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TRANSITION METAL POLYCHELATES WITH SALEN-TYPE SCHIFF BASE: SYNTHETIC, SPECTROSCOPIC, THERMAL, ELECTRICAL CONDUCTIVITY, BIOLOGICAL, AND COORDINATION ASPECTS

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ABSTRACT

Cr(III), Mn(III), Fe(III), Ti(III), Zr(IV), VO(IV), MoO_2(VI) and UO_2(VI) polychelates with salen type Schiff base 4,4′-*bis*[(*N*-butanessalicylaldimine-5)azo]biphenyl (BNBSAP) prepared from dye 4,4′-*bis*[(salicylaldimine-5)azo]biphenyl and 1,4-diaminobutanehave been characterized by elemental analyses, IR and electronic spectra, magnetic susceptibility measurements and thermogravimetric analysis.All the polychelatesare dark colouredsolid and sparinglysoluble in common organic solvents. ^{1}H-NMR spectrum ligand clearly indicates the presence of OH and azomethine groups. Thermogravimetric analysis confirms the coordination of H_2O in polychelates.The thermal data have also been analyzed for the kinetic parameters by using Horowitz-Metzger method. Solid state dc conductivity of ligand and its polychelates was measured in their compressed pellet form over 373-413K range of temperatures and all compounds show semiconducting behaviour. The Synthesise polychelateswere also screened for antimicrobial activity against various bacteria.

KEYWORDS: Polychelates, Thermal analysis, Electrical Conductivity, Biological Activity.

INTRODUCTION

Polymers have increasing interest over the last few decades in the fundamental research as well as in their potential applications in fields such as catalysis, ion exchange, photochemistry, selective separation, biological study, physical and materials chemistry [I-IV]. Chelate polymers are defined as materials in which metal ions are linked together with polyfunctional ligands and chelate polymers are also well known for their thermal stability [V]. The incorporation of transition metals into polymeric Schiff bases not only affects their physical characteristics, but also their chemical activity. Complexation of a metal ion to functional polymeric ligand changes its activity due to polymeric effect.Polymer–metal complexes are in general coordinating polymers containing one or more electron donor atoms such as N, S and O that can form coordination with most of the transition and toxic heavy metals.Among polymers those containing nitrogen as donor atoms have been synthesized and used in complexation of transition metal complexes. Various nitrogen containing ligands such as salicylaldiminatederivatives [VI]have been used in preparation of resins, adhesives, additives and catalysts [VII].This report deals with the synthesis and characterization of a polymeric Schiff base by condensation of 4,4*'-bis*[(salicylaldimine-5)azo]biphenyl with 1,4-diaminobutane. The resulting polymeric Schiff base readily form polymeric metal complexes with Cr(III), Mn(III), Fe(III), Ti(III), Zr(IV), VO(IV), MoO_2(VI) and UO_2(VI) ions. The coordination behaviour of the Schiff base polymer towards transition metal ions was investigated by IR, ^{1}H-NMR, UV–visible spectroscopy, magnetic moment measurements and thermal studies. The antimicrobial activity of the polymeric Schiff base and its polychelatesagainst the bacteria and fungi is also reported.

EXPERIMENTAL

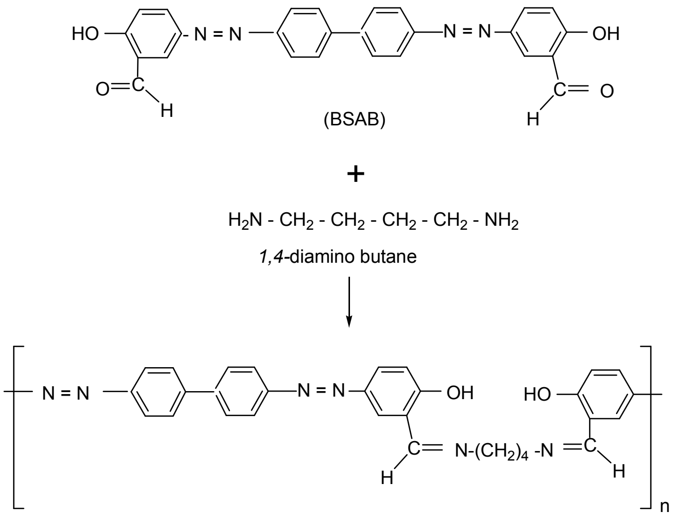
All the chemicals and solvents used were of AR grade obtained from Merck and SD's fine chemicals and used as received. Titanium trichloride ($TiCl_3$), Vanadylsulphatepentahydrate ($VOSO_4.5H_2O$), chromium chloride hexahydrate ($CrCl_3.6H_2O$), manganese triacetate dihydrate [$Mn(OAc)_3.2H_2O$], anhydrous ferric chloride ($FeCl_3$), zirconyloxychlorideoctahydrate ($ZrOCl_2.8H_2O$), 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 dehydrate, dioxo-molybdenum acetate dihydrate and zirconium diacetate were prepared by literature methods [VIII-XI].

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 [XII] 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 ^{1}H NMR spectrum of ligand was measured in *$CDCl_3$* using TMS as internal standard on BrukerAuance-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) $_4$]ascalibrant; diamagnetic corrections were made from Pascal's constants. The thermal stability of ligand and its polychelates have been evaluated fromrecording thermograms by Metzsch STA 409 thermal analyzer at a heating rate of 20^{o}C /min in air atmosphere over the temperature range 40- 700^{o}C. 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 polychelates 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 (M.P.).

Preparation of 4,4'-bis[(I-propanesalicylaldimine-5)azo]biphenyl polymer (BNBSAP)

The dye 4,4*'-bis*[(salicylaldimine-5)azo]biphenyl was prepared by diazotization (BSAB) [XIII]. A quantity of 4.25 g (0.01mol) of the dye (BSAB) was dissolved in 25ml DMF with heating. A solution of 1,4-diaminobutane 0.08 ml (0.01mol) in 25ml ethanol was added dropwise to this solution with constant stirring. A drop of concentrated H_2SO_4 was added as catalyst in the reaction mixture and it was further refluxed on an oil bath for about 3-4 h. The Schiff base ligand 4,4'-*bis*[(*N*-butane salicylaldimine-5)azo]biphenyl (BNBSAP) was separated out as a leaf brown color product, which was filtered washed with DMF and Ethanol and re-crystallized from DMF-ethanol mixture (1:1v/v) Yield: 65%, m.p.: 255°C.



4,4' - bis [(*N*-butanesalicylaldimine-*5*)azo] biphenyl BNBSAP

Reaction Scheme

^{1}H-NMR Spectral Study

Ligand shows expected signal at 10.59 and 8.10 δ ppm for OH and H-C=N proton respectively. Multipletes signals in the region 7.05 δ to 8.05 δ are due to aromatic protons.

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 (0.005mol) of metal salt and ligand were dissolved separately in minimum quantity (25ml) of hot ethanol and DMF respectively. Both the solutions were filtered and then mixed in hot condition with constant stirring. The reaction mixture was refluxed on sand bath for a 5-6h.The resulting coloured 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

Zirconyloxychlorideoctahydrate (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 oxozirconium (IV) diacetate. The Schiff base ligand(0.002 mol) was dissolved separately in hot methanol. To this 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 water followed by petroleum 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.

Biological Study

The ligand and its polychelateswere 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, Asapergillus Niger and Candida Albicians*using. Very dilute solutions of 100, 200 and 300 ppm of the compounds in DMSO were used for the studies. These discs were placed on the already seeded plates and incubated at 35°C for 24h. 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 polymer ligand reacts with metal salts in 1:1 molar ratio in mixed DMF-ethanol solvents and give polychelatesare 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 data

IR spectra

The free ligand (BNBSAP) exhibits IR bands at 3397 cm^{-1} (OH), 1634 cm^{-1} (C=N), 1281 cm^{-1} (C-O) and 1484 cm^{-1} (N=N). In the spectra of all polychelates (table 2), the band disappears due to hydrogen bonded OH of the ligand and at the same time phenolic C-O vibrations shifted towards higher frequency by 10-20 cm^{-1} indicating coordination of ligand to the metal ion through phenolic oxygen, after deprotonation of phenolic OH group. The azomethine ν (C=N) of the ligand shifted towards lower frequency by 10-25 cm^{-1} indicating coordination of C=N group through nitrogen [XIV, XV]. The shifting of the frequency region to lower side and appearance bands in the region 555-410 cm^{-1} confirms the participation of phenolic oxygen and azomethine nitrogen which are assignable to ν (M-O) and ν (M-N) stretching modes respectively [XVI, XVII].Polychelatesof Cr(III), Fe(III) and Ti(III) metal ions show three diagnostic bands for coordinated water molecules in the ranges 3350-3400 cm^{-1} (broad and strong), 1650-1660 cm^{-1} (medium sharp shoulder) for ν(OH) vibration and 825-835 cm^{-1} (strong, sharp) for ν (H_2O) [XIV,XVIII]. Mn(III)polychelate shows three bands at 1530, 1390 and 660 cm^{-1} respectively which may be due to monodentate coordination of acetate group (OAc) to Mn(III) and assigned to ν_{asym}(OCO) and ν_{sym}(OCO) and δ(OCO) vibrations [XIV,XVIII]. The IR spectrum of VO(IV)polychelate shows sharp band at 971 cm^{-1} due to ν (V=O) stretching vibrations which is characteristic of oxovanadium polymer. IR spectra of MoO_2(VI) and UO_2(VI) polychelates show strong and sharp band at 895 cm^{-1} and 915 cm^{-1} indicative of *cis*- MoO_2 and *trans*- UO_2 structures [XIX]. Absence of band at 840-960 cm^{-1} in the Zr(IV)polychelatefavors the formation of $Zr(OH)_2$ and which is further confirmed by appearance of new band at 1135 cm^{-1} which is assigned to δ Zr(OH).

Electronic Spectra and Magnetic moments study

The electronic spectrum of VO(IV) polychelate shows three bands at 13400, 16200 and 22730 cm^{-1}due to $d_{xy}(b_2)\rightarrow d_{xy}d_{yz}(e^*)$, $d_{xy}(b_2)\rightarrow d_{x2-y2}(b_1^*)$ and $d_{xy}(b_2)\rightarrow d_{z2}(a_1^*)$, transitions, respectively indicating that the vanadyl chelate has a square pyramidal geometry [XX]. The Cr(III) polychelateexhibits absorption bands at 16805, 21625 and 27580cm^{-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 [XXI, XXII]. The ligand field parameters, Dq, Racahinterelectronic repulsion parameter (B'), nephelauxetic ratio (β) and % covalency of metal-ligand bond have been calculated for Cr(III) polymer and the values for Dq, B', β, ν_2/ν_1 and % covalency are found to be 1680 cm^{-1}, 705 cm^{-1}, 0.766, 0.77 and 23.4. The

Racahinterelectronic repulsion parameter (B') for polychelates 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) polychelates shows bands at 13605, 16949 and 19120 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 Mn(III)ion [XXIII].TheFe (III)polychelateshows bands at 11494, 21740 and 27727 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 [XXIV]. The Ti(III) polychelate exhibits a broad band about at 18550 cm^{-1} due to $^2T_g \rightarrow ^2E_g$ transition towards distorted octahedral symmetry [XXV]. The magnetic moments of all polychelates was measured at room temperature. The VO(IV), Cr(III), Mn(III), Fe(III) and Ti(III)polychelatesexhibit magnetic moments of 1.69, 3.80, 4.93, 5.90 and 1.86 B.M respectively. These data are close to the reported values for these polychelates [XXVI]. The MoO_2(VI), Zr(IV) and UO_2(VI)polychelates complex are found to be diamagnetic as expected from their electronic configurations [XXVII].

TGA analysis

The structural characterization of BNBSAP and its polychelates were revealed by their thermogravimetric analysis. Thermogravimetric studies of the polychelateshave been carried out to estimate the contribution of weight losses during decomposition for determination of water molecules present in the chelates and to know their decomposition pattern. From the TG curves (figure 1), it is observed that all the polychelates, except Mn(III), decomposes in two steps, while Mn(III) polymer complex decompose in three steps. Thermograms of Cr(III), Fe(III) and Ti(III)polychelate shows the weight loss in the temperature range 160-180°Cindicating the removal of two coordinated water molecules [% wt loss obs/calcd: Cr(III) 5.80/5.77, Fe(III) 5.85/5.74, Ti(III) 5.90/5.81]. In case of Mn(III), VO(IV), MoO_2(VI) and UO_2(VI) polychelates negligible weight loss is observed up to 220°C suggest the absence of any water or solvent molecules in the polychelatecomplexes. In Zr(IV) polychelate weight loss corresponding to (OH)group [wt. loss obsed/calcd : 5.40/5.37] occurs above 180°C.In Mn(III)polychelate weight loss at ~290-300°C indicates[% wt loss obsd/calcd : 9.70/9.60] the presence of acetate group. In complex polymers after the elimination of water/acetate /OH group the polychelates of are found to be stable for a short while up to 250-300°C, but above this they show continues mass loss up to 700°C. This mass loss may be due to oxidative degradation of polychelates leading to formation of respective metal oxide. [% residue, obs./calcd: Cr_2O_3: 24.60/24.39, Mn_3O_4: 37.50/37.29, Fe_2O_3: 26.00/25.39, V_2O_5: 32.20/32.09, ZrO_2: 21.00/20.72, TiO_2 : 13.20/12.93, MoO_3 : 23.40/23.08, U_3O_8: 110.00/109.35]. From the thermal decomposition data various kinetic and thermodynamic parameters such as energy of activation (Ea), frequency factor (Z) and entropy change (ΔS) have been evaluated by employing Horowitz-Metzger method [XXVIII] 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 [XXIX].

Electrical Conductivity study

The electrical conductivity of all polychelates (table no. 1) show a tendency to increase by raising temperature which is shown in figure 2. The electrical conductivity of these polychelates lies in the range $2.68 \times 10^{-9} – 8.77 \times 10^{-13} \Omega^{-1} cm^{-1}$at 373 K. The order of electrical conductivity of BNBSAP polychelates at 373 K is found to be BNBSAP >Zr(IV) > VO(IV) > UO_2(VI) >Mn(III) > MoO_2(VI) > Fe(III) > Cr(III) > Ti(III). The activation energy of electrical conduction of these polychelatesis found to be in the range (0.892-1.217 eV) and increase in the order BNBSAP >Cr(III) >Zr(IV) > Fe(III) > VO(IV) > Ti(III) > MoO_2(VI) > UO_2(VI) >Mn(III). The increases start 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 [XXX]. The polychelates possess lower electrical conductivities 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 compounds .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 [XXX].

Biological study

Antibacterial screening of BNBSAP and its polychelates against *E. coli, S. abnoy, S. aeruginosa, B. subtilis* and antifungal activity against the fungi *A. niger*and*C. Albicas*were carried out. The results (figure 3 and table 4) reveals that ligand BNBSAP shows moderate activity against the bacterial and fungal strains. Cr(III), Fe(III), Ti(III), VO(IV) and MoO_2(VI) polychelates showed maximum antibacterial activity while polychelates of Ti(III), Mn(III), Fe(III) and Zr(IV) showed moderate antifungal activity. Fe(III) and Ti(III) polychelates show maximum antibacterial activity against *E.coli.*whereas Cr(III), VO(IV) and MoO_2(VI) polychelates shows good antibacterial activity against *B.subtilis* and fungal strain *C.albicans.* From the above results, it can be concluded that the ligand BNBSAP as well as its polychelates showed biocidal nature against all the micro-organisms studied. In general the results reveal that, the activity of the BNBSAPligand was found to be enhanced on complexation with metal ions. It has been observed that the metal complex polymershow enhanced antibacterial activity as compared to the free ligand against the same organism under identical experimental conditions. This is because of the chelation. According to Tweedy's chelation theory [XXXI], 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 [XXXII,XXXIII]. 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

Various physicochemical methods suggest that square pyramidal structure for Mn(III) and VO(IV) polymer, whereas octahedral to Ti(III), Cr(III), Fe(III), MoO_2(VI), Zr(IV) and UO_2(VI) polychelates as shown in fig. 4. IR spectra display the characteristic features of the Schiff base and indicate that ligand acts as dibasic in nature, coordinating via phenolic oxygen and azomethine nitrogen atoms. 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 sparingly soluble in common organic solvents. The extended nature of TG curves showing decomposition in a wide temperature range also indicating their polymeric nature.

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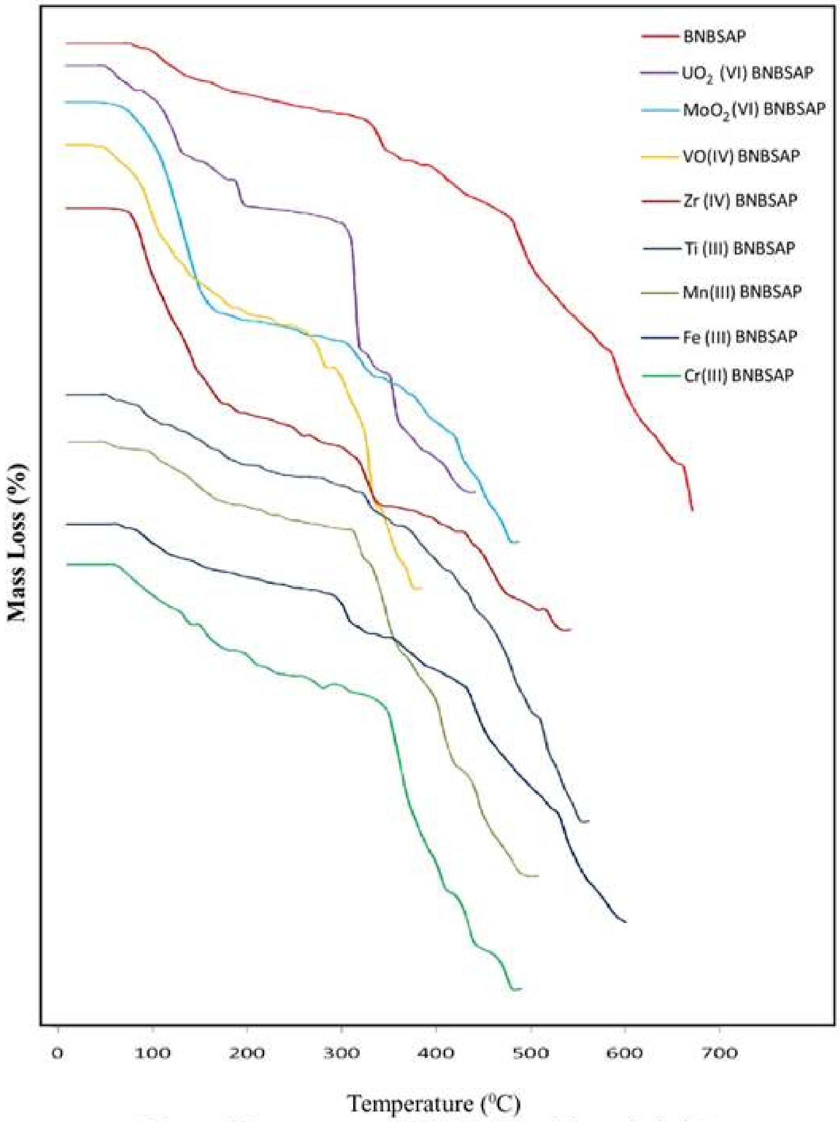


Fig. 1 Thermograms of BNBSAP and its polychelates

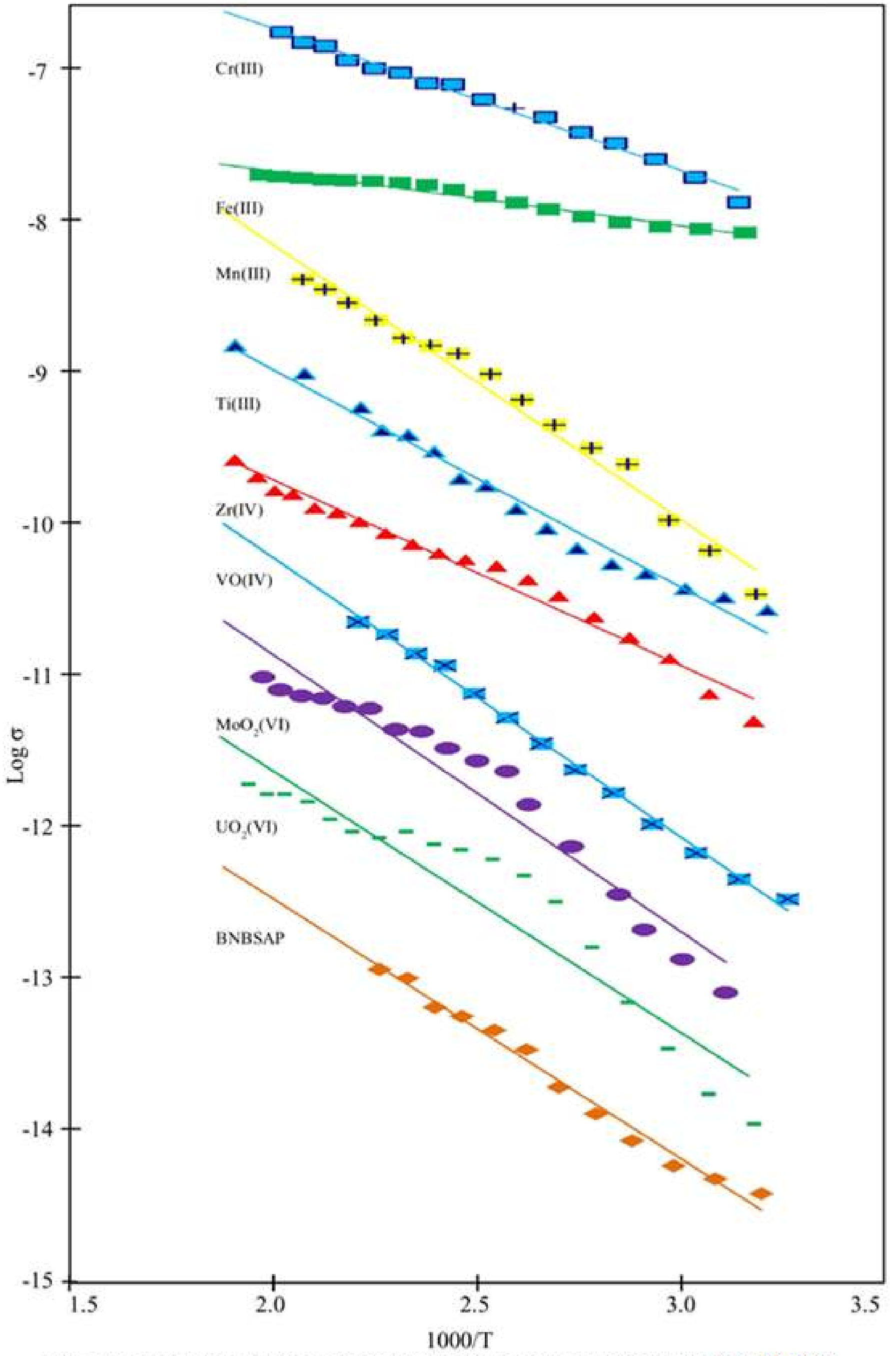


Fig. 2 SOLID STATE CONDUCTIVITY OF BNBSAP AND IT'S polychelates

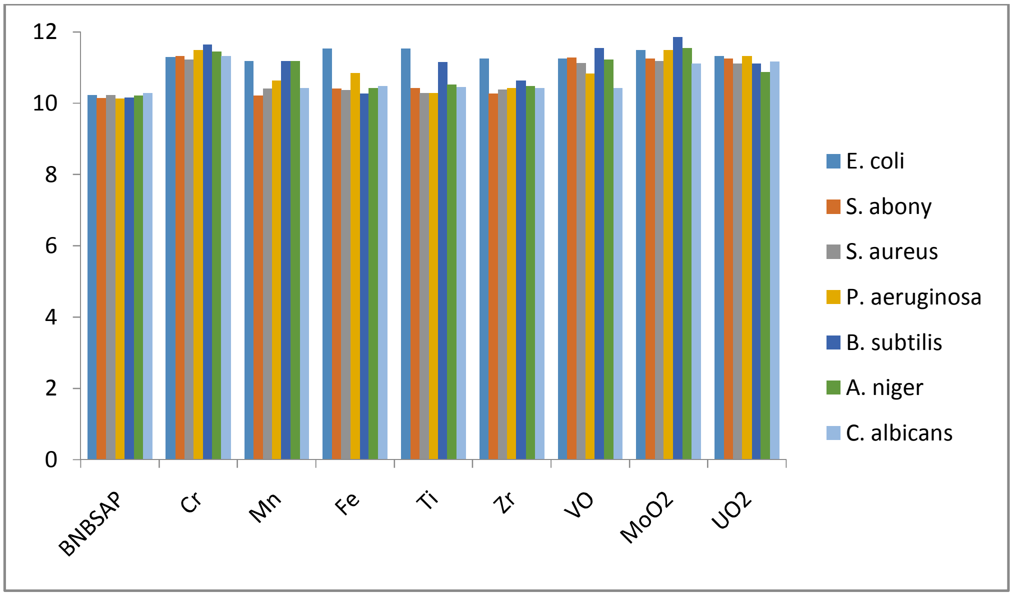
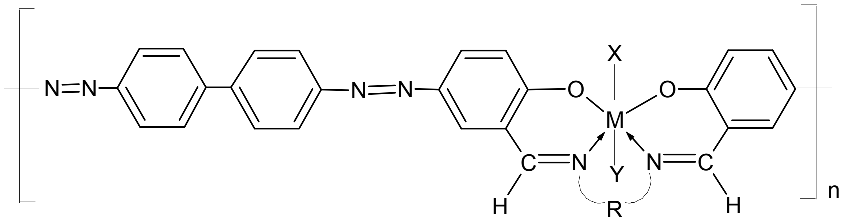
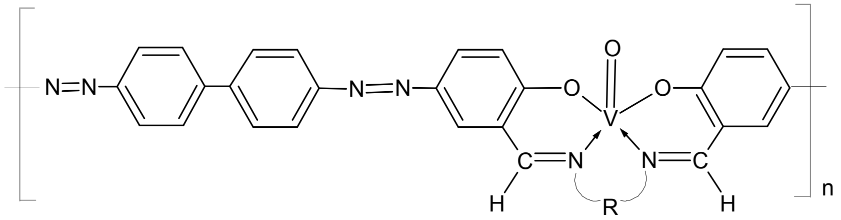


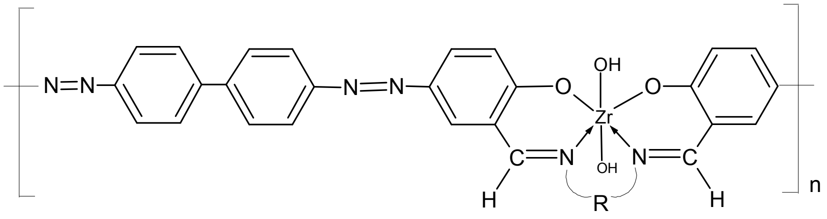
Fig. 3 Antimicrobial activity of BNBSAP and its polychelates



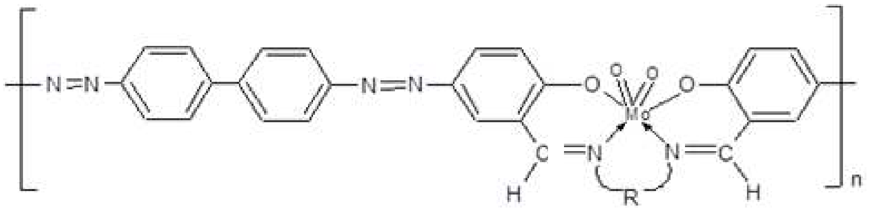
M = Cr(III), Fe(III) and Ti(III) polychelate X and Y = H_2O



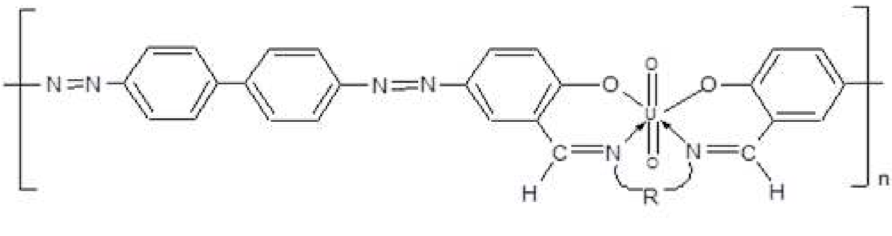
VO(IV) polychelate



Zr(IV)polychelate



MoO_2(VI) polychelate



UO_2(VI) polychelate

Fig. 4 Probable Structures of polychelates

Table 1: Analytical and electrical conductivity data of BNBSAPand its polychelates

Sr. No.	Proposed composition of the polychelates	σ ($\Omega^{-1}cm^{-1}$)	Ea (eV)	Band gap	Color	Elemental Analysis % Found (Calculated)			
						M	C	H	N
1	BNBSAP	$9.064x10^{-9}$	1.21	2.42	Dark brown	--	71.70 (71.71)	5.12 (5.17)	16.70 (16.73)
2	$\{[Cr\ BNBSAP.2H_2O]Cl\}_n$	$1.34\ x10^{-12}$	0.329	0.658	Dark brown	8.30 (8.34)	57.50 (57.78)	3.80 (3.85)	13.40 (13.48)
3	$[MnBNBSAP.OAc]_n$	$1.77\ x10^{-12}$	0.332	0.664	Brown	8.80 (8.95)	58.60 (58.63)	3.80 (3.90)	13.60 (13.68)
4	$\{[Fe\ BNBSAP.2H_2O]Cl\}_n$	$9.22\ x10^{-11}$	0.892	1.78	Brown red	8.90 (8.93)	57.12 (57.41)	3.65 (3.82)	13.25 (13.39)
5	$[VO\ BNBSAP]_n$	$8.77\ x10^{-13}$	0.396	0.792	Brown red	8.87 (8.99)	63.40 (63.49)	4.10 (4.23)	14.50 (14.81)
6	$[Zr(OH)_2\ BNBSAP]_n$	$2.68\ x10^{-9}$	0.329	0.658	Dark brown	15.60 (15.65)	56.80 (56.87)	3.65 (3.79)	13.20 (13.27)
7	$\{[Ti\ BNBSAP.2H_2O]Cl\}_n$	$2.24\ x10^{-11}$	0.349	0.698	Dark brown	7.70 (7.75)	57.99 (58.15)	3.70 (3.87)	13.58 (13.57)
8	$[MoO_2\ BNBSAP]_n$	$1.46\ x10^{-12}$	0.430	0.860	Dark brown	15.20 (15.28)	57.30 (57.32)	3.80 (3.82)	13.20 (13.27)
9	$[UO_2\ BNBSAP]_n$	$5.61\ x10^{-11}$	0.605	1.21	Dark brown	30.85 (30.90)	46.70 (46.75)	3.10 (3.11)	10.80 (10.90)

Table 2: IR Spectral data (cm^{-1}) of BNBSAP 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_2O/OAc/OH
1.	BNBSAP	3397	1634	1281	-	-	-	-	-	-
2.	$\{[Cr.BNBSAP.2H_2O]Cl\}_n$	-	1615	1300	555	480	-	-	-	3350, 1650, 835
3.	$\{[Fe.BNBSAP.2H_2O]Cl\}_n$	-	1615	1310	530	475	-	-	-	3400, 1655, 830
4.	$[Mn.BNBSAP.OAc]_n$	-	1610	1315	540	480	-	-	-	1530, 1390, 660
5.	$\{[Ti.BNBSAP.2H_2O]Cl\}_n$	-	1590	1290	525	485	-	-	-	3375, 1660, 825
6.	$[Zr(OH)_2BNBSAP]_n$	-	1600	1305	535	470	-	-	-	1135
7.	$[VO.BNBSAP]_n$	-	1590	1300	530	480	971	-	-	-
8.	$[MoO_2BNBSAP]_n$	-	1590	1310	525	485	-	895	-	-
9.	$[UO_2BNBSAP]_n$	-	1590	1315	410	475	-	-	915	-

Table 3: Thermal decomposition data of BNBSAP and its polychelates

Sr. No.	Compound	Half decom-position temp. (^oC)	Activation energy Ea (kJ mol^{-1})	Frequency factor Z (sec^{-1})	Entropy change -ΔS (Jmol^{-1}K^{-1})	Free energy change ΔG (kJmol^{-1})
1	BNBSAP	530	18.42	14.38	-38.57	21.57
2	$\{[Cr\ BNBSAP.2H_2O]Cl\}_n$	380	16.85	18.20	-39.27	19.18
3	$[MnBNBSAP.OAc]_n$	340	19.67	14.20	-37.71	23.77
4	$\{[Fe\ BNBSAP.2H_2O]Cl\}_n$	400	14.83	18.20	-31.95	25.56
5	$[VO\ BNBSAP]_n$	540	20.66	19.51	-36.36	21.86
6	$[Zr(OH)_2\ BNBSAP]_n$	350	23.59	22.02	-32.33	23.35
7	$\{[Ti\ BNBSAP.2H_2O]Cl\}_n$	360	22.21	18.07	-34.51	22.21
8	$[MoO_2\ BNBSAP]_n$	370	18.75	14.18	-28.13	27.41
9	$[UO_2\ BNBSAP]_n$	390	16.54	13.07	-25.17	26.54

Table 4: Antimicrobial Activity of BNBSAP 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	BNBSAP	10.22	10.14	10.22	10.12	10.16	10.21	10.28
2	$\{[Cr\ BNBSAP.2H_2O]Cl\}_n$	11.29	11.32	11.22	11.48	11.64	11.44	11.32
3	$[Mn\ BNBSAP.OAc]_n$	11.18	10.21	10.41	10.62	11.18	11.17	10.42
4	$\{[Fe\ BNBSAP.2H_2O]Cl\}_n$	11.52	10.41	10.36	10.84	10.26	10.42	10.48
5	$[VO\ BNBSAP]_n$	11.52	10.42	10.28	10.28	11.14	10.52	10.44
6	$[Zr(OH)_2\ BNBSAP]_n$	11.24	10.26	10.38	10.42	10.62	10.48	10.42
7	$\{[Ti\ BNBSAP.2H_2O]Cl\}_n$	11.24	11.28	11.12	10.82	11.54	11.22	10.42
8	$[MoO_2\ BNBSAP]_n$	11.48	11.24	11.18	11.48	11.84	11.54	11.10
9	$[UO_2\ BNBSAP]_n$	11.32	11.24	11.10	11.32	11.10	10.87	11.16

Concentration: 100 µg/ml