Synthesis, characterisation and electrochemical studies of dioxouranium (VI) complexes of dioxolenes with pyridine bases

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Mixed ligand complexes of the formulae UO₂(Ο₂)⁰(L---L)(H₂O)²⁻(2-5) where Ο₂ = dioxolenes viz pyrocatechol (2), tert-butylcatechol (3), di-tert-butylcatechol (4) and tetrachlorocatechol (5) and L---L = pyridine (b), bipyridine (c), o-phenanthroline (d) and dipyridylamine (e) have been prepared and characterised by elemental, IR, UV-vis and thermal analyses. Cyclic voltammograms suggest three successive redox responses. The catechol oxidation is highly sensitive to the nature of the substituents. The low energy transition in the visible region is dependent on the nature of the catechol and pyridine base used. This band is assigned to ligand-to-ligand charge transfer (LLCT) transition and is qualitatively assigned as 3b₁ (cat) → π* (base) transition.

The multidimensional growth of catechols and its derivatives in the field of coordination chemistry is rapidly increasing. The importance may be due to their frequent occurrence in living systems. Catechols are non-innocent ligands and exist in three different redox forms: catechols (Rcq, 1a), semiquinone (Sq, 1b) and quinones (Rq, 1c). The complexes of second and third row metals have shown marked difference in chemistry and charge distribution. Metal complexes containing reducing ligand as catechols and α-dimine/azoimine as oxidising ligand show a typical optoelectronic transition known as ligand-to-ligand charge transfer (LLCT) that has been recently studied. Functionalised platinum metal complexes of catechols have specific pharmacological properties. Use of catechols in the development of f-block chemistry is scarce. In this work we report uranyl complexes of catechols and their ternary complexes with mono and bidentate pyridine bases.

Materials and Methods

UO₂(NO₃)₂, 6H₂O (BDH), pyridine (py) (Loba), bipyridine (bpy), o-phenanthroline (ophen), dipyridylamine (dpa) (E Merck) were of reagent grades. Pyrocatechol (H₂cat), 4-tert-butylcatechol (H₂tdcat), 3,5-di-tert-butylcatechol (H₂dtbcat) and tetrachlorocatechol (H₂tccat) (Aldrich) were purified by crystallisation from benzene. Solvents were purified by reported procedures. Nitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulphuric acid. Tetrabutylammonium perchlorate (TBAP) was prepared and recrystallised by known procedures.

Electronic spectra were recorded using Schimadzu 160A spectrophotometer and infrared spectra were taken on a Perkin-Elmer 783 spectrophotometer. Microanalysis (C, H, N) were obtained using Perkin-Elmer 240C elemental analyser. Electrochemical measurements were performed on a EG&G PARC model 270 VERSTAT electrochemical instruments. All experiments were performed at 298K under dinitrogen atmosphere with a three electrode system Pt-bead as working, Pt as auxiliary and saturated calomel electrode as reference electrodes. Thermal studies were obtained from DT - 30, DT - 40 Shimadzu thermal analyser. All potential are referenced to SCE and are uncorrected for the junction contribution with TBAP as supporting electrolyte. Uranium was determined by standard procedure.

Preparation of complexes

UO₂L. 3H₂O (a)

A methanolic solution (30 ml) of catechol and LiOH.H₂O (1.2 mmol) were added with stirring to
UO$_2$(NO$_3$)$_2$. 6H$_2$O (1 mmol). The mixture was refluxed on a steam bath for 1 h. The brown solution evaporated slowly and the brown solid product so obtained was filtered, washed with methanol and dried over CaCl$_2$, yield 50 - 65%.

$UO_2L(pyy)H_2O$ (b)

To a suspension of $UO_2L_3H_2O$ (0.5 mmol) in methanol (20 ml) was added with stirring a solution of pyridine (0.5 mmol). The mixture was then heated with stirring for 1 h. Orange-brown crystalline product formed on cooling was collected by filtration and washed with methanol and dried over CaCl$_2$, yield 70-80%.

$UO_2L(bpy)H_2O$ (c)

To a suspension of $UO_2L_3H_2O$ (0.5 mmol) in methanol (20 ml) was added with stirring a solution of 2,2'-bipyridine (bpy) (0.5 mmol) in the same solvent (55 ml). The mixture was heated to reflux on steam bath for 30 min. Orange-brown crystalline product formed on cooling was collected by filtration, washed with methanol and dried over CaCl$_2$, yield 70-80%.

The complexes $UO_2L(ophen)H_2O$ (d), $UO_2L(dpa)H_2O$ (e) were prepared by identical procedure. The yields were 70-85%.

**Results and Discussion**

The complexes prepared together with analytical data are given in Table 1. The reaction of uranyl salts with catechols in methanol in 1:1 mole ratio under refluxing condition yielded brown coloured $UO_2L_3H_2O$ complex. The catechols used are abbreviated as pyrocatechol (H$_2$ cat), 4-tert-butylcatechol (Hrtbcat), 3,5-di-tert-butylcatechol (Hrtdtbcat) and tetrachlorocatechol (Hrtccat). The mixed complexes with pyridine bases viz pyridine (py), bipyridine (bpy), o-phenanthroline (ophen), dipyridylamine (dpa) were prepared either by reacting the complex with bases or from 1:1 mixture of respective catechol, base with one equivalent of uranyl salt. The complexes are orange-brown to brown in colour and sparingly soluble in ethanol, methanol, benzene, chloroform and acetone but soluble in DMSO and DMF. The list of complexes are given in Scheme 1. The conductance measurements in DMF solution exhibit non-electrolytic behaviour ($\Lambda_m = 5 - 12\ \Omega^{-1} cm^2 mol^{-1}$) and suggest that the chelates are covalently bonded in all the cases. The molecular weights could not be measured due to lack of specific arrangements.

The IR spectra of the complexes display strong absorption near 1475 - 1490 and 1520 - 1530 cm$^{-1}$ and suggest the binding of ionized hydroxyl groups of catechols to metal ions. The former absorption corresponds to skeletal vibration of catechol ring and the latter is assigned to $\nu$(C-O) vibration. These complexes show medium and weak vibrations at 480 - 535 and 460 - 510 cm$^{-1}$ respectively correspond to two $\nu$(U-O) vibrations. The weak band at 330 - 380 cm$^{-1}$ refers to $\nu$(U-N) vibration. The presence of a broad medium intense band 3340 - 3410 cm$^{-1}$ in the complexes is due to $\nu$(O - H) of coordinated water. The difference in spectra of (a) and others clearly exhibit the ring vibrations of pyridine bases. The bands are blue shifted from their free ligand values. The spectral data are presented in Table 1. All the complexes exhibit strong absorption in the range 910 - 930 cm$^{-1}$ and in assigned to $\nu_{as}$ ($O = U = O$). The force constant ($f_{O=O}$) of the $U = O$ bond has been calculated and the values 6.85 - 7.23 mdyn/A are used to calculate the $U = O$ bond length using Jones's formula and the values 1.71 - 1.73 A are in the expected range. $UO_2(dpa)O(O)H_2O$ (e) exhibit a sharp band 3230 - 3240 cm$^{-1}$ corresponding to $\nu$(N - H) which appears in free ligand, dpa at 3260 cm$^{-1}$. The mixed complexes (b-e) exhibit moderate intense band in the region 1600 - 1670 cm$^{-1}$ and are assigned to C = N stretching. This band is blue shifted in comparison to free ligand. In case of dipyridylamine, $\nu$(C = N) appears at 1610 and in complexes (e) it is shifted to 1660 - 1670 cm$^{-1}$.

The complexes remained almost insoluble in common organic solvents like benzene, acetonitrile, chloroform, dichloromethane and alcohols. The UV-vis spectra were recorded in saturated solution of DMSO. There are three well-defined spectral transitions; the band exhibited at 300 is ascribed to intral-
Table 1 — Elemental analyses and electrochemical data

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<th>Compound</th>
<th>Found(Calcd)%</th>
<th>Electrochemical data&lt;sup&gt;a,b&lt;/sup&gt;</th>
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<th>Sq/q</th>
<th>reductions,</th>
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<th>-Ep</th>
<th>Epc</th>
<th>Ei/2</th>
<th>ΔE&lt;sup&gt;s&lt;/sup&gt;</th>
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</table>

<sup>a</sup> In DMSO<sup>b</sup>; Supporting electrolyte TBAP; electrode Pt; solute concentration ~10<sup>-3</sup> M; scan rate 50 mV sec<sup>-1</sup>; potentials are in V vs. SCE<sup>s</sup>; E<sub>pa</sub> - E<sub>pc</sub> in V.

Gand charge transfer<sup>16</sup> and a band 400-480 nm absent in the free ligand may be due to apical oxygen → I<sup>-</sup>(U) transition<sup>11</sup>. The third transition in the range 550-900 nm, is most significant and the position of the band is highly dependent on the nature of substituent(s) in catechol frame and the type of pyridine.
base (s). This band may be assigned as a ligand-to-ligand charge transfer (LLCT) transition involving HOMO of catechols and the LUMO of \( \alpha \)-diimines. Due to insolubility in most organic solvents, the solvent effect of this band could not be investigated.

**Redox activities**

All the measurements were performed with three electrode system where platinum-bead is working electrode, platinum auxiliary electrode and the reference electrode is saturated calomel electrode (SCE). Tetrabutylammonium perchlorate was used as supporting electrolyte. The electron transfer behaviour of the complexes according to cyclic voltammetry is summarised in Table 1. A representative voltammogram is given in Fig. 1.

The complexes exhibit one or two redox processes positive to SCE and one at negative side. The couple at negative side is due to imine reduction of pyridine bases. As the solvent window does not go beyond +1.0 V, other reductions are not available. The reduction is quasi-reversible in character; counter peak appears on scan reversal at a large potential difference. In the anodic scan, the compounds undergo two successive one-electron oxidation process with varying degree of reversibility (Fig. 1) except tetrachlorocatecholato complexes. In compounds containing electron-donating catechols (tbcat, \((c)\); dtbcat, \((d)\), the first step oxidation is reversible while the second step is irreversible. For uranyl compounds, this anodic process is believed to be a ligand-based oxidation of the coordinated catechol (Rcq) to the semiquinone (Sq) state and finally to quinone (Rq) state (Eq. 1). The oxidation potentials of \([\text{UO}_2\text{(cat)(N,N)}]\) are similar irrespective of coligands (py/bpy/ophen) showing that HOMO is mainly from dioxolenes. But these complexes show a considerable change in the LLCT band position without marked change in redox potential as reported in earlier cases.

The presence of \(\text{Bu}^+\) groups in the catechol ring efficiently stabilizes the cation radical possibly through a hyperconjugative effect. On the other hand, catechol and tetrachlorocatechol are oxidised irreversibly even at high scan rate (500 mV s\(^{-1}\)) due to lack of sufficient electron influx into the semiquinone ring which needs for radical stabilization. The electron stoichiometry of the first step oxidation has been established by constant potential coulometric experiments. An interesting trend in the catechol-centered oxidation is that the potential (Epa) is shifted to more positive values (Table 1) as the substituents in the bound catechol ring become more electron-withdrawing. This is because the oxidation will be thermodynamically more facile when electron density flows into the catechol ring, leading to stabilization of the positive charge of the cation radical.

The reduction at the negative to SCE is responsible for the electron transfer to the LUMO mostly characterised by imine/diimine function. The observed first reduction potential is far away from the \(\text{UO}_2^{2+}\) / \(\text{UO}_2^+\) redox potential as the current height measurement suggest more than one electron transfer process. The first reduction potential follows the energy ordering, py(b) < bpy (c) < ophen (d). However, the spectro-electro correlation between the LLCT band and potential difference of the first oxidation of dioxolene and the first reduction of imine/diimine is difficult. The observed difference in redox potentials of an irreversible electron transfer process are controlled both by kinetic and thermodynamic parameters whereas the spectral transition LLCT is totally thermodynamic parameter. The potentials of the first reduction and oxidation can qualitatively be related to the nature of orbitals in these redox processes. These orbitals are involved in the CT transition as \(3b_1\) (cat) \(\rightarrow\) \(\pi^*\) (imine).

The complexes were subjected to thermal analysis in air atmosphere under non-isothermal conditions. The general behaviour consists of endothermic loss of \(\text{H}_2\text{O}, \text{L}\) or \(\text{L} - \text{L}\) in one or more steps followed by highly exothermic oxidative loss of the ligand at
-400°C. The final residue is invariably U₃ Os¹. In aquo complexes (2-5a), the mass loss starts at 110°C and the step ends at 160°C which is equivalent to three moles of water. Other complexes lose one mole of water at 120-175°C and co-ligands release at 300-550°C followed by the formation of a brown solid oxide. The ternary complexes are thus thermally stable.

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