the stoichiometric formula $UO_2(HL)NO_3$. 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 $-CH_2-$ 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 $UO_2(Ac)_2\cdot 2H_2O$, instead of with the nitrate, we always get a compound with stoichiometric formula UO_2L were both carboxylic groups are salificated.

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A28

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

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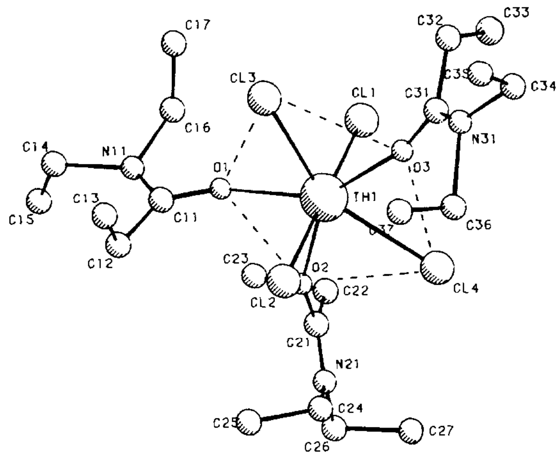

Fig. 1. Perspective view of the molecule $ThCl_4\cdot 3depa$.

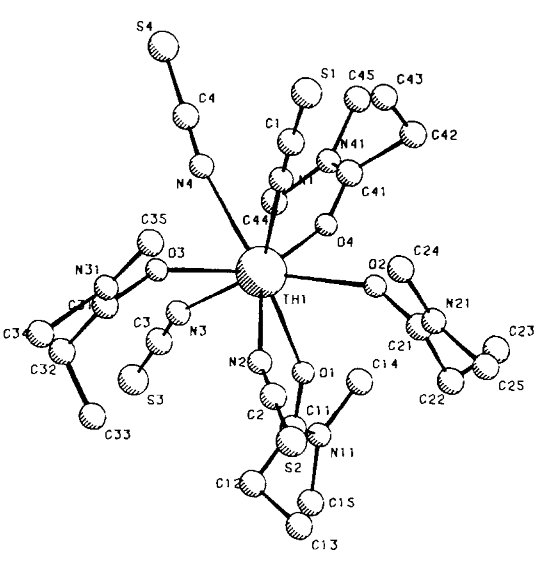

Fig. 2. Perspective view of the molecule $Th(NCS)_4\cdot 4dmpa$.

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 (=$EtCONEt_2$) the complexes $2UCl_4\cdot 5depa$ [1] and $ThCl_4\cdot 3depa$ [2] are obtained. The former has been shown [1] to be ionic, $[UCl_3(depa)_4]^+[UCl_5(depa)]^-$, 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 $U(NCS)_4(dmiba)_3$ (dmiba = $Me_2CHCONMe_2$). It was therefore of interest to determine the structure of $ThCl_4\cdot 3depa$ in order to ascertain whether the coordination geometry was again pentagonal bipyramidal, and also to investigate the structure of the probably 8-coordinate complex $Th(NCS)_4\cdot 4dmpa$ (dmpa = $EtCONMe_2$) the preparation of which has also been reported recently [2].

Crystal Data

$ThCl_4\cdot 3depa$ (*1*) ($ThC_{21}H_{45}Cl_4N_2O_3$) $M = 761.5$, monoclinic $P2_{1/n}$, $a = 18.107(4)$, $b = 10.347(2)$, $c = 17.867(4)$ Å, $\beta = 108.5(1)°$, $Z = 4$, $\lambda(MoK_\alpha)$ 0.71069 Å. 3126 reflections with $I \geqslant 2.5\sigma$ (I) used in the structure solution and refinement, $R = 0.046$, $R_w = 0.046$.

$Th(NCS)_4 \cdot 4dmpa$ (*2*) ($ThC_{24}H_{44}N_8O_4S_4$) M = 821.0, monoclinic $P_{2_1/a}$, a = 22.759(6), b = 13.763(4), c = 11.910(3) Å, β = 91.4(1)°, Z = 4, $\lambda(MoK_\alpha)$ 0.71069 Å. 3729 reflections with $I \geqslant 2.5\sigma(1)$ used in the structure solution and refinement, $R = 0.049$, $R_w = 0.053$.

The coordination geometry for (*1*) is pentagonal bipyramidal as shown in Fig. 1, with two chlorine atoms occupying the axial positions. This kind of geometry is common in seven-coordinate dioxouranium(VI) complexes, rather unusual for U(IV) compounds and the first example for that concerning mononuclear Th(IV) derivatives.

The Th–Cl axial bond distances (2.69 Å av.) are shorter respect to the Th–Cl equatorials (2.75 Å av.) as consequence of the different steric hindrance experienced by the anionic ligands.

The Th–O bond distances have an averaged value of 2.34 Å.

The coordination geometry for (*2*) (see Fig. 2) is nearly square antiprismatic. The substitution of the chlorine with the less hindering isothiocyanate ligand allows a higher coordination number around the thorium ion, while the change of the neutral ligand does not seem of some effect. The Th–N and Th–O bond distances have the averaged values of 2.50 Å and 2.38 Å respectively.

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A29

Actinide and Lanthanide Complexes with Bidentate Ligands. Crystal Structure of Methanolbis(N-phenylbenzoylhydroxamato)dioxouranium(VI)

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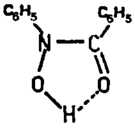
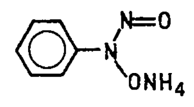
As a part of a study dealing with the interaction of a series of common and well known chelating ligands with some actinide and lanthanide ions we report here the synthesis and the physicochemical characterization of La^{3+}, Th^{4+} and UO_2^{2+} complexes of N-phenylbenzoylhydroxamic acid (HL^1) and cupferron (HL^2) (the ammonium salt of N-nitrosophenyl-hydroxylamine)



(HL^1)



(HL^2)

The crystal structure of methanolbis(N-phenylbenzoylhydroxamato)dioxouranium(VI), $UO_2(L^1)_2$-MeOH is also reported.

A projection of the $UO_2(L^1)_2$ MeOH molecule is shown in Fig. 1 together with the used numbering scheme. Two bidentate N-phenylbenzoylhydroxamato ions and one MeOH molecule are equatorially bonded to the uranyl group in the pentagonal bipyramidal coordination geometry. The coordinated solvent molecule confines with the NO group of one ligand and with the CO group of the other so that the entire molecule is asymmetric. The UO_2^{2+} group is linear with usual values (1.75 Å) for the U–O distances; the equatorial U–O (L) distances (mean 2.39 Å) and the U–O (MeOH) distance of 2.37 Å are normal, but it is noteworthy that the longest one U–O(3) = 2.42 Å involves the O(3) oxygen atom which makes a relatively strong hydrogen bond (2.59 Å) with the MeOH oxygen atom of the centrosymmetric unit. The C–O (mean 1.30 Å) and the N–O (mean 1.36 Å) bonds are partial double, and also the N–C(7) and N–C(20) bonds (mean 1.30 Å) are shortened, indicating the presence of electronic mesomery over the chelate moieties. The two ligands basically behave in the same way with respect to the metal atom; nevertheless it seems that the hydrogen bonding to O(3) plays an important role in determining some observed differences.

Thus we must note that, in addition to the above mentioned U–O(3) distance, the N(1)–O(3) distance is significantly longer than the corresponding N(2)–O(5) and that the U–O(3)–N(1) angle is significantly smaller than U–O(4)–C(7), whereas the corresponding angles in the adjacent ligand are comparable.

The phenyl rings are inclined by *ca.* 50° to the equatorial plane. The methanol molecule of the complex can be easily replaced in CH_2Cl_2, by other, more basic monodentate ligands as Ph_3PO, dmso, dmf or py according to the reaction:

$$UO_2L_2MeOH + A \longrightarrow UO_2L_2A + MeOH$$

($A = Ph_3PO$, dmso, dmf and py)

Reaction of UO_2^{2+} salts with cupferron under a variety of conditions always yielded $NH_4[UO_2(L^2)_3]$.