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Der Pharma Chemica, 2010, 2(3): 301-308

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Synthesis and Characterization of Some Chelate Polymers of poly-Schiff base Ligand

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Abstract

Chelate polymers of Cr^{III}, Mn^{III}, Fe^{III}, Ti^{III}, VO^{IV}, Zr^{IV}, MoO₂^{VI} and UO₂^{VI} with poly-Schiff base ligand derived from 4,4'-bis-[(salicylaldehyde-5)azo] biphenyl and 1,3-diaminopropane have been prepared and characterized by elemental analyses, spectral (IR and electronic spectra), magnetic and thermal data. All the chelate polymers are colored, stable under dry condition and insoluble in common organic solvents. The chelation is through the nitrogen of the azomethine group and oxygen of hydroxyl group of poly-Schiff base. Biological studies of the ligand and its chelate polymers have been assessed by screening them against various microorganisms.

Keywords Chelate polymers, Bis-bidentate ligand, Antimicrobial study.

INTRODUCTION

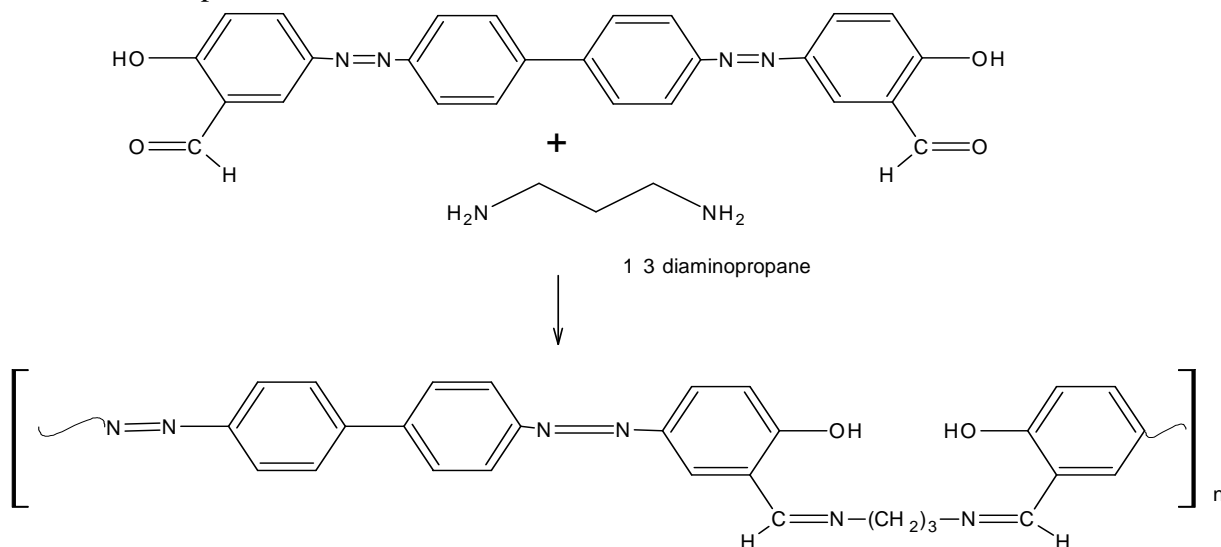
Schiff bases and related azomethines have attracted the attention of the investigators as very useful chelating ligands. Chelate polymers derived from polymeric Schiff bases have been received much attention in recent years due to their semiconducting, catalytic and biological properties [1]. Polymeric reagents have developed over the past decade from somewhat exotic and esoteric research activity into a fast growing field in applied and specific separations [2-3]. Literature survey reveals that though some work has been done on Schiff base polychelates of bivalent metal ions, but no work seems to have been done on the metal polychelates derived

from poly Schiff base involving higher valent metal ions. Therefore, it was thought interest to synthesized tetradentate poly-Schiff ligand, which would be able to form complexes with metal ions of different oxidation states. Thus, in this communication we report polyschiff base ligand, 4,4'-bis-[(N-diaminopropane Salicylaldehyde -5) azo] biphenyl (BNPSAP) and its chelate polymers with Cr(III), Mn(III), Fe(III), Ti(III), VO(IV), Zr(IV), MoO₂(VI) and UO₂(VI) ions. The chelate polymers have been characterized by various physicochemical methods in conjunction with thermogravimetric analysis data.

MATERIALS AND METHODS

All the chemicals were of A.R. grade and used without further purification. 4, 4'-bis-[(salicylaldehyde-5)azo] biphenyl ,Manganese (III) acetate dihydrate bis (acetylacetonato) -dioxomolybdenum (VI and zirconium acetate were synthesized according to the published procedures [4-6]. Chromium chloride hexahydrate, ferric chloride (anhydrous), titanium trichloride (anhydrous) and uranyl nitrate hexahydrate (S.D.'s fine chemicals) were used for synthesis

BNPSAP: 4, 4'-bis-[(salicylaldehyde-5)azo] was dissolved in hot DMF (25ml) and clear solution was obtained. Now 1,3-diaminopropane in ethanol (25ml) was added and reaction mixture was heated at reflux for 2h . To this mixture a drop of conc. H₂SO₄ was added as catalyst and further refluxed for six hours. On cooling to room temperature, a leaf brown dark solid formed was filtered, washed with ethanol and petroleum ether, and dried at ambient temperature. Yield: 72%, m.p. 260°C. The reaction scheme is as follows;



Scheme 1

Preparation of Metal Polychealates:

Equimolar quantities of Schiff base and metal salt (0.005 mol), [CrCl₃.6H₂O, Mn(OAc)₃.2H₂O, FeCl₃, TiCl₃, VOSO₄.5H₂O, ZrOCl₂.8H₂O, MoO₂(acac)₂.2H₂O and UO₂(NO₃)₂.6H₂O] were

dissolved separately in hot DMF (25ml) ,filtered and mixed in hot condition. The reaction mixture was refluxed for 6-8 h with constant stirring magnetically. On cooling to room temperature, the coloured complexes precipitated out was filtered, washed with hot water, alcohol, DMF and petroleum ether and finally dried under vacuum at room temperature. Yield 65-70 %

Elemental analysis (C-H-N) was carried out with a Carlo Erba 1108 analyzer in microanalytical laboratory, CDRI, Lucknow. Metal contents of the complexes were analyzed using standard methods [7] after decomposing the complexes with HNO₃ and H₂SO₄. IR spectra were recorded on a Perkin-Elmer-RX-1 spectrophotometer using KBr pellets. ¹H NMR spectrum of ligand was recorded in a mixed solvent (CDCl₃ + DMSO) on a Bruker AC-300 F spectrometer using TMS as an internal standard. The diffuse reflectance spectra of the chelate polymers were recorded on Cary-2390 spectrophotometer as MgO discs. Magnetic susceptibility was measured at room temperature by Gouy's method using Hg[Co(NCS)₄] as a calibrant and the diamagnetic corrections were made using Pascal's constants. Thermogravimetric analysis of the complexes was carried out on Perkin-Elmer TG-2 thermobalance in ambient air with a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

The reaction of 4, 4'-bis-[(Salicylaldehyde-5)azo] biphenyl and 1,3-diaminopropane yields a Schiff base (BNPSAP), the formation of which is supported by analytical and spectral data (Table I). All the chelate polymers are dark colored, air stable and insoluble in water and most of the common organic solvents but sparingly soluble in DMSO and DMF. Elemental analysis data suggested 1:1 (metal: ligand) stiochiometry. The ¹HNMR spectrum of Ligand in *d*₆-DMSO shows signals at δ 10.65, 8.99, 3.25 and 6.80-7.75 ppm due to phenolic, azomethine, methylene and aromatic protons respectively. The ¹HNMR spectrum clearly indicates the presence of OH and azomethine groups.

IR spectrum of ligand shows a broad band in the region 3200-3395 cm⁻¹ which may be due to intramolecular hydrogen bonding between phenolic hydrogen and azomethine nitrogen atoms [8]. Absence of this band in the spectra of polychelates indicates the breaking of hydrogen bonding and coordination of oxygen to the metal ion after replacement of proton of phenolic OH group. This is further confirmed by positive shift (30-80 cm⁻¹) of the ligand band observed at 1200 cm⁻¹ due to phenolic C-O stretch [9]. The strong band at 1626 cm⁻¹ (C=N) in the ligand spectrum shifted to lower frequency by 10-20 cm⁻¹ in the spectra of polychelates indicating participation of azomethine nitrogen in chelate formation. The ligand band observed at 1598 cm⁻¹ due to ν(N=N) remain unchanged in the spectra of polychelates indicating non involvement of azo group in the coordination [10-11]. The IR spectra of Cr^{III}, Ti^{III} and Fe^{III} polychelates show bands around 3350-3580, 1530-1540 and 790-840 cm⁻¹ could be assigned to OH stretching, rocking and wagging vibrations, respectively, showing presence of coordinated water molecules in these polychelates. In the Zr^{IV} polychelate, the absence of a band at 850-950 cm⁻¹ (Zr = O) favours the formation of Zr(OH)₂ and not Zr = O. The appearance of a new band at 1140 cm⁻¹ has been assigned to the δ Zr-OH [12-13]. The spectra of VO(IV) polychelate show new band at

around 973 cm^{-1} due to $\nu(\text{V}=\text{O})$ vibration [14]. The dioxo-metal complexes exhibit an IR spectral bands at 939 and 902 cm^{-1} due to $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$ vibrations respectively, indicating the existence of linear $\text{O}=\text{M}=\text{O}$ moiety in these polychelates [15]. In addition to the above bands all the complexes display the bands in the far-infrared region at 567 - 504 and 458 - 422 cm^{-1} tentatively assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations [16-17]. In Mn^{III} polychelates $\nu_{\text{asy}}(\text{COO})$ and $\nu_{\text{sy}}(\text{COO})$ occurs in the range of 1610 - 1614 and 1415 - 1426 cm^{-1} respectively. The band energy separation (210 - 240 cm^{-1}) between $\nu_{\text{asy}}(\text{COO})$ and $\nu_{\text{sy}}(\text{COO})$ is greater than 190 this and this indicate monodentate nature of acetate ion [18].

A study of diffuse reflectance spectra and magnetic moment provides important information about stereochemistry [19]. The diffuse reflectance spectrum of Cr^{III} polychelate exhibits three bands at 16880 , 22830 and 24890 cm^{-1} which may be assigned to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{A}_{1g}(\text{P})$ transitions, respectively for an octahedral geometry around chromium ion [20]. Cr^{III} polychelate has magnetic moment 3.88 B.M. in accordance with its spin only value. The Mn^{III} chelate has magnetic moment 4.95 B.M. and its electronic spectrum shows three bands at 13500 , 16550 and 1850 cm^{-1} due to ${}^5\text{B}_1 \rightarrow {}^5\text{B}_2$, ${}^5\text{B}_1 \rightarrow {}^5\text{A}_2$, and ${}^5\text{B}_1 \rightarrow {}^5\text{E}_1$ transitions, respectively, suggesting square pyramidal geometry for Mn^{III} polychelate [21]. Fe^{III} polychelate shows magnetic moment 5.78 B.M. corresponds to five unpaired electrons. The electronic spectrum of Fe^{III} polychelate displays three bands at 16667 , 23529 and 24411 cm^{-1} due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{D})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ transitions, respectively towards octahedral geometry [22]. The magnetic moment of Ti^{III} polychelate is found to be 1.78 B.M. corresponds to one unpaired electron. Its electronic spectrum shows broad band and double hump type of nature at 18450 cm^{-1} attributed to ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition suggesting an octahedral structure around Ti^{III} ion [23]. The observed magnetic moment for oxovanadium polychelate is 1.68 B.M. and its electronic spectrum shows bands at 11737 , 17240 and 25906 cm^{-1} due to $d_{xy} \rightarrow d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions, respectively corresponds to square pyramidal geometry [23]. The polychelates of Zr^{IV} , MoO_2^{VI} and UO_2^{VI} are found to be diamagnetic in nature as expected. The electronic spectra of $\text{Zr}(\text{IV})$, $\text{MoO}_2(\text{IV})$ and $\text{UO}_2(\text{VI})$ complexes do not furnish any characteristic d-d transition except charge transfer bands.

The synthesis of thermally stable polychelates is now a promising area in the chemistry of heat resistant polymers. Some of the polymers containing metal ion linked by chelate rings derived from organic groups show exceptional thermal stability. Aromatic backbone units are much more stable than aliphatic ones and they have significant higher melting temperatures. The thermogravimetric analysis studies of polychelates up to the decomposition point indicate that they are thermally stable. All polychelates show negligible weight loss up to 90 - 100°C indicating the absence of any lattice water molecules in these polychelates. In the case of Cr^{III} , Fe^{III} and Ti^{III} polychelates elimination of one coordinated water molecule takes place between temperature range 150 - 220°C . The Zr^{IV} polychelate show first loss starting just above 175°C is possibly due to the loss of coordinated DMF [24]. The polychelates of VO^{IV} , MoO_2^{VI} and UO_2^{VI} shows negligible loss up to temperature 200°C indicating absence of any water molecule. After elimination of coordinated water molecules chelates remain stable for a short while and thereafter there is a gradual weight loss observed in the temperature range 440 - 700°C and TG .

Table: I Analytical and magnetic data of polychelates

Sr. No.	Compound	Colour	Mol. wt* (Calcd)	Found (Calcd %)				Half decomp. Temp. (°C)	μ eff. (B.M.)
				M	C	H	N		
1	BNPSAP	Leaf Brown	410	-	71.45 (71.31)	5.12 (4.91)	17.85 (17.21)	140	--
2	{[Cr BNPSAP.Cl(H ₂ O)] _n }	Dark brown	531	8.60 (8.53)	57.50 (57.14)	4.55 (4.26)	20.17 (19.79)	220	3.88
3	[Mn BNPSAP. OAc] _n	Brown	521	9.98 (9.16)	62.35 (62.00)	4.27 (4.16)	14.70 (14.00)	230	4.95
4	{[Fe BNPSAPCl.(H ₂ O)] _n }	Brown red	534	9.38 (9.13)	57.12 (56.76)	4.80 (4.24)	14.15 (13.70)	265	5.78
5	[VO BNPSAP] _n	Brown red	474	9.80 (9.22)	63.50 (62.99)	4.12 (3.97)	15.80 (13.19)	225	168
6	[Zr(OH) ₂ BNPSAP DMF] _n	Dark brown	605	14.83 (15.06)	52.88 (53.53)	4.31 (4.33)	13.17 (13.87)	270	Dimag
7	{[Ti BNPSAP.Cl(H ₂ O)] _n }	Brown red	526	8.12 (7.50)	55.23 (54.37)	4.68 (4.06)	13.14 (13.12)	210	1.73
8	[MoO ₂ BNPSAP] _n	Brown red	519	17.08 (15.63)	60.24 (56.37)	4.02 (3.78)	14.93 (14.21)	205	Dimag
9	[UO ₂ BNPSAP] _n	Brown red	677	33.84 (32.87)	48.72 (48.06)	3.12 (3.03)	12.23 (11.60)	220	Dimag

* From analytical data & considering one unit.

Table: II Antimicrobial Activities of ligand and Complexes

S.N	Compound	Antimicrobial activity					Antifungal Activity	
		<i>E-Coli</i>	<i>S- Abony</i>	<i>S- Aureus</i>	<i>P- Aeruginosa</i>	<i>B- Subtilis</i>	<i>A-Niger</i>	<i>C-Albicians</i>
1	BNPSAP	9	10	8	12	11	10	8
2	{[Cr BNPSAP.Cl(H ₂ O)] _n }	12	11	13	13	13	14	9
3	[Mn BNPSAP. OAc] _n	15	12	10	14	13	11	10
4	{[Fe BNPSAP.Cl(H ₂ O)] _n }	11	12	9	13	12	15	9
5	[VO BNPSAP] _n	10	13	13	15	10	12	12
6	[Zr(OH) ₂ BNPSAP DMF] _n	10	12	11	14	12	11	10
7	{[Ti BNPSAP..Cl(H ₂ O)] _n }	14	13	10	14	12	10	11
8	[MoO ₂ BNPSAP] _n	11	11	12	15	13	13	11
9	[UO ₂ BNPSAP] _n	10	13	11	14	12	11	13

curve attain a constant level corresponds to the respective metal oxides. Thermal stability of polychelates follows the order $Zr^{IV} > Fe^{III} > Mn^{II} > VO^{IV} > Cr^{III} \sim UO_2^{VI} > Ti^{III} > MoO_2^{VI}$.

Antibacterial activity was evaluated by the paper disk plate method. The nutrient agar medium and 5mm diameter paper disks (Whatman no.1) were used. The compounds were dissolved in DMSO. The filter paper disks were soaked with different solutions of the compounds dried and then placed in the Petri plates previously seeded with test organism *E. Coli*, *S. abony*, *S. aureus*, *P.aeruginosa* and *B. subtilis*. The plates were incubated for 24 h at 37°C and the inhibition zone around each disc was measured. The antifungal activities of the ligand and its polychelates were studied against the fungi *A. Niger* and *C. albicans* using agar plate technique [25] at concentration of 1mg/ml in DMSO. Ligand and its all polychelates show antimicrobial activity against all test organisms used in the study. The zone of inhibition was observed after the incubation period of 24 h at 37°C for bacteria and 28°C for 48h for fungi. All the polychelates were shows inhibition zone diameter ranges between 10 to 15 mm as shown in Table II.

The experimental data suggest that the metal polychelates are more potent in inhibiting the growth of microorganisms than the ligand. The enhanced antimicrobial activity of the metal polychelates as compared to its ligand can be conveniently be explained by the chelation theory [26]. The pathogens secreting various enzymes, which are involved in the breakdown of activities, appear to be especially susceptible to inactivation by the ion of complexes. The polychelates facilitate their diffusion through the lipid layer of spore membrane to the site of action and ultimately killing them by combining with the OH & C=N groups of certain cell enzymes. The polychelates of Mn^{III} and Ti^{III} shows greater antibacterial activity towards *E. coli*, Cr^{III} and Fe^{III} shows greater antifungal activity for *A Niger* while all other polychelate showed moderate activity against all the bacterial and fungal cultures.

Acknowledgement

The authors are grateful to Sant Gadge Baba Amravati University authorities for providing research facilities, one of us (JBD) is also thankful to Dr. D.M. Ambhore, Principle, Jijamata Mahavidyalaya, Buldhana. (M.S.) for providing laboratory facilities.

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