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COORDINATION CHAIN POLYMERIC ASSEMBLIES OF TRIVALENT LANTHANIDES WITH MULTIDENTATE SCHIFF BASE
Synthetic, spectral investigation and thermal aspects

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The coordination chain polymers of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) with N,N'-di(*o*-thiophenyl)terephthalaldehydediimine have been prepared and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, magnetic measurements, infrared spectra, reflectance spectra and thermogravimetric analysis. A coordination number of seven around the metal ion is suggested. The thermal decompositions of the coordination polymers have been studied. The kinetic parameters have been calculated using Freeman-Carroll method. The thermodynamic activation parameters such as entropy (S^*), preexponential factor (A), enthalpy (H^*) and free energy of the decomposition (G^*) have been evaluated.

Keywords: *polymeric assemblies, Schiff base, spectral investigation, thermal study, trivalent lanthanides*

Introduction

The rational increase of structural dimensionality is an important synthetic goal in supramolecular systems, organometallics, polymers, and material chemistry. Lanthanide metal ions possess properties like 0D frameworks and built up of metal centers linked organic ligands have been extensively studied in recent years with especial interest in their utility for molecular recognition, separation, non-linear optical properties or for absorption, porous materials and catalytic purposes [1–8]. Lanthanide coordination polymers have opened up a lots of opportunities in growing fields of large social and economical impact, such as environmental, medical, surface, polymer, photochemical and nano sciences [9–14]. Lanthanide coordination chain polymeric assemblies are less common even though it offers various coordination-mode and variable coordination number, which is often used to furnish high-dimension coordination polymer as nodes [15–17]. In continuation of earlier work [18], we prepared N, N'-di(*o*-thiophenyl)terephthalal- dehydediimine, which react with lanthanide metal ions like La(III), Ce(III), Pr(III), Nd(III) and Sm(III). The coordination polymers have been characterized on the basis of elemental analysis, infrared spectra, reflectance spectra, magnetic measurements and thermogravim etric measurements. Suggested structure of the ligand is shown in Fig. 1.

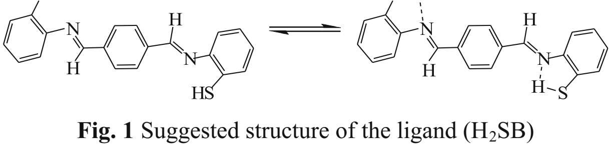

Fig. 1 Suggested structure of the ligand (H_2SB)

Experimental

Materials and methods

All the chemicals used were of analytical grade and used without further purification. Terephthalaldehyde, 2-aminothiophenol, and metal nitrates were purchased form E-Merck (India) Ltd., Mumbai. The organic solvents were purified from standard method [19].

Preparation of Schiff base

An ethanolic solution (100 mL) of terephthalaldehyde (1.34 g, 1 mmol) and an ethanolic solution (100 mL) of *o*-aminothiophenol (2.74 g, 2 mmol) were refluxed and a yellow crystalline solid was obtained immediately. The ligand was filtered, washed successively with ethanol and dried in air. The product was recrystallized in dimethyl formamide as insoluble in common organic solvents such as benzene, chloroform, and acetone.

Preparation of coordination polymers

The solution (100 mL) of metal nitrate (2 mmol) in dimethyl formamide was slowly added to a dimethyl formamide solution of the ligand (0.6 g, 2 mmol) in 1:1 mole ratio. The resulting mixture was heated for 10 h at 120°C to ensure complete precipitation and

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then allowed to cool overnight at room temperature. The obtained coordination polymer was filtered, washed with dimethyl formamide and dried in air. The coordination polymers are insoluble in all common organic solvents such as acetone, ethanol, chloroform, methanol, benzene, dimethyl formamide etc. The ^{1}H NMR and ^{13}C NMR spectral data are summarized in Table 1.

Table 1 ^{1}H NMR and ^{13}C NMR data of ligand

Compounds	^{1}H NMR	^{13}C NMR
H_2SB	3.33 (2H, s,-SH), 7.1-7.9(12H, Ar-H), 8.4(2H, s, CH=N),	C_1–160.2, C_2–126.4 C_3–130.1,C_4–127.8 C_5–136.0,C_6–115.5 C_7–176.0, C_8–138.3 C_9–128.4

Analytical procedure

The coordination polymers were analyzed for the metal contents by the EDTA titration technique [20]. Thermogravimetric analysis and differential thermal analysis were obtained with a model 5000/2960 SDTA, TA instrument (USA). The ^{1}H NMR and ^{13}C NMR were recorded on Bruker Avance (400 MHz). The magnetic moment have been obtained by Gouy's method using mercurytetrathiocyanatocobaltate(II) as a calibrant (λ_g = 16.44·10^{-6} C.G.S. unit at 20°C). Diamagnetic corrections were made using Pascal's constant. Infrared spectra were measured on a FT-IR Nicolet 400D spectrophotometer in KBr pellets. The reflectance spectra were measured on Beckman DK-2A spectrophotometer using MgO as a reference. The nitrogen, carbon and hydrogen were analyzed with a model 240 Perkin Elmer elemental analyzer.

Results and discussion

The analytical data and some physical properties are listed in Table 2. The reaction may be represented as follows.

$$M(NO_3)_3{\cdot}xH_2O+H_2SB\rightarrow$$
$$\rightarrow 1/n\{[MSB(H_2O)NO_3]{\cdot}H_2O\}_n+$$
$$+2HNO_3+(x-2)H_2O$$

where M=La(III), Ce(III), Pr(III), Nd(III) and Sm(III); H_2SB=di(*o*-thiophenyl)terephthalaldehydediimine.

All the coordination polymers exhibit 1:1 metal to ligand stoichiometry. Insolubility of the compounds in almost all solvents limits the determination of molecular masses. It is suggested that the compounds are coordination chain polymers [9] and suggested structure of the coordination chain polymer is shown in Fig. 2.

Magnetic measurements

The magnetic moment value among the trivalent lanthanide ions is due to the presence of unpaired '4f'

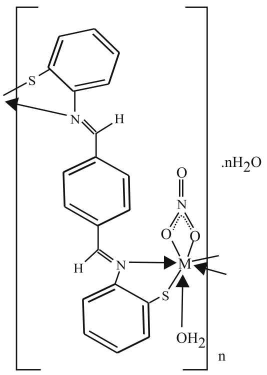

Fig. 2 Suggested structure of the coordination chain polymer $\{[La(SB)(H_2O)NO_3]{\cdot}H_2O\}_n$

Table 2 Analytical data of the coordination polymers

Coordination polymers Empirical formula	Formula mass	Found (Calcd.)/%					M.p./°C	$\mu_{eff.}$(B.M.) Found	Yield/%
		C	H	N	S	Metal			
H_2SB $C_{20}H_{16}N_2S_2$	348.487	68.95 (68.93)	4.62 (4.63)	8.07 (8.04)	18.42 (18.40)	–	232	–	60
$\{[La(SB)(H_2O)NO_3]{\cdot}H_2O\}_n$ $C_{20}H_{18}LaN_3O_5S_2$	583.412	41.16 (41.17)	3.14 (3.11)	7.2 (7.2)	10.89 (10.99)	23.88 (23.81)	>300	–	36
$\{[Ce(SB)(H_2O)NO_3]{\cdot}H_2O\}_n$ $C_{20}H_{18}CeN_3O_5S_2$	584.622	40.85 (41.09)	3.09 (3.10)	7.12 (7.19)	10.95 (10.97)	23.99 (23.97)	>300	2.30	36
$\{[Pr(SB)(H_2O)NO_3]{\cdot}H_2O\}_n$ $C_{20}H_{18}PrN_3O_5S_2$	585.412	41.07 (41.03)	3.12 (3.10)	7.21 (7.18)	10.97 (10.95)	24.10 (24.07)	>300	3.95	35
$\{[Nd(SB)(H_2O)NO_3]{\cdot}H_2O\}_n$ $C_{20}H_{18}NdN_3O_5S_2$	588.746	40.83 (40.80)	3.11 (3.08)	7.16 (7.14)	10.90 (10.89)	24.53 (24.50)	>300	3.60	38
$\{[Sm(SB)(H_2O)NO_3]{\cdot}H_2O\}_n$ $C_{20}H_{18}SmN_3O_5S_2$	594.866	40.40 (40.38)	3.08 (3.05)	7.09 (7.06)	10.81 (10.78)	25.30 (25.29)	>300	2.42	32

Table 3 Infrared spectral data (cm^{-1}) of the coordination polymers

Coordination polymer	$\nu_{C=N}$	$\nu_{M–N}$	$\nu_{M–O}$	$\nu_{M–S}$	$\nu_{C–S}$	$\nu_{C–H}$	$\nu_{C=C}$	ν_{SH}
H_2SB	1625	–	–	–	765	760	1530	2600
$\{[La(SB)(H_2O)NO_3]\cdot H_2O\}_n$	1582	520	445	410	760	763	1540	–
$\{[Ce(SB)(H_2O)NO_3]\cdot H_2O\}_n$	1595	515	440	420	755	765	1535	–
$\{[Pr(SB)(H_2O)NO_3]\cdot H_2O\}_n$	1595	515	445	425	750	770	1530	–
$\{[Nd(SB)(H_2O)NO_3]\cdot H_2O\}_n$	1596	520	435	415	750	763	1535	–
$\{[Sm(SB)(H_2O)NO_3]\cdot H_2O\}_n$	1580	525	440	425	755	769	1545	–

electrons. The magnetic measurements were carried out at room temperature and listed in Table 1. The compound of lanthanum(III) shows diamagnetism [17]. The compounds of the cerium (2.30 B.M.), praseodymium (3.95 B.M.), neodymium (3.60 B.M.) and samarium (2.42 B.M.) show paramagnetism.

Infrared spectra

The spectra of all the coordination polymers show the band about 3400 cm^{-1} due to the presence of coordinated water molecule [18]. The ligand shows the $\nu_{C=N}$ stretching band at 1625 cm^{-1}, which shifts to ~1582–1596 cm^{-1} in the coordination polymers indicating the involvement of the azomethine nitrogen in coordination. The two bands of medium intensity at ~1400 and ~1340 cm^{-1} are assigned to the vibration of the coordinated nitrate ion. The magnitudes of these bands indicate that the nitrate ion is coordinated in a bidentate fashion [21]. The band observed in all the coordination polymers at 520 cm^{-1} may be assigned to the $\nu_{M–N}$ mode [22]. The Schiff base shows a weak band at 2600 cm^{-1}, which is assigned to S–H group. This band vanished in the spectra of all the coordination polymers indicating that the SH group loses the thiol proton to form a covalent bond between sulfur and metal on chelation. The band observed at 765 cm^{-1} can be assigned to the $\nu_{C–S}$ for the ligand, which shifted to the lower frequency i.e. 750–760 cm^{-1} of all the coordination polymers. The band of medium intensity observed at 410–425 cm^{-1} is assigned to the $\nu_{M–S}$ mode [23–25]. The data are summarized in Table 3.

Electronic spectra

The electronic spectra of the nitrates of lanthanide are compared with the corresponding coordination polymers. La(III) and Ce(III) coordination polymers have no significant absorption in visible region. The absorption bands appear in the spectra of the coordination polymers of Pr(III), Nd(III) and Sm(III) are due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$ and $^6H_{5/2}$ to the excited J-levels of '4f' configuration, respectively. Some red shift or nephelauxetic effect is observed in these coordination polymers. The data are summarized in Table 4. In all the coordination polymers marked enhancement in the intensity of the bands has been observed. The red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these coordination polymers. From the β-values the covalence factor ($b^{1/2}$), Sinha parameter (δ%)

Table 4 Electronic spectral data (cm^{-1}) and related bonding parameters of coordination polymers

Coordination polymers	$Ln(NO_3)_3$ Electronic spectral bands	Compound's Electronic spectral bands	Energy levels	β	1–β	$b^{1/2}$	δ%	η
$\{[Pr(SB)(H_2O)NO_3]\cdot H_2O\}_n$	22470	22384	$^3H_4\to{}^3P_2$	0.9962	0.0038	0.0308	0.3814	0.0020
	21280	21186	$\to{}^3P_1$	0.9956	0.0044	0.0331	0.4419	0.0023
	20830	20661	$\to{}^3P_0$	0.9919	0.0081	0.0450	0.8166	0.0040
	16950	16790	$^3H_4\to{}^1D_2$	0.9906	0.0094	0.0484	0.9489	0.0047
$\{[Nd(SB)(H_2O)NO_3]\cdot H_2O\}_n$	19420	19278	$^4I_{9/2}\to{}^2G_{9/2}$	0.9927	0.0073	0.04627	0.7353	0.0036
	18993	18947	$^4G_{7/2}$	0.9976	0.0024	0.0244	0.2405	0.0012
	17390	17236	$^4G_{5/2}$	0.9912	0.0088	0.0469	0.8878	0.0044
	13420	13366	$^2S_{3/2}$	0.9960	0.0040	0.0316	0.4016	0.0020
	12500	12380	$^4F_{5/2}$	0.9904	0.0096	0.0489	0.9693	0.0048
	11446	11422	$^4F_{3/2}$	0.9979	0.0021	0.0229	0.2104	0.0010
$\{[Sm(SB)(H_2O)NO_3]\cdot H_2O\}_n$	24850	24728	$^6H_{5/2}\to{}^4F_{9/2}$ $^4F_{9/2}$	0.99351	0.0049	0.0350	0.4924	0.0024
	24100	24042	$^6P_{5/2}$	0.9979	0.0024	0.0244	0.2405	0.0012
	21600	21511	$^4I_{13/2}$	0.9959	0.0041	0.0320	0.4116	0.0020

Table 5 Thermoanalytical results (TGA and DTA) of the trivalent metal coordination polymers of H_2SB

Coordination polymer	TG range/°C	DTA_{max}/°C	Mass loss/% obs.(calc.)	Assignment
$\{[La(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–120	95(+)	3.42(3.07)	Loss of 1 lattice water molecule
	150–220	210(+)	2.98(3.07)	Loss of 1 coordinated water molecule
	270–450	430(–)	10.48(10.59)	Removal of nitrate
	450–650	580(–)	55.42(55.43)	Removal of the ligand
			72.30*(72.17)	Leaving La_2O_3 residue
$\{[Ce(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–130	81(+)	3.28(3.06)	Loss of 1 lattice water molecule
	130–310	197(+)	3.16(3.06)	Loss of 1 coordinated water molecule
	310–450	424(–)	10.71(10.56)	Removal of nitrate
	510–740	580(–)	55.13(55.31)	Removal of the ligand
			72.28*(72.02)	Leaving Ce_2O_3 residue
$\{[Pr(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–130	110(+)	2.96(3.06)	Loss of 1 lattice water molecule
	140–290	263(+)	3.35(3.06)	Loss of 1 coordinated water molecule
	310–470	408(–)	10.33(10.55)	Removal of nitrate
	500–690	621(–)	53.28(55.24)	Removal of the ligand
			69.61*(69.37)	Leaving Pr_2O_3 residue
$\{[Nd(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–130	87(+)	2.86(3.04)	Loss of 1 lattice water molecule
	130–230	211(+)	3.12(3.04)	Loss of 1 coordinated water molecule
	230–370	435(–)	10.31(10.49)	Removal of nitrate
	470-720	595(–)	54.66(54.92)	Removal of the ligand
			70.95*(71.52)	Leaving Nd_2O_3 residue
$\{[Sm(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–130	90(+)	2.57(3.00)	Loss of 1 lattice water molecule
	140–280	210(+)	3.36(3.00)	Loss of 1 coordinated water molecule
	280–430	399(–)	10.38(10.31)	Removal of nitrate
	530–730	615(–)	55.61(54.00)	Removal of the ligand
			71.92*(70.31)	Leaving Sm_2O_3 residue

(+) – endothermic; (–) – exothermic; *Total mass loss

(metal-ligand covalency%) and the covalency angular overlap parameter (η), have been calculated using the expression [26].

$$b^{1/2}=1/2(1-\beta)^{1/2},$$

$$\delta\%=[1-\beta/\beta]\bullet 100,$$

$$\eta=(1-\beta^{1/2})/\beta^{1/2}$$

The positive values for (1–β) and δ% in these coordination polymers suggest that the bonding between the metal and the ligand is covalent compared with the bonding between the metal and an aqua ion. The values of parameter (η) were found to be positive indicating covalent bonding.

Thermogravimetric analysis

The thermogravimetric analysis of the coordination polymers was carried out within a temperature range 30–800°C in N_2 atmosphere to establish their compositional differences as well as to ascertain the nature of associated water molecules. It has been observed that the loss in mass in the temperature range between 30–130°C for all coordination polymers corresponds to one lattice water molecule. The coordination polymers show loss in mass corresponding to one water molecule in the range 150–180°C indicating that this water molecule is coordinated to the central metal ion [27]. The TG curves indicate that in the temperature range 230–400°C the compounds start to loose nitrate ion. In the temperature range 400–800°C the Schiff base molecule is lost. In all of the cases the final products are metal oxides. These results are in good accordance with the composition of the coordination polymers. Thermoanalytical results (TG and DTA) of the trivalent metal coordination polymers of H_2SB are summarized in Table 5. TG-DTA curve of $\{[La(SB)(H_2O)NO_3]\cdot H_2O\}_n$ is shown in Fig. 3.

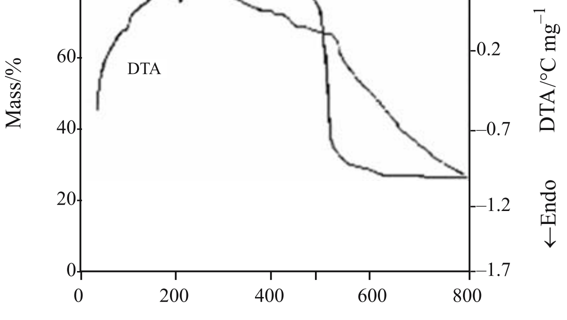

Fig. 3 TG-DTA curve of $\{[La(SB)(H_2O)NO_3]\cdot H_2O\}_n$

The stages of thermal decomposition of the coordination polymers can be written as under:

$$[M(SB)(NO_3)(H_2O)]_n nH_2O \xrightarrow{30\text{–}130℃} [M(SB)(NO_3)(H_2O)]_n nH_2O$$

$$[M(SB)(NO_3)(H_2O)]_n nH_2O \xrightarrow{150\text{–}180℃} [M(SB)(NO_3)]_n + n(H_2O)$$

$$[M(SB)(NO_3)]_n \xrightarrow{230\text{–}400℃} [M(SB)]_n + nNO_3$$

$$[M(SB)]_n \xrightarrow{400\text{–}800℃} M_2O_3 + (SB)_n$$

Calculation of thermodynamic parameters of the decomposed coordination polymers

The thermodynamic activation parameters of the coordination polymers upon thermal decomposition process, such as energy of activation (E_a) and order of reaction (n) were obtained graphically by employing the Freeman–Carroll [28] method using the following relation:

$$\left[\frac{\left(\frac{-E_a}{2.303R}\right)\Delta\left(\frac{1}{T}\right)}{\Delta\log w_r}\right] = -n + \frac{\Delta\log\left(\frac{dw}{dt}\right)}{\Delta\log w_r} \qquad (1)$$

where, T is the temperature in K, R is gas constant, $w_r=w_c-w$; w_c is the mass loss at the completion of the reaction and w is the total mass loss up to time t.

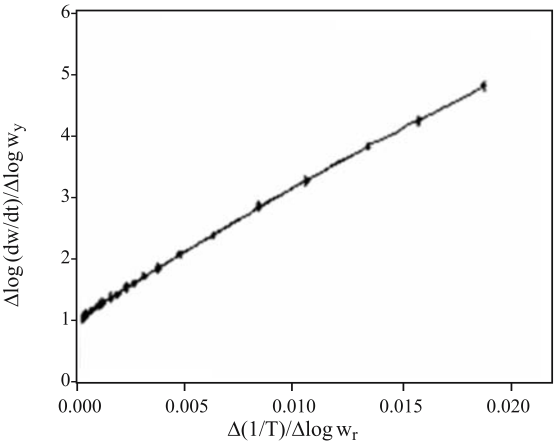

Fig. 4 Plot of [Δlog(dw/dt)/Δlog w_r] *vs.* [Δ(1/T)/Δlog w_r] for the Sm(III) coordination polymer

E_a and n are the energy of activation and order of reaction, respectively. A typical curve of [Δlog(dw/dt)/Δlog w_r] *vs.* [Δ(1/T)/Δlog w_r] for the Sm(III) coordination polymer is shown in Fig. 4. The slope of the plot gave the value of $E_a/2.303R$ and the order of reaction (n) was determined from the intercept.

The thermodynamic activation parameters of the decomposition process of coordination polymers such as entropy (S^*), preexponential factor (A), enthalpy (H^*) and free energy of the decomposition (G^*), were calculated using the following relations [29]:

$$E_a/RT_s^2 = A/\Phi\exp(-E_a/RT_s) \qquad (2)$$

Table 6 Thermodynamic data of the thermal decomposition of metal complexes

Coordination polymer	TG range/°C	E_a/kJ mol^{-1}	n	A/s^{-1}	S^*/J K^{-1}mol^{-1}	H^*/kJ mol^{-1}	G^*/kJ mol^{-1}
$\{[La(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–120	3.33	0.96	30.15	–97.88	2.54	11.84
	150–220	10.53	1.18	$1.19.10^2$	–96.59	8.78	29.06
	270–450	25.92	1.00	$2.27.10^2$	–95.92	22.34	63.59
	450–650	60.39	1.00	$5.93.10^4$	–93.95	55.57	110.06
$\{[Ce(SB)(H_2O)NO_3]\cdot H_2O\}_n$	60–140	3.38	0.98	74.97	–97.39	2.58	10.47
	180–280	10.76	1.11	$2.28.10^2$	–96.30	9.06	28.03
	350–480	29.32	1.00	$5.01.10^2$	–95.62	24.31	64.85
	540–680	59.77	1.00	$1.66.10^4$	–94.06	53.72	108.28
$\{[Pr(SB)(H_2O)NO_3]\cdot H_2O\}_n$	50–130	3.63	0.98	19.31	–98.09	2.72	13.51
	180–280	10.33	1.14	20.34	–97.47	8.15	33.79
	340–450	25.92	1.00	$3.90.10^2$	–95.73	22.53	61.59
	540–680	60.13	1.00	$2.14.10^4$	–94.21	54.97	113.48
$\{[Nd(SB)(H_2O)NO_3]\cdot H_2O\}$	50–130	3.61	0.97	85.61	–97.26	2.90	11.35
	130–230	10.33	1.39	$1.01.10^2$	–96.67	8.58	28.98
	230–370	26.49	1.00	$2.56.10^2$	–95.89	22.88	64.59
	370–780	60.69	1.00	$4.39.10^4$	–94.03	55.74	111.69
$\{[Sm(SB)(H_2O)NO_3]\cdot H_2O\}_n$	40–130	3.43	0.98	49.57	–97.58	2.67	11.46
	180–310	10.70	1.11	$1.25.10^2$	–96.56	8.86	29.14
	430–530	29.34	1.00	$1.48.10^3$	–95.22	25.99	64.08
	540–680	59.47	1.00	$2.38.10^4$	–94.19	54.39	111.85

$$S^*=2.303(\log Ah/KT)R \quad (3)$$

$$H^*=E_a-RT \quad (4)$$

$$G^*=H^*-T_sS^* \quad (5)$$

where, Φ is the heating rate, K is the Boltzman constant, h is the Plank constant and T_s is the peak temperature from DTG curve. According to the kinetic data obtained from DTG curves, all the complexes have negative entropy, which indicates that the studied coordination polymers have more ordered systems than reactants [30].

Thermal analysis data and structural interpretation

The TG curves of the La(III), Ce(III), Pr(III), Nd(III) and Sm(III) complexes consist of four stages of mass loss. For all the compounds studied, the activation energies of the thermal dehydration of all the coordination polymers are found to be in the range 3.33–3.61 kJ mol^{-1}. The activation energies of the loss of coordinated water molecule [31] and nitrate are found in the range of 10.33–10.70 and 25.92–29.34 kJ mol^{-1} respectively. Moreover, the activation energies for the removal of the ligand moiety in all the compounds are found in the range 59.47–60.69 kJ mol^{-1}. The thermodynamic parameter data are listed in Table 6 from which it is observed that all the coordination polymers have negative entropy values, which indicates that the activated complexes are formed spontaneously. The kinetic parameters, especially activation energy (E_a) is helpful in assigning the strength of the bonding of ligand moieties with the metal ion. The calculated (E_a) values of the investigated complexes, i.e. the stage of the formation of volatile gas products, are relatively high indicates that the ligand is strongly bonded to metal ion [32]. From the above data, the suggested structure of the coordination polymers is shown in Fig. 2.

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