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ON THE INDENYL COMPOUNDS OF ACTINIDE ELEMENTS

Part V : Some oxygen-donor complexes of indenyl actinide halides.

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ABSTRACT

The complexes $(\eta^5\text{-}C_9H_7)AnX_3.L_a.L_b$ (X = Cl or Br, An = U or Th, L_a = C_4H_8O (THF) or $(C_6H_5)_3PO$ (TΦPO), L_b = TΦPO or THF) have been prepared. Infrared, Raman, electronic and mass spectra as well as magnetic susceptibility measurements are reported and discussed. The solid-state molecular structure of $(\eta^5\text{-}C_9H_7)UBr_3.C_4H_8O.(C_6H_5)_3PO$ is reported. The complexes $(\eta^5\text{-}C_9H_7)AnX_3.\ 2(C_6H_5)_3PO$ in solution show a strong tendency to disproportionate giving $(\eta^5\text{-}C_9H_7)_3AnX$,2 $AnX_4.2(C_6H_5)_3PO$ and free ligand.

INTRODUCTION

Doretti and coworkers (1) have reported in 1972 the preparation of $(\eta^5\text{-}C_5H_5)UCl_3.2THF$. Recently, Bagnall and coworkers (2-3) have investigated the properties of this type of solvated species and the structure of some complexes has been established (4-6). As such compounds containing the indenyl entity have not previously been recorded, it was of interest

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to prepare them and to study some of their properties.

EXPERIMENTAL SECTION

$ThCl_4$, UCl_4, UBr_4 and $UCl_4.2(C_6H_5)_3PO$ were prepared according to published methods (3,7-10). Triphenyl phosphine oxide was prepared by reaction of an excess of $(C_6H_5)MgBr$ on $OPCl_3$ in ether (11). The crude product was neutralized, sublimed in vacuo and recrystallized from benzene. All experimental operations were carried out in a glove-box under purified nitrogen or argon (3,7-10) atmosphere. Vibrational, electronic and mass spectra were recorded as described previously (7-10). The magnetic susceptibility data were obtained with a Faraday balance.

PREPARATIVE METHODS

Trichloro (η^5-indenyl) bis(tetrahydrofuran) uranium(IV).

1.- C_9H_7Na (16,7 mmol) dissolved in THF was added over a period of 6 hours to a THF solution of UCl_4 (16,7 mmol) at room temperature. The green solution of the uranium salt became progressively deep red. After stirring (24 hrs), the red solution was filtered and concentrated at low temperature. The violet precipitate was filtered off and washed twice with n-pentane and vacuum dried at room temperature (yield > 70 %).

2.- $(\eta^5-C_9H_7)_3UCl$ (5 mmol) and UCl_4 (10 mmol) were dissolved in THF and the solution was stirred for two days at room temperature, its color turning gradually from brown to red. No change in the electronic spectrum of the solution was noted after 8 hours and no band $(\eta^5-C_9H_7)_3UCl$ was observed. The solution was evaporated until a violet product separated. The new compound was filtered off, washed with n-pentane and vacuum dried at room temperature (yield > 90 %).

The reddish tribromo (η^5-indenyl) bis(tetrahydrofuran) uranium and the pale yellow trichloro (η^5-indenyl) bis(tetrahydrofuran) thorium were prepared by the same method and with the same yields.

Trichloro (η^5-indenyl) tetrahydrofuran triphenyl phosphine oxide uranium(IV).

$(C_6H_5)_3PO$ (5 mmol) dissolved in THF was added (1 hr) to $(\eta^5-C_9H_7)UCl_3$. 2THF (5 mmol) in THF at - 70°C. After complete addition, the temperature was raised to 0°C. Around this temperature, a brick-red compound precipitated. The compound was filtered off, washed with cold THF (2x5 ml), with pentane (2x5 ml) and vacuum dried at 0°C (yield = 50 %).

The red tribromo (η^5-indenyl) tetrahydrofuran triphenyl phosphine oxide uranium(IV) and the pale yellow trichloro(η^5-indenyl) tetrahydrofuran triphenyl phosphine oxide thorium(IV) were prepared in the same manner.

Trichloro (η^5-indenyl) bis(triphenyl phosphine oxide) uranium(IV).

1.- $(\eta^5-C_9H_7)UCl_3$. 2THF (5 mmol) dissolved in THF was slowly reacted with 10 mmol $(C_6H_5)_3PO$ at - 70°C in THF. The solution was concentrated at low temperature until a pale brown solid formed. The compound was filtered off, washed with cold THF (3x5 ml) and immediately vacuum dried (yield = 50 %).

2.- UCl_4. 2TΦPO (1 mmol) and C_9H_7Na (1 mmol) were dissolved in one liter of THF and stirred at 0°C for 8 days. The solution was filtered and concentrated at low temperature. A pale brown compound was obtained in 50 % yield.
The analogous thorium compound was obtained in the same manner.

The complexes $(\eta^5\text{-}C_9H_7)AnX_3.THF$ and $(\eta^5\text{-}C_9H_7)AnX_3.T\Phi PO$ have been obtained by pumping respectively $(\eta^5\text{-}C_9H_7)AnX_3.2THF$ and $(\eta^5\text{-}C_9H_7)AnX_3.THF.T\Phi PO$ for 8 hrs at 60°C ($< 10^{-4}$ torr).

RESULTS AND DISCUSSION

The mobility of the THF ligand in the new complexes has been confirmed by recording the mass spectra at different temperatures. A typical spectrum is shown in Table II. At 180°C, when the first peaks corresponding to the indenyl-actinide complex are observed, we also note an important free-THF peak which disappears at higher temperatures. At 350°C, all the THF has been pumped out and we only observe peaks due to the fragmentation of THF-free complexes.

The THF adducts are very sensitive to oxygen and moisture while $(\eta^5\text{-}C_9H_7)AnX_3.2T\Phi PO$ are rather stable : only an exposure to air for many hours causes the complete decomposition of the complexes. On the other hand, the THF solutions of the phosphine oxide compounds are rather unstable. An addition of 10 % of pentane or heating at 30-40°C induces the disproportionation of the complexes :

$$3\ (\eta^5\text{-}C_9H_7)AnX_3.2T\Phi PO \rightleftarrows (\eta^5\text{-}C_9H_7)_3AnX + 2\ AnX_4.2T\Phi PO + 2T\Phi PO$$

In the case of uranium compounds, the solution turns from red to brown with precipitation of green $UX_4.2T\Phi PO$; $(\eta^5\text{-}C_9H_7)_3UX$ being identified by its electronic spectrum. At low temperature (t < 20°C), the THF solutions of uranium compounds are stable at least many days. The thorium complexes are more sensitive to disproportionation than the uranium analogues.

TABLE I. Analytical Results [a].

Compounds	C[b]	H[b]	An	Hal	P
$C_9H_7UCl_3$. 2 THF	33.90 (33.82)	3.80 (3.84)	39.6 (39.42)	17.0 (17.62)	
$C_9H_7UBr_3$. 2 THF	27.79 (27.70)	3.22 (3.15)	32.4 (32.29)	32.1 (32.52)	
$C_9H_7ThCl_3$. 2 THF	33.90 (34.16)	3.79 (3.88)	37.8 (38.22)	17.4 (17.79)	
$C_9H_7UCl_3$. THF	29.15 (29.37)	2.95 (2.84)	44.5 (44.77)	18.9 (20.01)	
$C_9H_7UBr_3$. THF	24.67 (23.48)	2.27 (2.27)	35.9 (35.79)	35.3 (36.05)	
$C_9H_7ThCl_3$. THF	29.67 (29.70)	3.13 (2.88)	44.1 (44.14)	20.2 (20.23)	
$C_9H_7UCl_3$. THF . TΦPO	45.86 (45.97)	3.70 (3.73)	29.1 (29.39)	13.0 (13.13)	3.7 (3.82)
$C_9H_7UBr_3$. THF . TΦPO	39.62 (39.47)	3.11 (3.21)	25.0 (25.23)	25.0 (25.41)	3.5 (3.28)
$C_9H_7ThCl_3$. THF . TΦPO	46.55 (46.31)	3.52 (3.76)	28.0 (28.86)	13.5 (13.23)	3.8 (3.85)
$C_9H_7UCl_3$. TΦPO	43.71 (43.95)	3.26 (3.00)	32.9 (32.26)	14.6 (14.42)	4.4 (4.20)
$C_9H_7UBr_3$. TΦPO	36.89 (37.22)	2.92 (2.55)	27.5 (27.32)	27.6 (27.52)	3.6 (3.55)
$C_9H_7ThCl_3$. TΦPO	43.87 (44.31)	3.18 (3.03)	30.9 (31.71)	14.9 (14.53)	4.0 (4.23)
$C_9H_7UCl_3$. 2 TΦPO	52.77 (53.19)	3.69 (3.67)	23.4 (23.43)	10.3 (10.47)	6.0 (6.10)
$C_9H_7ThCl_3$. 2 TΦPO	53.50 (53.51)	3.59 (3.69)	22.7 (22.97)	10.6 (10.52)	6.0 (6.13)

a) Theoretical values are given in parentheses.

b) C-H analyses were performed by G. Reuter. Analytische Laboratorien, Elbach (Germany).

TABLE II. Mass spectra of $(\eta^5\text{-}C_9H_7)UBr_3 . C_4H_8O . (C_6H_5)_3PO$ (62 eV).

m/e	t^b : 350°C R.I.[a]	t^b : 230°C R.I.[a]	t^b : 180°C R.I.[a]	Ion
791	3.2	-	-	$(C_9H_7)UBr_2 . (C_6H_5)_3PO^+$
756	6.3	-	-	$UBr_3 . (C_6H_5)_3PO^+$
711	27	-	-	$(C_9H_7)UBr . (C_6H_5)_3PO^+$
631	5.6	-	-	$(C_9H_7)U . (C_6H_5)_3PO^+$
513	58	75	75	$(C_9H_7)UBr_2^+$
433	31	38	40	$(C_9H_7)UBr^+$
353	100	100	100	$(C_9H_7)U^+$
72	-	-	V.S.[c]	$C_4H_8O^+$

a : Relative intensity.

b : Temperature of introduction.

c : Very strong.

In the infrared spectra of $(\eta^5\text{-}C_9H_7)AnX_3.2THF$ (figure 1), the characteristic absorption bands of η^5-bonded indenyl ligand can be observed around 1330, 1210, 785, 763, 756, 445 and 380 cm^{-1}

The two strong bands observed at 1013 and 856 cm^{-1} in $ThCl_4.2THF$ are shifted respectively to 996 and 842 cm^{-1} in $(\eta^5\text{-}C_9H_7)ThCl_3.2THF$ and to 996 to 840 cm^{-1} in $(\eta^5\text{-}C_9H_7)UCl_3.2THF$. They can be assigned to asymmetric and symmetric C-O-C stretching vibrations of the coordinated THF[3]. The corresponding Raman lines cannot be observed, the presence of THF being detected by a medium Raman line at 690 cm^{-1}.

In triphenyl phosphine oxide, the infrared band corresponding to the PO vibration is noted at 1190 cm^{-1} : this band

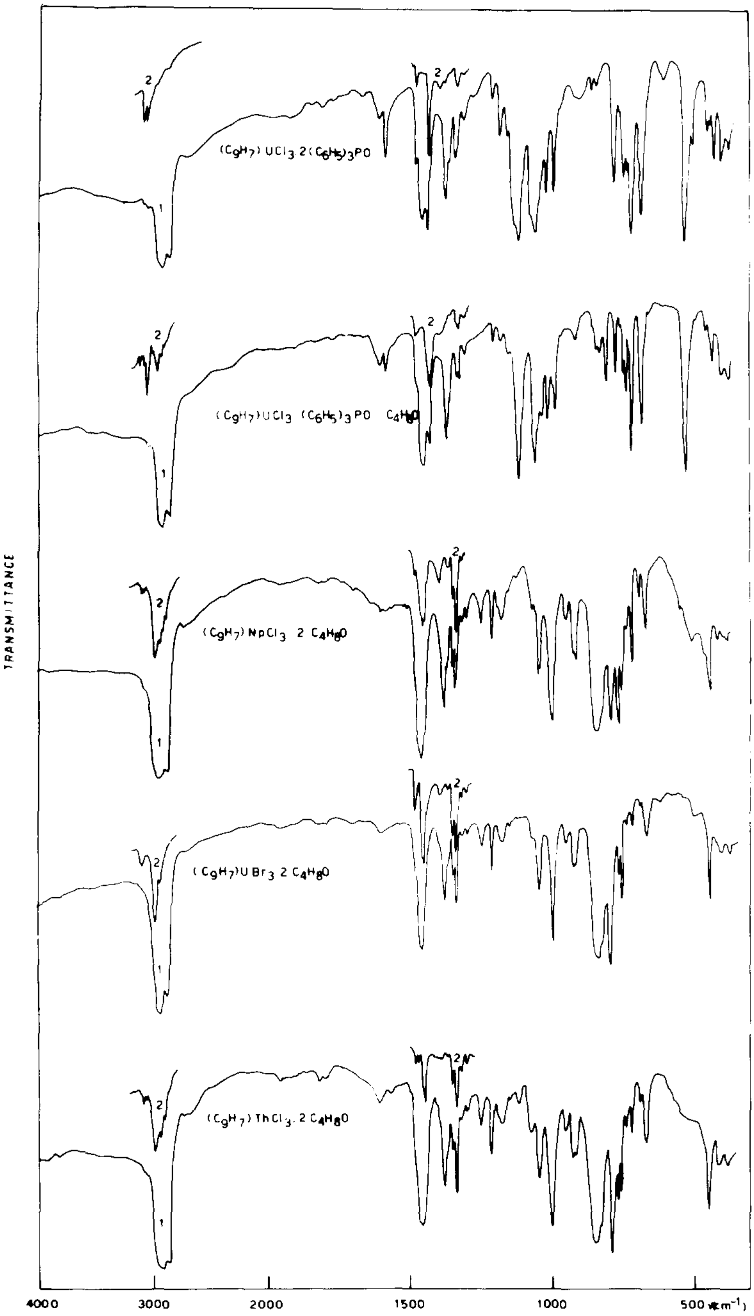

FIG. 1 INFRARED SPECTRA OF SOME INDENYL COMPOUNDS

(1. nujol mulls 2. hexachlorobutadiene mulls) is shifted to 1046 cm^{-1} in $ThCl_4.2T\Phi PO$ ($\Delta\nu$ = 144 cm^{-1}) and to 1045 cm^{-1} in $UCl_4.2T\Phi PO$ ($\Delta\nu$ = 145 cm^{-1}) by the coordination of the PO group to the actinide. The corresponding band is observed at 1067 cm^{-1} in $(\eta^5\text{-}C_9H_7)ThCl_3.THF.T\Phi PO$, at 1063 cm^{-1} in $(\eta^5\text{-}C_9H_7)UCl_3.THF.T\Phi PO$, at 1057 cm^{-1} in $(\eta^5\text{-}C_9H_7)UBr_3.THF.T\Phi PO$ and at 1060 cm^{-1} in the two $(\eta^5\text{-}C_9H_7)AnCl_3.2T\Phi PO$.

In the low frequency region, $(\eta^5\text{-}C_9H_7)AnCl_3.2THF$ presents one band at 260 cm^{-1} corresponding to the An-Cl vibration. The polarized Raman line at 275 cm^{-1} has been assigned to the same vibration. The UBr vibration is noted at 180 cm^{-1}.

The phosphine oxide adducts present a very large band around 260 cm^{-1} which corresponds probably to the superposition of two or more transitions in this frequency region.

The electronic spectra of the new complexes in benzene or in THF are very simple. In the range between 800 and 1600 nm, they only exhibit a strong band in the 1100-1200 nm region (table III).

Table III. Electronic spectra of the complexes in THF solution (principal feature : 800-1600 nm).

$(\eta^5\text{-}C_9H_7)UCl_3.2THF$	1162 nm
$(\eta^5\text{-}C_9H_7)UBr_3.2THF$	1166 nm
$(\eta^5\text{-}C_9H_7)UCl_3.THF.T\Phi PO$	1126 nm
$(\eta^5\text{-}C_9H_7)UBr_3.THF.T\Phi PO$	1127 nm
$(\eta^5\text{-}C_9H_7)UCl_3.2T\Phi PO$	1128 nm

This type of electronic spectra suggests the absence of other species in solution (3).

The magnetic susceptibility of the paramagnetic compounds has been measured between 77 K and room temperature (figure 2).

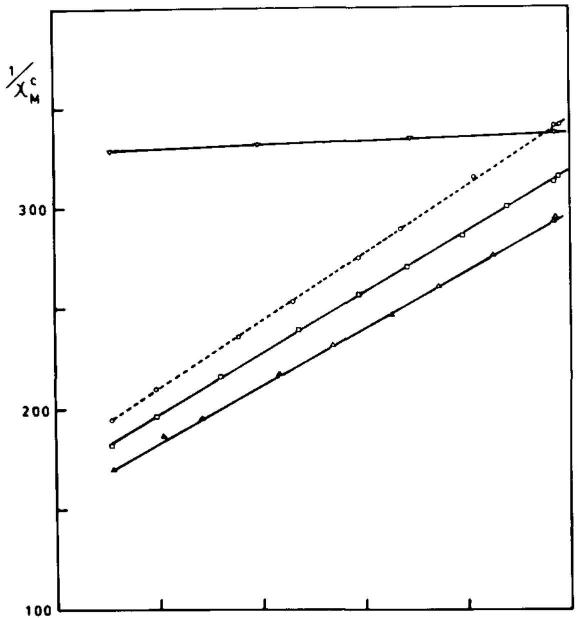

FIG. 2 MAGNETIC SUSCEPTIBILITY OF :

▼ $(C_9H_7)UCl_3.2(C_6H_5)_3PO$

● $(C_9H_7)UBr_3.(C_6H_5)_3PO.C_4H_8O$

□ $(C_9H_7)UCl_3.2C_4H_8O$

▲ $(C_9H_7)UBr_3.2C_4H_8O$

$(\eta^5-C_9H_7)UX_3.2T\Phi PO$ presents a magnetism practically independent of the temperature between 77 and 300 K. The same behaviour has been observed for $UCl_4.2T\Phi PO$, $(UCl_6)^{2-}$ and $(UBr_6)^{2-}$ which are known be species with a octahedral structure (12).
It is unlikely that the temperature dependent magnetism of the other indenyl compounds finds its origin in distortions of these molecules from a regular octahedral geometry. The single crystals of $(\eta^5-C_9H_7)UBr_3.THF.T\Phi PO$ were grown for crystallographic study (13)(figure 3). In this compound, the uranium atom is octahedrally coordinated to two oxygen atoms, one from $T\Phi PO$ and one

$(\eta^5\text{-}C_9H_7)UX_3.2THF$ and $(\eta^5\text{-}C_9H_7)UX_3.THF.T\Phi PO$ follow the Curie-Weiss law (table IV).

TABLE IV. Magnetic susceptibility data.

Complexes	θvalues	$\mu^{(a)}_{eff.}$	$\mu^{(b)}_{eff.}$
$(\eta^5\text{-}C_9H_7)UCl_3.2THF$	- 226	3,64	2,72
$(\eta^5\text{-}C_9H_7)UBr_3.2THF$	- 222	3,75	2,82
$(\eta^5\text{-}C_9H_7)UBr_3.THF.T\Phi PO$	- 204	3,41	2,62
$(\eta^5\text{-}C_9H_7)UCl_3.2T\Phi PO$	-	-	2,61
$UCl_4.2T\Phi PO$	-	-	2,03

(a) $\mu_{eff.} = 2{,}828 \sqrt{\chi_m^{corr} \, (T - \theta)}$

(b) $\mu_{eff.} = 2{,}828 \sqrt{\chi_m^{corr} \, 293}$

All results are corrected for the diamagnetic contribution of the molecular constituents.

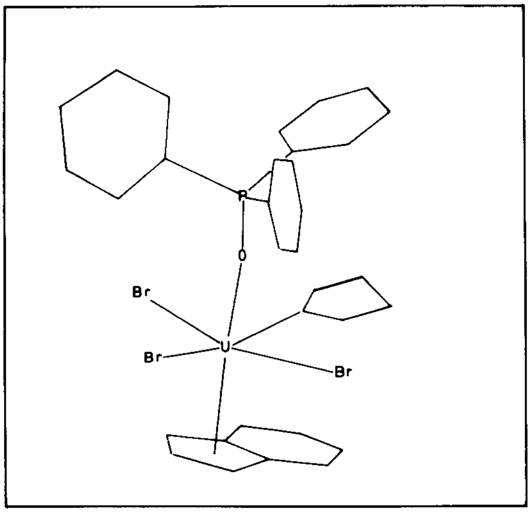

FIG. 3. STRUCTURE OF $(C_9H_7)\,UBr_3(C_6H_5)_3PO.C_4H_8O$

from THF which occupy cis position, to three bromide atoms and to the C_5 ring of the indenyl ligand which is placed in a trans position with respect to the TΦPO molecules. The coordination geometry of this new compound is similar to the structure of $UCl_4.2T\Phi PO$ and related compounds (4-6) in which TΦPO is also coordinated to the uranium atom in cis position. As expected by the magnetism measurements, the presence of indenyl anion induces a rather important distortion from perpendicularity of the angles subtended at the uranium atom. The value of the angles O (TΦPO)-U-Br and O (TΦPO)-U-O (THF) is around 80°. Complete data will be published (13).

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