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# Coordination Polymeric Assemblies of some d-Block Elements with Schiff Bases and its Characterization

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A few coordination chain polymeric assemblies of the type  $[M(SB)(H_2O)_2]_n$  [ $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$  and  $Cd(II)$ ,  $H_2SB^1 = 1,1'$ -dihydroxy-2,2'-(1-isonitriloethylidene-4-nitrilomethylidene)phenyl)diphenyl or  $H_2SB^2 = 1$ -thio-1'-hydroxy-2,2'-(1-isonitriloethylidene-4-nitrilomethylidene)phenyl)diphenyl have been investigated. Structural and spectroscopic properties have been studied on the basis of elemental analyses, infrared spectra,  $^1H$ -NMR,  $^{13}C$ -NMR, electronic spectra, magnetic measurements and thermogravimetric analyses. The Schiff bases act as bidentate tetradentate ligands and bonding occur through the nitrogen and oxygen or sulfur atoms. An octahedral geometry has been assigned to all the prepared coordination polymers. The coordination polymers are insoluble in common organic solvents like benzene, acetone, ethyl acetate, methanol, ethanol, chloroform, dimethyl formamide and dimethyl sulphoxide.

**Keywords:** spectroscopy; polymeric assemblies; schiff base; transition metal

## 1 Introduction

The rational increase of structural dimension is an important synthetic goal in supramolecular systems. The elegant pioneering studies of self-assembly of molecular squares containing metal ions by Lehn, Robson, Stang and Fujita in the past decade (1–4) demonstrated novel molecular architectures with many functional properties (5–7). Coordination polymers are usually known for their thermal stability (8, 9). However, some additional equally good applications have been reported, such as use as solar energy converters (10) and removal of  $SO_x$  and  $NO_x$  from the environment (11). The study of polymeric ligands and their metal complexes is very useful as a catalyst in metal separation and in bio-inorganic chemistry (12–14). These types of certain coordination polymers with Schiff bases have been reported from our laboratories earlier by M. N. Patel et al. (15–17). Herein, we report the preparation and structural properties of some coordination polymers of the  $[M(SB)(H_2O)_2]_n$  type and characterized on the basis of elemental analysis,  $^1H$ -NMR,  $^{13}C$ -NMR, magnetic measurements, thermal analysis and spectral studies. The suggested structure of the ligand and its resonance is shown in Figure 1.

## 2 Experimental

### 2.1 Materials and Methods

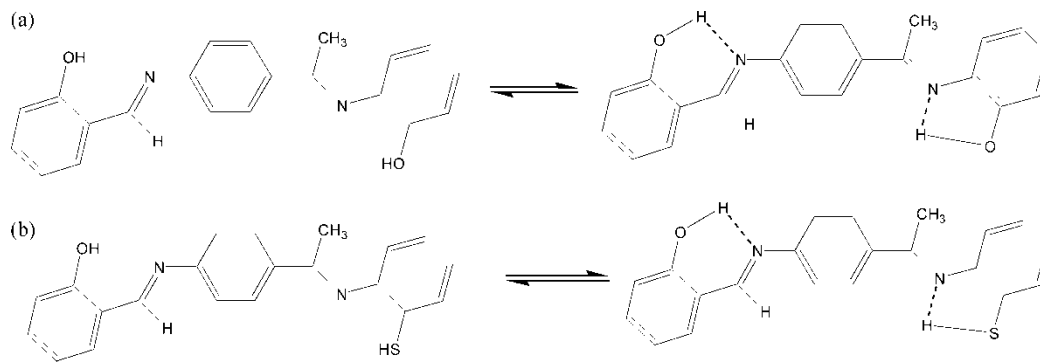
All the chemicals used were of analytical grade. *o*-Aminothiophenol was purchased from Lancaster, England. Salicylaldehyde, 4-aminoacetophenone, *o*-aminophenol and metal acetates were purchased from E. Merck (India) Limited, Mumbai. The organic solvents were purified by standard methods (18).

### 2.2 Preparation of the Schiff Bases

The preparation of salicylidene-4-aminoacetophenone was carried out by refluxing an ethanolic solution (100 mL) of 4-aminoacetophenone (10 mmol, 0.15 g) with an ethanolic solution (100 mL) of salicylaldehyde (10 mmol, 0.12 g) for 4 h and then allowed to cool overnight at room temperature. The formed yellow colored crystals were collected and dried in air. Yield = 0.21 g (78%), M.p. = 105°C.

An ethanolic solution (100 mL) of the salicylidene-4-aminoacetophenone (10 mmol, 0.24 g) and an ethanolic solution (100 mL) of *o*-aminophenol (10 mmol, 0.10 g) or *o*-aminothiophenol (10 mmol, 0.12 g) were mixed and refluxed for 10 h on a water bath and allowed to cool overnight at room temperature. The obtained crystals were filtered, washed successfully with water, ethanol, and dried in air. Yield = 0.22 g (64%), M.p.: 180°C for the ligand  $H_2SB^1$  and Yield = 0.19 g (60%), M.p.: 202°C for the ligand  $H_2SB^2$ .

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**Fig. 1.** Structure of the ligand, (a)  $\text{H}_2\text{SB}^1$  and (b)  $\text{H}_2\text{SB}^2$ .

### 2.3 Preparation of the Coordination Polymers

An ethanolic solution (100 mL) of metal acetate (20 mmol) and an ethanolic solution (100 mL) of  $\text{H}_2\text{SB}^1$  (20 mmol, 0.68 g) or  $\text{H}_2\text{SB}^2$  (20 mmol, 0.66 g) were mixed and refluxed on a water bath. The mixture was refluxed for 6 h to ensure complete precipitation. The mixture was then allowed to cool overnight at room temperature, and was filtered and washed with water and hot ethanol. The obtained coordination polymers were dried in air.

### 2.4 Physical Measurements

The magnetic moments have been obtained by a model 7304, Vibrating Sample Magnetometer, Lake Shore, USA. The vibrating sample magnetometer reports the total magnetic moment of a sample in emu. However, the end goal of the magnetic measurement is not the moment in emu, but to obtain the effective magnetic moment. Therefore, the magnetic moment can be converted to susceptibility units by realizing that  $1 \text{ emu} = 1 \text{ gauss} \cdot \text{cm}^3$ . The susceptibility of a sample has units of volume and is defined for paramagnetic material by the equation:

$$\chi(\text{cm}^3) = m(\text{emu})/H(\text{oersted})$$

The gram susceptibility,  $\chi_g$  was calculated using the expression:

$$\text{Gram susceptibility: } \chi_g = \chi(\text{cm}^3)/\text{mass}$$

The gram susceptibility was multiplied by the molecular weight of the sample to obtain molar susceptibility,  $\chi_M$ . A correction was applied for the diamagnetism of the ligands to get the corrected molar susceptibility  $\chi'_M$ . The effective magnetic moment was calculated from the expression:

$$\mu_{\text{efflig.}} = 2.84(\chi'_M \times T)^{1/2}$$

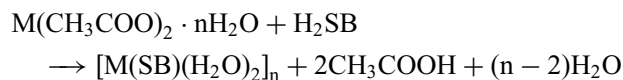
where T = absolute temperature (K).

Infrared spectra were recorded on a FT-IR Nicolet 400 D spectrophotometer in KBr pellets. Carbon, hydrogen, nitrogen and sulfur were analyzed with a model 240 Perkin-Elmer elemental analyzer.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a Bruker Avance (400 MHz). The metal contents of the mixed-ligand complexes were analyzed by

EDTA titration after decomposing the organic matter with a mixture of perchloric, sulfuric and nitric acids (1:1.5:2.5). Thermogravimetric analyses have been obtained by a model 5000/2960 SDTA, TA Instruments, USA. The TGA curves were obtained at a heating rate of  $10^\circ\text{C}/\text{min}$  in  $\text{N}_2$  atmosphere over the temperature range of  $50\text{--}800^\circ\text{C}$ . The reflectance spectra of the coordination polymers were recorded in the range  $1700\text{--}350 \text{ nm}$  (as  $\text{MgO}$  discs) on a Beckman DK-2A spectrophotometer.

## 3 Results and Discussion

The following reaction describes the formation of the coordination polymers:



Elemental analyses data, formula weights, colors, percentage yields, melting points and magnetic moment data are given in Table 1. The results of the elemental analyses of the Schiff bases  $\text{H}_2\text{SB}^1$  and  $\text{H}_2\text{SB}^2$  and its coordination polymers are in good agreement with those required by the proposed formula.

### 3.1 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ Spectra

The  $^1\text{H-NMR}$  spectra and  $^{13}\text{C-NMR}$  spectra of the ligands have been taken in  $\text{DMSO-d}_6$ . The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral data are reported along with the possible assignment in Table 2. The  $^1\text{H-NMR}$  spectra of ligand exhibit peaks at 6.6–7.5 ppm assigned to the aromatic protons. The singlet peak appeared at 8.3 and 8.4 ppm are assigned to azomethine protons ( $-\text{CH}=\text{N}-$ ). Phenolic  $-\text{OH}$  proton gives peaks at 4.9, and 5.3 ppm. The peaks appeared at 4.1 ppm is assigned to the  $-\text{SH}$  proton. In the case of  $^{13}\text{C-NMR}$  spectra peaks observed at 115.2–139.6 ppm are assigned to aromatic carbons. Peaks observed at 145.6, 155.7, 146.8, and 157.4 ppm are assigned to C-N carbons, while peaks at 164.9, and 164.9 corresponds to  $-\text{CH}=\text{N}-$  carbons, and

**Table 1.** Analytical data of the coordination polymers.<sup>a</sup>

Coordination polymers empirical formula	Formula weight	Colour	%Found (Calcd.)					M.p. (°C)	$\mu_{\text{eff.}}$ (B.M) (Calcd.)	Yield %
			C	H	N	S	Metal			
H <sub>2</sub> SB <sup>1</sup> C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	330.21	Yellow	76.35 (76.38)	5.48 (5.45)	8.50 (8.48)	—	—	180	—	64
H <sub>2</sub> SB <sup>2</sup> C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> OS	346.23	Yellow	72.80 (72.84)	5.15 (5.19)	8.05 (8.08)	9.22 (9.24)	—	202	—	60
[Mn(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> MnN <sub>2</sub> O <sub>4</sub>	419.14	Brown	60.12 (60.17)	4.71 (4.77)	6.73 (6.68)	—	13.06 (13.10)	>300	6.03 (5.92)	36
[Co(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> CoN <sub>2</sub> O <sub>4</sub>	423.16	Brown	59.66 (59.60)	4.80 (4.72)	6.60 (6.62)	—	13.90 (13.93)	>300	4.08 (4.01)	35
[Ni(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> NiO <sub>4</sub>	422.90	Green	59.72 (59.64)	4.74 (4.73)	6.65 (6.62)	—	13.82 (13.88)	>300	2.91 (2.83)	36
[Cu(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> CuN <sub>2</sub> O <sub>4</sub>	427.75	Green	58.90 (58.96)	4.61 (4.67)	6.51 (6.54)	—	14.80 (14.85)	>300	1.81 (1.73)	38
[Zn(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> Zn	429.60	Yellow	58.78 (58.71)	4.71 (4.66)	6.48 (6.52)	—	15.18 (15.22)	>300	—	32
[Cd(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> CdN <sub>2</sub> O <sub>4</sub>	476.62	Yellow	52.87 (52.92)	4.15 (4.19)	5.90 (5.87)	—	23.51 (23.58)	>300	—	40
[Mn(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> MnN <sub>2</sub> O <sub>3</sub> S	435.20	Brown	57.89 (57.95)	4.55 (4.59)	6.48 (6.43)	7.42 (7.36)	12.60 (12.62)	>300	6.01 (5.92)	39
[Co(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> CoN <sub>2</sub> O <sub>3</sub> S	439.20	Brown	57.48 (57.42)	4.50 (4.55)	6.30 (6.37)	7.23 (7.29)	13.47 (13.42)	>300	4.10 (4.01)	33
[Ni(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> NiO <sub>3</sub> S	438.96	Green	57.52 (57.45)	4.58 (4.55)	6.40 (6.38)	7.25 (7.29)	13.45 (13.37)	>300	2.94 (2.83)	30
[Cu(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> CuN <sub>2</sub> O <sub>3</sub> S	443.81	Green	56.80 (56.83)	4.52 (4.50)	6.28 (6.31)	7.23 (7.21)	13.35 (14.31)	>300	1.85 (1.73)	31
[Zn(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> SZn	445.66	Yellow	56.52 (56.59)	4.53 (4.49)	6.21 (6.28)	7.15 (7.18)	14.63 (14.67)	>300	—	35
[Cd(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> C <sub>21</sub> H <sub>20</sub> CdN <sub>2</sub> O <sub>3</sub> S	492.68	Yellow	51.25 (51.19)	4.00 (4.06)	5.73 (5.68)	6.54 (6.50)	22.85 (22.81)	>300	—	42

<sup>a</sup>H<sub>2</sub>SB<sup>1</sup> = 1,1'-dihydroxy-2,2'-(1-isonitriloethylidyne-4-nitrimethylidene-phenyl)diphenyl, H<sub>2</sub>SB<sup>2</sup> = 1-thio-1'-hydroxy-2,2'-(1-isonitriloethylidyne-4-nitrimethylidene-phenyl)diphenyl.

**Table 2.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data of ligands<sup>a</sup>

Compounds	<sup>1</sup> H-NMR	<sup>13</sup> C-NMR
H <sub>2</sub> SB <sup>1</sup>	4.9(2H, s-OH), 6.6–7.5(12H, m Ar-H), 8.3(1H, s, CH=N), 1.1(3H, s, Aliphatic)	15.1(Aliphatic), 115.2– 138.4(Aromatic), 151.2(C-OH), 152.6(C-OH), 145.6(C-N), 155.7(C-N), 165.8(CH=N), 168.9(C=N)
H <sub>2</sub> SB <sup>2</sup>	5.3 (1H, s-OH), 4.1(1H, s-SH), 6.7–7.5(12H, m Ar-H), 8.4(1H, s, CH=N), 1.1(3H, s, Aliphatic)	15.1(Aliphatic), 117.3– 139.6(Aromatic), 130.2(C-SH), 152.6(C-OH), 146.8(C-N), 157.4(C-N), 164.9(CH=N), 167.9(C=N)

<sup>a</sup>H<sub>2</sub>SB<sup>1</sup> = 1,1'-dihydroxy-2,2'-(1-isonitriloethylidyne-4-nitrimethylidene-phenyl)diphenyl, H<sub>2</sub>SB<sup>2</sup> = 1-thio-1'-hydroxy-2,2'-(1-isonitriloethylidyne-4-nitrimethylidene-phenyl)diphenyl.

peaks at 167.9, 168.9 due to >C=N- carbons. In case of <sup>13</sup>C-NMR, carbons bonded to hydroxyl group (-OH) give peak at 151.2 and 152.6, while carbon bonded to thiol group (-SH) gives at 130.2 ppm.

### 3.2 Electronic Spectra

The electronic spectra provide the most detailed information about the electronic structure. The electronic spectra of the coordination polymers have been studied in the solid state between 350 to 1700 nm. The electronic spectra of the Ni(II) coordination polymers (19) exhibit three bands at ~10,550, ~17,000 and ~25,000 cm<sup>-1</sup>, which may be due to the transitions <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F) (ν<sub>1</sub>), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) (ν<sub>2</sub>), and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) (ν<sub>3</sub>), respectively. The three bands for the Co(II) coordination polymers (20, 21) have been assigned to transitions <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F) (ν<sub>1</sub>), <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F) (ν<sub>2</sub>) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) (ν<sub>3</sub>) at ~9,200, ~18,200 and ~19,000 cm<sup>-1</sup>, respectively. The electronic spectra of the Cu(II) coordination polymers (22, 23) exhibit one band at

**Table 3.** Electronic parameters of the Co(II) and Ni(II) coordination polymers<sup>a</sup>

Coordination polymers	Observed band (cm <sup>-1</sup> )							10Dq
	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_2/\nu_1$	B	$\beta$	$\beta^0$	
[Co(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	9,300	18,180	18,940	1.95	717	0.73	26	10,419
[Ni(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	10,540	17,390	25,000	1.65	718	0.69	30	10,540
[Co(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	9,030	18,200	19,050	2.01	742	0.76	23	10,151
[Ni(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	10,525	16,930	25,000	1.60	690	0.67	32	10,525

<sup>a</sup>H<sub>2</sub>SB<sup>1</sup> = 1,1'-dihydroxy-2,2'-(1-isonitriloethylidyne-4-nitrimethylidenephényl)diphényl, H<sub>2</sub>SB<sup>2</sup> = 1-thio-1'-hydroxy-2,2'-(1-isonitriloethylidyne-4-nitrimethylidenephényl)diphényl.

~15,500 cm<sup>-1</sup> which may be attributed to the transition <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub>. These observations suggest an octahedral geometry for these coordination polymers. The electronic spectra of the Mn(II) coordination polymers exhibit three

weak absorption bands at ~15,000, ~19,500 and ~24,000 cm<sup>-1</sup>, which have been assigned to the transitions <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>T<sub>1g</sub>(G)( $\nu_1$ ), <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>T<sub>2g</sub>(G)( $\nu_2$ ) and <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>A<sub>1g</sub>, <sup>4</sup>E<sub>g</sub>(G)( $\nu_3$ ), respectively, in an octahedral

**Table 4.** Thermogravimetric data for the complexes<sup>a</sup>

Coordination polymers	TG range °C	Mass loss %		Assignment
		Found	Calculated	
[Mn(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.50	8.59	Loss of coordinated water molecule
	180–800	78.23	78.30	Loss of Ligand (SB <sup>1</sup> )
		17.09	16.92	Remaining mass of metal oxide
[Co(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.39	8.51	Loss of coordinated water molecule
	180–800	77.64	77.55	Loss of Ligand (SB <sup>1</sup> )
		19.67	19.59	Remaining mass of metal oxide
[Ni(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.53	8.52	Loss of coordinated water molecule
	180–800	77.71	77.60	Loss of Ligand (SB <sup>1</sup> )
		17.69	17.66	Remaining mass of metal oxide
[Cu(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.40	8.42	Loss of coordinated water molecule
	180–800	76.68	76.72	Loss of Ligand (SB <sup>1</sup> )
		18.70	18.59	Remaining mass of metal oxide
[Zn(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.49	8.38	Loss of coordinated water molecule
	180–800	76.33	76.39	Loss of Ligand (SB <sup>1</sup> )
		18.90	18.94	Remaining mass of metal oxide
[Cd(SB <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	7.61	7.56	Loss of coordinated water molecule
	180–800	68.78	68.85	Loss of Ligand (SB <sup>1</sup> )
		26.92	26.94	Remaining mass of metal oxide
[Mn(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.27	8.28	Loss of coordinated water molecule
	180–800	79.02	79.09	Loss of Ligand (SB <sup>2</sup> )
		16.23	16.29	Remaining mass of metal oxide
[Co(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.14	8.20	Loss of coordinated water molecule
	180–800	78.32	78.37	Loss of Ligand (SB <sup>2</sup> )
		18.93	18.88	Remaining mass of metal oxide
[Ni(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.19	8.21	Loss of coordinated water molecule
	180–800	78.47	78.41	Loss of Ligand (SB <sup>2</sup> )
		16.88	17.01	Remaining mass of metal oxide
[Cu(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	8.03	8.12	Loss of coordinated water molecule
	180–800	77.54	77.55	Loss of Ligand (SB <sup>2</sup> )
		17.89	17.92	Remaining mass of metal oxide
[Zn(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	7.96	8.08	Loss of coordinated water molecule
	180–800	77.41	77.23	Loss of Ligand (SB <sup>2</sup> )
		18.34	18.26	Remaining mass of metal oxide
[Cd(SB <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	150–180	7.37	7.31	Loss of coordinated water molecule
	180–800	69.91	69.86	Loss of Ligand (SB <sup>2</sup> )
		25.98	26.06	Remaining mass of metal oxide

field of Mn(II) ion (24). The ligand field splitting energy ( $Dq$ ), interelectronic repulsion parameter ( $B$ ) and nephelauxetic ratio ( $\beta$ ) and ratio  $\nu_2/\nu_1$  for the Co(II) and Ni(II) complexes have been calculated using the secular equations given by E. König (25) and are presented in Table 3.

### 3.3 Thermogravimetric Analyses

Thermogravimetric data is summarized in Table 4. It has been observed that all the coordination polymers show a loss in weight corresponding to establishing their compositional differences, as well as to find out the nature of water molecules in geometry of coordination polymer. The TG curves of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) coordination polymer show two decomposition temperature ranges about  $\sim 150$ – $180$  and  $\sim 180$ – $800^\circ\text{C}$ . The initial weight loss occurring in the  $\sim 150$ – $180^\circ\text{C}$  temperature range for all coordination polymers is attributed to a loss of two coordinated water molecules (26, 27), followed by liberation of ligand (SB) in between  $\sim 180$ – $800^\circ\text{C}$ . At last, the remaining weight is in good agreement with metal oxide. In all of the cases, the final products are metal oxides. These results are in good accordance with the composition of the coordination polymers.

### 3.4 Magnetic Measurements

The magnetic moment data are presented in Table 1. In the present case, the magnetic moment values of  $[\text{Mn}(\text{SB}^1)(\text{H}_2\text{O})_2]_n$  and  $[\text{Mn}(\text{SB}^2)(\text{H}_2\text{O})_2]_n$  are 6.03 and 6.01 B.M., respectively, which is within the limits of the spin-free value for five unpaired electrons, indicating that the coordination polymers are high-spin  $d^5$ -system with an octahedral geometry (28). The magnetic moment data of  $[\text{Co}(\text{SB}^1)(\text{H}_2\text{O})_2]_n$  and  $[\text{Co}(\text{SB}^2)(\text{H}_2\text{O})_2]_n$  are 4.08 and 4.10 B.M., respectively, suggesting an octahedral geometry (23). The magnetic moment data of  $[\text{Ni}(\text{SB}^1)(\text{H}_2\text{O})_2]_n$  and  $[\text{Ni}(\text{SB}^2)(\text{H}_2\text{O})_2]_n$  are 2.91 and 2.94 B.M., respectively, which are in the usual range expected for similar hexa-coordinated Ni(II) ions (29). The magnetic moment data of  $[\text{Cu}(\text{SB}^1)(\text{H}_2\text{O})_2]_n$  and  $[\text{Cu}(\text{SB}^2)(\text{H}_2\text{O})_2]_n$  are 1.81 and 1.85 B.M., respectively, which are very close to the spin-only value (1.73 B.M.) expected for one unpaired electron, which offers the possibility of an octahedral geometry (30). The magnetic moment determinations show that the Zn(II) and Cd(II) coordination polymers are diamagnetic.

### 3.5 IR Spectra

The IR spectra of the ligands and their coordination polymers were determined in order to assist in the identification of the ligands and coordination polymers. In the spectra of the ligands the strong bands at  $1625\text{ cm}^{-1}$  due to the vibration of the azomethine group. These bands are shifted in the coordination polymers toward lower values by  $\sim 10$ – $20\text{ cm}^{-1}$ ,

suggesting the coordination of the azomethine nitrogen (31) atom to the metal ion. In the spectra of the coordination polymers the bands observed at  $3200$ – $3300\text{ cm}^{-1}$  may be attributed to the vibration of water molecules coordinated to the metal ions (32). The coordination polymers exhibit absorption bands at  $\sim 860$  and  $\sim 710\text{ cm}^{-1}$  which are ascribed to rocking and wagging vibration (33) of coordinated water suggesting a six-coordinate structure for the coordination polymers. The spectra of the ligand  $\text{H}_2\text{SB}^1$  shows a medium sharp absorption band at  $3100\text{ cm}^{-1}$ , which may be due to a hydrogen-bonded phenolic hydroxyl group. This band is absent in the coordination polymers, indicating the deprotonation of the phenolic proton on the coordination polymers. Moreover, the strong band at  $1530\text{ cm}^{-1}$  due to  $\nu(\text{C-O})$  stretching (34) in the ligand have been shifted to the  $\sim 1540\text{ cm}^{-1}$  region in the coordination polymers. This shift towards higher absorption also suggests the formation of the (M-O) bond. In the coordination polymers new bands observed at  $\sim 480$  and  $\sim 430\text{ cm}^{-1}$  region due to  $\nu(\text{M-O})$  (35) and  $\nu(\text{M-N})$  (36) modes. The  $\nu(\text{SH})$  band (37) of the ligand  $\text{H}_2\text{SB}^2$  appears at  $\sim 2600\text{ cm}^{-1}$ . The absence of a band around  $\sim 2600\text{ cm}^{-1}$  in the spectra of all the coordination polymers indicates that the SH group loses the thiol proton to form a covalent bond between the sulfur and metal in all the coordination polymers. This fact is further supported by the appearance of new band in all the coordination polymers around  $\sim 410$ – $425\text{ cm}^{-1}$ , which may be assigned to the  $\nu(\text{M-S})$  model (38). The participation of the SH group in coordination polymers is ascertained from the shift of the  $\nu(\text{C-S})$  band (39, 40) to lower frequencies from  $\sim 765\text{ cm}^{-1}$  in the free ligand to  $\sim 750\text{ cm}^{-1}$  in the spectra of the coordination polymers. The suggested structure of the coordination polymer is shown in Figure 2.

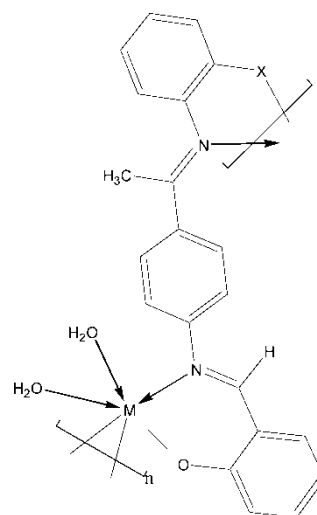
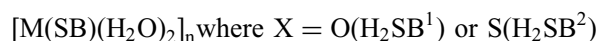


Fig. 2. Structure of the coordination polymers.

## 4 Conclusions

All of the coordination polymers are solid color and insoluble in 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 of coordination polymers in common organic solvents suggest their polymeric nature. An octahedral geometry has been assigned to all the prepared coordination polymers. The coordination polymers of Mn(II), Co(II), Ni(II), Cu(II) are paramagnetic, while Zn(II) and Cd(II) are diamagnetic in nature.

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