Synthesis and structure of neutral π-arene complex (η^6-C_6H_5Me)U($AlCl_4$)$_3$

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A new neutral π-arene complex of trivalent uranium, (η^6-C_6H_5Me)U($AlCl_4$)$_3$ (**1**), was obtained by the reductive Friedel—Crafts reaction. The crystal structure of **1** was determined by single crystal X-ray diffraction analysis. The U atom in **1** is bound to the C_6H_5Me group by the η^6 mechanism and is linked to the three $AlCl_4$ groups through two μ-Cl bridges. The coordination of the U atom is a distorted pentagonal bipyramid in which the center of the arene ring is in one apical position, and the bridging Cl atoms occupy the other vertices.

Key words: actinides, arene complexes, molecular structure, X-ray diffraction analysis.

The interest of researchers in π-arene complexes of f-elements is caused by the persisting discussion of the question of participation of the f-orbitals of metal atoms in binding to the ligand. In recent years, several π-arene complexes of lanthanides[1—4] and actinides[2,5—8] have been prepared. Most of these complexes were obtained under the conditions of the Friedel—Crafts reductive reaction from the corresponding lanthanide chlorides (La, Sm, Nd) or from uranium tetrachloride in the presence of aluminum. In the case of lanthanides, this reaction yields Ln^{III} complexes of the type (η^6-Arene)Ln($AlCl_4$)$_3$, though during the synthesis, reduction processes occur, as indicated by the red coloring of the reaction mixture.[1,4]

The reactions involving UCl_4 afford both U^{III} and U^{IV} complexes. The conditions in which the reaction is conducted, in particular, the solvent used, play an important role in the formation of one or another product. For example, in an arene solvent, tetravalent uranium is reduced to trivalent uranium, and the reaction yields complexes (η^6-C_6H_5Me)U($AlCl_4$)$_3$).[2,5] However, when the reaction of UCl_4, arene, and $AlCl_3$ was carried out in hexane, and the final product was then extracted with dichloromethane, multinuclear complexes of tetravalent uranium were obtained.[6,7]

All the obtained compounds are intensely colored crystals sensitive to oxygen and moisture. After isolation in the solid state, they are poorly soluble in hydrocarbon solvents[2] and decompose in polar coordinating solvents such as THF, pyridine, and acetonitrile.[7] It has also been noted that the U^{III} complex (η^6-$C_6H_3Me_3$)U(BH_4)$_3$ decomposes under the action of dichloromethane.[8] This may account for the fact that the reactions conducted in this solvent yield no complexes of trivalent uranium.[6,7]

The bond between the U atom and the ligand in neutral π-arene complexes is rather weak, and these compounds exist only in the absence of stronger donors. This makes it possible to obtain new compounds of this type by replacing one arene by another arene having a higher donor ability. In terms of their donor properties, alkylbenzenes taken as arenes can be arranged in the following sequence: benzene < toluene < mesitylene < hexamethylbenzene. In fact, a mesitylene ligand in (η^6-$C_6H_3Me_3$)U(BH_4)$_3$ is readily replaced by hexamethylbenzene, thus yielding a new complex, (η^6-C_6Me_6)U(BH_4)$_3$; however the attempts to replace it in a similar way by benzene or toluene were unsuccessful.[8]

Results and Discussion

In order to obtain the neutral π-arene uranium complex based on toluene, we carried out experiments in which the conditions of the Friedel—Crafts reaction varied. However, neither the direct reaction of UCl_4, $AlCl_3$, and toluene in the presence of aluminum foil nor the replacement of the solvent by hexane and

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dichloromethane and the replacement of the aluminum foil by zinc dust led to the desired product. We were able to obtain compound **1** only by adding one more reactant, naphthalene, to the reaction system. The presence of naphthalene in the system is necessary even in the first step of the reaction.

Since the Friedel—Crafts reaction involves electrophilic attack on the arene, one may assume that the higher is the π-donor ability of the arene, the more easily this attack occurs. Judging by the values of the ionization potential,[9] it is naphthalene (IP 8.12 eV) rather than toluene (IP 8.82 eV) that should have reacted. However, the real result is different. In all probability, the role of naphthalene in the reaction under consideration is due to its another property, namely, the positive electron affinity unlike that of toluene (0.152 and −1.3 eV, respectively).[9] It may be suggested that naphthalene participates in complex processes of intermolecular electron transfer between the components of the reaction system and thus facilitates these processes acting as an electron transferring reagent and promoting the reduction of U^{4+} to U^{3+}. Naphthalene is widely used as an electron transferring reagent in redox processes, for example, for the reduction of metal salts to zero-valent metals.[10]

The result obtained is also in agreement with the data on the stabilities of analogous π-arene complexes of d-transition metals. For example, in a sequence of the stability of the M—arene bond based on a great body of experimental results,[11] naphthalene is located after benzene, despite its lower IP and, correspondingly, higher donor ability (the IP values, eV, are given in parentheses)[9]: mesitylene (8.40) > *p*-xylene (8.44) > *m*-xylene (8.56) > toluene (8.82) > benzene (8.25) > naphthalene (8.12).

It has also been reported that a naphthalene ligand is easily replaced in these complexes by another arene ligand (benzene, toluene, *etc.*).[11]

We isolated the U^{III} complex **1** as dark-violet crystals. Regarding its solubility in various solvents, complex **1** does not differ from the previously obtained complexes based on benzene[5] and hexamethylbenzene.[2] Complex **1** isolated from a toluene solution is poorly soluble in toluene; it is insoluble in hexane, decomposes in benzene and THF, and is readily soluble in dichloromethane giving a black solution, from which an uranium-containing compound, whose composition is yet unknown, was isolated as a black powder. When the crystals of complex **1** are dissolved in thoroughly dried ethanol, a crimson-colored solution is produced, whose electronic absorption spectrum exhibits an absorption maximum in the 450—560 nm region; this may indicate that the solution contains uranium in an oxidation state of +3.[12] In air, the ethanolic solution is decolorized, and, as this take place, absorption bands typical of U^{VI} appear. Our attempts to crystallize the crimson-colored compound resulting from the removal of the solvent from the ethanolic solution were unsuccessful.

We obtained tentative data indicating that in an atmosphere of CO, the crystals of complex **1** absorb CO in a ratio of 0.5 : 1. A TLC analysis of the mixture of products obtained after hydrolysis of the reaction system showed the presence of a compound containing a carboxyl group.

An X-ray structural study showed that the structure of complex **1** is similar to that of the previously studied lanthanide complexes $(Me_6C_6)Sm(AlCl_4)_3$,[1,2] $(1,3\text{-}Me_2C_6H_4)Sm(AlCl_4)_3)$,[3] and $(C_6H_6)Ln(AlCl_4)_3$ (Ln = Nd, Sm).[4] The U atom is bound to the substituted benzene ring by the η^6-mechanism and is bound to the three $AlCl_4$ groups through two μ-Cl bridges (Fig. 1). The coordination of the U atom is a distorted pentagonal bipyramid in which one apical position is occupied by the geometric center of the arene ring and the other vertex is occupied by the Cl(6) atom. Both bridging atoms of two $AlCl_4$ groups (Cl(1), Cl(2), Cl(9), and Cl(10)) and one bridging atom of the third $AlCl_4$ group (C(5)) are located in the equatorial plane. The U atom deviates from the mean plane of the Cl(1)—Cl(2)—Cl(5)—Cl(9)—Cl(10) fragment by 0.54 Å, pointing away from the Cl(6) atom. The above-mentioned Cl atoms also deviate somewhat from the mean plane: Cl(1) 0.13 Å, Cl(2) −0.19 Å, Cl(5) 0.17 Å, Cl(9) −0.09 Å, Cl(10) −0.02 Å. The X—U—Cl(6) angle (where X is the geometric center of the arene ring) is 173.7°, and the X—U—C_{eq} and C(6)—U—Cl_{eq} angles vary over wide limits of 71.4—104.9°.

The bond between the U atom and the Cl atom in the apical position (U—Cl(6) 2.849(3) Å) is somewhat shorter than the distances to the Cl atoms in the axial positions, which are 2.867(3)—2.919(2) Å (the average value is 2.89(2) Å). A similar difference has been observed in the above-mentioned lanthanide derivatives $(Me_6C_6)Sm(AlCl_4)_3$,[1,2] $(1,3\text{-}Me_2C_6H_4)Sm(AlCl_4)_3)$,[3] and $(C_6H_6)Ln(AlCl_4)_3$ (Ln = Nd, Sm).[4]

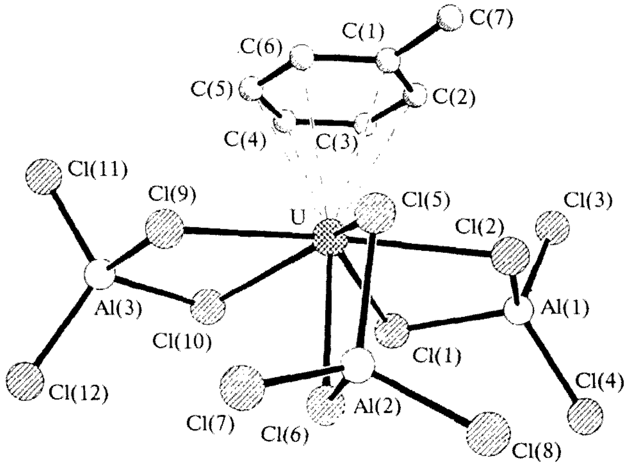

Fig. 1. General view of molecule **1**.

Table 1. Bond lengths (*d*) and selected bond angles (ω) in molecule **1**

Bond	d/Å	Angle	ω/deg
U—Al(1)	3.799(3)	Cl(1)—U—Cl(2)	69.5(1)
U—Al(3)	3.824(3)	Cl(1)—U—Cl(6)	80.8(1)
U—Cl(2)	2.891(2)	Cl(1)—U—Cl(10)	69.1(1)
U—Cl(6)	2.849(3)	Cl(2)—U—Cl(5)	71.4(1)
U—Cl(10)	2.867(3)	Cl(2)—U—Cl(6)	83.2(1)
U—C(2)	2.99(1)	Cl(5)—U—Cl(6)	71.4(1)
U—C(4)	2.91(1)	Cl(5)—U—Cl(9)	73.8(1)
U—C(6)	2.907(9)	Cl(6)—U—Cl(9)	78.6(1)
Al(1)—Cl(2)	2.188(3)	Cl(6)—U—Cl(10)	82.5(1)
Al(1)—Cl(4)	2.078(3)	Cl(9)—U—Cl(10)	69.6(1)
Al(2)—Cl(6)	2.200(4)	Cl(1)—Al(1)—Cl(3)	107.8(1)
Al(2)—Cl(8)	2.085(4)	Cl(2)—Al(1)—Cl(3)	111.2(2)
Al(3)—Cl(10)	2.204(3)	Cl(1)—Al(1)—Cl(4)	112.5(2)
Al(3)—Cl(12)	2.079(5)	Cl(2)—Al(1)—Cl(4)	109.4(1)
C(1)—C(3)	2.44(2)	Cl(3)—Al(1)—Cl(4)	117.1(2)
C(1)—C(6)	1.42(1)	Cl(5)—Al(2)—Cl(6)	98.8(1)
C(2)—C(3)	1.39(2)	Cl(5)—Al(2)—Cl(7)	107.8(1)
C(2)—C(6)	2.41(1)	Cl(6)—Al(2)—Cl(7)	112.5(2)
C(3)—C(5)	2.43(2)	Cl(5)—Al(2)—Cl(8)	112.7(2)
C(4)—C(6)	2.44(1)	Cl(6)—Al(2)—Cl(8)	108.6(1)
C(6)—C(7)	2.51(2)	Cl(7)—Al(2)—Cl(8)	115.2(2)
U—Al(2)	3.767(3)	Cl(9)—Al(3)—Cl(10)	96.8(1)
U—Cl(1)	2.881(2)	Cl(9)—Al(3)—Cl(11)	109.4(2)
U—Cl(5)	2.894(2)	Cl(10)—Al(3)—Cl(11)	110.1(2)
U—Cl(9)	2.919(2)	Cl(9)—Al(3)—Cl(12)	110.5(2)
U—C(1)	2.99(1)	Cl(10)—Al(3)—Cl(12)	110.9(2)
U—C(3)	2.94(1)	Cl(11)—Al(3)—Cl(12)	117.2(2)
U—C(5)	2.88(1)	U—Cl(1)—Al(1)	95.8(1)
Al(1)—Cl(1)	2.204(4)	U—Cl(2)—Al(1)	95.8(1)
Al(1)—Cl(3)	2.090(4)	U—Cl(5)—Al(2)	94.0(1)
Al(2)—Cl(5)	2.216(4)	U—Cl(6)—Al(2)	95.7(1)
Al(2)—Cl(7)	2.094(4)	U—Cl(9)—Al(3)	95.4(1)
Al(3)—Cl(9)	2.211(4)	U—Cl(10)—Al(3)	97.0(1)
Al(3)—Cl(11)	2.095(4)	C(2)—C(1)—C(6)	117.3(10)
C(1)—C(2)	1.40(1)	C(2)—C(1)—C(7)	123.7(9)
C(1)—C(5)	2.45(2)	C(6)—C(1)—C(7)	119.0(8)
C(1)—C(7)	1.49(2)	C(1)—C(2)—C(3)	122.0(10)
C(2)—C(4)	2.42(2)	C(2)—C(3)—C(4)	121.0(9)
C(3)—C(4)	1.40(2)	C(3)—C(4)—C(5)	118.0(10)
C(4)—C(5)	1.44(2)	C(4)—C(5)—C(6)	120.0(10)
C(5)—C(6)	1.38(2)	C(1)—C(6)—C(5)	121.7(9)

Experimental

All the reactions were carried out under argon. UCl_4 was prepared by a previously described procedure.[13] Aluminum chloride was sublimed immediately prior to use. Naphthalene was purified by sublimation. Aluminum foil was washed with acetone and dichloroethane and dried *in vacuo*. All the solvents were thoroughly purified by the standard procedures.[14]

Synthesis of $(\eta^6\text{-}C_6H_5Me)U(AlCl_4)_3$ (1). Freshly distilled toluene (40 mL) was added to a mixture of UCl_4 (0.7 g, 1.8 mmol), $AlCl_3$ (1.8 g, 13.5 mmol), and naphthalene (0.6 g, 4.7 mmol), and the mixture was stirred with heating for 30 min. During this period the salts dissolved, and the reaction mixture acquired a red-brown color. Aluminum foil was placed into the flask at room temperature, and 10 days later, dark-violet crystals grew on the foil. Separation from the mother liquor followed by drying *in vacuo* gave 0.97 g (63.8 %) of complex **1**.

Table 2. Coordinates of atoms (×10⁴) and equivalent isotropic heat factors U_{iso}* (×10³) in the structure of **1**

Atom	x	y	z	U_{iso}/Å^2
U	1331(1)	1040(1)	2643(1)	16(1)
Al(1)	2189(3)	1484(1)	5615(2)	19(1)
Al(2)	2314(3)	−799(2)	2959(2)	21(1)
Al(3)	2879(4)	1333(1)	200(2)	23(1)
Cl(1)	3187(3)	1808(1)	4322(2)	23(1)
Cl(2)	886(3)	672(1)	4722(2)	23(1)
Cl(3)	915(3)	2275(1)	5924(2)	31(1)
Cl(4)	3659(3)	1080(1)	6923(2)	29(1)
Cl(5)	185(3)	−314(1)	2507(2)	22(1)
Cl(6)	3647(3)	114(1)	3218(2)	27(1)
Cl(7)	2577(3)	−1364(1)	1640(2)	30(1)
Cl(8)	2652(3)	−1325(1)	4408(2)	36(1)
Cl(9)	1475(3)	523(1)	539(2)	25(1)
Cl(10)	3360(3)	1795(1)	1811(2)	25(1)
Cl(11)	1678(3)	1999(1)	−934(2)	35(1)
Cl(12)	4710(3)	927(2)	−135(2)	38(1)
C(1)	−1810(12)	1255(5)	2351(7)	24(3)
C(2)	−1191(12)	1765(5)	3067(8)	25(3)
C(3)	−336(11)	2262(5)	2786(7)	25(3)
C(4)	−85(12)	2282(5)	1757(8)	29(4)
C(5)	−697(12)	1760(6)	1010(9)	35(4)
C(6)	−1529(11)	1264(5)	1312(7)	21(3)
C(7)	−2780(11)	729(5)	2605(8)	26(3)

* The equivalent isotropic heat factors were determined as 1/3 of the trace of the orthogonalized $U(i,j)$ tensor.

X-ray diffraction analysis of 1 was carried out on a Siemens P3/PC diffractometer (−120 °C, λ(Mo-Kα), graphite monochromator, θ/2θ-scanning in the $2 < 2\theta < 50°$ range). The crystals were rhombic; at −120 °C, a = 9.649(2) Å, b = 19.844(4) Å, c = 12.812(3) Å, β = 103.95(3)°, V = 2380.8(9) Å^3, space group $P2_1/n$, Z = 4, d_{calc} = 2.334 g cm^{-3}, μ(Mo-Kα) = 7.93 mm^{-1}. 2927 independent reflections were measured, 3105 of these reflexes with $F > 4\sigma(F)$ were used in the refinement of the structure. The structure of complex **1** was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all the nonhydrogen atoms. The positions of H atoms were calculated based on ideal geometric conditions. The H atoms were refined in terms of the "rider" method with nonfixed isotropic heat parameters. In the final steps of the refinement, the following weighing scheme was used: $w^{-1} = \sigma^2(F) + 0.001F^2$. Absorption was taken into account using the DIFABS program.[15] The final residual values were: R = 0.040, R_w = 0.047, S = 1.04. The calculations were carried out on a personal computer using the SHELXTL PLUS program package.[16] The bond lengths and angles, the coordinates of the atoms, and their equivalent isotropic heat parameters for compound **1** are listed in Tables 1—2.

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