

Figure 3. ORTEP II view of the packing along [100] (dashed lines through U-Li nearest neighbors).

in the present compound. The two N atoms participate in the coordination of the Li atom owing to an endo-endo conformation of the bicyclic ligand. The Li atom lies at the center of a highly distorted octahedron, a skew-par-

allelogram bipyramid, made of the four O atoms and the two N atoms of the cryptand. The four atoms N(1), N(2), O(11), and O(16), oxygen atoms from the two shortest chains, are coplanar within 0.02 Å while the Li atom is displaced out of this plane by 1.01 (5) Å toward O(3) and O(6) (oxygen of the long chain). O(3) and O(6) are on the same side of this plane at 2.67 (2) and 2.66 (2) Å, respectively, and form with N(1) and N(2) an approximate plane (± 0.15 Å) containing Li, nearly orthogonal (92°) to the N(1)-N(2)-O(11)-O(16) plane.

The crystal packing is shown in Figure 3. No critical intermolecular distance is observed since all the C...C contacts are greater than 3.8 Å. However, this shortest intramolecular distances are observed between the α -carbon of butyl and some carbon atoms of Cp1 and Cp2 (3.2 and 3.4 Å), which may explain the relative freedom of the third Cp. Though the structure can be considered as a three-dimensional network with a marked ionic character, there exist shorter distances between metallic atoms U and Li (6.69 (1) and 6.48 (2) Å) in the [10 $\bar{1}$] direction compared to other lying from 8.39 (2) to 8.89 (2) Å, which define chains of alternating anions and cations.

Registry No. [Cp₃U-*n*-Bu]⁻[Li-2.1.1]⁺, 99476-34-3; Cp₃UC₄H₉⁻,Li⁺, 83999-88-6; Cp₃UCH₃⁻,Li⁺, 82762-08-1; Cp₃UC₆H₅⁻,Li⁺, 99476-32-1; Cp₃UC₄H₉, 37298-84-3; LiC₄H₉, 109-72-8; LiCH₃, 917-54-4; LiC₆H₅, 591-51-6; U, 7440-61-1; C, 7440-44-0.

Supplementary Material Available: Tables of observed and calculated structure factors, refined temperature factors, and positional parameters (18 pages). Ordering information is given on any current masthead page.

Syntheses, Structures, and Solid-State ¹³C NMR of Two η^6 -Arene Uranium(IV) Complexes, [U(C₆Me₆)Cl₂(μ -Cl)₃UCl₂(C₆Me₆)]AlCl₄ and U(C₆Me₆)Cl₂(μ -Cl)₃UCl₂(μ -Cl)₃UCl₂(C₆Me₆)

Gordon C. Campbell, F. Albert Cotton,* James F. Haw, and Willi Schwotzer

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Received May 29, 1985

Two complexes of U(IV) with hexamethylbenzene as an η^6 -ligand have been prepared and structurally characterized. [U(C₆Me₆)Cl₂(μ -Cl)₃U(C₆Me₆)Cl₂][AlCl₄] (1) crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.028$ (4) Å, $b = 8.716$ (3) Å, $c = 29.180$ (11) Å, $\beta = 93.70$ (2) $^\circ$, $V = 3814$ (4) Å³, and $Z = 4$. The complex cation consists of an face-sharing bioctahedron with the η^6 -C₆Me₆ moiety occupying one octahedral coordination site. [UCl₂(C₆Me₆)₂UCl₆] (2) is a molecular trinuclear complex. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.171$ (4) Å, $b = 13.484$ (3) Å, $c = 17.279$ (4) Å, $\beta = 102.74$ (2) $^\circ$, $V = 3902$ (3) Å³, and $Z = 4$. The molecules consist of two terminal octahedrally coordinated uranium atoms, each of which is bonded to a hexamethylbenzene. Each is sharing a trigonal (μ -Cl)₃ face with the central uranium atom which has a square-antiprismatic coordination sphere of chlorine atoms. This leads to a symmetrical bent chain of uranium atoms with a U...U...U angle of 142.2 $^\circ$ and a U...U distance of 4.033 (3) Å. Comparable bonds in both compounds are of equal length in a statistical sense, viz., U-Cl (bridge) = 2.75 [8], U-Cl (terminal) = 2.55 [2], and U-C(ring) = 2.93 [3] Å. Compound 2, which can be prepared in large quantities, was also subjected to a solid state ¹³C NMR study. It has a temperature-dependent spectrum with chemical shifts (at -53 $^\circ$ C) of 3.7 (CH₃) and -39.3 ppm (aromatic). At room temperature the two signals coincide at 8 ppm.

Introduction

Despite many examples of organometallic compounds of f-block elements with π -donor ligands the nature of the bonding interaction is still controversial. Most authors who have addressed this problem in the past appear to believe that the covalent contribution to the interaction between

the organic π -system and the uranium atom is of limited importance, and an entirely ionic model for cyclopentadienyl (Cp) and cyclooctatetraenyl (COT) complexes was suggested based on the results of Hückel calculations^{1,2}

(1) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* 1984, 23, 1633.

and a comparison of metric properties.³ Perhaps the strongest support for an ionic description stems from the conspicuous absence, with one exception, of π -complexes with neutral or cationic π -ligands. There is, on the other side, evidence that an f-orbital contribution to ligand bonding is not to be neglected.⁴

It appeared to us that further experimental and theoretical work pertinent to the above question had to involve nonanionic π -ligands.⁵ In such complexes, for which there is only one example, $U(\eta^6-C_6H_6)(AlCl_4)_3$, on record⁶ the π -ligand cannot be bonded by an ionic interaction and, consequently, there must be an appreciable amount of covalency.

In this paper we report the syntheses of two such complexes: $[(\eta^6-C_6Me_6)UCl_2(\mu-Cl)_3UCl_2(\eta^6-C_6Me_6)](AlCl_4)$ (1) and $[(\eta^6-C_6Me_6)UCl_2(\mu-Cl)_3UCl_2(\mu-Cl)_3UCl_2(\eta^6-C_6Me_6)]$ (2). Both compounds were isolated as crystalline solids and were stable enough to permit X-ray data collection at room temperature over several days. However, we found that the choice of solvents suitable either as reaction media or for spectroscopic studies was a very limited one, as the arene is easily displaced by even weak σ -donors. Because our options for characterization of the products were thus very restricted, we decided to turn an apparent disadvantage into an advantage by using these compounds to probe the applicability of solid-state NMR for structural problems involving paramagnetic actinide compounds.

Experimental Section

All operations were performed in a dry and anaerobic atmosphere of argon. UCl_4 was prepared from UO_3 by published procedures.⁷ $AlCl_3$ was sublimed immediately prior to use. Hexamethylbenzene (hmb) was of commercial origin (Kodak) and used as received. Solvents were distilled under argon from appropriate drying agents.

Preparation of $U_2Cl_7(C_6Me_6)_2AlCl_4$. Weighed amounts of UCl_4 (380 mg, 1 mmol), hmb (200 mg, 1.2 mmol), and $AlCl_3$ (500 mg) were placed in a Schlenk flask. Hexane (20 mL) was added and the suspension boiled under reflux for 12 h. During this time the appearance and color changed and a yellow greenish precipitate deposited at the walls of the Schlenk flask close to the solvent boundary. The slightly turbid hexane solution was decanted and 20 mL of CH_2Cl_2 added. Part of the solid dissolved to form a yellowish solution. Addition of zinc powder afforded a deep red solution within 2 h. It was filtered through Celite and layered with hexane. Well-defined crystals of 1 grew at the interlayer boundary within 36 h while an amorphous red precipitate, which has not been identified, was deposited at the bottom of the flask over a period of 1 week; yield 384 mg (63%).

Preparation of $U_3Cl_{12}(C_6Me_6)_2$. A mixture of 3.8 g of UCl_4 , 2 g of hmb, and 1 g of $AlCl_3$ in 50 mL of hexane was boiled under reflux for 18 h. The solvent was then decanted and the residue extracted with 50 mL of CH_2Cl_2 . A first crop of green crystals (1.8 g), which deposited upon standing at room temperature overnight, was isolated by filtration. A second crop of 0.6 g was isolated after the solution was kept at 5 °C for 72 h. More of 2 was deposited at -20 °C but was contaminated with a reddish precipitate. The isolated yield of pure (coarsely crystalline) product for the NMR study was 2.4 g. Once deposited, the

compound is no longer soluble in CH_2Cl_2 , and it dissolves in THF or acetonitrile only with decomposition to the corresponding UCl_4 solvates.

X-ray Crystallography. Because of their moderate air sensitivity the pale green plates of 1 as well as the dark-green prisms of 2 were mounted inside Lindemann capillaries. In each case a series of crystals was surveyed and the specimen chosen for data collection was a good diffractor of X-rays with a minimal anisotropy of absorption, as evaluated by an azimuthal scan of a reflection with an Eulerian χ angle close to 90°.

Structure 1. All geometric and intensity data were taken by a CAD-4 automated four-circle diffractometer equipped with monochromated Mo $K\alpha$ radiation.

The crystal orientation matrix and unit cell parameters were derived from a least-squares fit to the goniometer settings of 25 accurately located reflections in the range of $15^\circ \leq 2\theta \leq 31^\circ$. Data scans which employed an ω motion were made in the range of $5^\circ \leq 2\theta \leq 45^\circ$. The intensity data were corrected for Lorentz and polarization effects before structure factors were derived. An empirical absorption correction ($\mu(Mo K\alpha) = 88.6 \text{ cm}^{-1}$) was based on azimuthal scans of nine reflections near $\chi = 90^\circ$. In all there were 2408 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Systematically absent reflections uniquely identified the spacegroup as $P2_1/c$.

The position of the two uranium atoms in the crystallographic asymmetric unit were derived from a three-dimensional Patterson map. The remainder of the structure was located and refined, without difficulties, by an alternating sequence of least-squares cycles and difference maps. The last cycle gave residuals of $R = 0.048$ ($R_w = 0.053$) with a quality of fit of 1.389 for the fit of 343 variables to 2408 observations.

Structure 2. All data were obtained from a Syntex P1 automated four-circle diffractometer. The lattice vectors were identified by application of the automatic indexing routine to the positions of 15 reflections taken from a rotation photograph and located and centered by the diffractometer. Axial photographs confirmed the unit-cell dimensions and the monoclinic symmetry. The crystal orientation matrix and the unit cell were refined by a least-squares fit to the goniometer positions of 15 accurately located reflections in the range of $6^\circ \leq 2\theta \leq 30^\circ$. Intensity data were collected by the ω -scan technique in the range $5^\circ \leq 2\theta \leq 45^\circ$. The scan speed was variable in the range of 2–24°/min. The intensity data were corrected for Lorentz and polarization effects before structure factors were derived. An empirical absorption correction ($\mu(Mo K\alpha) = 126.25 \text{ cm}^{-1}$) was based on azimuthal scans of nine reflections near $\chi = 90^\circ$. Systematically absent reflections uniquely identified the space group as $P2_1/c$. A trial structure consisting of the three uranium atoms was obtained by direct methods (MULTAN). Iterative application of least-squares refinement and difference Fourier maps led to the development of the entire structure. All but one non-hydrogen atom (C(2)) were refined with anisotropic displacement parameters; the latter refined with a satisfactory isotropic displacement parameter. The last cycle gave residuals of $R = 0.043$ ($R_w = 0.053$) with a quality of fit of 0.958 for the fit of 347 parameters to 2807 observations with $F_o^2 \geq 3\sigma(F_o^2)$.

Many data pertaining to data collection and refinement are summarized in Table I.⁸ Fractional coordinates for 1 and 2 are listed in Tables II and III, respectively.

Tables IV and V summarize important bond lengths and angles for 1 and 2, respectively.

Solid-State NMR. Spectra of 2 were recorded at several temperatures on a Chemagnetics M100S NMR spectrometer at a ^{13}C frequency of 25.02 MHz. Cross polarization and magic-angle spinning were used.

Results and Discussion

Chemical Reactions. Among the relatively few examples of metal-metal bonding between very early transition metals (Ti, Zr) are the trinuclear organometallic clusters formed under reductive Friedel-Crafts conditions.⁹ In an

(2) Pyykkö, P.; Lohr, L. L., Jr. *Inorg. Chem.* 1981, 20, 1950.

(3) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* 1980, 13, 283.

(4) (a) Rösch, N.; Streitwieser, A. *J. Organomet. Chem.* 1978, 145, 195. (b) Veal, B. W.; Law, D. T. In "Lanthanide and Actinide Chemistry and Spectroscopy": Edelstein, N. M., Ed.; American Chemical Society: Washington, D.C., 1980; ACS Symp. Ser. No. 131. (c) Denning, R. G.; Norris, T. O. W.; Shom, I. G.; Snellgrove, T. R.; Woodward, D. R. *Ibid.* 1980, No. 131, 313–330.

(5) Cotton, F. A.; Schwotzer, W. *Organometallics* 1985, 4, 942.

(6) Cesari, M.; Pedretti, U.; Zazetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* 1971, 5, 439.

(7) Herman, T. A.; Suttle, J. F. *Inorg. Synth.* 1957, 5, 143.

(8) Crystallographic calculations were done with VAXSDP software on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University.

(9) Fischer, E. O.; Wawersik, T. *J. Organomet. Chem.* 1966, 5, 559.

Table I. Crystallographic Data

formula	U ₃ Cl ₁₁ AlC ₂₄ H ₃₆	U ₃ Cl ₁₂ C ₂₄ H ₃₆
fw	1217.6	1464.1
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
systematic absences	<i>h</i> 0 <i>l</i> , <i>l</i> = 2 <i>n</i> + 1; 0 <i>k</i> 0, <i>k</i> = 2 <i>n</i> + 1	<i>h</i> 0 <i>l</i> , <i>l</i> = 2 <i>n</i> + 1; 0 <i>k</i> 0, <i>k</i> = 2 <i>n</i> + 1
<i>a</i> , Å	15.028 (4)	17.171 (4)
<i>b</i> , Å	8.716 (3)	13.484 (3)
<i>c</i> , Å	29.180 (11)	17.279 (4)
β, deg	93.70 (2)	102.74 (2)
<i>V</i> , Å ³	3814 (4)	3902 (3)
<i>Z</i>	4	4
<i>d</i> _{calc} , g/cm ³	2.12	2.49
cryst size, mm	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.2
μ(Mo Kα), cm ⁻¹	88.60	126.25
data collectn instrument	Enraf-Nonius CAD-4	Syntex P1
radiatn (monochromated in incident beam)	Mo Kα	Mo Kα
orientatn reflctns, no., range (2θ)	25, 15 < 2θ < 31	15, 16 < 2θ < 30
temp, °C	25	5
scan method	ω scan	ω scan
data col range 2θ, deg	5 < 2θ < 45	5 < 2θ < 45
no. of unique data, total with <i>F</i> _o ² > 3σ(<i>F</i> _o ²)	2408	2807
no. of parameters refined	343	347
trans factors, max, min (exptl)	1.0, 0.73	1.0, 0.82
<i>R</i> ^a	0.048	0.043
<i>R</i> _w ^b	0.053	0.053
quality of fit indicator ^c	1.309	0.958
largest shift/esd, final cycle	0.31	0.08
largest peak, e/Å ³	1.5, 1.4 (around U1, U2)	0.79

^a $R = \sum \|F_o| - |F_c|\| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for U₃Cl₁₁AlC₂₄H₃₆^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
U1	0.28098 (6)	0.0517 (1)	0.02409 (3)	3.32 (2)
U2	0.33840 (6)	0.1421 (1)	0.15475 (3)	3.72 (2)
Cl1	0.8011 (4)	0.7043 (7)	0.4072 (2)	4.4 (2)
Cl2	0.6765 (4)	0.3841 (7)	0.3960 (2)	4.8 (2)
Cl3	0.5866 (4)	0.7045 (7)	0.4285 (2)	4.4 (2)
Cl4	0.6145 (4)	0.3612 (8)	0.5084 (2)	5.2 (2)
Cl5	0.8524 (4)	0.3783 (8)	0.4800 (3)	5.6 (2)
Cl6	0.6351 (5)	0.9257 (9)	0.3342 (3)	7.2 (2)
Cl7	0.5036 (4)	0.5669 (9)	0.3197 (2)	6.4 (2)
Cl8	0.1268 (5)	0.766 (1)	0.2988 (3)	8.4 (2)
Cl9	0.9478 (6)	0.380 (1)	0.0979 (3)	8.9 (3)
Cl10	0.7381 (6)	0.479 (1)	0.1274 (3)	11.1 (3)
Cl11	0.9211 (8)	0.647 (1)	0.1824 (4)	13.8 (4)
Al1	0.8708 (6)	0.445 (1)	0.1522 (3)	6.2 (2)
C1	0.756 (2)	0.859 (3)	0.5139 (8)	4.7 (6)
C2	0.674 (2)	0.821 (3)	0.5316 (8)	4.5 (6)
C3	0.671 (1)	0.687 (2)	0.5616 (8)	3.8 (5)
C4	0.752 (2)	0.600 (3)	0.5730 (8)	4.5 (6)
C5	0.834 (2)	0.652 (3)	0.5565 (9)	5.5 (7)
C6	0.834 (2)	0.775 (3)	0.5232 (8)	4.5 (6)
C7	0.758 (2)	1.000 (3)	0.485 (1)	7.8 (9)
C8	0.590 (2)	0.922 (3)	0.524 (1)	7.5 (8)
C9	0.586 (2)	0.651 (3)	0.5846 (9)	6.5 (7)
C10	0.752 (2)	0.467 (3)	0.6066 (9)	7.6 (8)
C11	0.920 (2)	0.573 (4)	0.573 (1)	9.0 (9)
C12	0.922 (2)	0.823 (3)	0.505 (1)	7.6 (9)
C13	0.774 (1)	0.420 (3)	0.2973 (8)	3.8 (6)
C14	0.696 (2)	0.435 (3)	0.2696 (8)	5.4 (7)
C15	0.671 (1)	0.581 (3)	0.2504 (8)	4.7 (6)
C16	0.730 (2)	0.710 (3)	0.2562 (8)	4.8 (7)
C17	0.807 (2)	0.698 (3)	0.2864 (7)	4.8 (6)
C18	0.830 (2)	0.552 (3)	0.3040 (8)	5.4 (7)
C19	0.804 (2)	0.264 (3)	0.3151 (9)	6.2 (7)
C20	0.633 (2)	0.299 (3)	0.261 (1)	8.8 (9)
C21	0.588 (2)	0.594 (4)	0.2164 (9)	8.4 (9)
C22	0.709 (2)	0.858 (3)	0.230 (1)	9 (1)
C23	0.867 (2)	0.839 (3)	0.294 (1)	8.2 (9)
C24	0.920 (2)	0.534 (3)	0.3304 (8)	5.7 (7)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations U₃Cl₁₂C₂₄H₃₆^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
U1	0.18196 (5)	0.27943 (7)	0.44100 (5)	2.92 (2)
U2	0.22146 (5)	0.52907 (7)	0.32673 (5)	2.78 (2)
U3	0.37833 (5)	0.65674 (7)	0.21490 (5)	2.66 (2)
Cl1	0.2974 (4)	0.1575 (6)	0.4589 (4)	5.2 (2)
Cl2	0.1947 (4)	0.3046 (6)	0.5893 (4)	5.5 (2)
Cl3	0.2021 (3)	0.3211 (4)	0.2936 (3)	3.2 (1)
Cl4	0.1060 (3)	0.4525 (5)	0.4129 (4)	4.1 (1)
Cl5	0.3006 (3)	0.4213 (5)	0.4585 (3)	3.5 (1)
Cl6	0.0916 (4)	0.5283 (5)	0.2228 (4)	4.1 (1)
Cl7	0.1942 (5)	0.6710 (6)	0.4118 (4)	5.7 (2)
Cl8	0.2994 (4)	0.4780 (5)	0.2078 (4)	3.9 (1)
Cl9	0.3804 (4)	0.6005 (5)	0.3670 (3)	4.2 (1)
Cl10	0.2308 (4)	0.7019 (5)	0.2288 (4)	4.2 (2)
Cl11	0.4978 (4)	0.5496 (5)	0.2093 (6)	7.2 (2)
Cl12	0.3286 (6)	0.6577 (6)	0.0661 (4)	7.1 (2)
C1	0.433 (2)	0.848 (2)	0.164 (1)	4.4 (6)
C2	0.375 (1)	0.871 (2)	0.207 (1)	2.9 (5)*
C3	0.391 (1)	0.851 (2)	0.289 (1)	4.2 (6)
C4	0.460 (1)	0.807 (2)	0.327 (1)	3.8 (6)
C5	0.516 (1)	0.781 (2)	0.280 (2)	4.4 (6)
C6	0.501 (1)	0.798 (2)	0.198 (2)	4.0 (6)
C7	0.420 (2)	0.880 (2)	0.076 (1)	9 (1)
C8	0.296 (2)	0.929 (2)	0.167 (2)	9 (1)
C9	0.335 (2)	0.892 (3)	0.340 (2)	9.7 (9)
C10	0.490 (3)	0.804 (2)	0.418 (2)	9 (1)
C11	0.598 (2)	0.734 (3)	0.326 (2)	8 (1)
C12	0.566 (1)	0.778 (3)	0.150 (2)	7.3 (8)
C13	0.111 (1)	0.083 (2)	0.390 (1)	4.0 (6)
C14	0.096 (1)	0.099 (2)	0.467 (1)	4.4 (6)
C15	0.044 (2)	0.173 (2)	0.480 (1)	4.3 (6)
C16	0.009 (1)	0.238 (2)	0.417 (2)	4.7 (6)
C17	0.025 (1)	0.227 (2)	0.337 (1)	4.4 (6)
C18	0.076 (1)	0.148 (2)	0.327 (1)	3.4 (5)
C19	0.155 (2)	-0.009 (2)	0.374 (2)	6.9 (9)
C20	0.135 (2)	0.032 (2)	0.538 (2)	7.5 (9)
C21	0.019 (2)	0.185 (3)	0.557 (2)	8 (1)
C22	-0.054 (2)	0.316 (3)	0.427 (2)	8 (1)
C23	-0.017 (2)	0.294 (2)	0.269 (2)	6.2 (7)
C24	0.089 (2)	0.121 (2)	0.243 (1)	6.2 (7)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $\text{U}_2\text{Cl}_{11}\text{AlCl}_2\text{H}_3\text{e}^a$

(a) Bond Lengths											
U1	U2	3.934 (1)	U1	C4	2.88 (2)	U2	C14	2.92 (3)			
U1	Cl1	2.763 (6)	U1	C5	2.96 (2)	U2	C15	2.83 (2)			
U1	Cl2	2.791 (6)	U1	C6	2.89 (2)	U2	C16	2.91 (2)			
U1	Cl3	2.701 (6)	U2	Cl1	2.732 (6)	U2	C17	2.91 (2)			
U1	Cl4	2.513 (7)	U2	Cl2	2.694 (6)	U2	C18	2.98 (3)			
U1	Cl5	2.507 (6)	U2	Cl3	2.796 (6)	Cl8	Al1	2.119 (13)			
U1	C1	2.94 (2)	U2	Cl6	2.521 (7)	Cl9	Al1	2.100 (13)			
U1	C2	2.96 (2)	U2	Cl7	2.529 (6)	Cl10	Al1	2.098 (12)			
U1	C3	2.90 (2)	U2	C13	2.98 (2)	Cl11	Al1	2.089 (14)			
(b) Bond Angles											
Cl1	U1	Cl2	74.6 (2)	Cl1	U2	Cl2	76.6 (2)	U1	Cl1	U2	91.4 (2)
Cl1	U1	Cl3	74.9 (2)	Cl1	U2	Cl3	73.9 (2)	U1	Cl2	U2	91.6 (2)
Cl1	U1	Cl4	155.7 (2)	Cl1	U2	Cl6	89.9 (2)	U1	Cl3	U2	91.4 (2)
Cl1	U1	Cl5	86.1 (2)	Cl1	U2	Cl7	155.8 (2)	Cl8	Al1	Cl9	103.8 (5)
Cl2	U1	Cl3	73.1 (2)	Cl2	U2	Cl3	73.1 (2)	Cl8	Al1	Cl10	108.2 (5)
Cl2	U1	Cl4	81.6 (2)	Cl2	U2	Cl6	153.6 (2)	Cl8	Al1	Cl11	110.4 (5)
Cl2	U1	Cl5	82.2 (2)	Cl2	U2	Cl7	89.4 (2)	Cl9	Al1	Cl10	109.6 (5)
Cl3	U1	Cl4	93.5 (2)	Cl3	U2	Cl6	81.5 (2)	Cl9	Al1	Cl11	110.2 (6)
Cl3	U1	Cl5	151.9 (2)	Cl3	U2	Cl7	83.3 (2)	Cl10	Al1	Cl11	109.6 (6)
Cl4	U1	Cl5	95.8 (2)	Cl6	U2	Cl7	94.5 (3)				

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

attempt to mimic their chemistry we originally reacted UCl_4 , AlCl_3 , hmb, and aluminum in a melt reaction. Although a reaction appeared to have occurred, we were unable to isolate uranium–arene complexes. The crude reaction mixture was insoluble in all but coordinating solvents from which we were able to isolate only the UCl_4 solvates.¹⁰ We then decided to perform the reaction in two steps: electrophilic addition of the UCl_4 – AlCl_3 complex in an inert solvent followed by reduction in a more polar but noncoordinating solvent. We realized that the choice of solvent for the first step was a limited one, indeed. Solvents with σ -donor capability will directly compete with the π -ligand, halohydrocarbons in the presence of AlCl_3 are electrophiles in their own right, and aromatic hydrocarbons will compete with hmb by mass action. We thus chose hexane in which the arylation of UCl_4 was completed in less than 12 h.

That the proposed reduction of the U(IV)–arene complex is yet to be achieved was obvious after successful structural characterization of 1. We then considered the possibility that 1 might be isolated directly from a CH_2Cl_2 extract of the reaction mixture. At the same time we reduced the amount of the Friedel–Crafts catalyst, AlCl_3 , from a massive excess to a near-stoichiometric quantity. While this did not, in fact, provide a way to prepare 1, it leads reproducibly to a structurally related trinuclear U(IV) complex, 2, which is unprecedented. In contrast to 1, which is difficult to isolate in pure form and large quantities, compound 2 is obtained in decent yields without contamination by slow crystallization from CH_2Cl_2 .

Structures. Crystals of 1 consist of an ordered array of dinuclear complex cations and AlCl_4 anions. Compound 2 is a trinuclear molecular complex. Perspective drawings are shown in Figures 1 and 2 for compounds 1 and 2, respectively.

The complex cation $\{[\text{U}(\text{C}_6\text{Me}_6)\text{Cl}_2]_2(\mu\text{-Cl})_3\}^+$ is conveniently described in terms of a face-sharing bioctahedron with the C_6Me_6 molecule occupying one ligand site. Important bond distances are U–Cl (bridge) = 2.75 [5] Å, U–Cl (terminal) = 2.58 [1] Å, and U–C (ring) = 2.92 [4] Å. The U...U distance is 3.937 (1) Å. The coordination of the uranium is discussed below in comparison with structure 2. The AlCl_4 anion is, within the error of the

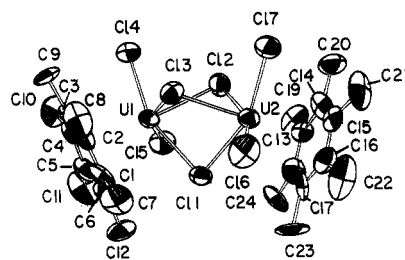


Figure 1. An ORTEP drawing of the $\{[\text{U}(\text{C}_6\text{Me}_6)\text{Cl}_2]_2(\mu\text{-Cl})_3\}^+$ cation, giving the atom labeling scheme. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

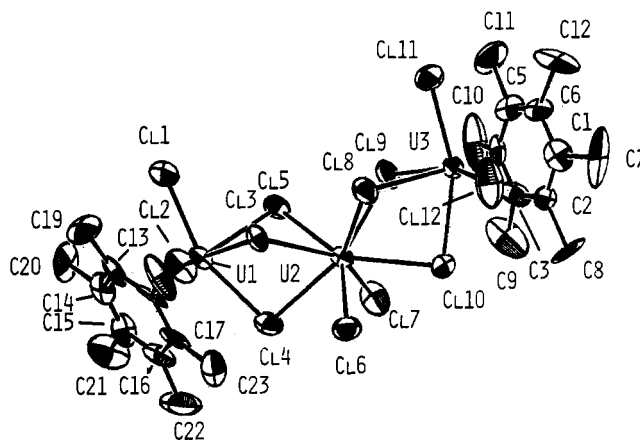


Figure 2. An ORTEP drawing of the $[(\text{C}_6\text{Me}_6)\text{UCl}_2(\mu\text{-Cl})_3\text{UCl}_2(\mu\text{-Cl})_3\text{UCl}_2(\text{C}_6\text{Me}_6)]$ molecule with the atom labeling scheme.

experiment, tetrahedral with average Al–Cl bond lengths of 2.10 [5] Å.

Complex 2 can be derived from 1 by formal insertion of a UCl_5^- subunit into the $(\mu\text{-Cl})_3$ bridge. The central uranium atom is thus eight-coordinate, and we can describe the coordination polyhedron as a square antiprism (SAP) with Cl(3), Cl(5), Cl(9), Cl(8) and Cl(4), Cl(7), Cl(10), Cl(6) defining the squares.¹¹ The distortion from the ideal SAP metric¹² stems from the significant differences in bond

(10) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* 1984, C40, 1186.

(11) A description as a kinked bicapped bigonal prism is also conceivable but we found that the distortions from the idealized geometry are more severe.

Table V. Table of Bond Distances (Å) and Bond Angles (deg) in $U_3Cl_{12}C_{24}H_{36}$

(a) Bond Distances											
U1	U2	4.035 (1)	U1	C18	2.96 (2)	U3	Cl9	2.728 (6)			
U1	Cl1	2.541 (7)	U2	U3	4.031 (1)	U3	Cl10	2.667 (7)			
U1	Cl2	2.546 (7)	U2	Cl3	2.867 (6)	U3	Cl11	2.529 (8)			
U1	Cl3	2.703 (6)	U2	Cl4	2.918 (7)	U3	Cl12	2.523 (7)			
U1	Cl4	2.666 (7)	U2	Cl5	2.789 (6)	U3	C1	2.94 (3)			
U1	Cl5	2.762 (6)	U2	Cl6	2.535 (5)	U3	C2	2.89 (2)			
U1	Cl3	2.97 (2)	U2	Cl7	2.519 (8)	U3	C3	2.90 (3)			
U1	Cl4	2.93 (3)	U2	Cl8	2.775 (7)	U3	C4	2.94 (2)			
U1	Cl5	2.97 (3)	U2	Cl9	2.833 (6)	U3	C5	2.92 (2)			
U1	Cl6	2.96 (2)	U2	Cl10	2.905 (7)	U3	C6	2.90 (2)			
U1	Cl7	2.97 (2)	U3	Cl8	2.755 (6)						
(b) Bond Angles											
Cl1	U1	Cl2	94.2 (2)	Cl4	U2	Cl5	70.3 (2)	Cl8	U2	Cl9	70.8 (2)
Cl1	U1	Cl3	89.4 (2)	Cl4	U2	Cl6	76.7 (2)	Cl8	U2	Cl10	70.7 (2)
Cl1	U1	Cl4	157.8 (2)	Cl4	U2	Cl7	74.7 (2)	Cl9	U2	Cl10	72.3 (2)
Cl1	U1	Cl5	84.1 (2)	Cl4	U2	Cl8	141.5 (2)	Cl8	U3	Cl9	72.6 (2)
Cl2	U1	Cl3	156.9 (2)	Cl4	U2	Cl9	136.1 (2)	Cl8	U3	Cl10	74.7 (2)
Cl2	U1	Cl4	89.8 (2)	Cl4	U2	Cl10	135.4 (2)	Cl8	U3	Cl11	83.9 (2)
Cl2	U1	Cl5	84.2 (2)	Cl5	U2	Cl6	140.4 (2)	Cl8	U3	Cl12	84.7 (2)
Cl3	U1	Cl4	78.8 (2)	Cl5	U2	Cl7	92.2 (2)	Cl9	U3	Cl10	77.8 (2)
Cl3	U1	Cl5	73.4 (2)	Cl5	U2	Cl8	104.4 (2)	Cl9	U3	Cl11	92.3 (3)
Cl4	U1	Cl5	74.5 (2)	Cl5	U2	Cl9	73.0 (2)	Cl9	U3	Cl12	155.8 (3)
U1	U2	U3	142.47 (3)	Cl5	U2	Cl10	144.5 (2)	Cl10	U3	Cl11	158.2 (2)
Cl3	U2	Cl4	72.2 (2)	Cl6	U2	Cl7	99.7 (2)	Cl10	U3	Cl12	88.6 (3)
Cl3	U2	Cl5	70.6 (2)	Cl6	U2	Cl8	88.1 (2)	Cl11	U3	Cl12	93.4 (3)
Cl3	U2	Cl6	79.0 (2)	Cl6	U2	Cl9	145.5 (2)	U1	Cl4	U2	92.4 (2)
Cl3	U2	Cl7	146.2 (2)	Cl6	U2	Cl10	75.1 (2)	U1	Cl5	U2	93.3 (2)
Cl3	U2	Cl8	70.3 (2)	Cl7	U2	Cl8	143.4 (2)	U2	Cl8	U3	93.6 (2)
Cl3	U2	Cl9	116.4 (2)	Cl7	U2	Cl9	83.8 (2)	U2	Cl9	U3	92.9 (2)
Cl3	U2	Cl10	133.4 (2)	Cl7	U2	Cl10	76.8 (2)	U2	Cl10	U3	92.6 (2)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

lengths for the bridging and the terminal chlorides. Consequently the deviations from the best plane including chlorides 3, 5, 9, and 8 (all bridging) are less than 0.1 Å while those of 4, 7, 10, and 6 are all 0.26 Å. The dihedral angle between the best planes is 2.2°. Each terminal octahedral uranium atom and the central square-antiprismatic one are then mutually sharing a trigonal face which leads to a bent arrangement of the three uranium atoms with an angle of 142.4° and an average U...U distance of 4.033 [3] Å. Other important averaged distances are U-Cl (terminal) = 2.53 [1] Å, U-Cl (bridge) = 2.78 [8] Å, and U-C (ring) = 2.94 [3] Å.

The coordination of the uranium atoms bonded to hmb deserves special attention. Both U atoms in 1 and the terminal U atoms in 2 have a distorted octahedral coordination with the hmb molecules occupying one site. There are two sources of distortion: First, hmb is a rather bulky ligand and, second, three of the five remaining chloride ligands are tied together as they constitute a μ_3 bridge. Consequently we find the U atom displaced from the meridional plane defined by the four chlorides cis to the hmb ligand. This deviation, which is easily seen in the ORTEP drawing, is on the average 0.53 Å in 1 and 0.48 Å in 2, while deviations of the Cl from the respective mean planes are less than 0.02 Å. No statistically significant deviations from planarity for the hmb moieties is seen in either structure. All aromatic carbon atoms are planar with none of the sums of bond angles deviating more than 1° from the theoretical value of 360°.

Turning our attention now to the U-C distances we find, in comparison with previously published data (Table VI), that the U-C bond lengths observed in 1 and 2 are among the longest on record. While it is understood that there

Table VI. Comparison of U(IV)-C π -Bond Lengths

compd	U-C(mean), Å	ref
(C ₆ H ₅) ₂ U	2.65	18
[(CH ₃) ₄ C ₆ H ₄] ₂ U	2.66	19
Cp ₂ U(C≡CPh)	2.68	20
CpU(2-Me-C ₃ H ₄) ₃	2.79 (Cp), 2.66 (term), 2.80 (centr)	21
U[(Cp) ₂ CH ₂]Cl ₂ (bpy)	2.72	22
(Cp) ₄ U	2.81	23
[U(η ³ -C ₃ H ₅) ₂ (O- <i>i</i> -Pr) ₂] ₂	2.68	24
U[(CH ₃) ₅ C ₅] ₂ [η ² -CO[N-(CH ₃) ₂]] ₂	2.78	25
Cp ₂ U[O ₂ C ₂ CHP(Me) ₂ (C ₆ H ₅)-Fe ₂ Cp ₂ (CO) ₂] ₂	2.89	26
U(η ⁶ -C ₆ H ₆)(AlCl ₄) ₃	2.91	6
{[U(η ⁶ -C ₆ Me ₆)Cl ₂] ₂ (η-Cl) ₃ }-AlCl ₄	2.92	this work
{[UCl ₂ (C ₆ Me ₆) ₂ UCl ₅]	2.94	this work

is no simple correlation between bond length and bond strength, this observation concurs with our experience that the hmb ligands are easily displaced.

Bonding. The nature of the bond between π -donor ligands and the actinide centers has attracted a great deal of attention. On the theoretical side it appears that extended Hückel analysis and relativistically parameterized extended Hückel calculations consistently evaluate the interaction between Cp⁻ and U⁴⁺ as well as between COT²⁻ and U⁴⁺ as being almost exclusively ionic.^{1,2} This view received support from an attempt to derive the ionic nature of these bonds from the metric properties of the compounds.³ SCF-X α scattered-wave MO studies on uranocene and thorocene, on the other hand, suggested a considerable amount of covalency in these compounds.^{4a}

Quite obviously, an ionic bonding model cannot be invoked for the two complexes presented here. Consistent with the high Lewis acidity of UCl₄ and the electron-rich character of C₆Me₆ the bonding can be visualized as a dative interaction of the arene with UCl₄. The composition

(12) (a) Hoard, J. L.; Silvertown, J. V. *Inorg. Chem.* **1963**, *2*, 235. (b) Blight, D. G.; Kepert, D. L. *Theor. Chim. Acta* **1968**, *11*, 51. (c) Kepert, D. J. *Chem. Soc.* **1965**, 4736.

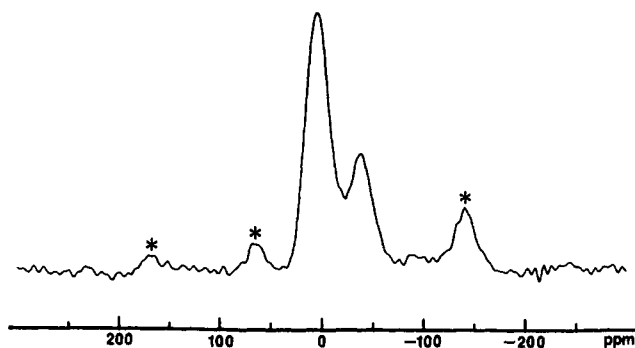


Figure 3. CP/MAS ^{13}C NMR spectrum $[(\text{C}_6\text{Me}_6)\text{UCl}_2(\mu\text{-Cl})_3\text{UCl}_2(\text{C}_6\text{Me}_6)]$ at -53°C . Spinning sidebands are labeled with asterisks.

of the metal acceptor orbitals is unknown. It cannot be considered surprising that both 1 and 2 are easily decomposed by efficient σ -donors such as pyridine or THF even though they are quite stable in a thermodynamic sense.

It is our experience that the above complexes are by no means isolated examples as we have observed (though not yet characterized) Friedel-Crafts type reactions of UCl_4 with other π -systems including pyrene and perilene. It was interesting to learn in a recent report about a Th-Ni interaction, i.e., a dative bond between a nucleophilic transition metal with Th(IV).¹³

Solid-State ^{13}C NMR. The insolubility of the title compounds in nondestructive solvents aroused our interest in solid-state analytical techniques other than X-ray crystallography. NMR spectroscopy, which is such a powerful tool in solution chemistry, came to mind, although we were concerned about possible difficulties related to the paramagnetism of U(IV). Spectra with good signal to noise ratios and with reasonable line widths were obtained in relatively short times (typically 45 min). At room temperature a single resonance, accompanied by the spinning sidebands, was detected at 8.0 ppm, i.e., 9.4 ppm upfield from the methyl resonance of solid hmb. It was tempting to assign this signal to the methyl groups of the complexed hmb and to rationalize the apparent absence of resonances due to the aromatic carbons in terms of broadening of the lines below detection level by paramagnetic relaxation. However, a careful evaluation of the intensity of the spinning sidebands and the powder pattern (obtained in a CP/MAS experiment without sample spinning) suggested an alternative (and correct) interpretation: the signal at 8.0 ppm consists of a superposition of two signals with almost identical isotropic chemical shift but different chemical shift anisotropies. In order to verify this interpretation, we recorded a set of spectra at temperatures between -105°C and $+23^\circ\text{C}$.¹⁴ It is well-known from solution NMR studies that chemical shifts of paramagnetic compounds are temperature dependent.¹⁵ This temperature dependence is in a first approximation a

Curie-Weiss behavior, possibly modified by temperature-dependent conformational changes or the presence of low-lying excited states. Important for our purpose is that the temperature shift increments will depend on the nature of the individual nuclei; i.e., the shifts of chemically different nuclei will be affected differently by temperature changes. This is exactly our observation, and a representative spectrum at -53°C is shown in Figure 3 while a composite drawing of the variable-temperature experiment was deposited with the supplementary material. While the chemical shift of the methyl groups is hardly affected at all ($\Delta\delta = 4.7$ ppm), the aromatic signal (identified by the larger size of the spinning sidebands due to the inherently larger chemical shift anisotropy) is shifted by 47.7 ppm.

Even with the fortuitous coincidence of the methyl and the aromatic signals resolved the spectrum still is deceptively simple. Inspection of the solid-state structure reveals virtual C_{2v} symmetry and nonequivalence of the carbons within the ring. There are two possible explanations for the observed signal averaging. It is conceivable that the chemical shift differences between the individual sites are obscured by the relatively broad lines. Alternatively, fast rotation (on the time scale of the experiment) of the hmb rings will lead to signal averaging. Dynamic processes of this type in the solid state are not unprecedented.¹⁶

A detailed study of the temperature dependence of this and other uranium organometallics is presently in progress and will be reported separately. We note that this represents the first CP/MAS ^{13}C NMR study of organoactinide compounds and that there is only one report of a solid-state NMR study of a paramagnetic compound on record.¹⁷ It is our impression that solid-state ^{13}C is widely applicable to organoactinides and thus represents a valuable tool for the synthetic chemist.

Acknowledgment. We thank the Robert A. Welch Foundation (F.A.C.) and the Center for Energy and Mineral Resources at Texas A&M University (J.F.H.) for financial support.

Registry No. 1, 99496-10-3; 2, 99496-11-4; hmb, 87-85-4; AlCl_3 , 7446-70-0; UCl_4 , 10026-10-5.

Supplementary Material Available: Two tables of observed and calculated structure factors, two tables of anisotropic displacement parameters, complete tables of bond lengths and bond angles, and a composite drawing of the CP/MAS ^{13}C NMR spectra between -74°C and 23°C (40 pages). Ordering information is given on any current masthead page.

(16) Fyfe, C. A. "Solid State NMR For Chemists"; C.F.C. Press: Guelph, 1984; pp 412-419.

(17) Chacko, V. P.; Ganapathy, S.; Bryant, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5491.

(18) Zalkin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **1969**, *91*, 5667.

(19) Hogson, K. O.; Raymond, K. N. *Inorg. Chem.* **1973**, *12*, 458.

(20) Atwood, J. L.; Hains, C. F.; Tsutsui, M.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 453.

(21) Day, V. W.; Ernst, R. D. Cited in "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 240.

(22) Secaur, C. A.; Day, V. W.; Ernst, R. D.; Kennelly, W. J.; Marks, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3713.

(23) Burns, J. H. *J. Organomet. Chem.* **1974**, *69*, 225.

(24) Brunelli, M.; Perego, G.; Lugli, G.; Mazzei, A. *J. Chem. Soc., Dalton Trans.* **1979**, 861.

(25) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Secaur Day, C.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206.

(26) Cramer, R. E.; Higa, K. T.; Pruskin, S. L.; Gilje, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6749.

(13) Ritchey, J. M.; Zoznlin, A. J.; Wroblewski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501.

(14) An attempt to acquire the spectrum at temperatures above ambient ended when the deldrin rotor in which the sample was packed shattered.

(15) Luke, W. D.; Streitzwieser, A., Jr. *ACS Symp. Ser.* **1980**, No. 131, 93.