Synthesis and characterization of complexes of early actinides with tridentate schiff base ligands

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A series of thorium(IV) and dioxouranium(VI) complexes have been synthesised with tridentate schiff base ligands (N_2O donor set) obtained by \textit{in situ} condensation of N, N-dimethylethylenediamine with o-hydroxy aromatic aldehydes such as salicylaldehyde (HL) or o-hydroxy naphthaldehyde (HL'). While with dioxouranium(VI), the ligands are coordinated in a neutral manner and act as tridentate donors forming complexes of the type UO_2(HL)X_2 or UO_2(HL')X_2 (X = Cl, I, NCS, NO_3, CH_3COO) with thorium(IV) they are coordinated as deprotonated tridentate ligands yielding complexes of the type Th(L')_2X_2 (X = I, NCS, NO_3). The IR spectra show that the thiocyanate group is actually N-bonded unidentate isothiocyanate and both the nitrate and the acetate groups are bonded in bidentate manner while the ligands are bonded in tridentate manner in these complexes. The PMR spectra confirm the mode of bonding of the ligands either as neutral or as deprotonated species. The thermogravimetric analyses indicate the stability of the complexes.

Experimental

Hydrated metal chlorides and nitrates (BDH) were used as such. The metal thiocyanates and iodides were obtained by metathesis of the nitrates with KCNS or KI, respectively. Anhydrous UO_2Cl_2.2THF was obtained as a free-flowing solid by refluxing UO_2Cl_2.2H_2O in dry THF for several hours, filtering the insoluble residues and removing the solvent \textit{in vacuo}. The salicylaldehyde and o-hydroxynaphthaldehyde were from S Merck and N,N-dimethyl ethylenediamine obtained from Fluka were used without further purification. The elemental analyses, electrical conductivity, IR and thermogravimetric measurements were performed as reported. The Th and U contents were determined as ThO_2 and U_3O_8 by heating in an electrical muffle furnace at 900°C. The \textsuperscript{1}H NMR spectra of complexes was recorded in DMSO-d_6 and CDCl_3 medium in a BRUKER 300MHz FTNMR machine.

Synthesis of ligands HL and HL'

The two ligands could not be isolated as solid products and were used as such after \textit{in situ} generation of the schiff bases by condensation of salicylaldehyde or o-hydroxynaphthaldehyde with N, N-dimethyl ethylenediamine in ethanol and refluxing. The ligands are abbreviated as HL and HL', respectively.

Synthesis of complexes

UO_2(HL)X_2 and UO_2(HL')X_2 (where X = Cl, I, NCSA, NO_3, CH_3COO)

To the ligand in ethanol was added the desired dioxouranium salt dissolved in ethanol slowly with continuous stirring in warm condition for 2h, when a resinous product separated out. On storing at 4°C for 12h, followed by decantation of the supernatant liquid and stirring for 1h with addition of diethyl ether, the desired product separated out. This was collected in a glass frit (G-3) and washed repeatedly with small aliquots of Et_2O and finally dried \textit{in vacuo}.

Th(L')_2X_2 (where X = I, NCS, NO_3)

On addition of the metal salt solution in ethanol to the ligand solution and on stirring for 2h, the yellow
solid separated out. This was collected, washed and dried as above.

Results and discussion
The characterization data of the complexes are presented in Table 1. Most of the complexes have a fairly high melting or decomposition temperature, are stable under ordinary conditions and are rather poorly soluble in organic solvents for molecular weight determinations. The stable Schiff base complexes of various metal ions are useful for selective chemical separation of several metal ions\(^{11-12}\) and indeed, the Schiff bases isolated from \(\alpha\)-hydroxy aromatic aldehydes and amines are known to be effective extractants for Cu(II) (ref. 13), Zr(IV), Th(IV) and U(VI) (ref. 14). Further interest arises in the Schiff base complexes due to their possible role as models for biological systems\(^{115}\). In what follows, we shall dwell upon the stoichiometry and coordination number of these actinide Schiff base complexes.

The interaction of thorium(IV) and dioxouranium(VI) salts with the synthesized Schiff bases in solution yield intensely coloured stable complexes of the type UO\(_2\)(HL)\(_2\) or UO\(_2\)(HL')\(_2\) where HL and HL' refer to the Schiff bases prepared through the reaction of salicylaldehyde or o-hydroxynaphthaldehyde, respectively, with the N-protected N,N-dimethylhexanediylamine and also the complexes Th(L')\(_2\)X\(_2\). In case of thorium(IV) complexes, the ligand acts as a deprotonated, uninegative, tridentate donor system whereas for the uranium(VI) complexes, the ligands are neutral and tridentate. This is borne out on the basis of analytical data and supported by IR and NMR investigations.

The formation of deprotonated complexes for Th\(^{4+}\) may be due to its large ionic potential as compared to that of UO\(_2^{2+}\). The conductivity measurements in dilute acetone solutions (ca. \(10^{-4} M\)) establish the non-electrolytic nature of these complexes, although due to partial solvolysis the conductance values increase in coordinating solvents like DMF or DMSO. The electrical conductivity values also remain unaltered in the presence of added triphenylphosphine oxide (TPPO) or trioctylphosphine oxide (TOPO), providing further evidence in favour of the covalent bonding of the anions and the non-electrolytic nature of the complexes.

The IR absorption bands of the complexes in the 4000-400 cm\(^{-1}\) region reveal apart from the uranyl vibrations, the ligand vibrational modes and the vibrations due to the polyatomic anions showing their bonding mode. The relative sharp bands at 890-915 cm\(^{-1}\) for all dioxouranium(VI) complexes are
assigned to the $v_{\text{as}}(\text{U-O})$ (ref. 16) of the linear $\text{UO}_2^{2+}$ moiety, while the $v_{\text{s}}(\text{U-O})$ appears at 740-780 cm$^{-1}$ as relatively weak band$^{17}$. So far as the ligand bands are concerned, certain important features merit discussion. While the carbonyl stretching frequencies of the aldehydes generally observed $\sim 1700$ cm$^{-1}$ is uniformly absent in all the complexes, a new IR band appears at 1615-1635 cm$^{-1}$ region due to the $v(\text{C=N})$ of the azomethine group providing evidence$^{18}$ in favour of the condensation of the amine and the aldehydes with the concomitant formation of the Schiff bases. The $v(\text{C=N})$ appears at $1350$ cm$^{-1}$, the phenolic $v(\text{C-O})$ at $1260$ cm$^{-1}$ and the phenyl ring vibrations are seen at $1595$ cm$^{-1}$ region in these complexes. For all the uranyl complexes, bands obtained $\sim 3150$ cm$^{-1}$ show the presence of phenolic OH groups, which are absent in the thorium complexes. This observation along with the PMR data show that the ligands are coordinated in a neutral manner in all $\text{UO}_2^{2+}$ complexes and as deprotonated uninegative ions for the $\text{Th}^{4+}$ complexes. The new vibrational modes at 620 and 520 cm$^{-1}$ region in the complexes may be attributed to the metal-nitrogen and metal-oxygen stretching frequencies, respectively$^{19}$.

As far as the polyatomic anions are concerned, the IR spectra of the nitrate complexes do not exhibit absorption bands near $1380$ cm$^{-1}$, where the free nitrate ion is known to absorb. The bands at 1480 and $1280$ cm$^{-1}$ are due to the $v(\text{NO})$ and $v_{\text{as}}(\text{NO})$ of the bidentate nitrate group$^{20}$. The thiocyanato complexes exhibit a sharp intense band at 2045-2060 cm$^{-1}$ and another at 810-840 cm$^{-1}$ of moderate intensity due to the $v(\text{C=S})$ and $v(\text{C=N})$, respectively, suggesting the coordination through the nitrogen end$^{21}$ and emphasising the ‘hard’ character of the dioxouranium(VI) and the thorium(IV) ions. The $v_{\text{as}}(\text{COO})$ and $v_{\text{s}}(\text{COO})$ at $1550$ and $1430$ cm$^{-1}$, respectively, suggest the bidentate coordination of acetate groups in the acetate complexes of uranium.

The $^{1}H$ NMR spectra of the complexes recorded in DMSO-$d_6$ and CDC$_3$ medium exhibit clear sharp signals due to the N-methyl groups at 2.7 ppm and 2.6 ppm, for the dioxouranium(VI) and thorium(IV) complexes, respectively. The aldiminic proton signal appear at 9.4 ppm for the dioxouranium(VI) and at 9.1 ppm for the Th(IV) complex. The multiplet signals at 6.7-7.7 ppm and 6.7-8.3 ppm in the dioxouranium(VI) and thorium(IV) complexes are assigned to the aromatic protons. Whereas a proton signal is seen at 11.00 ppm for the dioxouranium(VI) complexes assigned to the phenolic OH proton, the same is clearly absent in the thorium(IV) complexes indicating the deprotonation of the phenolic – OH group on complexation. These observations are in conformity with the results of IR investigations discussed above.

The thermogravimetric measurements indicate that the thermal decomposition of the complexes commences only above 120°C, proceeds in stages ultimately forming the respective oxides as the ultimate end product.

The results of the above investigations thus indicate that depending upon the anions and their mode of coordination dioxouranium(VI) complexes have a coordination number seven or nine, while thorium(IV) complexes have a coordination number eight or ten. Although such features are not commonly encountered in the widely studied chemistry of the transition metals, the large effective size coupled with the high charge of the two early actinide ions does explain the formation of complexes with coordination numbers greater than six$^{22}$.

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References