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Preparation and Thermodynamic Properties of UO_2^{2+} –Ethylene-1,2-Dioxydiacetate Complex

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It is known that actinide ions in aqueous solutions form stable complexes especially with ligands of the mono- and poly-carboxylic acid type, possessing charged oxygen donors. Neutral donor groups interact with the actinide ions only as additional donors, contributing to the stability of the complexes through the formation of chelate structures.

Previously we investigated the complex formation of the UO_2^{2+} ion with bicarboxylic ligands containing different functional groups in the carbon chain: oxydiacetic (oda), thiodiacetic (tda) and iminodiacetic (ida) acids [1]. As a result we concluded that the relative affinity of the three donor groups, present in the chain, towards a hard acceptor follows the order: $\text{NH} > \text{O} > \text{S}$. In fact the iminodiacetic and oxydiacetic ligands tend to form especially strong complexes with the UO_2^{2+} ion, with a coordination geometry in which one ligand is tridentate, forming a five atom ring, known as a particularly stable one. In order to verify whether more functional groups in the carbon chain influence the stability of the complexes formed, we extended our study to ligands of the type $\text{HOOC}-(\text{CH}_2-\text{X}-\text{CH}_2)_n-\text{COOH}$ where $\text{X} = -\text{O}-$, $-\text{NH}-$, and $n = 2, 3$. This report concerns the thermodynamic study of the complex formation of UO_2^{2+} with ethylene-1,2-dioxydiacetate (edoda, where $\text{X} = -\text{O}-$, $n = 2$) in aqueous solution.

The UO_2^{2+} –edoda system was investigated by both potentiometric and calorimetric titration methods. The changes in free energy were computed from the stability constants determined by potentiometric measurements, the enthalpy changes were measured by direct calorimetric titrations. All measurements were carried out at 25.0°C and in 1.00 mol dm^{-3} $\text{Na}(\text{ClO}_4)$, as constant ionic medium. Stability cons-

tants and enthalpy changes were calculated using MINIQUAD 75 and LETAGROP KALLE programs respectively.

The ligand was prepared by oxidation of triethylenglycol with nitric acid [2]. The purity had been checked by elemental analysis, determination of formula weight and NMR spectroscopy. The protonation constants of the ligand ($\log\beta_1^{\text{H}} = 3.71$ and $\log\beta_2^{\text{H}} = 6.77$) are in good agreement with those reported in the literature [3]. On that account for the heats of the proton ligand complexes' formation were taken the values given in the above cited paper.

The formation constants of the complexes formed were determined by potentiometric titration of different metal concentration solutions ($C_{\text{M}}^0 = 10$ to 30 mM) with ligand buffers ($\delta = C_{\text{H}_2\text{L}}/C_{\text{L}} = 0$ to 0.5). The obtained formation curves show good superimposition. In the ligand concentration range used, the metal ion seems to coordinate one ligand only, forming a complex of the type ML. The pH range used (pH = 2.0 to 3.5) allows to avoid the hydrolysis of the UO_2^{2+} ion.

The calculations of the thermodynamic properties based on the potentiometric and calorimetric investigations is in process. Our preliminary data show that the stability of the complex obtained is much smaller in comparison with the one formed with the inferior homologous (oda). Comparing the thermodynamic data for the two ligands (see Table) we can see that the difference in the stability of the complexes of the 1:1 type is due completely to an enthalpy effect, as the values for ΔS are almost equal. Such a difference in ΔH may be connected with a different geometry of coordination.

The available structural data for UO_2^{2+} –oda support the hypothesis of a chelate structure through the carboxylic and the ether groups [4].

In order to have comparable structural data for the ethylene-1, 2-dioxydiacetate we prepared the solid compounds. The reaction was conducted in ethanol and in water in order to get as close as possible to the thermodynamic experimental conditions.

We have obtained interesting results, though not quite coinciding with the thermodynamic part. In fact:

i) Starting from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and working in water and in ethanol we always get compound of

	$\log\beta_{\text{ML}}$	$-\Delta\text{G}^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)
UO_2^{2+} –oda	5.11	29.17	16.86	154.4
UO_2^{2+} –edoda	3.08	17.60	26.6	148.4

the stoichiometric formula $\text{UO}_2(\text{HL})\text{NO}_3$. The above formula is confirmed by elemental analysis; by the evidence of the nitrate ionic band at 1385 cm^{-1} , well distinguished on the IR spectrum; by the splitting of the band due to $-\text{CH}_2-$ nearby the carboxylic band in the NMR spectra. All that can confirm the salification of only one carboxylic group by the metal.

ii) On the contrary, in the same solvents, starting with $\text{UO}_2(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, instead of with the nitrate, we always get a compound with stoichiometric formula UO_2L were both carboxylic groups are salificated.

We thank the International Atomic Energy Agency, Vienna for the financial support to M. Taskaeva.

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The Crystal and Molecular Structures of Tetrachloro-tris(NN-diethylpropionamide)thorium(IV) and Tetra-N-thiocyanatotetrakis(NN-dimethylpropionamide)-thorium(IV)

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Amide complexes of thorium tetrachloride often adopt a different stoichiometry to those formed by the same ligand with uranium tetrachloride, a difference which can be ascribed to the smaller radius of the U(IV) centre as compared with that of Th(IV). For example, with the amide depa (=EtCONEt₂) the complexes $2\text{UCl}_4 \cdot 5\text{depa}$ [1] and $\text{ThCl}_4 \cdot 3\text{depa}$ [2] are obtained. The former has been shown [1] to be ionic, $[\text{UCl}_3(\text{depa})_4]^+[\text{UCl}_5(\text{depa})]^-$, with the 7-coordinate uranium atom in the cation adopting the rather unusual bipyramidal geometry which had already been observed [3] in the neutral complex $\text{U}(\text{NCS})_4(\text{dmiba})_3$ (dmiba = $\text{Me}_2\text{CHCONMe}_2$). It was

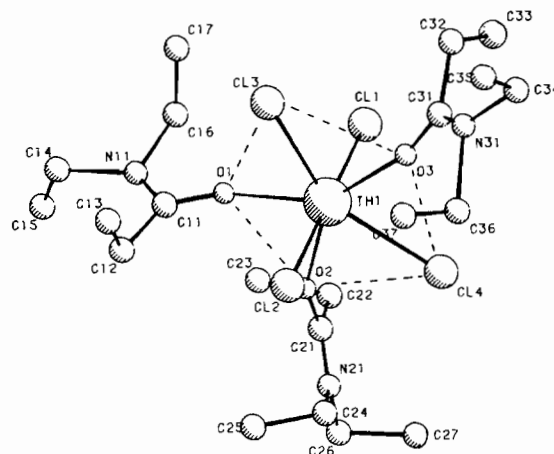


Fig. 1. Perspective view of the molecule $\text{ThCl}_4 \cdot 3\text{depa}$.

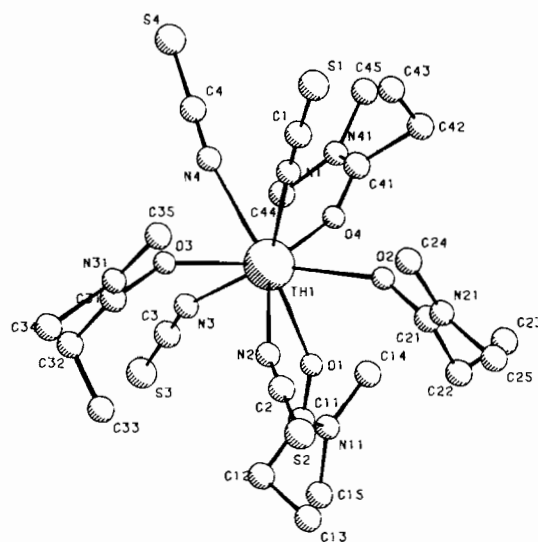


Fig. 2. Perspective view of the molecule $\text{Th}(\text{NCS})_4 \cdot 4\text{dmpa}$.

therefore of interest to determine the structure of $\text{ThCl}_4 \cdot 3\text{depa}$ in order to ascertain whether the coordination geometry was again pentagonal bipyramidal, and also to investigate the structure of the probably 8-coordinate complex $\text{Th}(\text{NCS})_4 \cdot 4\text{dmpa}$ (dmpa = EtCONMe_2) the preparation of which has also been reported recently [2].

Crystal Data

$\text{ThCl}_4 \cdot 3\text{depa}$ (I) ($\text{ThC}_{21}\text{H}_{45}\text{Cl}_4\text{N}_2\text{O}_3$) $M = 761.5$, monoclinic $P2_1/n$, $a = 18.107(4)$, $b = 10.347(2)$, $c = 17.867(4)$ Å, $\beta = 108.5(1)^\circ$, $Z = 4$, $\lambda(\text{MoK}\alpha) 0.71069$ Å. 3126 reflections with $I \geq 2.5\sigma(I)$ used in the structure solution and refinement, $R = 0.046$, $R_w = 0.046$.