Synthesis and characterization of dioxouranium(VI), oxovanadium(IV), thorium(IV), zinc(II), cadmium(II), mercury(II) and lead(II) complexes with propylenediamine-bis(isatin) Schiff base

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Some metal complexes of propylenediamine-bis(isatin) Schiff base ligand with dioxouranium(VI), oxovanadium(IV), Th(IV), Zn(II), Cd(II), Hg(II) and Pb(II) have been prepared and characterized by elemental analysis, IR, UV-visible, NMR spectra as well as molar conductivity and magnetic measurements. The data suggest a 1:1 (metal: ligand) stoichiometry for all the isolated complexes. The ligand behaves as neutral ONNO quadridentate for all chelates except for those prepared from the direct reaction of the free ligand with dioxouranium(VI), Zn(II) and Pb(II) where the ligand acts as dibasic quadridentate.

Although much attention has been directed to study the metal complexes of the Schiff base ligands derived from isatin7-12, no investigations have appeared in literature to describe the metal complexation of Schiff bases derived from isatin with aliphatic diamines. In view of the versatile importance of isatinSchiff bases derived from isatin with aliphatic diamines. In view of the versatile importance of isatin, we herein, deemed desirable to report the synthesis and characterization of the metal complexes of the Schiff base ligand formed by condensation of twofold amounts of isatin with propylenediamine.

**Experimental**

*Preparation of the propylenediamine-bis(isatin) Schiff base ligand*

A solution of isatin (0.02 mol) in pure ethanol (50 ml) was added dropwise at the ambient temperature to a solution of propylenediamine (0.01 mol) in ethanol (20 ml) with continuous stirring. The reaction mixture was refluxed on steam bath for 1 h and then concentrated in vacuo. The resulting reddish brown precipitate was filtered off and washed with ethanol and then dried in vacuo.

***Preparation of complexes by in situ method***

The following general procedure was adopted for the preparation of all the complexes. The metal salts viz., $\text{UO}_2(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, $\text{VOSO}_4\cdot 5\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2\cdot \text{H}_2\text{O}$, $\text{ThCl}_4$, $\text{HgCl}_2$ and $\text{Pb}(\text{CH}_3\text{COO})_2\cdot 3\text{H}_2\text{O}$, dissolved in water or ethanol (50 ml) were added to a solution of propylenediamine and isatin in ethanol (100 ml), the molar ratio being 1:1:2 (metal: propylenediamine: isatin). In case of oxovanadium complex, $\text{VOSO}_4\cdot 5\text{H}_2\text{O}$ was dissolved in a 1:1 hot mixture of $\text{CH}_3\text{OH}$ and $\text{CHCl}_3$. The resulting solution was heated under reflux with continuous stirring for 2 h. On cooling, the precipitate appeared which was filtered and washed with distilled water and then with absolute ethanol and dried in vacuo.

***Synthesis of dioxouranium(VI), Zn(II) and Pb(II) complexes***

To a solution of $\text{UO}_2(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, and $\text{Pb}(\text{CH}_3\text{COO})_2\cdot 3\text{H}_2\text{O}$ (0.01 mol) in ethanol (50 ml) was added to a solution of the ligand (0.01 mol) in DMF (50 ml). The reaction mixture was refluxed with stirring for 2 h. On concentration, the complexes were precipitated which were filtered off, washed with ethanol followed by ether and then dried in vacuo.

***Synthesis of oxovanadium(IV), Cd(II), Th(IV) and Hg(II) complexes***

To a suspension of propylenediamine-bis(isatin) ligand (0.01 mol) in ethanol (50 ml), was added a solution of $\text{CdCl}_2\cdot \text{H}_2\text{O}$, $\text{ThCl}_4$, and $\text{HgCl}_2$ (0.01 mol) respectively in water (30 ml) or a solution of $\text{VOSO}_4\cdot 5\text{H}_2\text{O}$ (0.01 mol) in a 1:1 hot mixture of $\text{CH}_3\text{OH}$ and $\text{CHCl}_3$ (40 ml). The reaction mixture was refluxed for 2 h with continuous stirring. On cooling, the precipitated complexes were filtered off, washed with ethanol followed by ether and dried in vacuo. These isolated complexes were found to be identical with those prepared by the in situ method as will be discussed later.
The electronic spectra of the resulting solid complexes in nujol mull were measured on Shimadzu UV-160A UV-visible recording spectrophotometer. The IR spectra were measured as KBr discs on Pye Unicam SP 1025 spectrometer. The conductivity measurements in freshly prepared DMF solution were made at ambient temperature using a YSI Model 35 conductance meter. The PMR spectra in deuterated DMSO were measured on a Varian EM 390 NMR Spectrophotometer. The chemical shifts are reported in δ ppm downfield from internal TMS. The magnetic measurements were determined by Faraday technique at 25°C.

Results and discussion
On the basis of the analytical data obtained (Table 1) for the resulting solid complexes, it was found that the complexes prepared by in situ method possess 1:1 (metal:ligand) stoichiometry of the general formula $M(H_2L)_mX_n\cdot nH_2O$ where $M=UO_2^{2+}, VO_2^{2+}, Th^{4+}, Zn^{2+}, Cd^{2+}, Hg^{2+}$ and $Pb^{2+}$; $H_2L$ is propylenediamine-bis(isatin) schiff base ligand and $X=$ the anionic species of chlorides, acetates and sulphates. The conductivity values given in Table 1 for the investigated metal chelates imply that they behave as electrolytes in DMF solution at the ambient temperature. This result proposes that the anionic species of acetates, sulphates and chlorides are mostly ionically bonded to the central metal ions from the outer sphere of coordination corroborating the proposed formulation of these chelates suggested by the elemental analyses.

The analytical data (Table 1) also revealed that two different types of complexes were isolated. The metal acetates of dioxouranium(VI), $Zn$ (II) and $Pb$ (II) react with the free ligand yielding neutral complexes of the general formula $ML\cdot nH_2O$. These complexes possess molar conductivity values less than 20 ohm$^{-1}\cdot$ mol$^{-1}\cdot$ cm$^2$ suggesting their non-electrolytic nature. On the other hand, the reaction of $VO(SO_4)_2\cdot 5H_2O, CdCl_2\cdot H_2O$, $ThCl_4$ and $HgCl_2$ with the free ligand yields complexes of the general formula $M(H_2L)_m\cdot nH_2O$. Their analytical, conductivity, IR and electronic spectral data were found to be identical to the corresponding data obtained for the metal complexes prepared by the in situ method.

The infrared spectra of the solid metal chelates are characterized mainly by the bands in the regions 3120-3150, 1680-1700 and 1620-1600 cm$^{-1}$ which may be assigned to the stretching frequencies of NH and $C=O$ groups of isatin residue and the bridging azomethine $C=N$ groups. The appearance of these bands implies the formation of the expected propylenediamine-bis(isatin) schiff base ligand. The vibrational positions of these bands indicate the participation of both nitrogen atom of azomethine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (Calcd.), %</th>
<th>$\Lambda$ ohm$^{-1}\cdot$ mol$^{-1}\cdot$ cm$^2$</th>
<th>$\mu_{eff}$ B M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylenediamine-bis(isatin) schiff has ligand</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$UO_2(H_2L)(CH_3COO)_2\cdot 2H_2O$</td>
<td>36.3</td>
<td>4.2</td>
<td>7.3</td>
</tr>
<tr>
<td>$Hg(H_2L)Cl_2\cdot H_2O$</td>
<td>36.5</td>
<td>2.4</td>
<td>9.4</td>
</tr>
<tr>
<td>$VO(H_2L)SO_4\cdot H_2O$</td>
<td>44.1</td>
<td>3.3</td>
<td>10.7</td>
</tr>
<tr>
<td>$Zn(H_2L)(CH_3COO)_2\cdot 2H_2O$</td>
<td>50.2</td>
<td>4.4</td>
<td>10.4</td>
</tr>
<tr>
<td>$Cd(H_2L)Cl_2\cdot 4H_2O$</td>
<td>41.6</td>
<td>3.2</td>
<td>10.2</td>
</tr>
<tr>
<td>$Th(H_2L)Cl_4\cdot 4H_2O$</td>
<td>29.6</td>
<td>3.2</td>
<td>7.4</td>
</tr>
<tr>
<td>$Pb(H_2L)(CH_3COO)_2\cdot 2H_2O$</td>
<td>39.6</td>
<td>3.8</td>
<td>8.3</td>
</tr>
<tr>
<td>$Zn(L)\cdot 2H_2O$</td>
<td>52.63</td>
<td>4.32</td>
<td>12.75</td>
</tr>
<tr>
<td>$UO_3L\cdot 4H_2O$</td>
<td>33.65</td>
<td>3.42</td>
<td>8.59</td>
</tr>
<tr>
<td>$PbL\cdot 3H_2O$</td>
<td>38.29</td>
<td>3.56</td>
<td>9.73</td>
</tr>
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</table>
group and the oxygen atom of carbonyl group of isatin moiety in the coordination with the central metal ion. Thus, the present ligand behaves as ONNO quadridentate neutral ligand forming cationic complexes (Structure I). Such coordinative behaviour has been observed for several structurally related ONNO chromophoric type ligands prepared by the condensation of aldehydes or ketones with diamines\(^{22-27}\).

![Structure I](image)

The appearance of a broad band in the range 3100-3090 cm\(^{-1}\) in the spectra of chelates of Th\(^{4+}\), UO\(_2\)\(^{2+}\) and neutral complexes can suggest the existence of coordinated water molecules. This was also suggested by the microanalytical data. For dioxouranium(VI) complex, a strong band appeared in the region 880-900 cm\(^{-1}\) indicating the linearity of O = U = O moiety. For oxovanadium(IV) chelate, the band due to the \(v(V = O)\) is observed at 960 cm\(^{-1}\). It is worth mentioning that the bands in the regions 1370-1410 and 1530-1590 cm\(^{-1}\) assigned, respectively, to \(v_{sym}(C=O)\) and \(v_{as}(C=O)\) for Pb(II), Zn(II) and dioxouranium(VI) complexes, support the above conductivity and analytical data and substantiate the formation of the cationic complexes.

The IR spectrum of the free ligand exhibits a medium intensity band at 3190 cm\(^{-1}\) and two strong bands at 1740 and 1660 cm\(^{-1}\). These bands can be assigned to \(v_{NH}\), \(vC = O\) and \(vC = N\) respectively. In the IR spectra of M(L).\(nH_2O\) complexes, where M = dioxouranium(VI), Zn(II) and Pb(II), the absence of the bands in the regions 3140-3190, 1370-1410 and 1530-1590 cm\(^{-1}\) assignable to \(v_{NH}\), \(v_{sym}(C=O)\) and \(v_{as}(C=O)\) respectively indicates that the ligand, in these chelates, behaves as dibasic chelating agent towards the central metal yielding neutral complexes.

The \(^1\)H NMR spectrum of the free ligand exhibits two multiplets at 2.9-3.6 and 7.3-7.8 ppm and a doublet at 11.8-11.6 ppm corresponding, respectively, to resonances resulting from the aliphatic protons of propylene chain, protons of the fused aromatic nuclei of isatin residues and the NH proton belonging to isatin moieties. The integration of the above \(^1\)H NMR signals yields the proton ratio 3:4:1, respectively, which is consistent with the above assignments. In the \(^1\)H NMR spectra of the cationic diamagnetic chelates of the type M(H\(_2\)L)\(_{X_n}\).\(nH_2O\) where M = Zn(II), Cd(II), Pb(II), Hg(II), dioxouranium(VI), the appearances of a signal due to resonance of NH proton of isatin moiety at almost the same position is considered as an additional evidence for shifting the tautomeric lactam-lactim equilibrium toward the keto form indicating involvement of the oxygen atom of position 2 of isatin moiety as actual keto group. This supports the above infrared spectral results. It is worth mentioning that the signals due to CH\(_3\) protons of acetate groups in dioxouranium(VI), Zn(II) and Pb(II) chelates may be overlapped by the multiplets due to aliphatic protons of propylene chain. On the other hand, it was found that the \(^1\)H NMR spectra of the neutral diamagnetic chelates of the type ML.\(nH_2O\) where M = Zn(II), dioxouranium(VI) and Pb(II) are similar to those of the cationic complexes with the exception that the signal due to NH proton of isatin moieties disappeared. This result provides an evidence for the deprotonation of NH proton upon complexation and supports the above infrared spectral data that the ligand acts as dibasic chelating agent.

The oxovanadium(IV) complex is paramagnetic and possesses the ambient temperature magnetic moment value of 1.53 BM. It is slightly less than the spin only value for one unpaired electron. The low magnetic moment may be ascribed to antiferromagnetic coupling of spin\(^{28}\). The electronic spectrum of this complex exhibits two d-d absorption bands in the regions 13250 and 25620 cm\(^{-1}\) which may be assigned to the \(2B_1 \rightarrow 2E\) and \(2B_2 \rightarrow 2A_1\) transitions respectively in square-pyramidal geometry.

The magnetische measurements indicate that both dioxouranium(VI) and Th(IV) complexes are diamagnetic as generally expected for 5 \(\sigma\) compounds. The electronic spectrum of uranyl complex reveals that the ligation has a relatively minor influence and the electronic spectrum is mainly dependent upon the triatomic U\(_2\)O\(_2\) moiety. A band observed at 21739 cm\(^{-1}\) is attributable to the transition from apical oxygens to \(f\) orbitals of the uranyl moiety\(^{29}\) and charge transfer arising from the equatorial ligand orbitals to the 5\(f\) and/or 6\(d\) orbitals of uranium.

Thorium(IV) and dioxouranium(VI) complexes are assigned six and eight coordination numbers respectively. They attained their coordination numbers by coordinating to the water molecules as evidenced by both IR and analytical data. The absorption bands appearing at 28570, 23800 cm\(^{-1}\) for Zn(II) chelate; 29154, 22779 cm\(^{-1}\) for Cd(II)
chelate; 36200, 29411 cm\(^{-1}\) for Pb(II) chelate; 28409, 25316 cm\(^{-1}\) for Th(IV) chelate and at 32258, 29411 cm\(^{-1}\) for Hg(II) chelate may be attributed to L \(\rightarrow\) L\(^*\) transitions.

References
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