Inorganica Chimica Acta, 139 (1987) 209–210

Crystal and Molecular Structure of a Novel Organoactinide Complex: $[U(C_5H_5)_3(NCCH_3)_2]^+[Th(C_5H_5)Cl_4(NCCH_3)]^-$ *

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The property of UCp_3X type molecules (Cp = cyclopentadienyl) of forming adducts has been unequivocally established when complexes $[UCp_3XY]^q$ were isolated and structurally characterized by X-ray diffraction. Examples of such complexes are known with electronic charges $q = 0, +1, -1$ in different salts: these are $[UCp_3(NCCH_3)(NCS)]$ [1], $[UCp_3(NCCH_3)_2]_2^+[UO_2Cl_4]^{2-}\cdot 2(C_4H_6)$ [2] and $[AsPh_4]^+[UCp_3(NCS)_2]^-$ [3]. The compound whose crystal structure is described below is unique in organoactinide chemistry since it contains simultaneously an organouranium component as cation and an organothorium component as anion.

Experimental

The title compound was obtained, under argon atmosphere, by addition of $ThCl_4$ to a solution of UCp_3Cl in CH_3CN. Well-shaped green single crystals appeared during recrystallization from a CH_3CN solution at 80 °C. The new compound was characterized by chemical analysis and infrared spectroscopy. X-ray intensities were recorded with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. $[UCp_3(NCCH_3)_2]^+[Th(C_5H_5)Cl_4(NCCH_3)]^-$ crystallizes in the monoclinic space group $P2_{1/c}$ with cell dimensions $a = 12.284(4)$, $b = 14.510(8)$, $c = 17.247(9)$ Å and $\beta = 96.77(1)°$. There are four molecules in the unit cell. The structure determination was solved by direct methods and refined by the least-squares method in a full-matrix approximation on 1411 unique reflections for which $I > 3\sigma(I)$. The agreement factors are $R = 0.042$ and $R_w = 0.047$ ($w = 1/\sigma^2(F_o)$).

Results and Discussion

The molecular structures of the cation and of the anion are presented in Figs. 1 and 2 respectively. Selected interatomic distances and angles are listed in Table I. In the cation, the coordination around the uranium atom is a trigonal bipyramid (pseudo D_{3h} symmetry), the centres of the three π-bonded cyclopentadienyl rings constituting the equatorial plane

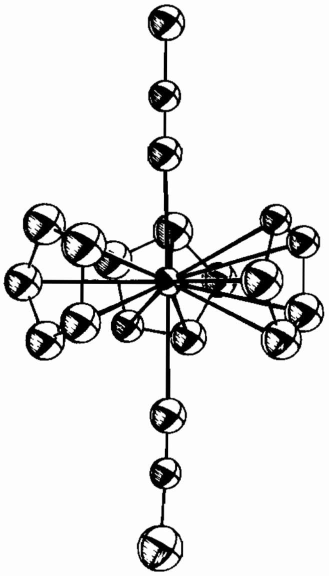

Fig. 1. View of the cation $[U(C_5H_5)_3(NCCH_3)]^+$.

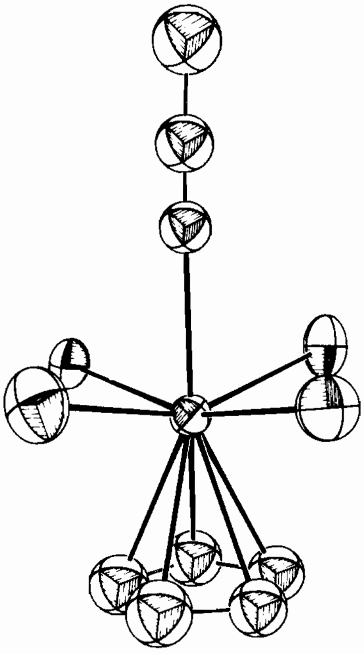

Fig. 2. View of the anion $[Th(C_5H_5)Cl_4(NCCH_3)]^-$.

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*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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0020-1693/87/$3.50

TABLE I. Selected Distances (A) and Angles (°)[a]

$[UCp_3(NCCH_3)_2]^+$		$[ThCpCl_4(NCCH_3)]^-$	
Bonds			
U–C(1)	2.76(3)	Th–C(16)	2.77(3)
U–C(2)	2.74(3)	Th–C(17)	2.78(3)
U–C(3)	2.76(3)	Th–C(18)	2.79(3)
U–C(4)	2.72(3)	Th–C(19)	2.74(3)
U–C(5)	2.66(3)	Th–C(20)	2.77(3)
U–C(6)	2.68(3)	Th–Cp(4)	2.51(3)
U–C(7)	2.71(3)	Th–Cl(1)	2.659(8)
U–C(8)	2.72(2)	Th–Cl(2)	2.670(8)
U–C(9)	2.80(3)	Th–Cl(3)	2.655(8)
U–C(10)	2.76(3)	Th–Cl(4)	2.646(9)
U–C(11)	2.74(3)	Th–N(3))	2.58(3)
U–C(12)	2.79(3)		
U–C(13)	2.75(3)		
U–C(14)	2.68(3)		
U–C(15)	2.67(3)		
U–Cp(1)	2.46(3)		
U–Cp(2)	2.47(3)		
U–Cp(3)	2.46(3)		
U–N(1)	2.50(3)		
U–N(2)	2.59(3)		
Angles			
		Cl(1)–Th–Cl(3)	87.0(3)
N(1)–U–N(2)	178.6(8)	Cl(1)–Th–Cl(4)	87.1(3)
Cp(1)–U–Cp(2)	119.3(9)	Cl(2)–Th–Cl(3)	89.5(3)
Cp(1)–U–Cp(3)	120.0(9)	Cl(2)–Th–Cl(4)	87.8(3)
Cp(2)–U–Cp(3)	120.7(9)	Cl(1)–Th–N(3)	81.9(6)
N(1)–U–Cp(1)	91.0(8)	Cl(2)–Th–N(3)	78.9(6)
N(2)–U–Cp(1)	89.6(8)	Cl(3)–Th–N(3)	74.5(6)
N(1)–U–Cp(2)	90.7(8)	Cl(4)–Th–N(3)	79.7(6)
N(2)–U–Cp(2)	90.1(8)	Cl(1)–Th–Cp(4)	101.0(7)
N(1)–U–Cp(3)	90.2(8)	Cl(2)–Th–Cp(4)	98.3(7)
N(2)–U–Cp(3)	88.4(8)	Cl(3)–Th–Cp(4)	100.7(7)
U–N(1)–C(1′)	179.0(2)	Cl(4)–Th–Cp(4)	105.2(7)
U–N(2)–C(2′)	178.0(2)	N(3)–Th–Cp(4)	174.3(8)

[a] Cp(1) denotes ring 1 centroid (C(1)···C(5)); Cp(2) denotes ring 2 centroid (C(6)···C(10)); Cp(3) denotes ring 3 centroid (C(11)···C(15)); Cp(4) denotes ring 4 centroid (C(16)··· C(20)).

of the bipyramid. The two acetonitrile ligands occupy the *trans* diaxial positions, being bonded to the uranium via the nitrogen atoms. The uranium in this cationic unit is formally eleven-coordinated if each η^5-Cp ligand is assumed to occupy three coordination sites. The two CH_3CN ligands are practically co-linear with the U–N bonds.

This cationic organouranium species has previously been observed in the complex $[UCp_3(NCCH_3)_2]_2$-$[UO_2Cl_4]\cdot 2(C_4H_6)$ whose crystal structure has been reported in the literature [2]. All bond distances and angles are in good agreement in the two structures. Here the average U–C distance is 2.73(3) Å. The ring centroid–U–ring centroid and ring centroid–U–N angles average respectively 120.0° and 90.0°.

The anion coordination polyhedron is a distorted octahedron. The cyclopentadienyl and the acetonitrile nitrogen atom occupy axial positions with the four chlorine atoms lying at the corners of a slightly puckered square constituting the equatorial plane. The thorium atom is formally eight-coordinated. The deviations from the best least-squares mean plane through the four chlorines are +0.075(8), +0.072(7), −0.073(8) and −0.074(8) Å, respectively, for the atoms Cl(1), Cl(2), Cl(3) and Cl(4). The thorium atom is 0.520(1) Å out of this equatorial mean plane toward the cyclopentadienyl ligand. The four equatorial ligands seem therefore to bend away from the penta-hapto cyclopentadienyl ligand. The Th–C distances average 2.77(3) Å, in agreement with the values reported for the penta-hapto Th–C bond lengths in $[Th(C_5H_4)(C_5H_5)_2]_2$ [4] and $[Th(C_5(CH_3)_5)_2(C_2(CH_3)_2O_2)]_2$ [5]. The average Th–Cl distance, 2.658(8) Å, is in agreement with the covalent radii sum. $[ThCpCl_4(NCCH_3)]^-$ is the first $AnX_4\cdot 2L$ (An = actinide; X = Cl or Br) type complex with a cyclopentadienyl ring as donor ligand. The intermolecular contacts in this compound are not of particular significance.

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