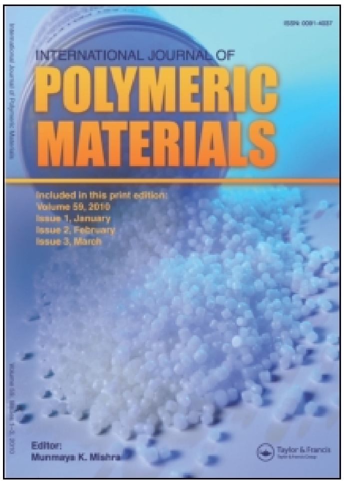

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Coordination Polymeric Chain Assemblies of Some Metal Ions with BHQPP

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Coordination Polymeric Chain Assemblies of Some Metal Ions with BHQPP

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A few coordination chain polymeric assemblies of the type $[M(H_2L)(H_2O)_2]_n \cdot xH_2O$ [where M = Mn(II), Cu(II) and Zn(II) x = 1; Co(II) and Ni(II) x = 2, H_2L = 2,2′-bis-4-[(8-hydroxy-5-quinoline methylenoxy) phenyl] propane] (BHQPP) have been investigated. Structural and spectroscopic properties have been determined by elemental analyses, infrared spectra, electronic spectra, magnetic measurements and thermogravimetric analyses. Magnetic moment and reflectance spectral studies reveal that an octahedral geometry is present in all the prepared coordination polymers. The kinetic parameters such as order of reaction (n) and the energy of activation (Ea) were determined using the Freeman–Carroll method. The pre-exponential factor (A), the activation entropy ($\Delta S^{\#}$), the activation enthalpy ($\Delta H^{\#}$) and the free energy of activation ($\Delta G^{\#}$) have been calculated.

Keywords coordination polymers, DTA and DSC studies, Freeman–Carroll method, TG/DTG

INTRODUCTION

The design of new coordination supramolecules and polymers based on transition metal compounds and multidentate organic ligands has attracted much interest in recent years [1–5]. Dependent on the nature of the metal and the coordination behavior of the ligand one can develop synthetic strategies to influence the one-, two- or three-dimensional arrangement in the crystal in a more directed way [6]. Furthermore, it is now realized that weak hydrogen bond(s) that involve O-H $\cdots$ O hydrogen bond stacking interactions also play

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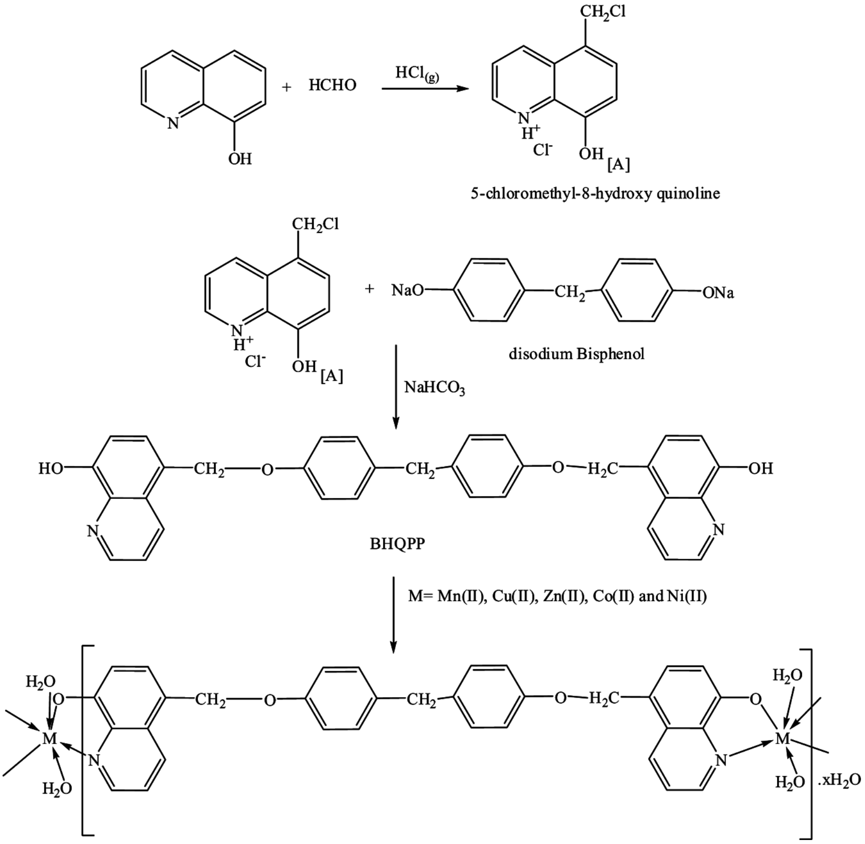
a significant and predictable structure determining role. Coordination polymers are usually known for their thermal stability [7,8]. However, some additional equally good applications have been reported, such as use of solar energy converters [9] and removal of SO_x and NO_x from the environment [10]. One major goal in this area is the preparation of new compounds with interesting properties such as functional materials in molecular magnetism [11–15], catalysis [16–19], optoelectronic devices and gas sorption [20–22]. The study of polymeric ligands and their metal complexes is very useful in metal separation and in bio-inorganic chemistry [23–25], but no detailed studies on coordination polymeric chain assemblies of transition metal ions with ligands have been carried out so far. Hence, information about the structural properties of coordination polymers with H_2L is important in order to examine the coordination abilities and complexation behavior of H_2L ligands and to investigate the building blocks for the supramolecular networks. The suggested structure of the coordination polymers is shown in Scheme 1.



Scheme 1: Synthesis and structure of the complexes.

EXPERIMENTAL

Materials

All the chemicals used were of analytical grade and used without further purification. The compound 8-hydroxy quinoline, formaldehyde, bisphenol and metal salts were purchased from E. Merck Ltd. (India).

Instruments

Carbon, hydrogen and nitrogen were analyzed with the Perkin Elmer, USA 2400-II CHN analyzer. The metal content of the coordination polymers were analyzed by the EDTA titration technique [26]. Infrared spectra ($4000–400\,cm^{-1}$) were recorded on Nicolet-400D spectrophotometer using KBr pellets. The reflectance spectra of the coordination polymers were recorded in the range of 1700–350 nm (as MgO discs) on a Beckman DK-2A spectrophotometer. The magnetic moments were obtained by the Gouy's method using mercury tetrathiocyanatocobaltate(II) as a calibrant ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 20°C). Diamagnetic corrections were made using Pascal's constant. A simultaneous TG/DTG and DTA had been obtained by a model 5000/2960 SDT, TA Instruments, USA. The experiments were performed in N_2 atmosphere at a heating rate of $10°C\,min^{-1}$ in the temperature range 50–800°C, using Al_2O_3 crucible. The sample sizes ranged from 4.5 to 10 mg. The DSC scans were recorded using DSC 2920, TA Instrument, USA, at a heating rate of $10°C\,min^{-1}$ in N_2 atmosphere over the temperature range of 50–400°C, using aluminum crucibles.

Preparation of Polymers of 2,2′-bis-4-((8-hydroxy-5-quinoline Methylenoxy) Phenyl) Propane) (BHQPP) (H_2L)

The literature procedure [27] with some modifications in the reaction time and work-up was followed. In a two-necked round-bottomed flask with magnetic stirrer, a reflux condenser and a dropping funnel, the compound 5-chloromethyl-8-hydroxyquinoline hydrochloride (23 g, 0.01 mol) was dissolved with bisphenol-A (17.5 g, 0.1 mol) in an acetone-water mixture. The resulting mixture was refluxed for 3 h with occasional shaking. The resulting suspension, which contained a green precipitate, was made alkaline with dilute aqueous ammonia and then filtered. The solid product was collected and dried to give H_2L (70% yield). Analysis for $C_{35}H_{30}N_2O_4$; Calculated (%): C, 77.49; H, 5.53; N, 5.16; Found: C, 77.19; H, 5.23; N, 4.87.

Synthesis of Coordination Polymers

The formed ligand H_2L (5 mmol, 3.13 g) was dissolved in 10 mL of DMF. To this solution, a methanolic solution of 25 mL metal nitrate (5 mmol) (1:1 molar ratio) was added slowly with constant stirring over a period of 30 min. The pH of the solution was adjusted to 5–6 with the dropwise addition of methanolic solution of sodium acetate. The resulting mixture was heated with stirring at reflux temperature for 4–5 h. The obtained coordination polymers were filtered off, washed with hot water, hot methanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous $CaCl_2$. The coordination polymers are insoluble in all common organic solvents like methanol, ethanol, chloroform, acetone, benzene, dimethyl formamide and dimethyl sulfoxide.

RESULTS AND DISCUSSION

The analytical and physical properties of the ligand H_2L and its coordination polymers are listed in Table 1. The following reaction describes the formation of the coordination polymers:

$$M(NO_3)_2 \cdot nH_2O + H_2L \rightarrow [M(H_2L)(H_2O)_2]_n \cdot xH_2O + 2HNO_3 + (n - x)H_2O$$

where M = Mn(II), Cu(II) and Zn(II), $x = 1$; Co(II) and Ni(II), $x = 2$.

All the coordination polymers are insoluble in all common organic solvents. It was not possible to characterize them by conventional methods such as osmometry, viscometry, and conductometry, as they are insoluble. The nature of the ligand, high thermal stability, metal–ligand ratio (1:1) and insolubility in all common organic solvents suggest their polymeric nature.

IR Spectra

The important infrared spectral bands and their tentative assignments for the synthesized ligand and its coordination polymers were recorded as KBr disks and are discussed here.

In the investigated coordination polymers, the bands observed in the region 3400–3450, 1295–1300, 860–870 and 715–717 cm^{-1} are attributed to –OH stretching, bending, rocking and wagging vibrations respectively, due to the presence of water molecules [28]. The presence of rocking band indicates the coordination nature of the water molecule [29]. The IR spectra of the H_2L show 1600 cm^{-1} and 1380 cm^{-1} bands corresponding to ν(C=N) and ν(C–O) respectively; on complexation these peaks shifted to a lower frequencies, 1588 cm^{-1} and 1367 cm^{-1}, due to coordination polymer formation. Weak bands around 519 cm^{-1} and 779 cm^{-1} are attributed to the ν(M–O) and ν(M–N) stretching frequencies [30].

Table 1: Analytical and physical data of the ligand H_2L and its coordination polymers.

Empirical formula of monomer unit	**Formula weight**	**Color (Yield %)**	**M.P. (°C)**	**Found (Calcd.) (%)**				**μ_{eff} (B.M.)**
				C	**H**	**N**	**M**	
H_2L	514.57	Yellowish brown (74)	201[d]	77.00 (77.03)	5.04 (5.09)	5.38 (5.44)	–	–
$(Mn(H_2L)(H_2O)_2)_n \cdot H_2O$ $C_{37}H_{40}MnN_2O_7$	635.61	Dark brown (68)	>300	66.08 (66.14)	5.67 (5.71)	4.32 (4.41)	8.57 (8.64)	6.01
$(Co(H_2L)(H_2O)_2)_n \cdot 2H_2O$ $C_{37}H_{42}CoN_2O_8$	625.19	Dark brown (64)	>300	67.11 (67.24)	5.50 (5.55)	4.42 (4.48)	9.37 (9.43)	4.06
$(Ni(H_2L)(H_2O)_2)_n \cdot 2H_2O$ $C_{37}H_{42}N_2NiO_8$	624.95	Dark green (72)	>300	67.19 (67.27)	5.45 (5.55)	4.41 (4.48)	9.23 (9.39)	2.91
$(Cu(H_2L)(H_2O)_2)_n \cdot H_2O$ $C_{37}H_{40}CuN_2O_7$	644.22	Dark brown (70)	>300	65.15 (65.25)	5.58 (5.63)	4.31 (4.35)	9.77 (9.86)	1.79
$(Zn(H_2L)(H_2O)_2)_n \cdot H_2O$ $C_{37}H_{40}N_2O_7Zn$	646.08	Brown (65)	>300	65.01 (65.07)	5.48 (5.62)	4.28 (4.34)	10.07 (10.12)	Diamag.

[d] decomposed, B.M. = Bohr magneton.

Magnetic Moments and Electronic Spectra

The information regarding geometry of the coordination polymers was obtained from their electronic spectral data and magnetic moment values. The reflectance spectrum of the Mn(II) coordination polymer shows absorption bands at ~15,050, ~19,970 and ~24,800 cm^{-1} assignable to $^6A_{1g} \rightarrow {}^4T_{1g}$ (ν_1), $^6A_{1g} \rightarrow {}^4T_{2g}$ (ν_2) and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4Eg (ν_3) transitions, respectively, in an octahedral environment around the Mn(II) ion [31]. The magnetic moment value of the Mn(II) coordination polymer was 6.01 B.M. due to a high-spin d^5-system with an octahedral geometry [32]. The observed magnetic moments 4.06 and 2.91 B.M., for the Co(II) and Ni(II) coordination polymers, respectively, are within the range for an octahedral geometry [33,34]. The reflectance spectrum of Co(II) coordination polymer (see Table 2) shows medium intensity bands at ~9,300, ~18,300 and ~19,050 cm^{-1}, which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively, of an octahedral geometry. The reflectance spectrum of the Ni(II) coordination polymer exhibits three bands at ~10,300, ~17,650 and ~24,000 cm^{-1} assignable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively, in an octahedral geometry. The reflectance spectrum of Cu(II) coordination polymer displays a broad band at ~15,450 cm^{-1} due to the $^2E_g \rightarrow {}^2T_{2g}$ transition and the observed magnetic moment is 1.79 B.M., which is close to spin-only value (1.73 B.M.) expected for an unpaired electron, offering the possibility of an octahedral geometry [35].

Thermal Studies

The thermodynamic activation parameters of the decomposition process of the coordination polymers, such as energy of activation (Ea) and order of reaction (n), were evaluated graphically by employing the Freeman–Carroll

Table 2: Electronic parameters of the Co(II) and Ni(II) coordination polymers[a].

Coordination polymers	**Observed bands (cm^{-1})**							
	ν_1	ν_2	ν_3	ν_2/ν_1	**B**	**β**	**B$_0$**	**10 Dq**
$(Co(H_2L)(H_2O)_2)_n \cdot 2H_2O$	9,300	18,180	18,940	1.95	717	0.73	26.0	10,419
$(Ni(H_2L)(H_2O)_2)_n \cdot 2H_2O$	10,500	17,500	24,600	1.67	707	0.69	31.4	10,500

[a] The ligand field splitting energy (10 Dq), interelectronic repulsion parameter (B) and covalency factor (nephelauxetic ratio)(â).

For the Co(II) and Ni(II) complexes were calculated using the secular equations:

For Co(II) complex	For Ni(II) complex
$10\ Dq = ½\ ((2\nu_1 - \nu_3) + (\nu_3^2 + \nu_1\nu_3 - \nu_1^2)^{1/2})$	$10\ Dq = \nu_1$
$15B = \nu_3 - 2\nu_1 + 10Dq$	$15B = (\nu_2 + \nu_3) - 3\nu_1$
$\beta = B/B_0$ (B_0 (free ion) = 917)	$\beta = B/B_0$ (B_0 (free ion) = 1030)
$\beta_0 = (1 - \beta) \cdot 100$	$\beta_0 = (1 - \beta) \cdot 100$

method [36] using the following relation:

$$[(-Ea/2.303\,R)\ \Delta\ (1/T)]\ \Delta \log w_r = -n + \Delta \log(dw/dt)\Delta \log w_r \qquad (1)$$

where T is the temperature in K, R is gas constant, $w_r = w_c - w$; w_c is the weight loss at the completion of the reaction and w is the total mass loss up to time t. Ea and n are the energy of activation and order of reaction, respectively. A typical curve of $[\Delta\log(dw/dt)/\Delta\log\ w_r]$ vs. $[\Delta\ (1/T)/\Delta\log w_r]$ for the Co(II) coordination polymer is shown in Figure 1. The slope of the plot gave the value of Ea/2.303 R and the order of reaction (n) was determined from the intercept.

The Thermal Behavior of the Prepared Coordination Polymers

Thermal data and kinetic parameters of the coordination polymers are given in Tables 3 and 4, respectively. Typical TG/DTG, DTA and DSC curves of the coordination polymer $[M(H_2L)(H_2O)_y]_n \cdot xH_2O$ (where M = Co(II), y = 2, x = 2) are presented in Figure 2. The thermal fragmentation scheme for Mn(II) and Ni(II) coordination polymers is shown below:

$$[M(H_2L)(H_2O)_y]_n \cdot xH_2O \xrightarrow[\text{Dehydration}]{50-130^\circ C} [M(H_2L)(H_2O)y]_n + xH_2O$$

[where M = Mn(II) and Ni(II), x = 2.]

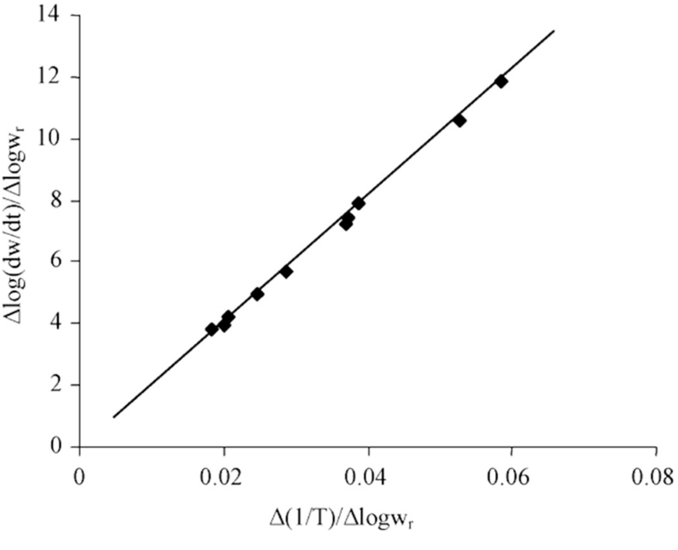


Figure 1: Freeman–Carroll plot for thermal dehydration of $(Co(H_2L)\ (H_2O)_2)_n \cdot 2H_2O$.

Table 3: Thermo-analytical data of the coordination polymers.

Heterochelates	**TG range (°C)**	**DTG$_{max}$ (°C)**	**DTA$_{max}$ (°C)**	**DSC$_{max}$ (°C)**	**Mass loss (%) obs. (calc.)**	**Assignment**
$(Mn(H_2L)(H_2O)_2)_n \cdot H_2O$	50–130	63.50	62.17	122.91	2.28 (2.45)	Loss of one lattice water molecule
	130–260	–	–	187.68	4.85 (4.90)	Loss of two coordination water molecules
				215		
	260–780	427.89	378.30	253.25	81.94 (81.80)	Removal of (H_2L) ligand molecule
				360.15	89.07 (89.15)	Leaving Mn_2O_3 residue
$Co(H_2L)(H_2O)_2)_n \cdot 2H_2O$	50–260	67.94	75.11	156.47	9.36 (9.51)	Loss of two lattice + two coordinated water molecule
	260–760	431.78	459.77	–	80.62 (80.57)	Removal of (H_2L) ligand molecule
					89.98* (90.08)	Leaving CoO residue
$(Ni(H_2L)(H_2O)_2)_n \cdot 2H_2O$	50–130	68.72	73.66	–	4.88 (4.76)	Loss of two lattice water molecule
	130–280	–	–	160.14	4.61 (4.76)	Loss of two coordination water molecules
	280–760	471.52	439.39	–	82.69 (82.58)	Removal of (H_2L) ligand molecule
					92.18* (92.10)	Leaving free Ni residue
$(Cu(H_2L)(H_2O)_2)_n \cdot H_2O$	50–240	60–66	66.15	161.33	7.17 (7.26)	Loss of one lattice + two coordinated water molecule
	240–720	495–73	407.68	274.15	82.09 (82.03)	Removal of (H_2L) ligand molecule
				358.97	89.26* (89.29)	Leaving CuO residue
$(Zn(H_2L)(H_2O)_2)_n \cdot H_2O$	50–230	62.94	64.61	149.06	7.15 (7.24)	Loss of one lattice + two coordinated water molecule
	230–740	521.91	503.75	–	83.86 (83.83)	Removal of (H_2L) ligand molecule
					91.01* (91.10)	Leaving free Zn residue

*Total mass loss.

Table 4: Kinetic parameters of the coordination polymers.

Compounds	**TG range ($^\circ$C)**	**Ea ($kJmol^{-1}$)**	**n**	**A (s^{-1})**	**$\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)**	**$\Delta H^{\#}$ ($kJmol^{-1}$)**	**$\Delta G^{\#}$ ($kJmol^{-1}$)**
$(Mn(H_2L)(H_2O)_2)_n \cdot H_2O$	50–130	3.52	0.00	0.13	−102.25	0.73	35.13
	130–260	5.19	1.50	0.11	−101.98	1.36	48.34
	260–780	45.35	1.00	$0.26 \cdot 10^3$	−95.67	39.52	106.58
$Co(H_2L)(H_2O)_2)_n \cdot 2H_2O$	50–260	3.80	0.00	0.15	−102.00	0.96	35.80
	260–760	81.40	1.00	$0.21 \cdot 10^6$	−93.60	75.50	141.00
$(Ni(H_2L)(H_2O)_2)_n \cdot 2H_2O$	50–130	3.18	0.00	0.15	−102.02	0.97	35.83
	130–280	4.90	1.49	0.12	−101.98	1.28	45.46
	280–760	101.02	1.00	$0.26 \cdot 10^6$	−93.00	94.83	164.07
$(Cu(H_2L)(H_2O)_2)_n \cdot H_2O$	50–240	3.36	0.00	0.12	−102.38	0.59	34.75
	240–720	69.88	1.00	$0.79 \cdot 10^4$	−94.45	63.49	136.09
$(Zn(H_2L)(H_2O)_2)_n \cdot H_2O$	50–230	3.15	0.00	0.13	−102.00	0.72	35.10
	230–740	44.10	1.00	$0.81 \cdot 10^2$	−96.10	37.60	114.00

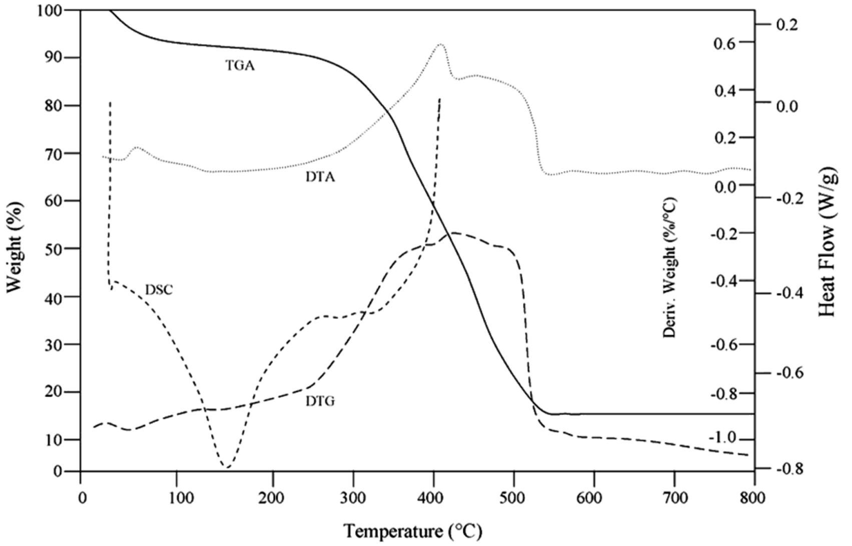


Figure 2: TGA/DTG, DTA and DSC curves of $(Co(H_2L)(H_2O)2)n \cdot 2H_2O$.

$$[M(H_2L)(H_2O)_y]_n \xrightarrow[\text{Removal of coordinated water molecules}]{130-280^{\circ}C} [M(H_2L)]_n + yH_2O$$

where $M = Mn(II)$, $Ni(II)$, $y = 2$.

$$[M(H_2L)]_n \xrightarrow[\text{Removal of } H_2L \text{ ligand molecule}]{280-780^{\circ}C} \text{metal residue}$$

where metal residue $= Mn_2O_3$ or free Ni residue, whereas for Co(II), Cu(II) and Zn(II) coordination polymers, the thermal fragmentation scheme is shown below.

$$[M(H_2L)(H_2O)_y]_n \cdot xH_2O \xrightarrow[\substack{\text{Removal of lattice water molecules} \\ + \text{ coordinated water molecule}}]{50-260^{\circ}C} [M(H_2L)]_n + yH_2O + xH_2O$$

where $M = Cu(II)$, $Zn(II)$, $y = 2$, $x = 1$ and $Co(II)$, $y = 2$, $x = 2$.

$$[M(H_2L)]_n \xrightarrow[\text{Removal of } H_2L \text{ ligand molecule}]{260-760^{\circ}C} \text{metal residue}$$

where metal residue $= CoO$, CuO or free Zn residue.

The anhydrous coordination polymers show great thermal stability up to 260°C; and in the second subsequent stage for Co, Cu and Zn coordination polymers whereas in the third subsequent stage for Mn and Ni coordination polymers, the decomposition and combustion of ligand (H_2L) occurs. The removal of ligand (H_2L) during decomposition leaves free metal for Ni and Zn [37,38] or metal oxides for Mn, Co and Cu as the final residue.

The thermodynamic activation parameters of the decomposition process of dehydrated complexes, such as activation entropy ($\Delta S^{\#}$), pre-exponential factor (A), activation enthalpy ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$), were calculated using the reported equations [39,40]. According to the kinetic data obtained from DTG curves, all the coordination polymers have negative entropy, which indicates that the studied coordination polymers have more ordered systems than the reactants [41]. The kinetic parameters, especially energy of activation (Ea) are helpful in assigning the strength of the coordination polymers. The calculated Ea values of the investigated coordination polymers for the first dehydration step are in the range 3.36–3.81 $\mathrm{kJ\,mol^{-1}}$ (Table 4). Based on the activation energy values, the thermal stabilities of the coordination polymers in a decreasing order is: Ni(II) > Co(II) > Mn(II) > Zn(II) > Cu(II).

It is evident that the thermal stabilities of the coordination polymers increase as the ionic radii decrease. The thermal stabilities of the Ni(II) and Mn(II) coordination polymers in the solid-state follow the general trend found by Irving and Williams [42] for the stabilities of complexes in solution. The Co(II), Cu(II) and Zn(II) coordination polymers deviate from this general behavior. Since the Irving–Williams series reflects electrostatic effects, this observation indicates that the water–metal interaction in these coordination polymers is almost of ion-dipole type.

CONCLUSIONS

The design and synthesis of a new tetradentate ligand (H_2L) have been successfully demonstrated. New Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) coordination polymeric assemblies were prepared. All the coordination polymers are insoluble in common organic solvents. It was not possible to characterize them by convectional methods, like osmometry, viscometry, conductometry, etc., as they are insoluble. The nature of the ligand, high thermal stability, metal–ligand ratio (1:1) and insolubility of these compounds suggest their polymeric nature. An octahedral geometry has been assigned to all the prepared polymers.

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