Eclipsed and Staggered Configurations for a Methyl-substituted Cyclo-octatetraenyl Dianion Complex of Uranium(IV): *X*-Ray Determination of the Structure of $U[C_8H_4(CH_3)_4]_2$

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Summary The crystal and molecular structure of bis-(1,3,5,7-tetramethylcyclo-octatetraenyl)uranium(IV) has been determined; the unusual crystal structure has two types of molecule with different rotomeric configurations around the two dianion rings on a central atom; in one form the methyl groups are approximately staggered and the other eclipsed.

STRUCTURAL studies of cyclo-octatetraenyl dianion π-complexes of actinides[1,2] and lanthanides[3] have been reported. Streitwieser and his co-workers have recently synthesized a substituted cyclo-octatetraene derivative, $U[C_8H_4Me_4]_2$ and have studied the contact shift of the proton magnetic resonance in order to estimate the degree to which *f*-orbitals are involved in the metal–ligand bonding.[4] Precise structural information was needed in order to evaluate the geometrically dependent contributions to the chemical shift. We were also interested in the relative configurations of the methyl groups on opposite rings as an indication of the rotomeric freedom of the rings in such complexes. We have determined the crystal and molecular structure of bis-(1,3,5,7-tetramethylcyclo-octatetraenyl)-uranium(IV) by *X*-ray diffraction methods.

Single crystals of the air-sensitive compound which were suitable for *X*-ray diffraction analysis were obtained by sealed tube sublimation under argon (*ca.* 650 mmHg) and were mounted in thin-walled quartz capillaries under argon. Precession photographs displayed symmetry and systematic absences consistent with the monoclinic space group $P2_1/c$. Accurate cell constants were determined by least-squares refinement of orientation and 2θ angles for 12 reflections which were centred on a Picker FACS-1 diffractometer. The lattice parameters are (Mo-$K_{\alpha1}$; $\lambda = 0{\cdot}70926$ Å): $a = 20{\cdot}224(5)$, $b = 12{\cdot}066(2)$, $c = 17{\cdot}467(4)$ Å, $\beta = 101{\cdot}57(2)°$; $D_c = 1{\cdot}74$ g cm^{-3}; $Z = 8$.

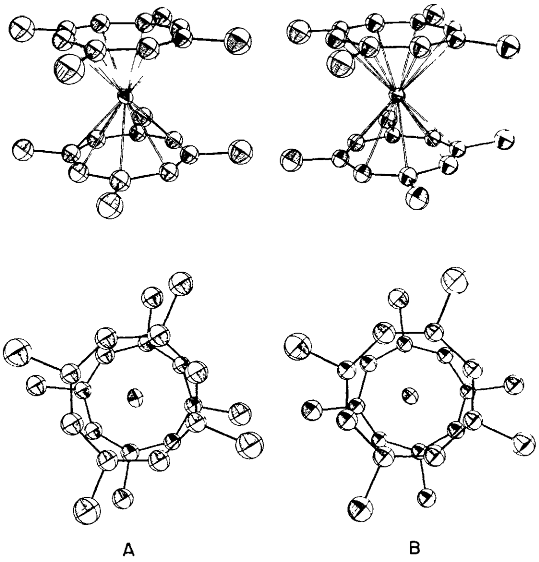

FIGURE. *The independent molecules of* $U[C_8H_4(CH_3)_4]_2$. *Thermal ellipsoids are drawn at the* 40% *probability contour.*

Intensities were collected using the θ—2θ scan technique for $2\theta < 70°$. The structure was solved by heavy-atom techniques. There are two crystallographically independent molecules in the unit cell. The two molecules differ in the rotomeric configuration of the ring methyl groups (see Figure). This model is being refined using full-matrix techniques. At the present level of refinement with the light atoms assigned isotropic temperature factors, 5188 independent reflections with $F^2 > 3\sigma(F^2)$ give $R = 6{\cdot}57\%$ (weighted R 8·43%).

In the planar dianion ligands, the C–C bonds are all of equal length within experimental error, and average 1·41(3) Å. The aromaticity of the rings is substantiated by the equal averages of two sets of alternate C–C bonds for each molecule; 1·418 and 1·416 Å for molecule (A) and 1·420 and 1·402 Å for molecule (B). The uranium–carbon bond lengths in both molecules are equal, and average 2·67(1) Å for (A) and 2·66(1) Å for (B). As the molecules are viewed down the molecular four-fold axis (see Figure), the ring carbon atoms in both molecules are rotated 14(2)° from being exactly eclipsed. In (A), the methyl groups are approximately eclipsed with respect to the other ring methyl groups, but in ring (B), the methyl groups are approximately staggered. The mean uranium–methyl carbon distances are 3·88(1) and 3·85(1) Å respectively for (A) and (B).

The existence of these two rotomers demonstrates absence of steric inhibition to rotation, even for the geometry in which the methyl groups on the two rings would be eclipsed. The rotation of the two rings from the carbon-eclipsed position represents a distinct departure from the D_{8h} molecular symmetry observed for the other di-π-cyclooctatetraene structures previously studied[1-3] and demonstrates that such symmetry does not represent a uniquely stable geometry.

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