observed in the compound $Cr(CO_2CH_2NH_2)_3 \cdot H_2O$.[23] Considering the distortion in the electron density distribution normally encountered in X-ray studies[24] for hydrogen atoms, the observed bond distances are close to the expected values.

Finally, returning to the coordination geometry of the vanadium, an alternative view[16a, 25] can be proposed in which the metal is formally four-coordinate in a distorted tetrahedral arrangement, each peroxo group bonding with one coordination site (*e.g.*, a vacant $sd^3$ hybrid) by means of a three-center bond. Such a proposal is not unreasonable, especially when the bond angles to the midpoints of the peroxo groups are examined: O(1)–V–($O_2$), 107.2 (1)°; O(1)–V–N(1), 97.5 (1)°; N(1)–V–($O_2$), 106.1 (1)°; ($O_2$)–V–($O_2$), 128.5 (1)°. The largest angle is attributed[19] to repulsion between the two peroxo groups, and the smallest angle is a response to this repulsion by the less strongly bound ammonia. This angle of 128.5 (1)° is not as large as corresponding angles observed[19] in diperoxochromium complexes.

## Calculations

All calculations were performed on an IBM 360/50 computer. Programs used were as follows: FORDAP, crystallographic Fourier summation and peak searching (A. Zalkin); BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury); ORFFE, Fortran crystallographic function and error program (W. R. Busing, K. O. Martin, and H. A. Levy); ORTEP, Fortran thermal ellipsoid plot program for crystal structure illustrations (C. K. Johnson); MEANPLANE, calculation of weighted mean planes through atom groups with esd's' (M. E. Pippy and F. R. Ahmed); MGTLS, a program to calculated translational, librational, and screw tensors for a molecule (K. N. Trueblood).

**Acknowledgments.**—The authors wish to thank Dr. P. G. Lenhert for making available his programs for the control of the diffractometer and the National Research Council of Canada whose financial support made this research possible.

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# Two Isostructural Actinide π Complexes. The Crystal and Molecular Structure of Bis(cyclooctatetraenyl)uranium(IV), $U(C_8H_8)_2$, and Bis(cyclooctatetraenyl)thorium(IV), $Th(C_8H_8)_2$

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*Received August 16, 1971*

Crystal and molecular structures of the two isostructural cyclooctatetraene dianion π complexes "uranocene" and "thorocene," $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, have been determined from three-dimensional X-ray diffraction data. The molecules both have $D_{8h}$ molecular symmetry. The heavy atom in each case is symmetrically π bonded to two aromatic cyclooctatetraene dianion rings related by a crystallographic inversion center. The mean uranium–carbon bond length is 2.647 (4) Å and the mean Th–C bond length is 2.701 (4) Å. The cyclooctatetraene dianion rings are planar with average C–C bond lengths of 1.392 (13) and 1.386 (9) Å for $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, respectively. Differences in the metal–carbon bond lengths in $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ can be calculated from the corresponding change in ionic radii. Deep green plates of $U(C_8H_8)_2$ have the following crystal data: monoclinic space group $P2_1/n$, cell constants $a$ = 7.084 (3), $b$ = 8.710 (3), $c$ = 10.631 (5) Å, and $\beta$ = 98.75 (3)°. For two fomula units in the cell, the calculated density is 2.29 g/cm³. Bright yellow plates of $Th(C_8H_8)_2$ have the same crystal structure with cell constants $a$ = 7.0581 (11), $b$ = 8.8192 (17), $c$ = 10.7042 (18) Å, and $\beta$ = 98.44 (3)°. The calculated density is 2.22 g/cm³. Both structures have been refined using full-matrix least-squares methods to unweighted $R$ factors of 2.09 and 2.07% for $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, respectively.

## Introduction

Following the initial characterization of bis(cyclooctatetraenyl)uranium(IV), "uranocene," by Streitwieser and Müller-Westerhoff[1] the synthesis and chemical properties for a number of 4f and 5f transition series π complexes containing cyclooctatetraene dianion have been reported.[2–6] It was originaly postulated that $U(C_8H_8)_2$ has a π-sandwich structure and that symmetry-allowed overlap of the 5f orbitals with the ligand molecular orbitals could contribute to the bonding.[1] Our preliminary report[7] showed the structure of $U(C_8H_8)_2$ to be a true π-sandwich complex with $D_{8h}$ molecular symmetry. The question of f-orbital participation in bonding has since become the subject of much renewed interest and speculation. Mössbauer studies on bis(cyclooctatetraenyl)neptunium(IV)[3] and proton magnetic resonance studies of $U(C_8H_8)_2$[8] and the substituted analog bis(1,3,5,7-tetramethylcyclooctatetraene)uranium(IV)[6] appear to confirm the presence of at least some π interaction between

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ligand molecular orbitals and metal 5f orbitals. Little is known of the structures of these and other $\pi$-carbocyclic complexes yet knowledge of the precise molecular structures is necessary in order to interpret their spectral and magnetic properties. The recently reported structure of $[Ce(C_8H_8)Cl \cdot 2OC_4H_8]_2$ is the only other structural report for an actinide or lanthanide compound containing $C_8H_8^{2-}$.[9]

After the characterization of $U(C_8H_8)_2$, the analogous thorium complex was synthesized.[2] Its physical and chemical properties were so different from those of the uranium compound that initially there was question as to whether the complex has the same $\pi$-sandwich structure. A structural study was begun in order to determine if the two complexes were indeed isostructural. Another reason for interest was to determine whether molecular details, such as metal–carbon bond lengths, could be calculated for isostructural actinide complexes using variations in lattice constants or ionic radii with the $U(C_8H_8)_2$ structure. This would be applicable to the structures of other $M(C_8H_8)_2$ complexes, such as the neptunium and plutonium compounds already synthesized. In this paper we report the completed structure of $U(C_8H_8)_2$ and its thorium analog, $Th(C_8H_8)_2$.

## Experimental Section

The syntheses of $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ have been reported previously.[1,2] Single crystals of both compounds suitable for X-ray analysis were obtained by high-vacuum ($\approx 10^{-3}$ mm), hot-tube sublimation of the pure powdered material. The highly oxygen-sensitive crystals were sealed in thin-walled quartz capillaries under a dry argon atmosphere; a small amount of Kel-F grease was used as an adhesive. Several large crystals exhibiting sharp extinction under polarized light were selected for precession photography. The diffraction patterns of both compounds displayed the Laue symmetry $2/m$ of the monoclinic system. Preliminary photographs taken with Polaroid film appeared to be body centered ($h + k + l = 2n$), and only upon careful examination of overexposed emulsion film photographs could weak reflections for which $h + k + l = 2n + 1$ be discerned. The diffractometer intensity data showed only absences $0k0$, $k \neq 2n$, and $h0l$, $h + l \neq 2n$. The space group $P2_1/n$ (an alternate setting of $P2_1/c$, $C_{2h}^5$) is consistent with these conditions.

**Data Collection.** $\mathbf{U(C_8H_8)_2}$.—The crystal selected for data collection was a deep green regular parallelepiped bounded by the following planes and their reciprocals: 011, $0\bar{1}1$, and $\bar{1}01$. The plane-to-plane distances are, respectively, 0.077, 0.077, and 0.062 mm. The crystal in its capillary was mounted on an eucentric goniometer head with its (101) direction parallel to the $\phi$ axis of a General Electric XRD-5 manual diffractometer equipped with a scintillation counter and a pulse height discriminator. The X-ray source was Mo $K\alpha_1$ radiation ($\lambda$ 0.70926 Å) and the diffracted beam was filtered through 3 mils of Zr foil. The receiving aperture was 2 × 10 mm and was positioned 15 cm from the crystal. Accurate cell constants were determined using a 2.0° takeoff angle and a narrow detector slit by careful hand measurement of the Bragg $2\theta$ angles for several high index reflections whose $K\alpha_1$ and $K\alpha_2$ peaks were well resolved. The crystal gave $\omega$ scan widths at half-height of less than 0.08°. The resultant cell parameters and their estimated standard deviations are summarized in Table I.

Intensity data were collected using the stationary-crystal, stationary-counter method. The intensities for the form $hkl$ with $0 \leq 2\theta \leq 35°$ were measured at a takeoff angle of 4.0° for 10-sec counts at the peak maximum. The background counts for a number of low-angle reflections and some high-angle reflections were measured by locating a minimum on the low-$2\theta$ side of the peak. The remaining backgrounds were estimated from a plot of background as a function of $2\theta$ for various combinations of the orientation angles $\phi$ and $\chi$. The intensities of the set of three approximately orthogonal standards were monitored every 100 reflections and no significant change was observed throughout the experiment. The observed intensities, $I$, after correction for background, were assigned standard deviations according to the formula $\sigma(I) = [I + 0.75B + (0.05I)^2]^{1/2}$ where the quantity $B$ was estimated from the expression $B = 650 - 10(2\theta) + 0.02I$ which gave a reasonable approximation of the actual background curve. The corrected intensities were then reduced to values of $F^2$ by applying Lorentz and polarization corrections.[10]

TABLE I

SUMMARY OF CRYSTAL DATA

| | Molecular formula | |
|---|---|---|
| | $U(C_8H_8)_2$ | $Th(C_8H_8)_2$ |
| Mol wt | 446.34 | 440.35 |
| Linear absorption coeff, $\mu$, cm$^{-1}$ | 186.0 | 166.4 |
| Max crystal dimensions, mm | 0.08 × 0.08 × 0.06 | 0.09 × 0.11 × 0.19 |
| Molecules/unit cell | 2 | 2 |
| Cell constants[a] | | |
| $a$, Å | 7.084 (3) | 7.0581 (11) |
| $b$, Å | 8.710 (3) | 8.8192 (17) |
| $c$, Å | 10.631 (5) | 10.7042 (18) |
| $\beta$, deg | 98.75 (3) | 98.44 (3) |
| Cos $\beta$ | −0.1521 (2) | −0.1468 (2) |
| Cell vol, Å$^3$ | 647.6 (10) | 659.0 (9) |
| Calcd density, g cm$^{-3}$ | 2.29 | 2.22 |

[a] Temperature of 22–24°, with Mo $K\alpha_1$ radiation ($\lambda$ 0.70926 Å).

The calculated absorption coefficient, $\mu$, is 186 cm$^{-1}$. The values of $\mu t$ for the minimum and maximum thicknesses varied from 1.1 to 1.49. Therefore an absorption correction was applied using a gaussian numerical integration program.[10] The applied corrections ranged from 5.4 to 8.0. After the final correction there were 543 reflections with $F^2 > \sigma(F^2)$ and these were used in the final refinement of the structure.

$\mathbf{Th(C_8H_8)_2}$.—A bright yellow crystal of $Th(C_8H_8)_2$ which extinguished sharply in polarized light was chosen for data collection. The irregularly shaped crystal was bounded by seven pairs of planes with maximum crystal dimensions (point to point) of approximately 0.09 × 0.11 × 0.19 mm. The crystal was mounted on a Picker FACS-1 four-circle diffractometer with its (010) axis nearly parallel to the $\phi$ axis of the instrument.

The optimum crystal orientation matrix and unit cell constants were determined by a least-squares refinement of the orientation and $2\theta$ angles for 12 carefully centered reflections whose $2\theta$ angles ranged from 39 to 60°.[11] The X-ray source and diffractometer parameters were identical with those used in the intensity measurements. The refined cell parameters are given in Table I. The crystal gave $\omega$ scans with widths at half-height of 0.06–0.08° for several low-angle reflections.

The intensity data were collected using a $\theta$–$2\theta$ scan mode with monochromatic Mo $K\alpha$ radiation. The diffracted beam was counted using a scintillation counter. The Bragg $2\theta$ angle for the graphite monochrometer crystal was 12.02° and the X-ray tube takeoff angle was 2.0°. The pulse height analyzer, centered on a Mo $K\alpha$ peak, was set to admit approximately 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 $2\theta$ scans were from 0.505° below the $K\alpha_1$ peak to 0.505° above the $K\alpha_2$ peak with a scan rate of 1.0°/min. Stationary 10-sec background counts were taken at the beginning and end of each scan. Attenuation of the diffracted beam was not needed since the strongest intensity was less than 10,000 cps.

During the experiment, the intensities of the three standard reflections, 600, 060, and 006, were measured every 60 reflections and showed no appreciable decrease. The 4927 reflections collected included almost two complete forms of intensity data ($\pm h, k, \pm l$) within a sphere of $0 \geq 2\theta \geq 50°$.

The data reduction and processing was accomplished by our program UCFACS as previously described.[12] The parameter $p$

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[9] K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **11**, 171 (1972).

[10] In addition to local programs for the CDC 6400 computer, the following programs or modifications were used: Zalkin's EULERA and AUDIT programs for diffractometer data processing and the 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; Dewar's FAME, a structure factor normalization program.

[11] Programs used for the PDP 8/I computer were those written by Busing and Levy, as modified by the Picker Corp.

[12] E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

TABLE II

POSITIONAL[a] AND ANISOTROPIC THERMAL PARAMETERS[b] FOR $U(C_8H_8)_2$ AND $Th(C_8H_8)_2$

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| U | 0 | 0 | 0 | 152.8 (15) | 63.2 (9) | 55.2 (7) | −7.7 (10) | −1.4 (5) | 8.7 (6) |
| $C_1$ | 0.2655 (21) | 0.2049 (13) | 0.2070 (13) | 311 (34) | 162 (26) | 110 (14) | 91 (26) | −91 (20) | −61 (15) |
| $C_2$ | 0.3397 (14) | 0.0936 (17) | 0.1092 (14) | 131 (23) | 202 (27) | 147 (17) | −11 (22) | −12 (17) | −12 (18) |
| $C_3$ | 0.2817 (16) | 0.2025 (15) | 0.0221 (12) | 231 (29) | 143 (20) | 110 (13) | −53 (21) | 54 (16) | −14 (14) |
| $C_4$ | 0.1154 (23) | 0.2864 (13) | −0.0115 (10) | 432 (45) | 103 (19) | 42 (11) | −95 (28) | −7 (15) | 1 (11) |
| $C_5$ | −0.0646 (21) | 0.2951 (14) | 0.0336 (16) | 304 (35) | 80 (18) | 153 (17) | 51 (22) | −151 (18) | −50 (15) |
| $C_6$ | −0.1440 (15) | 0.2184 (15) | 0.1296 (14) | 185 (25) | 121 (20) | 150 (17) | 4 (20) | 42 (18) | −89 (15) |
| $C_7$ | −0.0853 (21) | 0.1106 (18) | 0.2162 (12) | 373 (42) | 188 (28) | 107 (15) | −132 (29) | 79 (21) | −50 (16) |
| $C_8$ | 0.0829 (27) | 0.0261 (12) | 0.2505 (10) | 554 (56) | 86 (25) | 53 (10) | −118 (26) | −17 (18) | −18 (10) |
| Th | 0 | 0 | 0 | 133.8 (8) | 70.8 (5) | 49.0 (4) | −11 (3) | −3.1 (3) | −9 (1) |
| $C_1$ | 0.2643 (23) | 0.0269 (12) | 0.2081 (10) | 381 (40) | 103 (29) | 122 (10) | 63 (23) | −125 (16) | −26 (10) |
| $C_2$ | 0.3447 (16) | 0.0983 (15) | 0.1133 (12) | 124 (21) | 197 (20) | 170 (13) | −31 (20) | −15 (14) | −78 (14) |
| $C_3$ | 0.2855 (18) | 0.2073 (14) | 0.0255 (10) | 277 (32) | 167 (18) | 128 (11) | −117 (22) | 93 (17) | −57 (12) |
| $C_4$ | 0.1218 (29) | 0.2874 (16) | −0.0047 (9) | 416 (56) | 120 (20) | 65 (9) | −45 (30) | −21 (17) | 17 (10) |
| $C_5$ | −0.0596 (22) | 0.2999 (14) | 0.0358 (15) | 320 (46) | 55 (12) | 144 (14) | 38 (20) | −133 (15) | −43 (11) |
| $C_6$ | −0.1389 (16) | 0.2253 (14) | 0.1321 (12) | 193 (27) | 186 (20) | 156 (12) | −12 (20) | 40 (16) | −115 (13) |
| $C_7$ | −0.0809 (19) | 0.1166 (15) | 0.2194 (9) | 308 (36) | 235 (22) | 87 (9) | −51 (26) | 80 (16) | −57 (12) |
| $C_8$ | 0.0870 (26) | 0.0329 (14) | 0.2533 (8) | 539 (54) | 199 (37) | 50 (6) | −123 (33) | −17 (13) | 7 (9) |

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

introduced to avoid overweighting strong reflections was set to 0.04. The corrected intensities were converted to values of $F^2$ by application of Lorentz and polarization corrections. With a calculated linear absorption coefficient of 166.4 cm$^{-1}$, the values of $\mu t$ for the minimum and maximum crystal dimensions vary from 1.49 to 3.15. Due to loss of the data crystal before the exact measurement of plane-to-plane distances, an absorption correction by numerical integration could not be applied. However, the equant habit of the crystal made a spherical absorption correction a reasonable approximation. The value of $\mu r$ ($r$ is the mean radius of the crystal in centimeters) used in the correction was 1.0.

After the absorption correction, the two forms of $F_o^2$ were averaged to give 730 independent reflections with $F^2 > 3\sigma(F^2)$. Subsequent least-squares refinement on the averaged $F_o^2$ data gave values of $F_c^2$ which always were bracketed by the individual $F_o^2$ values for the two symmetry-related forms. Thus, although it was only possible to correct properly for the $2\theta$ dependence of the absorption, the relatively small orientation dependence has been largely removed by averaging data from two different regions of reciprocal space. The final refinement based on the average $F_o^2$ gave exceptionally good agreement between the observed and calculated magnitudes of the structure factors squared and indicates that our approximation to the absorption correction is very good. The $R$ factor for averaging on $F^2$ was 5.4% which compares well with the final least-squares $R$ factor on $F$ of 2.07%.

## Solution and Refinement of Structure

**$U(C_8H_8)_2$.**—The structure of $U(C_8H_8)_2$ was solved using Patterson techniques. Full-matrix, least-squares refinements on $F$ were used 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, respectively, and $w = 4F^2/\sigma^2(F^2)$. Neutral scattering factors for U and C atoms used in the refinements 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]

With two formula units per unit cell, the uranium atom can be located unambiguously at the origin with $\bar{1}$ ($C_i$) site symmetry. The uranium atoms thus contribute only to structure factors ($F_{hkl}$) which have $h + k + l = 2n$. That is, the uranium atoms form a body-centered cell within the true cell and only the carbon atoms contribute to those structure factors for which $h + k + l = 2n + 1$. Solution of the structure is then essentially a light-atom problem for those $F$'s where the sum of the three indices is odd.

A three-dimensional Patterson map easily confirmed the heavy-atom positions. The remainder of the map, however, was dominated by Fourier ripple peaks around the origin and no uranium–carbon vectors could be discerned. Least-squares refinement of the uranium position followed by a difference Fourier gave an electron density map in which peaks were very difficult to distinguish from noise, since only those $F$'s for which $h + k + l = 2n$ were phased by the uranium atom. This failure of the heavy-atom technique is to be expected for structures containing very heavy atoms which form a superlattice. In order to remove Fourier ripple peaks associated with the origin peak of the Patterson map, an origin-removed sharpened Patterson function was calculated.[10] Normalized structure factors, $E$'s, were calculated from the equation $E_{hkl} = F_{hkl}/\epsilon[\Sigma f_{j\,hkl}^2]^{1/2}$, where $F_{hkl}$ is the observed structure factor corrected for average thermal motion, $\epsilon$, a multiplicity factor, is the order of the point group of $hkl$ in reciprocal space, and $f_{j\,hkl}$ is the scattering factor of the $j$th atom at the $(\sin\theta)/\lambda$ value associated with $hkl$. The coefficients in the Patterson map were then $E^2 - 1$. The resultant map showed large peaks and relatively little ripple. The largest eight peaks in the map for vectors with reasonable uranium–carbon bond lengths were all approximately 2.6 Å in length and represented the eight different U–C vectors. Since the uranium atom is on the origin with $\bar{1}$ site symmetry, the coordinates of the peaks from the Patterson map are themselves the carbon coordinates $x$, $y$, $z$ or their Patterson mirror-related positions $x$, $\bar{y}$, $z$. These peaks clearly showed the sandwich structure of the molecule. The coordinates obtained from the Patterson map were used directly in a least-squares refinement (with all atoms isotropic) which converged in several cycles. As a test of our model, separate refinements on the full data set and a partial data set with $h + k + l = 2n + 1$ were carried out. The class of reflections for which $h + k + l$ is odd (which are weak but due *only* to the carbon and hydrogen scattering) converged with refinement of the carbon atom positional parameters to an unweighted $R$ factor of 11.4%. The unweighted $R$ factor including all data and refining only the uranium thermal parameter was 10.8%. Several additional least-squares cycles were run in which the uranium thermal parameters were anisotropic. Since the hydrogen atoms could only be approximately located in difference Fourier maps following this refinement, their positions were calculated by assuming a trigonal-planar geometry about the carbon atoms and C–H bond lengths of 1.0 Å. In the final anisotropic refinement, the hydrogen atom contributions to the structure factors were calculated from these fixed positions with isotropic thermal parameters of 5.0 Å$^2$. The extinction parameter was also varied.[16] The model converged to give final agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2$ (weighted $R$ factor) $= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ of 2.08 and 2.74%, respectively. The error in an observation of unit weight, defined as $[(\Sigma w(|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$, where $N_o$ and $N_v$ are the numbers of observations and variables, respectively, is 0.666. The final difference Fourier showed no peaks greater than 0.4 e/Å which were not within 1 Å of the uranium atom position.

The positional and anisotropic thermal parameters from the final least-squares cycle and their associated standard deviations are listed in Table II. The calculated hydrogen positions are

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[13] D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

[14] R. F. Steward, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[15] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[16] W. H. Zachariasen, *Acta Crystallogr., Sect. A*, **24**, 212 (1968).

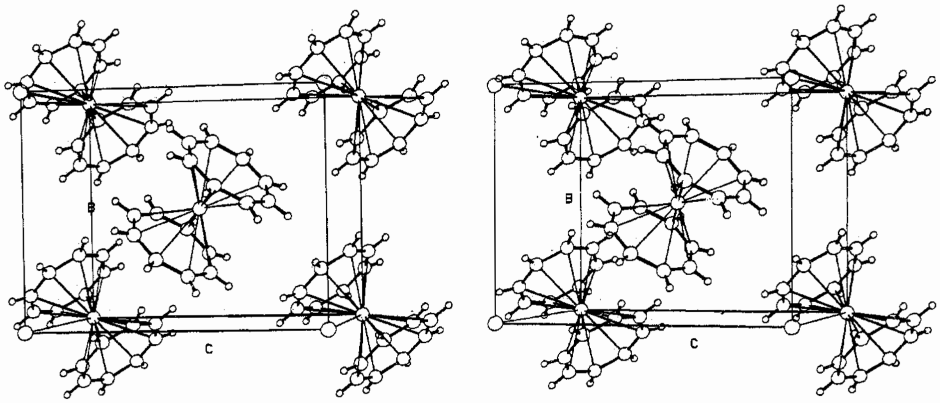

Figure 1.—A stereoscopic packing diagram of $U(C_8H_8)_2$ viewed normal to the *yz* plane. The origin is at the lower back left.

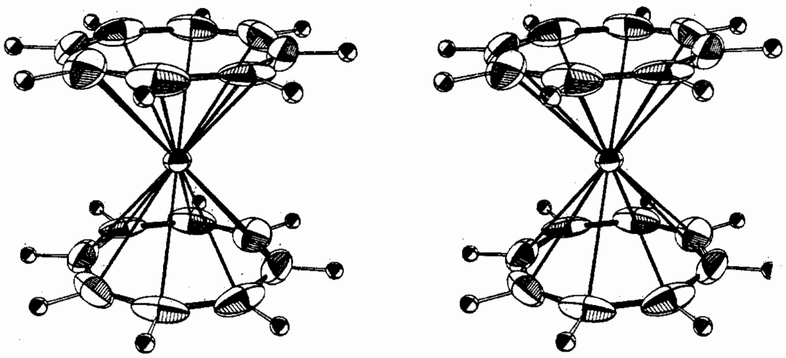

Figure 2.—A stereoscopic diagram of $Th(C_8H_8)_2$. Thermal ellipsoids are drawn at the 40% probability contour and the calculated hydrogen positions are included with *B* values of 1.0 Å². The numbering in the upper $C_8H_8^{2-}$ ring increases counterclockwise from $C_4$, the carbon at the far left in the upper ring.

TABLE III

CALCULATED HYDROGEN POSITIONS IN $U(C_8H_8)_2$ AND $Th(C_8H_8)_2$

| | $U(C_8H_8)_2$ | | | $Th(C_8H_8)_2$ | | |
|---|---|---|---|---|---|---|
| Atom | *x* | *y* | *z* | *x* | *y* | *z* |
| $H_1$ | 0.3450 | −0.0510 | 0.2540 | 0.3604 | −0.0501 | 0.2559 |
| $H_2$ | 0.4590 | 0.0620 | 0.1050 | 0.4852 | 0.0656 | 0.1049 |
| $H_3$ | 0.3700 | 0.2250 | −0.0280 | 0.3849 | 0.2363 | −0.0339 |
| $H_4$ | 0.1230 | 0.3480 | −0.0740 | 0.1327 | 0.3675 | −0.0775 |
| $H_5$ | −0.1480 | 0.3640 | −0.0080 | −0.1588 | 0.3738 | −0.0161 |
| $H_6$ | −0.2650 | 0.2500 | 0.1340 | −0.2780 | 0.6661 | 0.1405 |
| $H_7$ | −0.1770 | 0.0890 | 0.2640 | −0.1855 | 0.0877 | 0.2762 |
| $H_8$ | 0.0800 | −0.0410 | 0.3160 | 0.0797 | −0.0424 | 0.3278 |

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF ATOM VIBRATION IN $U(C_8H_8)_2$ AND $Th(C_8H_8)_2$ ALONG PRINCIPAL AXES (IN Å × $10^3$)

| $U(C_8H_8)_2$ | | | | $Th(C_8H_8)_2$ | | | |
|---|---|---|---|---|---|---|---|
| Atom | Axis 1 | Axis 2 | Axis 3 | Atom | Axis 1 | Axis 2 | Axis 3 |
| U | 147 (1) | 177 (1) | 206 (1) | Th | 144 (2) | 179 (2) | 194 (1) |
| $C_1$ | 170 (18) | 202 (20) | 318 (19) | $C_1$ | 168 (15) | 190 (24) | 396 (15) |
| $C_2$ | 139 (22) | 196 (17) | 372 (17) | $C_2$ | 154 (18) | 242 (14) | 357 (14) |
| $C_3$ | 196 (17) | 231 (15) | 281 (16) | $C_3$ | 175 (17) | 215 (11) | 351 (16) |
| $C_4$ | 152 (19) | 171 (20) | 350 (17) | $C_4$ | 179 (14) | 214 (18) | 339 (19) |
| $C_5$ | 136 (21) | 164 (20) | 410 (14) | $C_5$ | 123 (20) | 170 (19) | 396 (14) |
| $C_6$ | 133 (21) | 215 (15) | 333 (17) | $C_6$ | 158 (13) | 217 (15) | 369 (14) |
| $C_7$ | 197 (20) | 216 (16) | 327 (19) | $C_7$ | 172 (12) | 258 (16) | 340 (16) |
| $C_8$ | 120 (26) | 193 (17) | 393 (19) | $C_8$ | 166 (10) | 243 (20) | 399 (20) |

given in Table III and the root-mean-square amplitudes of vibration of all nonhydrogen atoms are given in Table IV.[17]

Solution of the structure for $Th(C_8H_8)_2$ followed directly from the $U(C_8H_8)_2$ results. Trial atomic positions with isotropic thermal parameters from $U(C_8H_8)_2$ were used in a least-squares refinement with the $Th(C_8H_8)_2$ data. The refinement converged in three cycles. Hydrogen atom positions were calculated as described for $U(C_8H_8)_2$. In the final anisotropic least-squares refinement the structure factor contributions from these fixed hydrogen positions were included and the extinction parameter was varied.[16] The final *R* factors are $R_1 = 2.07\%$ and $R_2 = 2.08\%$, with an error in an observation of unit weight of 0.616. The final difference Fourier showed no peaks greater than 0.56 e/Å³.

The $Th(C_8H_8)_2$ positional and anisotropic thermal parameters after the refinement are listed in Table II. The calculated hydrogen positions are listed in Table III. Table IV gives 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 crystal structures of $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, there are two molecules per unit cell. The heavy atoms occupy the symmetry-related positions 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ with $\bar{1}$ ($C_i$) site symmetry. A stereoscopic packing diagram of $U(C_8H_8)_2$ viewed normal to the *yz* plane is shown in Figure 1. The molecules alternate in a herringbone motif up the twofold screw axis, parallel to *b*. The molecular eightfold axis which passes through the center of the two rings and the uranium atom makes an angle of 40.9° with the *b* axis in $U(C_8H_8)_2$ and 44.6° with the *b* axis in $Th(C_8H_8)_2$. The crystal structures show no unusually short intermolecular nonbonded distances.

A stereoview of the $Th(C_8H_8)_2$ molecule is shown in Figure 2. The molecular structure consists of a central metal atom symmetrically $\pi$ bonded to two $C_8H_8^{2-}$ rings which are related by the inversion center at the heavy atom. In $U(C_8H_8)_2$, the uranium–carbon bonds are equal within experimental error and average 2.647

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[17] A listing of structure factors will appear following these pages in the microfilm edition of this volume of the 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, by referring to code number INORG-72-1083. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(4) Å. The thorium–carbon bonds in $Th(C_8H_8)_2$ are slightly longer and average 2.701 (4) Å. The mean ring-to-ring distance along the molecular eightfold axis is 3.847 (10) Å in $U(C_8H_8)_2$ and 4.007 (3) Å in $Th(C_8H_8)_2$. That is, one-half this distance (1.924 and 2.004 Å, respectively, for $U(C_8H_8)_2$ and $Th(C_8H_8)_2$) is the distance from the metal to the center of the dianion ring. The mean C–M–C angle for adjacent carbons in the dianion ring is 30.5 (3)° in $U(C_8H_8)_2$ and 29.7 (2)° in $Th(C_8H_8)_2$. Carbon–metal–carbon angles, where the two carbons are separated by three ring atoms and are on opposite sides of the dianion ring, average 86.80 (13)° for $U(C_8H_8)_2$ and 84.22 (16)° for $Th(C_8H_8)_2$. These angles and distances along with the planarity of the dianion ring establish almost exact $D_{8h}$ molecular symmetry for the π-sandwich structures. The bond lengths and angles for the inner coordination spheres are summarized in Table V. The thermal motion of the heavy atoms is nearly isotropic. See Table VI for the bond lengths and angles of the cyclooctatetraene dianions.

TABLE V
INNER COORDINATION SPHERE BOND LENGTHS (Å) AND ANGLES (DEG) IN $U(C_8H_8)_2$ AND $Th(C_8H_8)_2$

| $U(C_8H_8)_2$ | | $Th(C_8H_8)_2$ | |
|---|---|---|---|
| Atoms | Distance | Atoms | Distance |
| U–$C_1$ | 2.675 (11) | Th–$C_1$ | 2.698 (10) |
| U–$C_2$ | 2.637 (10) | Th–$C_2$ | 2.697 (11) |
| U–$C_3$ | 2.648 (11) | Th–$C_3$ | 2.705 (10) |
| U–$C_4$ | 2.635 (10) | Th–$C_4$ | 2.679 (14) |
| U–$C_5$ | 2.646 (11) | Th–$C_5$ | 2.714 (12) |
| U–$C_6$ | 2.643 (10) | Th–$C_6$ | 2.705 (9) |
| U–$C_7$ | 2.645 (11) | Th–$C_7$ | 2.700 (8) |
| U–$C_8$ | 2.648 (11) | Th–$C_8$ | 2.706 (8) |
| Mean U–C | 2.647 (4)[a] | Mean Th–C | 2.701 (4)[a] |
| Mean ring to ring distance | 3.847 (10)[b] | Mean ring to ring distance | 4.007 (3)[b] |
| Group | Angle | Group | Angle |
| Mean $C_i$–U–$C_{i+1}$ | 30.49 (28)[c] | Mean $C_i$–Th–$C_{i+1}$ | 29.74 (18)[c] |
| Mean $C_i$–U–$C_{i+4}$ | 86.80 (13)[d] | Mean $C_i$–Th–$C_{i+4}$ | 84.22 (16)[d] |

[a] Standard deviations for the mean values reported in this and subsequent tables were estimated from the variance using the equations $\sigma^2 = (\Sigma_{i=1}{}^n(x_i - \bar{x})^2)/(n - 1)$ and $\sigma_{\bar{x}} = 1/(\sqrt{n})\sigma$, where $\sigma$ is the standard deviation of an individual observation and $\sigma_{\bar{x}}$ is the standard deviation for the mean. [b] Half this number is the distance from the uranium to the center of the eight-membered ring. [c] Atoms $i$ and $i + 1$ are adjacent in the cyclooctatetraene ring. [d] Atoms $i$ and $i + 4$ are separated by three carbon atoms in the ring; half this value is the angle between the eightfold molecular symmetry axis and the carbon atom.

The cyclooctatetraene dianions in both compounds are planar and have average C–C bond lengths of 1.392 (13) and 1.386 (9) Å in $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, respectively. A weighted least-squares plane through the dianion ring of $U(C_8H_8)_2$ (Table VII) has all of the atoms within 0.02 Å of the plane with standard deviations of about 0.01 Å. In $Th(C_8H_8)_2$ all the atoms are within 0.008 Å of the weighted least-squares plane with a standard deviation of 0.01 Å. The planar rings in both compounds have the regular interior octagonal angle of 135.0°. The planarity of the ring and the mean bond lengths and angles demonstrate the aromatic nature of the 10-π-electron dianion rings in these structures. Another confirmation of the aromaticity is a comparison of the two averages for alternate sets of four carbon–carbon bonds. A comparison of these two averages is a much more severe test of the aromatic nature of the anion than bond-by-bond comparisons or the overall average. These averages, 1.396 (5) and 1.388 (27) Å in $U(C_8H_8)_2$ and 1.386 (12) and 1.387 (14) Å in $Th(C_8H_8)_2$, are equal within experimental error. The averages must be equal in an aromatic hydrocarbon ring. The relatively large anisotropic thermal motion of the $C_8H_8^{2-}$ ring carbon atoms is similar to that previously observed in structures containing $C_8H_8^{2-}$.[9,18] The preferential oscillation is around the eightfold symmetry axis with an average root-mean-square amplitude of vibration (see Table IV) along the major ellipsoid axis of 0.37 Å in $U(C_8H_8)_2$ and 0.39 Å in $Th(C_8H_8)_2$. This approximately represents the average thermal motion along the circumference of the $C_8H_8^{2-}$ ring. See Figure 3 for illustrations of the ring carbon atoms of $Th(C_8H_8)_2$.

TABLE VI
BOND LENGTHS (Å) AND ANGLES (DEG) FOR THE CYCLOOCTATETRAENE DIANIONS

| | Distance | |
|---|---|---|
| Bond | $U(C_8H_8)_2$ | $Th(C_8H_8)_2$ |
| $C_1$–$C_2$ | 1.389 (19) | 1.384 (18) |
| $C_2$–$C_3$ | 1.346 (17) | 1.366 (17) |
| $C_3$–$C_4$ | 1.386 (18) | 1.353 (21) |
| $C_4$–$C_5$ | 1.431 (21) | 1.415 (19) |
| $C_5$–$C_6$ | 1.407 (19) | 1.406 (18) |
| $C_6$–$C_7$ | 1.337 (18) | 1.359 (18) |
| $C_7$–$C_8$ | 1.401 (19) | 1.399 (17) |
| $C_8$–$C_1$ | 1.439 (23) | 1.408 (21) |
| Av C–C | 1.392 (13) | 1.386 (9) |
| Av of two sets of alternate C–C bonds | 1.396 (5)<br>1.388 (27) | 1.386 (12)<br>1.387 (14) |
| | Angle | |
| Group | $U(C_8H_8)_2$ | $Th(C_8H_8)_2$ |
| $C_8$–$C_1$–$C_2$ | 133.3 (11) | 135.7 (12) |
| $C_1$–$C_2$–$C_3$ | 136.7 (11) | 135.0 (12) |
| $C_2$–$C_3$–$C_4$ | 135.1 (11) | 134.1 (10) |
| $C_3$–$C_4$–$C_5$ | 135.0 (11) | 138.3 (13) |
| $C_4$–$C_5$–$C_6$ | 133.8 (11) | 131.6 (13) |
| $C_5$–$C_6$–$C_7$ | 135.8 (11) | 136.2 (12) |
| $C_6$–$C_7$–$C_8$ | 135.4 (12) | 135.2 (10) |
| $C_7$–$C_8$–$C_1$ | 135.8 (11) | 133.9 (10) |
| Av C–C–C interior angle | 135.0 (7) | 135.0 (4) |

TABLE VII
WEIGHTED LEAST-SQUARES PLANE FOR PLANE OF CYCLOOCTATETRAENE DIANION IN $U(C_8H_8)_2$ AND $Th(C_8H_8)_2$

| $U(C_8H_8)_2$ | | $Th(C_8H_8)_2$ | |
|---|---|---|---|
| Atom | Distance[a] | Atom | Distance[a] |
| $C_1$ | 0.021 (10) | $C_1$ | −0.005 (10) |
| $C_2$ | −0.013 (10) | $C_2$ | −0.006 (11) |
| $C_3$ | −0.001 (12) | $C_3$ | 0.001 (10) |
| $C_4$ | −0.001 (10) | $C_4$ | 0.001 (12) |
| $C_5$ | 0.009 (11) | $C_5$ | 0.000 (12) |
| $C_6$ | −0.001 (10) | $C_6$ | 0.003 (9) |
| $C_7$ | −0.008 (11) | $C_7$ | −0.008 (10) |
| $C_8$ | −0.003 (10) | $C_8$ | 0.001 (11) |
| Parameters from Eq of Plane[b] | | | |
| $A$ | 0.185 | $A$ | 0.188 |
| $B$ | 0.622 | $B$ | 0.628 |
| $C$ | 0.640 | $C$ | 0.645 |
| $D$ | 0.192 | $D$ | 0.200 |

[a] Distances in ångströms of individual atoms from weighted least-squares plane. [b] Equation for least-squares plane in monoclinic coordinates of the form $Ax + By + Cz - D = 0$.

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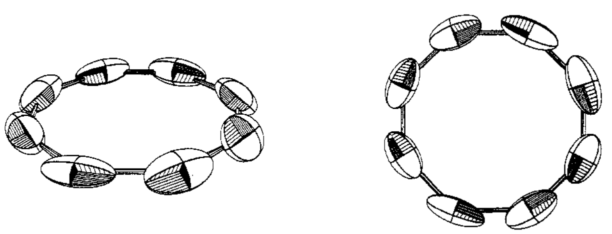

Figure 3.—The cyclooctatetraene dianion ring carbon atoms in $Th(C_8H_8)_2$ viewed perpendicular to the plane of the ring are shown on the right. The left view is rotated 65°. The numbering sequence increases sequentially in a clockwise direction from the upper right carbon atom, $C_1$, in both rings.

Comparison of the $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ structures demonstrates the ability to use ionic radii in predicting bond distances in an isostructural actinide (or lanthanide) series of organometallic $\pi$ complexes. The following comparisons are made using ionic radii calculated for a coordination number (CN) of IX (CN of VIII gives the same results; values for CN of X are not available). The thorium–carbon bond lengths can be estimated from the ionic radii of uranium (IV), 1.05 Å,[19] and thorium (IV), 1.09 Å.[19] The difference in these radii, when added to the average U–C bond length, predicts a Th–C bond length of 2.69 Å. This compares well with the observed value of 2.70 Å. An estimation can also be made for a lanthanide with a similar $\pi$-sandwich structure, $K(diglyme)Ce(C_8H_8)_2$.[20] The difference between the ionic radii of uranium(IV) and cerium(III), 1.15 Å,[19] predicts a Ce–C bond length of 2.75 Å. Preliminary structural results, before final refinement, give an experimental average Ce–C bond distance of 2.74 Å.[20] It is thus apparently possible to predict M–C bond lengths to within about 0.01 Å for these actinide and lanthanide $C_8H_8^{2-}$ complexes.

The general features of the bonding in $Th(C_8H_8)_2$ and $U(C_8H_8)_2$, as established by this study, are substantially identical. Questions regarding the relative importance of f-orbital involvement in the bonding of these compounds and how this may affect the relative reactivities of compounds such as $Th(C_8H_8)_2$ and $U(C_8H_8)_2$ cannot be directly answered by structural studies alone. It was observed by Streitwieser and Yoshida that $Th(C_8H_8)_2$, in contrast to $U(C_8H_8)_2$, is easily solvolyzed in solvents which can act as Lewis bases.[2] The degree to which f-orbital back-bonding explains the chemical differences in this series remains to be established by the magnetic resonance and spectroscopic studies which are in progress.

**Acknowledgment.**—We thank Professor A. Streitwieser, Jr., for his discussion of and interest in this work and N. Yoshida for supplying us with crystalline $Th(C_8H_8)_2$. We gratefully acknowledge the financial support of the National Science Foundation through Grants GP-13278 and GP-29764 and an NSF traineeship to K. O. H. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the University of California Computer Center for subsidized computer time. This research was supported in part by the Atomic Energy Commission (A. Z.).

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# The Molecular Structure of Chlorodinitrosylbis(triphenylphosphine)ruthenium Hexafluorophosphate–Benzene. A Complex Having Linear and Bent Nitrosyl Groups

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*Received July 19, 1971*

The crystal and molecular structure of the dinitrosyl complex $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]\cdot C_6H_6$ has been determined from three-dimensional single-crystal X-ray data collected by the $\theta$–$2\theta$ counter technique. The complex crystallizes in the monoclinic space group $P2_1/c$ in a cell of dimensions $a = 12.51$ (1), $b = 14.67$ (1), $c = 23.00$ (1) Å, $\beta = 91.8$ (2)°, and $V = 4219$ Å$^3$. There are four molecules per unit cell ($\rho_{exptl} = 1.49 \pm 0.01$ g/cm$^3$; $\rho_{calcd} = 1.484$ g/cm$^3$). The structure was solved by Patterson and Fourier methods and has been refined by a least-squares procedure to a conventional $R$ factor of 0.065 for 1522 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. The structure of the ruthenium dinitrosyl cation is a distorted square pyramid in which an apical nitrosyl group coordinates in a bent manner (Ru–N, 1.85 (2) Å; Ru–N–O, 138 (2)°) while a basal nitrosyl coordinates in a linear manner (Ru–N, 1.74 (2) Å; Ru–N–O, 178 (2)°). As such, this Ru(II) complex represents a striking illustration of the two different modes of coordination for nitrosyl. The average Ru–P and Ru–Cl distances are 2.426 (6) and 2.362 (6) Å, respectively. The bonding of the apical nitrosyl group in this and other closely related systems is discussed in terms of a simple orbital correlation diagram.

## Introduction

In 1967, Hodgson, *et al.*, reported the reaction between $IrCl(CO)(P(C_6H_5)_3)_2$ and $NO^+$ and showed that it yields a nitrosyl complex with a metal–nitrogen–oxygen bond angle of 124 (1)°.[2,3] Since the initial report of this system, other examples of nitrosyl coordination to group VIII metal ions exhibiting M–N–O angles approaching 120° have appeared.[4–8] From

[1] National Institutes of Health Predoctoral Fellow, 1969–1971.

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