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Synthesis and Structure of a π-Arene Complex of Uranium(III) - Aluminum Chloride*

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The synthesis of a π-arene uranium(III) complex with aluminum chloride obtained from UCl_4, $AlCl_3$ and Al in benzene, is reported. The isolated big black crystals are thermally stable up to 110°C and are immediately decomposed by moisture. The crystal and molecular structure of the complex is reported as determined by single crystal X-ray method.

Introduction

Up to now the organometallic chemistry of uranium offers few examples of complexes with aromatic type ligands. In fact, the carbocyclic species C_nH_n π-bonded in known compounds are restricted to the cases with $n=5$ and $n=8$.[1-2]

In the present paper we report the synthesis and the structure of a new complex in which a benzene ring π-linked to uranium atom; its empirical formula corresponds to $UAl_3Cl_{12} . C_6H_6$.

Experimental Section

Synthesis. The compound has been prepared by the method of Fisher,[3] by reacting UCl_4 (25 mmoles), sublimed $AlCl_3$ (80 mmole) and powdered aluminum (46 mmoles) in anhydrous benzene (50 ml). The mixture was refluxed for 7 hr and the brown suspension was filtered while hot under argon atmosphere. The red-brown filtrate solution was allowed to cool down to room temperature. After 2-3 days black crystals appeared on the walls of the Schlenk tube; the time of crystallization and the kind of the crystals varied as a function of the ratio $AlCl_3/UCl_4$ used. The compound is practically insoluble in all common organic solvents; polar solvents as THF, decompose the complex giving $AlCl_3$.base, UCl_3 and benzene. The amount of the last component, determined by gaschromatography, agrees with the proposed formula. Yield based on UCl_4 ranges between 70 and 80 per cent, depending on the purity of $AlCl_3$.

Anal. Found: C, 8.65; H, 0.61; Cl, 51.03; Al, 9.35; U, 30.17. Calcd for $C_6H_6Cl_{12}Al_3U$: C, 8.75; H, 0.73; Cl, 51.80; Al, 9.84; U, 29.29.

The product is thermally stable up to 110°C, it can be dried at 60-80°C in vacuum (10^{-2} mm Hg), and it is immediately decomposed by air.

I.R. Analysis. In the IR spectra bands are present at 3075, 1020, 740, 682, and 667 cm^{-1} which can be correlated to various modes of vibration of the aromatic rings. These absorptions, although shifted with relation to the analogous mode of imperturbed benzene, give no clear indication as the kind of bond between the benzene and the uranium. Bands that can be ascribed to bridge Al-halogen vibrations are present at 480 and 550 cm^{-1}.

X-ray Analysis. X-ray structural analysis was performed on a small black crystal of irregular prismatic shape (square cross section approximately 0.04 mm^2) enclosed in a capillary tube under nitrogen atmosphere. The crystal data are as follows: $UAl_3Cl_{12}C_6H_6$; MW=822.4; triclinic, space group $P\bar{1}$; $a=9.47$, $b=10.81$, $c=16.79$ Å, all ±0.02 Å; $\alpha=98.7°$, $\beta=86.5°$, $\gamma=122.9°$, all ±0.3°; $Z=2$; $D_c=1.914$ g cm^{-3}; $\mu(MoK\alpha)=26.76$ cm^{-1}.

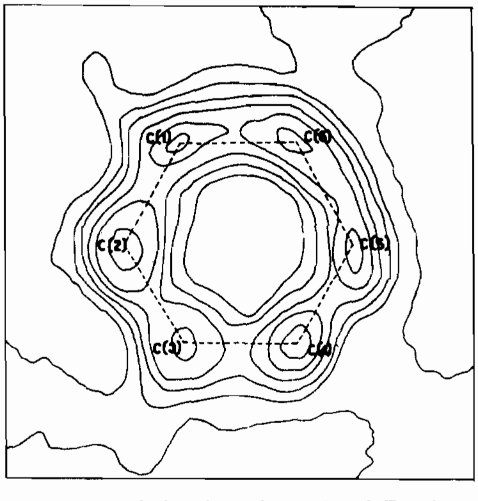

Figure 1. Section of the three-dimensional Fourier synthesis through the mean plane of carbon atom coordinates (equation of the plane referring to the crystallographic axes is, $0.6250x+0.3112y+0.0158z-3.3579=0$); contour lines drawn at arbitrary level units. See text.

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(1) L.T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *2*, 246 (1956); C. Wong, T. Yen, and T. Lee, *Acta Cryst.*, *18*, 340 (1965).

(2) A .Streitwieser and U. Mueller-Westerhoff, *J. Am. Chem. Soc.* *90*, 7364 (1968); A. Zalfin and K.N. Raymond, *J. Am. Chem. Soc.*, *91*, 5667 (1969).

(3) E.O. Fisher and W. Hafner, Z. *Naturforsch.*, *10b*, 655 (1955).

(4) A. Immirzi, *Ric. Sci.*, *37*, 743 (1967).

The intensities of 4268 independent reflections were collected by a Siemens automatic diffractometer using MoKα radiation. No absorption or extinction corrections were applied. All calculations were carried out with the programs written by A. Immirzi.[5] The structure was solved from the Patterson function by routine application of the heavy atom technique. Four cycles of block-diagonal least-square refinement, using isotropic temperature factors, lowered the residual to 0.16; five further cycles, using anisotropic temperature factors for the non-carbon atoms, gave a final overall R of 0.109. However the carbon atom coordinates obtained in the refinement were not so reliable as expected (expecially the carbon C(5) showed an inconsistent shift). Therefore the mean plane of the benzene was calculated (deviation from planarity was within 0.02 Å) using the coordinates of the final cycle of the least-quare; phased with the same coordinates, a section of Fourier map through the mean plane was performed and the carbon coordinates were definitely deduced by fitting a benzene ring model (C–C, 1.40 Å), as shown in Figure 1. The atomic coordinates, thermal parameters and standard deviations (with exception for carbon atoms) as obtained from the least-square refinement, are listed in Table I and II. Bond distances and angles are given in Table III; the most important non-bonded distances are listed in Table IV.

Table I. Atomic fractional coordinates of non-hydrogen atoms, with their extimated standard deviations, both multiplied by 10^4. For atom numbering see Fig. 3.

	x	y	z
U	678(1)	971(1)	2522(1)
Cl(1)	2498(8)	—3046(7)	2248(5)
Cl(2)	911(7)	—1233(6)	1412(4)
Cl(3)	—1833(8)	—4412(7)	2344(5)
Cl(4)	1052(7)	—955(6)	3395(4)
Cl(5)	—248(8)	868(7)	906(4)
Cl(6)	—867(14)	3650(10)	586(6)
Cl(7)	—4261(10)	243(11)	1120(6)
Cl(8)	—967(8)	2585(7)	2491(4)
Cl(9)	—2752(6)	—1370(6)	2571(3)
Cl(10)	—454(7)	1211(6)	4118(4)
Cl(11)	—3607(11)	—2365(9)	4495(5)
Cl(12)	—4670(9)	86(10)	3901(5)
Al(1)	632(8)	—2594(7)	2342(4)
Al(2)	—1687(9)	1896(8)	1242(5)
Al(3)	—3038(8)	—637(8)	3822(4)
C(1)	4015	2768	1879
C(2)	4289	2237	2513
C(3)	4010	2665	3308
C(4)	3457	3626	3459
C(5)	3177	4168	2830
C(6)	3457	3738	2028

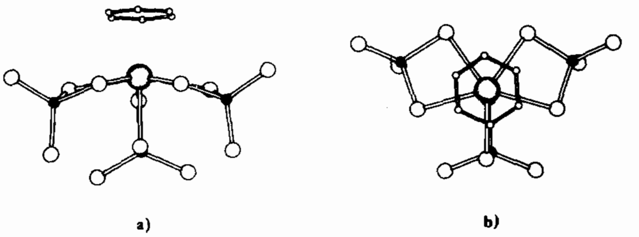

Figure 2. Projections of the molecule in the plane of the benene ring, b), and in a plane nearly perpendicular, a).

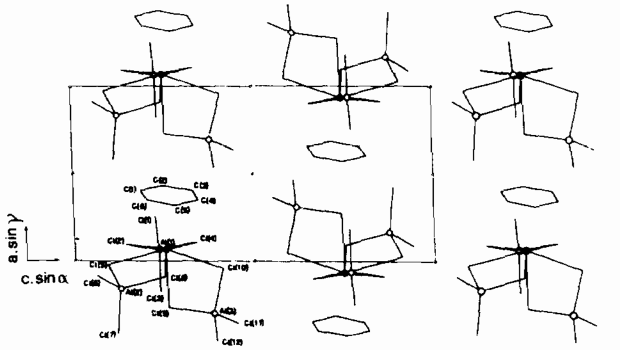

Figure 3. Molecular packing in the crystal state.

Results and Discussion

In Figure 2 two projections of the molecule, one parallel the other nearly perpendicular to the mean plane of the benzene, are given. It may be observed

Table II. Anisotropic temperature factors in the form, exp-($B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl$), with their extimated standard deviation, both multiplied by 10^4.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	271(3)	175(3)	361(5)	108(2)	28(2)	40(3)
Cl(1)	402(25)	339(27)	701(43)	254(22)	29(24)	103(25)
Cl(2)	446(24)	267(22)	367(32)	233(20)	57(19)	22(18)
Cl(3)	324(23)	243(23)	643(43)	60(20)	—9(22)	34(22)
Cl(4)	350(21)	197(19)	368(31)	144(17)	—28(17)	25(17)
Cl(5)	533(28)	482(30)	292(32)	395(26)	32(20)	10(21)
Cl(6)	1106(59)	577(41)	561(50)	606(44)	199(40)	286(34)
Cl(7)	428(31)	646(45)	670(50)	262(32)	—41(28)	—45(34)
Cl(8)	518(26)	357(25)	304(30)	346(23)	14(19)	—9(19)
Cl(9)	240(17)	294(21)	222(27)	92(16)	—15(14)	—26(16)
Cl(10)	316(21)	322(23)	256(30)	139(18)	—16(17)	—39(18)
Cl(11)	691(41)	442(35)	495(47)	181(31)	72(31)	242(30)
Cl(12)	436(28)	627(39)	536(41)	362(29)	32(24)	—42(29)
Al(1)	258(23)	154(23)	481(39)	115(20)	27(31)	63(21)
Al(2)	377(28)	355(30)	344(38)	272(25)	62(22)	92(24)
Al(3)	266(25)	338(30)	324(39)	132(23)	47(21)	77(24)

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(5) G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chemie, 61,* 69 (1963).

Table III. Bond lengths (Å) and bond angles with their extimated standard deviations.

U	— Cl(2)		= 2.895(7)
U	— Cl(4)		= 2.898(7)
U	— Cl(5)		= 2.870(6)
U	— Cl(8)		= 2.910(8)
U	— Cl(9)		= 2.838(7)
U	— Cl(10)		= 2.854(6)
Al(1)	— Cl(1)		= 2.066(10)
Al(1)	— Cl(3)		= 2.080(11)
Al(1)	— Cl(2)		= 2.213(10)
Al(1)	— Cl(4)		= 2.190(10)
Al(2)	— Cl(6)		= 2.083(15)
Al(2)	— Cl(7)		= 2.095(15)
Al(2)	— Cl(5)		= 2.185(12)
Al(2)	— Cl(8)		= 2.138(10)
Al(3)	— Cl(11)		= 2.128(14)
Al(3)	— Cl(12)		= 2.068(12)
Al(3)	— Cl(9)		= 2.186(10)
Al(3)	— Cl(10)		= 2.181(12)
U	— C(1)		= 2.91
U	— C(2)		= 2.91
U	— C(3)		= 2.92
U	— C(4)		= 2.92
U	— C(5)		= 2.92
U	— C(6)		= 2.91
Cl(2)	— U	— Cl(4)	= 69.5(0.1)
Cl(2)	— U	— Cl(5)	= 68.3(0.1)
Cl(5)	— U	— Cl(8)	= 68.8(0.1)
Cl(8)	— U	— Cl(10)	= 74.2(0.1)
Cl(4)	— U	— Cl(10)	= 72.5(0.1)
Cl(9)	— U	— Cl(2)	= 83.4(0.1)
Cl(9)	— U	— Cl(4)	= 80.6(0.1)
Cl(9)	— U	— Cl(5)	= 82.9(0.1)
Cl(9)	— U	— Cl(8)	= 79.3(0.1)
Cl(9)	— U	— Cl(10)	= 71.9(0.1)
U	— Cl(2)	— Al(1)	= 95.1(0.2)
U	— Cl(4)	— Al(1)	= 95.5(0.2)
U	— Cl(5)	— Al(2)	= 95.9(0.2)
U	— Cl(8)	— Al(2)	= 95.9(0.2)
U	— Cl(9)	— Al(3)	= 94.2(0.2)
U	— Cl(10)	— Al(3)	= 93.8(0.2)
Cl(1)	— Al(1)	— Cl(2)	= 110.5(0.2)
Cl(1)	— Al(1)	— Cl(4)	= 111.8(0.2)
Cl(1)	— Al(1)	— Cl(3)	= 116.7(0.2)
Cl(2)	— Al(1)	— Cl(3)	= 110.5(0.2)
Cl(2)	— Al(1)	— Cl(4)	= 97.2(0.2)
Cl(3)	— Al(1)	— Cl(4)	= 108.7(0.2)
Cl(5)	— Al(2)	— Cl(6)	= 109.3(0.3)
Cl(5)	— Al(2)	— Cl(7)	= 109.0(0.3)
Cl(5)	— Al(2)	— Cl(8)	= 98.1(0.2)
Cl(6)	— Al(2)	— Cl(7)	= 115.5(0.3)
Cl(6)	— Al(2)	— Cl(8)	= 114.1(0.2)
Cl(7)	— Al(2)	— Cl(8)	= 109.6(0.2)
Cl(9)	— Al(3)	— Cl(10)	= 99.8(0.2)
Cl(9)	— Al(3)	— Cl(11)	= 107.1(0.2)
Cl(9)	— Al(3)	— Cl(12)	= 111.2(0.2)
Cl(10)	— Al(3)	— Cl(11)	= 108.4(0.3)
Cl(10)	— Al(3)	— Cl(12)	= 111.4(0.2)
Cl(11)	— Al(3)	— Cl(12)	= 117.4(0.3)

Table IV. Important intra and intermolecular distances (Å)

C(1)	— Cl(2)	= 3.66
C(2)	— Cl(2)	= 3.65
C(3)	— Cl(4)	= 3.38
C(4)	— Cl(10)	= 3.41
C(5)	— Cl(8)	= 3.37
C(6)	— Cl(5)	= 3.56
Cl(5)	— Cl(5) (I)	= 3.47
Cl(6)	— Cl(6) (II)	= 3.35
Cl(3)	— Cl(6) (III)	= 3.72
Cl(1)	— Cl(5) (III)	= 3.68
Cl(3)	— C(1) (IV)	= 3.46
Cl(3)	— C(2) (IV)	= 3.52
Cl(4)	— Cl(12)(V)	= 3.68
Cl(7)	— C(2) (VI)	= 3.65
Cl(11)	— C(3) (VII)	= 3.73
Cl(12)	— Cl(12(VIII)	= 3.72

(I) x, y, z	(V) x+1, y, z
(II) x, y+1, z	(VI) x—1, y, z
(III) x, y+1, z	(VII) x, y, z+1
(IV) x—1, y—1, z	(VIII) x—1, y, z+1

that the molecular structure is made up of an uranium atom which coordinates three $AlCl_4$ tetrahedra, through U–Cl–Al bridge bonds and a benzene ring. The bridging chlorine atoms, Cl_b, form a pentagonal piramid, while the uranium atom lies on the centre of the basal plane but shifted outside, toward the benzen ring for nearly 0.5 Å; the benzene is parallel to the same basal plane. With another simpler scheme, uranius is linked to five chlorine atoms in a plane, while the two apical groups are constituted by a sixth chlorine and the benzene molecule.

The mean distance Al–Cl_b bond is 2.18 Å and for the other Al–Cl bonds is 2.09 (individual values ranging from 2.138 to 2.213 Å and from 2.066 to 2.128 Å respectively). This values may be compared with those found in the dimer CH_3Cl_2Al[5] where Al–Cl_b is 2.25 Å and Al–Cl 2.05 Å; the differences are in agreement with the electron donor character of the uranium atom. The mean Cl_b–Al–Cl_b angle is 98° and the mean Cl–Al–Cl 111.5°; the first angle is 8° greater with respect of that observed in the above mentioned dimer; this difference may be accounted by the lenght of the U–Cl_b bond, compared with that of Al–Cl_b. The mean distance of the U–Cl_b bonds is 2.88 Å (the individual values ranging from 2.838 to 2.911 Å). This value is noteworthy high and very close to the sum of the ionic radii ($1.11+1.81=2.92$ Å) given for Cl^{-1} and U^{+3}.

Following the procedure used by Wong *et al.*,[1] the bond order is approximatively 0.2, so that the ionic character for the U–Cl bond is about 0.87 ($0.80+(0.35 * 0.2)=0.87$, where 0.35 is the partial ionic character).

The data regarding the benzene ring are not very reliable as discussed above, however the planarity of benzene ought to be accepted. The mean U–C distance is 2.91±0.01 Å when carbon coordinates adjusted as described in the preceding section are considered. Moreover this value agrees perfectly with the values resulting from least-square refinement, which range from 2.91 to 2.93 Å. Therefore a standard deviation not exceeding 0.05 Å should be considered appropriate for this bond length. It is possible now to make significant comparison by considering the values found for U–C bond distance in $(\pi-C_5H_5)_3UCl$, 2.65 Å, and in $(\pi-{}_8H_8)_2U$, 2.74 Å. According Wong *et al.*, bond order may be tentatively deduced by extrapolating Zachariasen and Plettinger's[6] curve for U–O bond *versus* bond-length, assuming 2.19 Å for U–C single bond. In this way, bond order values for $(\pi-C_8H_8)_2U$ and $(\pi-C_5H_5)_3UCl$ approach to 0.5 and 0.17 respectively, while for the present compound a value near zero is derived. This result is in agreement with a lower electrophilic

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(6) W.H. Zachariasen and H.A. Plettinger, *Acta Cryst.*, *12*, 526 (1959).

Table V. Observed and calculated structure factors (x 10).

[illegible]

Table IV. (Continued)

character of benzene with respect to the other two rings; furthermore the high electronegativity of the six chlorine atoms surrounding the uranium must reduce the electron availability for bonding with the aromatic ring. These considerations besides the general stereochemical feature of the molecule should leave no question that the benzene is linked to uranium by a π–type bonding.

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