$Th(NCS)_4 \cdot 4dmpa$ (*2*) ($ThC_{24}H_{44}N_8O_4S_4$) M = 821.0, monoclinic $P2_1/a$, 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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3 K. W. Bagnall, Li Xing-fu, G. Bombieri and F. Benetollo, *J. Chem. Soc., Dalton Trans.*, 19 (1982).

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

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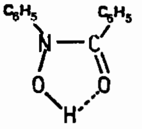
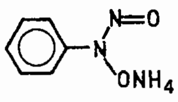
As a part of a study dealing with the interaction of a series of common and well known chelating ligands with some actinide and lanthanide ions we report here the synthesis and the physicochemical characterization of La^{3+}, Th^{4+} and UO_2^{2+} complexes of N-phenylbenzoylhydroxamic acid (HL^1) and cupferron (HL^2) (the ammonium salt of N-nitroso-phenyl-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 $NH_4[UO_2(L^2)_3]$.

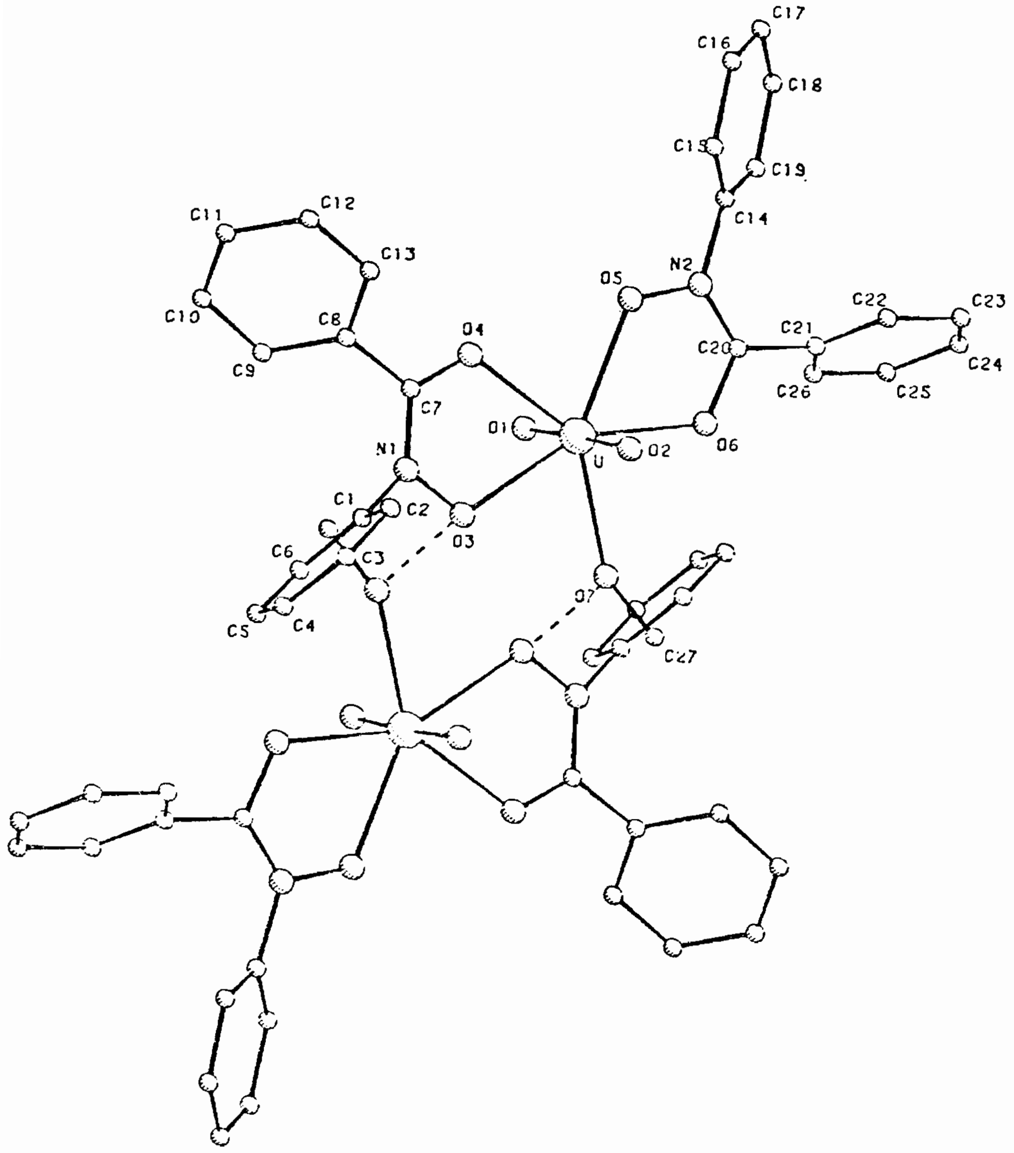


Fig. 1.

The high stability of the $UO_2(L^2)_3^-$ anion caused the failure of the attempts to prepare complexes of the type $UO_2(L^2)_2A$ (A = Ph_3PO, dmf, py), starting from uranyl(VI) salts and cupferron. Only a compound of formula $UO_2(L^2)_2Ph_3PO \cdot 3H_2O$ was obtained by reacting $UO_2(NO_3)_2(Ph_3PO)_2$ with cupferron in H_2O/MeOH solution. The presence of a molecule of water in the complex $Th(L^2)_4 \cdot H_2O$, obtained by reacting $Th(NO_3)_4 \cdot 5H_2O$ with cupferron in H_2O/MeOH solution, was easily determined by the thermogravimetric analysis but coordination of the water molecule to thorium was not immediately clear, even if reactions of the type:

$$Th(L^2)_4 \cdot H_2O + A \longrightarrow Th(L^2)_4A + H_2O$$

(where A is a monodentate ligand containing oxygen or nitrogens as donor atom), seem to support it. Lowering of the νP=O to 1160 cm^{-1} in Th-$(L^2)_4 \cdot Ph_3PO$ and of νC=O to 1617 cm^{-1} in Th-$(L^2)_4 \cdot$dma are evidences that Ph_3PO and dma are coordinated and that the most probable coordination number is 9 in these complexes. For the product obtained by reacting $Th(NO_3)_4 \cdot 5H_2O$ with an excess of cupferron in H_2O/MeOH, formulable as $NH_4[Th(L^2)_5] \cdot H_2O$, a c.n. 10 should be tentatively assumed for Th^{4+}, as it was proposed for the same atom in $Li[Th(trop)_5] \cdot H_2O$. A further X-ray investigation of these complexes is necessary in order to ascertain their coordination polyhedra. Attempts to grow good crystals for such investigation, were for the moment unsuccessful.

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Kinetics of the Exchange Reactions and the Formation Rate of the Lanthanide(III)-Ethylenediamine-Tetraacetate Complexes

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The kinetics of the substitution reactions of the metal ions in the lanthanide(III)-ethylenediamine-tetraacetate ($\mathrm{Lnedta^-} = \mathrm{LnY}$) complexes have been investigated in detail by isotopic-exchange [1–4] and spectrophotometric methods [5–7]. As a result, the main features of the mechanisms of the reactions are known. The exchange can take place by the proton catalyzed dissociation of complexes as well as by the direct attack of the exchanging metal on the complex. In the interval $3 < \mathrm{pH} < 6$ the dissociative path predominates and it is assumed that the relatively slow dissociation of complexes is followed by a fast reaction of the free ligand with the exchanging metal. The intimate mechanisms of these processes are not known and the possible role of the water-exchange rate of the metal ions has hardly been investigated.

Recently studying the kinetics of the exchange reactions between the Ceedta and $\mathrm{Ni^{2+}}$ or $\mathrm{Co^{2+}}$ ions we have shown [7] that the reactions of the free ligand formed by dissociation, depend on the water-exchange rate of both the outcoming and incoming metal ions. As a result the dissociation of the complex must be regarded as reversible reaction as it is described in the following scheme:

$$\mathrm{Ceedta^-} + \mathrm{H^+} \overset{K^H}{\rightleftharpoons} \mathrm{CeHedta} \tag{1}$$

$$\begin{tikzcd} \mathrm{CeHedta} \arrow[r, shift left, "k_{CeHY}"] & \mathrm{Ce^{3+}} + \mathrm{Hedta^{3-}} \arrow[l, shift left, "k^{Ce}_{H_iY}"] \arrow[d, shift right, "H^+"'] \\ & \mathrm{H_iedta^{(4-i)-}} \arrow[u, shift right] \end{tikzcd} \tag{2}$$

$$\mathrm{H_iedta^{(4-i)-}} + \mathrm{M^{2+}} \xrightarrow{k^M_{H_iY}} \mathrm{Medta^{2-}} + i\mathrm{H^+} \tag{3}$$

where the degree of protonation of the ligand, i, depends on the pH of the solution.

In the presence of $\mathrm{Ce^{3+}}$ and $\mathrm{M^{2+}}$ ion excess pseudo-first-order rate constants k_p can be obtained and from the dependence of the k_p values on the concentration of the $\mathrm{H^+}$, $\mathrm{Ce^{3+}}$ and $\mathrm{M^{2+}}$ ions, the formation rate constants $k^M_{H_iY}$ of the $\mathrm{Medta^{2-}}$ complex can be calculated [7]. With the application of this principle the formation rate constants of some Lnedta complexes have been determined, since in spite of the interest of these complexes their rate of formation has not been investigated [6].

For the determination of the formation rate constants $k^{Ln}_{H_iY}$ the kinetics of the following exchange reaction was investigated:

$$\mathrm{Ceedta^-} + \mathrm{Ln^{3+}} \rightleftharpoons \mathrm{Ce^{3+}} + \mathrm{Lnedta^-} \tag{4}$$

where Ln = Nd, Gd, Er and Y.

The formation rate constants can be determined only when the rate of formation of the Lnedta complexes can be slowed down with the increase of the concentration of the $\mathrm{Ce^{3+}}$ ions. This condition fulfills if $k_{Ce}^{-H_2O}[\mathrm{Ce^{3+}}] > k_{Ln}^{-H_2O}[\mathrm{Ln^{3+}}]/10$ ($k_{Ce}^{-H_2O}$ and $k_{Ln}^{-H_2O}$ are the characteristic water-exchange rate constants of the $\mathrm{Ce^{3+}}$ and the $\mathrm{Ln^{3+}}$ ions).

The exchange reactions (4) were followed by spectrophotometry at 280 nm (25 °C, I = 1 *M* KCl, cell length 4 cm). The concentration of the Ceedta was 4×10^{-4} *M*, while the pH as well as the concentration of the $\mathrm{Ce^{3+}}$ and $\mathrm{Ln^{3+}}$ ions were varied between 8×10^{-3} and 6×10^{-2} *M*. The concentration of the $\mathrm{Ln^{3+}}$ ions was always high enough ($[\mathrm{Ln^{3+}}] > [\mathrm{Ce^{3+}}]$) to make the exchange practically complete. With the application of these conditions the exchange reaction (4) can be treated as a first order one and its rate can be expressed as follows:

$$-\frac{d[\mathrm{CeY}]_t}{dt} = k_p[\mathrm{CeY}]_t \tag{5}$$

Taking into consideration all the possible reaction paths of the exchange the pseudo-first-order rate constant can be expressed with the following equation:

$$k_p = \frac{k^{Ln}_{CeY} + k^{Ln}_{CeHY}K^H_{CeY}[\mathrm{H^+}] +}{1 + K^H_{CeY}[\mathrm{H^+}]} + \frac{\sum_i k^{Ln}_{H_iY}\beta_i[\mathrm{H^+}]^i \;/K_{CeY}[\mathrm{Ce^{3+}}]}{1 + K^H_{CeY}[\mathrm{H^+}]}\,[\mathrm{Ln^{3+}}] \tag{6}$$

where k^{Ln}_{CeY} and k^{Ln}_{CeHY} are the rate constants of the reactions taking place by the direct attack of the $\mathrm{Ln^{3+}}$ ions on the $\mathrm{Ceedta^-}$ and CeHedta complexes. K_{CeY} is the stability constant, K^H_{CeY} is the protonation constant of the $\mathrm{Ceedta^-}$. β_i is the i-th protonation constant of the $\mathrm{edta^{4-}}$ ligand.

The formation rate constants have been calculated using eqn. (6) to computer fit the k_p values obtained at various $\mathrm{H^+}$, $\mathrm{Ce^{3+}}$ and $\mathrm{Ln^{3+}}$ concentrations. The results of the calculations indicated an appropriate fitting with the use of i = 1 and 2. The contribution