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Chloride and Oxinate Mixed Complexes of Uranium(IV) and Thorium(IV)

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Some new chloride and oxinate mixed complexes of general composition $MCl_{4-n}Ox_n$ (M = U(IV) and Th(IV); Ox = 8-hydroxyquinolinato; n = 1, 2) were synthesized by the reaction of uranium or thorium tetrachlorides with M'Ox (M' = Na, K, Tl) or $MgOx_2$. By using the oxine the formation of the adducts $MCl_4 \cdot 2HOx$ occurs, without the substitution of the chloride ions. By suspending $MCl_4 \cdot 2HOx$ in the presence of a strong base (Proton Sponge) MCl_2Ox_2 was formed immediately. The reaction of UCl_2Ox_2 and TlCp did not afford Cp_2UOx_2, which can be easily prepared by reaction of $Cp_2U(NEt_2)_2$ and HOx.

Introduction

Potentially chelating ligands such as β-diketonato and 8-hydroxyquinolinato anions easily form complexes with thorium(IV) and uranium(IV) ions with composition MOx_4 and MOx_4HOx (where M = Th(IV) and U(IV), HOx = 8-hydroxyquinoline) [1,2]. MOx_4 species can be obtained from MOx_4HOx by thermal dissociation of the neutral ligand HOx. However, no mixed ligand complexes such as $MOx_{4-n}Cl_n$ (n < 4) have been described to date. On the other hand the acetylacetonato anion gives rise to some interesting uranium(IV) mixed ligand complexes by partial replacement of the chloride ions of UCl_4 [3,4].

We carried out the similar reactions by using thorium and uranium tetrachlorides and oxinate anions in order to investigate the possibility of obtaining their corresponding mixed ligand complexes.

Experimental

Due to the general oxygen and moisture sensitivity of uranium(IV) and thorium(IV) derivatives, all the manipulations were carried out in controlled dry boxes, or under nitrogen atmosphere. The solvents were appropriately purified prior to use [5].

Commercially available reagent grade materials were employed, except in some particular cases in which they were prepared as reported below. UCl_4 was prepared following Herrmann and Suttle's method [6]. $Cp_2U(Net_2)_2$ was synthesized as described in [7].

KOx and NaOx were prepared by reaction of the corresponding metal hydroxides with oxine in methanol solution. TlOx and $MgOx_2$ were prepared by reaction of oxine with TlOEt (Et = C_2H_5) and Mg(n-Bu)$_2$(n-Bu = n-C_4H_9) respectively in toluene. $LiNEt_2$ was synthesized by reaction of diethylamine and lithium n-buthyl in n-hexane solution.

C, H, N Analyses were carried out by Mr. A. Berton of this Institute. Oxine and chloride contents were determined by bromometric and argentometric titrations respectively.

Cary 17D UV–Vis-NIR, Perkin Elmer 580 B IR, Varian FT 80A NMR, and V. G. ZAB 2F mass spectrometer, were used in order to perform the appropriate measurements.

UCl_2Ox_2 and $UCl_3Ox \cdot 2THF$

Mixtures containing UCl_4 and M'Ox (M' = Na, K, Tl) (a few millimoles of reagents) in 1:2 and 1:1 molar ratios respectively were stirred overnight at room temperature in 50–100 ml tetrahydrofurane (THF). The yellow-green and pale-green coloured solutions respectively were filtered and the solids having the same colour as the original solutions were obtained by addition of n-hexane (V(THF): V(n-hexane) = 1:3) in the 70–75% yields. An additional amount of the products was obtained by Soxhlet extraction with THF (5 hours) of the insoluble solids.

UCl_2Ox_2 is a yellow-green powder sparingly soluble in THF, CH_2Cl_2, $CHCl_3$, and CCl_4, and inso-

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TABLE I. Physico-Chemical Data of the Mixed Ligands Uranium(IV) and Thorium(IV) Complexes.

Compound	Colour	Elemental Analysis									
		Calcd. %					Found %				
		C	H	N	Cl	Ox[a]	C	H	N	Cl	Ox[a]
$\mathrm{UOxCl_3\cdot 2THF}$	Green	32.15	3.78	2.21	16.78	–	31.8	3.6	2.3	16.5	–
$\mathrm{UOx_2Cl_2}$	Yellow-Green	36.18	2.01	4.69	11.89	–	36.2	2.3	4.4	11.5	–
$\mathrm{UCl_4\cdot 2HOx}$	Pink	32.24	2.09	4.18	21.19	–	32.6	2.1	4.1	21.1	
$\mathrm{Cp_2UOx_2}$	Orange	51.22	3.35	4.27	–	43.90	50.7	3.1	4.1	–	43.5
$\mathrm{ThOxCl_3\cdot 2THF}$	Yellow	32.46	3.82	2.23	16.94	22.91	31.2	3.7	3.1	17.0	24.0
$\mathrm{ThCl_4\cdot 2HOx}$	Yellow	32.53	2.11	4.22	21.38	43.67	31.5	2.0	3.6	21.7	43.1
$\mathrm{ThOx_2Cl_2}$	Yellow	36.55	2.03	4.74	12.01	48.73	37.2	2.7	4.8	12.9	48.4

[a] The determinations have been carried out bromometrically. In the case of U(IV) derivatives the data were unreproducible, probably due to some oxidation processes of U(IV).

Main I.R. Absorption Bands ($\mathrm{cm^{-1}}$)

Compound	ν(C=N)(C=C) [8a,b,c]	ν(O–C)[8a,b,c]	δ(C–H)	ν(M–O) [8a,b,c]
$\mathrm{UOxCl_3\cdot 2THF}$ (THF 859 m)	1588s, 1550s, 1502s	1107s	821s, 730s	501m, 472m, 408m
$\mathrm{UOx_2Cl_2}$	1580s, 1549s, 1500s	1109s	829s, 736s	508m, 488m, 390w
$\mathrm{UCl_4\cdot 2HOx}$	1588s, 1550s, 1499m	1107s	820s, 737s	516s, 472m, 408w
$\mathrm{Cp_2UOx_2}$ (Cp: 1010m, 782s)	1593m, 1563s, 1491s	1102s	819s, 725s	504s, 479m, 390w
$\mathrm{ThOxCl_3\cdot 2THF}$ (THF 857m)	1585s, 1549s, 1500s	1109s	833m, 732s	512m, 490m, 410w
$\mathrm{ThCl_4\cdot 2HOx}$	1582s, 1550s, 1498s	1104s	821s, 728s	508m, 488m, 412m
$\mathrm{ThOx_2Cl_2}$	1584s, 1548s, 1500s	1108s	821s, 730s	510s, 487m, 411w

luble in benzene, toluene and in light aliphatic hydrocarbons.

$\mathrm{UCl_3Ox\cdot 2THF}$ is a pale-green powder having the same solubility previously observed for $\mathrm{UCl_2Ox_2}$.

$\mathrm{UCl_2Ox_2}$ and $\mathrm{UCl_3Ox\cdot 2THF}$ were obtained as insoluble solids also from $\mathrm{UCl_4}$ and $\mathrm{MgOx_2}$ in THF (in the 1:1 and 1:0.5 molar ratios respectively). This procedure seems to be preferable to the above one, as it is less time consuming.

$\mathrm{UCl_4\cdot 2HOx}$

$\mathrm{UCl_4}$ (0.76 g, 2 m*M*) was brought to react at room temperature with HOx (1.16 g, 4 m*M*) in THF (30 ml) under stirring; a pink powder formed immediately which was separated after three hours by filtration, washed several times with THF and dried *in vacuo*.

The pink product is almost insoluble in the most common inert organic solvents.

A THF suspension of this complex was stirred in the presence of proton sponge (1.8-bis(dimethylamino)naphthalene); the solvent becomes progres-

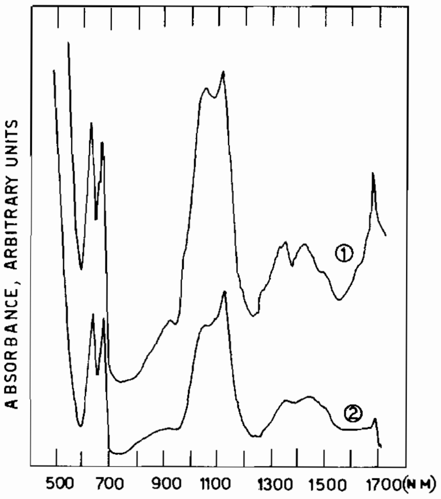


Fig. 1. Absorption spectra in THF solution of 1) $\mathrm{UOx_2Cl_2}$; 2) $\mathrm{UCl_4\cdot 2HOx}$ after 3–4 hours stirring with Proton Sponge.

TABLE II. ^{1}H n.m.r. Data of UOx_2Cl_2 and Cp_2UOx_2 in benzene-d_6 Solution (ppm from Benzene-d_6 as Internal Standard, T = 27 °C).

Compound	Chemical Shift (ppm)*	Assignments	J (Hz)
Cp_2UOx_2	–19.19(d)	C_7–H	$J_{6,7}$ = 7.7
	–5.20(t)	C_6–H	$J_{5,6}$ = 8.0 $J_{6,7}$ = 7.7
	–1.73(d)	C_4–H	$J_{3,4}$ = 7.5
	–0.16(d)	C_5–H	$J_{5,6}$ = 8.0
	8.90(dd)	C_3–H	$J_{2,3}$ = 4.6 $J_{3,4}$ = 7.5
	10.72(d)	C_2–H	$J_{2,3}$ = 4.6
	23.01(s)	Cp	
UOx_2Cl_2 (in CD_3CN)	–38.75(d)	C_7–H	$J_{6,7}$ = 8.0
	–18.94(t)	C_6–H	$J_{5,6}$ = 8.0 $J_{6,7}$ = 8.0
	–14.90(d)	C_5–H	$J_{5,6}$ = 8.0
	–13.79(d)	C_4–H	$J_{3,4}$ = 6.0
	–9.19(m)	C_3–H	$J_{2,3}$ = 4.4
	covered by the solvent	C_2–H	–

*The negative values represent downfield shifts, the positive ones are indicative of upfield shifts.

sively yellow-green and its optical spectrum (400–1700 nm) was identical to that of UCl_2Ox_2 (Fig. 1).

$ThCl_2Ox_2$, $ThCl_3Ox$ 2THF and $ThCl_4 \cdot 2HOx$ (all yellow products) were prepared as described for the corresponding uranium derivatives.

Cp_2UOx_2

a) Attempt at Synthesis from UCl_2Ox_2 and TlCp

UCl_2Ox_2 (1 m*M*) and TlCp (2 m*M*) in THF (30 ml) were stirred overnight at room temperature. The red brown solution was concentrated, added to an excess of n-hexane, and the brown precipitate separated and dried in the usual way. Contents of chloride ions, ^{1}H n.m.r. and visible-NIR spectra were identical to those corresponding to Cp_3UCl.

b) Synthesis from $Cp_2U(NEt_2)_2$ and HOx

Cp_2UOx_2 was easily prepared by reaction of $Cp_2U(NEt_2)_2$ [7] and HOx (1:2 molar ratio) in diethylether solution. A red-brown solid precipitated immediately. The compound was fully characterized by its ^{1}H n.m.r. and mass spectra, and by elemental analysis (Table I).

Results and Discussion

The reactions of uranium and thorium tetrachlorides with oxinate salts in tetrahydrofurane afford the title compounds MCl_2Ox_2 and $MCl_3Ox \cdot$ 2THF depending on the molar ratio of the reagents, following the pattern:

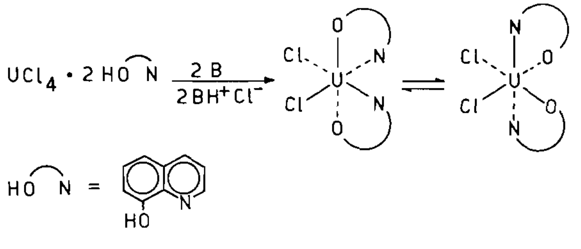
$$MCl_4 + M'Ox \longrightarrow MCl_3Ox\ 2THF + M'Cl$$

$$MCl_4 + 2M'Ox \longrightarrow MCl_2Ox_2 + 2M'Cl$$

M = U(IV), Th(IV)
M′ = Na, K

The obtained products are sparingly soluble in the most common organic inert solvents, the solubility decreasing on going from uranium to thorium derivatives.

Direct reaction of MCl_4 and the protonated ligand HOx (8-hydroxyquinoline) in THF does not cause replacement of halide ions with oxine, as occurs in basic aqueous or alcoholic media [1]. The only product obtained is MCl_4 2HOx, which, at least in the case of the uranium derivative, undergoes intramolecular substitution of halide by oxine in the presence of a strong base such as proton sponge (Scheme I):



The mode of ligation of the coordinated ligands can be inferred by the infrared absorptions [8a,b,c]. Thus in the range 1600–300 cm^{-1} the absorption bands assigned to the oxinate anion bound in the chelated form to the metallic ions are present and they seem only weakly influenced by the nature of

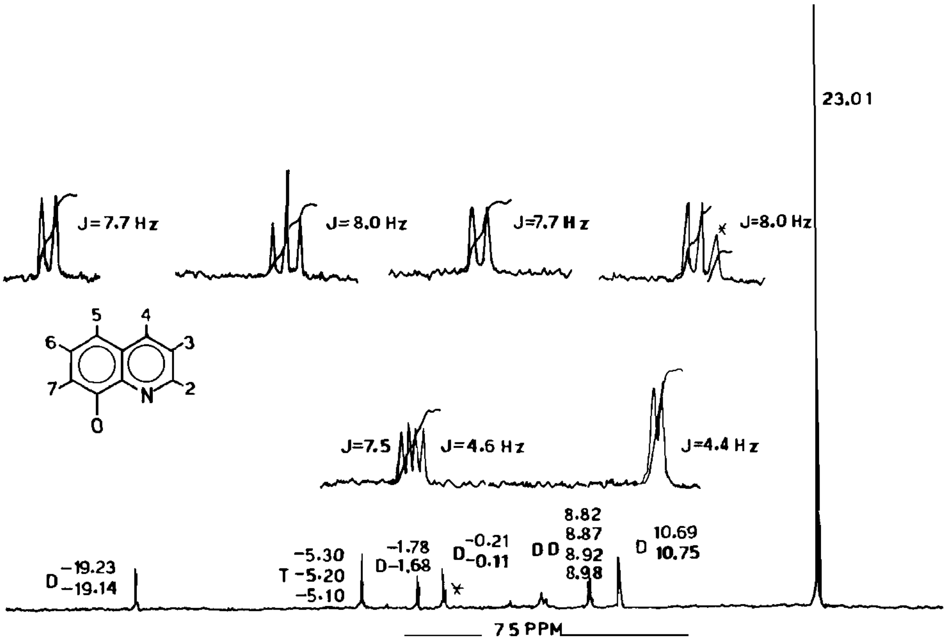


Fig. 2. ^1H n.m.r. spectrum of $CpUOx_2$ in benzene-d_6 (T = 27 °C; ppm from benzene-d_6 as internal standard; x = benzene-d_6).

the central atom or by the number of the coordinated oxinate groups.

The coordination of the oxinate anion with the paramagnetic uranium(IV) ion gives rise to isotropic shifts for the signals due to the protons of both the phenolic ring and the hetero-ring in the ligand, which provide a means of monitoring the electronic environments of the ligation modes. Thus, changes in the chemical shifts relative to their position for the free ligand yield information about the nature of the metal–ligand bonds. Observations that all the signals due to the protons of both the phenolic- and hetero-rings are isotropically shifted provide confirmation that the ligands are bound to the paramagnetic uranium(IV) ion in the chelated form (Table II).

Due to the low solubility of UCl_2Ox_2 the assignments of the signals of the oxinate groups were carried out by double resonance experiments on the more soluble Cp_2UOx_2, whose structure may reasonably be pseudo-octahedral, like UCl_2Ox_2. An attempt to prepare Cp_2UOx_2 from UOx_2Cl_2 and TlCp was unsuccessful as the only isolated product was Cp_3UCl, probably due to the reaction:

$$2\ TlCp + UCl_2Ox_2 \longrightarrow \text{'}Cp_2UCl_2\text{'} + 2TlOx$$
$$\rightleftharpoons$$
$$\tfrac{1}{2}CpUCl_3\cdot 25 + \tfrac{1}{2}Cp_3UCl$$

Cp_2UOx_2 is easily obtained from $Cp_2U(NEt_2)_2$, whose diethylamido groups are theoretically replaceable by all acids stronger than the diethylamine.

The presence in the ^1H n.m.r. spectrum of Cp_2UOx_2 (Fig. 2) of only one set of signals related both to the oxine and Cp protons indicates that the ligands in the molecule are magnetically equivalent. As far as the assignments of the oxine protons are concerned, by irradiating the doublet centered at −19.19 ppm (J = 7.7 Hz) the modification of the triplet at −5.20 ppm (J = 8.0 Hz) into a doublet (J = 8.0 Hz) is observed, while all the other signals are unchanged. Thus it can be argued that the doublet centered at −19.19 ppm is due to the protons *7* (or *2*) and the triplet at −5.20 ppm to the protons *6* (or *3*). In order to confirm these assignments, the triplet at −5.20 ppm is irradiated and as a consequence the two doublets at −19.19 ppm and at −0.16 ppm respectively, are changed in two singlets. In addition to the assignments of the protons *7* (or *2*) and *6* (or *3*) the latter behaviour indicates that the doublet centered at −0.16 ppm (J = 8.0 Hz) has to be assigned to the protons *5* (or *4*). In fact, by irradiating the doublet at −0.16 ppm the triplet at −5.20 ppm is transformed in a doublet (J = 7.7 Hz).

By making the double resonance on the doublet at −1.73 ppm (J = 7.5 Hz) the transformation of the doublet of doublets centered at 8.90 ppm into a doublet (J = 4.6 Hz) occurs, thus indicating that the doublet at −1.73 ppm may be assigned to the protons *4* or (*5*) and the doublet of doublets to the protons *3* (or *6*) (coupled both with the protons *2* $J_{2,3}$ = 4.6 Hz and with the protons *4* $J_{3,4}$ = 7.5 Hz). Finally, by irradiating the doublet at 10.72 ppm (J

= 4.6 Hz) the transformation of the doublet of doublets into a doublet (J = 7.5 Hz) is obtained; thus indicating that the doublet at 10.72 ppm may be assigned to the protons *2* (or *7*).

Moreover, by comparison of the isotropic shifts due to the α, β, γ, protons of the pentahaptocyclopentadienyl uranium(IV) alkoxydes reported in the literature [9] with those observed for Cp_2UOx_2, and taking into account that the value of the coupling constant (J = 4.6 Hz) of the doublet centered at 10.72 ppm is of the same order as observed for the $J_{2,3}$ = 4–5 Hz of the *2* and *3* quinoline protons, and is lower than the coupling constant of the *6* and *7* quinoline protons ($J_{6,7}$ = 7–8 Hz), the correct assignments of the oxinate protons are those reported in Fig. 2 and Table II.

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