

Ligand-bridged Polychelates of 4,4'-((4,4'-Biphenylenebisazo)-disalicylaldehyde phenylhydrazone

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ABSTRACT

Polymeric ligand-bridged metal chelates of VO(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared on interaction of 4,4'-((4,4'-biphenylenebisazo)-disalicylaldehyde phenylhydrazone with metal salts in *N,N*-dimethylformamide (DMF). All the polychelates are dark coloured powders, insoluble in water and common organic solvents. They have very poor solubility in DMF. All the polychelates are found to be non-charged chelate polymers from their conductivities in DMF. Their probable structures were determined from reflectance electronic spectral and magnetic measurements in conjunction with infrared spectroscopy. The diffuse reflectance spectra of VO(II), Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) polychelates have been analyzed in terms of ligand-field theory. Infrared spectra have been obtained to determine coordination sites of the ligand. The thermal, magnetic and conductivity measurements are discussed in light of the proposed assigned structure. All the polychelates are believed to have an octahedral stereochemistry. The semi-empirical AM1 calculation was also performed on ligand structure.

Key Words:

polychelates;
coordination polymers;
bis-azo dyes;
poly[Schiff] bases;
semi-empirical AM1 calculations;
diffuse reflectance spectra;
magnetic and conductivity measurements.

INTRODUCTION

Coordination polymers, i.e. polymers with inorganic elements in the backbone or as pendant groups, have unique property profiles that make them different from organic polymers.

Among the main features of coordination polymers are the following:

- The number and variety of elements that are found in these polymers as a result of the relatively high abundance of inorganic elements in the earth's crust,

- Strong bonds, which resist cleavage reactions,

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- Multiple valences for attachment of a wide variety of ligands,
- High thermal stability, and,
- The ability to tailoring new and interesting structures with endless variations. [1-4]

The demand for new polymeric materials with high thermal and chemical stability has stimulated research in many areas of polymer chemistry. Organic pigments are insoluble coordination complexes of organic compounds with metal ions, which are used in printing ink, plastics, rubber, and protective and decorative coatings. Polymeric coordinating reagents are a novel type of ligand which give polymeric metal complexes and have the physical properties of the polymer and the chemical properties of the ligand. Polychelates derived from poly[Schiff] bases have been extensively studied [5-7]; however, very little systematic work has been done on the preparation of the ligand-bridged polychelates derived from the symmetric bis-bifunctional derivatives of bis-azo dyes. In such derivatives, the chelating sites are widely separated so that the ligand can coordinate with two metal ions giving ligand bridged polychelates. Our laboratory has been exploring the chemistry of coordination polymers of this class of derivative for quite some time [8-11]. The present work describes the preparation of polychelates of VO(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) bridged with 4,4'-(4,4'-biphenylenebisazo)-disalicylaldehyde phenylhydrazine (PH-B-PH). An attempt has been made to decipher the stereochemistry of these polychelates using elemental analysis, semi-empirical AM1, as well as measurements of conductivity, mag-

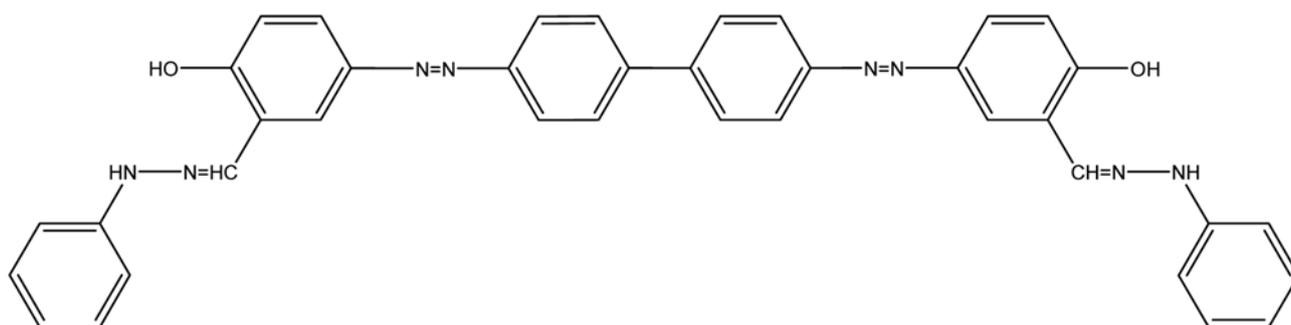
netic properties, and infrared and diffuse reflectance spectral data. The ligand used in the present study has the structure as given in Scheme I.

EXPERIMENTAL

Material and Instruments

All chemicals (reagent grades) were purchased from S.D. Fine chemicals, Boisor, and used after purification. Benzidine was used after recrystallization from hot water. DMF, salicylaldehyde and phenyl hydrazine were used after distillation following a standard procedures [12]. Hydrated metal nitrates were used as source of metal ions; and for V(IV) vanadyl sulphate was used.

The metal content was determined by gravimetric oxide method. Elemental analyses were done using a Perkin-Elmer 2400 Series-II CHN analyzer. IR Spectra (KBr pellets) were recorded on Nicolet-400D FTIR spectrophotometer. Magnetic susceptibility was measured using Lakeshore 7304 vibrating sample magnetometer. Conductivity of the complexes was measured using Systronics digital conductometer. For this purpose saturated solution of the compound was prepared in DMF and specific conductance at room temperature was measured using conductivity cell of known cell constant. The diffuse reflectance spectra of the complexes in solid state, diluted with MgO, were recorded on Beckman-DK-2A Spectrophotometer. The thermograms of all the polymeric chelates were obtained in dynamic nitrogen flux in the temperature range from 25°C to 350°C using an SDT 2960 TA thermoanalyzer.



(PH-B-PH)

Scheme I. Structure drawing of polymeric ligand.

Synthesis

The 4,4'-(4,4'-biphenylenebisazo)-disalicylaldehyde was prepared using the method reported by Karampurwala, Patel, and Shah [8]. The Schiff base with phenylhydrazine is described below.

Preparation of 4,4'-(4,4'-biphenylenebisazo)-disalicylaldehyde Phenylhydrazine (PH-B-PH)

PH-B-PH was obtained by refluxing a solution of *N,N*-dimethylformamide (DMF) (80 mL) of 4,4'-(4,4'-biphenylenebisazo)-disalicylaldehyde (10 mmol) with phenylhydrazine (20 mmol) on a sand bath for 2 h (Scheme II). The precipitated solid was filtered and washed with DMF and then with ethanol.

Preparation of the Polychelates

PH-B-PH (0.05 mole) was dissolved in DMF (100 mL) by refluxing. To the refluxing solution, a metal salt (0.05 mole) solution in DMF (60 mL) was added slowly. To the resultant refluxing mixture about 1 g of sodium acetate was added and the solution then was allowed to reflux for 2 h. The precipitated solid was filtered and washed well with hot DMF, followed by hot water and finally with ethanol. The products were dried at 45°C. The properties (elemental analyses, magnetic and conductivity data) and the electronic and IR spectral data are summarized in Tables 1, 2 and 3, respectively.

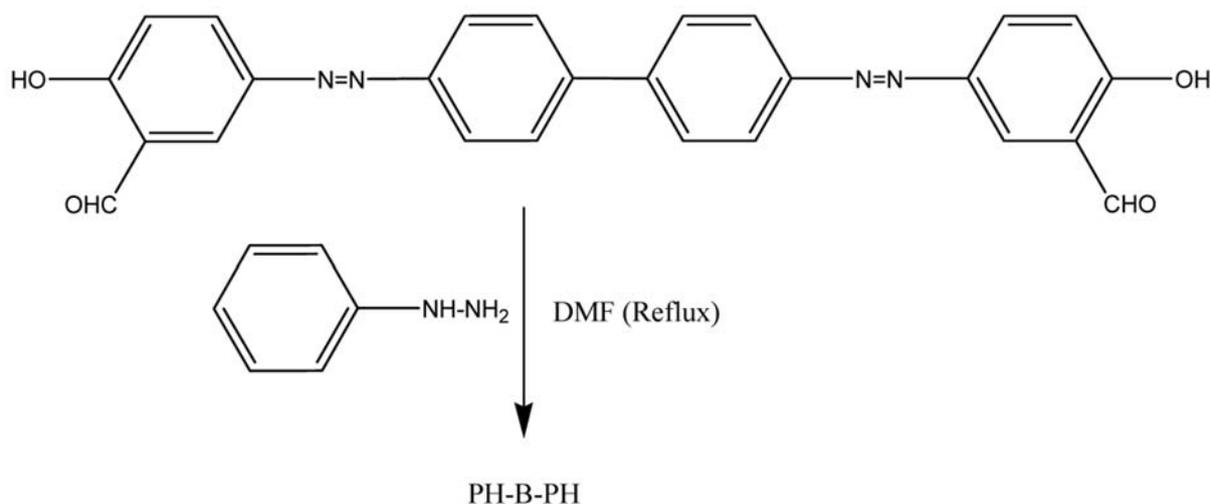
RESULTS AND DISCUSSION

The analytical data (Table 1) indicates a 1:1 metal-to-

ligand stoichiometry, and suggests a dibasic bis-bidentate nature of the ligand, and hence the formation of ligand-bridged polychelates. This polymeric character is also reflected in the low solubility in water as well as in coordinating and non-coordinating organic solvents. Molecular weight and molar conductance measurements could not be made because of low solubility. The low values of specific conductance in DMF indicate the non-electrolytic nature of these complexes.

The ligand structure was optimized using AM1 Hamiltonian using semi-empirical MO calculation software MOPAC [13]. The AM1 method was chosen among the various available methods in MOPAC because the present system contains too many nitrogen atoms and for such a system AM1 is more suitable [14]. The optimized minima are the true minima, as confirmed from Hessian calculations. The charges over the phenolic oxygen and azomethine nitrogen (-0.2493 and -0.2314, respectively) are more negative in comparison to other atoms of PH-B-PH, and suggest that these atoms are the coordinating atoms in the polymeric ligand.

The electronic spectra of azobenzene and its derivatives are characterized by two bands; an intense absorption band ($\epsilon \sim 10^4$) due to the $\pi \rightarrow \pi^*$ transition and a weak to moderate absorption band ($\epsilon \sim 600$) due to the $n \rightarrow \pi^*$ transition. The latter transition band sometimes overlaps with the strong $\pi \rightarrow \pi^*$ transition band [15]. The diffuse reflectance spectra of PH-B-PH and its Zn(II) polychelates show a band at 25000 and 22222 cm^{-1} , corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [15]. The observed shift



Scheme II

Table 1. Analytical, magnetic and conductivity data of the ligand and their polymeric chelates.

Compound	Yield (%)	Decomposition temp. (°C)	Analyses (%) : Found (calculated)				$\mu_{\text{eff.}}^{\#}$ (B.M.)	Specific conductance $\times 10^6$ (ohm ⁻¹ cm ²)
			M	C	H	N		
C ₃₈ H ₃₀ N ₈ O ₂ (PH-B-PH)	80	-	-	71.66 (72.38)	5.02 (4.76)	17.40 (17.77)	-	2.10
VO(PH-B-PH) H ₂ O	73	288	9.25 (9.38)	64.15 (63.96)	5.00 (4.20)	15.22 (15.70)	1.66 (1.73)	3.10
Cr(PH-B-PH)Cl H ₂ O	76	279	6.98 (7.08)	62.81 (62.16)	4.80 (4.09)	15.20 (15.26)	3.93 (2.92)	1.65
Mn(PH-B-PH)(H ₂ O) ₂	65	313	7.80 (7.64)	62.88 (63.42)	4.50 (4.45)	15.90 (15.57)	5.78 (5.91)	2.50
Co(PH-B-PH)(H ₂ O) ₂	70	300	8.46 (8.15)	62.15 (63.07)	3.98 (4.42)	15.90 (15.49)	4.89 (3.97)	2.50
Ni(PH-B-PH)(H ₂ O) ₂	75	284	8.09 (8.12)	63.50 (63.09)	4.05 (4.42)	16.02 (15.49)	3.65 (2.92)	1.15
Cu(PH-B-PH)(H ₂ O) ₂	65	284	8.57 (8.73)	63.00 (62.67)	4.76 (4.39)	16.00 (15.39)	1.79 (1.73)	3.20
Zn(PH-B-PH)(H ₂ O) ₂	75	336	8.84 (8.96)	62.40 (62.51)	4.00 (4.38)	16.02 (15.35)	D	1.25

Figures in parenthesis indicate spin only values.

towards the longer wavelength as compared to that of azobenzene may be due to the extensive conjugation between rings and -N=N- groups, which lowers the energy of the π^* orbital [16].

The VO(II) polychelates show bands at 20408, 16949, 11363 and 9808 cm⁻¹ in its diffuse reflectance spectrum. The latter three bands may be assigned to the

$dxy \rightarrow dz^2$, $dxy \rightarrow dx^2-y^2$ and $dxy \rightarrow dxz$, dyz transitions, respectively, and follow the cluster level scheme [17]. The former, high energy band may be due to the first spin-forbidden charge transfer transition. The spectrum of the VO(II) polychelates in pyridine is very similar to that of its diffuse reflectance spectrum. This suggests that there is no further coordination of

Table 2. Electronic spectral bands and their assignments.

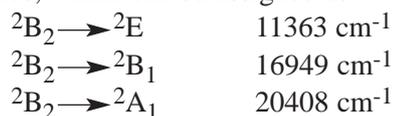
Compound	Band position (cm ⁻¹)	Assignments
PH-B-PH, Zn(II)	25000, 22222	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
VO(II)	20408, 16949, 11363, 9808	$dxy \rightarrow dz^2$, $dxy \rightarrow dx^2-y^2$, $dxy \rightarrow dxz$, $dxy \rightarrow dyz$
Cr(III)	20000, 15384, 10989	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}$, ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(v_1)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}$, 2E_g
Mn(II)	18868, 15873	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$
Co(II)	18181, 15384	${}^4T_{1g} \rightarrow {}^4T_{2g}(P)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$
Ni(II)	14925, 10000, 9000	${}^3A_{2g} \rightarrow {}^3T_{1g}(v_2)$, ${}^3A_{2g} \rightarrow {}^3T_{2g}(v_1)$
Cu(II)	13333, 11630	${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, 2E_g

Table 3. IR Spectral assignments of the ligand and their polymeric chelates (cm⁻¹).

Ligand	VO(II)	Cr(III)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
3350-3430	3325-3416 m,	3316-3425	3350-3440	3360-3475	3375-3500	3316-3425	3316-3408
m, br	br	m, br	m, br	m, br	m, br	m, br	m, br
3240 m, s	3240 m, s	3240 m, s	3240 m, s	3240 m, s	3240 m, s	3240 m, s	3240 m, s
1605 S, s	1600 s, s	1600 s, s	1600 s, s	1600 s, s	1600 s, s	1600 s, s	1600 s, s
1575 s, s	1580 w, sh	1580 w, sh	1580 w, sh	1580 m, s	1580 w, sh	1580 w, sh	1580 w, s
1280 s, s	1280 s, s	1280 m, sh	1280 m, s	1280 m, s	1280 s, sh	1275 m, s	1280 s, s
1105 m, s	1110 w, s	1115 m, s	1115 w, s	1125 m, s	1112 m, s	1115 m, s	1115 m, s

s s = strong sharp, m s = medium sharp, w s = weak sharp, m br = medium broad, m sh = medium shoulder, w sh = weak shoulder.

pyridine and there is no change of stereochemistry of the VO(II) polychelates in a donor solvent. This also confirms the tetragonally distorted octahedral structure for the polychelates. The coordination polymer of V(IV) containing a VO group cannot have symmetry higher than C_{2v}. Such a five coordinated V(IV) usually shows three bands below 30000 cm⁻¹ at room temperature [18]. In the present study we have observed three bands, which can be assigned as:



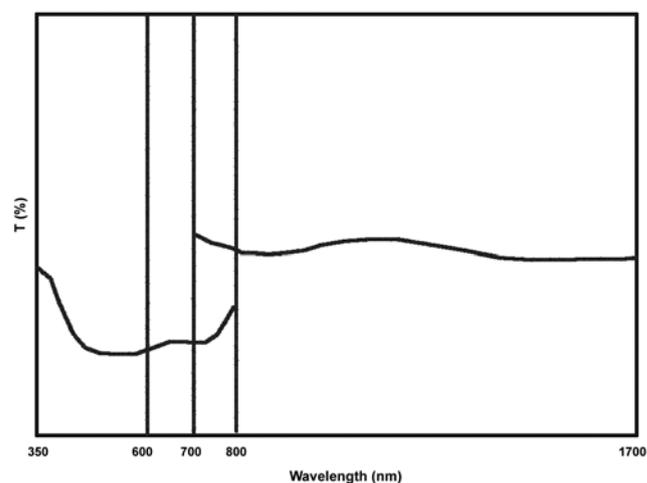
This suggests the square pyramidal coordination around V(VI) [8]. This polymer shows some solubility in pyridine. The saturated solution of the VO(II) polychelates was prepared in pyridine and its electronic spectrum was recorded. This spectrum was compared with the diffuse reflectance spectrum of VO(II) polychelate obtained in solid state, in absence of pyridine. Both these spectra are quite similar and there is no change in band position. This suggests that there is no further coordination of pyridine and there is no change of stereochemistry of the VO(II) polychelates in a donor solvent. This confirms the penta coordination around V(VI).

The diffuse reflectance spectrum of the Cr(III) polychelates exhibits bands at 10989, 15384 and 20,000 cm⁻¹, which presumably contains d-d transitions. The low energy band may be a spin-forbidden transition corresponding to the $4A_{2g}(F) \rightarrow 4T_{2g}$, $2E_g$ transitions. The latter two high energy bands may be assigned to the $4A_{2g}(F) \rightarrow 4T_{2g}(v_1)$ and $4A_{2g}(F) \rightarrow 4T_{1g}$ transitions, respectively, which are typical of an octahedral Cr(III) [14]. Using the ligand field theory of

spin-allowed transitions [19], we have calculated the transition energy corresponding to the $4A_{2g}(F) \rightarrow 4T_{1g}(P)(v_3 = 32616 \text{ cm}^{-1})$ for $B_{35} = 431 \text{ cm}^{-1}$ and $\beta_{35} = 0.47$. The reduction of B_{35} and β_{35} (if β_{35} is 1 then there is no covalent character but because the value is lowered by 0.53 it indicates considerable covalent character, β_{35} is a ratio of $B_{\text{complex}}/B_{\text{free ion}}$) indicates a considerable amount of covalent character in the M-L bonds. [20] The values for the $B_{55} = 575 \text{ cm}^{-1}$ and $\beta_{55} = 0.63$ have been calculated from the energy of the spin-forbidden transition, and are indicative of a π type interaction between Cr(III) and the ligand [20].

The Mn(II) polychelates show bands at 18868 and 15873 cm⁻¹ corresponding to the $6A_{1g} \rightarrow 4T_{2g}(G)$ and $6A_{1g} \rightarrow 4T_{2g}(G)$ transitions, respectively, assuming an octahedral structure for this polychelates [19].

The diffuse reflectance spectrum of the Co(II) polychelates shows shoulder at 18181 and 15384 cm⁻¹ on

**Figure 1.** Diffuse reflectance spectrum of Ni(II) polychelate.

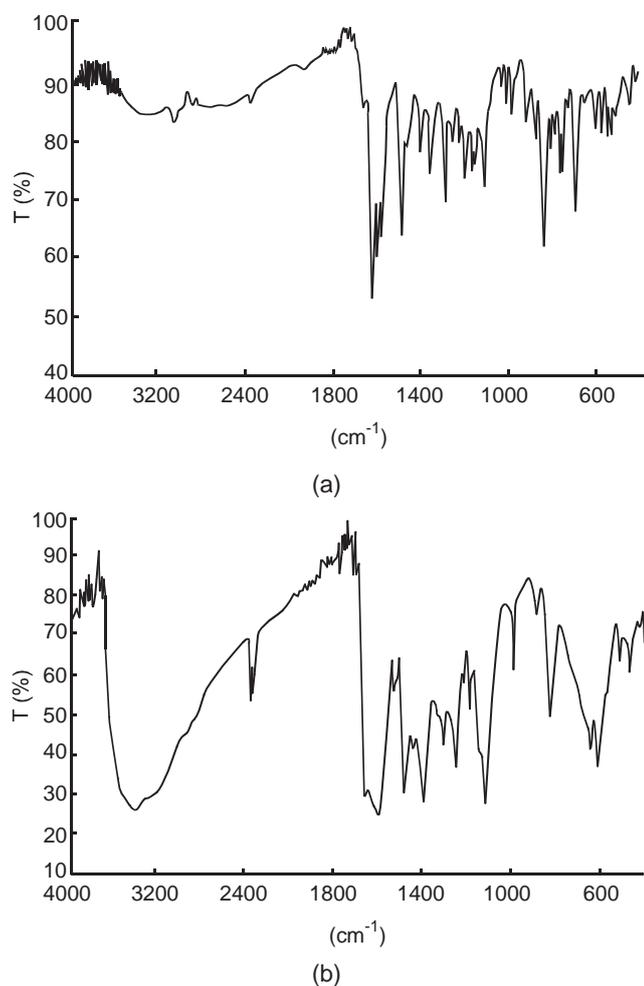


Figure 2. Infrared spectra of ligand (a) and its Ni(II) polychelate (b).

the high energy ligand band. Considering an octahedral structure for this polychelate, the observed shoulders may correspond to the ${}^4T_{1g} \rightarrow {}^4T_{2g}(P)$, ${}^6T_{1g} \rightarrow {}^4A_{2g}$ transitions, respectively [19].

The Ni(II) polychelates show a weak and a very broad band in the region 9000-10000 cm^{-1} , which may be due to the ${}^3A_{2g} \rightarrow {}^4T_{2g}(v_1)$ transition in an octahedral symmetry [18]. The shoulder at 14925 cm^{-1} may be due to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(v_2)$ transition. The weak and broad nature, with some signs of splitting of the v_1 band (Figure 1) suggests tetragonal distortion in the polychelate.

The diffuse reflectance spectrum of the Cu(II) polychelates exhibits a medium broad band around 11630 cm^{-1} and a broad band around 13333 cm^{-1} . Considering the distorted octahedral structure of the polychelate, the observed bands may correspond to the

${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$, 2E_g transitions, respectively [18, 21].

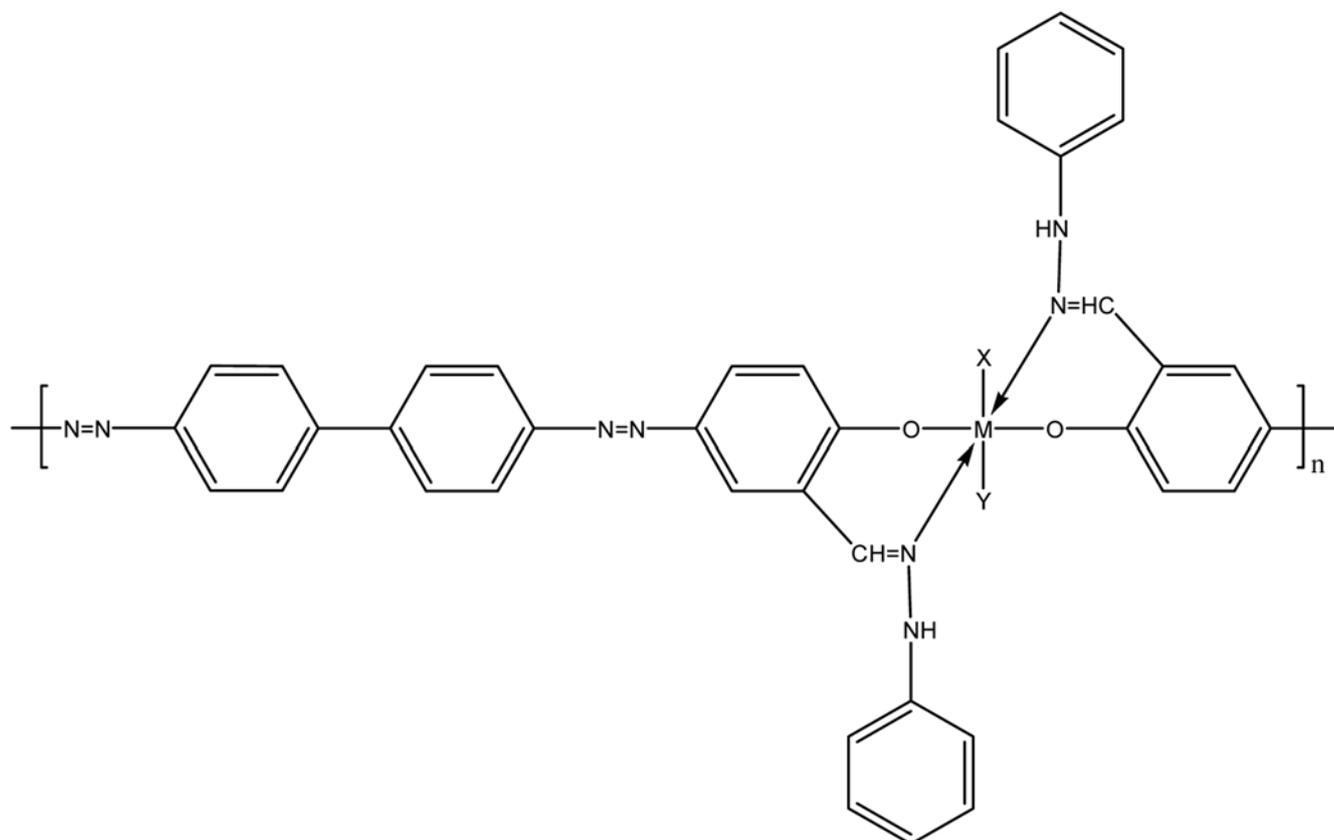
The magnetic moment of the VO(II) polychelates is a slightly less than the spin only value. This may be due to the antiferromagnetic exchange coupling between the pairs of the vanadyl ions as suggested by Ballhausen and Gray [22]. The magnetic moments of the Co(II), Cu(II), Cr(III) and Mn(II) polychelates are in the required range for an octahedral geometry around these metal ions. The magnetic moments of the Ni(II) polychelates show a deviation from the spin-only value, which may be due to the second order Zeeman effect [23].

The infrared spectral data of the ligand and its polymeric chelates are listed in Table 3. The infrared spectrum of the ligand has given strong and broad band centered at 3420 cm^{-1} , which is assigned to OH [18]. There is also a band at 1280 cm^{-1} , which may be assigned to the in-plane OH bending vibration. All polychelates show both of these bands, which may be due to the presence of the water molecules. The ligand as well as the polychelates shows a band at 3240 cm^{-1} due to NH. The ligand shows strong and sharp bands at 1605 cm^{-1} and 1575 cm^{-1} , which may be due to the $\nu_{N=N}$ and $\nu_{C=N}$, respectively [24]. All the polychelates show a strong and broad band at ~ 1600 cm^{-1} , which may be due to both $\nu_{N=N}$ and $\nu_{C=N}$ (Figure 2).

The sharp ligand band at 1105 cm^{-1} is representative of the phenolic C-O vibration. On chelation a small shift ($\Delta\nu = 5$ cm^{-1}) toward higher frequency is observed in all the polychelates (Table 3), which suggests coordination through the phenolic oxygen.

The TG curves of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) polymeric chelates show a mass loss in the range 120-220°C indicating the presence of two coordinated molecules of water, thus supporting octahedral geometry as suggested by the spectral and magnetic studies. A thermogram of the VO(II) and Cr(III) polychelate shows a weight loss at $\sim 140^\circ\text{C}$, which may be due to one coordinated water molecule.

The thermograms of all the polychelates show the presence of water. The losses in weight of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) polymeric chelates in the range 120-220°C, are 4.98%, 4.94%, 4.97, 4.95 and 5.0% respectively, which correspond to two water molecules. VO(II) and Cr(III) polychelate show a weight loss of 2.5 % and 2.4 %, respectively, at $\sim 140^\circ\text{C}$ corre-



n = degree of polymerization; $X = Y = \text{H}_2\text{O}$ when $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$; $X = \text{Cl}, Y = \text{H}_2\text{O}$ when $M = \text{Cr(III)}$; $X = \text{O}, Y = \text{H}_2\text{O}$ when $M = \text{V(IV)}$

Figure 3. Suggested structure of polychelate.

responding to one molecule of water per repeating unit of polychelates, which may be due to one coordinated water molecule.

The decomposition temperatures are listed in Table 1 and reveal the following thermal order of stability: $\text{Zn(II)} > \text{Mn(II)} > \text{Co(II)} > \text{VO(IV)} > \text{Cu(II)} / \text{Ni(II)} > \text{Cr(III)}$.

From the above studies the general structure of polychelates under investigations may be suggested as shown in Figure 3.

CONCLUSION

On the basis of above studies it shows that the polymeric Schiff base ligand coordinates through its phenolic oxygen and azomethine nitrogen atoms, giving octahedral environment around metal ions, resulting in to ligand bridged coordination polymers. All the polymers

have good thermal stability.

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REFERENCES

1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley, 398 (1978).
2. Allcock H.R., *Developments at the Interface of Inorganic, Organic and Polymer Chemistry*, C & EN. March 18, 22 (1985).
3. Stevens M.P., *Polymer Chemistry: An Introduction*, 2nd ed., Oxford University, 487 (1990).

4. Rahimi A., Inorganic and organometallic polymers: A review, *Iran. Polym. J.*, **13**, 149-163 (2004).
5. Patel N.H., Patel K.M., Patel K.N., Patel M.N., Coordination chain polymers of some transition metals with Schiff base, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1031-1039 (2001).
6. Roy S.M., Juneja H.D., Munshi K.N., Synthesis and Structural Features of Some First row Transition Series Metal bis (BIURET)polymeric Chelates, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1611-1621 (2001).
7. Garribbaa E., Miceraa G., Zemab M., Monomeric versus dimeric structures in ternary complexes of manganese(II) with derivatives of benzoic acid and nitrogenous bases: Structural details and spectral properties, *Inorg. Chim. Acta.*, **357**, 2038-2048 (2004).
8. Karampurwala A.M., Patel R.P., Shah J.R., Synthesis and properties of chelate polymers of VO(II), Mn(II), Zn(II), Fe(III) and Cr(III) with Schiff base of 5,5'-methylene bis-salicylaldehyde with aniline, *Angew. Makromol. Chem.*, **89**, 57-64 (1980).
9. Karampurwala A.M., Patel R.P., Shah J.R., Spectral, thermal and magnetic properties of chelate polymers, *J. Macromol. Sci.-Chem.*, **15**, 431-438 (1981).
10. Deshpande U.G., Shah J.R., Coordination polymers. V. Spectral, thermal and magnetic properties of polychelates derived from 4,4'-phenylenebisazodisalicylic acid, *J. Macromol. Sci.-Chem.*, **21**, 21-28 (1984).
11. Suthar H.B., Shah J.R., Polychelates of tetrafunctional bisoxime, *Angew. Makromol. Chem.*, **130**, 147-153 (1985).
12. Perrin D.D., Armarego W.L.F., Perrin D.R., *Purification of Laboratory Chemicals*, Pergamon, 2nd ed. (1981).
13. Stewart J.J.P., MOPAC 7.0 *Quantum Chemistry Program Exchange*, University of Indiana, Bloomington, IN, USA (1989).
14. Jadeja R.N., Shirsat R.N., Suresh E., Ab initio study and its comparison with x-ray crystal structure of 4-[1-(4-chloro-phenylamino)-ethyl]-5-methyl-2-p-tolyl-2,4-dihydro-pyrazol-3-one, *Struc. Chem.*, **16**, 515-520 (2005).
15. Gore P. H., Wheeler O.H., Absorption spectra of aromatic azo and related compounds. III. Substituted azobenzenes, *J. Org. Chem.*, **26**, 3295-3298 (1961).
16. Griffiths J., *Colour and Constitution of Organic Molecules*, Academic, Oxford, (1976).
17. Ortolano T.R., Selbin J., McGlynn S.P., Electronic structure, spectra, and magnetic properties of oxycations. V. The electronic spectra of some vanadyl complexes, *J. Chem. Phys.*, **41**, 262-268 (1964).
18. Jadeja R.N., Parmar N.J., Oxovanadium(IV), Cr(III), Fe(III), Fe(II), Ni(II), Zn(II) and UO₂(VI) chelates from ONNO donor Schiff bases, *Synth. React. Inorg. Met.-Org. & Nano Met. Chem.*, **35**, 111-117 (2005).
19. Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam-London-New York, (1968).
20. Parikh P.M., Shah J.R., Studies on six coordinate octahedral chromium(III) chelates with Schiff base derived from 4-acetyl-3-methyl-1-(3-chlorophenyl)-2-pyrazoline-5-one, *Synth. React. Inorg. Met.-Org. Chem.*, **15**, 769-778 (1985).
21. Jadeja R.N., Shah J.R., Suresh E., Paul P., Synthesis and structural characterization of some Schiff bases derived from 4-[(arylimino)ethyl]-3-methyl-1-(4'-methylphenyl)-2-pyrazolin-5-one and spectroscopic studies of their Cu(II) complexes, *Polyhedron*, **23**, 2465-2475 (2004).
22. Ballhausen C.J., Gray H.B., The electronic structure of the vanadyl ion, *Inorg. Chem.*, **1**, 111 (1962).
23. Saxena C.P., Khadikar P.V., Studies on some mixed ligand complexes of Ni(II), *J. Inorg. Nucl. Chem.*, **43**, 603-605 (1981).
24. Rana A.K., Shah N.R., Patil M.S., Karampurwala A.M., Shah J.R., Polychelates derived from 4,4'-(4,4'-biphenylenebisazo)di(salicylaldehyde oxime), *Makromol. Chem.*, **182**, 3387-3395 (1981).