J Therm Anal Calorim (2010) 100:645–650
DOI 10.1007/s10973-009-0510-9

Synthesis, thermal degradation, and kinetic parameters studies of some coordination polymers

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Received: 24 March 2009 / Accepted: 18 September 2009 / Published online: 31 October 2009

Abstract This article describes synthesis and route of thermal degradation and studies of kinetic parameters of some coordination polymers of first transition series metal ions viz. Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The newly synthesized ligand and its coordination polymers have been characterized by various instrumental techniques. The thermal degradation studies have been studied at different heating rates to determine the apparent activation energy, order of reaction, entropy change, free energy change, apparent entropy change, and frequency factor using Sharp–Wentworth and Freeman–Carroll methods. Thermo gravimetric analysis (TGA) has been used to determine the thermal stability of coordination polymers. The decomposition temperatures of the polymers were defined by half decomposition curve technique.

Keywords Coordination polymers · Thermal studies and kinetic parameters

Introduction

The thermal stabilities of bis salicylidene adipic dihydrazone and their complexes with divalent metal ion have been studied [1]. Coordination polymers have been found to own a wide range of applications such as molecular separation and pollution prevention in air, liquid, and water systems where they can be used as ion exchangers and molecular sieves [2]. Coordination polymers of adipyl bis-phenyl hydrazide and succinyl bis-hydrazide with transition metal ions have been synthesized for exhibiting good thermal stability [3]. Metal containing coordination polymers can be used as adsorbents, sensors, and catalysts [4]. The coordination polymers have been characterized on the basis of elemental analysis, infrared spectra, reflectance spectra, and thermo gravimetric analysis (TGA).

Experimental

Materials

All chemicals used were of AnalaR grade. Solvents were double distilled before used.

(1) 2-Aminobenzothiazole → (Himedia, India)
(2) Pimelic acid → (SRL, India)
(3) Benzene, $SOCl_2$, DMF → (S.D. Fine Chem., India)
(4) Manganese acetate, Cobalt acetate, Nickel acetate → (E. Merck, Germany)
(5) Copper acetate, Zinc acetate → (S.D. Fine Chem., India)

Instruments

Microanalysis for C, H, N, and S were carried out on Eassuperuser, Elemental Analyser system GmbH, Access: VarioEL Superuser, NEERI. Infrared spectra in the region 4,000–400 cm^{-1} were recorded in the solid state (KBr pallets) in Pharmacy Dept., RTMNU, NAGPUR, using FTIR-101A SHIMADZU. Reflectance spectra were done in Chemistry

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Dept. RTMNU, Nagpur on GBC Model Cintra 10 E, UV–Visible Spectrophotometer in the range of 300–1,100 nm. The slit width was kept at 5.00 nm, while the scan speed was maintained at 60 nm min^{-1}. The thermal studies of all the coordination polymers have been done at Vishveshwarya National Institute of Technology, Nagpur, using TGA–SDTA-851, METTLER, TOLENDO. The thermocouple used was Pt–Pt–Rh, with a temperature range of 10–1,200 °C and the heating rate was 5, 10, and 15 °C min^{-1}. The thermal analysis was carried out in an air atmosphere.

Synthesis of ligand pimeloyl-bis-2-aminobenzothiazole

Pimeloyl-bis-2-aminobenzothiazole (PBAB) ligand was prepared by the reaction of acid dichloride with 2-aminobenzothiazole in dry benzene medium. Acid dichloride was prepared by the standard method [5]. The acid dichloride was taken in 250 mL round bottomed flask and to it (0.2 M) 2-aminobenzothiazole was added, and was refluxed for about 4–5 h at 70–80 °C. A granular solid was obtained and separated by filtration and purified by giving repeated washings with hot dry benzene and ethanol. The ligand is reported for the first time in this study and hence, characterized by elemental, infrared spectral, and H-NMR studies. The reaction of ligand formation has been shown in Fig. 1. The physico-chemical properties and elemental data of ligand have been given in Tables 1 and 2.

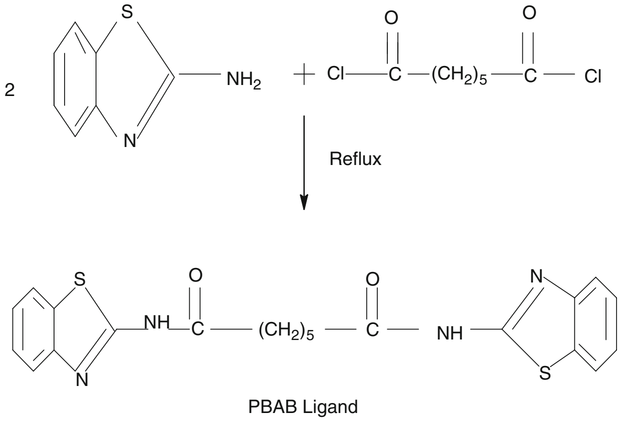


Fig. 1

Table 1 Elemental analysis of ligand PBAB

Ligand	Carbon/%	Hydrogen/%	Nitrogen/%	Sulfur/%
(PBAB)	Found	Found	Found	Found
	Calculated	Calculated	Calculated	Calculated
	59.43	4.71	13.20	15.09
	59.57	4.04	13.14	15.02

Table 2 Physico-chemical properties of PBAB ligand

Ligand	Empirical formula	Formula weight	Color	Melting point/°C	Solubility
PBAB	$C_{21}H_{20}O_2N_4S_2$	424	Off white	178	DMF

Synthesis of coordination polymers of PBAB ligand

Coordination polymers of pimeloyl-bis-2-aminobenzothiazole with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized by dissolving metal acetate in minimum amount of DMF, and were added to a solution of pimeloyl-bis-aminobenzothiazole in 1:1 mole ratio in 50 mL DMF. The reaction mixtures were refluxed in an oil bath at about 150 °C for 6–7 h. The products formed were filtered, washed thoroughly first with hot DMF and then with absolute alcohol and dried under IR lamp. These newly synthesized coordination polymers were found to be insoluble in almost all organic solvents such as alcohol, acetone, chloroform, carbon tetrachloride, DMF, dioxan, DMSO etc. The purity of these coordination polymers was ascertained by repeated washings with DMF and alcohol.

Results and discussion

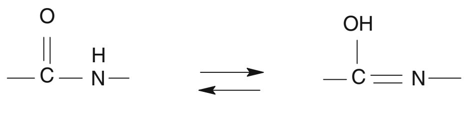
Composition of the polymeric unit

The composition of the polymeric unit was assigned on the basis of elemental analysis. Thermal studies have been used to ascertain the presence of water of crystallization as well as coordination. On the basis of elemental analysis, infrared spectra, reflectance spectra, and thermal studies, the proposed structure of these coordination polymers have been shown in Fig. 2. The analytical data are given in Table 3 and physico-chemical properties of the coordination polymers of pimeloyl-bis-2-aminobenzothiazole are given in Tables 4 and 5.

Infrared spectral studies

The spectra of ligand show the band around 3292.9 cm^{-1} due to the presence of the –NH– group [6]. However, in the case of polymers, this frequency is disappearing. The sharp band of C=O stretching is observed at 1653.2 cm^{-1} [7]. IR spectra of ligand as well as polymers show a peak in the region 2930–2947 cm^{-1} which may be due to the $–CH_2$ stretching. Medium band observed in the range between 1257.7 cm^{-1} may be assigned due to the C–N exocyclic group frequency [8].

It has been found that bis-ligand undergoes keto-enol tautomerism during polymerization as follows:



Keto(I) Enol(II)

This has been proved by the fact that the band observed at 1653.2 cm^{-1} due to the C=O stretching mode in the case of ligand disappears and new band is observed around 1390–1470 cm^{-1} in polymers which clearly indicates that the C=O band disappears due to formation of the C=N as a result of enolization [9]. This is further supported by the appearance of C–O band around 1024–1092 cm^{-1} in the case of polymers [10]. The C–S stretching vibration is observed in region of 700–600 cm^{-1}, since there is no considerable change in band frequencies of ligand and their coordination polymers, it gives evidence that sulfur has not participated in bonding with the metal. The band observed in all the coordination polymers at 428–456 cm^{-1} may be assigned to the υ_{M-N} mode [11]. The band observed at 615–618 cm^{-1} in coordination polymer may be assigned to the υ_{M-O} mode [12].

Medium band appearing in the range of 750–790 cm^{-1} in the case of few coordination polymers may be attributed to the presence of water of coordination [13].

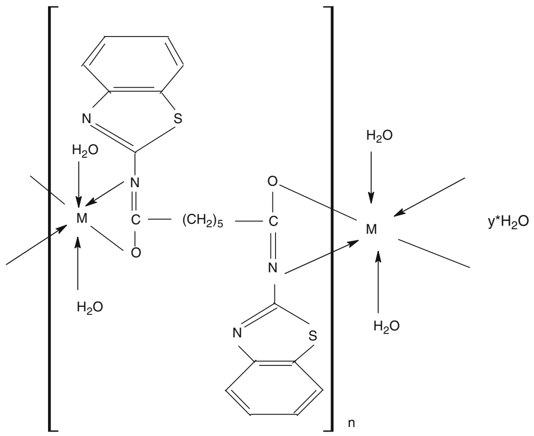


Fig. 2 Proposed structure: the proposed structure of the coordination polymers of pimeloyl-bis-2-aminobenzothiazole, M = metal ion, Mn(II),Co(II), Ni(II), Cu(II), and Zn(II). Y*H_2O—lattice water. H_2O is absent in Zn(II), Cu(II), Mn(II) polymers. $y = 1$ for Co(II), Ni(II), Mn(II) and Zn(II) PBAB coordination polymers and $y = 0$ for Cu(II) PBAB coordination polymers. *H_2O is absent in Cu(II) PBAB coordination polymer

Electronic spectral studies of PBAB coordination polymers

The $\{[Cu(II)\,(PBAB)]\}_n$ polymer exhibited a band at 25.00 and 14.28 kK which may be assigned to $^{2}B_{1g} \rightarrow {}^{2}E_{g}$ and $^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, respectively for square planar geometry [14]. The $\{[Co(II)\,(PBAB)\,(H_2O)_2]H_2O\}_n$ polymer exhibited a band at 19.04 kK which is assigned to $^{4}T_{1g} \rightarrow {}^{4}T_{1g(P)}$ for octahedral geometry [15]. For$\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$ polymer, the band observed at 23.52 and 14.81 kK which may be due to $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}$ (P) and $^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) transition, respectively, having octahedral geometry [16]. The $\{[Mn(II)\,(PBAB)]\,H_2O\}_n$ exhibited a band at 24.09 kK which is assigned to $^{6}A_1 \rightarrow {}^{4}E(G)$ for tetrahedral geometry [17]. Since $\{[Zn(II)(PBAB)]H_2O\}_n$ is a d^{10} system and hence is diamagnetic in nature, however, on the basis of elemental analysis, IR spectra, and thermal decomposition data, its most probable geometry is suggested to be tetrahedral. The electronic spectral data of coordination polymers are given in Table 6.

Table 3 Elemental analysis of PBAB coordination polymers

Coordination polymers	C/% Calculated Found	H/% Calculated Found	N/% Calculated Found	S/% Calculated Found	M/% Calculated Found
$\{[Mn(II)(PBAB)]H_2O\}_n$	52.61	4.17	11.69	13.36	12.06
	52.79	4.21	11.70	13.28	11.46
$\{[Co(II)(PBAB)(H_2O)_2]H_2O\}_n$	48.56	3.85	10.79	12.33	11.5
	48.31	4.03	10.72	12.36	11.35
$\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$	48.58	3.85	10.79	12.33	11.41
	48.57	3.75	10.63	12.60	11.35
$\{[Cu(II)(PBAB)]\}_n$	51.68	4.10	11.48	13.12	13.69
	51.67	4.54	11.98	13.17	13.03
$\{[Zn(II)(PBAB)]H_2O\}_n$	51.49	4.08	11.44	13.07	13.63
	51.53	4.04	11.41	13.15	13.36

Table 4 Physico-chemical properties of PBAB coordination polymers

Coordination polymers	Colour	Empirical formula	Formula weight
$\{[Mn(II)(PBAB)]H_2O\}_n$	White	$MnC_{21}H_{20}O_3N_4S_2$	494.93
$\{[Co(II)(PBAB)(H_2O)_2]H_2O\}_n$	Light pink	$CoC_{21}H_{24}O_5N_4S_2$	534.93
$\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$	Light green	$NiC_{21}H_{24}O_5N_4S_2$	534.69
$\{[Cu(II)(PBAB)]\}_n$	Dirty green	$CuC_{21}H_{18}O_2N_4S_2$	485.54
$\{[Zn(II)(PBAB)]H_2O\}_n$	White	$ZnC_{21}H_{20}O_3N_4S_2$	505.39

Table 5 IR spectral assignments of PBAB ligand and its coordination polymers/cm^{-1}

Compound	–NH	C=O	C–N	C–S	M–O	M–N	H–O–H	$-CH_2$	C–O	C=N
PBAB	3292.9	1653.2	1257.7	674	–	–	–	2947	–	–
Mn(II)	–	–	–	659.7	615.4	428.2	–	2930.2	1091.8	1390.8
Co(II)	–	–	–	681	615.4	432.1	787.1	2936	1091.8	1412.1
Ni(II)	–	–	–	681	617.3	432.1	756.2	2934.1	1024.3	1412.1
Cu(II)	–	–	–	681	617.3	436	–	2932.2	1068.7	1469.9
Zn(II)	–	–	–	698.3	615.4	455.3	–	2943.7	1091.8	1398.6

Thermal studies of coordination polymers

Freeman–Carroll [18] and Sharp–Wentworth [19] methods have been used to determine the kinetic parameters of the coordination polymers.

Freeman–Carroll method

The dynamic (non-isothermal) analysis of all the coordination polymers has been carried out from room temperature to 900 °C in the air atmosphere.

In this method, following expression is used to evaluate various kinetic parameters:

$$\frac{\Delta \log\left(\mathrm{d}W/\mathrm{d}t\right)}{\Delta \log W_\mathrm{r}} = \left(-Ea/2.303R\right)\frac{\Delta\left(1/T\right)}{\Delta \log W} + n$$

where $\mathrm{d}W/\mathrm{d}t$ is the rate of change of weight with time, $W_r = W_c - W$, where W_c is the weight loss at completion of reaction or at a definite time t, T is temperature, R is gas constant, and n is the order of reaction.

Hence, by plotting

$$\frac{\Delta \log\left(\mathrm{d}W/\mathrm{d}t\right)}{\Delta \log\ W_\mathrm{r}} \text{ versus } \frac{\Delta\left(1/T\right)}{\Delta \log W}$$

n is obtained as an intercept on former axis and E_a is the slope of the line.

Sharp–Wentworth method

The following expression is used to evaluate activation energy:

$$Log\left(\frac{\mathrm{d}C/\mathrm{d}T}{1-C}\right) = \log\left(A/\beta\right) - \left(-E_\mathrm{a}/2.303R\right) \times \frac{1}{T}$$

where B is the linear heating rate, $\mathrm{d}T/\mathrm{d}t$.

Therefore, a linear plot of

$$\log\left(\frac{\mathrm{d}C/\mathrm{d}T}{1-C}\right) \quad \text{versus} \quad 1/T$$

is obtained whose slope gives the value of E_a and A may be evaluated from intercept. The linear relationship confirmed

Table 6 Electronic spectral assignments of coordination polymers

S. No.	Coordination polymers	Absorbance/kK	Assignments	Stereochemistry
1	Mn(II)PBAB	24.09	$^6A_1 \rightarrow {}^4E(G)$	Tetrahedral
2	Co(II)PBAB	19.04	$^4T_{1g} \rightarrow {}^4T_{1g(P)}$	Octahedral
3	Ni(II)PBAB	23.52	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
		14.81	$^3A_{2g} \rightarrow {}^3T_{1g}\ (F)$	
4	Cu(II)PBAB	25.00	$^2B_{1g} \rightarrow {}^2E_g$	Square planar
		14.28	$^2B_{1g} \rightarrow {}^2B_{2g}$	

that assumed order ($n = 1$) is correct. In order to economize the space only representative TG curve of $\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$ at heating rate of 10 °C/min has been shown in Fig. 3. Thermodynamic parameters have been calculated on the basis of thermal activation energy data and kinetic parameters of PBAB coordination polymers at different heating rates are given in Tables 7, 8, and 9. From the given data, it can be observed that the values of thermodynamic parameters indicate a common reaction mode.

The thermogram of Ni(II) PBAB coordination polymer shows loss in weight up to 120 °C, which may be due to loss of one molecule of lattice water. From 130 to 230 °C, the loss in weight is observed due to loss of two coordinated

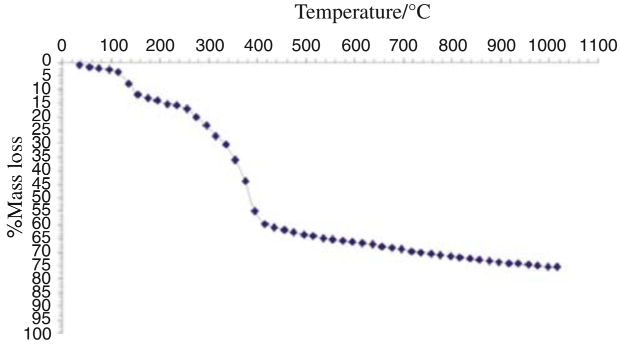


Fig. 3 Thermogram of $\{[Ni(II)\ (PBAB)\ (H_2O)_2]\ H_2O\}_n$ coordination polymer at 10 °C min^{-1}

Table 7 Heating rate = 5 °C min^{-1}

Coordination polymers	Activation energy (E_a)/ kJ mol^{-1}		Entropy change Δ(S)/J	Free energy change Δ(*F*)/kJ	Frequency factor (*Z*)/S^{-1}	Apparent entropy change (*S**)/J	Order of Reaction (*n*)	Decomposition Temperature/°C
	FC	SW						
$\{[Mn(II)(PBAB)]H_2O\}_n$	29.01	28.72	−157.30	104.32	2478.32	−185.54	0.55	310
$\{[Co(II)(PBAB)(H_2O)_2]H_2O\}_n$	16.39	16.34	−162.99	103.37	193.28	−206.61	1.01	300
$\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$	25.45	26.04	−155.52	106.31	865.19	−194.97	0.7	360
$\{[Cu(II)(PBAB)]\}_n$	30.24	29.83	−171.09	112.65	2264.35	−186.43	0.65	320
$\{[Zn(II)(PBAB)]H_2O\}_n$	27.45	27.53	−154.89	101.71	1237.36	−191.73	0.62	340

Table 8 Heating rate = 10 °C min^{-1}

Coordination polymers	Activation energy (E_a)/ kJ mol^{-1}		Entropy change Δ(S)/J	Free energy change Δ(*F*)/kJ	Frequency factor (*Z*)/S^{-1}	Apparent entropy change (*S**)/J	Order of Reaction (*n*)	Decomposition temperature/°C
	FC	SW						
$\{[Mn(II)(PBAB)]H_2O\}_n$	31	30.86	−191.99	117.97	8168.42	−175.9	0.7	330
$\{[Co(II)(PBAB)(H_2O)_2]H_2O\}_n$	16.28	17.14	−201.17	115.45	633.76	−196.8	1	310
$\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$	25.41	25.03	−193.64	118.93	2855.21	−185.4	0.65	390
$\{[Cu(II)(PBAB)]\}_n$	29.67	29.33	−201.92	121.14	7094.22	−177.3	0.75	350
$\{[Zn(II)(PBAB)]H_2O\}_n$	27.62	27.83	−192.95	115.02	4869.06	−180.6	0.7	360

Table 9 Heating rate = 15 °C min^{-1}

Coordination polymers	Activation energy (E_a)/ kJ mol^{-1}		Entropy change/ Δ(S)/J	Free energy change *Δ(F)*/kJ	Frequency factor (*Z*)/ (s^{-1})	Apparent entropy change (*S**)/J	Order of reaction (*n*)	Decomposition temperature/°C
	FC	SW						
$\{[Mn(II)(PBAB)]H_2O\}_n$	26.21	26.18	−155.28	106.50	910.99	−194.28	0.55	320
$\{[Co(II)(PBAB)(H_2O)_2]H_2O\}_n$	16.30	16.27	−176.46	105.26	138.41	−209.53	1.04	310
$\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$	25.59	25.66	−159.30	111.38	946.91	−194.00	0.65	360
$\{[Cu(II)(PBAB)]\}_n$	29.38	29.59	−173.47	113.14	2121.35	−186.69	0.7	340
$\{[Zn(II)(PBAB)]H_2O\}_n$	27.49	27.44	−165.82	108.14	1236.03	−191.87	0.82	350

water molecules. After 230–720 °C, a gradual mass loss is observed, due to decomposition of coordination polymer then it forms stable species. The decomposition temperatures of polymers were determined by half decomposition curve technique.

Conclusions

On the basis of elemental analysis, infrared spectra, reflectance spectra, and thermal studies at different heating rates, the $\{[Mn(II)(PBAB)]H_2O\}_n$ and $\{[Zn(II)(PBAB)]H_2O\}_n$ coordination polymers are having tetrahedral geometry, whereas $\{[Ni(II)(PBAB)(H_2O)_2]H_2O\}_n$ and $\{[Co(II)(PBAB)(H_2O)_2]H_2O\}_n$ coordination polymers have octahedral geometry, and $\{[Cu(II)(PBAB)]\}_n$ is having square planar geometry, and order of reaction has been found to be approximately one, and have thermal stability in the order Ni(II) > Zn(II) > Cu(II) > Mn(II) > Co(II).

Acknowledgements Authors are thankful to the Head of the Department of Chemistry; Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, for providing the laboratory facilities to carry out this study.

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