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Research Article

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Syntheses, spectral characterization, thermal properties and DNA cleavage studies of a series of Co(II), Ni(II) and Cu(II) polypyridine complexes with some new schiff-bases derived from 2-chloro ethyl amine

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Abstract: In the present study nine polypyridine complexes $[M(N–N)_2(L^{1–3})](OAc)_2.(nH_2O)$; M = Ni(II), Co(II) and Cu(II); $(N\text{-}N)_2$ = 1,10-phenanthroline $(phen)_2$; $(L^{1–3})$ = ligands derived from 2-chloro ethyl amine, 2-hydroxy-3,5-diiodo benzaldehyde L^1/ 2-hydroxy-1-naphthaldehyde L^2 and 2-hydroxy-3,5-diiodo acetophenone L^3 have been synthesized. The structures of the compounds were determined with the aid of elemental analysis and FT-IR, UV-Vis.,^{1}H NMR, ESR spectroscopic methods, magnetic measurements and conductance measurements, further analyzed by powder XRD and thermal studies. FT-IR, UV-Vis. and ^{1}H-NMR spectral studies indicate the ligands are bidentate. The observed anisotropic *g* values indicate the presence of Cu(II) in an octahedral environment. The powder XRD patterns of complexes recorded in the range (2θ = 0–80°) and average crystallite size (d_{XRD}) was calculated using Scherrer's formula. Thermal decomposition profiles of complexes show high decompound temperatures indicating a good thermal stability. Binding of the complexes with calf thymus DNA (CT DNA) has been investigated by gel electrophoresis.

Keywords: 2-chloro ethyl amine, Schiff bases,1,10-phenanthroline and polypyridine complexes.

1. INTRODUCTION

Schiff base containing nitrogen and oxygen donor atoms and their transition metal complexes play an important role in inorganic research due to their unique coordinative and pharmaceutical properties [1-5]. They have been extensively studied in great details for their various crystallographic, structural and magnetic features. They also play important roles in supramolecular assemblies, metallo-dendrimers and formation of stable complexes [6,7]. Among these, polypyridine complexes of Schiff base ligands do have significant interest because of their excellent chemical, electrochemical and photochemical properties as well as potential biological applications such as antitumor, anticandida, antimycobacterial and antimicrobial activities [8-10]. Furthermore, the interaction of these complexes with DNA has gained

much attention due to their possible applications as new therapeutic agents [11-13]. Present investigation deals with the syntheses, spectral characterization, thermal properties and DNA cleavage studies of series of Co(II), Ni(II) and Cu(II) polypyridine complexes with three new Schiff base ligands derived from 2-chloro ethyl amine.

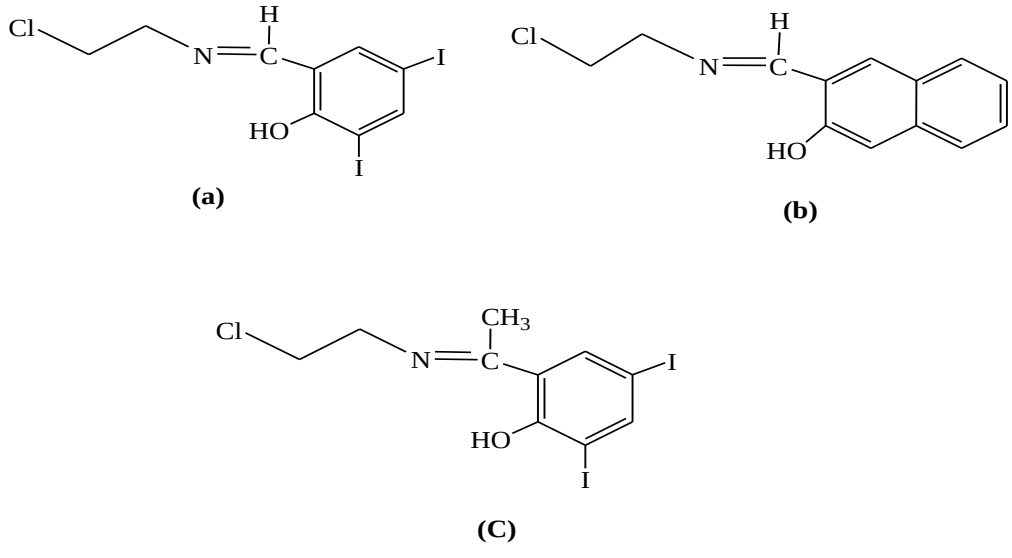
2. EXPERIMENTAL

2.1. Materials

The metal precursor complexes $[Ni(phen)_2](OAc)_2.4H_2O$, $[Co(phen)_2](OAc)_2.6H_2O$, and $[Cu(phen)_2](OAc)_2.H_2O$ were synthesized by a method similar to one described previously [14]. All other chemicals were purchased from Aldrich and used without further purification.

2.2. Physical Measurements

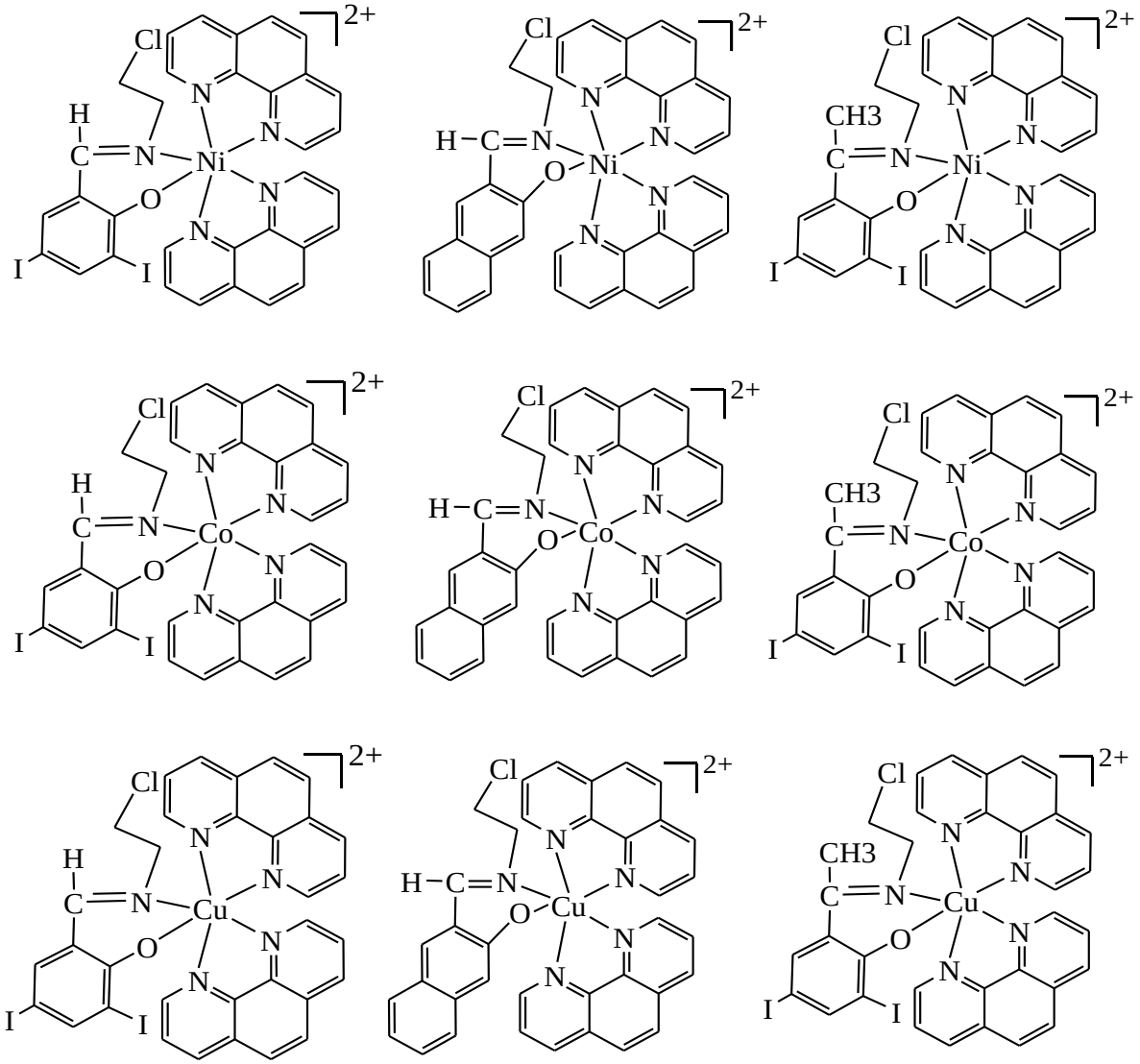
The elemental analysis for C, H and N was done using a Perkin-Elmer elemental analyzer and analysis of metal was carried out by EDTA titration method. ^{1}H-NMR spectra were obtained on a Bruker AM400 MHz instrument with Me_4Si as internal reference. The IR spectra were recorded on a JASCO FT/IR-410 spectrometer in the range 4000–400 cm^{-1} using KBr disc method. Electronic spectra were recorded on a Perkin Elmer Lambda-25 UV/Vis spectrometer in the range 200–600 nm. Magnetic susceptibility measurement were carried out by the Gouy method at room temperature using $Hg[Co(SCN)_4]$ as a reference for callibrant. Conductivities of a 10^{-3} M solution of the complexes were measured in DMSO at 25 ºC using a CMD 750 WPA model conductivity meter. Powder XRD was recorded on a Rigaku Dmax X-ray diffractometer with Cu Ka radiation. ESR measurements (solid state) at room temperature were carried out using a Varian E-109, X-band spectrometer. Thermal analysis was carried out in air (25-700 ºC) using a Shimadzu DT-30 thermal analyzer.



Scheme 1. Structure of ligands (a) L^1, (b) L^2 and (c) L^3.

2.3. Synthesis of ligands

The Schiff base ligands were synthesized according to the general procedure. An ethanolic solution of 2-chloro ethyl amine and 2-hydroxy-3,5-diiodo benzaldehyde L^1/2-hydroxy naphthaldehyde L^2 or 2-hydroxy-3,5-diiodo acetophenone L^3 (1mmol) was boiled under reflux for 2h. in presence of catalytic amount of $SnCl_2.2H_2O$. The structures of ligands are presented in Scheme 1**.**



Scheme 2. Proposed structure of metal complexes (4)–(12).

2.4. Synthesis of complexes

The complexes were prepared by refluxing a solution of (1 mmol) of metal precursor complexes $[Ni(phen)_2](OAc)_2.4H_2O$, $[Co(phen)_2](OAc)_2.6H_2O$ and $[Cu(phen)_2](OAc)_2.H_2O$ with the respective ligands L^1–L^3 (1 mmol) in aqueous ethanol (20 ml) for 4h. The solid obtained were filtered, washed with ethanol and then dried. The proposed structures of complexes are shown in Scheme 2.

Table 1. Physical and analytical data of ligands and their complexes.

No.	Compound	Formula	M.W.	Yield	Elemental analysis(%) Found/(Calcd.) (%)			
					C	H	N	M
(1)	L^1	$C_9H_9NOCl_2I_2$	472	85	21.63(22.88)	1.85(1.90)	3.44(2.96)	–
(2)	L^2	$C_{10}H_{11}NOCl_2I_2$	270	90	23.81(24.69)	1.96(2.26)	3.13(2.88)	–
(3)	L^3	$C_{13}H_{13}NO\ Cl_2$	486	78	56.89(57.77)	3.92(4.81)	4.71(5.18)	–
(4)	$[Ni(phen)_2(L^1)](OAc)_2$	$C_{37}H_{30}N_5O_5Cl_2I_2Ni.4H_2O$	1080	90	40.92(41.11)	3.80(3.51)	6.90(6.48)	4.80(5.46)
(5)	$[Ni(phen)_2(L^2)](OAc)_2$	$C_{41}H_{34}N_5O_5Cl_2Ni.4H_2O$	978	78	59.96(60.53)	4.25(4.29)	7.21(7.15)	5.65(6.03)
(6)	$[Ni(phen)_2(L^3)](OAc)_2$	$C_{38}H_{35}N_5O_5Cl_2I_2Ni.4H_2O$	1094	80	41.14(41.68)	3.44(3.65)	6.13(6.39)	5.21(5.39)
(7)	$[Co(phen)_2(L^1)](OAc)_2$	$C_{37}H_{30}N_5O_5Cl_2I_2Co.4H_2O$	1080	90	40.89(41.11)	3.31(3.51)	6.58(6.48)	5.14(5.46)
(8)	$[Co(phen)_2(L^2)](OAc)_2$	$C_{41}H_{34}N_5O_5Cl_2Co.4H_2O$	978	78	60.13(60.53)	4.25(4.29)	7.10(7.15)	5.73(6.03)
(9)	$[Co(phen)_2(L^3)](OAc)_2$	$C_{38}H_{35}N_5O_5Cl_2I_2Co.4H_2O$	1094	80	41.92(41.68)	3.80(3.65)	5.97(6.39)	5.18(5.39)
(10)	$[Cu(phen)_2(L^1)](OAc)_2$	$C_{37}H_{30}N_5O_5Cl_2I_2Cu..H_2O$	1031	90	43.48(43.06)	2.79(3.10)	6.71(6.78)	5.90(6.20)
(11)	$[Cu(phen)_2(L^2)](OAc)_2$	$C_{41}H_{34}N_5O_5Cl_2Cu.H_2O$	929	78	63.16(63.72)	3.25(3.87)	7.17(7.53)	5.81(6.03)
(12)	$[Cu(phen)_2(L^3)](OAc)_2$	$C_{38}H_{32}N_5O_5Cl_2I_2Cu.H_2O$	1045	80	43.12(43.63)	3.10(3.25)	6.33(6.69)	5.94(6.12)

2.5. DNA cleavage studies

For the gel electrophoresis study super coiled pBR 322 DNA (0.1 μg) was treated with the complexes in 50 mM tris-HCl, 18 mM NaCl buffer (pH 7.2), and then the solution was incubated in dark for (1 hr) was irradiated for 30 min inside the sample chamber of Perkin-Elmer LS 55 spectroflurometer (λ_{ex} = 456 $\pm$ 5 nm, slit width = 5 nm, slit width = 5 nm). The samples were analyzed by electrophoresis for 30 min at 75 V in Tris-acetate buffer containing 1% agarose gel. The gel was stained with 1 $\mu g/ml^{-1}$ ethidium bromide and photographed under UV light.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis

Elemental analysis data confirmed that the complexes have a 1:2:1 molar ratio between the metal and ligands. i.e. one mole of metal salt reacted with two moles of 1,10-phenanthroline and one mole of ligands L^1/L^2 or L^3 to give the corresponding metal complexes. The elemental analysis data for ligands and complexes is given in Table.1. All the compounds show the analytical results close to the theoretical values indicating the presence of two types of ligands.

3.2. IR Spectra

The IR spectral data of ligands and their complexes are given in Table 2. The spectra of free Schiff base ligands L^1, L^2 and L^3 showed the broad bands at 3444 cm^{-1} were due to stretching vibrations of phenolic OH [15-17]. These bands were absent in all the complexes, indicating deprotonation on coordination of the Schiff base ligands to metal ion. In addition, the bands at 1346–1350 cm^{-1} attributed to the phenolic C–O stretching vibrations of the free ligands were blue-shifted to 1341–1431 cm^{-1} upon complexation suggesting the involvement of the phenolic oxygen atom in the coordination [18-20]. The imine (C=N) functional group of the free ligands was observed as strong bands between 1670–1643 cm^{-1} were red-shifted to 1642–1586 cm^{-1} in the spectra of the complexes, indicating coordination of azomethine nitrogen of the Schiff base ligands to metal ion [21-23]. Thus it can be concluded that the schiff bases are bidentate, coordinating via phenolic O and the azomethine N. Furthermore, the infrared spectra of free Schiff base ligands showed the bands at 3070–3093 cm^{-1} and 2877–2889 cm^{-1} were due to the stretching vibrations of (C–H) and (CH_2). The bands observed at 1296–1249 cm^{-1} and 655–582 cm^{-1} were due to the stretching vibrations of (C–N) and (C–Cl) [24,25]. These bands were shifted to negative frequencies after complexations. The presence of water molecules in the complexes was indicated by broad absorption bands at 3425–3390 cm^{-1}. The mode of coordination of the Schiff base ligands was further supported by the appearance of two new weak bands in the lower frequency region at 570–520 cm^{-1} and 478–416 cm^{-1}. These bands were assigned to the M–N and M–O stretching vibrations, respectively [19,16].

3.3. Electronic Spectra

The electronic spectra of the ligands and their metal complexes in DMSO solvent, magnetic moments and molar conductivities are given in Table 3. Three absorption bands were observed in the electronic spectra of the free Schiff base ligands L^1, L^2 and L^3 in the 264–430 nm, 264–435 nm and 261–434 nm range respectively were assigned to π–π* and n–π* transitions. The bands observed at 350 nm, 316 nm and 349 nm were assigned to the π–π* transitions of the azomethine, which were shifted to 411–437 nm range in the electronic spectra of complexes indicating the azomethine nitrogen was involved in coordination [20,21]. The bands observed at 264 nm were assigned to the π–π* transitions of the phenol [25]. The absorption bands at about 270 nm were originated from π–π* transitions of phenanthroline ring in all the complexes [16,17]. The electronic spectra of Ni(II) complexes exhibited three well defined bands in the range of 250–450 nm. These bands were assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions

which corresponds to octahedral geometry [26,27]. The electronic spectra of Co(II) complexes exhibited three bands in the range of 261–529 nm. These bands were assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions which corresponds to octahedral geometry. Cu(II) complexes exhibited three bands in the range of and 256–421 nm. These bands were assigned to $^2A_{1g} \rightarrow {}^2B_{1g}$ and $^2Eg \rightarrow {}^2B_{1g}$ transitions which corresponds to octahedral geometry [28,29]. The weak absorption bands in the spectra of complexes were contribution from spin allowed metal to ligand charge transfer, MLCT [20].

Table 2. IR spectral (cm^{-1}) assignment of ligands and their complexes.

Compound	Assignment (cm^{-1})									
	ν(OH), H_2O	ν(OH), phenol	ν(C=N),	ν(C=O),	ν(C–N),	ν(C–H),	ν(CH_2),	ν(C–Cl),	ν(M–N),	ν(M–O)
(1)	–	3444	1662	1346	1296	3070	2877	632	–	–
(2)	–	3421	1670	1350	1269	3093	2877	582	–	–
(3)	–	3444	1643	1346	1249	3074	2889	655	–	–
(4)	3400	–	1614	1431	1239	3053	2860	631	570	416
(5)	3413	–	1586	1426	1220	3050	2870	641	520	420
(6)	3421	–	1625	1427	1225	3060	2860	661	525	423
(7)	3425	–	1642	1360	1239	3050	2870	619	559	478
(8)	3421	–	1607	1347	1218	3055	2860	620	559	465
(9)	3405	–	1619	1341	1224	3049	2874	619	552	467
(10)	3390	–	1609	1425	1213	3069	2829	619	557	427
(11)	3398	–	1619	1426	1211	3055	2830	620	569	425
(12)	3390	–	1610	1425	1215	3060	2830	620	560	425

The molar conductance data of the complexes were measured in DMSO solution for the 0.001 M solutions. The Ni(II) complexes showed the molar conductivity in the range of 143.27–145.65 Ω^{-1} cm^2 mol^{-1} indicating that it is 2:1 type of electrolyte. The Co(II) complexes showed the molar conductivity in the range of 71.64–74.72 Ω^{-1} cm^2 mol^{-1} indicating that it is 1:1 type of electrolyte. The Cu(II) complexes were non electrolytes due to their low values of molar conductivity in the range of 11–14 Ω^{-1} cm^2 mol^{-1} [33].

Table 3. Electronic spectral data (nm) of the ligands and their metal complexes in DMSO solvent , magnetic moments and molar conductivities.

S. no.	Compound	Electronic absorption bands (nm)	Λc (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
(1)	L^1	264, 280, 350, 430	–	–
(2)	L^2	264, 316, 356, 435	–	–
(3)	L^3	261, 290, 349, 434	–	–
(4)	$[Ni(phen)_2(L^1)](OAc)_2$	250, 276, 414	143.27	3.15
(5)	$[Ni(phen)_2(L^2)](OAc)_2$	270, 310, 412, 450	147.91	1.42
(6)	$[Ni(phen)_2(L^3)](OAc)_2$	265, 315, 437	145.65	2.73
(7)	$[Co(phen)_2(L^1)](OAc)_2$	261, 360, 411, 529	72.39	4.62
(8)	$[Co(phen)_2(L^2)](OAc)_2$	265, 371, 427	74.72	4.58
(9)	$[Co(phen)_2(L^3)](OAc)_2$	266, 350, 433	71.64	4.86
(10)	$[Cu(phen)_2(L^1)](OAc)_2$	256, 279, 421	12.00	1.84
(11)	$[Cu(phen)_2(L^2)](OAc)_2$	263, 318, 402	11.00	1.79
(12)	$[Cu(phen)_2(L^3)](OAc)_2$	267, 290, 414	14.00	1.91

The magnetic moment values for the Ni(II) complexes lies in the range 1.42–3.15 B.M. corresponding to two unpaired electrons which may be considered to possess an octahedral geometry [26,30]. The magnetic moment values for the Co(II) complexes reported here in the range 4.58–4.86 B.M. show that there are three unpaired electrons indicating a high spin octahedral configuration [31]. Cu(II) complex has magnetic moment value 1.79–1.91 B.M. corresponding to one unpaired electron which offer possibility of octahedral geometry [32].

3.4. ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of ligands and their complexes were recorded in DMSO as a solvent are summarized in Table 4. The ^{1}H-NMR spectra of ligands L^1, L^2 and L^3 displayed broad signals at 9.90–11.80 ppm were assigned to OH of phenol [15-17]. The metal complexes of these ligands did not show any proton signal to the phenolic OH range suggesting the participation of phenolic oxygen in

Table 4. ^{1}H-NMR data (in DMSO-d_6) for the ligands and their complexes.

S. no.	Compound	NMR band shift: δ ppm
(1)	L^1	2.40(s, 4H, CH_2–CH_2), 8.10(s, 2H, ArH), 8.30(s, 1H, ArH), 9.90(s, 1H, OH)
(2)	L^2	2.40(s, 4H, CH_2–CH_2), 7.20(d, 1H, ArH), 7.40(t, 2H, ArH), 7.60(t, 1H, ArH), 7.85(d, 1H, ArH), 8.10(d, 1H, ArH), 8.90(d, 1H, ArH), 10.81(s, 1H, OH)
(3)	L^3	2.40(s, 4H, CH_2–CH_2), 2.75(s, 3H, CH_3), 7.70(d, 1H, ArH), 8.10(d, 1H, ArH), 11.80(s, 1H, OH)
(4)	$[Ni(phen)_2(L^1)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 7.60(s,2H, ArH), 7.90(d, 1H, ArH), 8.20(s, 6H, phen protons), 8.60(s, 4H, phen protons), 8.80(s,.6H, phen protons)
(5)	$[Ni(phen)_2(L^2)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 7.10(t, 2H, ArH), 7.30(m, 2H, ArH), 7.50(d, 2H, ArH), 7.70(q, 1H, ArH), 7.90(t, 4H, phen protons), 8.20(d, 6H, phen protons), 8.70(s, 4H, phen protons), 9.00(s, 2H, phen protons)
(6)	$[Ni(phen)_2(L^3)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 2.65(s, 3H, CH_3), 7.50(s, 1H, ArH), 7.80(s, 1H, ArH), 8.00(s, 4H, phen protons), 8.30(s, 4H, phen protons), 8.80(d, 4H, phen protons), 8.90(s, 4H, phen protons)
(7)	$[Co(phen)_2(L^1)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 7.50(s,2H, ArH), 7.85(d, 1H, ArH), 8.00(s, 6H, phen protons), 8.10(s, 4H, phen protons), 8.60(s,.6H, phen protons)
(8)	$[Co(phen)_2(L^2)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 7.20(s, 2H, ArH), 7.50(m, 4H, ArH), 7.60(s, 1H, ArH), 8.00(s, 6H, phen protons), 8.30(d, 6H, phen protons), 8.60(s, 4H, phen protons)
(9)	$[Co(phen)_2(L^3)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 2.70(s, 3H, CH_3), 7.50(s, 1H, ArH), 7.60(s, 1H, ArH), 7.90(s, 4H, phen protons), 8.10(s, 6H, phen protons), 8.60(d, 6H, phen protons)
(10)	$[Cu(phen)_2(L^1)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 7.65(s,2H, ArH), 7.80(d, 1H, ArH), 8.00(s, 6H, phen protons), 8.20(s, 4H, phen protons), 8.60(s,.6H, phen protons)

		8.60(s, 4H, phen protons)
(11)	$[Cu(phen)_2(L^2)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 7.10(s, 2H, ArH), 7.20(m, 2H, ArH), 7.40(d, 2H, ArH), 7.60(s, 1H, ArH), 8.10(s, 4H, phen protons), 8.20(d, 6H, phen protons), 8.60(s, 4H, phen protons), 8.80(s, 2H, phen protons)
(12)	$[Cu(phen)_2(L^3)](OAc)_2$	1.90(s, 4H, CH_2–CH_2), 2.60(d, 6H, OAc), 2.70(s, 3H, CH_3), 7.50(s, 1H, ArH), 7.80(s, 1H, ArH), 8.40(s, 4H, phen protons), 8.60(s, 4H, phen protons), 8.80(d, 4H, phen protons), 8.90(s, 4H, phen protons)

coordination, after complete deprotonation. The signal due to the imine group at about 8.10 ppm as singlet provided evidence for the formation of the Schiff bases which was shifted downfield at about 7.80 ppm in the ^{1}H-NMR spectra of the complexes indicating the coordination of ligands to the metal ion through azomethine nitrogen [21-23]. A signal observed as singlet at 2.40 ppm was due to ethyl protons. The aromatic protons were appeared in the 7.20–8.90 ppm range. A signal observed as singlet at 2.75 ppm in the ^{1}H-NMR spectra of ligand L^3 was due to methyl protons [24,25]. All these protons were shifted downfield in the ^{1}H-NMR spectra of the complexes indicating the coordination of ligands to the metal ion [17]. The additional signals in the spectra of complexes at 7.90–9.00 ppm were assigned to phen protons and a signal at 2.60 ppm is due to acetate group [15,16]. The conclusions drawn from these studies lend further support to the mode of bonding discussed in their IR spectra. The number of protons calculated from the integration curves and those obtained from the values of the expected CHN analyses agree with each other.

3.5. Mass spectra

Mass spectra of ligands were performed to determine their molecular weight and fragmentation pattern. The molecular ion peaks were observed at *m/z* 472, *m/z* 270 and *m/z* 486 confirming their formula weights (FW) for L^1, L^2 and L^3 respectively, which are same as the calculated m+ values [23,25]. The mass spectra of L^1 and L^3 are shown in Figure 1.

3.6. Powder XRD

Powder XRD patterns of complexes show the sharp crystalline peaks indicating their crystalline phase. The diffraction pattern of complexes is measured in the range (2θ = 0–80°) are shown in Figure 2. The crystallite size of the complexes d_{XRD} is estimated from XRD patterns by applying full width half maximum of the characteristic peak to Scherrer's equation using the XRD line broadening method which is as follows:

$$d_{XRD} = 0.9\lambda/\text{FWHM}\cos\theta$$

where λ is the wavelength used, FWHM is the full width at half maxima, and θ is the diffraction angle.

From the observed d_{XRD} patterns, the average crystallite sizes for the Ni(II) complexes are found to be 72, 69 and 71 nm. The average crystallite sizes for the Co(II) are 67, 72 and 78 nm and for the Cu(II) complex is found to be 85, 82 and 78 nm. The appearance of crystallinity in the complexes is due to the inherent crystalline nature of metal compounds [34-36].

3.7. ESR Spectra

The X-band ESR spectra of complexes was recorded in DMSO at room temperature. The spectra of copper complexes (a) and (b) exhibited anisotropic signals with g values $g_{\|}$ = 2.17 and $g_{\perp}$ = 2.04, and $g_{\|}$ = 2.14 and $g_{\perp}$ = 2.03 respectively, which is a characteristic of the axial symmetry. The observed g-tensor values were $g_{\|}$ (2.23) > $g_{\perp}$ (2.17) > g_e (2.04) suggested the complexes have octahedral geometry [37,38]. An exchange coupling interaction between two Cu(II) ions was explained by Hathaway expression G = ($g_{\|}$ - 2)/($g_{\perp}$ - 2). If the value G > 4.0, the exchange interaction is negligible and if G < 4.0, a considerable exchange coupling is present in the complex. In the present complexes, the 'G' value (4.25) is > 4 indicating that there is no interaction in the complexes [39]. In addition the absence of a half field signal at 1600 G corresponding to DM = ±2 transitions indicates the absence of any Cu–Cu interaction in the complexes [40,41]. Kivelson have shown that for an ionic environment $g_{\|}$ is 2.3 or larger, but for a covalent environment $g_{\|}$ is less than 2.3. The $g_{\|}$ values for the present complexes were 2.17, indicating a significant degree of covalency in the metal–ligand bond [42]. ESR spectra of complexes (a) and (b) are shown in Figure 3.

(L^1)

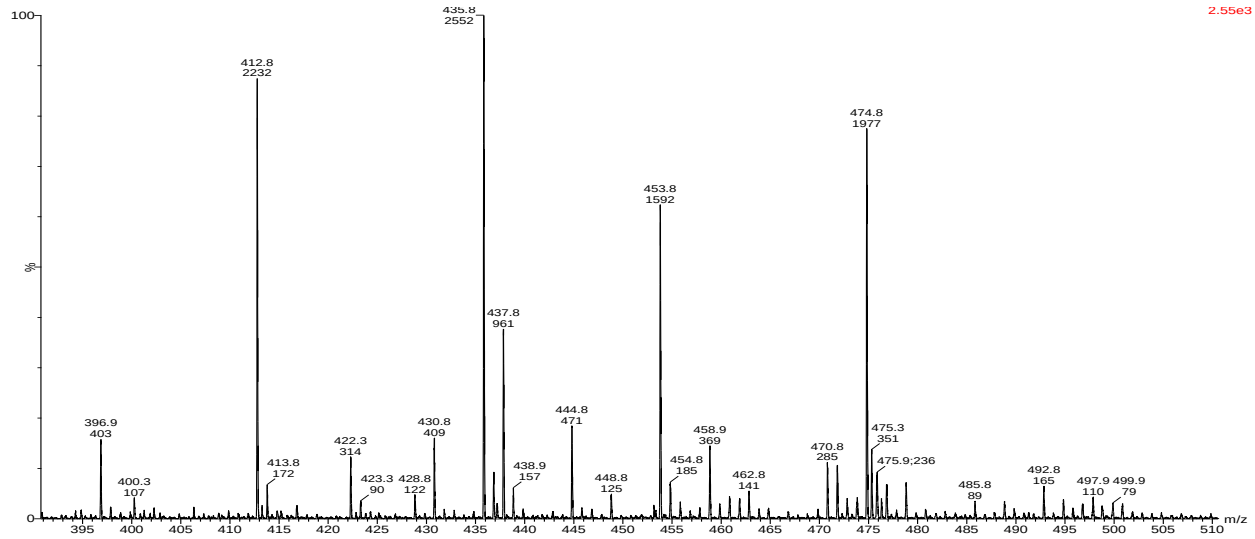


Figure 1. Mass spectra of the ligands L^1 and L^3 (continued)

(L^3)

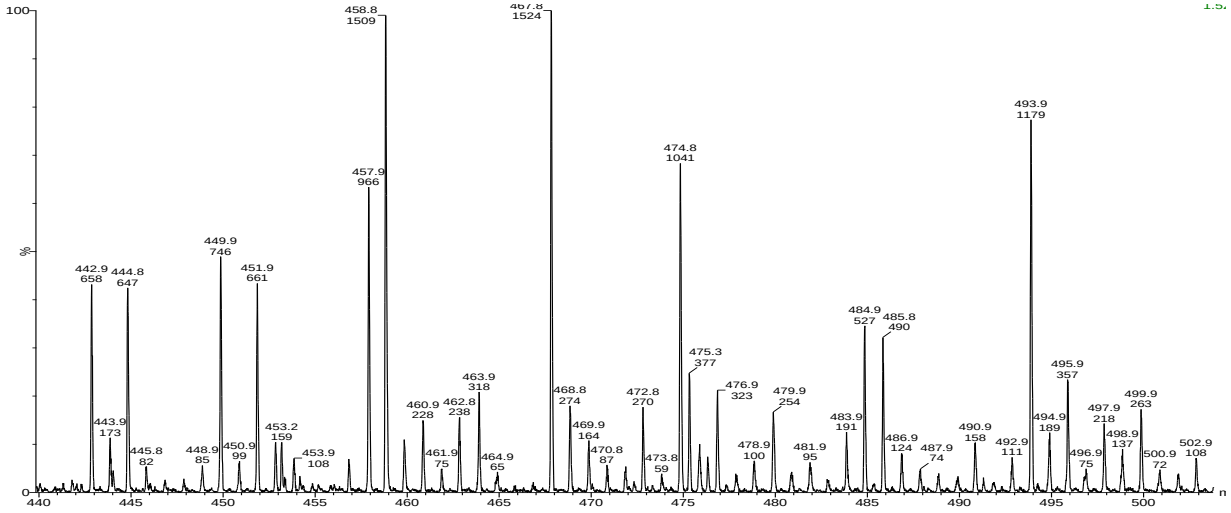
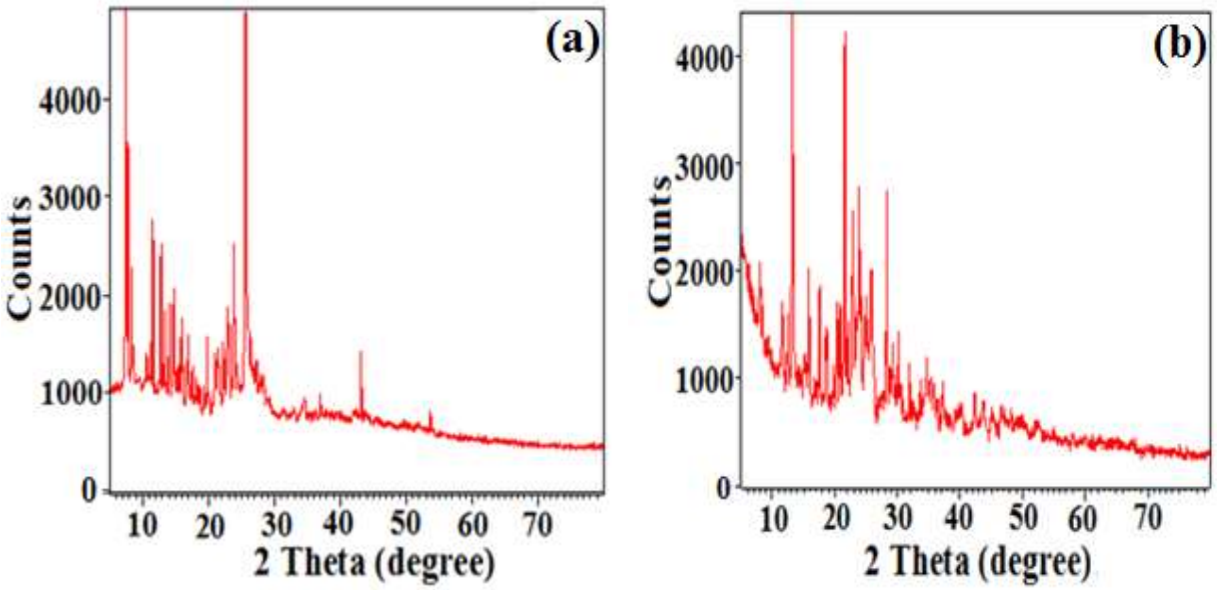


Figure 1. Mass spectra of the ligands L^1 and L^3.



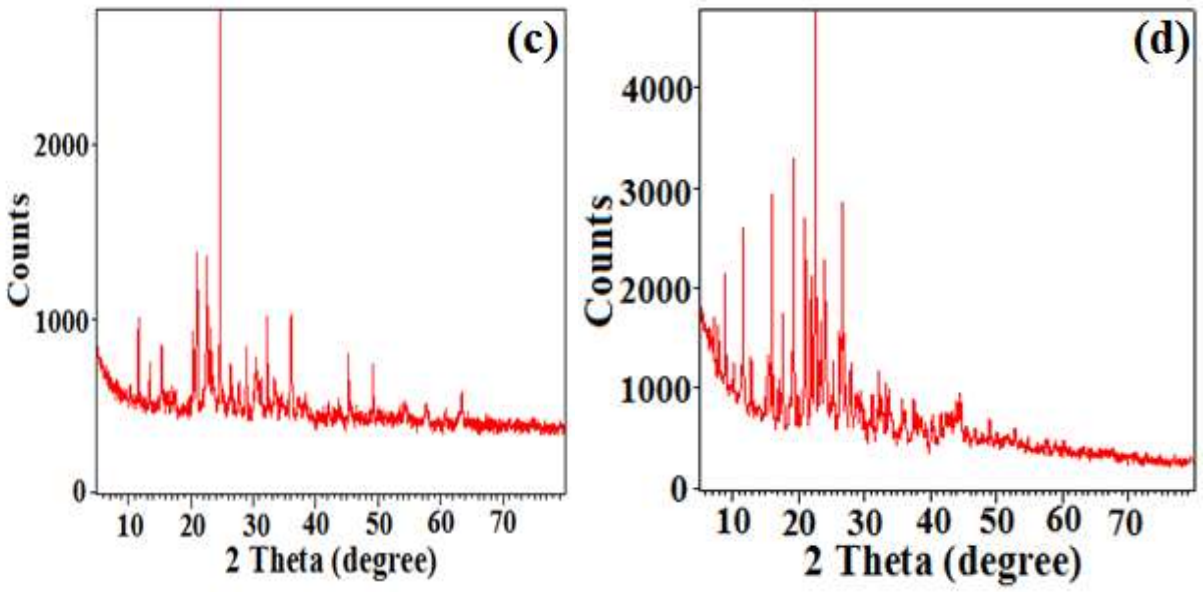


Figure 2. Powder XRD patterns of the (a) $[Ni(phen)_2(L^2)](OAc)_2$, (b) $[Ni(phen)_2(L^3)](OAc)_2$, (c) $[Co(phen)_2(L^3)](OAc)_2$ and (d) $[Cu(phen)_2(L^2)](OAc)_2$ complexes.

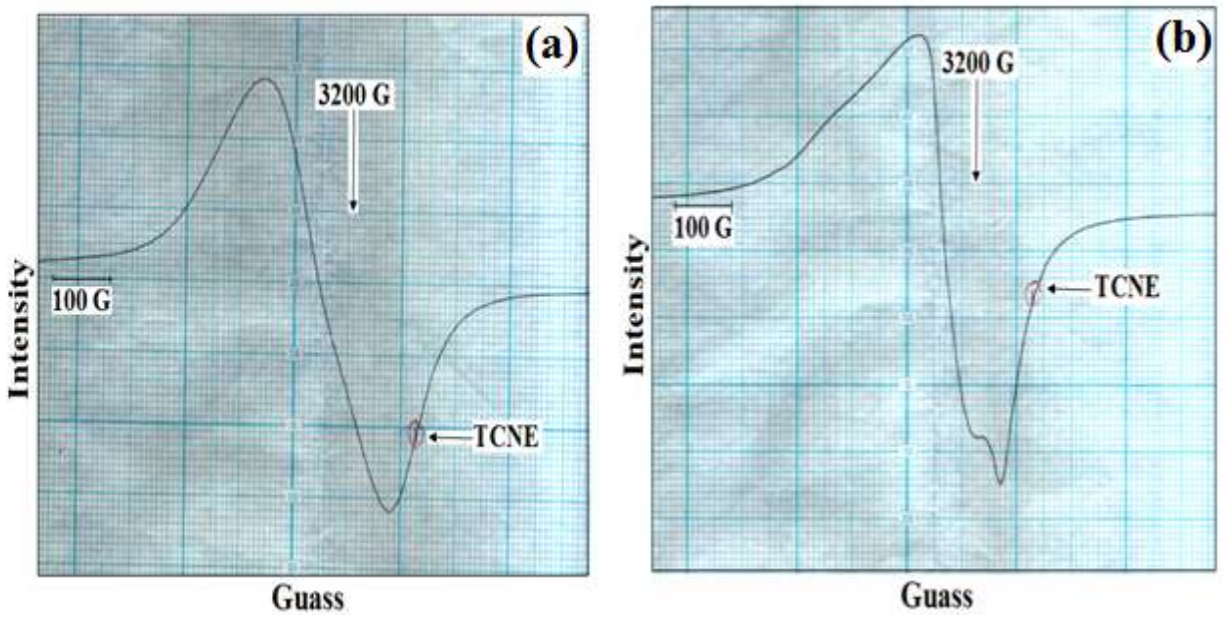


Figure 3. The ESR spectra of the (a) $[Cu(phen)_2(L^2)](OAc)_2$ and (b) $[Cu(phen)_2(L^1)](OAc)_2$ complexes.

3.8. Thermogravimetric study

Thermogravimetric studies have been made in the temperature range 25–700 °C. The thermal stability data of all the complexes are listed in Table 5. Thermal decomposition curves of the complexes

showed a similar sequence of three decomposition steps [43-45]. given in Figure 4. The first decomposition step for all the complexes occurred in the temperature range of 25–140 °C. The observed mass losses obtained for Ni(II) complexes were 6.19 %, 5.37% and 5.10%; for Co(II) complexes were 6.52%, 7.16% and 5.89% and for Cu(II) complexes were 1.68%, 1.87% and 1.57% which were attributed to the decomposition of absorbed water molecules. The second decomposition step occurred in the

Table 5. Thermogravimetric data of complexes.

S. no.	Compound	Temperature (°C)	T.G.A. Found (Calcd) (%)	Assignment	Loss type
(1)	$[Ni(phen)_2(L^1)](OAc)_2$	25–110	6.19(6.66)	Dehydration process	$4.H_2O$
		110–435	43.54(44.07)	Decomposition	Phen ligand + Acetate
		435–690	44.16(44.79)	Decomposition	Schiff base ligand
		> 690	-	Residue	NiO
(2)	$[Ni(phen)_2(L^3)](OAc)_2$	25–140	5.10(6.58)	Dehydration process	$4.H_2O$
		140-425	43.18(43.51)	Decomposition	Phen ligand + Acetate
		425–620	44.24(44.33)	Decomposition	Schiff base ligand
		>620	-	Residue	NiO
(3)	$[Co(phen)_2(L^3)](OAc)_2$	25–110	5.89 (6.58)	Dehydration process	$4.H_2O$
		110-435	43.12 (43.51)	Decomposition	Phen ligand + Acetate
		435–690	44.17(44.33)	Decomposition	Schiff base ligand
		>690	-	Residue	CoO
(4)	$[Cu(phen)_2(L^2)](OAc)_2$	25–110	1.87(1.93)	Dehydration process	$1.H_2O$
		110-350	51.28(51.23)	Decomposition	Phen ligand + Acetate
		350–690	28.26(28.95)	Decomposition	Schiff base ligand
		>690	-	Residue	CuO

temperature range of 100–435°C corresponding to observed mass losses for Ni(II) complexes were 43.54%, 46.19% and 43.18%; for Co(II) complexes were 44.35%, 47.19% and 43.12% and for Cu(II) complexes were 48.25%, 51.28% and 44.57% due to the decomposition of phenanthroline ligand and acetate. The third decomposition step occurred in the temperature range of 435–690°C corresponds to observed mass losses for Ni(II) complexes were 44.16%, 26.94% and 44.24%; for Co(II) complexes were 44.14%, 27.12% and 44.17% and Cu(II) complexes were 44.61%, 28.26% and 46.29% which were assigned to the final decomposition of Schiff base ligand from metal chelates. The horizontal thermal curves observed above 690°C correspond to a metal oxide residue.

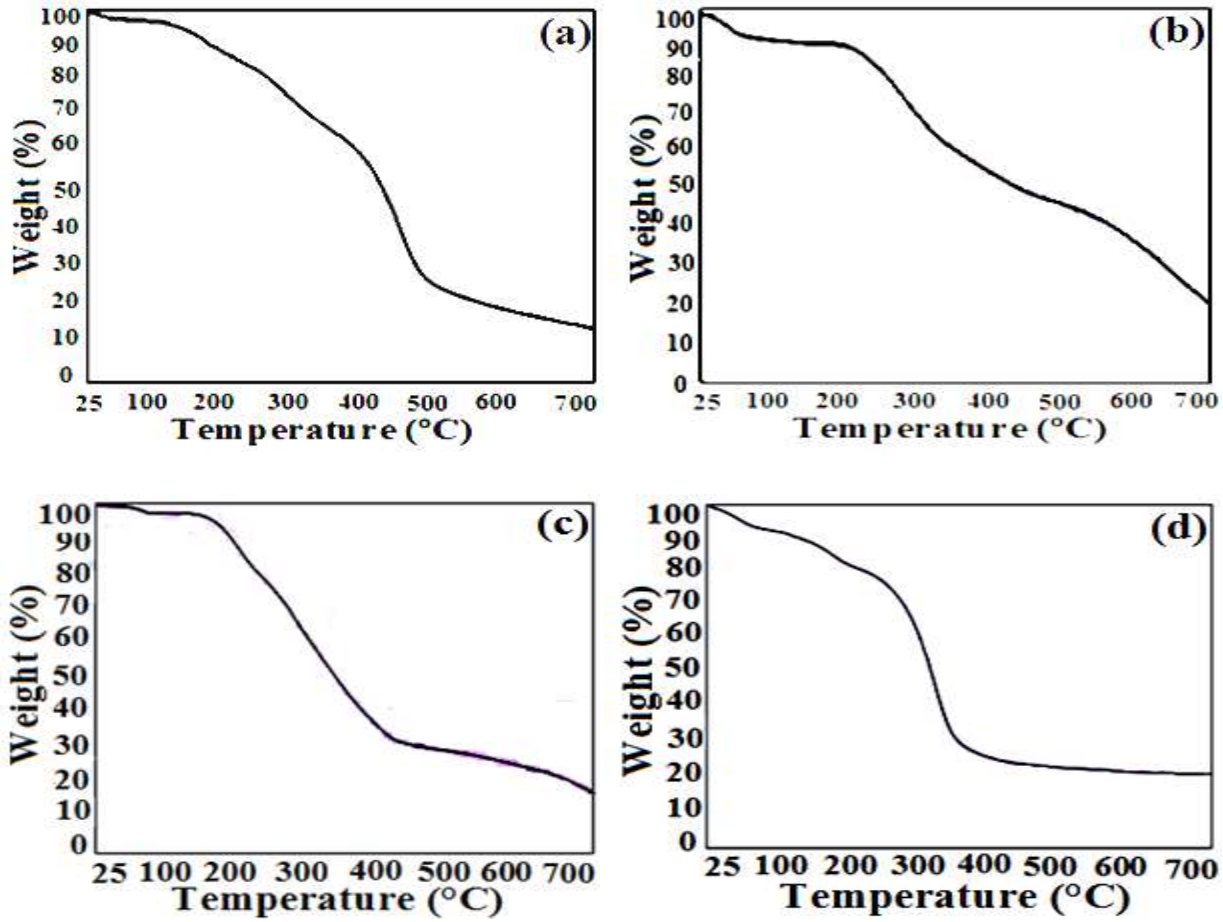


Figure 4. The TGA curves of the (a) $[Ni(phen)_2(L^1)](OAc)_2$, (b) $[Ni(phen)_2(L^3)](OAc)_2$, (c) $[Co(phen)_2(L^2)](OAc)_2$ and (d) $[Co(phen)_2(L^3)](OAc)_2$ complexes.

3.9. DNA cleavage studies

The cleavage reaction on plasmid DNA is monitored by agarose gel electrophoresis. When circular plasmid DNA is subject to electrophoresis, relatively fast migration is observed for the supercoil form (form I). If scission occurs on one strand (nicking), the supercoil will relax to generate a slower moving open circular form (form II). If both strands are cleaved, a linear form (form III) that migrates between form I and form II is generated [12,13,46]. Figure 5 shows gel electrophoresis separation of pBR 322 DNA after incubation with complexes and irradiation at 457 nm lane (6-10). No DNA cleavage was

observed for controls in which the complex was absent (lane N). It is evident from Fig. 5 that the complexes bind to DNA by intercalation mode and found to promote cleavage of plasmid pBR 322 DNA from the supercoiled form I to the open circular form II upon irradiation. Further studies are being done to clarify the cleavage mechanism.

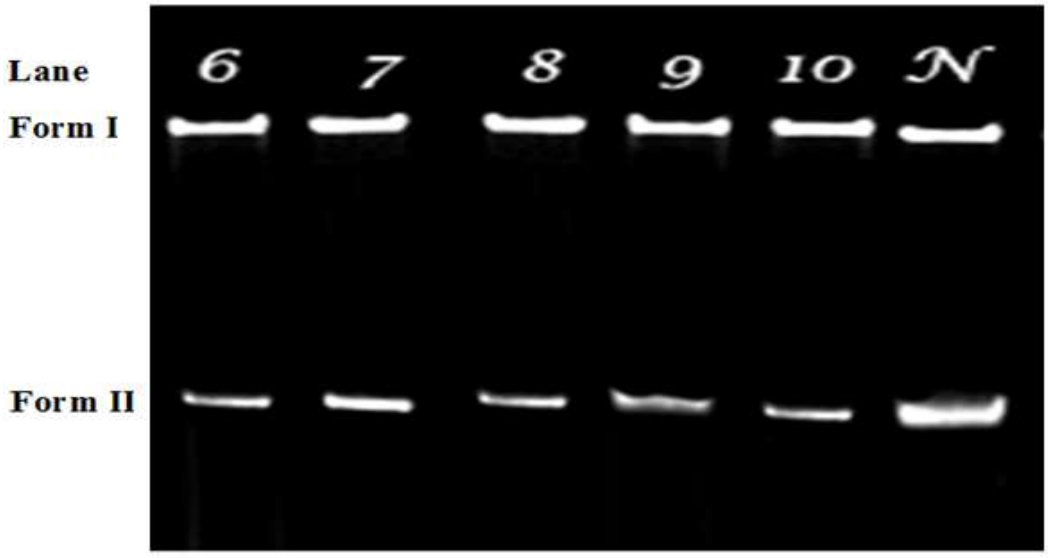


Figure 5. Gel electrophoresis diagram of the complexes, Lane N: control DNA; Lane 6: DNA + $[Ni(phen)_2(L^1)](OAc)_2$; Lane 7: DNA + $[Ni(phen)_2(L^2)](OAc)_2$; Lane 8: DNA + $[Co(phen)_2(L^1)](OAc)_2$; Lane 9: DNA + $[Co(phen)_2(L^3)](OAc)_2$; Lane 10: DNA + $[Cu(phen)_2(L^1)](OAc)_2$.

4. CONCLUSION

Three new Schiff base ligands derived from 2-chloro ethyl amine and their nine Co(II), Ni(II) and Cu(II) polypyridine complexes were synthesized and characterized. Based on the above observations of the elemental analysis, UV-Vis., IR, ^{1}H-NMR, ESR spectral data, magnetic measurements and conductance measurements it is possible to determine the type of coordination of the ligands in their complexes. The spectral data reveal that all the complexes were six coordinated and possess octahedral geometry around the metal ion. Powder XRD indicates the crystalline state of the complexes. Thermal property measurements show that the complexes have good thermal stability. The supercoiled DNA is cleaved in the electrophoresis by complexes which confirms that the complexes are having the ability to act as a potent DNA cleavaging agent.

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The authors declare no conflict of interest

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