Synthesis, characterization, electrical and biological studies of Cr(III), Mn(III), Fe(III), Ti(III), VO(IV), Th(IV), Zr(IV) and UO₂(VI) polychelates with bis-bidentate Schiff base

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The polychelates of Cr(III), Mn(III), Fe(III), Ti(III), VO(IV), Th(IV), Zr(IV) and UO₂(VI) with bis-bidentate Schiff base derived from 4,4'-bis[salicylaldehyde-5]-azo diphenyl methane and aniline have been synthesized. The resulting compounds have been characterized on the basis of elemental analyses, reflectance and infrared spectral studies, magnetic measurements and thermogravimetric analysis and are found to have the general formula [M(BPSADM)x(H₂O)]. The ligand (H₂BPSADM) acts as a bis-bidentate molecule coordinating through the phenolic oxygen and azomethine nitrogen atoms. The thermal data have been analyzed for the kinetic parameters by using Broido’s method. The thermal stability of these chelates decreases in the order Zr(IV) > Th(IV) > Cr(III) > Fe(III) > VO(IV). The thermal activation energy lies in the range 38.68 to 55.18 kJ mol⁻¹ and the decomposition follows first order kinetics. The solid state properties of the ligand and its polychelates have been studied over the temperature range 313-493 K and the chelates are found to show semiconducting behaviour. The activation energy of the electrical conduction lies in the range 0.912 to 0.315 eV. The ligand and its polychelates have also been screened for their antimicrobial activities using various microorganisms and all of them have been found to be moderately active against the organisms.

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The polychelates derived from bis-ligands have received much attention in recent years due to their semiconducting, catalytic and biological properties. Studies on the divalent metal chelates with symmetric as well as unsymmetric Schiff base ligands have been reported extensively due to their biological relevance. Even metal complexes of ligand having azo groups find a place in the literature due to their use as model biological systems. But the literature on metal complexes with Schiff base ligands having azo groups is limited. In view of the above significant properties, therefore it was worthwhile to study the polychelates of tri-, tetra- and hexavalent metal ions with Schiff base ligand containing an azo group. In the present work we describe the synthesis of 4,4'-bis[(N-phenyl salicylaldimine-5)-azo] diphenyl methane [H₂BPSADM] (structure I) and its polychelate with Cr(III), Mn(III), Fe(III), Ti(III), VO(IV), Th(IV) and UO₂(VI) ions and their characterization by elemental analyses, magnetic susceptibilities, diffuse reflectance and IR spectral studies in conjunction with thermogravimetric analysis and solid state conductivity measurements. The antimicrobial activity of the ligand as well as chelates against S. aureus, E. coli, S. typhi and P. aeruginosa have also been reported.

Experimental

All the chemicals used were of A R grade. Solvents were purified and dried before use according to standard procedure. The metal salts used were chromium chloride hexahydrate, manganese triacetate dihydrate, ferric chloride, vanadyl sulphate pentahydrate, zirconylchloride octahydrate, thorium nitrate pentahydrate, titanium chloride and uranyl nitrate hexahydrate. Salicylaldehyde (E Merck, India) and diamino diphenyl methane (Fluka, Switzerland) were used. The IR spectra (KBr) were recorded on a Perkin-Elmer-842 spectrophotometer in the 400-4000 cm⁻¹ region at RSIC, Punjab University, Chandigarh. The ¹H NMR spectrum of ligand was taken in d₆-DMSO using TMS as an internal standard on a 90 MHz Perkin-Elmer R-32, spectrophotometer. The reflectance spectra of the solid compounds suitably diluted with MgO, were recorded on a Carl-Zeiss, DMR-21 spectrophotometer at RSIC, IIT, Chennai. Thermogravimetric analysis of the chelates were carried out on a simple manually operated thermobalance fabricated in our laboratory. The instrument was calibrated using crystallised copper sulphate pentahydrate. Samples were run under a dynamic air atmosphere, with a heating rate of 10°C min⁻¹. Magnetic measurements were carried out at room temperature by Gouy method using Hg[Co(SCN)₄] as calibrate. The diamagnetic

[Diagram of H₂BPSADM (I)]
correction of metal-ligand system was calculated using the Pascal’s constant. Microanalysis of C, H and N was carried out at the RSIC, Punjab University, Chandigarh. The metal contents were determined by standard method after decomposing chelates with conc. HNO₃. The solid state conductivity was measured in their pellet form using micro voltmeter over 313-493 K temperature range. The biological screening of the ligand and chelates was carried out using disc diffusion method.

**Synthesis of 4,4’-bis[salicylaldehyde-5]-azo] diphenyl methane**

A prediazotised solution of 4,4’-diaminodiphenyl methane (10.4 g) was added slowly into a cold solution (0±1°C) of salicylaldehyde (6.1g) in sodium carbonate (23 g) and water (100 ml) with constant stirring. The stirring was continued further for 3.5 h. The complete conversions to an intermediate compounds took place when there was no blue colour with alkaline ‘H’ acid. To this mixture a second mole of well stirred salicylaldehyde (6.1g) in the minimum quantity of sodium hydroxide solution was added slowly and stirring was continued until the reaction was complete. Then the reaction mixture was acidified with cold, dilute hydrochloric acid. The precipitated azo compound was filtered, washed with hot water and air dried. Yield: 75 %, m.p. 220°C.

**Synthesis of H₂BPSADM**

To a refluxing methanolic (30 ml) solution of 4,4’-bis-[salicylaldehyde-5]-azo] diphenyl methane (2.5 g, 0.005 mol), an ethanolic solution (25 ml) of aniline (1g, 0.01 mol) was added in 1:2 molar ratio. A drop of conc. H₂SO₄ was added as a catalyst and the reaction mixture was further refluxed on a water bath for 3 h. The solution was cooled and the isolated leaf brown solid was filtered, washed with water, ethanol and methanol and recrystallized from 1:1 DMF-ethanol mixture, yield: 65%, m.p 290°C.

**Synthesis of polychelates**

All the metal polychelates were isolated by the following general method. To a solution of the ligand (0.005 mol) in DMF (25 ml), a solution of the metal salt (0.005 mol) in ethanol (25 ml) was added with constant stirring. The reaction mixture was refluxed on an oil bath for 3-4 h. The coloured products obtained were filtered, washed thoroughly first with hot water, DMF and ethanol and finally with acetone to remove unreacted reactants and dried in an electric oven at 80°C to constant weight, Yield: 70-75%.

**Results and discussion**

The reaction of 4,4’-bis[salicylaldehyde-5]-azo] diphenyl methane with aniline yield the Schiff base I (H₂BPSADM), the formulation of which is supported by analytical and spectral data. The ¹H NMR spectrum of a ligand in DMSO-d₆ shows signals at δ7.60 and 9.99 ppm due to azomethine H(C=N) and phenolic group protons. This ‘downfield phenomenon’ is attributed to the existence of hydrogen bonding in ligand. The Schiff base displays a multiplet at 6.80-7.31 ppm and a singlet at 1.25 ppm due to aromatic protons and methylene protons respectively. The IR spectrum of the ligand shows bands at 3025, 1614, 1250 and 1508 cm⁻¹ corresponding to u(0H), u(C=N), u(C-O) and u(N=N) groups, respectively.

The reaction of Schiff base with metal ions yielded polychelates, which are found to be quite stable in atmosphere and non-hygroscopic in nature. The analytical data (Table 1) indicates that the metal-ligand stoichiometry is 1:1 in all the polychelates. The resulting polychelates are found to be coloured solids and insoluble in water and most of the organic solvents but are sparingly soluble in DMF and DMSO only.

The ligand H₂BPSADM shows a medium broad band at 3020 cm⁻¹ which may be assigned to the phenolic OH stretching vibrations. The stretching frequency for the free OH occurs at 3600 cm⁻¹. The observed shift to lower frequency indicating the presence of intramolecular hydrogen bonding as part of a resonating ring system. This band disappears in spectra of all polychelates indicating the dissociation of phenolic hydrogen with bond formation between metal and oxygen. This is further supported by the shift to higher frequency (14-45 cm⁻¹) of u(C-O) vibrations from 1250 in ligand to 1254-1295 cm⁻¹ in the polychelates and also confirmed by the appearance of a new, low-intensity band in the region at 506-590 cm⁻¹ in the spectra of the polychelates due to u(M-O) vibrations. A strong and sharp band at 1614 cm⁻¹ in the spectrum of the ligand due to u(C=N), shows a shift to lower frequency by 20-24 cm⁻¹ in the spectra of all polychelates, which indicates the coordination of azomethine nitrogen to the metal ions. This is again supported by the appearance of a new, low-intensity band in the region 406-460 cm⁻¹ in the polychelates are attributable to u(M-N) vibrations. A moderately sharp band occurs at 1508 cm⁻¹ in the spectra of ligand and polychelates due to u(N=N) and
no change in its position suggests the indifferent nature of the azo group towards coordination. In the oxovanadium(IV) and dioxouranium(VI) polychelates strong bands at 960 and 913 cm\(^{-1}\) are assigned to \(\nu(\text{V=O})\) and \(\nu(\text{O=U=O})\) modes, respectively. Broad and strong bands in the polychelates of Cr(III), Fe(III), VO(IV), Zr(IV), Th(IV) and Ti(III) in the region 3395-3401 cm\(^{-1}\) due to \(\nu(\text{OH})\) and sharp shoulder at 1640-1648 cm\(^{-1}\) due to \(\nu(\text{H}_2\text{O})\) indicate the presence of water molecules and a strong sharp band at 835 cm\(^{-1}\) due to the (H\(_2\)O) rocking mode suggests these water molecules as coordinated ones. The Mn(III) polychelates show two additional bands at 1520 and 1391 cm\(^{-1}\) due to \(\nu_\text{as}(\text{O=C=O})\) and \(\nu_\text{as}(\text{O=C=O})\) stretching frequency, respectively of acetato group. The difference between \(\nu_\text{as}\) and \(\nu_\text{as}\) of 129 cm\(^{-1}\) indicates that the acetato group is coordinated as a monodentate ligand, it further exhibits a band at 666 cm\(^{-1}\) due to \(\delta(\text{OCO})\) which is considered a diagnostic band for a monodentate ligand. Thus, the IR data suggest that the Schiff base behaves as a dibasic, bis-bidentate nature of the ligand and its coordination to metal ions through the phenolic oxygen and azomethine nitrogen atoms.

The diffuse reflectance spectrum of the Cr(III) chelate exhibits three bands at 16,880, 22830 and 24980 cm\(^{-1}\) which may be assigned to \(^4\!A_{2g} \rightarrow ^4T_{1g}(F)\) and \(^4\!A_{2g} \rightarrow ^4T_{2g}(P)\) transitions, respectively for an octahedral stereochemistry. Cr(III) chelate has magnetic moment 3.85 B.M. in accordance with the spin only value for three unpaired electrons corresponding to high-spin octahedral Cr(III) complexes. The magnetic moment of Mn(III) polychelate was found to be 4.92 B.M. suggesting presence of four unpaired electrons. Mn(III) polychelate shows bands at 13530, 16530, 18080, and 28370 cm\(^{-1}\) due to \(^5\!B_1 \rightarrow ^5\!B_2\), \(^5\!B_1 \rightarrow ^5\!A_1\), \(^5\!B_1 \rightarrow ^5\!E\) and LMCT transitions, respectively towards square pyramidal geometry. The Fe(III) chelate has magnetic moment 5.19 B.M. suggesting the presence of five unpaired electrons and high spin octahedral geometry. The electronic spectrum of Fe(III) chelate exhibits three bands at 10,890, 23095 and 28,490 cm\(^{-1}\) assignable \(^6\!A_{1g} \rightarrow ^4T_{1g}, ^6\!A_{1g} \rightarrow ^4T_{2g}, ^6\!A_{1g} \rightarrow ^4E_g\) transitions, respectively in an octahedral geometry. The observed magnetic moment of VO(IV) polychelate is 2.00 B.M. The higher value of magnetic moment may be due to the presence of orbital contribution. Its electronic spectrum shows three bands at 10845, 19230 and 26180 cm\(^{-1}\) corresponds to transitions, \(d_{x^2-y^2}(b_2) \rightarrow d_{xy}(e_g)\), \(d_{x^2-y^2}(b_2) \rightarrow d_{xy}(b_1)\) and \(d_{xy}(b_2) \rightarrow d_{xy}(a_1)\), respectively, towards octahedral geometry. The electronic spectrum of Ti(III) chelate shows only one broad band at 18,450 cm\(^{-1}\) due to \(^2\!T_{2g} \rightarrow ^2E_g\) transition for

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**Table 1—Analytical, thermal and electrical data of the polychelates**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound</th>
<th>Metal (Calcd.)</th>
<th>(\mu) eff (BM)</th>
<th>Decomp. temp. (°C)</th>
<th>(E_a) kJ mol(^{-1})</th>
<th>E.C. Cond. ((\Omega^{-1}) cm(^{-1}))</th>
<th>(E_a) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H(_2)BPSADM</td>
<td>Leaf Brown</td>
<td>-</td>
<td>260</td>
<td>41.50</td>
<td>4.67 \times 10^{-12} (_a)</td>
<td>0.429</td>
</tr>
<tr>
<td>2</td>
<td>[(Cr(BPSADM)(_2))(H(_2)O)(_2)]</td>
<td>Gray Brown</td>
<td>7.33</td>
<td>38.5</td>
<td>315</td>
<td>55.18</td>
<td>4.37 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>3</td>
<td>[(Mn(BPSADM)(OAC))(_n)]</td>
<td>Light Brown</td>
<td>7.37</td>
<td>49.2</td>
<td>325</td>
<td>52.20</td>
<td>3.85 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>4</td>
<td>[(Fe(BPSADM)(H(_2)O)(_2)]</td>
<td>Black Brown</td>
<td>7.77</td>
<td>59.1</td>
<td>285</td>
<td>42.76</td>
<td>3.06 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>5</td>
<td>[(VO(BPSADM)(H(_2)O)]</td>
<td>Light Brown</td>
<td>7.03</td>
<td>2.00</td>
<td>280</td>
<td>50.15</td>
<td>1.62 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>6</td>
<td><a href="H(_2)O">(Zr(BPSADM)</a>(_2)]</td>
<td>Sand Stone</td>
<td>12.00</td>
<td>2.34</td>
<td>330</td>
<td>41.43</td>
<td>2.22 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>7</td>
<td>[(Th(BPSADM)(H(_2)O)(NO(_3))(_2)]</td>
<td>Black Brown</td>
<td>26.67</td>
<td>2.96</td>
<td>322</td>
<td>42.50</td>
<td>2.96 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>8</td>
<td>[(Ti(BPSADM)(H(_2)O)]</td>
<td>Sand Stone</td>
<td>6.44</td>
<td>2.01</td>
<td>290</td>
<td>38.65</td>
<td>2.96 \times 10^{-12} (_a)</td>
</tr>
<tr>
<td>9</td>
<td>[(UO(_2)(BPSADM))]</td>
<td>Black Brown</td>
<td>26.50</td>
<td>2.53</td>
<td>320</td>
<td>99.34</td>
<td>2.53 \times 10^{-12} (_a)</td>
</tr>
</tbody>
</table>

\(a = 40^\circ\text{C}, b = 220^\circ\text{C}\)
an octahedral geometry. The broad and double hump nature of the Ti(III) spectrum indicates the presence of Jahn-Teller distortion. It has magnetic moment 2.01 B.M. The Zr(IV), Th(IV) and UO₂(VI) polychelates as expected, are diamagnetic in nature and their electronic spectra do not furnish any characteristic d-d transitions except charge transfer bands.

The thermogravimetric analysis of polychelates indicate that they decompose in two stages. The rate of thermal degradation of the ligand is more than that of polychelates. It is also observed that there is no weight loss up to 100°C indicating the absence of lattice water molecules in all chelates. In the case of the Cr(III), Fe(III), Zr(IV), Th(IV) and Ti(III) polychelates elimination of two coordinated water molecule takes place between 140-220°C, while the VO(IV) polychelate loses one coordinated water molecules in this range. The polychelates of Mn(III) and UO₂(VI) show negligible weight loss up to 200°C indicating the absence of any water molecules. Once the coordinate water was eliminated, the chelates remain stable for a short while and thereafter the second stage of degradation starts in which the weight loss occurs continuously at higher rate till a constant weight was obtained at 580-700°C due to the formation of stable metal oxides. The thermal stability of the chelates decreases in the order Zr>Mn>Th>UO₂>Cr>Ti>Fe>VO. The order of thermal decomposition and corresponding activation energies have been evaluated from the figures generated using Broiido's equation. The plots of ln [ln (t/y)] vs 1/T were found to be linear corresponding to first order kinetics. The slope of plots yields the thermal activation energy (Ea) of decomposition which lies between 38.65 - 53.15 kJ mol⁻¹.

The solid state conductivity of the ligand and its polychelates was studied over a 313-493 K temperatures range. The room temperature conductivity (σ) of the polychelates lies in the range 3.63 x 10⁻¹⁰ to 1.62 x 10⁻¹² cm⁻¹ suggesting their semiconducting nature. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relation σ=σ₀ exp(-Ea/kT), where σ₀ is constant, Ea activation energy of conduction process, T is absolute temperature and K is Boltzman constant. When logσ is plotted against 1/T a linear dependence was observed, also suggesting the semiconducting behaviour of the ligand and its polychelates. The lower temperature region has lower slopes with lower Ea values, whereas higher temperature region has higher slopes and higher energy of activation. This break observed in plots i.e. phase transition in case of the ligand may be attributed to two molecular structures having keto and enol forms which exchange the conduction at different thermal stabilities (Structure II). Since there is no significant difference in the conductivity values of the diamagnetic and paramagnetic chelates. It may be presumed that similar types of conduction mechanisms exist in all chelates.

The antimicrobial activity of ligand and its chelates has been studied by disc diffusion method. Seven days old cultures of E.coli, S. typhi, S. aureus and P. aeruginosa were used as test organisms which were grown on nutrient agar (NA) medium. Solutions of the complexes (1 µg/ml) in DMSO were used for the studies. Growth was compared with DMSO as control and growth inhibition zone diameters were measured in mm. The free ligand shows less activity towards all the species (growth inhibitor zone 6-7 mm) than the chelates. Titanium chelate shows very high activity (9-12 mm), whereas polychelates of Cr(III), Mn(III) and Fe(III) show moderate activity. The other polychelates are less active towards the microorganisms. In general, E. coli was found to be more sensitive toward all the complexes, while S. typhi is least affected by the polychelates. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells. Normally the inhibition activity of the compounds increases with increase in the concentration of the solution.

Conclusion
The formation of polymeric chain may be expected for a ligand with two chelating sites which for a sterical reason can not interact with the same metal ions. The formation of chelate polymer is also supported by the fact that all the chelates obtained are coloured amorphous solid and insoluble in water and common organic solvents. The extended nature of TG curves with a very slow decomposition in a wide range of temperature also indicates their polymeric nature. On
the basis of physicochemical studies, all the polychelates may have octahedral geometry except Mn(III) chelate, which may have square pyramidal structure and the general Structure (III) has been proposed for the polychelates.

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\begin{align*}
\text{For } M = \text{Cr(III), Fe(III), Zr(IV), Th(IV), Ti(III), Zn(II), X= Y = H, O} \\
\text{VO(IV)} : & \quad X = H_2O \text{ and } Y = O \\
\text{Mn(III)} : & \quad X = OAc \text{ and } Y = N\text{H} \\
\text{UO(VI)} : & \quad X = Y = O
\end{align*}
\]

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References