



ORIGINAL ARTICLE

Synthesis, characterisation and thermal degradation behaviour of some coordination polymers by using TG–DTG and DTA techniques



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Thermal stability

Abstract The four chelate polymer complexes commonly called as coordination polymers of Mn(II), Co(II), Ni(II) and Cu(II) ions with *fbmpc* (*fbmpc* = fumaroyl *bis* (paramethoxyphenylcarbamide)) were synthesized and characterised by elemental analyses, infrared spectroscopy, diffuse reflectance, magnetic moment susceptibility, thermal analysis, X-ray diffraction, electrical conductivity and scanning electron microscopy technique (SEM). SEM investigations of coordination polymers were found in different shapes and sizes, though they are synthesized from a single ligand. Each metal ion is coordinated by a *bis* (bidentate) manner through oxygen atom of the carboxylato group and the nitrogen atom of an amide group of ligand and two aqua ligands by coordinated

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bond which formed 6-member heterocyclic ring. In the present article, the main aim of research study is to find out the comparative studies of coordination polymers such as thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), electrical conductivity and morphology behaviour. Furthermore, the electrical conductivities of chelating ligand and coordination polymers were determined in the solid state powder form. The electrical conductivities measurements of undoped and doped ligand, coordination polymers were carried out at room temperature by the four probe technique using an electrometer. Thermal degradation studies of the coordination polymers have been carried out from a non-isothermal condition under nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The decomposition steps and thermal stabilities of these complexes were confirmed by thermal analysis techniques (TG/DTG/DTA). The thermal studies inferred the presence of crystallized water in all coordination polymers, whereas coordinated water was found in Ni(II) and Cu(II) ions.

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1. Introduction

Nowadays an immeasurable attention is being paid in the synthesis and thermal degradation characterisation of coordination and organometallic coordination polymers of divalent transition metal ions. The beauty of coordination polymer is thermal stability. The nanoscale particles of transition metal coordination polymers have huge thermal stability and tremendous potential applications [1,2]. Various studies have been reported on thermal stability, synthesis, morphological and applications of transition metal organic coordination polymers with derivative of dicarboxylic [3–7], amines [8], aromatic mono/dicarboxylic acid [9,10], substituted thiourea salt and bidentate ligand [11–13]. Actually, the supramolecular skeleton of coordination polymer is formed due to the polydentate ligand. These polydentate ligands designed the heterocyclic rings by combining with metal ions, hence they possess excellent structure with beautiful artistic which have high dimensional supramolecular network [14–17]. In spite of valuable importance to polydentate ligand synthesis, and design in contemporary coordination chemistry there are very few glib and high yielding methods for the generation of functionalized ligand scaffold [18–23]. Furthermore, deprotonated organic amide and dicarboxylate are being widely used as polydentate ligand in metal coordination chemistry since they possess noteworthy topography, such as bidentate linking modes and probability of triply coordinated oxygen atoms [24–28]. In that respect, the coordination chemistry of fumaric dicarboxylic acids, $^-\text{OOC}-\text{CH}=\text{CH}-\text{COO}^-$ has been extensively investigated. Various examples of transition metals derivatives of fumaric dicarboxylic acids possessing fascinating and magnificent structural features have already been published [29,30]. Herein, we have emphasised metal derivative of fumaric acid containing amide moieties and found out its overwhelming thermal stability properties by the thermal analysis techniques. The thermal analysis techniques, such as thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and derivative thermogravimetry (DTG) were widely applied in studying the thermal behaviour and structure of inorganic compounds, complexes and coordination polymers of transition metal ions [31–35].

The present work reported the synthesis and spectroscopic characterisation of coordination polymer, which were characterised by XRD, SEM and thermal decomposition (TG/DTG/DTA) techniques. SEM studies were significantly helpful to

determine the particle sizes and identify the distinct morphology for ligand and coordination polymers. The obtained results from thermal analysis permitted us to obtain information concerning the structure of coordination polymers including their thermal behaviour and degradation. The presence of lattice and coordinated water molecules in coordination polymers (Fig. 1) was investigated by these (TG/DTG/DTA) techniques and determined by the endothermic and exothermic effects connected with melting, dehydration, decomposition and crystallisation. Also, we present comparative studies of coordination polymers of a particular ligand with various metal ions. The thermal decomposition of organic moieties occurs in two or three steps with the formation of metal oxides as the final residue. The main objective of this article is to introduce the thermal degradation behaviours and thermal stability of coordination polymers of divalent transition metal ions.

2. Experimental

2.1. Materials and measurements

All the chemicals were reagent grade and used without purification. Thermal degradation of coordination polymers was carried out in the range $28\text{--}1220\text{ }^{\circ}\text{C}$ at a heating rate of

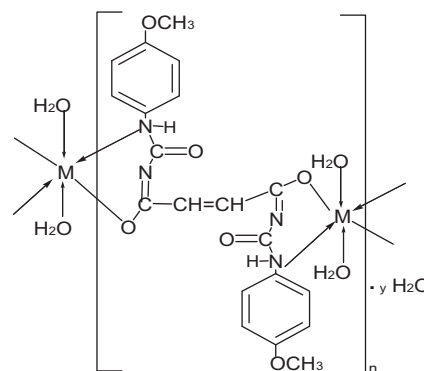


Figure 1 The propose structure of coordination polymers of *fbmpc* where $M=\text{Mn(II)}$, Co(II) , Ni(II) , Cu(II) ions and H_2O -coordinated water were present in Ni(II) and Cu(II) ions, whereas $\cdot y\text{ H}_2\text{O}$ -lattice water present in Mn(II) , Co(II) , Ni(II) and Cu(II) ions.

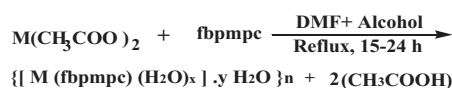
10 °C/min under nitrogen atmosphere. Scanning electron microscopic images were scanned at energy of 20 kV with magnification $\times 1500$ and diffuse reflectance absorption studies were recorded in the range 200–600 nm. The magnetic susceptibility measurements at room temperature were carried out by Gouy's method. IR spectra of the ligand and its coordination polymer were recorded by using KBr pellets in the range 4000–400 cm^{-1} on Shimadzu FT-IR-8101A spectrophotometer. The electrical conductivity values of all samples were measured with an electrometer. The pellets were hydraulically pressed to 1687.3 kg/cm^2 . The iodine doping was carried out by exposure of the pellets to iodine vapour at atmospheric pressure and room temperature in a desiccator.

2.2. Preparation of coordination polymers

Chelating ligand was synthesized according to previously published work [36–38]. In the present work four coordination polymers have been synthesized. The coordination polymers were synthesized by dissolving metal acetate (10 mmol) and ligand (5 mmol) separately in 25 ml hot dimethylformamide (Scheme 1). The solutions of metal acetate and bis-ligand were filtered and mixed in hot condition and the mixture was refluxed in an oil bath. The temperatures of the reaction mixture were maintained at 140–150 °C. The coordination polymers appeared after 20–24 h. The products obtained were filtered, washed thoroughly with hot dimethylformamide, dimethylsulphoxide and alcohol was used to remove the unreacted reactant, if any present. Finally, the polymers were dried. The purity of products was ascertained by repeated washing with hot DMF and ethanol. The obtained polymers were stable and coloured at room temperature. The synthesized coordination polymers to assign the geometry were characterised by elemental analysis, IR spectroscopy, diffuse reflectance, XRD and magnetic measurements.

2.3. Method

Thermogravimetric analyses of coordination polymers were performed by TG/DTG/DTA techniques at a heating rate of 10 °C/min under N_2 atmosphere. We assume initial decomposition temperature (T_i) due to the degradation of ligand, not by hydration of water and half decomposing temperature (T_h) and final decomposing temperature (T_f) due to degradation of organic moieties in order to confirm their thermal stability behaviour as well as recorded decomposition temperature of coordination polymers at 5%, 10% and 20% mass loss (T_5 , T_{10} and T_{20}). The point obtained at the intersection of tangent to the peak of DTG curve is called as peak temperature (T_{DTG} or T_m) i.e., the maximum mass loss at temperature. The matter released at each step of the degradation was identified through attributing the mass loss at given step to the similar mass calculated from molecular formula of investigated polymer, comparing that with literature values for relevant complexes and considering their temperature.



Scheme 1 Preparation of coordination polymer.

3. Results and discussion

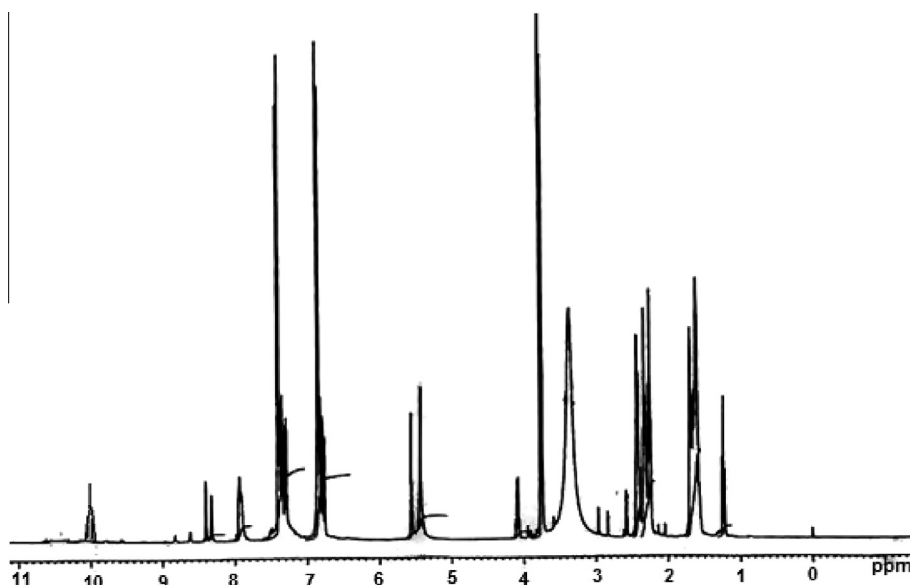
3.1. Synthesis and characterisation of coordination polymers

The chelating ligand formed by condensation of fumaric dichloride with paramethoxyphenylcarbamide would generate structurally interesting thermally stable coordination polymers. The coordination polymers were synthesized by condensation of transition metal salts ($\text{M}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$ where $\text{M}=\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$) with polydentate chelating ligand i.e., fumaroyl bis (paramethoxyphenylcarbamide) (*fbmpc*) in mixed solvent of dimethylformamide-ethanol. Here, we have synthesized coordination polymers via several trial methods of different ratios of dimethylformamide and ethanol solvent. The best result was obtained from the equimolar ratio of both the solvents i.e., EtOH/DMF. The reaction of $\text{M}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$ with *fbmpc* in EtOH/DMF required different time, out of four coordination polymers copper(II) required much more time i.e., 24 h. Mn(II) was found to be in cement colour with yield 69.8%, Co(II) in pink with yield 68.2%, Ni(II) in green with yield 65.1% and Cu(II) in blue colour with yield 64.9%. The yield of polymer, molecular weight, and empirical formula weight are given in Table 1. Furthermore, the solubility was investigated with 0.01 g in 2 ml of solvent. These products were insoluble in common organic solvents. However, chelating ligand showed a high solubility in mixture of dimethylformamide-alcohol. Due to the high molecular weight, multiple double bonds, multifunctional group and heterocyclic ring formation the result showed a high insolubility and thermal stabilities for all the coordination polymers than a ligand. The molecular composition of inorganic complexes i.e., coordination polymer may generally be formulated as $\{[\text{M}(\text{fbmpc})(\text{H}_2\text{O})_x] \cdot y\text{H}_2\text{O}\}_n$ on the basis of elemental analysis and thermogravimetry analysis. The proposed structure of coordination polymers (Fig. 1) has been deduced by elemental analysis, IR, diffuse reflectance, magnetic moment, thermal, SEM, and XRD techniques. TG/DTG and DTA studies decide whether aqua molecules are placed either inside or outside of Werner's sphere of attraction.

The electronic spectral data of ligand were found at 263, 288 nm and 290, 308 nm. The first peak is attributed to the aromatic benzene ring $\pi-\pi^*$ and the second peak due to $n-\pi^*$ transition, then this transition is shifted to lower wavelength with high intensity. This shift indicated the donation of a lone pair of electrons of nitrogen in ligand to the central metal ion. ^1H NMR spectra of *fbmpc* showed a multiplet at δ 6.7–7.8 ppm that may be due the presence of aromatic protons. 3H of the 4-methoxy phenyl ring produces a singlet at δ 3.6 ppm. Hydrogen of $-\text{CONH}$ produces a singlet at δ 10.0 ppm. Proton NMR spectra of methylene proton show multiplet for 2H of methylene of at δ 1.9–3.2 ppm. Proton NMR spectra of ligand are displayed in Fig. 2. The infrared spectrum of free *fbmpc* contains a band for NH group at 3310 cm^{-1} . The N–H frequencies of ligand shifted towards a lower or higher frequency in all polymers which confirmed the coordination formation. But, a broad peak found after chelation at 3400–3700 cm^{-1} may be due to the $-\text{OH}$ group frequency of lattice water which merged with the N–H group followed by a sharp peak at 742–759 cm^{-1} assignable to rocking and wagging vibrations which may be due to the co-ordination water in coordination polymers [39]. A

Table 1 Physicochemical data of coordination polymers.

Ligands/polymers	Colour	Mol. formula	Mol. Wt.	Yield%
fbmpc	Creamish	C ₂₀ H ₂₀ N ₄ O ₆	412	79.3
{Mn(fbmpc)} H ₂ O _n	Cement	C ₂₀ H ₂₀ N ₄ O ₇ Mn	482.93	69.8
{Co(fbmpc)} 3H ₂ O _n	Chocolate	C ₂₀ H ₂₄ N ₄ O ₉ Co	522.93	68.2
{Ni(fbmpc) (H ₂ O) ₂ } 3H ₂ O _n	Shine black	C ₂₀ H ₂₈ N ₄ O ₁₁ Ni	558.69	65.1
{Cu(fbmpc) (H ₂ O) ₂ } 2H ₂ O _n	Black	C ₂₀ H ₂₆ N ₄ O ₁₀ Cu	545.54	64.9

**Figure 2** Proton NMR spectra of ligand.

representative IR data have been shown in Table 2. The presence of a perceptible band for C=O was found at 1665 cm⁻¹ in free ligand, whereas in coordination polymers it was shifted towards the lower frequency relative to the band of the parent ligand which indicates the chelation, then ultimately strengthened the C=N bond as result of polymerization. It happened due to the enolization of C=O to C=N mode and is represented in Scheme 2.

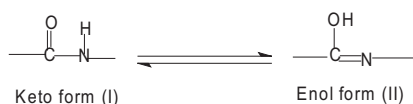
This suggests, a covalent mode of ligand moiety by —OH group to central metal ion, whereas the coordination mode through a nitrogen atom. This indicates the bidentate nature of the chelating ligand. The coordination mode of *fbmpc* in coordination polymers is shown in Scheme 3.

A noteworthy medium weak peak was observed at 413–429 cm⁻¹ and 545–612 cm⁻¹ in all coordination polymers which were assigned to the $\nu(\text{M-O})$ and $\nu(\text{M} \leftarrow \text{N})$ [40]

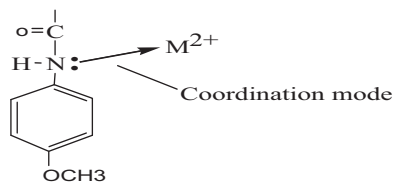
Table 2 Infrared, magnetic moment, reflectance spectra and assignment for coordination polymers.

Polymers	—NH	C=O	M—O	M—N	H—OH	C=N	μ_B	Absorbance	Assignments	Geometry
<i>fbmpc</i>	3310s	1665s	—	—	—	—	—	—	—	—
Mn(II)	3306s	1658s	417	589	3448s,—	1531	5.41	16,420 18,248 24,154	⁶ A ₁ (S) → ⁴ T ₂ (G) ⁶ A ₁ (S) → ⁴ E(G) ⁶ A ₁ (S) → ⁴ A ₁ (G)	Tetrahedral
Co(II)	3487s	1649s	429	612	3487s,—	1543	3.72	15,408 16,339	⁴ A ₂ (F) → ⁴ T ₁ (P) ⁴ A ₂ (F) → ⁴ T ₁ (F)	Tetrahedral
Ni(II)	3268s	1639s	428	545	3474s,742b	1549	2.76	16,474 26,385	³ A _{2g} (F) → ³ T _{2g} (F) ³ A _{2g} (F) → ³ T _{1g} (P)	Octahedral
Cu(II)	3448s	1629s	413	549	3448s,759b	1544	1.98	13,245 14,534 17,211	² B _{1g} → ² B _{2g} ² B _{1g} → ² E _g ² B _{1g} → ² A _{1g}	Distorted Octahedral

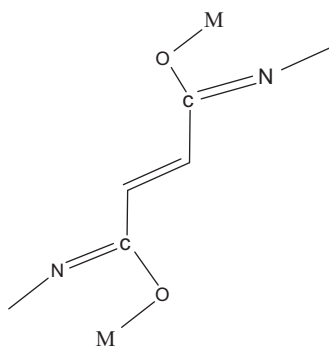
s = stretching and b = bending vibration frequency in coordination polymers.



Scheme 2 Keto-enol tautomerism and covalent mode of *fbpmc* in coordination polymers during polymerization.



Scheme 3 Coordination mode of *fbpmc* in coordination polymer.



Scheme 4 Asymmetric chelation mode of *fbpmc* in coordination polymers.

respectively. Metal ions in polymer were linked to each of the carboxylato group by covalent bond in the asymmetric chelation mode (Scheme 4). The coordination geometry of Mn(II) and Co(II) ions is tetrahedral and consists of two N-atom and two O-atom of *fbpmc*, whereas the geometry of Ni(II) and Cu(II) ions consists of two N-atoms and two O-atoms of *fbpmc* and two coordinated water molecules. The equatorial coordination site was occupied by two N-atoms of amide and two O-atoms of carboxylato anion by *bis* bidentate manner of *fbpmc*, while the axial position was occupied by two coordinated aquo ligands in Ni(II) and Cu(II).

The diffuse reflectance data and curves are tabulated and presented in Table 1 and Fig. 3 respectively. This study is genuinely helpful for determining the geometry of coordination polymers. The diffuse reflectance of Mn(II) shows peaks at $24,154\text{ cm}^{-1}$, $16,420\text{ cm}^{-1}$ and $18,248\text{ cm}^{-1}$ which may be assigned to ${}^6A_1(S) \rightarrow {}^4A_1(G)$, ${}^6A_1(S) \rightarrow {}^4T_2(G)$ and ${}^6A_1(S) \rightarrow {}^4E(G)$ transitions favours four coordinating tetrahedral geometry [41] respectively and obtained magnetic moment value μ_B : 5.412 B.M, hence it indicates that spins free with corresponding to paramagnetic nature. The reflectance spectra of Co(II) and Ni(II) exhibited two bands at $16,339\text{ cm}^{-1}$, $15,408\text{ cm}^{-1}$ and $16,474\text{ cm}^{-1}$, $26,385\text{ cm}^{-1}$ assigned to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ and ${}^3A_2g(F) \rightarrow {}^3T_2g(F)$, ${}^3A_2g(F) \rightarrow {}^3T_1g(P)$ transition corresponding to tetrahedral and octahedral

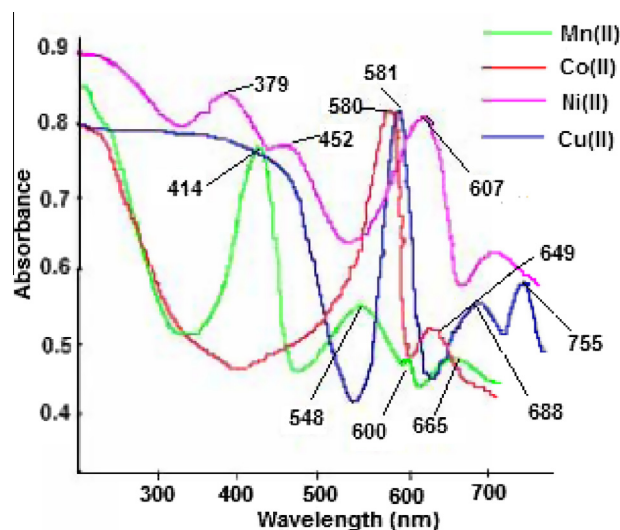


Figure 3 Diffuse reflectance spectra of coordination polymers.

environmental around Co(II) and Ni(II) ions [42,43,39] respectively. Magnetic moment value for Co(II) and Ni(II) were found as μ_B : 3.72 and 2.76 B.M which indicates high-spin coordination polymers. The reflectance spectrum of Cu(II) is expected to consist allowed transitions ($13,245\text{ cm}^{-1}$, $14,534\text{ cm}^{-1}$ and $17,211\text{ cm}^{-1}$) namely ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$. These bands suggested distorted-octahedral geometry around Cu(II) ion [44,39] and supported by magnetic moment value μ_B : 1.98 B.M.

3.2. Morphological behaviour

The morphological behaviours of divalent transition metal coordination polymers were characterised by X-ray diffraction and scanning electron microscopy techniques. X-ray diffraction analyses of coordination polymers were carried out in solid state form. The X-ray diffractograph of Mn(II), Co(II) and Ni(II) showed broad weak peaks, which indicates the amorphous powder nature and does not exhibit any anisotropic behaviours. Though, these coordination polymers show an amorphous structure they are not soluble in common organic solvents such as alcohol, chloroform, carbon tetrachloride, dimethylsulphoxide and dimethylformamide. However, the powder X-ray diffraction pattern of Cu(II) exhibits some long fine peaks, as well as the data show a hallow pattern in the region $2\theta = 10\text{--}80^\circ$. This indicates weak crystallinity with pseudo orthorhombic structure.

SEM images of coordination polymers were recorded at energy of 20 kV with magnification $\times 5000$ which are displayed in Fig. 4a–d. This technique is helpful to classify the distinct morphology of ligand and coordination polymers. The distinct morphology of coordination polymers is conspicuous the formation of new product. The morphologies of coordination polymers are found in different shapes and sizes, though they are synthesized from a single ligand. The morphology of Mn(II) polymer (Fig. 4a) is found beads shape as well as appeared like stack of globule droplet or beads in long chain. The bigger size of droplet is due to the mishmash of various single beads. Each bigger beads diameter is found 851.53 nm, whereas small bead have 80 nm sizes. The micrograph of

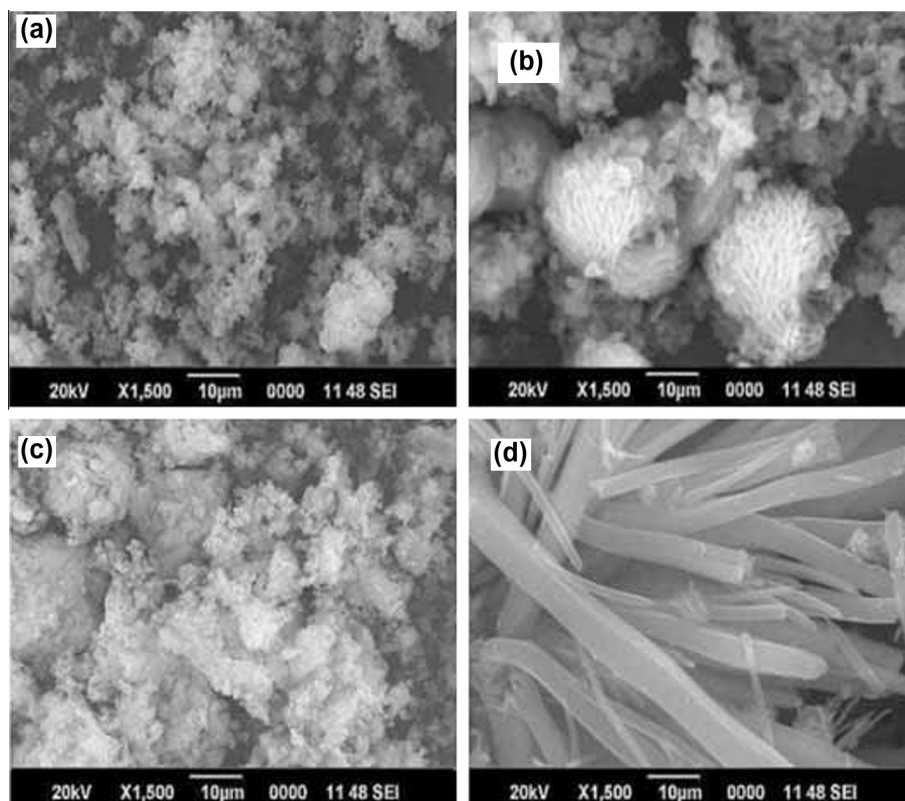


Figure 4 SEM image of coordination polymers of (a) Mn(II), (b) Co(II), (c) Ni(II) and (d) Cu(II).

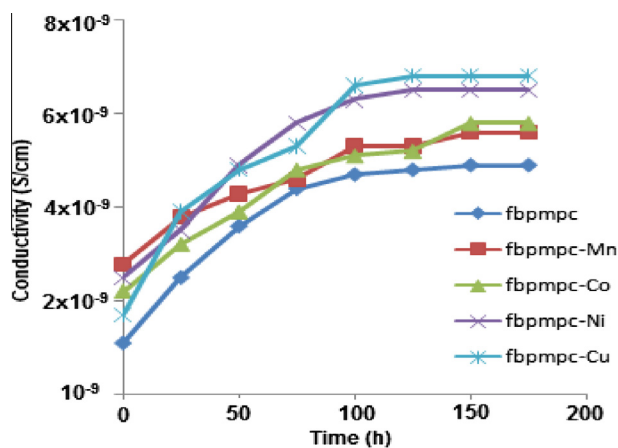


Figure 5 Electrical conductivities changes of I₂-doped *fbpmc* and coordination polymers vs. doping time at 30 °C.

Co(II) (Fig. 4b) showed jelly fish type structure i.e., seen as a bundle of fibres of polymer having diameter size 90 nm. It revealed that the polymerization took place. The SEM of Ni(II) (Fig. 4c) is unclear, but showed some small irregular shaped particles entrapped in bigger one and unite to give cotton shape structure, which indicates the aggregation of number of polymer chains. The image of Cu(II) (Fig. 4d) shows smart look with fine sharp and rod shape structure or tentacles, which indicates semi crystalline nature. Each tentacle has different lengths and diameters. The diameter of each bigger tentacle shape is found to be 935.22 nm, whereas fine sharp

tentacle has 100 nm sizes. The fine shape tentacles structure is due to the aggregation of various monomers leading to the polymerization. Consequently, scanning electron microscope studies divulge the synthesized metal coordination polymers were in polymeric form.

3.3. Electrical conductivity study

The electrical conductivities studies of coordination polymers were carried out in powdered form. The four probe method was used to carry out the study using an electrometer. The electrical conductivities of *fbpmc*, *fbpmc*-Mn, *fbpmc*-Co, *fbpmc*-Ni and *fbpmc*-Cu were found to be in range 1.1×10^{-9} – 6.8×10^{-9} S/cm. Herein, it was seen that the electrical conductivities increases when the material doped with iodine. Fig. 5 shows the results for *fbpmc* and its metal coordination polymers doped with iodine for various time at 30 °C. It was found that the conductivity increases steadily with doping time, but then levels off. The important thing is that the long doping times are needed to obtain more electrical conductivity. The maximum conductivities were measured as 6.8×10^{-9} S/cm, the increase in electrical conductivity of coordination polymers imply that the charge-transfer complex between materials and dopant iodine is formed without interrupting. The maximum conductivity values for *fbpmc*, *fbpmc*-Mn, *fbpmc*-Co, *fbpmc*-Ni and *fbpmc*-Cu were found to be 4.9×10^{-9} , 5.6×10^{-9} , 5.8×10^{-9} , 6.5×10^{-9} and 6.8×10^{-9} S/cm respectively. According to these values, the highest conductivity was observed in *fbpmc*-Cu coordination polymer. Only small noteworthy differences were found in electrical conductivity values of *fbpmc*-Mn, *fbpmc*-Co,

fbmpc-Ni and *fbmpc*-Cu. Nitrogen atom is very electronegative element having tendency of coordinating with iodine molecule. This happened because all these belong to a similar class of metal coordination polymers. The conductivity values of other metal coordination polymers had been measured by the same techniques and present results agreed with reported literature [45].

3.4. Thermal studies of coordination polymers

TG/DTG/DTA curves of coordination polymer are displayed in Figs. 6–9 and their thermal decomposition data are tabulated in Tables 3 and 4. Thermal decomposition of all the coordination polymers was carried out at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere over the temperature range 28–1220 $^{\circ}\text{C}$. The structural transformation is observed by TG curves which is supported by DTG and DTA studies. Thermal analysis has proved to be useful in determining the crystal water content in the coordination polymers and their thermal stability as well as decomposition mode under controlled heating rate. The matter released at each step of degradation was identified through attributing the mass loss at given step to the similar mass calculated from molecular formula of investigated polymer, comparing that with literature values for relevant coordination polymers considering their temperature. The thermal stability properties were evaluated by TG/DTG/DTA methods whose results revealed good thermal stability for all the synthesized coordination polymers. Moreover, the limited oxygen index values were calculated on the basis of

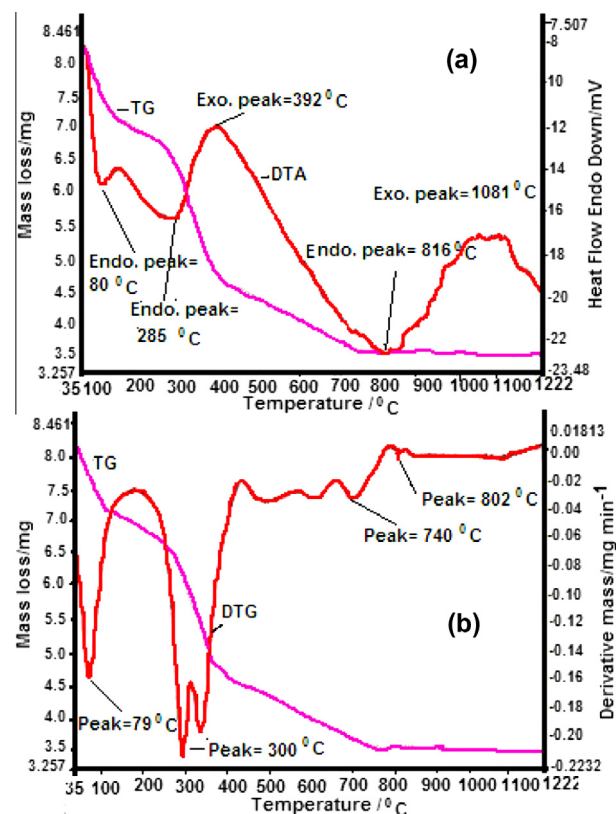


Figure 7 (a) TG/DTA and (b) TG/DTG curves of Co-coordination polymer.

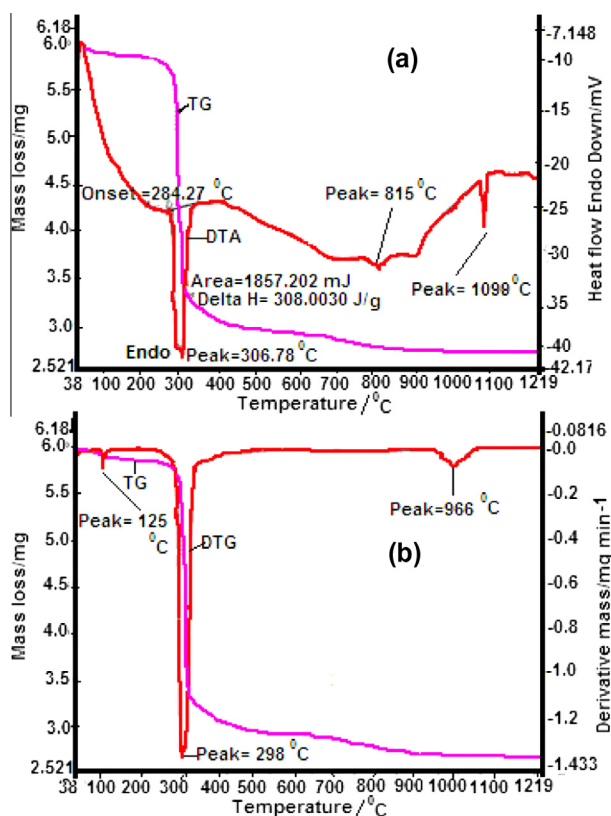


Figure 6 (a) TG/DTA and (b) TG/DTG curves of Mn-coordination polymer.

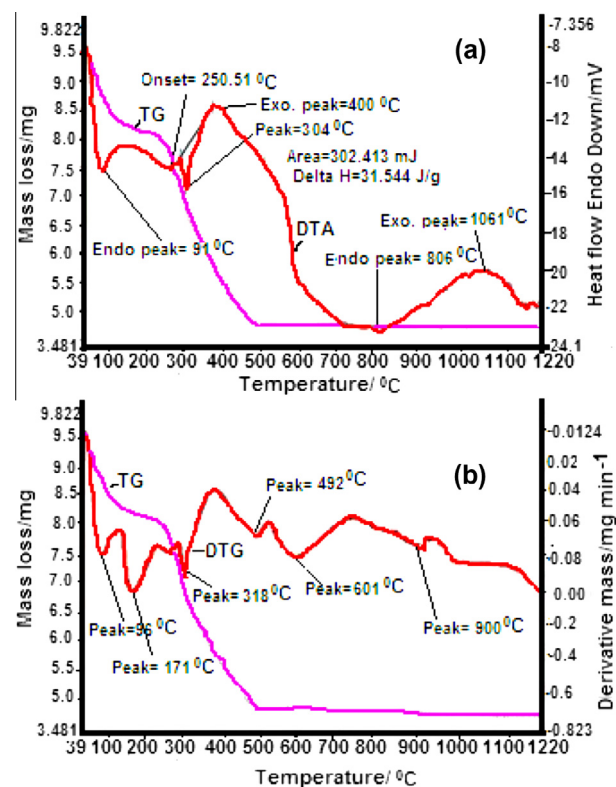


Figure 8 (a) TG/DTA and (b) TG/DTG curves of Ni-coordination polymer.

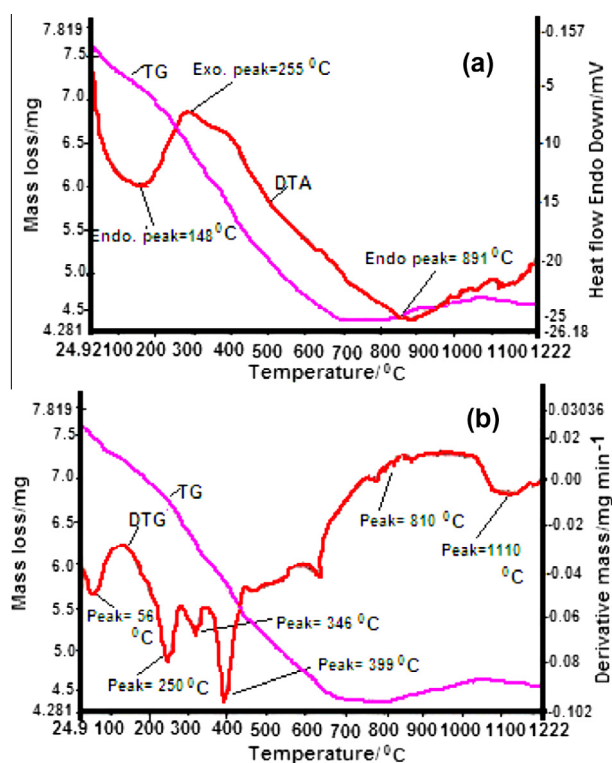


Figure 9 (a) TG/DTA and (b) TG/DTG of curves Cu-coordination polymer.

char yield obtained at 1200 °C and revealed good thermal stability of the coordination polymers.

3.4.1. Thermal degradation

The newly synthesized divalent transition metal coordination polymers were found to be highly thermally stable as

compared to its *bis* (bidentate) ligand. In general, it was observed that the sequence of degradation that takes place in these coordination polymers starts with dehydration of adsorbed water followed by the release of coordination water and then fragments of the backbone. This seems like a multi-step decomposition process. However, a close investigation of TG/DTG/DTA curves of Mn(II) (Fig. 6) revealed the thermal decomposition profile which occurs through three steps. The initial step of degradation at 42–140 °C with T_{DTG} at 125 °C, correspond to 3.2% (Calc. 3.7%) mass loss may be due to the removal of lattice water. Moreover, it was supported by elemental analysis and IR data. But no T_{DTG} and T_{DTA} peaks were found for coordinated water molecules. The initial step of decomposition in TG curve was found to be in temperature range 35–165 °C, 39–150 °C and 24–150 °C associated with T_{DTG} peaks at 79 °C, 96 °C and 52 °C for Co(II), Ni(II) and Cu(II) coordination polymers respectively, hence the low temperature range corresponding to this transformation indicates the presence of loss of lattice water and these values are further supported by elemental analysis, IR data. Releasing of adsorbed lattice water in coordination polymer was reported with good agreement [46–48].

In this dehydration process, the ease of adsorbed water desolvation in these coordination polymers suggests the weak interaction of water or no role in the lattice forces and occupies in the crystal voids. The small differences in the T_{DTG} values (125, 79, 96 and 56 °C), the endothermic peaks with small differences in the T_{DTA} values (80 and 91 °C) suggest that the adsorbed water in these coordination polymers may be identical. Hence, the strength of the dehydration DTG peaks indicates that the rate of dehydration in these coordination polymers is almost same. This process is followed immediately by removal of coordinated water molecules from the inner sphere of coordination polymer compound and yielding stable anhydrous intermediate. At a higher temperature, this intermediate undergoes further degradation involving ligand

Table 3 TG/DTG/DTA data and assignments of coordination polymers.

Polymers	Step	DTG_{max}	Temperature Range (°C)	DTA (T_{DTA})		Weight loss Obs/Calc	Assignment
		T_{DTG}		Endo	Exo		
Mn(II)	1st	125	42–140	—	—	3.2/3.7	–1H ₂ O (lattice water)
	2nd	298	255–500	306	—	40.3/42.6	–50% ligand
	3rd	966	500–1219	815,1099	—	40.9/42.6	–50% ligand
Residue of MnO							
Co(II)	1st	79	35–162	80	—	11.2/10.3	–3H ₂ O (lattice water)
	2nd	300,722	200–740	285	392	42.1/43.3	–55% ligand
	3rd	740,802	740–1222	816	1081	35.3/35.2	–45% ligand
Residue of CoO							
Ni(II)	1st	96	39–150	91	—	10.4/9.6	–3H ₂ O (lattice water)
	2nd	171,221	150–250	268	—	6.9/6.4	–2H ₂ O (coord. water)
	3rd	318,492	250–500	304	400	48.3/51.6	–70% ligand
	4th	601,900	500–1220	806	1061	22.1/22.12	–30% ligand
Residue of NiO							
Cu(II)	1st	56	24–150	148	—	7.3/6.5	–2H ₂ O (lattice water)
	2nd	250	150–260	—	255	6.4/6.5	–2H ₂ O (coord water)
	3rd	346,399	260–700	400	—	38.1/41.5	–55% ligand
	4th	810,1110	700–1222	891	1100	32.9/33.9	–45% ligand
Residue of CuO							

Table 4 Thermal behaviour data of coordination polymers.

Polymers	TG								
	^a T_i	^b T_{max}	^c T_f	^d T_h	^e $T_{5\%}$	^f $T_{10\%}$	^g $T_{20\%}$	^h Char yield%	ⁱ LOI
Mn(II)	250	125,298,966	926	465	282	284	298	85.3	51.6
Co(II)	200	79,300,722	800	412	79	100	305	88.6	52.9
Ni(II)	255	143,321,822	1008	⁵⁰⁰	118	289	316	87.7	52.5
Cu(II)	260	52,346,810	1110	⁷⁰⁰	135	215	342	84.7	51.3

^a The initial degradation temperature due to ligand in coordination polymers.

^b Peak temperature.

^c Final step decomposing temperature.

^d Half decomposing temperature.

^{e-g} Temperature corresponding to 5%, 10%, 20% weight losses.

^h Decomposed material left undecomposed after TG analysis at 1200 °C.

ⁱ LOI (limiting oxygen index).

fragmentation, which occurs in multistep. Also in our previous study on thermal stability of coordination polymer by TG/DTG/DTA analysis [49] it shows a medium difference in their T_{DTG} and T_{DTA} values for lattice water, but shows multi step mechanism in thermal degradation of backbone (ligand) and coordination of water (copper ion).

The second step decomposition in TG curves (Figs. 8 and 9) shows the slow rate of mass losses between 150 and 260 °C for Ni(II) and Cu(II) may be due the loss of coordinated water, which demonstrate a great stability of coordination polymer. This stability can be correlated with the coordination ring as well as the strong interaction between the metal ion and chelating ligand with oxygen donor atom. The reported temperature range was valid for various coordination polymers [50,51]. The Ni(II) loss its two coordinated water molecules at 150–250 °C associated with T_{DTG} peak at 221 °C and endothermic T_{DTA} peak at 268 °C corresponding to the loss of 6.9% (Calc.6.4%) of two water molecules. However, in Cu(II) the second step is displayed at 150–260 °C corresponding to the removal of coordinated water of 6.4% (Calc. 6.5%) associated with T_{DTG} peak at 250 °C and one endothermic T_{DTA} peak at 255 °C. The thermal degradation data and various decomposition temperatures of coordination polymer are shown in Table 3.

The last step degradation profile in all coordination polymers was loss of organic moieties. The 50% mass loss of ligand in Mn(II) coordination polymer (Fig. 6a and b) between 262 and 500 °C (Obs.40.3%, Calc.42.6%) at second step is associated with T_{DTG} peak at 298 °C and T_{DTA} peak at 306 °C. The remaining 50% mass loss of ligand was found at the third step (500–1219 °C) with a T_{DTG} peak at 966 °C and T_{DTA} peak at 815 °C. In the second step (200–740 °C) for Co(II) coordination polymer (Fig. 7a and b) two T_{DTG} peaks were found at 300,722 °C and exothermic T_{DTA} peaks at 392 corresponding to the release of 55% ligand, whereas the fourth step was decomposed at 400–560 °C with mass loss of about 45% with T_{DTG} peaks at 740 °C, 802 °C and one endothermic and exothermic T_{DTA} peaks at 816 °C and 1081 °C, which corresponds to the released of remaining ligand. The observed mass loss (70%) in Ni(II) coordination polymer (Fig. 8a and b) at the third step (250–500 °C) with two T_{DTG} peaks at 301, 822 °C and one endothermic T_{DTA} peak at 304 °C and one exothermic T_{DTA} peak at 400 °C corresponds to mass loss 48.3% (Calc. 51.6%), while at the fourth step (500–1220 °C) released 30% ligand (Obs. 22.1%, Calc. 22.1%) with two T_{DTG} peak at

605, 900 °C and T_{DTA} peak at 806 and 1061 °C and formed metal oxide.

The mass loss of 55% ligand (Obs. 38.1%) in Cu(II) (Fig. 9c and d) at the third step (260–700 °C) associated with T_{DTG} peaks at 300 °C, 399 °C and T_{DTA} peak at 400 °C hence, it corresponds to mass loss of the ligand. The mass loss at the fourth step (700–1222 °C) with T_{DTG} peaks at 810 °C, 1110 °C and two T_{DTA} peaks at 891 °C, 1100 °C corresponds to the loss of remaining 45% ligand (Obs. 32.9%, Calc. 33.9%), the residue obtained later is metal oxide. It was interesting but surprising to note from TG/DTG/DTA data for all the coordination polymers that, the thermal degradation reaction of the transition metal coordination polymers results in the formation of their metal oxide.

3.4.2. Thermal stability

From, above interpretation of TG/DTG/DTA curves of all coordination polymers show the presence of lattice water, however Ni(II) and Cu(II) polymers show the presence of coordinated water. On the basis of TG/DTG/DTA analyses the coordination polymers were found to be thermally stable, however Cu(II) polymer shows highly thermal stability among the other coordination polymers. At the stage after release of coordination water and backbone the manganese, cobalt, nickel and copper ions in the coordination polymers were converted from multiple bonding to lower bonding. Hence, consequently metal ions with lower coordination number, where the repulsion between electron pairs decreases. Therefore, the electronegativity of metal ion becomes the predominant factor in the stability. This was evident in complete degradation of the backbone structure of the metal ions in the coordination polymers, if the initial decomposition temperature due to the backbone was considered then the high thermal stability was found for copper ion. It was due to the high electronegativity values as compared to other ions. Furthermore, the dehydration process, the ease of lattice and coordinated water in coordination polymers suggest almost identical. The initial decomposition temperature due to backbone in coordination polymer found small difference which may be due to the identical detachment of organic moieties suggesting same thermal stability at this stage, except cobalt ion. But, at half decomposition temperature and final decomposition temperature in coordination polymers a greater difference has been found, implying distinct thermal stability. If we look at the thermal stability on the

basis of half decomposition temperature, the copper ion shows a greater thermal stability. However, if we look on the basis of final decomposition temperature, the copper ion shows greater thermal stability. Hence, over all more thermal stability was shown by copper coordination polymer due to the high electronegativity and small ionic sizes. Furthermore, the thermal stability of coordination polymer is measured on the basis of char yield as summarized in Table 4. Char residue left after decomposition was in range 67–88%. More residue value was obtained for Ni(II) and Cu(II) at 1219–1222 °C. It was also well supported for high value of thermal stability for coordination polymers. In the above discussion the rate of releasing ligand in coordination polymers was somewhat comparable, but in some polymers it was contrary, this may be due to the different kinetic nature of polymers at the transition state.

Therefore, it was concluded that the thermal stability at the second and the third steps for Ni(II) and Cu(II) was more; this might be due to the slow degradation of coordinated water, organic ligand and formation of metal oxide, while a low value was obtained at the first step due to the weakly bonded lattice water. In conclusion, the thermal studies were significantly helpful for the elucidation of crystallisation of water, decomposition temperature and thermal stability of coordination polymers for each degradation step in thermal analysis processes. Furthermore, in order to check out the more thermal stability of coordination polymers, the initial decomposition temperature due to ligand, half decomposition temperature and final decomposition temperature are compared graphically. A graph of decomposition temperature vs. atomic number has been plotted and shown in Fig. 10. The coordination polymers of Cu(II) and Ni(II) were present on the peaks of the curve. This means that these two coordination polymers were more stable at the beginning of organic ligand decomposition than those on the bottom of the curve, Co(II) and Mn(II). Hence, a greater thermal stability was revealed for Cu(II) ion. Additionally, a graph of ionic radii of divalent transition metal ions against atomic number is plotted and displayed in Fig. 11.

Fig. 11 also suggests same order of thermal stability for coordination polymers. This study shows that there was a relationship between the ionic radius of the divalent transition metal ions and the thermal stability of the coordination polymers. From Fig. 11, it was concluded that the ionic radius of manganese and copper has top position, whereas the cobalt and nickel at bottom of the graph, hence copper shows a high

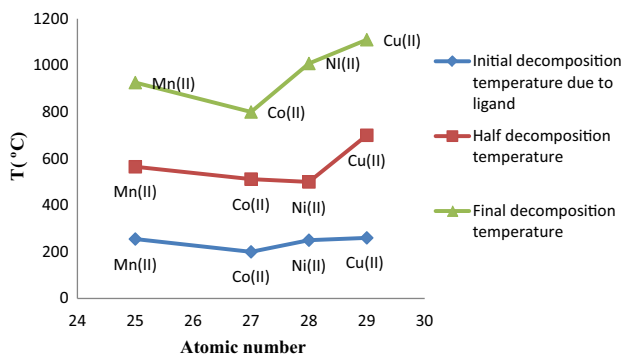


Figure 10 Decomposition temperatures of transition metal ions of coordination polymers vs. atomic number.

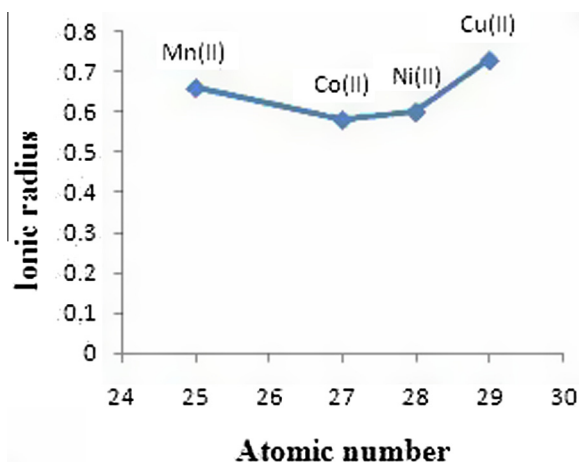


Figure 11 Ionic radius of divalent metal ions vs. atomic number.

thermal stability compared to other metal ions. Consequently, the thermal stabilities of coordination polymers increase as the ionic radii of divalent transition metals increase.

In an epilogue, complete backbone (ligand) decomposition has been taken place in two steps for Mn(II) (250–1219 °C), for Co(II) (200–1222 °C), for Ni(II) (255–1220 °C) and for Cu(II) (260–1222 °C). The initial peak temperature due to a ligand $T_i(T_{DTG})$ was found for Mn(II) at 298 °C, for Co(II) at 300 °C, for Ni(II) at 318 °C and for Cu(II) at 346 °C, however, a half decomposition temperature was observed for Mn(II), at 465 °C, Co(II), at 412 °C, Ni(II) at 500 °C and Cu(II) at 700 °C, whereas a final step decomposition temperature (T_f) was found for Mn(II), at 926 °C, for Co(II) at 800 °C, for Ni(II) at 1008 °C and for Cu(II) at 1110 °C. Therefore, on the basis of $T_i(T_{DTG})$, $T_h(T_{DTG})$, $T_f(T_{DTG})$ and the thermal stability of divalent transition metal coordination polymers were of the order: Cu(II) > Ni(II) > Mn(II) > Co(II). The higher thermal stability (1110 °C) due to the completion of the backbone degradation can be attributed to the higher electronegativity of copper compares to other metal ions, proving the predominant role of the electronegativity in the stability. The higher thermal stability shown by copper ion also reflects that it may be due to the smaller ionic sizes. Finally, it was disclosed that the entire coordination polymers have high degradation temperature with high thermal stability; therefore these may be used as thermally stable materials.

4. Conclusions

In this study, we have synthesized four novel coordination polymers of divalent transition metal ions with *fbpmc* chelating ligand that belongs to a class of coordination chemistry. Coordination polymers were structurally characterised by combined study of spectroscopic, magnetic susceptibility and thermal analysis. Apart from this, XRD and SEM studies confirmed the size and morphological behaviour of coordination polymers. The electrical conductivity value of copper coordination polymer was higher than the other coordination polymers. Furthermore, the detailed thermal study (TG–DTG) played an important role to confirm the number and nature of water molecules in coordination polymers. Also, DTA

technique was vital benefit to find out the dehydration of adsorbed water molecules in coordination polymers. Thermal analyses evoke although the four coordination polymers were of a particular ligand with different transition metal ions, yet the thermographs displayed different patterns and no identical decomposition. Finally, on the basis of $T_i(T_{DTG})$, $T_h(T_{DTG})$, $T_f(T_{DTG})$ and char yield value the high thermal stability was shown for copper(II) ion as compared to other ions.

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