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Organoactinide Complexes
Part I. Synthesis and Structure of Tris(cyclopentadienyl)uranium Fluoroalkoxides*

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In the rapidly growing area of organoactinide chemistry [1] the use of fluorinated ligands has been virtually ignored. Only a very small number of fluorine-containing organouranium and thorium complexes are known [2–6]. Well characterized examples are Cp_3UF [3, 4], $[\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2U(\mu\text{-}BF_4)(\mu\text{-}F)]_2$ [5] and $[\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2UF]_2$ [6]. We report here the synthesis and structural characterization of a series of tris(cyclopentadienyl)uranium(IV) fluoroalkoxides, Cp_3UOR_f (**1**).

Experimental

All reactions were carried out under rigorous exclusion of oxygen and moisture using a glovebox and standard Schlenk techniques.

Synthesis of Cp_3UOR_f (1)

Equimolar amounts (3.0 mmol) of Cp_3UCl [7] and $NaOR_f$ [8] were reacted in THF solution (50 ml) at room temperature for 24 h. After filtration through a thin layer of Celite filter aid the filtrate was evaporated to dryness. Recrystallization of the residue from toluene gave red–brown crystalline complexes (**1**) in 60–80% yield. All compounds gave satisfactory elemental analyses. NMR details are shown in Table I.

Crystal Data for 1c

Dark red single crystals were obtained by slow evaporation of a THF solution. $C_{19}H_{15}Cl_3F_6OU$: $M = 717.7$, orthorhombic, space group *Pcmn*, $Z = 4$, $a = 8.244(2)$, $b = 12.413(4)$, $c = 20.819(6)$ Å, $\mu = 76.8\ \text{cm}^{-1}$ (Mo Kα), $2\theta_{\max} = 65°$. The structure was solved by routine heavy atom methods and refined to $R = 0.056$, $R_w = 0.057$ for 2183 reflections (with $|F| > 5\sigma F$).

Results and Discussion

Cp_3UCl cleanly reacts with lithium or sodium fluoroalkoxides in THF solution to give red–brown crystalline complexes of the type Cp_3UOR_f (**1**)

$$Cp_3UCl + {}^{-}OR_f \xrightarrow[24\text{ h},\ 20\ °\text{C}]{\text{THF}} Cp_3UOR_f$$

$$-Cl^{-} \qquad (60\text{–}80\%\ \text{yield})$$

$R_f = CH_2CF_3, C(CF_3)_2CH_3, C(CF_3)_2CCl_3,$
$C(CF_3)_2CF(CF_3)_2, C_6F_5$

The new organouranium fluoroalkoxides (**1**) are soluble in aromatic hydrocarbons and significantly more volatile than Cp_3UCl (e.g. **1b** sublimes at *ca.* 120 °C/0.1 mm). The structure of $Cp_3UOC(CF_3)_2CCl_3$ (**1c**) was determined by X-ray diffraction. This represents the first structural characterization of an organouranium alkoxide of the type Cp_3UOR [9, 10]. Figure 1 shows a SCHAKAL drawing of **1c**. The central part of the molecule is the nearly linear U–O–C unit. The U–O distance (2.23 Å) is slightly longer than those found for binary uranium alkoxides (2.03–2.13 Å) [11, 12]. With an average U–C(Cp) distance of 2.74(1) the Cp_3U unit closely resembles other tris(cyclopentadienyl)uranium complexes [2].

TABLE 1. NMR Spectroscopic Characterization of Cp_3UOR_f (Solvent: C_6D_6)

	1a	1b	1c	1d	1e
R_f	CH_2CF_3	$C(CF_3)_2CH_3$	$C(CF_3)_2CCl_3$	$C(CF_3)_2CF(CF_3)_2$	C_6F_5
^{1}H NMR (ppm)	δ 0.2 (s, Cp), − 10.4 (CH_2)	δ 0.2 (s, Cp), − 9.2 (s, CH_3)	δ 0.2 (s, Cp)	δ 0.15 (s, Cp)	δ 0.3 (s, Cp)
^{19}F NMR (ppm)	δ −8.4 (t, CF_3)	δ − 94.8, (q, CF_3)	δ −97.1 (s, CF_3)	δ − 83.7, − 100.7 (m, CF_3), − 202.1 (m, CF)	δ − 136.8 (m, *o*–F) − 165.0 (m, *m*–F) − 169.5 (m, *p*–F)

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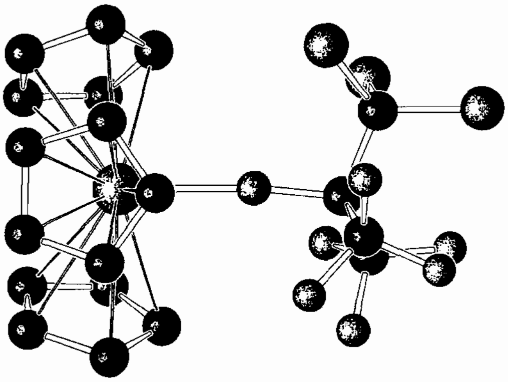

Fig. 1. Structure of **1c**. Selected bond lengths (Å) and angles (°): U–O, 2.23(1); O–C, 1.43(2); U–C(Cp), 2.74(1) (av.); U–Cp, 2.45(1) (av.); U–O–C, 175(1)

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