

Novel bi-metallic uranyl complexes - Redox chemistry in aqueous solutions

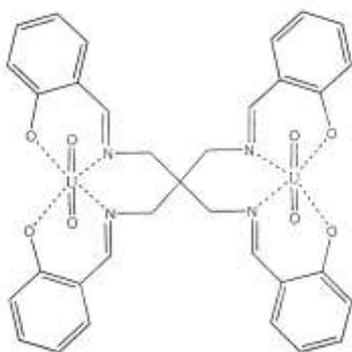
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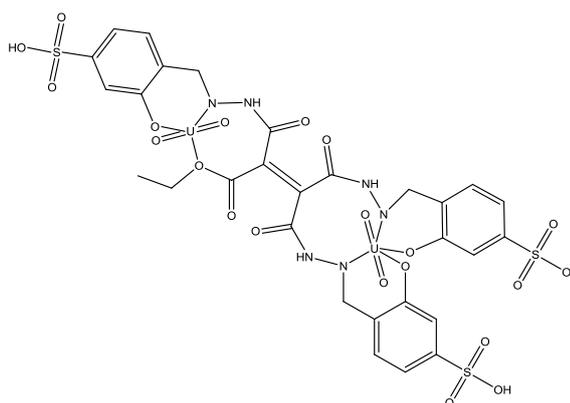
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The synthesis of organic ligands which can accommodate two uranium atoms at different oxidation states, mixed valency being then achieved by redox chemistry at room temperature is definitely a challenge in coordination chemistry. The following complexes were synthesized and characterized by elemental analysis, NMR, MS, IR and UV-vis.



$(\text{UO}_2)_2\text{L}^1$



$(\text{UO}_2)_2\text{L}^2$

L^1 forms a bimetallic complex with two uranyl centres which dissolves in organic solvents, but the complex (and not the ligand) dissolves in 90:10 v/v $\text{H}_2\text{O}/\text{CH}_3\text{OH}$. From the Job-plot the binding constant of the new complex may be approximated as $K \sim 8 \times 10^{17} \text{ M}^{-2}$.

$(\text{UO}_2)_2\text{L}^1$ is reduced radiolytically by $\cdot\text{CH}_2\text{O}^-$ (at pH 10) but not by $\cdot\text{CH}_2\text{OH}$ with

$k = 3.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The ligand, L^1 , is not reduced by $\cdot\text{CH}_2\text{OH}$ and precipitates in the presence of water or base. Preliminary electrochemical results in methanol show two irreversible reduction waves at -1.05 and at -1.73 V vs. SCE.

L^2 forms a bimetallic complexes with both two uranyl and two U(IV) centres which are

water soluble. From the Job-plot in water at pH 5, the binding constants of the new complexes, uranyl and U(IV), may be approximated as $K \sim 4 \times 10^{10} \text{ M}^{-2}$ and $K \sim 2 \times 10^9 \text{ M}^{-2}$ respectively.

Preliminary electrochemical results at pH 5, for $(\text{UO}_2^{2+})_2\text{L}^2$ show two irreversible reduction waves at -0.30 and -0.93 V vs. SCE.

Pulse radiolytic results for the same complex, $(\text{UO}_2^{2+})_2\text{L}^2$, in water at pH 5, show that both e^-_{aq} and $\text{CO}_2^{\cdot -}$ reduce both the complex and the ligand on similar time scales, 200 μs and 6 ms in two reactions in which the first reaction obeys first order kinetics while the second one obeys second order kinetics.

Detailed data will be presented.

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