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Rotomeric Configurations of a Methyl-Substituted Cyclooctatetraene Dianion Complex of Uranium(IV). Crystal and Molecular Structure of Bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV), $U(C_8H_4(CH_3)_4)_2$

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The crystal and molecular structure of bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV), $U(C_8H_4(CH_3)_4)_2$, has been determined from three-dimensional X-ray data collected by counter methods. There are two crystallographically independent π-carbocyclic sandwich molecules per unit cell. In both cases the uranium atom is symmetrically bonded to two planar, methyl-substituted cyclooctatetraenyl dianion rings. The U–C bond lengths are equal and average 2.658 (6) Å. The C–C bond lengths within the four aromatic rings are also equal and average 1.409 (7) Å. The two rings in both molecules, when viewed down the molecular symmetry axis, are rotated 14° from a conformation in which the ring carbon atoms are eclipsed. However, the two molecules differ in the relation of the substituent methyl groups. In molecule A the methyl groups are approximately eclipsed and in molecule B the methyl groups are approximately staggered. All 16 independent methyl groups are bent inward an average of 4.1° from the planes of the dianion ring carbons toward the uranium atom. The rotomeric conformation is discussed relative to the well-characterized substituted ferrocenes and two hypotheses are proposed for the nonplanarity of the methyl groups. The complex sublimes easily to give large, burgundy red plates with the following crystal data: monoclinic space group, $P2_1/c$, cell constants $a = 20.224$ (5), $b = 12.066$ (3), $c = 17.467$ (6) Å, $\beta = 101.57$ (2)°. For eight formula units per cell the calculated density is 1.74 g/cm^3. The structure has been refined with full-matrix least-squares methods using 4341 independent reflections for which $F^2 > 3\sigma(F^2)$ to a standard unweighted R factor of 3.68%.

Introduction

Following the initial synthesis[2,3] and single-crystal structure determination[4,5] of bis(cyclooctatetraenyl)uranium(IV), "uranocene," there has been renewed interest in the degree of covalent bonding in these π-carbocyclic complexes and particularly in the extent to which there is contribution to this bonding from the uranium 5f orbitals. Contact shift proton magnetic resonance is one technique which can be used to study the electronic interactions in these complexes, if the molecular structures of the complexes are well enough known so that the geometrically dependent contributions to the chemical shift can be evaluated. The original nmr study of $U(C_8H_8)_2$ by Edelstein, La Mar, Mares, and Streitwieser[6] was interpreted using the molecular parameters of the single-crystal structure and indicated a large positive net contact shift that suggested some form of covalency. However, in the absence of data which would indicate the type of ligand molecular orbital (σ or π) containing the delocalized spin, no attempt could be made to evaluate the possible role of f orbitals in such covalency. Methyl substitution on the π-carbocyclic ring provides a useful technique for characterizing the mechanism of spin delocalization in these ligands. For spin in the π orbitals it is well known that an attached ring proton and methyl group proton exhibit hyperfine coupling constants of comparable magnitude but of opposite sign; for spin in σ orbitals the coupling constants are of the same sign with the ring methyl shift attenuated 3–5 times the ring proton shift.

In order to utilize this approach in the interpretation of the $U(C_8H_8)_2$ spectrum, Streitwieser and coworkers prepared and studied the nmr spectrum of bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV).[7] The derived contact shifts were of opposite signs for the methyl and ring protons and the result has been interpreted as being consistent with f-orbital participation in the bonding of these complexes.

There were three main reasons for interest in the structure of $U(C_8H_4(CH_3)_4)_2$. First, we wished to compare the geometry with that of the previously studied parent compound, $U(C_8H_8)_2$,[4,5] and that of the thorium homolog, $Th(C_8H_8)_2$;[5] this information was needed for the nmr studies. Second, we wanted to determine which of the possible rotomeric conformations involving the relative orientations of the methyl groups and the dianion rings exist in the solid state, the object being to determine indirectly the ease of rotation of one ring with respect to another around the molecular symmetry axis. Third, we wanted to take advantage of the opportunity to measure the relative planarity of the tetramethylcyclooctatetraenyl ligand. Any concave or convex distortion of the unsubstituted cyclooctatetraenyl dianion ring cannot be determined by X-ray diffraction studies because the substituent hydrogen atoms are not located with sufficient accuracy. Replacement of the ring-substituent hydrogen atoms by a methyl group makes this measurement possible.

The preliminary structural results for $U(C_8H_4(CH_3)_4)_2$ appeared earlier.[8] In the present paper we report the full anisotropic refinement and completed structure determination for this unusual compound.

Experimental Section

The synthesis of $U(C_8H_4(CH_3)_4)_2$, $U(TMCOT)_2$, has been reported previously.[7] Single crystals of the complex suitable for X-ray structural studies were prepared by slow sublimation under a definite temperature gradient and argon pressure in a sealed tube. Pure $U(TMCOT)_2$ (50 mg) obtained from a previous sublimation was placed in a small copper crucible in a glass sublimation tube. The tube was evacuated to 20 μ and heated with a cold flame 4–6 cm above the crucible to clean the inner walls. The tube was pressurized

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(1) (a) National Science Foundation Trainee, 1969–1972. (b) Alfred P. Sloan Fellow.

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with argon to 650 mm and sealed. The sublimation was carried out at 270° in a heated block over a period of 24 hr. Crystals obtained in this way were well formed and ranged in size up to as large as 0.08 × 0.08 × 0.07 mm. The air- and moisture-sensitive crystals were mounted with Corning high-vacuum silicon grease in thin-walled quartz capillaries under an argon atmosphere. A series of precession photographs showed monoclinic symmetry with the following systematic absences: $h0l, l \neq 2n$; $0k0, k \neq 2n$. Space group $P2_1/c$ [C_{2h}^5] is the only choice consistent with these conditions.

Data Collection

The crystal selected for data collection was a burgundy red parallelepiped bounded by the following seven planes: $\bar{1}00$, $2\bar{1}0$, $\bar{2}10$, 110, $\bar{1}\bar{1}0$, 001, $00\bar{1}$. The perpendicular distances to each of these planes from the intersection point of the $2\bar{1}0$, 110, and 001 planes are respectively 0.025, 0.0, 0.021, 0.0, 0.024, 0.0, and 0.014 mm. The crystal gave ω-scan widths at half-height of 0.08, 0.09, and 0.08° for the 400, 040, and 004 reflections, respectively.

The crystal was mounted in a capillary with the $2\bar{1}0$ axis approximately parallel to the ϕ axis of a Picker FACS-1 four-circle diffractometer. The X-ray source was Mo Kα_1 radiation (λ 0.70926 Å) and the X-ray tube takeoff angle was 2.0°. The Bragg 2θ angle for the graphite monochromator crystal was 12.02°. The pulse height analyzer, centered on an Mo Kα peak, was set to admit about 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a receiving aperture of 7 × 7 mm. The optimum crystal orientation matrix and unit cell constants were determined by least-squares refinement[9] of 12 carefully centered high-angle reflections for which the Kα_1 and Kα_2 peaks were well resolved. The 12 reflections had 2θ values ranging from 39 to 50°. These refined cell parameters are given in Table I along with other pertinent crystal data.

The intensity data were collected using a θ-2θ scan mode with the same instrument settings that were used for determining the cell constants. The 2θ scans were from 0.5° below the Kα_1 peak to 0.5° above the Kα_2 peak with a scan rate of 1.0°/min. Stationary 10-sec background counts were taken at the start and end of each scan and copper foil attenuators were automatically inserted to maintain the count rate for a given reflection below 10^4 counts/sec.

During the experiment, the intensities of the three standard reflections 400, 060, and 004 were measured every 75 reflections as a check on the stability of the crystal and the instrument. The 14,507 reflections collected comprised only one unique form ($\pm h, k, l$) within a sphere of $0 \geqslant 2\theta \geqslant 60°$.

After 8 hr of data collection it was observed that the 2θ scans were no longer exactly centered in the scan range. Thus, a new orientation matrix was calculated and data collection resumed. A closer check as data collection progressed showed that the 2θ maxima were slowly shifting out of the center of the scan range. Whenever the scan reached 0.15-0.2° off center, a new orientation matrix was calculated and data collection resumed. This was done about 14 times during the course of data collection. Some of the intensity could not be reproduced by optimization of the orientation; this was apparently due to crystal decomposition. After completion of the data set, one source of the problem was discovered. The originally clear white silicon grease was red, indicating that some of the crystal had dissolved, and the crystal was slowly changing position in the grease.

The data reduction and processing were accomplished by our program UCFACS as described previously.[10] The parameter p introduced in the expression for $\sigma(F^2)$ to avoid overweighting the strong reflections was set to 0.04. The corrected intensities were converted to values of F by application of Lorentz and polarization corrections. The F^2 values of the standards showed maximum anisotropic losses in intensity of 4.4, 8.5, and 21.6%, respectively, for the three standards mentioned above.

Our decay correction program CHORT, which has been previously described,[11] was used to correct the F^2 values for this decay. As a check, a comparison of F^2's of standards taken at the beginning and end of data collection always agreed within 2% after the decay correction.

The calculated absorption coefficient, μ, is 114.1 cm^{-1}. An absorption correction was applied using a gaussian numerical integration program.[12] The applied corrections to F^2 ranged from 3.2 to 5.9 with an average correction of 4.1. After this correction, those data measured more than once were averaged and those for which $F^2 < 3\sigma(F^2)$ were rejected. This resulted in a set of 4341 independent reflections which were used in the final refinement.

Table I. Summary of Crystal Data

Mol formula	$U(C_8H_4(CH_3)_4)_2$
Mol wt	558.55
Linear absorption coeff μ	114.13 cm^{-1}
Calcd density	1.74 g/cm^3
Crystal dimensions	0.25 × 0.28 × 0.14 mm
Space group	$P2_1/c$, monoclinic
Molecules/unit cell	8
Cell constants[a]	$a = 20.224$ (5), $b = 12.066$ (3), $c = 17.467$ (6) Å; $\beta = 101.57$ (2)°; $\cos\beta = 0.2006$ (3)
Cell volume[a]	4175.8 Å^3

[a] Mo Kα_1 radiation, λ 0.70926 Å; ambient temperature of 23°.

Solution and Refinement of the Structure

The positions of the two independent uranium atoms were easily established from a three-dimensional Patterson map. Three cycles of least-squares refinement of the scale factor and uranium coordinates with isotropic temperature factors phased the structure sufficiently so that 35 carbon atoms could be located in the subsequent difference Fourier. Three additional cycles of refinement of these positions followed by another difference Fourier revealed the remaining positions of all the nonhydrogen atoms.

The full-matrix weighted least-squares refinements were carried out on F in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral U and C were taken from the values tabulated by Cromer and Mann[13] and those for neutral hydrogen were from Stewart, Davidson, and Simpson.[14] The calculations included both $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion effects of the uranium atom.[15]

After convergence of the isotropic model with all nonhydrogen atoms to a standard weighted R factor of 8.4%, two cycles of full-matrix least-squares refinement were run with anisotropic thermal parameters. In an attempt to locate the hydrogen atoms, a difference Fourier on F was calculated in which all data with $(\sin\theta)/\lambda > 0.4$ were rejected. No clearly defined atom positions could be found for either the ring or methyl group hydrogens. The hydrogen atom positions for the ring hydrogens were then calculated by assuming trigonal-planar geometry and C-H bond lengths of 1.0 Å. The methyl hydrogens were not included in the calculations. In the final anisotropic refinement the ring hydrogen atom contributions to the structure factors were calculated from these fixed positions and the temperature factors for all hydrogen atoms were set to 6.0 Å^2.

Inspection of the most intense reflections suggested the presence of secondary extinction effects so the extinction parameter was varied in the final refinements.[16] The least-squares refinement with 452 variables and 4341 observations took 955 sec per cycle of central processor time on the CDC 7600 computer. The refinement converged to give final agreement factors of

$$R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.0368$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.0461$$

The final error in an observation of unit weight, defined as $[(\Sigma w \cdot (|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$, is 1.04. A final difference Fourier showed no peaks greater than 0.6 e/Å^3 which were not within 1 Å of the uranium atoms.

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(9) Programs used for the PDP 8/I computer were those written by Busing and Levy, as modified by Picker Corp.

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(12) In addition to local programs for the CDC 7600 computer, the following programs or modifications were used: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group least-squares version of the Busing-Levy ORFLS program; ORFFE, a function and error program by Busing and Levy; Johnson's ORTEP thermal ellipsoid plot program; AGNOST, an absorption correction program written by P. Coppens, L. Leiserowite, and D. Rabinovich and modified by W. Haton, J. Edmonds, J. Ibers, and D. Cahen.

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Table II. Positional[a] and Anisotropic Thermal[b] Parameters for Molecule A

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U_1	0.12594(2)	0.24186(4)	0.21585(2)	14.9(1)	47.5(3)	25.7(1)	-0.7(3)	5.4(1)	5.9(4)
C_{11}	0.1528 (8)	0.4422 (10)	0.2804 (10)	29 (5)	54 (10)	41 (8)	-14 (6)	12 (5)	-12 (7)
C_{12}	0.2030 (7)	0.3712 (10)	0.3183 (7)	23 (4)	71 (10)	26 (6)	-3 (5)	3 (4)	0 (6)
C_{13}	0.2480 (6)	0.2937 (11)	0.2995 (8)	18 (4)	84 (11)	26 (6)	-9 (5)	-6 (3)	14 (6)
C_{14}	0.2592 (5)	0.2496 (12)	0.2294 (8)	15 (3)	76 (10)	45 (6)	4 (7)	4 (3)	10 (11)
C_{15}	0.2316 (7)	0.2604 (12)	0.1484 (8)	27 (4)	76 (11)	45 (6)	-10 (7)	19 (4)	0 (9)
C_{16}	0.1825 (7)	0.3342 (10)	0.1082 (7)	27 (4)	59 (9)	32 (6)	-3 (5)	13 (4)	-2 (6)
C_{17}	0.1390 (7)	0.4169 (11)	0.1279 (8)	25 (5)	81 (11)	28 (6)	-17 (6)	-3 (4)	25 (7)
C_{18}	0.1267 (7)	0.4593 (10)	0.2020 (11)	18 (4)	63 (9)	26 (8)	0 (5)	1 (5)	2 (8)
C_{11M}	0.1136 (8)	0.5109 (12)	0.3316 (9)	47 (7)	98 (14)	45 (8)	3 (7)	19 (6)	-33 (8)
C_{13M}	0.2923 (8)	0.2376 (14)	0.3717 (9)	37 (5)	155 (20)	51 (7)	18 (9)	-15 (5)	28 (11)
C_{15M}	0.2602 (8)	0.1779 (12)	0.0974 (10)	36 (6)	105 (14)	62 (9)	11 (7)	26 (6)	-10 (9)
C_{17M}	0.0919 (8)	0.4670 (12)	0.0526 (10)	40 (7)	106 (14)	41 (9)	2 (7)	1 (6)	27 (8)
C_{21}	0.0318 (7)	0.2025 (11)	0.3013 (8)	22 (4)	81 (11)	37 (6)	-9 (5)	13 (4)	12 (6)
C_{22}	0.0828 (7)	0.1228 (11)	0.3231 (8)	28 (5)	83 (11)	29 (6)	-5 (6)	13 (4)	15 (6)
C_{23}	0.1190 (8)	0.0457 (10)	0.2837 (10)	24 (5)	58 (10)	57 (9)	5 (5)	18 (5)	19 (7)
C_{24}	0.1183 (8)	0.0233 (9)	0.2055 (10)	35 (6)	56 (8)	22 (7)	3 (6)	8 (5)	-7 (8)
C_{25}	0.0820 (7)	0.0598 (11)	0.1323 (9)	25 (5)	63 (10)	43 (7)	-11 (6)	10 (5)	-13 (7)
C_{26}	0.0332 (6)	0.1409 (10)	0.1103 (7)	18 (4)	74 (10)	28 (6)	-13 (5)	0 (4)	2 (6)
C_{27}	-0.0031 (6)	0.2182 (10)	0.1477 (8)	18 (3)	77 (12)	36 (6)	0 (5)	5 (4)	11 (6)
C_{28}	-0.0036 (5)	0.2401 (11)	0.2261 (8)	16 (3)	61 (10)	45 (6)	3 (6)	9 (3)	5 (8)
C_{21M}	0.0137 (7)	0.2645 (13)	0.3704 (8)	42 (5)	135 (17)	41 (6)	10 (8)	26 (5)	-18 (10)
C_{23M}	0.1778 (7)	-0.0154 (12)	0.3412 (9)	29 (5)	122 (15)	46 (8)	22 (7)	7 (5)	40 (8)
C_{25M}	0.1049 (8)	0.0027 (12)	0.0622 (10)	30 (6)	127 (15)	33 (8)	-4 (7)	2 (5)	-24 (9)
C_{27M}	-0.0498 (7)	0.2959 (13)	0.0891 (9)	25 (5)	144 (16)	46 (8)	19 (7)	-5 (5)	14 (8)

[a] Fractional cell coordinates. [b] Values of β are multiplied by 10^4; the form of the thermal correction is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Positional[a] and Anisotropic Thermal[b] Parameters for Molecule B

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U_2	0.62429(2)	0.24712(5)	0.35534(2)	15.1(1)	46.2(3)	22.5(2)	-1.0(2)	3.8(1)	-0.8 (3)
C_{31}	0.6198 (8)	0.4544 (9)	0.4081 (9)	32 (6)	45 (8)	19 (7)	1 (5)	10 (5)	3 (6)
C_{32}	0.6668 (7)	0.3962 (9)	0.4645 (7)	31 (5)	58 (9)	14 (5)	-8 (5)	6 (4)	-7 (5)
C_{33}	0.7213 (6)	0.3229 (10)	0.4699 (8)	20 (4)	60 (9)	37 (6)	-5 (5)	0 (4)	-6 (6)
C_{34}	0.7536 (6)	0.2799 (10)	0.4115 (9)	13 (3)	72 (11)	44 (6)	3 (4)	3 (3)	1 (6)
C_{35}	0.7498 (6)	0.2875 (9)	0.3310 (8)	21 (4)	58 (9)	39 (7)	-4 (5)	10 (4)	-3 (6)
C_{36}	0.7041 (7)	0.3453 (10)	0.2737 (8)	28 (5)	58 (9)	34 (6)	-4 (5)	15 (4)	-8 (6)
C_{37}	0.6465 (7)	0.4188 (10)	0.2674 (9)	26 (5)	44 (8)	41 (7)	-11 (5)	9 (5)	11 (6)
C_{38}	0.6153 (7)	0.4614 (9)	0.3295 (10)	15 (4)	44 (8)	34 (8)	3 (4)	2 (4)	1 (6)
C_{31M}	0.5663 (7)	0.5207 (11)	0.4389 (9)	34 (5)	102 (13)	43 (7)	23 (7)	17 (5)	-5 (8)
C_{33M}	0.7459 (8)	0.2734 (14)	0.5535 (8)	39 (5)	170 (20)	25 (6)	10 (9)	-7 (4)	16 (9)
C_{35M}	0.7993 (7)	0.2102 (10)	0.3018 (9)	26 (4)	82 (11)	60 (8)	6 (5)	24 (5)	-12 (7)
C_{37M}	0.6141 (8)	0.4485 (12)	0.1818 (9)	29 (6)	110 (14)	21 (7)	5 (7)	4 (4)	6 (7)
C_{41}	0.4928 (6)	0.2129 (9)	0.3463 (8)	18 (3)	64 (10)	33 (6)	-4 (4)	7 (4)	-4 (6)
C_{42}	0.5251 (6)	0.1663 (10)	0.4212 (8)	20 (4)	64 (10)	33 (6)	0 (5)	10 (4)	-4 (6)
C_{43}	0.5794 (7)	0.0955 (10)	0.4409 (7)	23 (4)	71 (10)	25 (5)	-3 (5)	6 (4)	14 (6)
C_{44}	0.6272 (7)	0.0363 (10)	0.4015 (11)	12 (4)	55 (9)	46 (10)	4 (5)	6 (5)	8 (7)
C_{45}	0.6351 (7)	0.0334 (9)	0.3310 (10)	24 (5)	55 (9)	31 (7)	10 (5)	16 (4)	9 (6)
C_{46}	0.6029 (8)	0.0771 (10)	0.2559 (9)	27 (5)	57 (9)	45 (8)	-7 (6)	12 (5)	-20 (7)
C_{47}	0.5477 (7)	0.1510 (10)	0.2331 (7)	26 (4)	74 (10)	22 (5)	-16 (5)	5 (4)	-4 (6)
C_{48}	0.5024 (6)	0.2092 (9)	0.2708 (8)	22 (4)	61 (9)	28 (6)	-2 (5)	4 (4)	-1 (5)
C_{41M}	0.4947 (8)	0.2083 (12)	0.4902 (9)	48 (6)	103 (14)	41 (7)	13 (7)	31 (5)	-12 (7)
C_{43M}	0.6820 (7)	-0.0268 (12)	0.4618 (8)	37 (6)	122 (15)	34 (7)	27 (7)	3 (5)	29 (8)
C_{45M}	0.6386 (8)	0.0488 (12)	0.1859 (10)	25 (6)	112 (14)	24 (8)	8 (7)	5 (5)	-21 (7)
C_{47M}	0.4543 (7)	0.2889 (11)	0.2160 (9)	21 (4)	100 (13)	49 (7)	10 (6)	-11 (4)	13 (7)

[a] Fractional cell coordinates. [b] Values of β are multiplied by 10^4; the form of the thermal correction is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Positional and thermal parameters from the final least-squares cycle are given in Tables II and III. Tables IV and V list the hydrogen atom positions and the rms amplitudes of vibration along the principal axes of the thermal ellipsoids for all nonhydrogen atoms.[17]

Description of Structure and Discussion

In the structure, there are two crystallographically independent molecules, A and B, which differ only in their molecular conformation. Neither molecule A nor molecule B is

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(17) A listing of structure factors will appear following these pages in the microfilm edition of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-458.

Table IV. Calculated Positions for Ring Hydrogen Atoms on Cyclooctatetraene Rings[a]

Molecule A				Molecule B			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H_{12}	0.2098	0.3810	0.3777	H_{32}	0.6581	0.4115	0.5196
H_{14}	0.2967	0.1924	0.2397	H_{34}	0.7911	0.2263	0.4360
H_{16}	0.1765	0.3251	0.0483	H_{36}	0.7138	0.3299	0.2193
H_{18}	0.0890	0.5172	0.1927	H_{38}	0.5766	0.5132	0.3050
H_{22}	0.0986	0.1181	0.3831	H_{42}	0.4530	0.2609	0.3514
H_{24}	0.1540	−0.0348	0.2001	H_{44}	0.5890	0.0800	0.5003
H_{26}	0.0187	0.1457	0.0509	H_{46}	0.6775	−0.0117	0.3269
H_{28}	−0.0374	0.3006	0.2317	H_{48}	0.5381	0.1661	0.1744

[a] Calculated positions. Trigonal-planar geometries are assumed for the carbon atoms. A C–H bond length of 1.0 Å and an isotropic thermal parameter of 6.0 Å^2 were assumed.

Table V. Root-Mean-Square Amplitudes of Vibration of All Nonhydrogen Atoms Along Principal Axes (Å × 10^3)

Molecule A				Molecule B			
Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
U_1	163 (1)	180 (1)	207 (1)	U_2	172 (1)	181 (1)	186 (1)
C_{11}	170 (19)	222 (23)	274 (21)	C_{31}	155 (31)	184 (17)	252 (23)
C_{12}	195 (20)	213 (18)	237 (17)	C_{32}	133 (25)	201 (17)	258 (19)
C_{13}	149 (21)	202 (18)	284 (18)	C_{33}	180 (20)	220 (17)	250 (20)
C_{14}	173 (17)	227 (23)	271 (22)	C_{34}	159 (19)	232 (18)	259 (19)
C_{15}	169 (19)	241 (20)	284 (19)	C_{35}	188 (18)	208 (17)	247 (19)
C_{16}	185 (19)	207 (17)	248 (19)	C_{36}	180 (20)	204 (17)	264 (19)
C_{17}	148 (23)	192 (21)	314 (20)	C_{37}	140 (21)	241 (20)	257 (21)
C_{18}	178 (25)	209 (27)	218 (18)	C_{38}	164 (20)	187 (18)	230 (27)
$C_{11}M$	165 (25)	302 (22)	326 (21)	$C_{31}M$	171 (21)	265 (20)	317 (19)
$C_{13}M$	168 (24)	347 (22)	265 (24)	$C_{33}M$	163 (23)	306 (19)	359 (21)
$C_{15}M$	188 (22)	293 (19)	329 (22)	$C_{35}M$	157 (21)	254 (17)	317 (19)
$C_{17}M$	197 (25)	285 (23)	322 (22)	$C_{37}M$	173 (28)	240 (23)	288 (18)
C_{21}	153 (21)	244 (19)	265 (17)	C_{41}	184 (18)	210 (18)	316 (17)
C_{22}	154 (22)	249 (20)	265 (18)	C_{42}	177 (19)	215 (17)	234 (19)
C_{23}	180 (22)	197 (21)	310 (22)	C_{43}	163 (21)	215 (20)	249 (17)
C_{24}	164 (28)	212 (21)	264 (22)	C_{44}	150 (24)	199 (18)	265 (26)
C_{25}	183 (19)	220 (20)	274 (20)	C_{45}	153 (25)	183 (19)	263 (20)
C_{26}	163 (20)	208 (19)	257 (18)	C_{46}	174 (20)	220 (21)	285 (21)
C_{27}	186 (18)	209 (19)	258 (19)	C_{47}	178 (20)	190 (19)	270 (18)
C_{28}	170 (16)	211 (19)	261 (18)	C_{48}	200 (18)	208 (19)	216 (16)
$C_{21}M$	155 (24)	315 (19)	328 (21)	$C_{41}M$	141 (24)	288 (19)	339 (20)
$C_{23}M$	173 (22)	249 (21)	353 (20)	$C_{43}M$	163 (23)	268 (20)	345 (19)
$C_{25}M$	192 (26)	253 (22)	324 (19)	$C_{45}M$	160 (29)	221 (25)	308 (19)
$C_{27}M$	177 (22)	295 (21)	339 (19)	$C_{47}M$	154 (22)	277 (18)	317 (20)

constrained to have any symmetry higher than 1. In both molecules the central uranium is symmetrically π bonded to the two cyclooctatetraene rings. Molecule A has mean U-C bonds which are equal within experimental error and average 2.658 (4) Å. The average U-C bond in molecule B has the same value, 2.657 (6) Å. The mean value of the C-C bond length for molecules A and B is only two standard deviations longer than the average U-C bond in $U(C_8H_8)_2$ and thus the bond length in the methyl-substituted derivative is not significantly longer as compared to the parent compound. The ring-to-ring distance along the molecular symmetry axis for both A and B is essentially identical and averages 3.836 (9) Å, which again compares very closely with the analogous value observed in $U(C_8H_8)_2$ of 3.847 (10) Å. Half of this distance, 1.918 Å, is the average distance from the uranium atom to the center of the tetramethylcyclooctatetraene dianion ring. The mean C-M-C angle for adjacent carbons in the four dianion rings is 30.8 (16)°. The mean C-M-C angle for the four rings where the two carbons are separated by three ring atoms and are on opposite sides of the dianion ring is 87.7 (15)°. These angles and distances along with the planarity of the dianion rings establish that the molecular coordination of the uranium atoms in the methyl-substituted complex is almost identical with that in the parent compound $U(C_8H_8)_2$, with the exception of the rotomeric conformation of the ligands to be discussed later. The bond lengths and angles for the inner coordination spheres of molecules A and B are summarized in Tables VI and VII.

The ring carbon atoms for all four independent tetramethylcyclooctatetraene dianions are coplanar. The individual C-C distances and averages for each ring are summarized in Table VIII. The overall mean C-C distance is 1.409 (7) Å. This value is not significantly different from the mean value observed for $U(C_8H_8)_2$, 1.396 (5) Å, since the two values differ by less than three standard deviations. A weighted least-squares plane through each of the dianion rings (Table IX) shows that each of the rings is planar. The four planar rings have the regular interior octagonal angle of 135.0° (Table VII). The averages of alternate sets of C-C bonds for each of the four independent dianion rings are also each equal within five standard deviations. Although perhaps statistically significant, we do not regard this as a chemically significant difference. The planarity, interior average C-C-C angle, and average of alternate sets of C-C bonds confirm the aromaticity of each of the 10-π-electron aromatic dianion rings.

The thermal motion shows a preferential oscillation around the molecular axis in all of the dianion rings (as has been observed in the other structures of cyclooctatetraene complexes[5,11,18,19]) with an average root-mean-square amplitude of vibration (see Table V) along the major ellipsoid axis of 0.26 Å. This value, however, is 0.11 Å smaller than the same average for $U(C_8H_8)_2$. This is an expected consequence of the methyl substitution since the methyl groups should reduce thermal motion by both inter- and intramolecular effects.

The crystal structure is composed of two interpenetrating lattice arrays. These two arrays are identical in shape and the molecules within each array have the same orientation in space but one array is composed exclusively of molecules of type A and the second is composed exclusively of type B.

(18) P. A. Kroon and R. B. Helmoldt, *J. Organometal. Chem.*, **25**, 451 (1970).

(19) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **11**, 3030 (1972).

Table VI. Inner Coordination Sphere Bond Lengths (Å)

Molecule A		Molecule B	
Atoms	Distance[a]	Atoms	Distance[a]
U-C_{11}	2.676 (12)	U-C_{31}	2.674 (12)
U-C_{12}	2.636 (12)	U-C_{32}	2.637 (11)
U-C_{13}	2.678 (12)	U-C_{33}	2.668 (12)
U-C_{14}	2.659 (11)	U-C_{34}	2.632 (11)
U-C_{15}	2.649 (11)	U-C_{35}	2.701 (12)
U-C_{16}	2.637 (12)	U-C_{36}	2.639 (12)
U-C_{17}	2.656 (12)	U-C_{37}	2.671 (12)
U-C_{18}	2.635 (12)	U-C_{38}	2.624 (11)
U-C_{21}	2.688 (12)	U-C_{41}	2.665 (12)
U-C_{22}	2.644 (12)	U-C_{42}	2.688 (12)
U-C_{23}	2.663 (12)	U-C_{43}	2.636 (11)
U-C_{24}	2.645 (11)	U-C_{44}	2.666 (12)
U-C_{25}	2.688 (13)	U-C_{45}	2.630 (12)
U-C_{26}	2.648 (12)	U-C_{45}	2.667 (13)
U-C_{27}	2.658 (13)	U-C_{47}	2.641 (12)
U-C_{28}	2.661 (11)	U-C_{48}	2.647 (12)
Mean U-C	2.658 (4)	Mean U-C	2.657 (6)

[a] Standard deviations for the mean values reported in this and subsequent tables were estimated from the variance using the equations $\sigma^2 = (\Sigma_{i=1}{}^{n}(x_i - \overline{x})^2)/(n-1)$ and $\sigma(\overline{x}) = \sigma/\sqrt{n},$ where σ is the standard deviation of an individual observation and $\sigma(\overline{x})$ is the standard deviation of the mean.

Table VII. Bond Angles (deg) for the Cyclooctatetraene Dianion

Molecule A				Molecule B			
Group	Angle	Group	Angle	Group	Angle	Group	Angle
C_{18}-C_{11}-C_{12}	131.4 (14)	C_{28}-C_{21}-C_{22}	131.8 (12)	C_{38}-C_{31}-C_{32}	129.3 (13)	C_{48}-C_{41}-C_{42}	136.7 (12)
C_{11}-C_{12}-C_{13}	138.9 (13)	C_{21}-C_{22}-C_{23}	136.7 (14)	C_{31}-C_{32}-C_{33}	140.5 (13)	C_{41}-C_{42}-C_{43}	131.0 (12)
C_{12}-C_{13}-C_{14}	134.0 (12)	C_{22}-C_{23}-C_{24}	133.5 (14)	C_{32}-C_{33}-C_{34}	130.8 (13)	C_{42}-C_{43}-C_{44}	138.2 (12)
C_{13}-C_{14}-C_{15}	137.7 (12)	C_{23}-C_{24}-C_{25}	137.0 (14)	C_{33}-C_{34}-C_{35}	139.7 (12)	C_{43}-C_{44}-C_{45}	133.2 (14)
C_{14}-C_{15}-C_{16}	130.5 (13)	C_{24}-C_{25}-C_{26}	133.0 (13)	C_{34}-C_{35}-C_{36}	130.3 (12)	C_{44}-C_{45}-C_{46}	138.4 (15)
C_{15}-C_{16}-C_{17}	137.1 (13)	C_{25}-C_{26}-C_{27}	137.6 (13)	C_{35}-C_{36}-C_{37}	139.6 (13)	C_{44}-C_{45}-C_{46}	132.0 (14)
C_{16}-C_{17}-C_{18}	133.3 (12)	C_{26}-C_{27}-C_{28}	132.7 (12)	C_{36}-C_{37}-C_{38}	128.4 (14)	C_{45}-C_{46}-C_{47}	136.5 (13)
C_{17}-C_{18}-C_{11}	136.8 (13)	C_{27}-C_{28}-C_{21}	137.5 (12)	C_{37}-C_{38}-C_{31}	141.2 (14)	C_{46}-C_{47}-C_{48}	133.8 (12)
Mean C-C-C in ring 1	135.0 (11)	Mean C-C-C in ring 1	135.0 (9)	Mean C-C-C in ring 1	135.0 (20)	Mean C-C-C in ring 2	135.0 (9)

Molecule A		Molecule B	
Group	Angle	Group	Angle
Mean C_i-U-C_{i+1}	30.8 (16)	Mean C_i-U-C_{i+1}	30.74 (18)
Mean C_i-U-C_{i+4}	87.7 (19)	Mean C_i-U-C_{i+4}	87.64 (17)

[a] Atoms i and $i + 1$ are adjacent in the cyclooctatetraene dianion ring. Atoms i and $i + 4$ are separated by three carbon atoms in the ring. Half this value is the angle between the molecular axis and the ring carbon atoms.

The two arrays are related to one another by a translation in the reciprocal lattice **a*** direction of 9.88 Å. This translation is not along a real cell translation direction and so it does not repeat. The two arrays both contain sheets of molecules which lie in planes perpendicular to **c** and form a herringbone motif of alternating orientations of their respective molecular symmetry axes. A stereoscopic packing diagram of the contents of one unit cell is shown in Figure 1. The vertical axis of the figure is **b** and the horizontal axis is **a**. The direction of view is $-z \sin \beta$ (*i.e.*, **c*** comes directly out of plane of the figure). Since the β angle is 101.57° the diagram in Figure 1 is rotated 11.57° to the left from an orientation in which the view direction would be **c**.

There is a second type of pseudotranslation in the structure. Since the y coordinates of all molecules A and B are approximately $\pm{}^1/_4$, the glide operation $(x, {}^1/_2 - y, {}^1/_2 - z)$ becomes a translation of ${}^1/_2$ along **c** for the center of the molecules. This can be seen in Figure 1 along the direction of view; the molecules in the foreground are related to those directly behind them by a translation of ${}^1/_2$ along **c** and differ by approximately 90° in the orientations of their molecular symmetry axes. The molecule in the lower left foreground of Figure 1 is type A. The molecule in the lower right foreground is type B. The molecules in the upper left and right foreground are types B and A, respectively.

The approximate value of $\pm{}^1/_4$ for the y coordinates of all of the molecules in the structure also means that there are repeating sheets of molecules perpendicular to **b**. These sheets at $y = \pm{}^1/_4$ contain very regular rectangular arrays of molecules. Two adjacent corners along the **c** direction are type A and their centers are separated by 8.736 Å. The other two corners are type B and are separated by 8.734 Å. The distance between types A and B (along the **a*** direction) is 9.88 Å and the corner angle of the rectangle is 92.4°.

As seen from the similarities of their interpenetrating lattices, the crystal environments of molecules of types A and B are similar. The angle between the molecular symmetry axis of type A and the crystal axis **b** is 45.7°. The angle between the molecular symmetry axes of molecules of type A related by the **c** glide is 88.6°. The corresponding angles for type B are 38.6 and 77.2°, respectively. Although the two types of crystallographically independent molecules are similar in this structure, they differ in one striking way. The two molecules (Figure 2) have different relative orientations of the substituent methyl groups; in molecules of type A the methyl groups are nearly eclipsed and in type B they are staggered!

The general similarity of the crystal environment of types A and B leads immediately to the question of why two distinct rotomeric conformers should exist. We believe the answer lies in a detailed consideration of the intermolecular methyl-methyl interactions in the crystal. The van der Waals contact distance for methyl groups is approximately 4.00 Å.[20] There are many interactions of methyl groups in this structure near, or much less than, this value. Those methyl-methyl distances less than 4.36 Å are summarized in Table X. In many cases there is a kind of "interlocking gear" arrangement for adjacent molecules in which the teeth of the gears are the methyl groups. This links the orientations of the rings through a complex three-dimensional network. However, one feature does stand out. There are more, and stronger, *inter*molecular methyl-methyl contacts for type A than for type B. The *intra*molecular contacts for type A are much more severe than for type B. The distances between the eclipsed methyl groups range from 3.73 to

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(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

Table VIII. Bond Lengths (Å) for the Cyclooctatetraene Dianions

Molecule A				Molecule B			
Bond	Distance	Bond	Distance	Bond	Distance	Bond	Distance
C_{11}-C_{12}	1.390 (19)	C_{21}-C_{22}	1.407 (18)	C_{31}-C_{32}	1.413 (18)	C_{41}-C_{42}	1.454 (17)
C_{12}-C_{13}	1.389 (17)	C_{22}-C_{23}	1.442 (18)	C_{32}-C_{33}	1.401 (17)	C_{42}-C_{43}	1.379 (16)
C_{13}-C_{14}	1.394 (17)	C_{23}-C_{24}	1.388 (20)	C_{33}-C_{34}	1.415 (17)	C_{43}-C_{44}	1.479 (18)
C_{14}-C_{15}	1.420 (18)	C_{24}-C_{25}	1.411 (20)	C_{34}-C_{35}	1.395 (17)	C_{44}-C_{45}	1.273 (20)
C_{15}-C_{16}	1.412 (18)	C_{25}-C_{26}	1.389 (18)	C_{35}-C_{36}	1.404 (17)	C_{45}-C_{46}	1.443 (20)
C_{16}-C_{17}	1.419 (18)	C_{26}-C_{27}	1.424 (17)	C_{36}-C_{37}	1.451 (17)	C_{46}-C_{47}	1.423 (18)
C_{17}-C_{18}	1.459 (21)	C_{27}-C_{28}	1.396 (17)	C_{37}-C_{38}	1.454 (19)	C_{47}-C_{48}	1.417 (17)
C_{18}-C_{11}	1.381 (20)	C_{28}-C_{21}	1.437 (18)	C_{38}-C_{31}	1.361 (19)	C_{48}-C_{41}	1.372 (16)
Mean C-C in ring 1	1.408 (10)	Mean C-C in ring 2	1.411 (7)	Mean C-C in ring 1	1.412 (11)	Mean C-C in ring 1	1.405 (23)
Av of 2 sets of alternate C-C bonds	1.414 (18) 1.402 (12)	Av of 2 sets of alternate C-C bonds	1.395 (5) 1.429 (7)	Av of 2 sets of alternate C-C bonds	1.422 (11) 1.402 (19)	Av of 2 sets of alternate C-C bonds	1.448 (17) 1.364 (32)
C_{11}-$C_{11}M$	1.550 (19)	C_{21}-$C_{21}M$	1.525 (18)	C_{31}-$C_{31}M$	1.527 (18)	C_{41}-$C_{41}M$	1.543 (17)
C_{13}-$C_{13}M$	1.549 (17)	C_{23}-$C_{23}M$	1.578 (19)	C_{33}-$C_{33}M$	1.564 (17)	C_{43}-$C_{43}M$	1.567 (18)
C_{15}-$C_{15}M$	1.524 (18)	C_{25}-$C_{25}M$	1.554 (19)	C_{35}-$C_{35}M$	1.530 (16)	C_{45}-$C_{45}M$	1.577 (19)
C_{17}-$C_{17}M$	1.580 (18)	C_{27}-$C_{27}M$	1.559 (18)	C_{37}-$C_{37}M$	1.548 (19)	C_{47}-$C_{47}M$	1.553 (16)

Bond	Overall mean distance	Bond	Overall mean distance
Ring C-C	1.409 (7)	Ring C-methyl C	1.552 (3)

Table IX. Weighted Least-Squares Plane for the Plane of Cyclooctatetraene Dianion Rings[a]

	Molecule A				Molecule B			
	Ring 1		Ring 2		Ring 1		Ring 2	
C_{11}	−0.014 (13)	C_{21}	−0.010 (12)	C_{31}	−0.010 (13)	C_{41}	−0.009 (11)
C_{12}	−0.013 (12)	C_{22}	0.012 (13)	C_{32}	0.016 (12)	C_{42}	−0.003 (12)
C_{13}	0.026 (12)	C_{23}	0.000 (14)	C_{33}	−0.007 (11)	C_{43}	0.003 (12)
C_{14}	0.020 (13)	C_{24}	0.010 (15)	C_{34}	−0.014 (12)	C_{44}	−0.003 (13)
C_{15}	−0.041 (12)	C_{25}	−0.021 (13)	C_{35}	0.014 (11)	C_{45}	0.016 (13)
C_{16}	0.006 (12)	C_{26}	0.002 (11)	C_{36}	0.001 (12)	C_{46}	−0.016 (13)
C_{17}	0.029 (12)	C_{27}	0.020 (12)	C_{37}	−0.011 (12)	C_{47}	−0.006 (11)
C_{18}	−0.007 (14)	C_{28}	−0.012 (12)	C_{38}	0.005 (12)	C_{48}	0.020 (12)
A	14.38		14.59		12.3		4.66
B	8.52		8.35		9.46		3.62
C	−2.99		−2.65		−0.046		0.277
D	5.13		13.7		11.9		3.17

[a] Distances in angstroms and individual atoms from weighted least-squares planes. The equation for the least-squares plane in monoclinic coordinates is of the form $Ax + By + Cz - D = 0$.

Table X. Summary of Intermolecular Nonbonded Methyl-Methyl Distances Less Than 4.3 Å

Atoms	Distance[a]	Atoms	Distance[a]
$C_{11}M$, $C_{21}M$	3.73*	$C_{23}M$, $C_{33}M$	**3.78**
$C_{11}M$, $C_{25}M$	4.07	$C_{23}M$, $C_{35}M$	4.23
$C_{11}M$, $C_{27}M$	4.02	$C_{23}M$, $C_{37}M$	4.33
$C_{11}M$, $C_{35}M$	4.00	$C_{23}M$, $C_{44}M$	4.03
$C_{13}M$, $C_{15}M$	4.25	$C_{25}M$, $C_{25}M$	4.36
$C_{13}M$, $C_{23}M$	3.80*	$C_{27}M$, $C_{33}M$	4.14
$C_{13}M$, $C_{37}M$	4.16	$C_{31}M$, $C_{31}M$	**3.78**
$C_{13}M$, $C_{42}M$	4.22	$C_{31}M$, $C_{42}M$	4.20*
$C_{13}M$, $C_{44}M$	**3.82**	$C_{31}M$, $C_{42}M$	**3.79**
$C_{13}M$, $C_{46}M$	4.20	$C_{31}M$, $C_{46}M$	4.35
$C_{15}M$, $C_{25}M$	3.73*	$C_{31}M$, $C_{46}M$	4.29
$C_{15}M$, $C_{31}M$	4.15	$C_{31}M$, $C_{48}M$	4.19
$C_{15}M$, $C_{44}M$	**3.95**	$C_{33}M$, $C_{35}M$	4.26
$C_{15}M$, $C_{48}M$	4.27	$C_{33}M$, $C_{44}M$	4.07*
$C_{17}M$, $C_{17}M$	**3.88**	$C_{35}M$, $C_{46}M$	3.98*
$C_{17}M$, $C_{21}M$	4.29	$C_{37}M$, $C_{42}M$	4.17
$C_{17}M$, $C_{27}M$	3.69*	$C_{37}M$, $C_{48}M$	3.91*
$C_{17}M$, $C_{27}M$	**3.77**	$C_{42}M$, $C_{48}M$	4.19
$C_{17}M$, $C_{24}M$	4.20	$C_{44}M$, $C_{48}M$	4.33
$C_{21}M$, $C_{25}M$	4.07	$C_{46}M$, $C_{48}M$	4.19
$C_{23}M$, $C_{27}M$	**3.82**		

[a] Asterisked values are intramolecular methyl-methyl distances and boldface values are short intermolecular methyl-methyl contacts.

3.80 Å and average 3.76 Å. For the corresponding distances in the nearly staggered conformation of type B the range is from 3.91 to 4.20 Å and the average is 4.04 Å. Thus in type B the methyl groups for the two rings of the molecule are just at the contact distance while in type A they are nearly 0.3 Å less than this value, and in type A must be strongly repelling one another. Apparently the greater intramolecular methyl-methyl contacts of molecule A are sufficient to force it into what must be a higher energy conformation. Any rotation away from the observed conformation relieves some intramolecular strain but at too great an expense in decreased intermolecular methyl-methyl distances and resultant increase in energy.

The two rings in both molecules A and B, when viewed down the molecular symmetry axes (Figure 2), are rotated 14° from a configuration in which the ring carbon atoms are eclipsed. (In a perfectly staggered geometry this rotation angle would be 22.5°.) The equal value of this angle for both molecules is a coincidence of the structure. The observation of the eclipsed, D_{8h} geometry (in $U(C_8H_8)_2$ and $Th(C_8H_8)_2$[5]), the staggered, D_{8d} geometry (in $Ce(C_8H_8)_2^-$[19]), and now a geometry intermediate between these two extremes demonstrates the very small energy barrier to rotation that must exist for these cyclooctatetraene dianion complexes.

A wide range of rotomeric configurations has been observed for the substituted metallocene series of π-$C_5H_5^-$ organometallic complexes of the transition metals. In ferrocene, the original crystallographic study[21] established that the

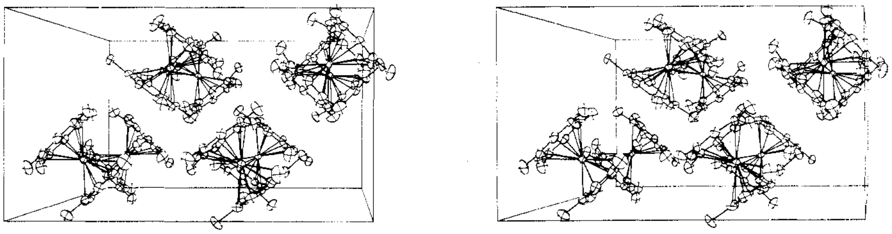
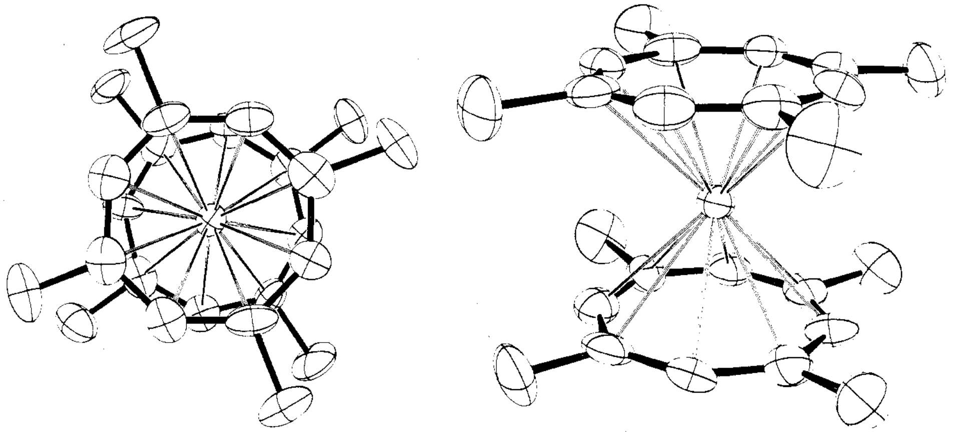
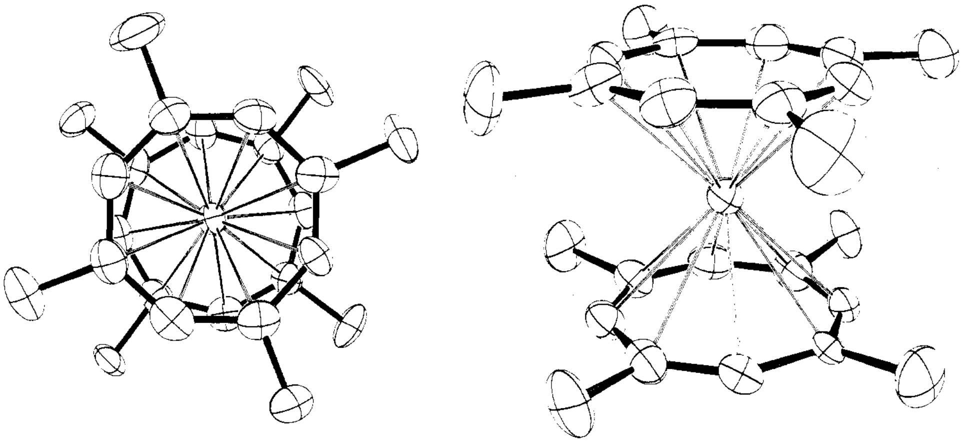


Figure 1. A stereoscopic packing diagram of $U(C_8H_4(CH_3)_4)_2$ viewed normal to the *xy* plane. The origin is at the lower back left corner, the horizontal axis is *a*, and the vertical is *b*.



MOLECULE A



MOLECULE B

Figure 2. The two crystallographically independent molecules A and B in the crystal structure of $U(C_8H_4(CH_3)_4)_2$.

C_5H_5 anion rings were staggered in crystalline $Fe(C_5H_5)_2$ but for $Ru(C_5H_5)_2$ they are eclipsed.[22] As substituents are placed on the cyclopentadienide ring, the rotomeric conformation of the rings changes in ferrocene derivatives. Extensive crystallographic studies have centered around ferrocene derivatives and much has been said about the relationship between orientation and intermolecular forces *vs.* intramolecular carbon–carbon repulsions.[23] In studies of carbonyl-substituted ferrocenes Palenik[24,25] has suggested that in the absence of steric constraints, the preferred conformation for ferrocene derivatives is eclipsed. It has also been suggested that there may be some correlation between the electron inductive effect of the substituent on the $C_5H_5^-$ ring and the resultant rotomeric conformation of the ferrocene derivative in the solid state.[26] The question of rotomeric conformation in ferrocene derivatives is, however, still largely unsettled.

The most unique feature of this methyl-substituted derivative can be seen from inspection of Table XI. All of the methyl groups are bent inward toward the central metal from the plane of the cyclooctatetraene dianion ring. The angle of this bend ranges from 0.82 to 6.45°, corresponding to distances of 0.01 and 0.2 Å from the appropriate least-

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Table XI. Angular Orientation of Methyl Groups and Their Perpendicular Distances from Least-Squares Planes

Methyl carbon	Bond angle,[a] deg	Distance to plane,[b] Å	Methyl carbon	Bond angle,[a] deg	Distance to plane,[b] Å
$C_{11}M$	5.76	0.144	$C_{31}M$	0.82	0.041
$C_{13}M$	2.24	0.035	$C_{33}M$	6.45	0.178
$C_{15}M$	5.19	0.182	$C_{35}M$	5.26	0.106
$C_{17}M$	1.59	0.007	$C_{37}M$	4.69	0.125
$C_{21}M$	2.51	0.062	$C_{41}M$	2.64	0.071
$C_{23}M$	7.43	0.195	$C_{43}M$	5.52	0.108
$C_{25}M$	1.77	0.022	$C_{45}M$	4.64	0.099
$C_{27}M$	4.33	0.142	$C_{47}M$	4.53	0.147

[a] This is the angle A–B–C formed by the methyl group (A), the ring carbon (B) to which it is attached, and the carbon opposite (C) in the COT^{2-} ring (A is separated from C by three carbons). In all cases the angle of bend is toward the uranium atom. [b] Perpendicular distance to the appropriate least-squares plane whose coefficients are given in Table IX.

squares plane. The average angle and distance are 4.1° and 0.10 Å, respectively. Examples of nonplanarity of substituents with respect to the plane of the cyclopentadienide anion in substituted ferrocenes are known. Hirotsu, Higuchi, and Shimada observed that in 1,1′-bis(pentamethyldisilanyl)ferrocene[27] the silicon atoms bend out of the carbon five-membered ring plane about 0.03 Å away from the metal. Kaluski and Struchkov found that the chlorine atoms in dichlorodiferrocenyl[28] were coplanar with the five-membered ring while in diethyldiferrocenyl the methylene carbon of the ethyl group bonded to the ring was bent in toward the iron atom 1.8° from the plane.[29] In both biphenylylferrocene[30] and *N*-formylaminomethylferrocene[31] the carbon atom bonded to the five-membered rings appears to be coplanar within 0.03 Å. In the recently reported structure of 2,2-dicyanovinylferrocene[23d] the carbon atoms of the vinyl group which are bonded to the five-membered rings appear to be bent slightly toward the central metal though no mention is made of this fact. There appears as yet to be no significant trend in the substituted ferrocene series with respect to the orientation of substituents directly attached to the ring and the plane of the five-membered ring itself.

One very recent structure analysis does show the same type of concave ring distortion as observed in $U(C_8H_4(CH_3)_4)_2$. In the low-temperature neutron diffraction study of $Cr(h^6\text{-}C_6H_6)(CO)_3$ Rees and Coppens have found that the benzene ring exhibits a convex distortion with the hydrogen atoms bent in an average of 1.7° toward the chromium atom.[32] Although substantially smaller than the distortion observed in $U(C_8H_4(CH_3)_4)_2$, a convex distortion of carbocyclic rings in sandwich structures appears to be a general phenomenon. It is particularly interesting that the same effect should be observed in both a 3d and a 5f transition metal compound.

In $U(C_8H_4(CH_3)_4)_2$ there is no question that in the case of both molecules A and B all of the methyl groups bend in toward the metal. van der Waals attraction cannot account for this convex bending in both types of molecules. In fact, as pointed out in the discussion of the crystal structure, molecule A has intramolecular methyl–methyl contacts 0.3 Å shorter than the sum of the van der Waals radii of two methyl groups. In spite of this short contact distance, the methyl groups on molecule A are on an average bent inward toward the uranium atom as much as those in molecule B. There are also no intermolecular effects which would force all of the methyl groups to bend inward, though undoubtedly some of the short intermolecular contacts (Table X) affect the degree to which individual methyl groups are displaced from the plane of the cyclooctatetraene dianion ring.

Both intermolecular packing effects and intramolecular van der Waals attraction thus unambiguously can be ruled out as explanations for the inward bending of the methyl groups in molecules A and B, and explanations of this phenomenon must be found in the electronic structure of the molecules. One possible explanation would involve the overlap of the pπ orbitals on the cyclooctatetraene dianion ring with the uranium metal orbitals. Overlap of the metal 5f orbitals with the ligand molecular orbitals of cyclooctatetraene dianion has been shown to be of significance in these types of actinide organometallic complexes.[3,6,7] The inward bending of the methyl substituents makes each carbon slightly pyramidal with the π orbital of the $C_8H_8{}^{2-}$ ring bent inward toward the uranium atom. This change provides greater directionality for overlap between the π orbitals and the metal orbitals. This slight bending and change of hybridization would result in only a small loss in the conjugation energy of the aromatic system.

A second explanation can be based on stereochemical effects of the π-electron density. In an uncoordinated $C_8H_8{}^{2-}$ ring, the π cloud of electrons above and below the plane would be symmetrical. The approach and coordination of the highly charged metal ion would result in two effects: (1) slight polarization of the ligand electron density toward the metal and, more important, (2) the contraction in volume (but not in total electron charge) of the electron density on the side of the ring adjacent to the metal ion. In the same way that nonbonded electron pairs in the Gillespie-Nyholm model are stereochemically more active than bonding electron pairs,[33] the electron density on the side of the dianion ring away from the metal atom would repel the methyl groups more than the electron density on the adjacent side of the ring, since the density on the side of the ring away from the metal electron density occupies a relatively larger volume of space. The result for the structure would be the observed inward bend of the methyl groups as a result of the nonbonded interactions of these groups with the higher electron density in the π system on the side opposite the metal ion. The effect would be expected to be more important for the more highly charged actinide cations than for the 2+ cations of the transition

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metals and this is in agreement with the observations in substituted ferrocenes and, more important, with the Cr(h^6-C_6H_6)(CO)$_3$ structure.

A test of these hypotheses would be found in the molecular structure of a ring-substituted lanthanide complex. Here, the 4f orbital involvement is not nearly as important as in the actinides and inward tilting of the $p\pi$ orbitals on the ligands should not be as important. Since the charge on the central lanthanide ions is 3+, the orbital contraction effect should be intermediate between that observed in the transition metals and the actinides. We plan to pursue this by carrying out a detailed structure analysis of a TMCOT complex of zirconium, hafnium, or a lanthanide.

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Studies with Heptavalent Neptunium. Identification and Crystal Structure Analysis of $LiCo(NH_3)_6Np_2O_8(OH)_2 \cdot 2H_2O$[1]

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The compound $LiCo(NH_3)_6Np_2O_8(OH)_2 \cdot 2H_2O$ was precipitated from a LiOH solution of Np(VII) by slowly diffusing in a solution of $Co(NH_3)_6Cl_3$. It was identified by combining elemental chemical analyses and single-crystal X-ray diffraction. The analog containing Na was produced from a NaOH solution of Np(VII), but no similar product was obtained from KOH solutions. The crystals are monoclinic (space group $C2/c$) with $a = 10.739$ (4), $b = 10.450$ (4), $c = 15.013$ (5) Å, and $\beta = 116°\ 38\ (5)'$; $Z = 4$. There are two independent Np atoms in the asymmetric unit, and each is coordinated by an octahedron of O atoms which make four short and two long bonds. These octahedra are linked through two of their O atoms into chains along c with the long axes of the octahedra alternately parallel and perpendicular to the chain. Lithium ions share four O atoms with three octahedra and are also linked to two H_2O molecules, while the $Co(NH_3)_6{}^{3+}$ octahedra lie between chains and cross-link them. The presence of OH^- ions and H_2O molecules is deduced from structural chemical considerations and chemical analyses. The existence of the $[NpO_4(OH)_2]^{3-}$ ion in solution is proposed and an explanation is offered for the manner in which the crystalline precipitates are formed.

Introduction

The heptavalent state of the transuranic elements neptunium and plutonium was reported by Spitsyn and coworkers[2] in 1969. They found Np(VII) and Pu(VII) to be rather stable in alkaline solution but unstable in acid. By choosing cations sufficiently soluble in alkali, they were able to make several solid compounds of Np(VII) and Pu(VII). The only one characterized by chemical analysis was formulated as $Co(NH_3)_6NpO_5 \cdot 3H_2O$, I. Following this discovery, a number of workers[3-5] prepared compounds of Np(VII) by solid-state reactions between alkali peroxides and dioxides or hydroxides of Np(V) and Np(VI). The compounds were produced as fine powders; hence little or nothing was learned of their structures.

Because $NpO_2{}^+$ and $NpO_2{}^{2+}$ are well-known ionic species, as is the uranyl ion, $UO_2{}^{2+}$, in which U(VI) is isoelectronic with Np(VII), Spitsyn, *et al.*,[2] reasoned that $NpO_2{}^{3+}$ may also exist and exhibit the same linear, double-bonded configuration as these three ions. Thus, when they prepared the compound above, they suggested that the $NpO_5{}^{3-}$ ion is present and has a linear O=Np=O group within it. Independently, Jorgensen[6] proposed that in solution the ion is hexagonal-bipyramidal *trans*-$[NpO_2(OH)_6]^{3-}$.

It was primarily to establish experimentally the configuration of the ion containing heptavalent Np that we undertook our study.

Experimental Section

Preparation of Compounds. The oxidation of Np to the heptavalent state was done essentially as described by Spitsyn, *et al.*,[2] and refined by Zielen and Cohen.[7] High-purity $^{237}NpO_2$, with less than 10 ppm of other actinides present, was obtained from the Isotopes Division of Oak Ridge National Laboratory. In a typical preparation of a Np(VII) solution, 200 mg of NpO_2 was dissolved in HNO_3, evaporated to dryness, and taken up in 5 ml of 1 N $HClO_4$. Addition of solid $NaNO_2$ reduced this to a blue-green solution of Np(V). To this was added an excess of 2.5 N LiOH to precipitate out gray Np(V) hydroxide. The solid was centrifuged off, washed with 1 N LiOH, and then suspended in 50 ml of 1 N LiOH in a bubbler flask. Ozone produced by a semimicro ozonizer described by Bonner[8] was bubbled through this suspension for 1 hr, causing dissolution of the hydroxide and producing a clear, pink solution of Np(VI). With continued ozone flow, the solution soon darkened and after another hour was very dark green. This solution was ~0.015 N in Np(VII) and served as stock for compound preparation.

Simultaneous dropwise addition of solutions of 0.02 N $Co(NH_3)_6Cl_3$ and 0.015 N Np(VII) to a stirred solution of 1 N LiOH yielded brilliant green platelets of I whose largest dimension was less than

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