Polychelates of salen-type Schiff base : Synthesis, characterization, thermal, electrical conductivity and biological study

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Abstract : Metal polychelates of the type $[ML.(2H_2O)X]Y$ where M = Cr^{III}, Mn^{III}, Fe^{III}, Ti^{III}, Zr^{IV}, VO^{IV}, MoO_2^{VI}, UO_2^{VI}; X = H_2O, Y = Cl with 4,4′-bis[(I-propanesalicylaldimine-5)azo]biphenyl (L) have been synthesized. Their structures have been proposed on the basis of elemental analysis, magnetic susceptibility measurements, IR and diffuse reflectance spectra and thermogravimetric analyses. ^1H NMR spectrum of the ligand clearly indicates the presence of OH and azomethine groups. The polychelates are dark colored and insoluble in common organic solvents. Their thermograms showed the loss of water of hydration in first step followed by decomposition of ligand molecule. The thermal data have also been analyzed for the kinetic parameters using Horowitz-Metzger method. The electrical conductivity of ligand and its polychelates showed semiconducting behavior. All the polychelates were found to be active against a variety of bacteria.

Keywords : Polychelates, TGA, electrical conductivity, antimicrobial activity.

Introduction

The branch of polymer-metal complexes has been developed as an interdisciplinary area involving chemistry, electrochemistry, metallurgy, environmental protection and material science. The chelate polymers constitute an important category of compounds in this area. The study of chelate polymers, initiated nearly five decades ago, is now regarded as one of the developing frontier areas of coordination chemistry. The potential applications of such polymers are, for example, as surface coating on metals and glasses, adhesives, semiconductors. The polymer metal chelates were also found to act as electrochromic materials, since the color of the polymer varies with oxidation state of the metal ion present in the chelate. The diverse range of co-ordination numbers and geometries which exist with transition elements offer the possibility of accessing polymers with unusual conformational, mechanical, and morphological characteristics. However, the development of the area of transition metal-based polymer science has been held up by considerable synthetic difficulties. The prodigious growth of the published literature on Schiff base complexes dictates certain limitations as far as spectral and magnetic investigations are concerned.

It is seemed advantageous to design and prepare a polymer bound Schiff base, which would be form complexes with variety of transition metals, and therefore has a large range of applications. Polychelates derived from bisbidentate ligands have been seemed advantageous due to their semiconducting, catalytic properties and biomedical potentials[1–8]. Some polychelates have shown activities as carcinogenic and antitumor because of their specific structures[9]. They also possess various biological activities such as fungicidal and insecticidal[10]. Polychelates can be used as dyes which react with wood silk and modified cellulose fibers[11] and analytical reagents for the determination of metal ions[12,13]. In the view of the importance associated with this class of polychelates, it was thought of interest to design polymer Schiff base 4,4′-bis[(I-propanesalicylaldimine-5)azo]biphenyl and its polychelates with Cr^{III}, Mn^{III}, Fe^{III}, Ti^{III}, VO^{IV}, Zr^{IV}, MoO_2^{VI} and UO_2^{VI} ions. All the polychelate compounds were characterized by physico-chemical techniques.

Experimental

All the chemicals and solvents used were of analytical grade procured from Merck and SD's fine chemicals and used as received. Titanium trichloride ($TiCl_3$), vanadyl

sulphate pentahydrate ($VOSO_4.5H_2O$), chromium chloride hexahydrate ($CrCl_3.6H_2O$), manganese triacetate dihydrate [$Mn(OAc)_3.2H_2O$], anhydrous ferric chloride ($FeCl_3$), zirconyl oxychloride octahydrate ($ZrOCl_2.8H_2O$), dioxo-molybdenum acetate dihydrate [$MoO_2(OAc).2H_2O$] and uranyl nitrate hexahydrate [$UO_2(NO_3)_2.6H_2O$] were used without further purification. Manganese triacetate dihydrate, dioxo-molybdenum acetate dihydrate and zirconium diacetate were prepared by literature methods[14–16].
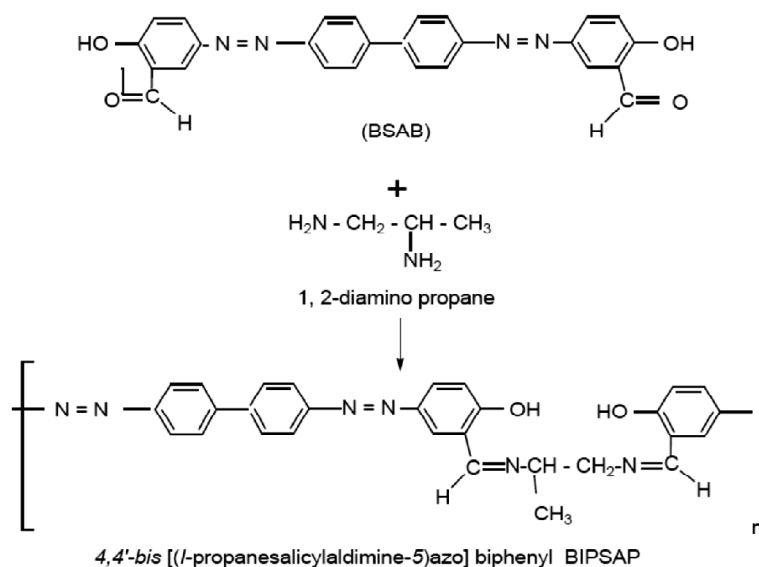
Physical measurements :

The microanalyses of carbon, hydrogen and nitrogen were performed on a Carlo Erba 1108 elemental analyzer at SAIF, Central Drug Research Institute (CDRI), Lucknow, India. The metal contents of the complexes were determined by standard methods[17] after decomposing the organic matter with a mixture of $HClO_4$, H_2SO_4 and HNO_3 (1 : 1.5 : 2.5). The infrared spectra of ligand and its polychelates were recorded on Perkin-Elmer spectrophotometer 597 by using KBr pellets at SAIF, Panjab University, Chandigarh, India. The ^1H NMR spectrum of ligand was measured in $CDCl_3$ using TMS as internal standard on Bruker Auance-II 400 NMR spectrometer at SAIF, Panjab University, Chandigarh, India. Magnetic susceptibilities were determined on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were made from Pascal's constants.

The thermal stability of ligand and its polychelates have been evaluated for recording thermograms by Metzsch STA 409 thermal analyzer at a heating rate of 20 ºC/min in air atmosphere over the temperature range 40–700 ºC. The electrical conductivity of compounds was measured in their pellet form using Zentech resistivity meter over a temperature at 373–413 K. Diffuse reflectance spectra of the solid complexes suitably diluted with magnesium oxide were recorded on a Varien Cary 5E UV-NIR spectrophotometer at SAIF, IIT, Chennai, India. Antimicrobial study of the polychelates was carried out at Nicholas Piramal (I.) Ltd., Prithampur, District Dhar (Madhya Pradesh).

Preparation of 4,4′-bis[(I-propanesalicylaldimine-5)azo]biphenyl (BIPSAP) :

The dye 4,4′-bis[(salicylaldimine-5)azo]biphenyl was prepared by diazotization[18]. To a boiling solution of dye 4.25 g (0.01 mol) of the 4,4′-bis[(salicylaldimine-5)azo]biphenyl (BSAB) in 25 ml DMF; a ethanolic solution (25 ml) of 1,2-diaminopropane 0.08 ml (0.01 mol) was added with constant stirring. A drop of concentrated H_2SO_4 was added as catalyst and the reaction mixture was refluxed on a oil bath for about 3 h. The Schiff base ligand 4,4′-bis[(I-propanesalicylaldimine-5)azo]biphenyl (BIPSAP) was separated out as a dark brown product, which was filtered washed with DMF, ethanol and petro-ether and finally re-crystallized from DMF-ethanol mix-

(BSAB)

+

$H_2N - CH_2 - CH - CH_3$
$\quad\quad\quad\quad | $
$\quad\quad\quad\quad NH_2$

1, 2-diamino propane

4,4′-bis [(*I*-propanesalicylaldimine-5)azo] biphenyl BIPSAP

Scheme

ture (1 : 1 v/v). Yield : ~70%, m.p. 268 °C.

^{1}H NMR spectrum (Fig. 1) of BIPSAP shows expected signal at δ 10.99, 8.06 and 6.80–7.31 ppm corresponding to phenolic, azomethine and aromatic protons respectively.

Synthesis of polychelates :

All the polychelates were prepared by reaction of metal salts with Schiff base ligand by using equimolar ratio (1 : 1) by general method. Equimolar proportions (0.005 mol) of metal salt and ligand were dissolved separately in minimum quantity (25 ml) of hot ethanol and DMF respectively. Both the solutions were filtered and then mixed in

ligand solution, a freshly prepared oxozirconium(IV) diacetate solution was added with continuous stirring and mixture was refluxed for 3–4 h. The product obtained was filtered, washed 2–3 times with DMF, hot ethanol petro-ether and dried at room temperature.

Synthesis of MoO$_2$^{VI} polychelate :

Ammonium molybdate (30 g) was dissolved in 100 ml of water and acetyl acetone (40 ml) was added with constant stirring. The pH of reaction mixture was adjusted to 3.5 by using 10% HNO$_3$ with constant stirring. The light yellowish green solid begins to precipitate after 1.5–2 h. A yellow MoO$_2$(acac)$_2$ obtained was filtered, washed with
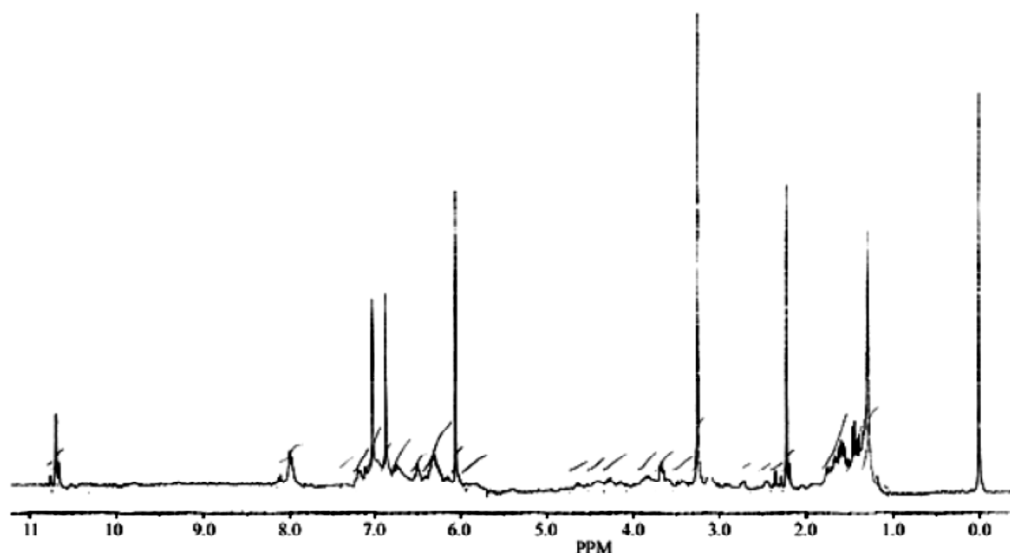

Fig. 1. ^{1}H NMR spectra of BIPSAP ligand.

hot condition with constant stirring. The reaction mixture was refluxed on sand bath for a 5–6 h. The resulting colored product so obtained on cooling was filtered, washed well with DMF, hot ethanol and finally with acetone to remove unreacted ligand and metal salts and dried over anhydrous calcium chloride in a desiccator.

Synthesis of Zr^{IV} polychelate :

Zirconyl oxychloride octahydrate (0.64 g, 0.002 mol) was dissolved in 10–15 ml of methanol and to this a methanolic solution of anhydrous sodium acetate (0.32 g, 0.04 mol) 15 ml was added and stirred for 5 min. The separated sodium chloride was filtered off from oxozironium(IV) diacetate. The Schiff base ligand (0.002 mol) was dissolved separately in hot methanol. To this

water followed by ether and dried. To resulting MoO$_2$(acac)$_2$, a solution (10 ml) of ligand (0.05 mol) was added in a portion with stirring and mixture was further refluxed for 3 h. The product obtained was filtered, washed with 2–3 times with DMF and ethanol followed by ether and dried at room temperature.

Antibacterial and antifungal study :

The ligand and its polychelate were screened by the disc diffusion method for their *in vitro* antibacterial activity in DMSO against the bacterial strains *Escherichia coli, Salmonella abony, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis, Aspergillus niger* and *Candida albicans* using. Solutions of 100, 200 and 300 ppm of the compounds in DMSO were used for the stu-

dies. These discs were placed on the already seeded plates and incubated at 35 °C for 24 h. The activity was determined by measuring the diameter (mm) of zones showing complete inhibition. For antifungal study Zapek-Dox agar (CDA) media was used.

Results and discussion

The condensation of 4,4′-bis[(salicylaldimine-5)azo]biphenyl (BSAB) with 1,2-diaminopropane gives Schiff base. Elemental analyses, IR and ^1H NMR spectral studies confirm its structure. The ligand reacts with metal salts in 1 : 1 molar ratio in mixed DMF-EtOH solvents. All the polychelates are colored solids with high melting points. The polychelates are non-hygroscopic and are stable in air, insoluble in methanol, ethanol, chloroform and acetone but sparingly soluble in DMF and DMSO. The analytical data suggest 1 : 1 (metal : ligand) ratio for all the complexes (Table 1). The elemental analysis data are in consistent with the theoretical expectations.

IR spectra :

The important diagnostic bands in the infrared spectra were assigned and the bands positions are shown in Fig.

2 and Table 2. The IR spectrum of the ligands exhibits a medium intensity band at 3393 cm^{-1} due to intramolecular hydrogen bonded hydroxyl group ν(OH). Absence of this band in all the spectra of polychelates indicates the breaking of hydrogen bond and coordination of oxygen atom to the metal after deprotonation. This is further supported by the upward shifts of ν(C-O) (phenolic) band at 1281 cm^{-1} by 10–12 cm^{-1} in polychelates suggest the coordination of ligand through phenolic oxygen via deprotonation. The infrared spectrum of ligand shows a strong band about at 1630 cm^{-1} due to azomethine stretch ν(C=N). In all polychelates this band shifted to lower energy by 20–25 cm^{-1} which is indicative of the azomethine nitrogen coordination of the ligand[19]. The negative shift may be attributed to the formation of coordinate bond by donation of lone pair of electrons from nitrogen to metal ion thereby decreasing electron density on nitrogen and it, therefore, withdraws electrons from the $>$C=N- π bond. The characteristic band at 1495 cm^{-1} due to ν(N-N) stretching remains unchanged in all polychelates indicating that azo group is not participating in coordination. In the spectra of polychelates Cr^{III}, Fe^{III} and Ti^{III} broad band in the range 3360–3900 cm^{-1} can be

Table 1. Analytical and electrical conductivity data of BIPSAP and its polychelates

| Sr. no.	Proposed composition of the polychelates	σ (Ω^{-1} cm^{-1})	E_a (eV)	Band gap	Color	Elemental analysis (%) : Found (Calcd.)			
						M	C	H	N
1.	BIPSAP	1.02×10^{-6}	2.39	4.78	Dark brown	–	71.40 (71.31)	5.15 (4.91)	17.80 (17.21)
2.	{[Cr BIPSAP·2H$_2$O]Cl}$_n$	6.15×10^{-13}	0.880	1.76	Dark brown	8.50 (8.53)	57.40 (57.14)	4.56 (4.26)	14.15 (13.79)
3.	[Mn BIPSAP·OAc]$_n$	9.02×10^{-13}	1.652	3.30	Brown	9.80 (9.16)	62.40 (62.00)	4.30 (4.16)	14.30 (14.00)
4.	{[Fe BIPSAP·2H$_2$O]Cl}$_n$	1.61×10^{-11}	0.660	1.32	Brown red	9.30 (9.13)	57.50 (56.76)	4.50 (4.24)	14.20 (13.70)
5.	[VO BIPSAP]$_n$	1.42×10^{-9}	0.440	0.880	Brown red	9.40 (9.22)	63.50 (62.99)	4.15 (3.97)	15.80 (15.19)
6.	[Zr(OH)$_2$ BIPSAP]$_n$	4.2×10^{-11}	0.517	1.034	Brown	16.30 (15.99)	57.10 (56.21)	4.25 (4.20)	14.22 (13.57)
7.	{[Ti BIPSAP·2H$_2$O]Cl}$_n$	8.5×10^{-12}	0.208	0.416	Brown red	8.20 (7.50)	55.10 (54.37)	4.60 (4.06)	13.25 (13.12)
8.	[MoO$_2$ BIPSAP]$_n$	3.90×10^{-12}	0.372	0.744	Brown red	17.10 (15.63)	60.30 (56.37)	4.10 (3.78)	14.70 (14.21)
9.	[UO$_2$ BIPSAP]$_n$	1.87×10^{-12}	0.787	1.57	Brown red	33.80 (32.87)	48.50 (48.06)	3.15 (3.03)	12.30 (11.60)
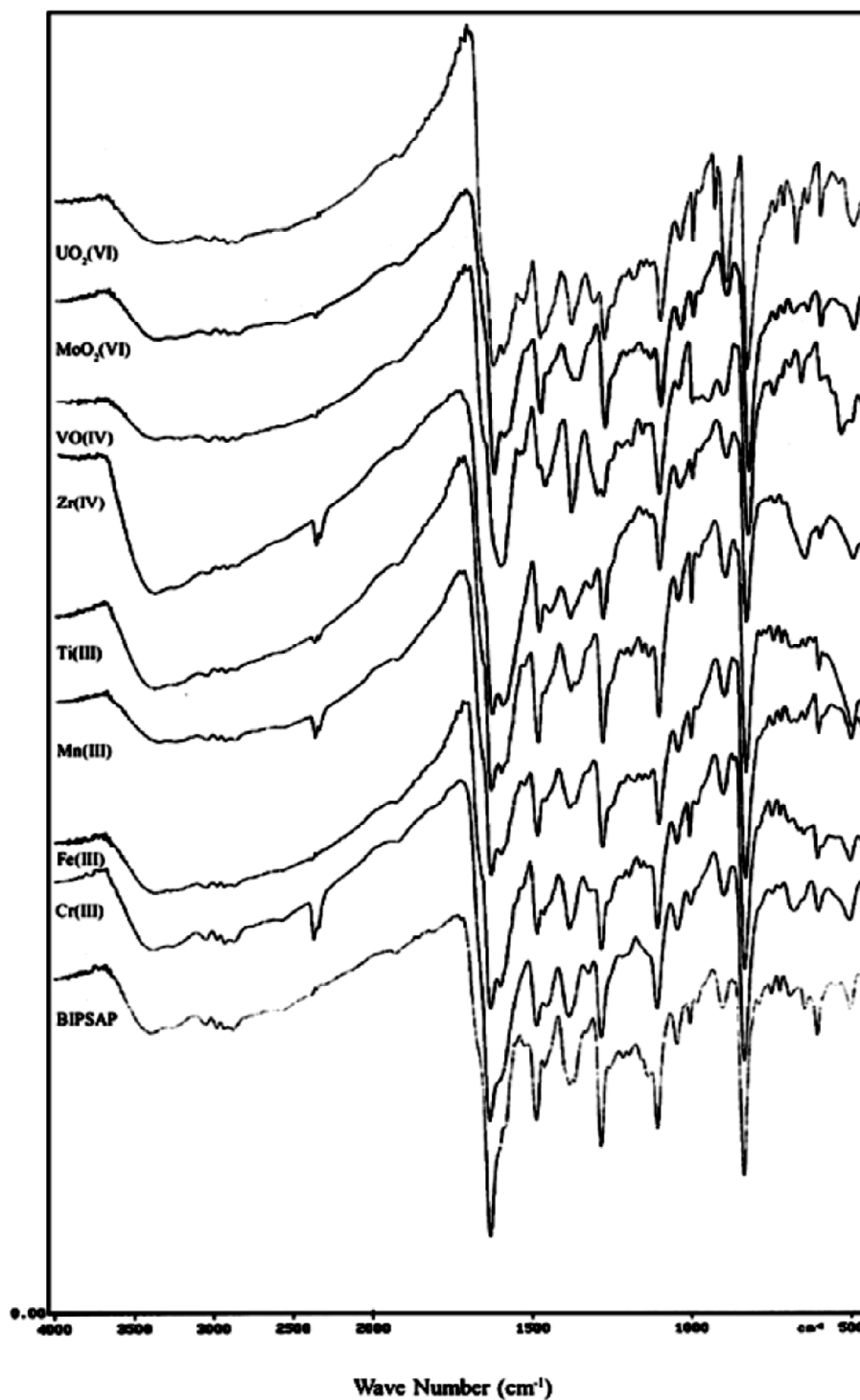
Fig. 2. IR spectra of BIPSAP and its polychelates.

assigned to $\nu(OH)$ stretching vibration of coordinated water molecules as evidenced by the spectra in the region 1650–1655 cm^{-1} (medium sharp shoulder) for $\nu(OH)$ vibration and 835–840 cm^{-1} (strong and sharp) for ν H$_2$O, presence confirmed by elemental and thermal analyses as well. The Mn^{III} polychelate shows three bands at 1525, 1390

Table 2. IR spectral data (cm^{-1}) of BIPSAP and its polychelates

Sr. no.	Ligand/Polychelate	O-H	C=N	C-O	M-O	M-N	V=O	O=Mo=O	O=U=O	H$_2$O/OAc/OH
1.	BIPSAP	3394	1630	1281	–	–	–	–	–	–
2.	{[Cr BIPSAP·2H$_2$O]Cl}$_n$	–	1620	1300	540	470	–	–	–	3360, 1650, 860
3.	[Mn BIPSAP·OAc]$_n$	–	1618	1310	540	480	–	–	–	3370, 1660, 865
4.	{[Fe BIPSAP·2H$_2$O]Cl}$_n$	–	1620	1300	535	470	–	–	–	1530, 1390, 660
5.	[VO BIPSAP]$_n$	–	1615	1290	530	480	–	–	–	3400, 1650, 865
6.	[Zr(OH)$_2$ BIPSAP]$_n$	–	1615	1295	535	485	–	–	–	1140
7.	{[Ti BIPSAP·2H$_2$O]Cl}$_n$	–	1615	1300	540	485	974	–	–	–
8.	[MoO$_2$ BIPSAP]$_n$	–	1618	1290	530	485	–	890	–	–
9.	[UO$_2$ BIPSAP]$_n$	–	1620	1290	545	470	–	–	915	–

and 667 cm^{-1} respectively which may be due to (OCO), ν_{sym}(OCO) and δ(OCO) vibrations of OAc to Mn^{III} ion[20]. The IR spectra of VO^{IV}, MoO$_2$^{VI} and UO$_2$^{VI} polychelates show medium bands at 974, 890 and 915 cm^{-1}, which may be attributed to V=O, O=Mo=O and O=U=O respectively. Formation of Zr(OH)$_2$ is favored by appearance of new band around at 1140 cm^{-1} [21]. In the ranges 530–545 and 470–485 cm^{-1} two supplementary bands tentatively assigned to stretching vibrations of ν(M-O) and ν(M-N) can be observed in the spectra of polychelates. Thus from above discussion, it is conclude that the BIPSAP ligand act as dibasic tetradentate nature towards all the metal ions.

Electronic spectra :

The electronic spectrum of VO^{IV} complex shows three bands at 13500, 16320 and 23310 cm^{-1} due to $d_{xy}(b_2) \rightarrow d_{xy}d_{yz}(e^*)$, $d_{xy}(b_2) \rightarrow d_{x^2-y^2}(b_1^*)$ and $d_{xy}(b_2) \rightarrow d_{z^2}(a_1^*)$, transitions, respectively indicating that the vanadyl complex has a square pyramidal geometry. The Cr^{III} complex exhibits absorption bands at 16680, 21850 and 27380 cm^{-1} due to the $^4A_{2g} \rightarrow {}^4T_{2g}$ (F), $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{2g}$ (P), transitions, respectively suggesting an octahedral geometry around the Cr^{III} ion[22,23]. The ligand field parameters, Dq, Racah interelectronic repulsion parameter (B'), nephelauxetic ratio (β) and % covalency of metal-ligand bond have been calculated for Cr^{III} complex and the values for Dq, B', β, ν_2/ν_1 and % covalency are found to be 1669 cm^{-1}, 702 cm^{-1}, 0.763, 0.76 and 27.2. The Racah interelectronic repulsion parameter (B') for complex is found to be lower than the free ion values (918 cm^{-1}) suggesting delocalization of electron on metal into molecular orbital covering both the metal and the

ligand i.e. the appreciable covalent character in the metal-ligand bond. The electronic spectrum of Mn^{III} complex shows bands at 13793, 16949 and 19230 cm^{-1} which may be assigned to $^5B_1 \rightarrow {}^5B_2$, $^5B_1 \rightarrow {}^5A_1$ and $^5B_1 \rightarrow {}^5E$, transitions, respectively towards square pyramidal geometry around metal ion[24]. The Fe^{III} complex shows bands at 11627, 22222 and 25974 cm^{-1} due to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$, transitions, respectively in an octahedral symmetry. The Ti^{III} complex exhibits a broad band about at 18600 cm^{-1} due to $^2T_g \rightarrow {}^2E_g$ transition towards distorted octahedral symmetry.

Magnetic moments :

The magnetic moments of all complexes was measured at room temperature. The VO^{IV}, Cr^{III}, Mn^{III} and Fe^{III} complexes exhibit magnetic moments of 1.74, 3.85, 4.86 and 5.92 B.M. respectively. These data are close to the reported values for these complexes[20]. The MoO$_2$^{VI}, Zr^{IV} and UO$_2$^{VI} complex are found to be diamagnetic as expected from their electronic configurations[21].

TG analysis :

The thermal behavior of all the polychelates was studied in air in 40–700 °C temperature range. Thermograms of Cr^{III}, Fe^{III}, Ti^{III}, VO^{IV}, Zr^{IV}, MoO$_2$^{VI} and UO$_2$^{VI} polychelates indicate two stage decomposition (Fig. 3). Cr^{III}, Fe^{III} and Ti^{III} polychelates show weight loss corresponds to the presence of two coordinated water molecules in these complexes [% wt. loss obsd./calcd : Cr^{III} : 6.00/5.91, Fe^{III} : 6.00/5.87, Ti^{III} : 6.10/5.95]. The first step of decomposition is fast as compared to second step. This may be due to the fact that the non-coordinated part of ligand decomposes first (~250–300 °C) while actu-
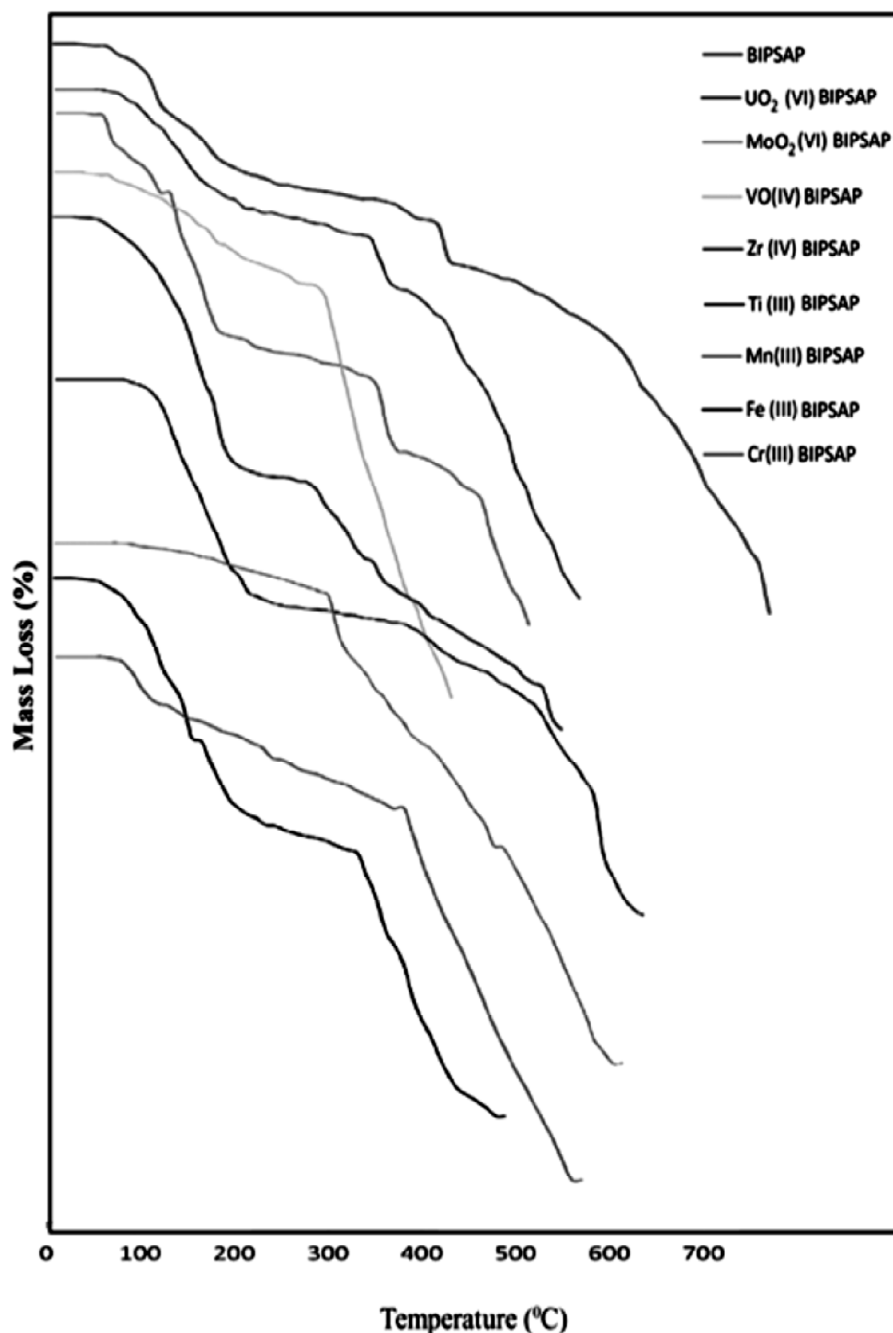
Fig. 3. Thermograms of BIPSAP and its polychelates.

ally coordinated moiety decomposes latter and finally forms metal oxide about at ~690 °C. In polychelates VO^{IV}, MoO_2^{VI} and UO_2^{VI} gradual weight loss observed in the range 300–630 °C leading to decomposition of polychelates, in Mn^{III} polychelate weight loss observed at ~300 °C indicates the loss of acetate group from polychelate [% wt. loss obsd./calcd. : 10.00/9.83]. Weight loss corresponding to (OH) group in Zr^{IV} polychelate found to be 5.49% at temperature ~180 °C. Above this temperature, the nature of curve is almost horizontal indicating formation of corresponding stable metal oxide [% residue, obsd./calcd. : Cr_2O_3 : 25.00/24.95, Mn_3O_4 :

Table 3. Thermal decomposition data of BIPSAP and its polychelates

Sr. no.	Compound	Half decomposition temp. (°C)	Activation energy E_a (kJ mol^{-1})	Frequency factor Z (s^{-1})	Entropy change $-\Delta S$ (J mol^{-1} K^{-1})	Free energy change ΔG (kJ mol^{-1})
1.	BIPSAP	520	39.20	29.32	–26.74	38.84
2.	{[Cr BIPSAP·2H$_2$O]Cl}$_n$	440	40.07	34.06	–26.35	41.39
3.	[Mn BIPSAP·OAc]$_n$	360	36.56	33.67	–26.81	42.87
4.	{[Fe BIPSAP·2H$_2$O]Cl}$_n$	490	29.21	37.67	–26.79	43.02
5.	[VO BIPSAP]$_n$	470	42.42	30.97	–26.47	41.81
6.	[Zr(OH)$_2$ BIPSAP]$_n$	320	36.35	36.50	–26.86	43.37
7.	{[Ti BIPSAP·2H$_2$O]Cl}$_n$	360	37.56	35.73	–27.81	46.47
8.	[MoO$_2$ BIPSAP]$_n$	350	34.43	39.89	–26.69	44.31
9.	[UO$_2$ BIPSAP]$_n$	480	32.57	33.30	–26.45	43.35

38.60/38.16, Fe$_2$O$_3$: 26.10/25.97, V$_2$O$_5$: 33.15/32.91, ZrO$_2$: 23.00/22.19, TiO$_2$: 13.50/13.22, MoO$_3$: 27.00/26.61, U$_3$O$_8$: 111.50/111.37]. From the thermal decomposition data various kinetic and thermodynamic parameters such as activation energy (E_a), frequency factor (Z) and entropy change (ΔS) have been evaluated by employing Horowitz-Metzger method[25] and values are summarized in Table 3. The values of kinetic parameters obtained are quite consistent which indicate that the similar types of chemical changes take place during degradation of all complexes. The negative values of entropy of activation suggest highly ordered transition state than individual reactants and the reactions are slower than normal. Thermal stability order of polychelates is found to be : BIPSAP > Mn^{III} > UO$_2$^{VI} > Cr^{III} > Ti^{III} > Zr^{IV} > MoO$_2$^{VI} > Fe^{III} > VO^{IV}.

Electrical conductivity study :

The temperature dependence of electrical conductivity of BIPSAP and its polychelates has been shown in Fig. 4 and results are tabulated in Table 1. The electrical conductivity of BIPSAP and its polychelates at 373 K lie in the range 1.02×10^{-6} – 9.02×10^{-13} Ω^{-1} cm^{-1} which suggests semiconducting nature of polychelates. Plots of log σ vs 1000/T are found to be linear over studied temperature range indicating their semi-conducting nature and obey Arrhenius equation. The activation energy of electrical conduction of these polychelates lies in the range 0.208–1.652 eV and electrical conductivity follows the order : BIPSAP > Fe^{III} > Cr^{III} > UO$_2$^{VI} > Mn^{III} > Zr^{IV} > Ti^{III} > MoO$_2$^{VI} > VO^{IV}.

The electrical conductivity increases when charge carriers have enough activation energy, also during the increase of temperature the mobility of these carriers increases. This is the property of a typical semiconductor[26]. The polychelates possess lower electrical conductivity and activation energy values than those of the free ligand. This could be attributed to the scattering mechanism and/or to the polymeric nature of complexes. The observed low value of electrical conductivity may be attributed to low molecular weight due to which the extent of conjugation becomes low or to undesirable morphology due to pressing of the sample into hard brittle pellet form[26].

Biological study :

BIPSAP and its polychelates were screened for their antibacterial and antifungal activity. The ligand is sensitive against all the bacterial and fungal strains. Fe^{III}, Cr^{III}, Ti^{III} and Zr^{IV} polychelates shows (Table 4) maximum antibacterial activity while MoO$_2$^{VI} and UO$_2$^{VI} showed moderate antibacterial activity. Ti^{III} and VO^{IV} polychelates showed maximum antifungal activity whereas Cr^{III}, Mn^{III}, Zr^{IV}, MoO$_2$^{VI} and UO$_2$^{VI} showed moderate antifungal activity in comparison with the ligand. From the above results, it can be concluded that the ligand as well as its polychelates showed biocidal nature against all the bacterial and fungal strains used under present study. In general the results reveal that the activity of the ligand was found to be enhanced on complexation with metal ions. It has been observed that the metal complexes show enhanced antibacterial activity as compared to the free ligand
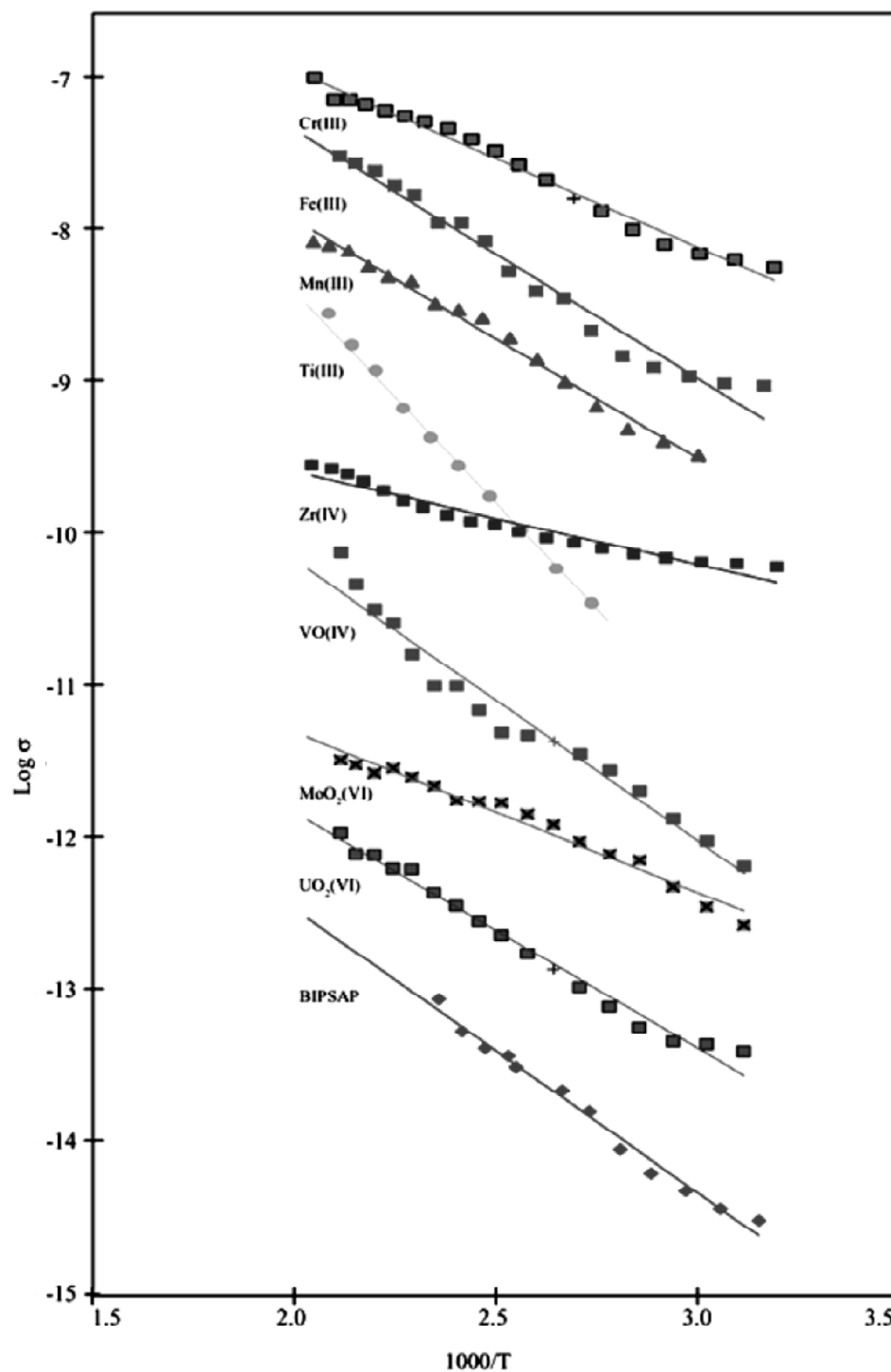
Fig. 4. Solid state conductivity of BIPSAP and its polychelates.

against the same organism under identical experimental conditions. This is because of the chelation. According to Tweedy's chelation theory[27], the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor groups and possible π electron delocalization over the whole ring[28,29].

Table 4. Antimicrobial activity of BIPSAP and its polychelates

Sr. no.	Name of ligand and polychelates	Antimicrobial activity					Antifungal activity	
		← Zones of inhibition (in mm) →						
		E. coli ATCC 8739	*S. abony* NCTC 6017	*S. aureus* ATCC 6538	*P. aruginosa* ATCC 9027	*B. subtilis* ATCC 6633	*A. niger* ATCC 16404	*C. albicans* ATCC 10231
1.	BIPSAP	10.26	11.24	11.25	11.12	11.18	10.88	10.87
2.	{[Cr BIPSAP·2H$_2$O]Cl}$_n$	11.24	11.40	11.31	11.42	11.36	10.92	11.25
3.	[Mn BIPSAP·OAc]$_n$	10.36	11.64	11.65	11.40	11.33	11.12	11.26
4.	{[Fe BIPSAP·2H$_2$O]Cl}$_n$	11.11	11.34	11.36	11.64	11.84	11.60	11.32
5.	[VO BIPSAP]$_n$	11.25	11.42	11.46	11.85	11.85	11.10	11.24
6.	[Zr(OH)$_2$ BIPSAP]$_n$	11.28	11.52	11.46	11.64	11.84	11.23	11.44
7.	{[Ti BIPSAP·2H$_2$O]Cl}$_n$	11.12	11.64	11.39	11.48	11.34	11.34	11.54
8.	[MoO$_2$ BIPSAP]$_n$	10.42	11.36	11.42	11.42	11.48	11.22	11.14
9.	[UO$_2$ BIPSAP]$_n$	11.11	11.36	11.38	11.45	11.37	11.36	11.24

This increases the lipophilic character of the metal chelate which favors its permeating through the lipid layer of bacterial membranes. The toxicity increases with increase in concentration of the complexes. This is because of the chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with donor groups and also due to the delocalization of π electrons over the whole chelate ring. Thus chelation increases lipophilic character in the complexes and results in enhancement of activity.

Conclusion

New polychelates were synthesized and characterized by various physicochemical methods and suggest square pyramidal structure for Mn^{III} and VO^{IV} polychelates, whereas octahedral to Ti^{III}, Cr^{III}, Fe^{III}, MoO$_2$^{VI}, Zr^{IV} and UO$_2$^{VI} polychelates. IR spectra display the characteristic features of the Schiff base and indicate that ligand acts as dibasic ONNO tetradentate, coordinating via phenolic oxygen and azomethine nitrogen atoms. Thermal study revealed that complexes are thermally stable and follow common reactions. The solid-state electrical conductivity of complexes increases with increase in temperature and suggesting their semiconducting behavior. The formation of macromolecular chain may be expected for a ligand with two chelating sites, which for steric reasons cannot interact with the same metal ion. The formation of chelate polymer is also supported by the fact that all chelates obtained are insoluble in water and common organic solvents. The extended nature of TG curves showing decomposition in a wide temperature range also indicating their polymeric nature. The polychelates are biologically active and showed enhanced antimicrobial activities compared to the free ligand.

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