Research Article

Characteristic Studies of Hexamethylene Diamine Complexes

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Preparation and chemical analysis of Mn(II), Fe(III), Co(II), Ni(II), and Zn(II) complexes with Schiff base L [*o*-HOC₆H₄CH=N(CH₂)₆N:CHC₆H₄OH-*o*] are the main tasks of this work. The octahedral (M₂L₂·*n*H₂O·X) complexes in 1:1 M:L ratio (X = NO₃⁻ or Ac⁻ group, L = ligand) were prepared by involving the hydroxylic group in ortho position. All complexes were characterized on the basis of elemental analysis, UV, IR, ¹H NMR, Gc/Ms, thermogravimetric analysis, magnetic measurements, molar conductance, and electrical conductivity. The obtained data indicate that all the investigated compounds behave as semiconductor materials.

1. Introduction

The chemistry of transition metal complexes of Schiff base compounds has attracted a lot of interest in the field of bioinorganic and coordination chemistry [1–4]. The presence of ion pair on the nitrogen atom of imino group enables the coordination of numerous metal cations [5]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to possess unusual configuration that is structurally labile and their sensitivity to molecular environments [6, 7]. Schiff base can also accommodate different anions of the same center metal involving various coordination modes, thereby allowing successful synthesis of homo- and heterometallic complexes with varied stereochemistry. This feature is employed for modeling active sites in biological system [8–11]. In regard to importance of these compounds, many literatures have been published in this field. In view of this recently, multicomponent has much attention, and many of them have been reported. The desired Schiff base was obtained when 1,6-hexanediamine was condensed with salicylaldehyde. The structures of Mn(II), Fe(III), Co(II), Ni(II), and Zn(II) complexes were confirmed by elemental analysis, infrared and UV-Visible spectra, thermogravimetric analysis, magnetic measurements, and molar conductance.

2. Experimental

2.1. Physical Measurements. Infrared measurements were carried out on Perkin Elmer spectrophotometer model 1430

in range from 200 to 4000 cm⁻¹. Ultraviolet and visible spectra were carried out on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer in the range 190–500 nm. The solution spectra of ligands and complexes were carried out in 10⁻⁶ M of DMF. ¹H-NMR spectra were recorded using a Varian spectrometer, 200 MHz. Thermal gravimetric analysis (TGA) data were measured from room temperature to 650°C at heating rate of 10°C/min. The data were obtained using a Shimadzu TGA-50H instrument. Mass spectra of the compounds were recorded on a Hewlett Packard mass spectrometer model MS 5988. Samples were introduced directly to the probe; fragmentations were carried out at 300°C and 70 eV. Molar conductivities were measured using WAP, GMP 500 conductivity meter. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a magnetic susceptibility balance, Sherwood Scientific, Cambridge Science Park, Cambridge, UK. Effective magnetic moments were calculated from the expression $\mu_{\text{eff}} = 2.84(X_M)^{1/2}$ B.M., where X_M is molar susceptibility.

2.2. Synthesis of *N,N'*-Hexamethylenebis(Salicylideneimine) Schiff Base L (HBS). The ligand was synthesized by slowly adding salicylaldehyde (5.47 mL, 44.86 mmole) in 100 mL methanol to 1,6-hexanediamine (3 g, 25.81 mmole). The reaction mixture was heated to reflux for 2 hr. The yellow product obtained was filtered off and washed with few amount of methanol and then diethylether, and fine crystals were

SCHEME 1: Schematic representation for the formation of Schiff base ligand L (HBS).

obtained by recrystallization from methanol. The ligand obtained was soluble in 1,2-dichloromethane, chloroform, and partially soluble in methanol and ethanol. The yield was (7 g, 83.73%), m.p. 72°C, Calc. for $C_{20}H_{24}N_2O_2$: C, 74.07; H, 7.41; N, 8.64, Found: C, 73.65; H, 7.77; N, 8.59%. The reaction for the formation of L (HBS) is illustrated in Scheme 1.

2.3. Synthesis of Schiff Base Metal Complexes: Reaction of $Mn(NO_3)_2 \cdot 6H_2O$ with L (HBS). A pink solution of $Mn(NO_3)_2 \cdot 6H_2O$ (0.42 mL, 2 mmole) in methanol (30 mL) was added gradually with constant stirring to a solution of the ligand L (HBS) (0.32 g, 1 mmole) in methanol (30 mL). The solution was refluxed for 2 hr. The dark green precipitate was deposited after evaporation of part of the solvent which was collected and washed with methanol and then diethylether. The product obtained was insoluble in methanol, ethanol, 1,2-dichloromethane, and chloroform but soluble in dimethylsulfoxide and dimethylformamide. The yield was (0.39 g, 43.64%), m.p. > 300°C.

2.4. Reaction of $Fe(NO_3)_3 \cdot 9H_2O$ with L (HBS). A yellow solution of $Fe(NO_3)_3 \cdot 9H_2O$ (0.81 g, 2 mmole) in methanol (30 mL) was added gradually with constant stirring to a solution of the ligand L (HBS) (0.32 g, 1 mmole) in methanol (30 mL). The solution was refluxed for 2 hr. The color changed to blood red and reddish brown. Precipitate was obtained and washed with small amounts of methanol and then diethylether. The precipitate was insoluble in ethanol, methanol, 1,2-dichloromethane, and acetone but soluble in dimethylformamide and dimethylsulfoxide. The yield was (0.75 g, 66.25%), m.p. > 300°C.

2.5. Reaction of $Co(NO_3)_2 \cdot 6H_2O$ with L (HBS). A red solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.58 g, 2 mmole) in methanol (30 mL) was added gradually with constant stirring to a solution of the ligand L (HBS) (0.32 g, 1 mmole) in methanol (30 mL). The reaction mixture was refluxed for 2 hr. Dark green precipitate was filtered off and dried. The product obtained was insoluble in 1,2-dichloromethane, chloroform, methanol, and ethanol but soluble in dimethylformamide and dimethylsulfoxide. The yield was (0.27 g, 30.23%), m.p. > 300°C.

2.6. Reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with L (HBS). A green solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.58 g, 2 mmole) in methanol

(30 mL) was added gradually with constant stirring to a solution of the ligand L (HBS) (0.32 g, 1 mmole) in methanol (30 mL). The solution was refluxed for 2 hr. The green precipitate deposited after evaporation. Part of the solvent was collected and washed with small amounts of methanol and then diethylether. The product obtained was insoluble in ethanol, methanol, and 1,2-dichloromethane but soluble in dimethylformamide and dimethylsulfoxide. The yield was (0.32 g, 35.43%), m.p. > 300°C.

2.7. Reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with L (HBS). A solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.44 g, 2 mmole) in methanol (30 mL) was added gradually with constant stirring to a solution of the ligand L (HBS) (0.32 g, 1 mmole). The solution was refluxed for 2 hr. Yellowish white precipitate obtained was filtered and washed with small amount of methanol and then diethylether. The yield was (0.61 g, 78.63%), m.p. > 300°C.

3. Results and Discussion

All the complexes provide satisfactory C, H, N, and metal analyses and confirm the general composition $[M_2L_2(H_2O)]$ and $[M_2L_2X_2(H_2O)]$, where L = ligand, X = NO_3^- , or Ac^- , M = Mn(II), Fe(III), Ni(II), Co(II), and Zn(II). The isolated solid complexes are stable in air. The analytical and physical properties of the prepared complexes are given in Table 1.

3.1. Electronic Spectral and Magnetic Susceptibility Measurements. The electronic spectrum of Mn(II) complex shows a band at 721 nm. This band is assignable to $d-d$ transition. The band at 316.52 nm may be attributed to phenolate $O(\pi\pi) \rightarrow Mn(d\pi^*)$ ligand and to metal charge transfer [12]. The band at 256.46 nm is due to $\pi-\pi^*$ (azomethine) ligand transitions. The magnetic moment (5.65 B.M.) is additional evidence for octahedral structure. The conductance of Mn(II) complex in DMF is 25.8 $\mu S/cm$. The low value of conductance indicated that the complex is nonelectrolyte. The electronic spectrum of Fe(III) complex shows a broad band at 415.20 nm. This is mainly due to charge-transfer (CT) band. The absorption bands at 257.7 and 276 nm are attributed to $\pi-\pi^*$ (azomethine) ligand and $n-\pi^*$ transitions [13] (see Table 3).

The value of the magnetic moment of the Fe(III) complex is 5.08 B.M. which falls in the range of values corresponding to low-spin octahedral complexes of Fe(III) ions. The conductance of Fe(III) complex in DMF is 7.18 $\mu S/cm$. The low value of conductance indicated that the complex is nonelectrolyte.

The electronic spectrum of the green Ni(II) complex showed three bands. The spectrum of octahedral Ni(II) consists of three bands which are accordingly assigned as ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. The ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition was not observed due to the fact that it occurs in the near infrared and is out of the range of the used instrument. The ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition is observed at 734.91 nm. The third band due to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ is observed at 369.73 nm, which refers to the charge-transfer transition.

The value of the magnetic moment of Ni(II) complex is 2.52 B.M. The conductance of Ni(II) complex in DMF is

SCHEME 2: Mass fragmentation pattern of the Schiff base L (HBS), ligand.

TABLE 1: Physical data of ligand (HBS) and corresponding metal complexes.

Ligand/complex Mol. formula	(Yield) % M.wt	Colour	M.P. °C (L : M)	Elemental analyses (Found) Calc. %			
				C	H	N	M
L (HBS)	(83.73)	Yellow	72	(73.65)	(7.77)	(8.59)	
C ₂₀ H ₂₄ N ₂ O ₂	324			74.07	7.41	8.64	
1-[Mn ₂ (L) ₂ (H ₂ O) ₄]	(43.64)	Dark	>300	(57.59)	(5.76)	(6.51)	(12.67)
C ₄₀ H ₅₂ N ₄ O ₈ Mn ₂	826.08	green	(1 : 2)	58.10	6.29	6.77	13.33
2-[Fe ₂ (H ₂ L)(NO ₃) ₆ (H ₂ O) ₂].6H ₂ O	(66.25)	Reddish	>300	(24.6)	(3.95)	(10.9)	(12.08)
C ₂₀ H ₄₀ N ₈ O ₂₈ Fe ₂	952	brown	(1 : 2)	25.21	4.20	11.76	11.76
3-[Co ₂ (HL) ₂ (NO ₃) ₂ (H ₂ O) ₂]	(30.23)	Dark	>300	(50.67)	(5.35)	(9.70)	(13.08)
C ₄₀ H ₅₀ N ₆ O ₁₂ Co ₂	923.8	green	(1 : 1)	51.95	5.41	9.09	12.70
4-[Ni ₂ (L)(NO ₃) ₂ (H ₂ O) ₆]	(35.43)	Green	>300	(36.12)	(4.19)	(8.76)	(17.83)
C ₂₀ H ₃₄ N ₄ O ₁₄ Ni ₂	671.4		(1 : 2)	35.75	5.05	8.33	17.49
5-[Cu ₂ (HL) ₂ (Ac) ₂ (H ₂ O) ₂]	(47.00)	Dark	>300	(57.06)	(5.94)	(6.70)	(13.80)
C ₄₄ H ₅₆ N ₄ O ₁₀ Cu ₂	927.3	green	(1 : 1)	56.95	6.04	6.04	13.70
6-[Zn ₂ (HL) ₂ (Ac) ₂ (H ₂ O) ₂]	(78.63)	Yellowish	>300	(57.55)	(5.10)	(6.24)	(13.41)
C ₄₀ H ₄₈ N ₄ O ₆ Zn ₂	930.8	white	(1 : 1)	56.72	6.01	6.02	13.85

SCHEME 3: Continued.

SCHEME 3: Mass fragmentation pattern of $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$.

SCHEME 4: Continued.

SCHEME 4: Mass fragmentation pattern of $[\text{Ni}_2(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_6]$.

$4.20\ \mu\text{S}/\text{cm}$. The low value of conductance indicated that complex is nonelectrolyte.

$\text{Zn}(\text{II})$ chelate is diamagnetic and has octahedral geometry, and the electronic spectra show absorption bands at 367.24 nm attributed to charge transfer. The conductance of $\text{Zn}(\text{II})$ and complexes in DMF is $6.12\ \mu\text{S}/\text{cm}$. The low value of conductance indicated that complex is nonelectrolyte. Electronic spectral studies, magnetic studies and conductance of the metal complexes of ligand L (HBS) are given in Table 4.

3.2. IR Spectra. Chemical reaction at the amino group of 1,6-hexanediamine with salicylaldehyde would affect massively the molecular symmetry of 1,6-hexanediamine. The infrared

spectrum of 1,6-hexanediamine is therefore basically retained for the reaction product. Some spectral changes are expected to appear as being associated with the formation of new species at the expense of vanished amino group. Confirming this is the disappearance of the vibrational absorptions characteristic of the amino group at 3200 cm^{-1} and 3120 cm^{-1} (asymmetric and symmetric of NH_2 group, resp.). Consistent with the shift and change of intensity for methylene group at 2930 cm^{-1} and 2854 cm^{-1} asymmetric and symmetric of CH_2 , 1460 cm^{-1} corresponding δ asymmetric CH_2 in plane bending, 1400 cm^{-1} δ symmetric CH_2 in plane bending and 881 cm^{-1} (γ CH_2 out of plane deformation). At the expense of vanished amino group species, new spectral absorption

TABLE 2: Important IR bands of HBS ligand and its complexes (1–6) with their assignments.

Ligand/complex	ν_{OH}	ν_{CH} aromatic	ν_{CH} sym./asym.	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{NO}_3^-}$	ν_{Ac^-}
L (HBS)	3445 (br)	3061 (w)	2931 (m) 2897 (w)	1631 (v.s)	1162 (w)	—	—	—	—
1-[Mn ₂ (L) ₂ (H ₂ O) ₄]	3399 (br)	3052 (v.w)	2927 (m) 2856 (w)	1608 (v.s)	1145 (m)	454 (v.w)	407 (w)	—	—
2-[Fe ₂ (H ₂ L)(NO ₃) ₆ (H ₂ O) ₂].6H ₂ O	3356 (br)	—	2919 (w) 2851 (w)	1629 (m)	1047 (w)	581 (v.w)	427 (m)	1382 (s) 1047 (w) 837 (w)	—
3-[Co ₂ (HL) ₂ (NO ₃) ₂ (H ₂ O) ₂]	3425 (br)	3056 (v.w)	2924 (m) 2854 (w)	1614 (v.s)	1139 (w)	586 (w)	463 (v.w)	1320 m 1028 (w) 850 (w)	—
4-[Ni ₂ (L)(NO ₃) ₂ (H ₂ O) ₆]	3424 (br)	—	2925 (m) 2856 (w)	1616 (s)	1142 (w)	462 (w)	395 (w)	1323 (w) 1039 (w) 754 (w)	—
5-[Cu ₂ (HL) ₂ (Ac) ₂ (H ₂ O) ₂]	3446 (br)	3020 (v.w)	2919 (m) 2849 (w)	1624 (v.s)	1147 (m)	522 (w)	470.(w)	—	1535 (s) 1347 (w)
6-[Zn ₂ (HL) ₂ (Ac) ₂ (H ₂ O) ₂]	3418 (br)	3011 (v.w)	2922 (m) 2850 (m)	1622 (v.s)	1188 (m)	457 (w)	411 (m)	—	1535 (s) 1347 (w)

TABLE 3: Electronic spectral data of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II)-HBS complexes.

Complex	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$ and C.T. (nm)	d-d transition	Magnetic moment	Conductance $\mu\text{S}/\text{cm}$
1-[Mn ₂ (L) ₂ (H ₂ O) ₄]	256, 316	987.19	5.65	25.8
2-[Fe ₂ (H ₂ L)(NO ₃) ₆ (H ₂ O) ₂].6H ₂ O	257, 276, 415	—	5.08	7.18
3-[Co ₂ (HL) ₂ (NO ₃) ₂ (H ₂ O) ₂]	247, 271	—	1.87	3.22
4-[Ni ₂ (L)(NO ₃) ₂ (H ₂ O) ₆]	267, 322, 369	656 734	2.52	4.20
5-[Cu ₂ (HL) ₂ (Ac) ₂ (H ₂ O) ₂]	272, 305, 363	697	2.73	4.86
6-[Zn ₂ (HL) ₂ (Ac) ₂ (H ₂ O) ₂]	298, 367	—	0.93	6.12

(Figure 1) appears to be associated with the newly formed species. Consistent with this is the appearance of new absorption at 3445 cm^{-1} (broad) characteristic of ν_{OH} stretch and appear anew absorption band at 1631 cm^{-1} characteristic of $\nu_{\text{C=N}}$ stretch. Also vibrational absorption characteristic of the benzene ring vibrations and OH should therefore appear to confirm the chemical reaction. Indeed, new characteristic absorption bands appear at 1502 and 1460 cm^{-1} which are characteristic of the benzene ring vibration. New absorption appear at 1280 and 763 cm^{-1} can be assigned to the deformation consistent with this is the appearance of new absorption characteristic of $\nu_{\text{C-O}}$ which appears at 1211 cm^{-1} . The most important bands in the IR spectrum of the complexes are compared to their ligands in Table 2 along with their tentative assignment. The positions of these bands provide significant indications regarding the bonding sites of the ligand molecule when complexed to metal cations, hydroxyl group in ortho position, and imino group. The ν_{OH} band at 3445 cm^{-1} is absent from the IR spectra of the ligand which overlapped with H₂O coordinate, but it can be indicated by shift of the $\nu_{\text{C-O}}$ band. But the ν_{OH} (H₂O coordination) at 3421 cm^{-1} is present, indicating that central metal is coordinated by water

molecule and OH in ortho position. This coordination is confirmed by the presence of two new bands in the range of $\nu_{\text{M-O}}$ therefore different of nature of oxygen. Further in the spectrum of ligand the medium band observed at 1631 cm^{-1} can be characterized by $\nu_{\text{C=N}}$ frequency. This vibrational absorption characteristic to C=N shift towards lower wave number by $20\text{--}35\text{ cm}^{-1}$ Table 2 in the spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to central metal atom these complexes consistent with this the metal-nitrogen bond are indicated by the absorptions in the region $454\text{--}586\text{ cm}^{-1}$ from IR data [14, 15], it can be inferred that the (L) 1,6-hexanediamine function as bidentate at each end of L through their hydroxyl oxygen and azomethine N atom. Also, all the complexes show bands due to the metal-nitrogen and metal-oxygen bonds.

The NO_3^- ion is coordinated to the metal ion as unidentate in case of complexes (1), (2), (3), and (4) with C_2v symmetry. Each unidentate nitrate group has three nondegenerate modes of vibrations (ν_s , ν'_s , and ν_{as}) which appeared in the ranges ($1315\text{--}1360$), ($1040\text{--}1028$), and ($810\text{--}830$) cm^{-1} [16].

On the other hand, acetate anion can, however, coordinate in monodentate, bidentate, or bridging bidentate

TABLE 4: Solid State of the Elictrical Conductivity for ligand (HBS) and its metal complexes(1-6)

Compound	T _c (°K)	E ₁ (eV) at lower temp.	E ₂ (eV) at higher temp.	σ_1 ($\Omega^{-1}\text{cm}^{-1}$) at 298 K	σ_2 ($\Omega^{-1}\text{cm}^{-1}$) at higher temp (°K)
L (HBS)	—	—	0.0116	1.435×10^{-11}	5.622×10^{-10}
Mn(II)	378 K	0.062	1.945	3.708×10^{-11}	2.233×10^{-8}
Fe(III)	369 K	0.098	0.540	1.035×10^{-10}	1.289×10^{-8}
Co(II)	488 K	0.0039	1.848	1.370×10^{-11}	1.100×10^{-9}
Ni(II)	—	—	0.0109	9.171×10^{-12}	1.696×10^{-11}
Cu(II)	—	—	0.0059	5.135×10^{-12}	1.005×10^{-11}
Zn(II)	—	0.0042	—	1.435×10^{-11}	5.617×10^{-11}

T_c: transition temperature for the ligand and metal complexes; E₁: activation energy in the lower temperature; E₂: activation energy in the higher temperature; σ_1 : electrical conductivity measured at lower temperature; σ_2 : electrical conductivity measured at higher temperature.

FIGURE 1: Infrared spectra of L (HBS), Mn(II), Fe(III), Co(II), and Ni(II)-HBS complexes.

FIGURE 2: ¹H-NMR spectrum of ligand L (HBS). FIGURE 3: ¹H-NMR spectrum of [Zn₂(HL)₂(Ac)₂(H₂O)₂].

FIGURE 4: Mass spectrum of the Schiff base L (HBS), ligand.

manner [17]. The monodentate behavior of acetate group in the investigated complex is deduced from the frequency difference ($\Delta\nu$) between ν_{asCOO^-} and ν_{sCOO^-} . The value is higher than 185 cm^{-1} indicating a monodentate behavior.

3.3. ¹H-NMR Spectra. The ¹H-NMR of L shows four types of signals: methylene protons, aromatic protons, hydroxyl, and azomethine proton at 1.194–3.519 ppm, 6.6–7.4 ppm, 8.3–8.5 ppm, and 13.4–13.6 ppm, respectively. The signals of methylene are not influenced corresponding to chelation, but

FIGURE 5: TGA curve of $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$. FIGURE 6: TGA curve of $[\text{Cu}_2(\text{HL})_2(\text{Ac})_2(\text{H}_2\text{O})_2]$. FIGURE 7: TGA curve of $[\text{Zn}_2(\text{HL})_2(\text{Ac})_2(\text{H}_2\text{O})_2]$. FIGURE 8: Electrical conductivity of $[\text{Mn}_2(\text{L})_2(\text{H}_2\text{O})_4]$. FIGURE 9: Electrical conductivity of $[\text{Fe}_2(\text{H}_2\text{L})(\text{NO}_3)_6(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$. FIGURE 10: Electrical conductivity of $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$.

the multiplet due to the aromatic protons is broader and shifts to lower field, indicating that the chelation perturbs the electron density distribution through the phenyl ring to some extent. The hydroxyl signal at 13.4 ppm disappeared and azomethine signal was shifted, thus indicating that $\text{CH}=\text{N}$ and OH group are involved in chelation. Figure 2 depicts ^1H -NMR of ligand **L**.

The $\text{Zn}(\text{II})$ complex is diamagnetic as expected, and its geometry is octahedral. The ^1H -NMR spectrum of $\text{Zn}(\text{II})$ complex, $[\text{Zn}_2(\text{HL})_2(\text{Ac})_2(\text{H}_2\text{O})_2]$ in $\text{CF}_3\text{COOD} + \text{DMSO}-d_6$, is shown in Figure 3.

It is observed that the signals of methylene are influenced by chelation, but the multiplet due to the aromatic protons is broader and shifts to lower field, indicating that the chelation perturbs the electron density distribution through the phenyl ring to some extent. The hydroxyl signal and the azomethine signal are shifted, thus indicating that $\text{CH}=\text{N}$ and OH groups are involved in chelation.

FIGURE 11: Representative structures of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II)-HBS complexes.

3.4. Mass Spectra. The electron impact mass spectrum of the free ligand confirmed the proposed formula of ligand by showing a peak at 324 due to molecular ion (parent peak). The series of peaks, in the ranges of 65, 76, 77, 91, 93, 94, 107, 123, 121, 121, 119, 120, 134, 148, 162, 176, 190, 204, 230, and 231, may be corresponding to various fragments, and their intensity gives an idea of stability fragments (Figure 4). Mechanism Scheme 2. The mass spectrum of Co(II) complex, $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$, the proposed formula of the complex by showing a base peak at 381.9 m/z . The series of peaks at 380.9, 364.9, 288.9, 261.9, 247.9, 233.9, 219.9, 205.9, 191.9, 177.9, 120, 119, 93, 76, 77, and 51 m/z may correspond to various fragments, and their intensity gives an idea of the stability of these fragments. The mass fragmentation pattern of $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ is depicted in Scheme 3.

The mass spectrum of Ni(II) complex $[\text{Ni}_2(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_6]$ confirms the proposed formula of the complex by showing a base peak at 380.7 m/z . The series of peaks at 380.7, 364.7, 288.7, 261.7, 247.7, 233.7, 218.7, 191.7, 177.7, 150.7, 92, 93, 77, 76, and 51 m/z may correspond to the various fragments, and their intensity gives an idea of the stability of these fragments. The mass fragmentation pattern of $[\text{Ni}_2(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_6]$ is depicted in Scheme 4.

3.5. Thermogravimetric Analysis. TGA curve of $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ shows four stages. The first one from 25 to 252°C corresponds to loss of two coordinated water molecules and N_2O_4 (Calc./Found %; 13.855/13.734%) from

the total weight of the complex. The second stage from 252 to 335°C corresponds to the loss of $\text{C}_7\text{H}_5\text{NO}_2$ (Calc./Found %; 16.964/16.852%). Third stage from 335 to 359°C corresponds to the loss of $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}$ (Calc./Found %; 34.806/33.865%). The last stage from 359 to 800°C corresponds to loss of C_5H_{10} (Calc./Found %; 16.248/16.867%). Figure 5 shows the TGA curve of $[\text{Co}_2(\text{HL})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$.

TGA curve of $[\text{Cu}_2(\text{HL})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ complex shows three stages. The first one is from 25 to 258°C with loss of coordinated water molecules (Calc./Found %; 3.88/3.38%) from the total weight of the complex. The second stage from 258 to 296°C corresponds to the loss of two acetate groups and $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$ (Calc./Found %; 29.62/29.11%). The third stage is from 296 to 650°C and due to the gradual decomposition of the complex it corresponds to the loss of $\text{C}_8\text{H}_{14}\text{N}_2\text{O}_2$ & C_7H_7 (Calc./Found %; 41.61/41.63%). Figure 6 shows the TGA curve of $[\text{Cu}_2(\text{HL})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$.

TGA curve of $[\text{Zn}_2(\text{HL})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ complex shows four stages. The first one from 25 to 400°C corresponds to the loss of two coordinated water molecules, two acetate groups, and two $\text{N}=\text{CH}$ (Calc./Found %; 22.346/22.530%) from the total weight of the complex. The second stage from 400 to 500°C corresponds to the loss of C_3H_6 (Calc./Found %; 5.811/5.344%). The third stage from 500 to 581°C corresponds to the loss of C_2H_4 (Calc./Found %; 4.112/3.856%). The last stage from 581 to 800°C corresponds to loss of $\text{C}_2\text{H}_3\text{N}$ (Calc./Found %; 6.280/6.734%). Figure 7 shows the TGA curve of $[\text{Zn}_2(\text{HL})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$.

3.6. *The Electrical Conductivity of the Metal Complexes of Ligand L (HBS).* The values of the electrical conductivity (σ) and activation energies of the metal complexes of ligand L (HBS) with Mn(II), Fe(III), Co(II), and Ni(II) are collected in Table 4. They lie in the range of semiconducting materials. The activation energy of thermal decomposition step is determined from the slope of the straight line of $\ln \sigma$ and $1/T$ (K) relationship. Blotting $\ln \sigma$ against $1/T$ (K), as shown in Figures 8, 9, and 10, of the investigated complexes yielded two lines over the given temperature ranges and obeyed Arrhenius equation. This may be due to phase transition or packing or change of chemical structure during the increase of temperature.

4. Conclusion

In conclusion, the Schiff bases derived from 1,6-hexanediamine are bonded to the metal ions as tetradentate ligand. The two bonding sites are the oxygen of the deprotonated hydroxyl group of benzene ring and nitrogen of azomethine which lead to stable six-membered chelating ring. The experimental data suggest the structure shown in Figure 11 for metal chelates under investigation.

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