

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Synthesis, spectral investigation and thermal aspects of coordination polymeric chain assemblies of some transition metal ions with bis-pyrazolones

C.K. Modi*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat 388120, India

ARTICLE INFO

Article history: Received 19 April 2008 Received in revised form 23 May 2008 Accepted 24 June 2008

Keywords: Coordination polymers Tautomeric studies of H₂SB Freeman-Carroll method TG/DTG DTA and DSC studies

ABSTRACT

A few coordination chain polymeric assemblies of the type $[M(SB)(H_2O)_2]_n \cdot XH_2O$ or $[VO(SB)-(H_2O)]_n \cdot H_2O$ [where M = Mn(II), Cu(II) and Zn(II), x = 1; Co(II) and Ni(II) x = 2, $H_2SB = (4Z, 4'Z)-4,4'-(2,2'-(4,4'-methylenebis(4,1-phenylene)bis(azanediyl))bis(1-hydroxy ethan-2-yl-1-ylidene))-bis(3-methyl-1-phenyl-1$ *H*-pyrazol-5(4H)-one)] have been investigated. Structural and spectroscopic properties have been studied on the basis of elemental analyses, infrared spectra, ¹H and ¹³C NMR spectra, electronic spectra, magnetic measurements and thermo gravimetric analyses. FT-IR, ¹H and ¹³C NMR studies reveal that the ligand (H₂SB) exists in the tautomeric enol form in both the states with intramolecular hydrogen bonding. Magnetic moment and reflectance spectral studies reveal that an octahedral geometry has been assigned to all the prepared coordination polymers. The kinetic parameters such as order of reaction (*n* $) and the energy of activation (<math>E_a$) have been reported using 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.

© 2008 Elsevier B.V. All rights reserved.

1. 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 [1,2]. Dependent on the nature of the metal and the coordination behavior of the ligand one can develop synthetic strategies to influence the one-, twoor three-dimensional arrangement in the crystal in a more directed way [3]. Furthermore, it is now realized that weak hydrogen bond(s) that involve O-H...O hydrogen bond stacking interactions also play a significant and predictable structure determining role. Their representing reliable and ubiquitous supramolecules show that they already have been applied in a broad range of systems and have analogues in the context of coordination supramolecules and polymers [1a,1b]. Coordination polymers are usually known for their thermal stability [4,5]. However, some additional equally good applications have been reported, such as use solar energy converters [6] and removal of SO_x and NO_x from the environment [7]. One major goal in this area is the preparation of new compounds with interesting properties such as functional materials in molecular magnetism [8], catalysis [9], optoelectronic devices and gas sorption [10]. The

E-mail addresses: chetank.modi1@gmail.com, modi_ck@yahoo.co.in.

study of polymeric ligands and their metal complexes is very useful as a catalyst in metal separation and in bio-inorganic chemistry [11–13].

Pyrazolone and its derivatives form an important class of such compounds and have attracted considerable scientific and applied interest. Furthermore, 4-acyl-pyrazolone derivatives have the potential to form different types of coordination compounds due to the several electron-rich donor centers [14-16] and tautomeric effect of the enol form and keto form [17-20]. Therefore, the 4-acyl-pyrazolone derivatives are broadly used in many fields, especially in biological, clinical and analytical applications [21-23]. The flexibility and conformational freedom of 4-acetyl-pyrazolone ligands give rise to a variety of interesting structural motifs. In the previous work, the present author have synthesized a series of 4-acyl-pyrazolone derivatives and reported several transition metal complexes [24-26], but no detailed studies on coordination polymeric chain assemblies of transition metal ions with bis-pyrazolones as a ligand have been carried out so far. Hence, information about the structural properties of coordination polymers with bis-pyrazolones is important to examine further the coordination abilities and complexation behavior of pyrazolone-based ligand and to investigate the building blocks for the supramolecular networks. The suggested structure of the ligand (H₂SB) is shown in Scheme 1.

^{*} Tel.: +91 2692 226856; fax: +91 2692 236475.

^{1386-1425/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2008.06.024



Scheme 1. Synthesis and structure of the ligand (H₂SB).

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade and used without further purification. The compound 1-phenyl-3-methyl-2-pyrazoline-5-ol was purchased from E. Merck Ltd. (India). 4,4'-Methylenedianiline and chloroacetyl chloride were purchased from Qualigens Fine Chemicals, India and used without further purification.

2.2. Instruments

Carbon, hydrogen and nitrogen were analyzed with the PerkinElmer, USA 2400-II CHN analyzer. The metal content of the coordination polymers were analyzed by the EDTA titration technique [27]. A 100 mg sample of the vanadyl coordination polymer was placed in a silica crucible, decomposed by gentle heating and then treated with 1–2 ml of concentrated HNO₃, 2–3 times. Orange colored residues (V₂O₅) were obtained after decomposition and complete drying [28]. Infrared spectra $(4000-400 \text{ cm}^{-1})$ were recorded on Nicolet-400D spectrophotometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded on a model Advance 400 Bruker FT-NMR instrument and DMSO-d₆ used as a solvent. 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 tetrathiocyanato cobaltate(II) as a calibrant (χ_g = 16.44 \times 10 $^{-6}$ c.g.s. units at 20 $^\circ$ 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, U.S.A. The experiments were performed in N_2 atmosphere at a heating rate of $10 \,^{\circ}C \,min^{-1}$ in the temperature range 50–800 °C, using Al₂O₃ crucible. The sample sizes are ranged in mass from 4.5 to 10 mg. The DSC was recorded using DSC 2920, TA Instrument, U.S.A. The DSC curves were obtained at a heating rate of $10 \,^\circ C \, min^{-1}$ in N_2 atmosphere over the temperature range of 50-400 °C, using aluminum crucible.

2.3. Synthesis of (Z)-4-(2-chloro-1-hydroxyethylidene)-3methyl-1-phenyl-1H-pyrazol-(4H)-one

The literature procedure [29] 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, compound 1-phenyl-3-methyl-2-pyrazoline-5-ol (17.07 g, 0.098 mol) was dissolved in dry dioxane (100 mL), and then Ca(OH)₂ (10.37 g, 0.14 mol) was added. Chloroacetyl chloride (7.97 mL, 0.1 mol) was added drop wise with precaution, as this reaction was exothermic. During this addition the whole mass was converted into a thick paste. After the complete addition, the reaction mixture was heated to reflux for about 4h and then it was cooled to room temperature. The mixture was poured slowly into 2 M chilled HCl (200 mL) with constant stirring until the light yellow precipitate was formed. The colored crystals thus obtained were separated by filtration and recrystallized from methanol-chloroform mixture (MeOH:CHCl₃ = 80:20). Yield 64%, mp: 80°C. Elemental analysis found (%) C, 57.52; H, 4.41; N, 11.23; calculated for C₁₂H₁₁ClN₂O₂: C, 57.49%; H, 4.42%; N. 11.17%.

2.4. Synthesis of (4Z,4'Z)-4,4'-(2,2'-(4,4'-methylenebis(4,1-phenylene)bis(azanediyl))bis(1-hydroxy ethan-2-yl-1-ylidene))-bis(3-methyl-1-phenyl-1H-pyrazol-5(4H)-one) (H₂SB)

The performed ligand 4-(2-chloro-1-hydroxyethylidene)-3methyl-1-phenyl-1*H*-pyrazol-(4*H*)-one (10 mmol, 2.50 g) was dissolved in 50 mL of rectified spirit. To this solution, a solution of 4,4'-methylenedianiline (5 mmol, 0.99 g) in rectified spirit (25 mL) was added dropwise with constant stirring. Then a solution of anhydrous K₂CO₃ (10 mmol, 1.38 g) in rectified spirit (25 mL) was added in it. The resulting mixture was then refluxed for 5–7 h. The reaction mixture was then poured into crushed ice with constant stirring when a light brown precipitate was obtained. It was filtered, washed several times with water and dried in vacuo. Yield 67%. Elemental analysis found (%) C, 70.96; H, 5.48; N, 13.52; calculated for C₃₇H₃₄N₆O₄: C, 70.91%; H, 5.47%; N, 13.41%. FT-IR (KBr, cm⁻¹): 3390

Table 1
Analytical and physical data of the ligand H ₂ SB and its coordination polymers ^a

Empirical formula of monomer unit	Formula weight	Color (yield %)	mp (°C)	Found (calculated) (%)			μ_{eff} (B.M.)	
				С	Н	Ν	М	
H ₂ SB, C ₃₇ H ₃₄ N ₆ O ₄	626.70	Yellowish brown (74)	171 ^b	70.96 (70.91)	5.48 (5.47)	13.45 (13.41)	-	-
$[Mn(SB)(H_2O)_2]_n \cdot H_2O, C_{37}H_{38}MnN_6O_7$	734.68	Dark brown (68)	>300	60.67 (60.57)	5.24 (5.22)	11.53 (11.45)	7.54 (7.49)	6.01
$[Co(SB)(H_2O)_2]_n \cdot 2H_2O, C_{37}H_{40}CoN_6O_8$	756.69	Dark brown (64)	>300	58.83 (58.81)	5.35 (5.34)	11.29 (11.12)	7.91 (7.80)	4.06
$[Ni(SB)(H_2O)_2]_n \cdot 2H_2O, C_{37}H_{40}N_6NiO_8$	756.45	Dark green (72)	>300	58.85 (58.83)	5.32 (5.34)	11.18 (11.12)	7.81 (7.77)	2.91
$[Cu(SB)(H_2O)_2]_n \cdot H_2O, C_{37}H_{38}CuN_6O_7$	743.29	Dark brown (70)	>300	59.92 (59.87)	5.18 (5.16)	11.30 (11.32)	8.63 (8.56)	1.79
$[Zn(SB)(H_2O)_2]_n H_2O, C_{37}H_{38}N_6O_7Zn$	745.15	Brown (65)	>300	59.81 (59.72)	5.17 (5.15)	11.33 (11.29)	8.84 (8.79)	Diamagnetic
$[VO(SB)(H_2O)]_n \cdot H_2O, C_{37}H_{36}N_6O_7V$	728.67	Brown (66)	>300	61.12 (61.07)	5.02 (4.99)	11.59 (11.55)	7.07 (7.00)	1.81

^a H₂SB = (4Z,4'Z)-4,4'-(2,2'-(4,4'-methylenebis(4,1-phenylene)bis(azanediyl))bis(1-hydroxy ethan-2-yl-1-ylidene))bis(3-methyl-1-phenyl-1H-pyrazol-5(4H)-one). ^b Decomposed.

 ν (O−H) of hydroxy ethylidene group, 3145 ν (N−H), 2820 ν (−CH₃), 1630 ν (C=O) of pyrazol-5-one, 1590 ν (C=N) of pyrazolone-ring [30]. ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 2.46 (6H, s, 2CH₃); 3.39 (2H, m, CH₂); 4.10 (4H, s, 2CH₂); 6.54 (2H, s, 2NH); 7.15–7.99 (18H, m, 4Ph-ring); 12.83 (2H, s, 2O−H···O hydrogen bonds). ¹³C NMR (400 MHz, DMSO- d_6): δ (ppm) = 16.40 (C8), 39.8 (C24), 61.40 (C2), 99.42 (C4), 112.8 (C21 and 23), 118.68 (C19), 124.77 (C13 and 15), 125.97 (C17), 129.31 (C12 and 16), 130.58 (C18 and 20), 139 (C14), 143.20 (C22), 146.87 (C5), 159.99 (C3), 167.12 (C1).

2.5. Synthesis of coordination polymers

The performed ligand H_2SB (5 mmol, 3.13 g) was dissolved in 10 mL of DMF. To this solution, the methanolic solution of 25 mL metal nitrate (5 mmol) or an aqueous solution (25 mL) of VOSO₄·5H₂O (5 mmol, 1.45 g) was added slowly with constant stirring over the period of 30 min in 1:1 molar ratio. The pH of the solution was adjusted 5–6 with the drop wise addition of methanolic solution of sodium acetate in it. 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 CaCl₂. The coordination polymers are insoluble in all common organic solvents like methanol, ethanol, chloroform, acetone, benzene, dimethyl formamide and dimethyl sulfoxide.

3. Results and discussion

The analytical and physical properties of the ligand H_2SB and its coordination polymers are listed in Table 1. The following reaction describes the formation of the coordination polymers:

$$M(NO_3)_2 \cdot nH_2O + H_2SB \rightarrow [M(SB)(H_2O)_2]_n \cdot xH_2O$$

$$+2HNO_3+(n-x)H_2O$$

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

$$VOSO_4 \cdot 5H_2O + H_2SB \rightarrow [VO(SB)(H_2O)]_n \cdot H_2O + H_2SO_4 + 3H_2O$$

All the coordination polymers are insoluble in all common organic solvents. It was not possible to characterize them by conventional 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 in all common organic solvents suggest their polymeric nature.

3.1. IR spectra

The important infrared spectral bands and their tentative assignments for the synthesized ligand H_2SB and its coordination polymers were recorded as KBr disks and are discussed.

The molecular structure of the ligand H₂SB is such that they can exist in six tautomeric forms as shown in Fig. 1. Detailed solution and solid-state studies of this ligand were carried out to establish their geometry. The IR spectrum of this ligand exhibits two characteristic bands at 3390 and 1630 cm⁻¹, which can either be assigned to $\nu(O-H)$ of the pyrazolone group and $\nu(C=O)$ of the lateral chain, respectively for the tautomeric form (Fig. 1A) or $\nu(O-H)$ and $\nu(C=O)$, respectively for the tautometric form (Fig. 1D) of the ligand. We assigned these two peaks to ν (O–H) and ν (C=O), respectively for the later form based on the information obtained from ¹H and ¹³C NMR studies in solution state (discussed later). The observed low frequency of ν (O–H) with respect to the free hydroxyl group is believed to be due to intramolecular H-bonding between H of OH of hydroxyethylidene group of the lateral chain and oxygen of pyrazolone-ring as illustrated in Fig. 1D'. All of these data suggest that hydrogen bond exists in the free ligand H₂SB.

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



Fig. 1. Possible tautomers of the ligand H₂SB (3).

vibrations, respectively due to the presence of water molecules [31]. The presence of rocking band indicates the coordination nature of the water molecule [32]. The ν (N–H) band at 3145 cm⁻¹ of the free ligand (H₂SB) is unaffected in the spectra of polymers that indicate non-involvement of this group. The infrared spectra of all the coordination polymers show a considerable negative shift $10-15 \text{ cm}^{-1}$ in ν (C=O) absorption of the pyrazolone group, indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the oxygen atom of the ligand. Meanwhile, the new absorption bands attributed to $\nu(C-O^-)$ [33] are observed at 1323–1326 cm⁻¹. From these observations, it is concluded that the ligand reacts in enol form with prototropy, which incorporates into proton transfer through oxygen atom of the lateral chain forming covalent bond with the metal ion. The oxovanadium(IV) coordination polymer exhibits a strong absorption band near ~958 cm⁻¹, which has been assigned to ν (V=O) band [24]. In the far-IR region, two new bands at 480-495 and 420-435 cm⁻¹ in the coordination polymers are assigned to ν (M–O)_{pyrazolone} and ν (M–O)_{lateral chain}, respectively. It is thus believed that the oxygens of the pyrazolone-ring and hydroxyethylidene group of the lateral chain are coordinated to metal ions.

3.2. Tautomerism studies of $H_2SB(\mathbf{3})$

Specifically the tautomerism of 1-aryl-4-acyl-pyrazolones has been the subject of various studies [34–40]. Based upon ¹H and ¹³C NMR studies, Kurkovskava et al. [35] concluded that in CDCl₃ solution, and at low temperature, 4-acetyl- and 4-benzoyl derivatives are mainly present in the associated OH form (\mathbf{A}') (Fig. 1) with a minor portion of NH form (B). In the case of the ligand H₂SB (3), the possible tautomers are shown in Fig. 1. Relevant ¹H and ¹³C NMR data of the compound **3** are given in Section 2. Data agree with the existence of enol form. ¹H NMR chemical shift for the OH group was observed at δ 12.83 ppm. This signal disappeared when a D₂O exchange experiment was carried out. It can be assigned either to OH of pyrazolone-ring or OH of hydroxvethylidene group of the lateral chain, in either case it is strongly deshielded because of hydrogen bonding with the other oxygen atom. It may be noted that the integration of this signal perfectly matches with one proton and there is no other fragment(s) of this signal, which suggests that only one tautomeric form of the ligand exists in solution under the experimental conditions. Any temperature-dependent experiments have not been carried out. Comparing with the solid-state study, we prefer to assign this signal to OH of the lateral chain; however, assignment of this peak to OH of the pyrazolone-ring cannot be ruled out provided solid-state structural evidence is not considered [41]. On the basis of ¹³C signal for the carbonyl carbon of the pyrazolone-ring is observed at 166 ppm [42] clearly correspond to a ketone form (Fig. 1**D**[']). These values are very close to those already reported by other authors [35]; showing that the pyrazole-5-ol form (Fig. 1A and A') can be excluded. The presence of ethanone form of the lateral chain (Fig. 1C) is not likely because this form requires an additional signal set (approximately at 195.0–204.5 ppm) [37] in ¹³C NMR spectra, clearly correspond to a ketone form of the lateral chain, which was not observed. The presence of a CH form (C) is not likely because it is known that proton transfer between pyrazole C4 and OH is usually slow [35,43]. Consequently, in DMSO- d_6 solution, the ligand (H₂SB) (**3**) exist mainly as hydroxyethylidene form (Fig. 1**D**') with intramolecular hydrogen bond, in agreement with other reports [35,36,44,45].

3.3. Magnetic moments and electronic spectra

The information regarding geometry of the coordination polymers were 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 ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$ (υ_1), ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (υ_2) and ${}^{6}A_{1g} \rightarrow {}^{4}A_{1g}$, ${}^{4}E_{g}$ (υ_3) transitions, respectively, in an octahedral environment around the Mn(II) ion [46]. The magnetic moment value of the Mn(II) coordination polymer was 6.01 B.M. due to a high-spin d⁵-system with an octahedral geometry [47]. 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 [48,49]. The reflectance spectrum of Co(II) coordination polymer shows medium intensity bands at ~9,300, ~18,300 and ~19,050 cm⁻¹, which may be assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F) (\upsilon_1)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F) (\upsilon_2)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ (υ_{3}) transitions, respectively, of an octahedral geometry. The reflectance spectrum of the Ni(II) coordination polymer exhibit three bands at ~10,300, ~17,650 and ~24,000 cm^{-1} assignable to ${}^3A_{2g}(F) \to {}^3T_{2g}(F)$ (υ_1), ${}^3A_{2g}(F) \to {}^3T_{1g}(F)$ (υ_2) and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ (υ_{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 ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ 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 [50]. The reflectance spectrum of oxovanadium(IV) coordination polymer exhibits three spin-allowed transitions at ~13,350, ~15,980 and ~23,850 cm⁻¹, which have been assigned to ${}^{2}B_{2} \rightarrow {}^{2}E(\upsilon_{1})$, ${}^{2}B_{2} \rightarrow {}^{2}B_{1}(\upsilon_{2})$ and ${}^{2}B_{2} \rightarrow {}^{2}A_{1}(\upsilon_{3})$ transitions, respectively [24]. The oxovanadium(IV) coordination polymer exhibits magnetic moment corresponding to the spin-only value of 1.80 B.M. The Zn(II) coordination polymer is diamagnetic as expected for d^{10} system. The values of the electronic parameters, such as the ligand field splitting energy (10 Dq), Racah interelectronic repulsion parameter (B), nephelauxetic ratio (β) and ratio v_2/v_1 for the Co(II) and Ni(II) coordination polymers have been calculated using the secular equations given by König [51] and are summarized in Table 2. The β values indicate that the coordination polymers have appreciable covalent character [52]. The suggested structure of the coordination polymers are shown in Fig. 2.

3.4. Thermal studies

The thermodynamic activation parameters of the decomposition process of the coordination polymers such as energy of activation (E_a) and order of reaction (n) were evaluated graphically

Table 2

Electronic parameters of the Co(II) a	and Ni(II) coordination polyme	rs
---------------------------------------	--------------------------------	----

Electronic parameters of the		amación polymers						
Coordination polymers	Observed bands (cm ⁻¹)			υ_2/υ_1	В	β	β_0	10 Dq
	υ_1	υ_2	υ_3					
$\frac{[Co(SB)(H_2O)_2]_n \cdot 2H_2O}{[Ni(SB)(H_2O)_2]_n \cdot 2H_2O}$	9, 300 10, 500	18,180 17,500	18,940 24,600	1.95 1.67	717 707	0.73 0.69	26.0 31.4	10,419 10,500



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



Fig. 2. Suggested structure of the coordination polymers.

by employing the Freeman–Carroll method [53] using the following relation:



Fig. 3. Freeman–Carroll plot for thermal dehydration of $[Co(SB)(H_2O)_2]_n \cdot 2H_2O$.

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*. E_a 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 Fig. 3. The slope of the plot gave the value of $E_a/2.303R$ and the order of reaction (*n*) was determined from the intercept.

3.4.1. 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. The typical TG/DTG, DTA and DSC curves of the coordination polymer $[M(SB)(H_2O)_y]_n \cdot xH_2O$ (where M = Co(II), y = 2, x = 2) are represented in Fig. 4. The thermal fragmentation scheme for Mn(II), Ni(II) and VO(IV) coordination polymers is shown below:

 $[\mathsf{M}(\mathsf{SB})(\mathsf{H}_2\mathsf{O})_y]_n \cdot x\mathsf{H}_2\mathsf{O}_{\substack{\mathsf{SD}-\mathsf{130^\circ C}\\\mathsf{dehydration}}}^{\mathsf{50}-\mathsf{130^\circ C}} [\mathsf{M}(\mathsf{SB})(\mathsf{H}_2\mathsf{O})_y]_n + x\mathsf{H}_2\mathsf{O}$

where M = Mn(II), VO(IV), x = 1 and Ni(II), x = 2.

$$[M(SB)(H_2O)_y]_{n \text{ removal of coordinated water molecules}} [M(SB)]_n + yH_2O$$

Table 3	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
$[Mn(SB)(H_2O)_2]_n \cdot H_2O$	50–130 130–260	63.50 -	62.17 (+)	122.91 (+) 187.68 (+) 215 (+)	2.28 (2.45) 4.85 (4.90)	Loss of one lattice water molecule Loss of two coordinated water molecules
	260-780	427.89	378.30 (-)	253.25 (+) 360.15 (+)	81.94 (81.80) 89.07 ^a (89.15)	Removal of (SB) ligand molecule Leaving Mn ₂ O ₃ residue
$[Co(SB)(H_2O)_2]_n \cdot 2H_2O$	50-260	67.94	75.11 (+)	156.47 (+)	9.36 (9.51)	Loss of two lattice + two coordinated water molecules
	260-760	431.78	459.77 (–)	-	80.62 (80.57) $89.98^{a} (90.08)$	Removal of (SB) ligand molecule Leaving CoO residue
[Ni(SB)(H ₂ O) ₂] _n ·2H ₂ O	50–130 130–280 280–760	68.72 - 471.52	73.66 (+) - 439.39 (–)	- 160.14 (+) -	4.88 (4.76) 4.61 (4.76) 82.69 (82.58) 92.18 ^a (92.10)	Loss of two lattice water molecules Loss of two coordinated water molecules Removal of (SB) ligand molecule Leaving free Ni residue
$[Cu(SB)(H_2O)_2]_n \cdot H_2O$	50-240	60.66	66.15 (+)	161.33 (+)	7.17 (7.26)	Loss of one lattice + two coordinated water molecules
	240-720	495.73	407.68 (-)	274.15 (+) 358.97 (+)	82.09 (82.03) $89.26^{a} (89.29)$	Removal of (SB) ligand molecule Leaving CuO residue
$[Zn(SB)(H_2O)_2]_n \cdot H_2O$	50-230	62.94	64.61 (+)	149.06 (+)	7.15 (7.24)	Loss of one lattice + two coordinated water molecules
	230–740	521.91	503.75 (-)	-	83.86 (83.83) 91.01 ^a (91.10)	Removal of (SB) ligand molecule Leaving free Zn residue
[VO(SB)(H ₂ O)] _n ·H ₂ O	50–130 130–250 250–700	60.51 - 448.61	65.28 (+) - 433.18 (-)	132.58 (+) 207.88 (+) 342.91 (+)	2.51 (2.47) 2.50 (2.47) 82.31 (82.44) 87.32 ^a (87.38)	Loss of one lattice water molecule Loss of one coordinated water molecule Removal of (SB) ligand molecule Leaving V ₂ O ₅ residue

(+) Endothermic and (-) exothermic.

^a Total mass loss.

The anhydrous coordination polymers show great thermal stawhere M = Mn(II), Ni(II), y = 2 and VO(IV), y = 1. bility up to 260 °C; and in the second subsequent stage for Co, Cu 280-780°C $[M(SB)]_n \xrightarrow{280-780^{\circ}C}{metal residue*}$ and Zn coordination polymers whereas in the third subsequent stage for Mn, Ni and VO coordination polymers, the decomposition and combustion of ligand (H₂SB) occurs. The removal of ligand where metal residue^{*} = Mn_2O_3 , V_2O_5 or free Ni residue. (H₂SB) undergoes decomposition forming free metal ion for Ni and Whereas for Co(II), Cu(II) and Zn(II) coordination polymers, the Zn [24,54] or metal oxides for Mn, Co, Cu and V as the final residue. thermal fragmentation scheme is shown below: 50–260°C $[M(SB)(H_2O)_y]_n \cdot xH_2O \xrightarrow{50-260^\circ C}_{\text{removal of lattice water molecules}+coordinated water molecules}} [M(SB)]_n + yH_2O + xH_2O$ where M = Cu(II), Zn(II), y = 2, x = 1 and Co(II), y = 2, x = 2. The thermodynamic activation parameters of the decomposition process of dehydrated complexes such as activation 260-760°C $[M(SB)]_n \xrightarrow[removal of H_2SB ligand molecule]{260-760°C} metal residue*$ entropy ($\Delta S^{\#}$), pre-exponential factor (A), activation enthalpy $(\Delta H^{\#})$ and free energy of activation $(\Delta G^{\#})$, were calculated using where metal residue* = CoO, CuO or f ree Zn residue. the reported equations [55,56]. According to the kinetic data

Table 4

Kinetic barameters of the coordination bolymers	Kinetic	parameters	of the	coordination	polymers
---	---------	------------	--------	--------------	----------

Riffette parameters of	the coordination p	orymers					
Compounds	TG range (°C)	$E_{\rm a}$ (kJ mol ⁻¹)	п	A (s ⁻¹)	$\Delta S^{\#}$ (J K ⁻¹ mol ⁻¹)	$\Delta H^{\#}$ (kJ mol ⁻¹)	$\Delta G^{\#}$ (kJ mol ⁻¹)
$[Mn(SB)(H_2O)_2]_n \cdot H_2O$	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	$0.26 imes 10^3$	-95.67	39.52	106.58
$[Co(SB)(H_2O)_2]_n \cdot 2H_2O$	50-260	3.80	0.00	0.15	-102.00	0.96	35.80
	260-760	81.40	1.00	$0.21 imes 10^6$	-93.60	75.50	141.00
$[Ni(SB)(H_2O)_2]_n \cdot 2H_2O$	50-130	3.81	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	0.26×10^6	-93.00	94.83	164.07
$[Cu(SB)(H_2O)_2]_n \cdot H_2O$	50-240	3.36	0.00	0.12	-102.38	0.59	34.75
	240-720	69.88	1.00	0.79×10^4	-94.45	63.49	136.09
$[Zn(SB)(H_2O)_2]_n \cdot H_2O$	50-230	3.51	0.00	0.13	-102.00	0.72	35.10
	230-740	44.10	1.00	$0.81 imes 10^2$	-96.10	37.60	114.00
$[VO(SB)(H_2O)]_n \cdot H_2O$	50-130	3.39	0.00	0.12	-102.00	0.61	34.80
	130-250	4.66	1.50	0.07	-103.00	0.65	50.00
	250-700	61.20	1.00	0.49×10^{4}	-94 60	55 30	122.00



Fig. 4. TGA/DTG, DTA and DSC curves of $[Co(SB)(H_2O)_2]_n \cdot 2H_2O$.

obtained from DTG curves, all the coordination polymers have negative entropy, which indicates that the studied coordination polymers have more ordered systems than reactants [57]. The kinetic parameters, especially energy of activation (E_a) is helpful in assigning the strength of the coordination polymers. The calculated E_a values of the investigated coordination polymers for the first dehydration step are in the range 3.36–3.81 kJ mol⁻¹ (Table 4). Based on the activation energy values the thermal stabilities of the coordination polymers in the decreasing order is: Ni(II) > Co(II) > Mn(II) > Zn(II) > Cu(II) > VO(IV).

It is evident that the thermal stabilities of the coordination polymers increase as the ionic radii decrease. The thermal stabilities of the Ni(II), Mn(II) and VO(IV) coordination polymers in the solid-state follow the general trend found by Irving and Williams [58] 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.

4. Conclusions

The design and synthesis of a new tetradentate ligand (H_2SB) have successfully demonstrated. FT-IR, ¹H and ¹³C NMR studies reveal that this ligand exists in the tautomeric enol form in the solid and solution with intramolecular hydrogen bonding. New Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and VO(IV) 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.

Acknowledgements

The author would like to present his deep thanks and gratitude to the University Grant Commission, New Delhi [Grant No. F.31-153/2005 (SR)] for financial support. The author also thanks the Head, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India, for providing the necessary laboratory facilities. Analytical facilities provided by the SAIF, Central Drug Research Institute, Lucknow, India and the Sophisticated Instrumentation Centre for Applied Research & Testing (SICART), Vallabh Vidyanagar, Gujarat, India is gratefully acknowledged.

References

- [1] (a) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
- (b) G.-Q. Zhang, G.-Q. Yang, J.-S. Ma, Cryst. Growth Des. 6 (2006) 357; (c) A.K. Ghosh, D. Ghoshal, J. Ribas, G. Mostafa, N.R. Chaudhuri, Cryst. Growth Des. 6 (2006) 36;
- (d) S.-Q. Zang, Y. Su, Y.-Z. Li, H.-Z. Zhu, Q.-J. Meng, Inorg. Chem. 45 (2006) 2972.
 Y. Xu, D. Yuan, B. Wu, L. Han, M. Wu, F. Jiang, M. Hong, Cryst. Growth Des. 6 (2006) 1168.
- [3] C. Nather, J. Greve, I. Jeb, Chem. Mater. 14 (2002) 4536.
- [4] A. Bajpai, S. Rai, U.D.N. Bajpai, Polym. J. (Tokyo) 29 (1997) 44;
- A. Bajpai, S. Rai, U.D.N. Bajpai, Chem. Abstr. 126 (2006) 126137.
- [5] K. Tokaji, I. Tomita, T. Endo, Macromolecules 30 (1997) 7386.
- [6] D.H. Grayson, J.M. Kelly, Sol. Energy R and D, Eur. Community, Ser. D. (Photo Chem., Photo Electrochem., Photobiol. Processes) 99 (51–57) (1983) 178958; D.H. Grayson, J.M. Kelly, Chem. Abstr. 99 (51–57) (1983) 178958.
- 7] N. Toshima, Kogya Zairyo, Chem. Abstr. 39 (1991) 451991.
- [8] (a) M. Kurmoo, H. Kumagai, M. Akita-Tanaka, K. Inoue, S. Takagi, Inorg. Chem. 45 (2006) 1627;
 - (b) Y.-Z. Tang, X.-S. Wang, T. Zhou, R.-G. Xiong, Cryst. Growth Des. 1 (2006) 11; (c) K. Takaoka, M. Kawano, T. Hozumi, S.-I. Ohkoshi, M. Fujita, Inorg. Chem. 45 (2006) 3976;

(d) S. Midollini, A. Orlandini, P. Rosa, L. Sorace, Inorg. Chem. 44 (2006) 2060;

- (e) S.K. Ghosh, J. Ribas, P.K. Bharadwaj, Cryst. Growth Des. 5 (2005) 623.
- [9] (a) S.A. Zimmerman, J.G. Ferry, Biochemistry 45 (2006) 5149;
 (b) P.K. Padma, G.K. Andrey, R.K. James, J. Phys. Chem. B 110 (2006) 3841;
 (c) D.A. Dickie, G. Schatte, M.C. Jennings, H.A. Jenkins, S.Y.L. Khoo, J.A.C. Clyburne, Inorg. Chem. 45 (2006) 1646;
- (d) Y. Lu, Y. Xu, E. Wang, J. Lu, C.-W. Hu, L. Xu, Cryst. Growth Des. 5 (2005) 257.
 [10] (a) T.J. Barton, L.M. Bull, W.G. Klemperer, D.A. Loy, B. McEnaney, M. Misono, P.A. Monson, G. Pez, G.W. Scherer, J.C. Vartuli, O.M. Yaghi, Chem. Mater. 11 (1999) 2633;
 (b) H. Li, M. Eddaoudi, T.L. Groy, O.M. Yaghi, J. Am. Chem. Soc. 120 (1998) 8571;

(c) B. Chen, M. Eddaoudi, S.T. Hyde, T.M. Reineke, M. o'Keeffe, O.M. Yaghi, Science 291 (2001) 1021.

- [11] J.D. Joshi, N.B. Patel, S.D. Patel, J. Macromol. Sci. A: Pure Appl. Chem. 43 (2006) 1167.
 [12] N.B. Patel, G.P. Patel, J.D. Joshi, J. Macromol. Sci. A: Pure Appl. Chem. 42 (2005)
- 931. [13] H. Matsui, H. Hasegawa, M. Yoshihara, J. Macromol. Sci. A: Pure Appl. Chem. 42
- (2005) 869.
- [14] A.K. El-Sawaf, D.X. West, Trans. Met. Chem. 23 (1998) 417.

- [15] N. Kalarani, S. Sangeetha, P. Kamalakannan, D. Venkappayya, Russ. J. Coord. Chem. 29 (2003) 845.
- [16] F. Marchetti, C. Rettinar, R. Pettinari, A. Cingolani, D. Leonesi, A. Lorenzotti, Polyhedron 18 (1999) 3041.
- [17] O.N. Kataeva, A.T. Gubaidullin, I.A. Litvinov, O.A. Lodochnikova, L.R. Islamov, A.I. Movchan, G.A. Chmutova, J. Mol. Stuct. 610 (2002) 175.
- [18] Y. Akama, A. Tong, Microchem. J. 53 (1996) 34.
- [19] Y. Akama, A. Tong, N. Matsumoto, T. Ikeda, S. Tunaka, Vib. Spectrosc. 13 (1996) 113
- [20] F. Marchetti, C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 2909.
- [21] M.F. Iskander, L. Sayed, A.F.M. Hefny, S.E. Zayan, J. Inorg. Nucl. Chem. 38 (1976) 2209.
- [22] H. Adams, D.E. Fenton, G. Minardi, E. Mura, M. Angelo, Inorg. Chem. Commun. 3 (2000) 24.
- [23] Z.Y. Yang, R.D. Yang, F.S. Li, K.B. Yu, Polyhedron 19 (2000) 2599.
- [24] C.K. Modi, M.N. Patel, J. Therm. Anal. Cal. 94 (2008) 247.
- [25] C.K. Modi, I.A. Patel, B.T. Thaker, J. Coord. Chem. 61 (2008) 3110.
- [26] K.R. Surati, B.T. Thaker, C.K. Modi, Russ. J. Coord. Chem. 34 (1) (2008) 25.
- [27] A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, third ed., Longman, London, 1975, 433pp.
- [28] N.H. Furman, Standard Methods of Chemical Analysis, vol. I, sixth ed., D. Van Nostrand Company, Inc., New Jersey, 1962, 1211pp.
- [29] B.S. Jensen, Acta Chem. Scand. 13 (1959) 1668.
- [30] C.K. Modi, B.T. Thaker, Indian J. Chem. 41A (2002) 2544.
 [31] H.M. Parekh, P.K. Panchal, M.N. Patel, J. Therm. Anal. Cal. 86 (2006) 803.
- [32] M.S. Masoud, M.F. Amira, A.M. Ramadan, G.M. El-Ashry, Spectrochim. Acta, Part A 69 (2008) 230.
- [33] L. Liu, D. Jia, Y. Ji, Synth. React. Inorg. Met.-Org. Chem. 32 (2002) 739.
 [34] J. Elguero, C. Marzin, A.R. Katritzky, P. Linda, Adv. Heterocycl. Chem. 1 (1976) 313
- [35] L.N. Kurkovskaya, N.N. Shapet'ko, A.S. Vitvitskaya, A.Y. Kvitko, J. Org. Chem. USSR (Engl. Transl.) 13 (1977) 1618, Original paper: Zh. Org. Khim, 13 (1997) 1750

- [36] W. Holzer, K. Mereiter, B. Plagens, Heterocycles 50 (1999) 799.
- [37] A.B. Uzoukwu, S.S. Al-Juaid, P.B. Hitchcock, J.D. Smith, Polyhedron 12 (1993) 1719.
- [38] Y. Akama, M. Shiro, T. Ueda, M. Kajitani, Acta Cryst. C51 (1995) 1310.
- [39] J.A.M. Guard, P.J. Steel, Aust. J. Chem. 47 (1994) 1453.
- [40] A.A. Soliman, Spectrochim. Acta, A 67 (2007) 852.
- [41] R.N. Jadeja, J.R. Shah, E. Suresh, P. Paul, Polyhedron 23 (2004) 2465.
- [42] H.-O. Kalinowski, S. Berger, S. Braun, ¹³C NMR-Spektroskopie, Georg Thieme Verlag, Stuttgart, New York, 1984, pp. 174–176.
- [43] A.R. Katritzky, M. Karelson, P.A. Harris, Heterocycles 32 (1991) 329.
- [44] E.C. Okafor, Spectrochim. Acta, A 40 (1984) 397.
- [45] R.N. Jadeja, J.R. Shah, Polyhedron 26 (2007) 1677.
- [46] N.H. Patel, H.M. Parekh, M.N. Patel, Trans. Met. Chem. 30 (2005) 13.
- [47] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amster-
- dam, 1984. [48] P.K. Panchal, M.N. Patel, Synth. React. Inorg. Met.-Org. Chem. 34 (2004) 1277.
- [49] M.M. Patel, R. Manavalan, J. Macromol. Sci. Chem. A 19 (1983) 951.
- [50] A.N. Speca, M. Karayannis, L.L. Pytleuski, J. Inorg. Nucl. Chem. 35 (1973) 3113.
- [51] E. König, Structure and Bonding, Springer Verlag, New York, 1971, pp. 9, 175.
- [52] S. Chandra, M. Pundir, Spectrochim. Acta, A 69 (2008) 1.
- [53] E.S. Freeman, B. Carroll, J. Phys. Chem. 62 (1958) 394.
- [54] S.B. Jagtap, R.C. Chikate, O.S. Yemul, R.S. Ghadage, B.A. Kulkarni, J. Therm. Anal. Cal. 78 (2004) 251.
- [55] M. Sekerci, F. Yakuphanoglu, J. Therm. Anal. Cal. 75 (2004) 189.
- [56] A.A. Abou-Hussen, N.M. El-Metwally, E.M. Saad, A.A. El-Asmy, J. Coord. Chem. 58 (2005) 1735.
- M.E. El-Zaria, Spectrochim. Acta, A 69 (2008) 216. [57]
- [58] H. Irving, R.J.P. Williams, J. Chem. Soc. (1953) 3192.