Loss of $3\text{C}_2\text{H}_2, \text{NH}_3, \text{CH}_4$	
(1)	39-70	50	1 st	4.71 (4.73)	Loss of $2\text{H}_2\text{O}$	MnO + 4C Carbon atoms residue
	70-232	218	2 nd	13.22 (13.14)	Loss of $2\text{H}_2\text{O}, 4\text{CH}_4$	
	232-387	545	3 rd	8.00 (7.8)	Loss of $\text{C}_2\text{H}_2, 2\text{NH}_3$	
	388-770	637	4 th	60.8 (61.2)	Loss of $10\text{C}_2\text{H}_2,$	

(2)	26-83	57.91	1 st	10.70 (11.0)	H ₂ O, N ₂ , Br ₂ Loss of 5H ₂ O	CoO + 7C Carbon atoms residue
	83-536	520	2 nd	39.4 (039.0)	Loss of 2H ₂ O, Br ₂ , C ₂ H ₂ , NH ₃ , CH ₄	
	537-762	629	3 rd	37.20 (37.4)	Loss of N ₂ , 10C ₂ H ₂ , H ₂ O	
(3)	32-62	50	1 st	2.10 (2.5)	Loss of H ₂ O	CuO
	63-226	161	2 nd	23.40 (22.6)	Loss of 2HBr	
	226-731	678	3 rd	64.20 (64.8)	Loss of 15C ₂ H ₂ , 2N ₂ , H ₂ O	
(4)	26-230	55,209	1 st	7.70 (8.4)	Loss of 2CH ₃ OH	½ ZnO
	230-395	335	2 nd	13.8 (14.0)	Loss of HBr, C ₂ H ₂	
	396-778	489,611	3 rd	73.70 (72.4)	Loss of HBr, 12C ₂ H ₂ , NH ₃ , 4CH ₄ , 1½ H ₂ O	

15C₂H₂, 2N₂, H₂O with a mass loss of 64.2 (calc. 64.8). The subsequent steps corresponding to removal of the organic part of the ligand leaving copper oxide and carbon residue [18,27].

The thermogravimetric curve of Zn(II) complex (4) shows three decomposition steps within the temperature range 30-800 °C. The first step of decomposition within the temperature range 26-230 °C corresponding to loss of 2CH₃OH with a mass loss of 7.7 (calc.8.4). The second step of decomposition within the temperature range 230-395 °C corresponding to loss of HBr, C₂H₂ with a mass loss of 13.8 (calc. 14.0). The third step of decomposition within the temperature range 396-778 °C corresponding to loss of HBr, 12C₂H₂, NH₃, 4CH₄, 1½ H₂O with a mass loss of 73.7 (calc. 72.4). The subsequent steps corresponding to removal of the organic part of the ligand leaving zinc oxide and carbon residue.

The thermogravimetric curve of Co(II) complex (2) shows three decomposition steps within the temperature range 30-800 °C. The first step of decomposition within the temperature range 26-83 °C corresponding to loss of 5H₂O with a mass loss of 10.7 (calc.11.0) the second step of decomposition within the temperature range 83-536 °C corresponding to loss of 2H₂O, C₂H₂, Br₂, NH₃, CH₄ with a mass loss of 39.4 (calc. 39.0) . the third step of decomposition within the temperature range 537-762 °C corresponding to loss of N₂, 10C₂H₂, H₂O with a mass loss of 37.2 (calc. 37.4) the subsequent steps corresponding to removal of the organic part of the ligand leaving cobalt oxide carbon residue.

The thermogravimetric curve of Cu(II) complex (3) shows three decomposition steps within the temperature range 30-800 °C. The first step of decomposition within the temperature range 32-62 °C corresponding to loss of H₂O with a mass loss of 2.1 (calc.2.5). The second step of decomposition within the temperature range 63-226 °C corresponding to loss of 2HBr with a mass loss of 23.4 (calc. 22.14) . The third step of decomposition within the temperature range 226-731 °C corresponding to loss of

4. Conclusions

In this work, synthesis and characterization of a Schiff base (HL) and its complexes are reported. The results obtained can be summarized as follows:

1. Elemental analysis and IR spectra are used to prove the stoichiometry and formulation of the complexes.
2. The new compound behaves as monobasic bidentate ligand when react with M(II) salt and undergo coordination through the Schiff base nitrogen and oxygen atom of the phenolic group.
3. The thermal properties of the ligand (HL) and its M(II) complexes were investigated by thermogravimetry analysis (TGA).
4. Thermal data suggested that the ligand is more stable as compared to complexes due to the presence of water molecules in outside of the coordination sphere.

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