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

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The synthesis of some new chloride and tropolonato mixed complexes of the general composition $MCl_{4-n}Trop_n \cdot mL$ *(*$M = U^{IV}, Th^{IV}$*; n = 1, 2, 3; m = 1/2, 2/3, 1, 2 and 3; L = DME, THF, LiCl and 18-crown-6) by the reaction of uranium and thorium tetrachlorides with M′Trop (M′ = Tl and Li) is described. The residual chloride atoms in* $UTropCl_3 \cdot THF$ *undergo further substitution reactions involving TlCp, while* $UTrop_2Cl_2 \cdot THF$ *shows a different behaviour toward TlCp, since* Cp_3UCl *as one of the main reaction products is obtained. Protolysis of* $Cp_2U(NEt_2)_2$ *by HTrop affords a mixture of* $CpUTrop_3$ *and* Cp_2UTrop_2*. Finally both* $UTropCl_3 \cdot THF$ *and* UCl_4 *react directly with HTrop, the nature of the resulting products depending on the reaction solvent.*

Introduction

To date tropolonato complexes either of transition or non-transition metals [1–3] have been prepared with the aim of understanding the coordination mode of this potentially chelating ligand as a function of the properties of the metal ion. Some uranium(IV) and thorium(IV) tropolonato complexes with a high coordination number have been reported [3–5] having the general composition: $MTrop_4 \cdot L$ (where $M = U^{IV}$ and Th^{IV}; L = DMSO and DMF) and $M'MTrop_5$ (where M′ = Li and $M = U^{IV}$ and Th^{IV}; M′ = Na, K and $M = Th^{IV}$). In such complexes the tropolonato anion behaves as a chelating ligand. On the contrary, no mixed-ligand complexes containing both tropolonato and some other anionic groups corresponding to a general formula $MTrop_{4-n}X_n \cdot aL$ ($M = U^{IV}, Th^{IV}$; n = 4; a = 1 and 2) have been reported. These mixed-ligand complexes may be in principle very interesting as intermediates in the synthesis of some other complexes by substitution both of X and L. Previous examples of a similar nature are represented by acetylacetonato and oxinato uranium(IV) and thorium(IV) derivatives [6–10].

Experimental

Materials and Methods

All operations involving the manipulation of uranium(IV) and thorium(IV) complexes were performed in a purified nitrogen filled glove box. The UCl_4 was prepared as reported in the literature [11]. Commercial anhydrous $ThCl_4$ (Alfa-Ventron), tropolone (Aldrich), 18-crown-6 (Fluka), 2,2′-bipyridine (Carlo Erba) and thallium(I) ethoxide (Aldrich) were used without any further purification. Cyclopentadiene was obtained by thermal decomposition of its dimer immediately before use. Thallium(I) tropolonate and thallium(I) cyclopentadienide were obtained in almost quantitative yields by adding a small excess of HTrop and HCp, respectively, to a solution of Tl(OEt) in toluene at room temperature; lithium tropolonate was obtained by adding a small excess of the tropolone to a solution of n-butyllithium in n-hexane. The solids were separated by filtration, washed several times with toluene and dried *in vacuo*. $Cp_2U(NEt_2)_2$ was synthesized according to a previously developed procedure [12]. The solvents (THF, DME, toluene, benzene, n-pentane and diethyl ether) were purified according to literature methods [13]. Common abbreviations are as follows: HTrop = tropolone, DME = 1,2-dimethoxyethane, DMSO = dimethyl sulfoxide, DMF = N,N-dimethylformamide, THF = tetrahydrofuran, Et_2O = diethyl ether, HCp = cyclopentadiene and $HNEt_2$ = diethylamine.

Proton nmr spectra were recorded on a Varian FT-80A spectrometer. The sample solutions (C_6D_6, CD_2Cl_2 and $CDCl_3$) were prepared inside the glove box and the tubes were then sealed. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer using Nujol mulls sandwiched between KBr plates in a O-ring-sealed, air-tight holder.

Electronic spectra were recorded on a Cary 17D spectrophotometer by using well-stoppered quartz cells. Mass spectra were recorded on a V. G. Organic Ltd. ZAB 2F instrument (E.I. = 70 eV, probe temperature = 160 °C).

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UTropCl$_3$·THF and ThTropCl$_3$·3THF

To a suspension of UCl$_4$ (0.380 g, 1 mmol) or of ThCl$_4$ (0.374 g, 1 mmol) in 20 ml of THF, TlTrop (0.325 g, 1 mmol) was added in several portions, at room temperature and under magnetic stirring. The mixture was reacted overnight and after filtration and washing of the solid residue, the solution was concentrated to 5 ml. Addition of diethyl ether (20 ml) to the concentrated solution caused the precipitation of a solid which was filtered off, washed several times with diethyl ether (5 ml portions) and dried *in vacuo*. The yields were ≅75%.

UTrop$_2$Cl$_2$·THF and ThTrop$_2$Cl$_2$·2THF

UCl$_4$ (0.380 g, 1 mmol) or ThCl$_4$ (0.374 g, 1 mmol) were suspended in THF (20 ml) at room temperature. TlTrop (0.650 g, 2 mmol) was added and stirring was continued overnight. After this time, the mixtures were handled as in the procedures reported above and the compounds were obtained in good yields (≅70%).

UTrop$_2$Cl$_2$·½DME·½LiCl

To a solution of UCl$_4$ (0.380 g, 1 mmol) in DME (20 ml) LiTrop (0.256 g, 2 mmol) in DME (10 ml) was added at room temperature under stirring. After 20 hours the light-brown precipitate was filtered, washed several times with DME (5 portions, 2 ml), and dried under vacuum. The crude product was Soxhlet-extracted for 3 hours with DME. The chloride contents of the products before and after Soxhlet extraction remained unchanged. The yield was ≅70%.

The Reaction of UCl$_4$ (UTrop$_3$Cl·THF and UTropCl$_3$·DME) with HTrop

UCl$_4$ and UTropCl$_3$·THF (1 mmol) were reacted with HTrop (in molar ratio 1:1 and 1:4 respectively) in THF at room temperature for six hours. In both reactions a red microcrystalline product precipitated, which was filtered, washed with THF and dried. The analytical data (Table I) were in agreement with a formulation UTrop$_3$Cl·THF (80% yield). When carrying out the same reactions between UCl$_4$ and HTrop (molar ratio 1:4) in DME, the only isolated dark-red product was UTropCl$_3$·2HTrop (80% yield).

The Reaction of ThCl$_4$·2DME and HTrop

By reacting ThCl$_4$·2DME and HTrop (molar ratio 1:4) in THF at room temperature for eight hours a pale yellow product was isolated, which analysed as ThTrop$_2$Cl$_2$·½DME (80% yield).

Substitution of Coordinated THF of MTropCl$_{4-n}$·xTHF (M = U^{IV} and Th^{IV}) by 18-Crown-6- and 2,2′-Bipyridine

An excess of the ligands 18-crown-6 and 2,2′-bipyridine, respectively, were slowly added to THF solutions of UTropCl$_3$·THF, UTrop$_2$Cl$_2$·THF and ThTropCl$_3$·3THF, respectively, at room temperature. Stirring was continued for 24 hours, and solid products progressively precipitated. These were separated by filtration, washed with THF and dried *in vacuo* (85% yields).

Attempts of a Synthesis of Cp$_2$UTrop$_2$

a) To UTrop$_2$Cl$_2$·THF (0.624 g, 1 mmol) dissolved in THF (20 ml) TlCp (0.538 g, 2 mmol) was added at room temperature. After 20 hours of stirring, the solid formed was filtered off and washed with THF and the resulting solution was concentrated *in vacuo* to 5 ml. Then n-pentane (50 ml) was added and a brown solid partially soluble in benzene precipitated (0.3 g). On the basis of analytical and spectroscopic data (^{1}H nmr and vis–nir) the benzene-soluble material was identified as a mixture containing mainly Cp$_3$UCl. No further analysis was performed.

b) To a Cp$_2$U(NEt$_2$)$_2$ (0.512 g, 1 mmol) n-hexane (20 ml) solution HTrop (0.122 g, 2 mmol) dissolved in Et$_2$O (20 ml) was added at room temperature, and the mixture was allowed to react under stirring for 24 hours. The dark-brown solid formed was filtered and washed several times with n-hexane. The crude product was identified, by ^{1}H nmr analysis, to be a mixture containing as main product CpUTrop$_3$. By Soxhlet extraction of the crude product with THF for 2 hours pure insoluble CpUTrop$_3$ was obtained. The filtered solution evaporated to dryness contained a mixture of products hardly separable in which Cp$_2$UTrop$_2$ was identified by its mass spectrum. Mass spectra: Cp$_2$UTrop$_2$: M^+ = 610 m/e (16); $M^+ - Cp$ = 545 m/e (100); $M^+ - 2Cp$ = 480 m/e (5). CpUTrop$_3$: M^+ = 666 m/e (6); $M^+ - Cp$ = 601 m/e (100). ^{1}H nmr (solvent CDCl$_3$, ppm from C$_6$D$_5$-H as internal standard; T = 27 °C): 6.35 (t, 6H, 3,5-H, J = 10.3 Hz); 2.78 (t, 3H, 4-H, J = 10.3 Hz); 1.24 (d, 6H, 2,6-H, J = 10.3 Hz); −16.75 (s, 5H, Cp).

CpUTropCl$_2$

To a suspension of UTropCl$_3$·THF (0.357 g, 1 mmol) in THF (30 ml) TlCp (0.269 g, 1 mmol) was added in several portions at room temperature. The stirring was continued for six hours, then the TlCl was filtered off, and the volume of the resulting solution was reduced to 5 ml under vacuum. By addition of Et$_2$O (30 ml) a yellow solid precipitated, which was filtered, washed with Et$_2$O and dried (≅65% yield). The mass spectrum presented the parent ion M^+ = 495 m/e.

CpUTrop$_2$Cl

A suspension of UCl$_4$ (0.380 g, 1 mmol), TlCp (0.269 g, 1 mmol) and TlTrop (0.650 g, 2 mmol) was stirred overnight in THF (20 ml). The red solution was filtered, reduced to small volume and a

TABLE I. Analytical Data of the Mixed-ligand Complexes Involving Uranium(IV) and Thorium(IV).

Compound	Colour	Calcd. %				Found %			
		C	H	N	Cl	C	H	N	Cl
UTropCl$_3$·THF	olive-green	24.56	2.44		19.79	25.42	2.80		20.01
ThTropCl$_3$·3THF	white	33.75	4.33		15.74	33.58	4.02		16.02
UTrop$_2$Cl$_2$·THF	hazel	34.67	2.91		11.38	34.33	2.98		11.43
ThTrop$_2$Cl$_2$·2THF	white	38.31	3.80		10.29	37.75	3.57		10.31
UTrop$_2$Cl$_2$·½DME·½LiCl	light-brown	31.07	2.45		14.38	30.68	2.37		14.13
UTrop$_3$Cl·THF	red	42.33	3.27		5.00	41.58	3.08		5.38
UTropCl$_3$·2HTrop	brick-red	35.52	2.41		14.99	34.63	2.93		14.95
ThTrop$_2$Cl$_2$·½DME	white	34.97	2.57		12.91	33.08	2.28		12.58
[UTropCl$_3$]$_2$·18-crown-6	light-yellow	26.11	2.87		17.80	27.16	2.43		18.01
[UTrop$_2$Cl$_2$]$_2$·18-crown-6	hazel	35.13	3.25		10.38	34.82	3.45		11.02
[ThTropCl$_3$]$_3$·[18-crown-6]$_2$	white	28.32	3.33		16.73	28.27	3.46		16.58
[UTropCl$_3$]$_2$·[2,2′-bipy]$_3$	red	37.74	2.45	6.01	15.20	38.08	2.68	6.28	15.37
CpUTrop$_3$	red	46.83	3.03			46.07	2.95		
CpUTropCl$_2$	yellow	29.09	2.04		14.32	28.66	2.13		14.42
CpUTrop$_2$Cl	red	39.27	2.60		6.11	38.56	2.48		5.98

TABLE II. The Near-infrared Spectra of the Uranium Complexes in the Range 1000–1300 nm.

Compound	Solvent	Absorption
UTropCl$_3$·THF	THF	1000sh, 1100sh, 1130s
UTrop$_2$Cl$_2$·THF	THF	1000s, 1080s, 1140s
UTrop$_3$Cl·THF	CH$_2$Cl$_2$	1050sh, 1100s
[UTropCl$_3$]$_2$·18-crown-6	water	1060s, 1180sh
[UTrop$_2$Cl$_2$]$_2$·18-crown-6	methanol	1055s, 1100sh
CpUTrop$_2$Cl	THF	1102s, 1180s, 1190sh
CpUTropCl$_2$	THF	1002s, 1030s, 1050sh, 1150s, 1290s

(Relative intensity: s = strong, sh = shoulder)

precipitate obtained after addition of n-hexane. The yield of the isolated CpUTrop$_2$Cl is low because of its slight solubility in THF, so the initial precipitate (containing probably TlCl mixed with the uranium compound) was Soxhlet extracted with THF during a period of some hours. The new product is identical to the first one.

As far as the ^{1}H nmr spectra are concerned, only some organometallic derivatives show, in organic deuterated solvents, a solubility suitable for recording unambiguous spectra.

Results and Discussion

The reaction of uranium(IV) and thorium(IV) tetrachlorides with M′Trop (where M′ = Li, Tl), affords the substitution of one or more chloride atoms depending on the molar ratios of the reagents, giving rise to mixed-ligand complexes of the general formula MTrop$_n$Cl$_{4-n}$·mL (M = U^{IV}, Th^{IV}; L = DME, THF, 18-crown-6, and 2,2′-bipyridine). These mixed-ligand complexes behave as Lewis acids being able to coordinate extra neutral ligands (Lewis bases) such as THF, 18-crown-6, 2,2′-bipyridine and, in the case of UTrop$_2$Cl$_2$·½DME·½LiCl, probably the chloride anion by forming Cl-bridged species. These coordination compounds seem to be stable against oxygen and moisture, whilst their organometallic derivatives are sensitive to the above agents. The solubility of the coordination compounds is good in water and methanol without apparent immediate decomposition and decreases in THF with an increase of the tropolonato groups bonded to the metal. The organometallic derivatives are rather soluble both in THF and benzene or toluene,

TABLE III. Main I.r. Absorption Bands (cm^{-1}) of the Mixed-ligand Uranium(IV) and Thorium(IV) Complexes.

Compound	Tropolonato		18-crown-6	THF	Cp	DME
	ν(C=O)	ν(C=C)				
$UTropCl_3 \cdot THF$	1585s	1510s		845m		
$ThTropCl_3 \cdot 3THF$	1590s	1513s		860m		
$UTrop_2Cl_2 \cdot THF$	1583s	1508s		863m		
$ThTrop_2Cl_2 \cdot 2THF$	1589s	1512s		860m		
$UTrop_3Cl \cdot THF$	1592s	1518s		868m		
$[UTrop_2Cl_2]_2 \cdot$ 18-crown-6	1593s	1521s	835m			
$[ThTropCl_3]_3 \cdot$ [18-crown-6]$_2$	1593s	1519s	830m			
$CpUTropCl_2$	1588s	1510s			1008m, 785s	
Cp_2UTrop_2	1595s	1513s			1012m, 782s	
$CpUTrop_3$	1593s	1515s			1017m, 788s	
$UCl_2Trop_2 \cdot$½DME·½LiCl	1594s	1519s				870s

(Relative intensity: s = strong, m = medium)

the relative solubility depending also in this case on the number of tropolonato groups.

The electronic spectra (Table II) of the uranium derivatives are typical of species containing a high formal coordination number (⩾8) [15] which could be reached in solution also by association processes leading to the formation of oligomeric products.

The infrared spectra in the range 1600–600 cm^{-1} (Table III) show the characteristic absorption bands of the chelating tropolonato and cyclopentadienide anions as well as those of the other coordinated ligands [1, 3, 14]. Only small variations of the band positions occur for the various complexes almost independently both on the metal and the different ligands. Worth noting is the decrease of the C=O stretching frequency along the series:

	ν(C=O) cm^{-1}
HTrop	1613
NaTrop	1610
$Th(Trop)_4$	1599
$U(Trop)_4$	1598
Our Complexes	1595–1583

which can be interpreted as an increased involvement of the oxygen atoms in covalent bonding to the metal atoms.

The reaction of HTrop with UCl_4 in various molar ratios depends on the nature of the reaction solvent, since by using THF a substitution of the chloride by tropolonato anions to afford $UTropCl_3 \cdot THF$ is observed, while by using DME as solvent a slightly soluble product with the composition $UTropCl_3 \cdot 2HTrop$ separated. The exact formulation of these adducts and particularly the mode of ligation [16] of HTrop to the central metal deserves further structural information. Efforts to obtain suitable crystals are underway.

By carrying out the reaction of $ThCl_4$ in DME with HTrop (in the molar ratio ¼) only substitution of chloride ions takes place by formation of $ThTrop_2Cl_2 \cdot$½DME.

With the aim of verifying the potential use of the mixed chloride and tropolonato complexes of uranium(IV) as starting materials for the synthesis of new organometallic derivatives, some reactions with TlCp have been carried out. $UTropCl_3$ reacts with TlCp giving the expected species $CpUTropCl_2$ following the scheme:

$$UTropCl_3THF + TlCp \xrightarrow[THF]{R.T.} CpUTropCl_2 + TlCp$$

while $UTrop_2Cl_2$ produces Cp_3UCl as one of the main products by reaction with two mol of TlCp. This behaviour parallels that of UOx_2Cl_2 [17] suggesting that in both cases a multi-step reaction takes place involving intermediates which undergo Cp ligand redistribution. On the other hand, if an equimolar $UTrop_2Cl_2$ and TlCp mixture is brought into reaction, the expected $CpUTrop_2Cl$ is formed in good yield.

A convenient route towards organometallic species seems to be the controlled protolysis of $Cp_2U(NEt_2)_2$ leading also to the substitution of the amido groups by tropolonate anions; indeed one cyclopentadienyl group, too, may be cleaved, but the formed $CpUTrop_3$ can be easily separated from the reaction mixture by taking advantage of the slight solubility of the former complex in THF. Its ^1H nmr spectrum ($CDCl_3$) shows four signals in the ratio 6:3:6:5, which on the basis of their multiplicities and of double resonance measurements have been assigned to 3,5-H, 4-H, 2,6-H (of the tropolonate groups) and to cyclopentadienyl protons respectively. The presence of only four signals is indicative of a high symmetry in the molecule making the three tropolonate groups magnetically equivalent. Comparison of the ^{1}H nmr spectra of $CpUTrop_3$ with that of the similar compound $CpU(acac)_3$ [10] shows that the isotropic shifts of the cyclopentadienyl protons are quite close ($CpUTrop_3$: Cp = −16.75 ppm; CpU-(acac): Cp = −14.03 ppm), while the other protons show a slightly different behaviour, reflecting both the different nature of the diketones involved and the greater rigidity of the tropolonate ring compared with that of the acetylacetate group.

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