Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 3, 803–807

TRANSITION METAL(II) IONS WITH DINEGATIVE TETRADENTATE SCHIFF BASE

Synthetic, thermal, spectroscopic and coordination aspects

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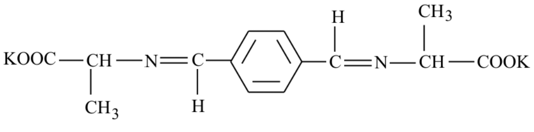
Some new coordination polymers of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), obtained from the interaction of metal acetate with dipotassium salt of N,N'-di(carboxyethylidene)terephthalaldehydediimine (K_2SB) are described. The products, which have been characterized by elemental analyses, magnetic measurements, thermogravimetric analyses, electronic and infrared spectral studies, have composition, $[M(SB)(H_2O)_2]_n$. These colored coordination polymers are non-hygroscopic and quite stable at room temperature. On the basis of analytical data and IR studies, a 1:1 metal to ligand stoichiometry has been suggested to these coordination polymers. The IR studies have also revealed that ligands are coordinated to metal ion through carboxy oxygen and azomethine nitrogen. All the studies suggested tetradentate nature of the ligand with octahedral symmetry of the coordination polymers. All the coordination polymers are insoluble in acetone, ethanol, chloroform, methanol, benzene, DMF and DMSO. The thermal decomposition of the coordination polymers is studied and indicates that not only the coordinated water is lost but also that the decomposition of the ligand from the coordination polymers is necessary to interpret the successive mass loss.

Keywords: *coordination polymers, spectroscopic analyses, tetradentate Schiff base, thermal analyses, transition metal*

Introduction

The interest in the construction of coordination polymers by linking transition metal ions with polydentate ligands has been constantly growing over the past years [1–7]. Coordination polymers (chelate polymers) are defined as materials in which metal ions are linked together with di- or polyfunctional ligands. Coordination polymers are usually known for their thermal stability [8, 9]. However, other equally important applications have been reported such as their use as solar energy converters [10] and their ability to remove SO_x and NO_x from the environment [11]. The choice of the metal ions, the ligand design, the counter ions and the solvents can have a considerable effect on the final architecture of the coordination polymers and particularly its dimensionality [12]. In continuation of earlier work [13] herein we describe synthesis, characterization and thermal studies of the coordination polymers with Schiff base. The structure of the Schiff base is shown in Scheme 1.



Scheme 1 Structure of the Schiff base (K_2SB)

Experimental

Reagent and solvents

All the chemicals used were of analytical grade. Terephthalaldehyde, *DL*-alanine, potassium hydroxide and metal acetate were purchased from E. Merck (India) Ltd., Mumbai. The organic solvents were purified by standard methods [14].

Synthesis of ligand

A solution of potassium hydroxide (20 mmol, 1.12 g) in 50 mL absolute alcohol was added to *DL*-alanine (20 mmol, 1.78 g). The mixture was stirred until it dissolved in the ethanol–KOH solution. Then an ethanolic solution (100 mL) of terephthalaldehyde (10 mmol, 1.34 g) was added quickly. The mixture was heated on a water bath for an hour. A yellow crystalline solid was obtained on cooling at room temperature. The product was filtered, washed with ethanol and dried in a vacuum desiccator. Yield: 56%; *m.p.*: >360°C.

Synthesis of the coordination polymers

The methanolic solution of 100 mL metal acetate (10 mmol) was added slowly to a methanolic solution (100 mL) of dipotassium salt of N,N'-di(carboxyethylidene)terephthalaldehydediimine (K_2SB)

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1388–6150/$20.00

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Table 1 Analytical and physical data of Schiff base and its coordination polymers[a]

Empirical formula of monomer unit	Colour (yield/%)	Found (calcd.)/%				*m.p.*/°C
		C	H	N	metal	
K_2SB $C_{14}H_{14}K_2N_2O_4$	yellow (56)	47.75 (47.72)	3.98 (3.97)	7.96 (7.94)	–	>360
$[Mn(SB)(H_2O)_2]_n$ $C_{14}H_{18}MnN_2O_6$	brown (47)	46.01 (46.05)	4.99 (4.93)	7.63 (7.67)	15.01 (15.04)	>360
$[Co(SB)(H_2O)_2]_n$ $C_{14}H_{18}CoN_2O_6$	brown (53)	45.57 (45.55)	4.87 (4.83)	7.56 (7.58)	15.71 (15.96)	>360
$[Ni(SB)(H_2O)_2]_n$ $C_{14}H_{18}NiN_2O_6$	green (50)	45.52 (45.58)	4.88 (4.84)	7.54 (7.59)	15.73 (15.91)	>360
$[Cu(SB)(H_2O)_2]_n$ $C_{14}H_{18}CuN_2O_6$	green (52)	44.93 (44.99)	4.84 (4.81)	7.43 (7.49)	17.05 (17.00)	>360
$[Zn(SB)(H_2O)_2]_n$ $C_{14}H_{18}ZnN_2O_6$	yellow (49)	44.73 (44.77)	4.76 (4.79)	7.47 (7.45)	17.36 (17.41)	>360
$[Cd(SB)(H_2O)_2]_n$ $C_{14}H_{18}CdN_2O_6$	yellow (46)	39.76 (39.79)	4.29 (4.26)	6.67 (6.62)	26.57 (26.60)	>360

[a] K_2SB=dipotassium salt of N,N'-di(carboxyethylidene)terephthalaldehydediimine

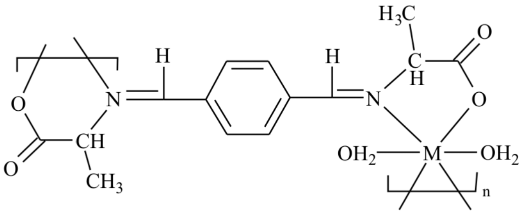
(10 mmol, 3.52 g) in 1:1 mole ratio. The mixture was heated for 8 h at 80°C to ensure complete precipitation and then allowed to cool overnight at room temperature. The obtained coordination polymers were filtered, washed with methanol and dried in air. The coordination polymers are insoluble in all common organic solvents like acetone, ethanol, methanol, chloroform, benzene, dimethyl formamide and dimethyl sulfoxide.

Results and discussion

Table 1 lists the analytical data for the ligand (K_2SB) and their coordination polymers with metal ions. The coordination polymers are of the general formulae $[M(SB)(H_2O)_2]_n$ and were prepared by following reaction.

$$M(CH_3COO)_2+K_2SB\rightarrow [M(SB)(H_2O)_2]_n+2CH_3COOK$$

The formation of coordination polymers having 1:1 metal–ligand mole ratio facilitated by loss of two potassium ions from Schiff base ligand. The polymeric compounds were insoluble in common organic compounds and, therefore, precluded the determination of molecular mass. Elemental analyses, physical properties and infrared data provide good evidence that the chelates are polymeric in nature [15]. The suggested structure of the coordination polymers is shown in Scheme 2.



Scheme 2 Structure of the coordination polymers; $[M(SB)(H_2O)_2]_n$ where *M*=Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Infrared spectra

In order to study the binding mode of Schiff base to the metal ion in the coordination polymers, the IR spectrum of the free ligand was compared with the spectra of the corresponding coordination polymers. The infrared spectra of the coordination polymers are shown in Fig. 1. In the spectra of the Schiff base, a strong band at 1635 cm^{-1} is attributable to the –C=N group, indicates the formation of the Schiff base. On coordination, due to possible drift of the lone pair density towards the metal ion, the azomethine –C=N bond is expected to absorb at lower frequency in the coordination polymers. The band observed at ~1605–1615 cm^{-1} indicates the coordination of the azomethine nitrogen to the metal ion [16]. In all the coordination polymers, a new band is seen in the 525–535 cm^{-1} region, which is probably due to the formation of M–N bonds [17]. The infrared spectra of the coordination polymers exhibit a broad band in the region 3300–3500 cm^{-1} is due to $\nu_{O–H}$ and other bands at ~850 and ~715 cm^{-1} are due to the rocking and wagging mode of the OH group [18]. The presence of later band indicates the coordination nature of the water molecule [19]. The two absorption bands occurring near 1595 and 1400 cm^{-1} in the Schiff base (K_2SB) corresponding to the asymmetric and

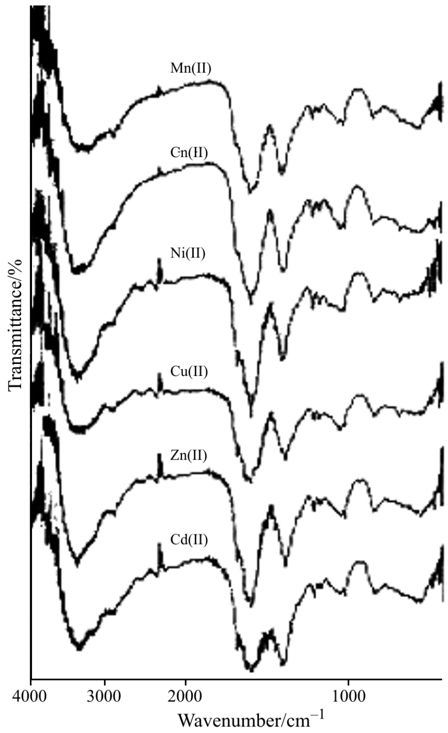


Fig. 1 Infrared spectra of the coordination polymers

symmetric stretching vibration bands of the ionic carboxy group ν_{COO}, in the coordination polymers are shifted to lower frequencies ~1585 and 1390 cm^{-1}, respectively [20]. The appearance of a new band at 415–420 cm^{-1} due to $\nu_{M\text{–}O}$ [21] further confirms the coordinated nature of the carboxylate groups. The coordination polymers show sharp band in the range 750–780 and 1525–1535 cm^{-1} are due to aromatic $\nu_{C\text{–}H}$ and $\nu_{C=C}$, respectively. The band in the range 1370–1390 cm^{-1} is due to $\nu_{C\text{–}CH_3}$.

Magnetic moments and electronic spectra

The information regarding geometry of the coordination polymers is obtained from their electronic spectral data and magnetic moments. For the Co(II) coordination polymer, the reflectance spectra exhibits the bands of medium intensity at ~9200, ~18000 and ~19000 cm^{-1}, which are assigned to the transitions $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ (ν_3), respectively, of an octahedral cobalt(II) coordination polymer [22] and the magnetic moment value is 4.19 B.M. The electronic spectra of the Ni(II) coordination polymer exhibits absorption bands at ~10500, ~18165 and ~24100 cm^{-1} attributed to $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ (ν_3) transitions, respectively, in an octahedral geometry [23]. The value of the magnetic moment (2.92 B.M.) may be taken as additional evidence for their octahedral structure. The ground state of Mn(II) is $^6A_{1g}$. The Mn(II) coordination polymer in an octahedral field should have three transitions corresponding to $^6A_{1g}\rightarrow{}^4T_{1g}$ (ν_1~15000 cm^{-1}), $^6A_{1g}\rightarrow{}^4T_{2g}$ (ν_2~19600 cm^{-1}) and $^6A_{1g}\rightarrow{}^4A_{1g}$, ^4E_g (ν_3~24500 cm^{-1}) in increasing order of energy. The magnetic moment value of the Mn(II) coordination polymer is 6.18 B.M., suggesting an octahedral geometry [24]. The Cu(II) coordination polymer display a broad band at ~15500 cm^{-1} due to the $^2E_g\rightarrow{}^2T_{2g}$ transition and the magnetic moment value is 1.78 B.M., which are close to spin-only value (1.73 B.M.) expected for an unpaired electron, which offers the possibility of an octahedral geometry [25]. Electronic spectral data and magnetic moments of coordination polymers are summarized in Table 2. 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 ν_2/ν_1 are presented in Table 3. The Zn(II) and Cd(II) coordination polymers are diamagnetic as expected for d^{10} systems.

Thermogravimetric studies

The thermogravimetric analysis for the coordination polymers was carried out within a temperature range from 50 to 800°C in N_2 atmosphere to establish their compositional differences as well as to ascertain the na-

Table 2 Electronic spectral data and magnetic moments of coordination polymers[a]

Coordination polymers	Absorption/cm^{-1}	Transition	μ_{eff}/B.M. (calcd.)
$[Mn(SB)(H_2O)_2]_n$	15000 19600 24500	$^6A_{1g}\rightarrow{}^4T_{1g}$ $^6A_{1g}\rightarrow{}^4T_{2g}$ $^6A_{1g}\rightarrow{}^4A_{1g}$, ^4E_g	6.18 (5.92)
$[Co(SB)(H_2O)_2]_n$	9200 18000 19000	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4T_{1g}(p)$	4.19 (3.87)
$[Ni(SB)(H_2O)_2]_n$	10500 18165 24100	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}(F)\rightarrow{}^3T_{1g}(p)$	2.92 (2.83)
$[Cu(SB)(H_2O)_2]_n$	15500	$^2E_g\rightarrow{}^2T_{2g}$	1.78 (1.73)

[a] K_2SB=dipotassium salt of N,N'-di(carboxyethylidene)terephthalaldehydediimine

Table 3 Electronic parameters of the Co(II) and Ni(II) coordination polymers[a]

Coordination polymers	Observed bands/cm^{-1}			ν_2/ν_1	*B*	β	β°	10 Dq
	ν_1	ν_2	ν_3					
$[Co(SB)(H_2O)_2]_n$	9200	18000	19000	1.95	728	0.75	25	10320
$[Ni(SB)(H_2O)_2]_n$	10500	18165	24100	1.73	717	0.69	31	10500

[a] K_2SB=dipotassium salt of N,N'-di(carboxyethylidene)terephthalaldehydediimine

The ligand field splitting energy (10 Dq), interelectronic repulsion parameter (*B*) and covalency factor (nephelauxetic ratio) β for the Co(II) and Ni(II) coordinating polymers have been calculated using the secular equations given by König [30]

for Co(II) complexes	for Ni(II) complexes
$10\ Dq=1\backslash 2[(2\nu_1-\nu_3)+(\nu_3^2+\nu_1\nu_3-\nu_1^2)^{1/2}]$	$10\ Dq=\nu_1$
$15B=\nu_3-2\nu_1+10\ Dq$	$15B=(\nu_2+\nu_3)-3\nu_1$
$\beta=B\backslash B_0\ [B_0(\text{free ion})=971]$	$\beta=B\backslash B_0[B_0(\text{free ion})=1030]$
$\beta°=(1-\beta)\cdot 100$	$\beta°=(1-\beta)\cdot 100$

Table 4 Thermogravimetric data[a]

Coordination polymers	TG range/°C	Mass loss estimated (calcd.)/%	Assignment	Activation energy, E_a/kcal mol^{-1}
$[Mn(SB)(H_2O)_2]_n$	150–180	9.81 (9.86)	loss of two coordinated water molecules	4.12
	180–800	80.53 (80.57)	decomp. of ligand and formation of metal oxide	
$[Co(SB)(H_2O)_2]_n$	150–180	9.74 (9.75)	loss of two coordinated water molecules	5.45
	180–800	77.59 (77.53)	decomp. of ligand and formation of metal oxide	
$[Ni(SB)(H_2O)_2]_n$	150–180	9.79 (9.76)	loss of two coordinated water molecules	3.66
	180–800	79.76 (79.76)	decomp. of ligand and formation of metal oxide	
$[Cu(SB)(H_2O)_2]_n$	150–180	9.67 (9.63)	loss of two coordinated water molecules	4.66
	180–800	78.74 (78.71)	decomp. of ligand and formation of metal oxide	
$[Zn(SB)(H_2O)_2]_n$	150–180	9.53 (9.58)	loss of two coordinated water molecules	5.28
	180–800	78.36 (78.32)	decomp. of ligand and formation of metal oxide	
$[Cd(SB)(H_2O)_2]_n$	150–180	8.58 (8.51)	loss of two coordinated water molecules	4.05
	180–800	69.69 (69.61)	decomp. of ligand and formation of metal oxide	

[a] K_2SB=dipotassium salt of N,N'-di(carboxyethylidene)terephthalaldehydediimine

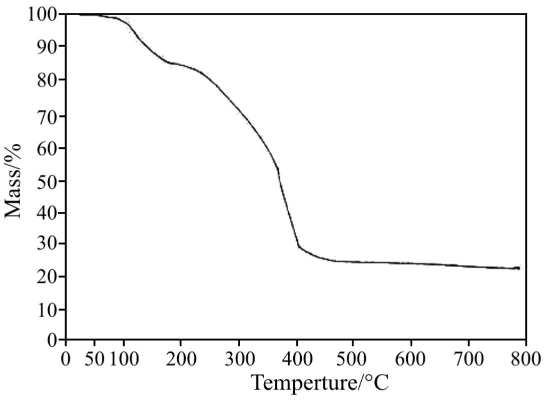


Fig. 2 Thermogravimetric curve of the $[Ni(SB)H_2O)_2]_n$ coordination polymer

ture of associated water molecules [26]. The Thermogravimetric curve of the coordination polymer is shown in Fig. 2. The determined temperature ranges, percent mass losses and thermal effects accompanying the changes in the coordination polymers on heating are given in Table 4, which revealed the following findings.

The TG curves of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) coordination polymers show a two-decomposition steps within the temperature ranges of 150–180 and 180–800°C. The first estimated mass losses (%) for $[M(SB)(H_2O)_2]_n$ coordination polymers are of 9.81 (9.86), 9.74 (9.75), 9.79 (9.76), 9.67 (9.63), 9.53 (9.58) and 8.58 (8.51) within the temperature range of 150–180°C may be attributed to the loss of two coordinated water molecules [27] of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) coordination polymers, respectively. The second estimated mass losses (%) for $[M(SB)(H_2O)_2]_n$ coordination polymers are of 80.53 (80.57), 77.59 (77.53), 79.76 (79.74), 78.74 (78.71), 78.36 (78.32) and 69.69 (69.61) within the temperature range of 180–800°C may be attributed to the loss of ligand molecule and formation of metal oxide of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) coordination polymers, respectively.

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 in the 3.66–5.45 kcal mol^{-1} range. The relative high E_a value indicates that the ligand is strongly bonded to metal ion [28]. Based on the activation energy values, the thermal stability of the coordination polymers in the decreasing order is: Co>Zn>Cu>Mn>Cd>Ni [29].

Acknowledgements

We wish to express our gratitude to the Head, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India, for providing the necessary laboratory facilities.

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Received: August 5, 2005
Accepted: November 11, 2005

DOI: 10.1007/s10973-005-7284-5