

# Coordination Polymers: Preparation, Physicochemical Characterization, Thermal and Biological Evaluation of Thiosemicarbazide Polychelates

Raza Rasool · Sumaiya Hasnain · Nahid Nishat

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**Abstract** Coordination polymers were prepared by the condensation reaction of salicylaldehyde and thiosemicarbazide with formaldehyde, transition metal acetates Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). Structural and spectral properties have been studied by elemental, spectral (FT-IR, <sup>1</sup>H NMR, and UV–Vis), and thermogravimetric analysis. The geometry of the chelated coordination polymers was confirmed by magnetic susceptibility measurements and UV–Visible spectroscopy. Antimicrobial screening was done against microbes such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Staphylococcus aureus*, *Staphylococcus typhi*, *Candida albicans*, *Microsporium canis*, *Aspergillus niger*. In vitro antimicrobial activity was determined by the Agar Well Diffusion method and result show that all the coordination polymers exhibited better antimicrobial activity than their parent polymeric Schiff base. Coordination polymers were found to be more stable than their corresponding ligand as deduced by on thermogravimetric analysis. Because of antimicrobial and thermal behavior, these coordination polymers have broad range of applications as thermally resistant as well as antimicrobial-biocidal and antifouling coating materials.

**Keywords** Coordination polymers · UV–Visible spectroscopy · Thiosemicarbazide · Formaldehyde

## 1 Introduction

Coordination polymers provide a great opportunity for obtaining materials with desired properties by using designed monomers with different combinations and functionalities. The properties of polymeric material are due to its structure. Metal coordination, selection of ligand, topology and geometry etc. are responsible for various physicochemical properties. Organic polymers when used on the surface as adhesives or coatings, microorganism causes rupturing of these coatings through bonding and disbonding. But when metal chelating polymers are used, it protects the adhered surface due to its biocidal behavior and thus deterioration can be avoided. Besides biocidal behavior, the thermal stability of these organic polymers is also enhanced by metal insertion into the polymeric backbone. Active hydroxyl and azomethine groups in Schiff base polymers containing conjugated bonds have been studied [1]. Polymeric Schiff bases usually show basic properties owing to the presence of a C=N linkage in backbone. Interest has been focused on preparing composites and graphite materials resistant to high temperatures, photoresistors, thermostabilizers, epoxide oligomers, block copolymers, antistatic and flame resistant materials [2–6]. Schiff bases polymers demonstrate antimicrobial activity against various bacteria, yeast, and fungi [7, 8].

Metal incorporation into the polymers also possesses wide application as catalysts, impregnants, textile sizers, aqueous thickeners, adhesives, resins, and in the biomedical field [9–12]. Nitrogen and sulphur atoms play a key role in metal coordination at active sites of numerous ligands. Important class of nitrogen and sulphur atom donor ligands are thiosemicarbazones, particularly for transition metals [13, 14]. Remarkable biological activities have been exhibited by thiosemicarbazone complexes ranging from anti-fungal,

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R. Rasool · S. Hasnain (✉) · N. Nishat  
Materials Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India  
e-mail: hasnain.sumaiya@gmail.com

anti-bacterial, anti-inflammatory, anti-viral to anti-tumour, activities [15–19].

A lot of inclination towards the complexation of thiosemicarbazones with iron, has been reported because of its pharmaceutical application [20] as potential antitumor agents, with aromatic thiosemicarbazones, copper complexes affected the mechanism of leukemic transformations by inhibiting the replication and triggering apoptotic processes [21]. At present, as far as biological activities are concerned, much study on transition metal complexes of thiosemicarbazones has been done. Keeping all the above facts in our mind, here we record the synthesis, characterization, thermal and biological activity of newly developed thiosemicarbazide based polymeric ligand and its coordination polymers. All synthesized polymeric compounds were characterized by elemental analysis, various spectral techniques like  $^1\text{H}$  NMR, FT-IR, UV–Visible spectra and in addition to antimicrobial activity, thermal stability of all polymeric compounds have also been discussed.

## 2 Experimental

### 2.1 Materials and Microbial Strains

Salicylaldehyde, thiosemicarbazide, ethanol, formaldehyde (37–41 %) (S.D. Fine), DMF, DMSO, acetone, sodium hydroxide (Merck). Barbituric acid, transition metal acetates (Qualingens): Manganese(II) acetate tetrahydrate  $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ , Cobalt(II) acetate tetrahydrate  $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ , Nickel(II) acetate tetrahydrate  $[\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ , Copper(II) acetate monohydrate  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ , Zinc(II) acetate dihydrate  $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$  were used without further purification. Elemental analysis of C, H and N of all polymeric compounds was carried out using elemental analyzer system GmbH Vario ELIII. All microorganisms were provided by the culture collection center of Microbiology Laboratory, Department of Microbiology (A.M.U. Aligarh).

### 2.2 Synthesis of Monomeric Schiff Base

Monomeric Schiff base, *N,N'*-bis (Salicylidene) thiosemicarbazide Schiff base (yield 72 %) and other polymeric compounds have been synthesized and synthetic method has been illustrated as supporting information.

### 2.3 Synthesis of Polymeric Schiff Base (STFB)

Polymeric Schiff base was synthesized by adding formaldehyde (0.02 mol, 1.5 cm<sup>3</sup>) into monomeric Schiff base (0.01 mol, 2.99 gm) in molar ratio of (2:1) Polymeric Schiff base STFB was obtained 70 % yield.

### 2.4 Synthesis of Coordination Polymers

Coordination polymers of [Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were prepared by using equimolar ratio (1:1) of polymeric ligand (AGP) and metal(II) acetates. The polychelate of manganese [STFB-Mn(II)] 81 % yield. The above procedure was adopted for the synthesis of other coordination polymers and yields are given in Table 1.

## 3 Antimicrobial Assessment

In vitro antimicrobial activity against *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Staphylococcus aureus*, *Staphylococcus typhi*, *Candida albicans*, *Microsporium canis*, *Aspergillus niger*, was adopted for measuring the effectiveness of the synthesized polymeric Schiff base (STFB) and its corresponding coordination polymers. Wells were dug in media with the help of a sterile metallic borer with centers of at least 25 mm. Recommended concentration (100  $\mu\text{l mL}^{-1}$ ) of the test sample [1 mg  $\text{mL}^{-1}$  in dimethylsulphoxide (DMSO)] was introduced in the corresponding wells. Other wells supplemented with DMSO and reference antimicrobial drugs served as negative and positive controls, respectively. Plates were incubated immediately at 37 °C for 20 h. Activity was determined by measuring the diameter (millimeters) of zones showing complete inhibition. Kanamycin was used as a standard drug for antibacterial activity and, Miconazole for antifungal activity.

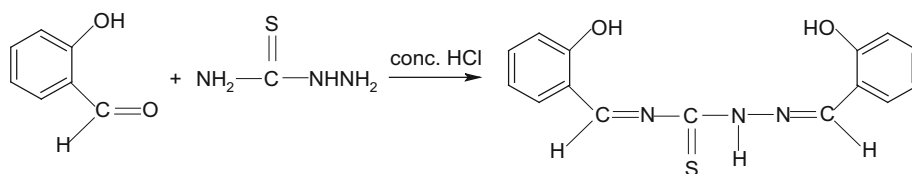
## 4 Measurements

Elemental analysis was carried out using elemental analyzer system GmbH Vario ELIII. Percentage of metals in the coordination polymers was determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA) after decomposition with fuming  $\text{HNO}_3$ . FT-IR spectra were recorded on a Perkin Elmer IR spectrophotometer (Model 621) using KBr discs in the range (4,000–400  $\text{cm}^{-1}$ ).  $^1\text{H}$  NMR spectra were recorded on a JEOL-GSX 300 MHz FX 1000 FT NMR spectrometer. Ultra violet–visible (UV–Vis) spectra were taken on a Perkin Elmer Lambda (EZ-201) spectrophotometer in solution form. Magnetic susceptibility of the powder samples were measured on a vibrating sample magnetometer (Model 155). Comparative thermal behavior of polymeric Schiff base (STFB) and its coordination polymers were recorded with TG analyzer (Perkin Elmer Pyris Diamond) at a heating rate of 20 °C  $\text{min}^{-1}$  in nitrogen atmosphere.

**Table 1** Elemental analysis for polymeric Schiff base and its coordination polymers

Compounds	Empirical formula	(Yield %)	Elemental analysis (%) <sup>a</sup>				
			Carbon	Hydrogen	Nitrogen	Sulphur	Metal
STFB	[C <sub>21</sub> H <sub>17</sub> N <sub>5</sub> O <sub>5</sub> S] <sub>n</sub>	70	55.49 (55.87)	3.89 (3.80)	15.45 (15.51)	7.17 (7.10)	– –
STFB-Mn(II)	[C <sub>21</sub> H <sub>15</sub> N <sub>5</sub> O <sub>5</sub> SMn·2H <sub>2</sub> O] <sub>n</sub>	81	46.71 (46.67)	3.39 (3.54)	13.10 (12.96)	6.13 (5.93)	10.23 (10.17)
STFB-Co(II)	[C <sub>21</sub> H <sub>15</sub> N <sub>5</sub> O <sub>5</sub> SCo·2H <sub>2</sub> O] <sub>n</sub>	68	46.45 (46.33)	3.61 (3.52)	12.93 (12.86)	5.98 (5.89)	10.87 (10.83)
STFB-Ni(II)	[C <sub>21</sub> H <sub>15</sub> N <sub>5</sub> O <sub>5</sub> SNi·2H <sub>2</sub> O] <sub>n</sub>	72	46.44 (46.35)	3.59 (3.52)	13.03 (12.87)	5.91 (5.89)	10.89 (10.79)
STFB-Cu(II)	[C <sub>21</sub> H <sub>15</sub> N <sub>5</sub> O <sub>5</sub> SCu] <sub>n</sub>	75	49.25 (49.17)	3.05 (2.95)	13.77 (13.65)	6.29 (6.25)	12.44 (12.39)
STFB-Zn(II)	[C <sub>21</sub> H <sub>15</sub> N <sub>5</sub> O <sub>5</sub> SZn] <sub>n</sub>	76	49.08 (48.99)	3.14 (2.94)	13.71 (13.60)	6.31 (6.23)	12.63 (12.70)

<sup>a</sup> Observed value (calculated)

**Scheme 1** Synthetic route to the monomeric Schiff base

## 5 Results and Discussion

### 5.1 Composition and Chemistry

Ligand was prepared in two steps by the polycondensation reaction. Firstly, monomeric Schiff base was prepared by the reaction of salicylaldehyde with thiosemicarbazide in 2:1 molar ratio according to Scheme 1. In the second step, polymeric Schiff base was prepared by the condensation of monomeric Schiff base with formaldehyde according to Scheme 2 in slight basic medium. These compounds were soluble in DMF, DMSO and insoluble in common polar organic solvents, such as ethanol, methanol, acetone and water. These are stable at room temperature and are non hygroscopic. The desired coordination polymers having the stoichiometry ratio 1:1 were obtained in quantitative yields by the interaction of an equimolar amount of metal(II) acetates with polymeric Schiff base STFB in DMF as shown in Scheme 3. Elemental analysis data of all polymers show that experimentally determined percentage values of C, H, N, S and M were also in very good agreement with calculated values, results being depicted in Table 1. A slight deviation in elemental analysis may be due to the polymeric nature of the compounds, as the value

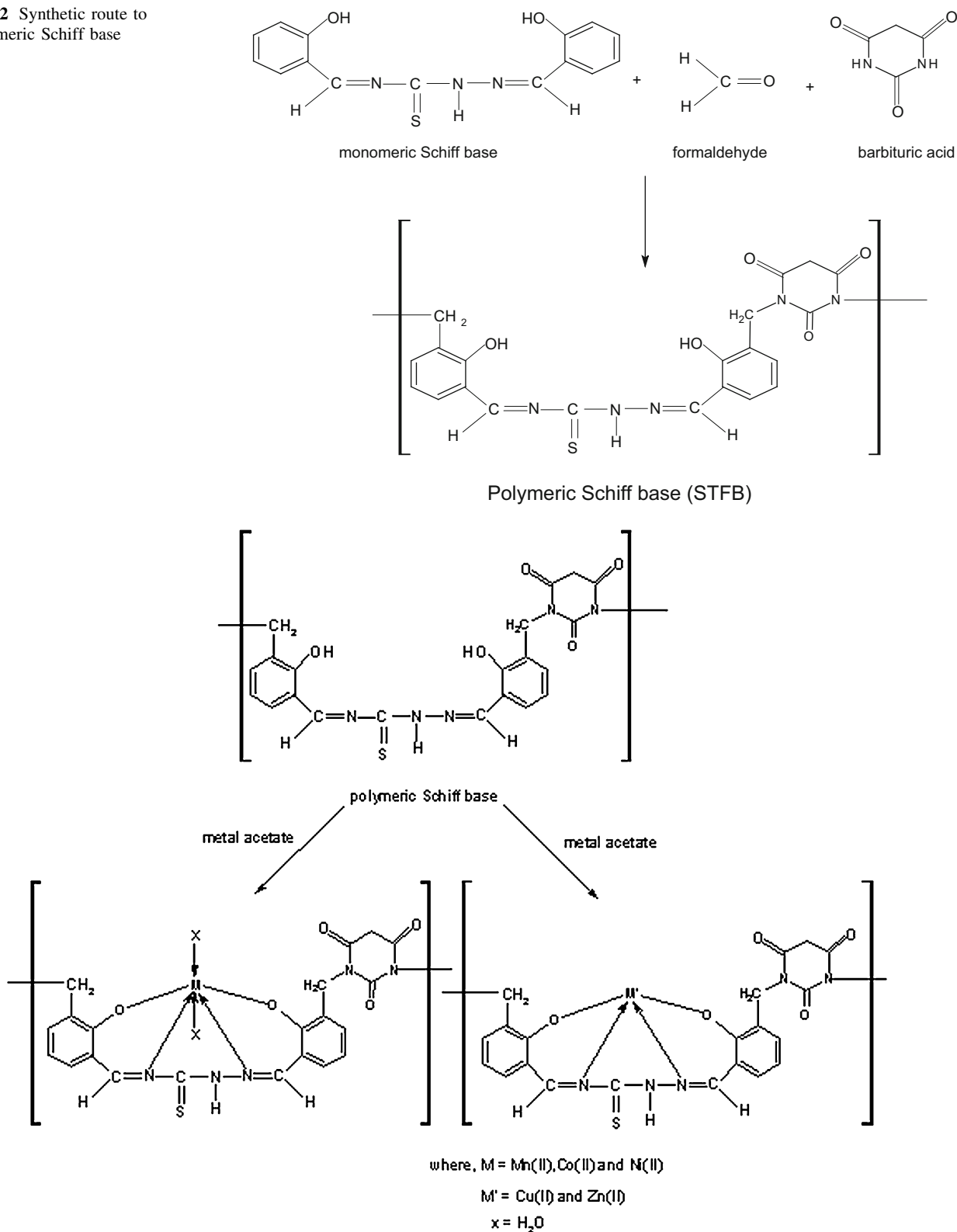
of end groups are not taken into account for theoretical reasons.

Elemental analysis data was in agreement with the proposed formula of polymers and confirmed octahedral geometry for [STFB-Mn(II), STFB-Co(II) and STFB-Ni(II)] while square planar geometry for STFB-Cu(II) and tetrahedral environment around STFB-Zn(II).

### 5.2 FT-IR Spectra

FTIR spectra of polymeric Schiff base and its coordination polymers with their assignments are given in the Table 2 and Fig. 1. Phenolic –OH stretching for the absorption frequency of polymeric Schiff base STFB appeared at 3,422 cm<sup>-1</sup>. These very broad bands disappear in the spectra of all coordination polymers, suggesting the involvement of hydroxyl oxygen in bond formation [22]. In the ligand, band at 1,246 cm<sup>-1</sup> for STFB correspond to phenolic (C–OH) group appeared but in the coordination polymers these bands shifted to lower frequency by 17–23 cm<sup>-1</sup>, indicating the coordination of metal to oxygen [23]. Peaks for azomethine group were observed at 1,620 cm<sup>-1</sup> for the ligand (STFB), while these bands

**Scheme 2** Synthetic route to the polymeric Schiff base (STFB)



**Scheme 3** Synthetic route to coordination polymers of STFB

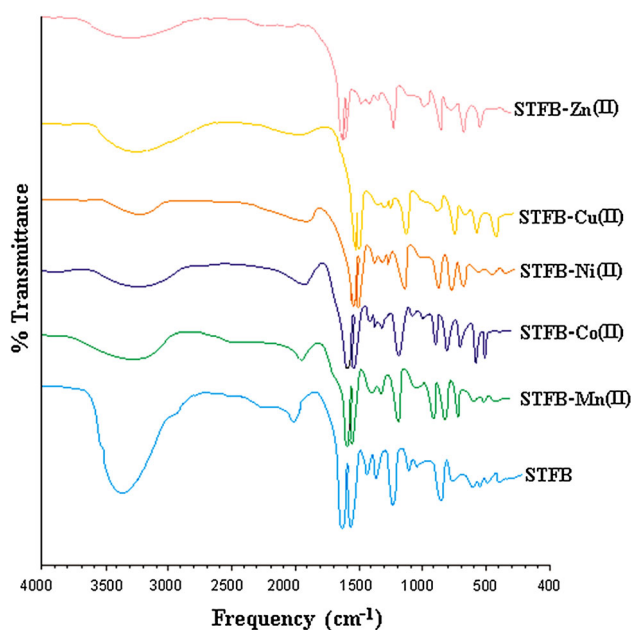
shifted to lower frequency by  $8\text{--}25\text{ cm}^{-1}$  in coordination polymers, thus indicating the coordination of metal to nitrogen. Lowering in the IR frequency indicates the

coordination of metal through the azomethine nitrogen [24]. Coordination polymers exhibited broad band in the region of  $3,330\text{--}3,166\text{ cm}^{-1}$  suggesting the presence of

**Table 2** FT-IR spectral bands of polymeric Schiff base and its coordination polymers

Compounds	OH	C–O	C=N	C=O	C=S	M–O	M–N	M–H <sub>2</sub> O
STFB	3422(b)	1246(m)	1620(m)	1611(m)	835(s)	–	–	–
STFB-Mn(II)	–	1229	1600(m)	1605(m)	835(s)	661(m)	535(m)	965(m), 750(w)
STFB-Co(II)	–	1226	1597(m)	1604(m)	834(s)	646(m)	567(m)	942(w), 743(w)
STFB-Ni(II)	–	1223	1595(m)	1608(m)	835(s)	656(m)	550(m)	954(m), 755(w)
STFB-Cu(II)	–	1231	1605(m)	1604(m)	833(s)	678(m)	518(m)	–
STFB-Zn(II)	–	1228	1612(m)	1609(m)	835(s)	670(m)	544(m)	–

*b* broad, *s* strong, *m* medium, *w* weak

**Fig. 1** FT-IR spectra of STFB and its coordination polymers

coordinated or absorbed H<sub>2</sub>O molecule [25]. Peaks at 1,590–1,487 cm<sup>-1</sup> are attributed to aromatic C=C stretch, C=S sharp signal also appeared at 835–833 cm<sup>-1</sup> which shows no change in the frequency of STFB and STFB-M(II) which confirming that sulphur is not involved in bond formation. No peak is observed at 2,600–2,400 cm<sup>-1</sup> which shows that thiosemicarbazide remains in its thio-keto form [26].

Coordinated water shows medium to weak intensity bands at 965–942 cm<sup>-1</sup> (rocking), 755–743 cm<sup>-1</sup> (wagging) in spectra of STFB-Mn(II), STFB-Co(II) and STFB-Ni(II) polychelates but not observed in the spectra of STFB-Cu(II) and STFB-Zn(II) polychelates. This difference suggests the presence of coordinated water molecule in Mn(II), Co(II) and Ni(II) polychelates. Bands at 567–518 cm<sup>-1</sup> indicate M–N bonding while M–O band appears at 678–646 cm<sup>-1</sup> [27].

### 5.3 <sup>1</sup>H NMR Spectra

<sup>1</sup>H NMR spectra of Schiff base, polymeric Schiff base and its Zn(II) polychelate was carried out in DMSO-d<sub>6</sub> at room temperature using TMS as internal standard is shown in Fig. 2. Aromatic protons show multiple resonance signals between 6.40 and 8.12 ppm for Schiff base, STFB and STFB-Zn(II) [28]. The signals observed in Schiff base have slight deviation as compared to polymeric Schiff base. Methylene proton of Ph–CH<sub>2</sub>–N– group show a sharp resonance signal at 3.50 ppm in STFB, due to the polymerization of salicylaldehyde-formaldehyde unit with barbituric acid moiety, whereas the resonance signals found at 3.15 ppm in STFB, indicate the presence of methylene group (–CH<sub>2</sub>–) of barbituric acid. Results of <sup>1</sup>H NMR spectra reveal that barbituric acid moiety is attached to the polymeric Schiff base with methylene group of formaldehyde. Phenolic OH signals are observed in case of, Schiff base and polymeric Schiff base STFB at 5.00–5.10 ppm [29], while in coordination polymers of Zn(II), signals for phenolic proton disappeared which suggested the coordination of phenolic group to the metal. Formation of Ar–O–M and a significant shifting in all other peaks was observed due to the drifting of electrons towards the metal centre. Azomethine linkage appears at 8.32 ppm [30] in polymeric Schiff base STFB, which show the shifting in coordination polymers interpreting the participation of nitrogen of azomethine in M–N bond formation.

### 5.4 Electronic Spectra

Electronic spectra of all the synthesized polymers, STFB and STFB-M(II) were recorded at room temperature using DMSO as a solvent and transitions with assignments obtained by fitting the observed spectrum to the Tanabe-Sugano diagram, are tabulated in Table 3. Electronic spectrum of STFB-Mn(II) exhibited three bands at 14,810, 18,139 and 23,134 cm<sup>-1</sup> which corresponds to <sup>4</sup>T<sub>1g</sub>(G) ← <sup>6</sup>A<sub>1g</sub>(F), <sup>4</sup>T<sub>2g</sub>(G) ← <sup>6</sup>A<sub>1g</sub>(F) and <sup>4</sup>A<sub>1g</sub>(G) ← <sup>6</sup>A<sub>1g</sub>(F) transitions, respectively. Magnetic moment of STFB-Mn(II) was

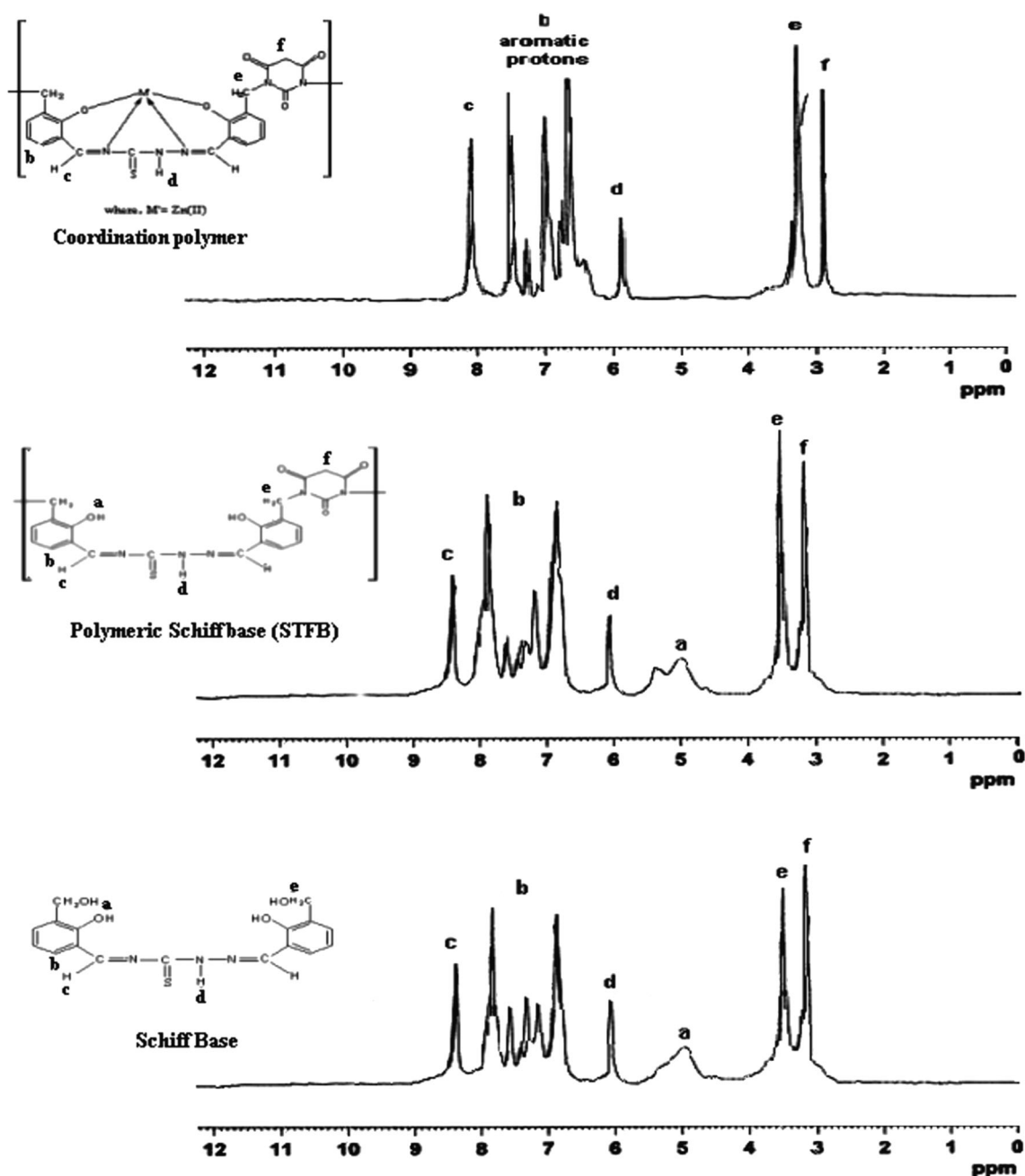


Fig. 2 <sup>1</sup>H NMR

found 5.65 B.M., suggesting the presence of five unpaired electrons. The above data were used to calculate the crystal field parameter (10Dq), Racah parameter (B) and Nephelauxetic effect ( $\beta$ ) and the covalency parameter ( $\beta\%$ ) values. The values of ligand field parameters 10Dq, B and  $\beta$  are listed in table indicating the covalent nature of compound and suggest the octahedral environment around the Mn(II) ion [31].

STFB-Co(II) has a magnetic moment of 4.60 B.M., [32] and showed three bands at 9,865, 16,674, 21,170  $\text{cm}^{-1}$

which were assigned to  ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ ,  ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$  and  ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$  transitions, respectively and the value of 10Dq, B and  $\beta$  indicate an octahedral environment around Co(II) ion [33].

The octahedral STFB-Ni(II) was expected to be paramagnetic owing to two unpaired d-electrons, and the experimental magnetic moment was found 2.83 B.M. [34]. The electronic spectrum showed three bands at 8,545, 13,970, 22,920  $\text{cm}^{-1}$  were assigned to  ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ ,  ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$  and  ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$  transitions for

**Table 3** Magnetic susceptibility, Electronic transitions and ligand field parameters

Compounds	Magnetic moment (B.M.)	Electronic transitions (cm <sup>-1</sup> )	Assignment	Geometry	B	10Dq (cm <sup>-1</sup> )	β	β°%
STFB-Mn(II)	5.65	23,134 18,139 14,810	<sup>4</sup> A <sub>1g</sub> (G) ← <sup>6</sup> A <sub>1g</sub> (F) <sup>4</sup> T <sub>2g</sub> (G) ← <sup>6</sup> A <sub>1g</sub> (F) <sup>4</sup> T <sub>1g</sub> (G) ← <sup>6</sup> A <sub>1g</sub> (F)	Octahedral	771	3,857	0.80	20
STFB-Co(II)	4.60	21,170 16,674 9,865	<sup>4</sup> T <sub>1g</sub> (P) ← <sup>4</sup> T <sub>1g</sub> (F) <sup>4</sup> A <sub>2g</sub> (F) ← <sup>4</sup> T <sub>1g</sub> (F) <sup>4</sup> T <sub>2g</sub> (F) ← <sup>4</sup> T <sub>1g</sub> (F)	Octahedral	940	9,879	0.84	16
STFB-Ni(II)	2.83	22,920 13,970 8,545	<sup>3</sup> T <sub>1g</sub> (P) ← <sup>3</sup> A <sub>2g</sub> (F) <sup>3</sup> T <sub>1g</sub> (F) ← <sup>3</sup> A <sub>2g</sub> (F) <sup>3</sup> T <sub>2g</sub> (F) ← <sup>3</sup> A <sub>2g</sub> (F)	Octahedral	723	9,399	0.66	34
STFB-Cu(II)	1.75	26,123 17,120	charge transfer <sup>2</sup> A <sub>1g</sub> ← <sup>2</sup> B <sub>1g</sub>	Square planar	–	–	–	–

**Table 4** Thermal properties of polymeric Schiff base (STFB) and its coordination polymers

Compounds	Weight left (%) at the indicated temperature (°C)							Characteristic weight left (%) at 800 °C
	100	200	300	400	500	600	700	
STFB	94	80	50	32	21.6	9	4	0.2
STFB-Mn(II)	95	92	65	47	36	26	19	8
STFB-Co(II)	97	88	61.5	44	38	29	23	7
STFB-Ni(II)	95.8	87	68.8	50	40	24	17	7.5
STFB-Cu(II)	99	91	71	59.6	48	31.7	22	14
STFB-Zn(II)	97	86	58	46	32	23	13	6.5

Heating rate of 20 °C min<sup>-1</sup> in nitrogen atmosphere

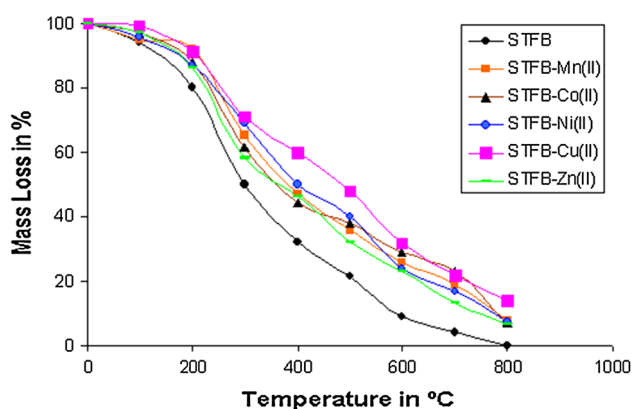
STFB-Ni(II). Crystal field parameters were in favor of octahedral geometry for STFB-Ni(II) [35]. The above discussion very strongly indicates an octahedral geometry around the central metal ion in the coordination polymers of Mn(II), Co(II), Ni(II). It accounts for the occupation of two coordinating sites by H<sub>2</sub>O out of six in making the octahedral environment.

Metal polychelate STFB-Cu(II) exhibited two bands at 17,120 and 26,123 cm<sup>-1</sup> due to <sup>2</sup>A<sub>1g</sub> ← <sup>2</sup>B<sub>1g</sub>(F) and charge transfer, respectively, which indicate square-planar geometry and the magnetic moment values of STFB-Cu(II) is found 1.75 B.M., in accordance with square planar geometry [36]. The diamagnetic nature and absence of d–d transition in Zn(II) represent tetrahedral geometry.

### 5.5 Thermogravimetric Analysis

TGA thermogram of all synthesized polymers and data are tabulated in Table 4 and Fig. 3. Thermal data revealed that the thermal stability of coordination polymers is higher than that of the parent ligand and did not decomposed

easily even at high temperature. TGA of coordination polymers shows no sharp weight loss was observed in the TGA curves of polymeric Schiff base (STFB) indicating their polymeric nature. In Mn(II), Co(II) and Ni(II) coordination polymers of STFB, thermogram curve show a 5–14 % weight loss corresponding to two water molecules up to 150–180 °C [37]. IR studies also support the presence of water molecules in these coordination polymers. In case of STFB-Cu(II) and STFB-Zn(II) coordination polymers, weight loss correspond to the loss of solvent or absorbed water molecules up to 130 °C while for STFB a steady and regular loss of weight was observed and at 300 °C the weight loss was about 50 %. Maximum rate of decomposition for the ligand was at 700 °C and almost entire ligand was lost by 800 °C, whereas in coordination polymers of STFB the weight loss was 86–93.5 %. This suggests that all coordination polymers show higher thermal stability than their corresponding polymeric ligand STFB, due to chelation. Another factor responsible for increased thermal stability of the coordination polymers is increase in molecular weight due to joining of two different polymer



**Fig. 3** Thermogram of STFB and its coordination polymers

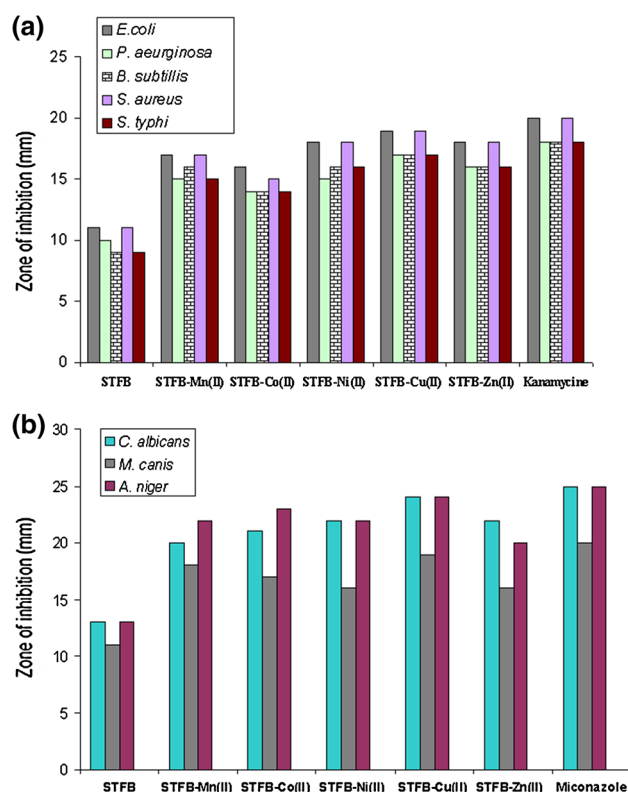
chains. Thermal stability of the polymeric compounds of STFB was in the order STFB-Cu(II) > STFB-Mn(II) > STFB-Ni(II) > STFB-Co(II) > STFB-Zn(II) > STFB. The greater stability of Cu(II) metal polychelate compared with other coordination polymers is in agreement with the spectrochemical series [38], according to which Cu(II) metal polychelate is always more stable than other coordination polymers.

### 5.6 Antimicrobial Activity

Polymeric Schiff base STFB and its coordination polymers individually exhibited varying degrees of inhibitory effects on growth of bacterial and fungal strains tested by agar well diffusion method [39]. Results represented in Fig. 4a, b which shows the newly synthesized STFB and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes possess good biological activity. The results of these investigations indicated that the synthesized polymers showed good antimicrobial activity. The polymer metal complexes show moderate to high biocidal action compared to the ligand against most of the strains. These polymers show better antibacterial activity compared to polymers reported by Hasnain et al. [26] and Nishat et al. [27], while the antifungal activities were better in latter cases.

Investigation revealed that the antimicrobial activity of polymeric Schiff base compound increases after metal chelation, as chelation reduces the polarity of central metal ion by partial sharing of positive charge with donor groups [40]. This process increases the lipophilic nature of central metal ion [41], which in turn favors its permeation to the lipid layer of membrane.

This enhanced biological activity can be rationalized to their structures possessing an additional C=N bond and chelation. It has also been observed [42] that solubility, conductivity, thermal stability, and dipole moment are influenced by the presence of metal ions. Cu(II) has



**Fig. 4** **a** Antibacterial activity of STFB and its coordination polymers. **b** Antifungal activity of STFB and its coordination polymers

stronger interaction with N and O donor atoms by which lipophilic nature is enhanced. The results of antifungal and antibacterial screening indicate that coordination polymers of Cu(II) possess best activity compared to other coordination polymers.

## 6 Conclusions

Polymeric Schiff base STFB and its coordination polymers were prepared in good yield and characterized by various microanalytical, magnetic, spectroscopic and thermal techniques. Thermal stability and antimicrobial behavior of all polymers were analyzed by using some bacteria and fungi. All polymeric compounds were soluble in DMF and DMSO, but insoluble in common organic solvents, giving opportunity to use these materials as solvent resistant coating materials. The incorporation of metal ion in organic backbone enhances thermal as well as antimicrobial activity. STFB-Cu(II) can be used for medical and biomaterial applications requiring thermal sterilization owing to stability at high temperatures while STFB-Cu(II) may be used as antimicrobial and antifouling coating for various projects.



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## References

1. S.C. Suh, S.C. Shim, *Synth. Met.* **114**, 91–95 (2000)
2. K.I. Aly, A.A. Khalaf, *J. Appl. Polym. Sci.* **77**, 1218–1229 (2000)
3. M. Grigoras, C.O. Catanescu, *J. Macromol. Sci. C* **44**, 131–173 (2004)
4. R.H. Baughman, J.L. Bredas, R.R. Chance, R.L. Elsenbaumer, L.W. Shacklette, *Chem. Rev.* **82**, 209–222 (1982)
5. F.R. Diaz, J. Moreno, L.H. Tagle, G.A. East, D. Radic, *Synth. Met.* **100**, 187–193 (1999)
6. A.V. Ragimov, B.A. Mamedov, S.G. Gasanova, *Polym. Int.* **43**, 343–346 (1997)
7. I. Kaya, H.Ö. Demir, A.R. Vilayetoglu, *Synth. Met.* **126**, 183–191 (2002)
8. I. Kaya, A.R. Vilayetoglu, H. Topak, *J. Appl. Polym. Sci.* **85**, 2004–2013 (2002)
9. H. Matsuda, K. Kanaoka, *J. Appl. Polym. Sci.* **30**, 1229–1239 (1985)
10. N. Nishat, R. Rasool, S.A. Khan, S. Parveen, *J. Coord. Chem.* **64**, 4054–4065 (2011)
11. H. Matsuda, *J. Appl. Polym. Sci.* **22**, 3371–3386 (1978)
12. J.H. Silver, A.P. Hart, E.C. Williams, S.L. Cooper, S. Charef, D. Labarre, M. Jozsfowivz, *Biomaterials* **13**(6), 339–344 (1992)
13. J.S. Chandra, Y.A.S.J.P. Kumari, P.N.V.V.L.P. Rani, Y. Sunandamm, *Ind. J. Adv. Chem. Sci.* **2**(1), 32–37 (2013)
14. S.B. Padhye, G.B. Kauffmann, *Coord. Chem. Rev.* **63**, 127–160 (1985)
15. P. Bindu, M.R.P. Kurup, T.R. Satyakeerty, *Polyhedron* **18**, 321–331 (1999)
16. J.P. Scovill, D.L. Klayman, C.F. Franchino, *J. Med. Chem.* **10**, 1261–1264 (1982)
17. A.K. Nandi, S. Chaudhri, S.K. Mazumdar, S. Ghosh, *J. Chem. Soc. Perkin Trans.* **2**(11), 1729–1733 (1984)
18. M.A. Ali, D.A. Chowdhary, M. Naziruddin, *Polyhedron* **5**, 595–598 (1984)
19. M.E. Hossain, M.N. Alam, J. Begum, M.A. Ali, M. Nazimuddin, F.E. Smith, R.C. Hynes, *Inorg. Chim. Act.* **249**, 207–213 (1996)
20. M. Baldini, M.B. Ferrari, F. Bisceglle, P.P.D. Aglio, G. Pelos, S. Pinelli, P. Tarasconi, *J. Inorg. Chem.* **43**, 7170–7179 (2004)
21. R.H.U. Borges, E. Paniago, H. Beraldo, *J. Inorg. Biochem.* **65**, 267–275 (1997)
22. N. Chantarasiri, T. Damrongkosit, W. Jangwong, D. Sridaeng, S. Suebphan, *Eur. Polym. J.* **40**, 1867–1874 (2004)
23. S. Saydam, E. Yilmaz, *Spectrochim. Acta A* **63**, 506–510 (2006)
24. M. Joseph, M. Kuriakose, M.R.P. Kurup, E. Suresh, A. Kishore, S.G. Bhat, *Polyhedron* **25**, 61–70 (2006)
25. H.H. Freedman, *J. Am. Chem. Soc.* **83**, 2900–2905 (1961)
26. S. Hasnain, M. Zulfequar, N. Nishat, *J. Coord. Chem.* **64**(6), 952–964 (2011)
27. N. Nishat, M. Zulfequar, Asma, S. Hasnain, *J. Coord. Chem.* **63**(7), 1273–1281 (2010)
28. N. Nishat, R. Rasool, S. Parveen, Manisha, S.A. Khan, *Int. J. Polym. Mat.* **61**, 41–56 (2012)
29. N. Nishat, S. Dhyani, S. Hasnain, Manisha, *Polym. Bull.* **64**, 523–536 (2010)
30. N. Nishat, Asma, S. Dhyani, *J. Coord. Chem.* **62**(18), 3003–3011 (2009)
31. F. Cotton, G. Wilkinson, C. Murillo, M. Bochmann, *Advanced inorganic chemistry*, 6th edn. (Wiley, New York, 1999)
32. N. Nishat, S. Hasnain, Manisha, Asma, *J. Appl. Polym. Sci.* **124**, 3971–3979 (2012)
33. A.B.P. Lever, *Inorganic electronic spectroscopy*, 2nd edn. (Elsevier, Amsterdam, 1984)
34. F.A. Cotton, G. Wilkinson, *Advanced inorganic chemistry* (Wiley, New York, 1962)
35. E. König, *Structure and bonding* (Springer, Berlin, 1971)
36. N. Nishat, S. Parveen, S. Dhyani, Asma, *J. Coord. Chem.* **62**(7), 1091–1099 (2009)
37. S.Y. Jang, Y.H. Ha, S.W. Ko, W. Lee, J. Lee, S. Kim, Y.W. Kim, W.K. Lee, H.J. Ha, *Bioorg. Med. Chem. Lett.* **14**, 3881–3883 (2004)
38. I.V. Szmercsanyi, A. Szilagy, *J. Therm. Anal.* **18**(2), 235–246 (1980)
39. N. Nishat, S. Hasnain, S. Dhyani, Asma, *J. Coord. Chem.* **63**(21), 3859–3870 (2010)
40. N. Raman, A. Kulandaisamy, A. Shunmugasundaram, K. Jeyasubramanian, *Trans. Met. Chem.* **26**, 131–135 (2001)
41. N. Nishat, S.A. Khan, R. Rasool, S. Parveen, *J. Inorg. Organomet. Polym.* **21**, 673–681 (2011)
42. R. Rasool, S. Hasnain, N. Nishat, *Des. Monomers Polym.* **17**(3), 217–226 (2014)