

Research Article

Synthesis, Spectral Characterization, Studies of Schiff Base Complexes as Antitumor Agent

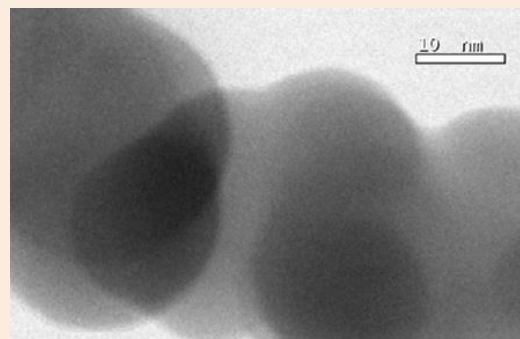
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Abstract

Schiff-base complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been synthesized and characterized by elemental, spectral and thermal studies. The conductance data indicate the non electrolytic nature of the complexes. The IR spectra of the prepared complexes were suggested that the metal coordinate with bipyridine, azomethine and N atom of benzoxazole. The physico-chemical studies revealed octahedral geometry or distorted octahedral geometry around metal ion. The EPR spectra of copper complex were recorded and their salient feature was reported. Thermal properties and decomposition kinetics of all complexes is investigated.

Keywords: Antitumor, Schiffbase, Metal Complex

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Introduction

In the recent years, there has been considerable interest in the chemistry of transition metal complexes of Schiff's bases [1,2]. They have played important role in the coordination chemistry [3]. This is due to the fact that Schiff's bases, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts[4-9], light emitting diode [10], corrosion inhibitor [11], potentiometric sensor [12,13], intermediates to obtain of some heterocyclic compounds[14], to synthesize of conjugate polymers containing azomethine bond[15] and their wide spectrum biological activities [16,17]. Studies during the past few years on Schiff bases containing chelating groups in their structures (especially nitrogen, oxygen and sulfur) have attract attention, due to its activity as electrochemical compounds [18], photo-chromism [19], determining of some cations[20], complexing towards heavy metals [21], antimicrobial activities[22], intermediates for synthesis of heterocyclic compounds containing sulfur and nitrogen atoms[23] and catalytically active materials in asymmetric catalysis [24]. In addition, Sulfanilamide are important class of drugs with several types of pharmacological agents possessing antibacterial, antithyroid, diuretic, hypoglycaemic, and anti-carbonic anhydrase [25,26]. Bioactive metal (II) complexes derived from Schiff base derivatives exhibit promising antibacterial and anti-malarial activities [27], as catalysts for specific DNA cleavage reactions[28]. Recently, copper (II) complexes were employed as catalysts in the aerobic oxidation of benzylic alcohols and the corresponding ligand structures in solution and solid state [29]. In this respect, encourage us to synthesis, spectroscopic and antimicrobial studies of Schiff's base and its cobalt(II), nickel(II), copper(II), and zinc(II) complexes. The structures of the compounds are characterized by using IR, UV, NMR, mass, TGA, EPR spectroscopic techniques.

Experimental**Materials**

All chemicals used in the present work were of highest purity and of the analytical reagent grade (AR). The solvents used were either spectroscopic pure from BDH or purified by the recommended method [30].

Physical methods

All melting points reported for the compounds were measured on a melting point SMP. The FT-IR spectra (200-4000 cm^{-1}) of the investigated compounds were reported as KBr discs using FT-IR 8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER (Shimadzu). The Electronic spectra were recorded on Shimadzu UV-Vis (1601) PC Spectrophotometer equipped with a 10 mm quartz cells, Personal Spectroscopy Software Version 3.6 Shimadzu, Tcc-240 A controller-stability $\pm 0.1^\circ\text{C}$ Shimadzu. The Conductance measurements were carried out in DMF solutions for HL complexes using a conductivity meter Metrohm-712 at $25^\circ\text{C} \pm 0.1^\circ\text{C}$. Elemental analysis for C, H, and N was performed by elemental analyzer and the metal determination was carried out using Perkin Elmer 3100(U.S.A). The NMR measurements were carried out on a Varian Gemini-200, using deuterated dimethyl sulfoxide(DMSO- d_6) solvent. The chemical shifts (δ) were given down field relative to tetramethylsilane (TMS), as internal stander. Mass spectrum was carried out using MSQP 1000 EX Shimadzu. TGA and DTA curves were obtained using NETZSCH-geratebanBestell-Nr 348472 C Electronic Spin Resonance (ESR) Spectrum was recorded on the Bruker ELXSYS 500 E X-band, detection for peak without need any calibration. Magnetic measurements were measured at room temperature using a magnetic susceptibility balance (Johnson Matthey alfa product, Model No.MKI). Diamagnetic corrections calculated from Pascal's constants.

Synthesis

Preparation of the Schiff base N-(2-(benzo[d]oxazol-2-yl)phenyl)-1-phenylmethanimine).

Add benzaldehyde (10 mmol) in 20 ml absolute ethanol dropwise with stirring, to 2-(benzo[d]oxazol-2-yl)aniline (10 mmol) in 20 ml absolute ethanol. After the complete addition, the reaction mixture was heated under reflux for 5 h with continuous stirring. The yellow solid product was precipitated, then filtered off and recrystallized from absolute ethanol. The yield was (85 %), and its melting point was 120°C .

Preparation of the metal complexes

Metal complexes of L ligand was prepared by the addition of a hot solution 60°C of the appropriate metal chloride (1 mmol) and biphenyl(1 mmol)in ethanol (50 ml) to the well stirred hot solution of the Schiff base (2 mmol) in the same solvent (25 ml). The mixture was left under reflux with continuous stirring for 2 h where upon the solid complexes precipitated. The obtained solid was washed with ethanol followed by diethyl ether and dried in vacuum over anhydrous calcium chloride. The analytical data of the complexes are collected in Table 1.

Table 1 Physical data of Ligand (L) and corresponding metal complexes

Cpd	Yield (%)	Color	m.p.($^\circ\text{C}$)	M. F. M.Wt.	Elemental analyses % calculated (found)				$^a\Lambda_m$	Δb
					M	C	H	N		
L	85	Yellow	120-122	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$ 298	—	80.53 80.52	4.69 4.73	9.39 9.39	-	-
MnL_2BP	50	Blue	>300	$\text{C}_{50}\text{H}_{36}\text{MnN}_6\text{O}_2$ 808	6.80 6.80	74.34 74.34	4.46 4.49	10.40 10.40	1.77	12.42
CoL_2BP	86	green	>300	$\text{C}_{50}\text{H}_{36}\text{CoN}_6\text{O}_2$ 811	7.26 7.26	73.98 73.98	4.43 4.47	10.35 10.35	1.80	15.66

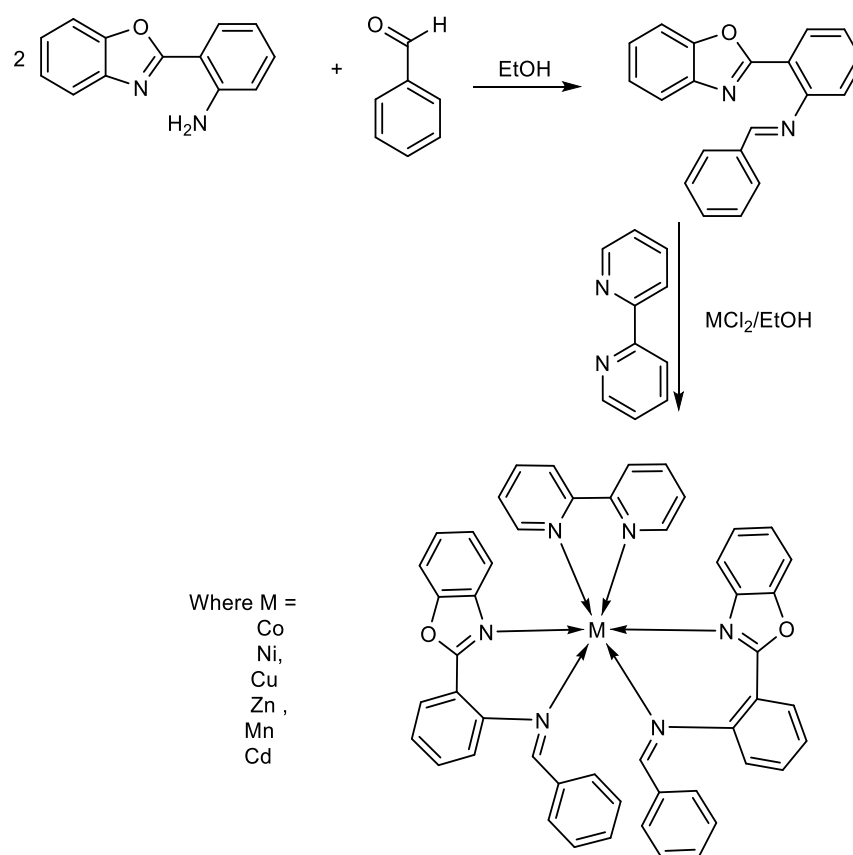
NiL₂ BP	72	Red	>300	C ₅₀ H ₃₆ N ₆ NiO ₂ 812	7.22 7.23	73.98 74.00	4.44 4.46	10.35 10.36	1.70	16.32
CuL₂ BP	61	Dark brown	>300	C ₅₀ H ₃₆ CuN ₆ O ₂ 816	7.78 7.76	73.56 73.55	4.44 4.40	10.29 10.35	1.70	17.20
ZnL₂ BP	52	Brown	>300	C ₅₀ H ₃₆ N ₆ O ₂ Zn 818	7.99 8.02	73.39 73.39	4.43 4.43	10.27 10.28	Di	15.36
CdL₂ BP	80	Dark brown	>300	C ₅₀ H ₃₆ CdN ₆ O ₂ 865	12.99 13.06	69.40 69.45	4.19 4.26	9.71 10.73	Di	16.32

(a) Magnetic moment values, μ_{eff} is the magnetic moment of the metal ions B.M : (Bohr magnetone)

(b) Molar conductance ($\text{Ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$) was measured in ($10^4 \text{mol}^{-1} \text{m}^{-1}$) DMF solvent

Results and discussion

The Schiff base ligand, L has been prepared by the condensation between 2-(benzo[d]oxazol-2-yl)aniline with benzaldehyde, (1:1 molar ratio) in EtOH as shown in scheme 1. The the purity of the ligand and the complexes was checked by T.L.C. Schiff base ligand L give the complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) salts. The complexes were synthesized according to **scheme 1**.



Scheme 1: synthesis of the complexes of Schiff bases ligand (**HL**) with Co(II), Ni(II), Cu(II), Zn(II) , (Mn) and Cd ions .

Characterization of ligand L

The IR spectrum (Table 2) of Schiff base ligand (L) is given in synthetic procedures. Vibration bands with the wave numbers of 3064 cm^{-1} ($\nu\text{C-H}$, Ar-H), 1655 cm^{-1} ($\nu\text{C=N}$ free), 1545 cm^{-1} ($\nu\text{C=C}$), 1212 cm^{-1} ($\nu\text{C-O}$, Ar-O) was observed for Schiff base ligand (L) [30]. Also, Schiff base ligand L with strong band at 1212 cm^{-1} of the stabilization of C-O bond [31]. L ligand shows bands at 1535, 1435, 1325 and 1155 cm^{-1} due to C=N ring [31], respectively. ^1H NMR spectral data of the ligand (Table 3) relative to TMS in DMSO- d_6 give further support of the suggested structures of the ligands. The broad signal for the methine proton of the characteristic azomethine group for Schiff base, $-\text{N}=\text{CH}-$ was observed at 8.64 ppm. In the region of 7.33-7.77 ppm chemical shifts were assigned for hydrogen of the aromatic ring. The UV-vis spectrum of the ligand shows three bands in the range 225, 286 and 370 nm which can be assigned to $\pi-\pi^*$ transitions within the aromatic rings, $\pi-\pi^*$ transitions within C=N and intramolecular charge transfer (CT) transition with the whole molecule. The electron impact mass spectrum of the free ligand, confirms the proposed formula by showing a peak at 298 u. The series of peaks in the range, i.e. 76, 118, 105 and 180, attributable to different fragments of the ligand. These data suggest the condensation of keto group with amino group. The molecular ion peak (298 u) is in good agreement with the suggested molecular formula indicated from elemental analyses ($\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$).

Characterization of the metal complex

Elemental analyses

Analytical data of ligand and their complexes are presented in **Table 1**. The experimental elemental analyses results of the complexes are in good compliance with the theoretical calculations. The data show the complexation of 1:2 [metal:ligand] ratio of the formulae of $[\text{M}(\text{L})_2\text{BP}]$. Conductivity values for the $[\text{Mn}(\text{L})_2\text{BP}]$, $[\text{Co}(\text{L})_2\text{BP}]$, $[\text{Ni}(\text{L})_2\text{BP}]$, $[\text{Cu}(\text{L})_2\text{BP}]$, $[\text{Zn}(\text{L})_2\text{BP}]$ and $[\text{Cd}(\text{L})_2\text{BP}]$ compounds in MeOH are in the range of 2.91-1.03 ($\Omega^{-1}\text{ cm}^3\text{ mol}^{-1}$) indicating that they are non-electrolytes [33]. Single crystals of the compounds could not be isolated from any organic solution, thus no definite structures can be described. However, the analytical and spectroscopic data enables us to predict possible structures as shown in **scheme 1**.

IR-spectra

Table 2 Wave numbers (Harmonic Frequency (cm^{-1}), IR assignments L ligand and its complexes with their assignments

Assignments	L	Co	Ni	Cu	Zn	Mn
vs(BP)	-	3385	3271br	3345	3188	3280br
$\nu(\text{C=N})_{\text{azomethine}}$	1655	1581	1563	1535	1540	1557
$\nu(\text{C-O})$	1212	1217	1208	1216	21.44	1202
$\nu(\text{C-H})_{\text{aromatic}}$	3080	3356	3065	3113	3077	3074
$\nu(\text{C=C})_{\text{phenyl}}$	1545	1581	1550	1594	69.9	1565
$\delta(\text{O-M-O})$	-	-	-	-	-	189
$\delta(\text{O-M-N})$	-	-	-	-	-	218
$\nu(\text{M-N})_{\text{Schiff base}}$	-	334	334	356	360	362

On comparing the IR-spectra of the free ligand with the IR spectra ligand (**Table 2**) of their complexes the following can be pointed out:

(i) The IR spectra of complexes displayed absorption bands at 1535–1581 cm^{-1} which can be assigned to C=N stretching frequency of coordinated ligand, whereas for free ligand this band was at 1655 cm^{-1} . The shift to lower frequencies (as compared to free ligand) indicated donation of the lone pair of electrons on azomethine nitrogen to metal center in complexes

(ii) For all complexes two new bands appear in their IR spectra at 3310 and 3250 cm^{-1} respectively these can be assigned to $\nu_{\text{M-N}}$ of new biphenyl ring.

(iii) The other bands of in the IR spectra of the free ligand still lie at the same position in the IR spectra of the complexes. These indicate that these groups did not contribute to the coordination of the metal ions in the complexes.

(iv) For all complexes two new bands appear in their IR spectra at 334–362 cm^{-1} which are absent from the IR spectra of the free ligands, these can be assigned to $\nu_{\text{M-N}}$ bands, respectively.

NMR spectra

A comparison of ^1H NMR spectrum of diamagnetic Zn(II) and Cd(II) complexes with the spectrum of the corresponding L Schiff base (Table 3), showed that, the chemical shift observed for the bipyridine ring protons at 8.25-9.25 ppm and not observed in the ligand, which confirmed the bonding of oxygen to the metal ions (N-M). Moreover, coordination of nitrogen atom of the ligand to Zn(II) and Cd(II) was indicated by a shift of the imine carbon proton signal to upper field region 7.54 ppm in comparison with that of the free ligand, inferring coordination through the azomethine nitrogen atom 8.64 ppm of the ligand, suggesting deshielding of the azomethine proton and proving its contribution to the covalent bond formed with the metal. Besides, the displacement of chemical shifts of azomethine hydrogen, the aromatic protons multiplets were displaced upper field region around δ 7.37-7.72 ppm.

Table 3 ^1H NMR data for the ligand δ (ppm)/J (Hz)

H-Type	Ligand	Zn(II)	Cd(II)
CH=N	8.64	7.54	7.54
CH _{Arm}	7.33-7.77 (m, 1H)	7.37-7.72	7.37-7.72
CH _{Bipyridine}	-	8.25-9.25	8.25-9.25

Mass spectra

The mass spectra of complexes showed peaks attributed to the molecular ions m/z at 808, 811, 812, 816, 818 and 865 M^+ for manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes, respectively. This data is in good agreement with the proposed molecular formula for these complexes i.e. $[\text{Mn}(\text{L})_2 \text{BP}]$, $[\text{Co}(\text{L})_2 \text{BP}]$,

[Ni(L)₂BP], [Cu(L)₂BP], [Zn(L)₂BP] and [Cd(L)₂BP]. The purity of the ligand and their complexes were checked using LC-mass technique. This confirms the formation of the Schiff-base frame.

Molar conductance

The molar conductance of the metal ion complexes under investigation are measured for 10⁻³ M solution in DMF. The results of molar conductance are listed in (Table 1) and indicate that all the complexes under investigation are non-electrolytes [34].

Magnetic and Electronic Spectral Studies

The room temperature magnetic moment of the manganese (II) complex lies at 5.95 B.M. corresponding to five unpaired electrons. Electronic spectrum of Mn(II) complex (Table 4) exhibit four weak intensity absorption, these bands may be assigned to the transitions: ⁶A_{1g} → ⁴T_{1g}(4G), ⁶A_{1g} → ⁴E_g, ⁴A_{1g}(4G) (10B + 5C) and ⁶A_{1g} → ⁴E_g(4D) (17B + 5C), ⁶A_{1g} → ⁴T_{1g}(4P) (7B + 7C), respectively [35]. The Co(II) complex showed the magnetic moment 4.85 B.M. at room temperature. The electronic spectrum of the cobalt(II) complex (Table 4), display absorption in the region 56-160 (Lmol⁻¹cm⁻¹). These bands may be assigned to the transitions: ⁴T_{1g}(F) → ⁴T_{2g}(F) (ν₁), ⁴T_{1g} → ⁴A_{2g} (ν₂) and ⁴T_{1g}(F) → ⁴T_{1g}(P) (ν₃), respectively. It is difficult to give the assignments for the fourth band and it may be due to charge transfer. The position of bands suggest octahedral geometry of Co(II) complex [36]. The magnetic moment was measured which gave 2.12 B.M., for Ni(II) complex, which lies in the range (2.9–3.3 B.M.) of the Ni(II) octahedral complexes [37]. Electronic spectrum of Ni(II) complex (Table 4) displays the assigned to ³A_{2g}(F) → ³T_{2g}(F) (ν₁), ³A_{2g}(F) → ³T_{1g}(F) (ν₂) and ³A_{2g}(F) → ³T_{1g}(P) (ν₃) transitions, respectively. It suggests octahedral geometry of Ni(II) complex [36]. The observed magnetic moment of the Cu(II) complex is 2.25 B.M., which confirms the octahedral structure of this complex [36,37].

Table 4 Magnetic moment and electronic spectral data of the complexes

Complex	μ _{eff} (B.M.)	Band assignments	λ _{max} (cm ⁻¹)	ε (Lmol ⁻¹ cm ⁻¹)	Geometry
[MnL ₂ BP]	5.15	⁶ A _{1g} → ⁴ T _{1g} (4G)	14,100	56	Octahedral
		⁶ A _{1g} → ⁴ E _g	20,764	91	
		⁴ A _{1g} (4G), ⁶ A _{1g} → ⁴ E _g (4D),	19,620	132	
		⁶ A _{1g} → ⁴ T _{1g} (4P)	24,232	156	
[CoL ₂ BP]	4.85	⁴ T _{1g} (F) → ⁴ T _{2g} (F), ⁴	10,372	56	Octahedral
		⁴ T _{1g} → ⁴ A _{2g} (F),	14,362	75	
		⁴ T _{1g} → ⁴ T _{1g} (P),	18,746	94	
		Charge transfer			
[NiL ₂ BP]	2.96	³ A _{2g} (F) → ³ T _{2g} (F),	18012	30	Octahedral
		³ A _{2g} (F) → ³ T _{1g} (F),	22,856	36	
		³ A _{2g} (F) → ³ T _{1g} (P)	27,285	130	
[CuL ₂ BP]	2.25	² B _{1g} → ² B _{2g} ,	11,788	67	Octahedral
		² B _{1g} → ² A _{1g} ,	14,813	74	
		² B _{1g} → ² E _g dx ₂ -y ₂ ,	18,312	85	
		dz ² , dxz, dyz → dx ² -dy ²	22,300	144	

The Zn(II) and Cd(II) complexes are diamagnetic as expected and its geometry is most probably octahedral similar to the Mn(II), Co(II), Ni(II) and Cu(II) complexes of the L ligand.

EPR spectra

The EPR spectrum of the Mn(II), Co(II), Ni(II) and Cu(II) complexes were recorded as a polycrystalline sample at room temperature [38]. The various ligand field parameters were calculated (Table 5), The value of Dq has been calculated from Orgel energy level diagrams using the ν_3/ν_1 ratio [35], also, the value for B (free ion) were calculated. The β low values for Mn(II), Co(II) and Ni(II) indicate that, the covalent character of metal ligand σ -bond is low (Table 5). The EPR spectra for Cu(II) complex exhibit an anisotropic characteristic for hexagonal geometry of copper(II) complex [39].

The anisotropic g - values have been calculated by Kneubuhl's methods [40] and by methods reported earlier [41] viz. $G = (g_{\perp} - 2)/(g_{\parallel} - 2)$, which measures the exchange interaction between the copper centers in polycrystalline samples, have been calculated. The calculated g -values are reported in Table 5. According to Hathaway [42-45], if $G > 4$, this value indicates to a considerable exchange interaction in solid complex.

The Zn(II) and Cd(II) complexes are diamagnetic as expected and its geometry is most probably octahedral similar to the Mn(II), Co(II), Ni(II) and Cu(II) complexes of the L ligand.

Table 5 Ligand field parameters and EPR spectral data of the complexes

Complex	Ligand field parameters					EPR spectral data at RT (for CO(II) LNT)						
	G	Dq (cm^{-1})	B	B	LFSE (kJ mol^{-1})	g_{\parallel}	g_{\perp}	g_{iso}	g_{av}	A_{\parallel}	A_{\perp}	A_{av}
[MnL ₂ BP]	1.25	382	625	0.80	0.0	–	–	2.00	–	–	–	–
[CoL ₂ BP]	1.95	311	523	0.62	45	5.88	3.08	–	–	–	–	–
[NiL ₂ BP]	–	934	764	0.72	135	–	–	–	–	–	–	–
[CuL ₂ BP]	2.0	–	–	–	–	2.2	–	–	–	–	–	–

Powder XRD and SEM analysis

Single crystals of the ligand L and its complexes could not be isolated due to their polycrystalline nature. Therefore, powder diffraction data were obtained for the ligand L and its complexes, the peaks were indexed by the crystal system and the particle size of the complex was calculated (Table 6), using the standard equation of Scherrer [46].

TEM image for the complex 1 is given in Figure 1. The morphology of complex was observed to have spherical particles of 10 nm averaged diameter. This is lying in good agreement with the calculated value (5 nm) obtained from Scherrer's equation.

Table 6 Powder XRD spectral data of [CuL₂BP]

Peak no.	2θ	Flex width	d-value	Intensity	I/I ₀
1	21.8	–	3.9560	412	100
2	22.5	–	4.3521	348	87
3	18.9	–	4.6264	120	32
4	25.4	1.891	3.5264	141	36
5	27.3	1.178	3.2547	124	32
6	30.2	1.178	2.9468	182	46

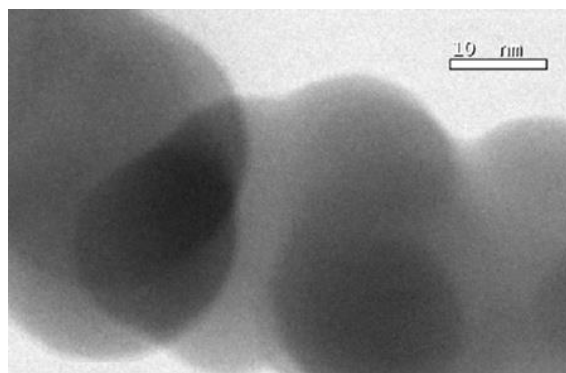
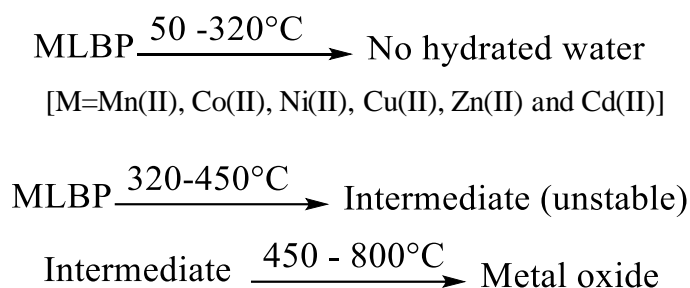


Figure 1 TEM image pattern for the [CuL₂BP] complex

Thermal decompositions of complexes

Thermal behaviors of complexes were investigated by TG/DSC techniques. The thermogravimetric analysis for the complexes was carried out within temperature ranging from room temperature to 800 °C. The TG/DTG curves of complexes Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are given in Figure 2. All the complexes were stable up to 3200 °C as no mass loss was observed below 320 °C, eliminated the possibility of water molecule outside the coordination sphere.

In general, the stages of thermal decomposition of the complexes can be written as shown:



Intermediates formed in the subsequent steps ultimately have undergone violent decomposition to give the respective metal oxides. The thermodynamic activation parameters of decomposition processes of dehydrated complexes namely activation energy (E), enthalpy (ΔH), entropy (ΔS) and free energy of decomposition (ΔG) (Tables 7), were evaluated by employing the Horowitz–Metzger [47] (HM), Coats–Redfern [47] (CR) methods and were helpful in assigning the strength of the complexes. According to the kinetic data obtained from the TG curves, all the complexes have negative entropy which indicates that, the complexes are formed spontaneously. The negative value of entropy also indicates a more ordered activated state that may be possible through the chemisorption of oxygen and other decomposition products. The negative values of the entropies of activation are compensated by the values of the enthalpies of activation, leading to almost the same values for the free energy of activation [48].

Finally, from the elemental analysis, molar conductivity, UV-visible spectral data, magnetic measurements, IR spectral data and EPR, we could confirm the type of coordination of Schiff base **L** ligand in its metal complexes, as dibasic ligand. All the prepared complexes were in the octahedral geometrical structures as shown in Scheme 1.

Conclusion

The Schiff base complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) derived from N-(2-(benzo[d]oxazol-2-yl)phenyl)-1-phenylmethanimine (**L**), were synthesized and characterized on the basis of analytical and spectral data.

The coordination of the L ligand to the metal ions takes place through N donor atoms of oxazol ring and azomethene group. Spectral characterizations of the new complexes showed that Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) forms six coordinate octahedral complexes with 1:2 (metal:ligand) stoichiometry. Powder XRD data enabled us to say that these complexes are of nano-sized.

Table 7 Kinetic parameters evaluated by Coats–Redfern equation

Compound	Stage	Decomposition range (°C)	A(S ⁻¹)	E _a (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)	ΔG (kJ/mol)
[MnL ₂ BP]	1st	487	84.63 × 10 ⁷	114.57	110.12	-0.034	152
	2nd	589	13.21 × 10 ⁷	143.45	143.56	-0.072	184
	3rd	868	98.75 × 10 ⁹	176.42	171.34	-0.098	243
[CoL ₂ BP]	1st	447	24.66 × 10 ⁵	137.43	132.42	-0.064	167
	2nd	546	54.32 × 10 ⁷	149.28	144.56	-0.073	196
	3rd	832	43.74 × 10 ¹⁰	168.56	160.85	-0.095	229
[NiL ₂ BP]	1st	456	4.96 × 10 ⁷	46.98	113.99	-0.045	163
	2nd	578	6.87 × 10 ⁷	131.89	139.86	-0.074	185
	3rd	799	49.14 × 10 ⁹	182.88	183.18	-0.095	257
[CuL ₂ BP]	1st	465	3.04 × 10 ⁹	40.44	52.46	-0.031	163
	2nd	577	5.42 × 10 ¹¹	71.79	73.78	-0.070	184
	3rd	800	2.87 × 10 ⁶	110.57	102.67	-0.093	195
[ZnL ₂ BP]	1st	476	44.68 × 10 ⁶	55.78	53.64	-0.096	153
	2nd	586	8.96 × 10 ¹⁰	83.89	92.84	-0.077	195
	3rd	872	33.85 × 10 ⁹	162.32	157.45	-0.122	218
[CdL ₂ BP]	1st	448	6.69 × 10 ⁹	37.56	77.12	-0.038	157
	2nd	634	17.39 × 10 ⁷	114.76	105.45	-0.112	184
	3rd	798	8.83 × 10 ⁶	122.12	124.20	-0.096	192

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