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Bis(cyclopentadienyl) Actinide(IV) Compounds. I. The Structure of Dichlorobis(pentamethyl-η^5-cyclopentadienyl)uranium(IV) and Dichlorobis(pentamethyl-η^5-cyclopentadienyl)thorium(IV)

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Abstract. $[UCl_2(C_{10}H_{15})_2]$, $M_r = 579.40$, orthorhombic, $Fmm2$, $a = 14.913\,(3)$, $b = 17.348\,(3)$, $c = 8.168\,(2)$ Å, $V = 2113\,(1)$ Å^3, $Z = 4$, $D_x = 1.821$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.5385$ mm^{-1}, $F(000) = 1104$, $T = 295\,(1)$ K, $R = 0.049$ for 436 observed reflections $[I > 3\sigma(I)]$. $[ThCl_2(C_{10}H_{15})_2]$, $M_r = 573.41$, orthorhombic, $Fmm2$, $a = 14.939\,(4)$, $b = 17.535\,(5)$, $c = 8.201\,(2)$ Å, $V = 2148\,(2)$ Å^3, $Z = 4$, $D_x = 1.773$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.4334$ mm^{-1}, $F(000) = 1096$, $T = 295\,(1)$ K, $R = 0.045$ for 548 observed reflections $[I > 3\sigma(I)]$. The two complexes are isostructural. The coordination geometry about the actinide atom is that of a distorted tetrahedron of symmetry C_{2v}, formed by the two Cl atoms and the centroids of the two cyclopentadienyl ligands. The corresponding bond angles in the two molecules are remarkably alike. The molecular geometry appears to be heavily influenced by intramolecular non-bonded interactions.

Introduction. $MX_2(C_5H_5)_2$ compounds are rather unstable for the actinide elements. While the structures of a number of Ti^{4+} and Zr^{4+} compounds of this type have been reported (Bruce, 1978, 1979), the only actinide compound for which both a synthesis and structure have been reported is bis(cyclopentadienyl)bis(tetrahydroborato)uranium, $[U(C_5H_5)_2(BH_4)_2]$ (Zanella, de Paoli, Bombieri, Zanotti & Rossi, 1977); attempts to prepare $[UCl_2(C_5H_5)_2]$ have not yet succeeded.

Alkylation of the cyclopentadienyl rings greatly improves the solubility and crystallizability of the resulting actinide complexes and the following bis(pentamethylcyclopentadienyl)actinide(IV) complexes have been synthesized and characterized by X-ray diffraction: $[Th\{C_5(CH_3)_5\}Cl\{COCH_2(CH_3)_3\}]$ (Fagan, Manriquez, Marks, Day, Vollmer & Day, 1980); $[Th\{(CH_3)_5C_5\}_2\{CH_2C(CH_3)_3\}_2]$ (Bruno, Smith, Fair, Schultz, Marks & Williams, 1986); $[Th\{(CH_3)_5C_5\}_2\{CH_2Si(CH_3)_3\}_2]$ (Bruno, Marks & Day, 1983). We report here the syntheses and structures of $[UCl_2\{C_5(CH_3)_5\}]$ and $[ThCl_2\{C_5(CH_3)_5\}]$. The structure of a pyrazole adduct of $[U\{C_5(CH_3)_5\}Cl_2$ (Eigenbrot & Raymond, 1982) has also been reported.

Experimental. Synthesis of the title complexes was by reaction of uranium (or thorium) tetrachloride and potassium pentamethylcyclopentadienyl in stoichiometric proportions and extraction with *n*-pentane. Single crystals were obtained by sublimation under high vacuum at 373 K (393 K). (Where details for thorium are different they are given in parentheses.) Crystals 0.30 × 0.30 × 0.25 mm (0.30 × 0.07 × 0.07 mm) were sealed in thin-walled glass capillaries

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under nitrogen, and used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation using ω–2θ scans; index range h 0/16, k 0/17, l 0/8 (h 0/17, k 0/20, l 0/9). Cell parameters were determined from 25 reflections with $4 < 2\theta < 20°$ ($3 < 2\theta < 39°$). Three standard reflections were measured at 30 min intervals and anisotropic decay correction was applied to the data [total decay 1.0% (1.2%)]. Lorentz–polarization corrections were applied. For the U complex, empirical absorption corrections were applied using the program *DIFABS* (Walker & Stuart, 1983), with transmission coefficients of 0.69–1.20. For the Th complex empirical absorption corrections were made by the method of North, Phillips & Mathews (1968), with transmission factors of 0.85–1.00. 838 (1880) observed reflections [$I > \sigma(I)$], corresponding to 437 (560) unique reflections [$R_{\rm int} = 0.058$ (0.030)], were measured in the range $4 < 2\theta < 46°$ ($4 < 2\theta < 50°$). Both structures were solved by direct methods and Fourier techniques, with full-matrix least-squares refinement on F. H atoms were not located. The systematic absences are compatible with space groups *Fmmm* (No. 69), *F*222 (No. 22) and *Fmm*2 (No. 42); in space group *Fmmm* or *F*222, the molecule would be required to have symmetry D_{2h} or D_2, not consistent with the expected tetrahedral coordination of the actinide atom; space group *Fmm*2 was confirmed by the solution. The last cycles of refinement $\{w = \sigma(F_o)^{-2}$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o)^2 = [\sigma^2(I) + (0.06I)^2]^{1/2}/{\rm Lp}\}$ were carried out on 436 (548) independent reflections with $F^2 > 3\sigma(F^2)$, and 33 (32) variables, with anisotropic thermal motion for An and Cl atoms, and a secondary-extinction coefficient (refined to $g = 3.69 \times 10^{-6}$ for the U complex; no extinction correction for the Th complex). The final agreement factors were $R = 0.048$ (0.045), $wR = 0.061$ (0.055), $S = 2.098$ (1.67); final $(\Delta/\sigma)_{\rm max}$ were less than 0.01; maximum and minimum heights in final difference Fourier maps were 0.86 (1.00) and −0.77 (−0.91) e Å^{-3}. Calculations were performed with the Enraf–Nonius (1986) *SDP* programs; atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic coordinates are given in Table 1,* distances and angles in Table 2, and the molecular structure is illustrated in Fig. 1.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$B_{\rm eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

For the Th complex, C atoms were refined isotropically.

	x	y	z	$B_{\rm eq}$
U complex				
U	0.000	0.000	0.000	2.04 (2)
Cl	0.1306 (6)	0.000	−0.208 (1)	5.1 (2)
C(1)	0.000	0.153 (3)	−0.01 (1)	7.0 (9)
C(2)	0.075 (2)	0.139 (2)	0.081 (4)	4.9 (5)
C(3)	0.048 (2)	0.110 (2)	0.226 (4)	5.2 (5)
C(1′)	0.000	0.183 (6)	−0.18 (2)	14 (3)
C(2′)	0.173 (3)	0.152 (3)	0.061 (6)	10 (1)
C(3′)	0.120 (6)	0.109 (4)	0.37 (1)	14 (2)
Th complex .				
Th	0.000	0.000	0.000	2.72 (1)
Cl	0.1335 (5)	0.000	−0.2036 (9)	5.8 (1)
C(1)	0.000	0.155 (2)	0.00 (3)	7.2 (6)
C(2)	0.077 (1)	0.137 (1)	0.101 (3)	5.4 (4)
C(3)	0.046 (2)	0.111 (1)	0.233 (3)	5.8 (4)
C(1′)	0.000	0.182 (5)	−0.17 (1)	16 (3)
C(2′)	0.171 (2)	0.153 (2)	0.060 (5)	9.5 (9)
C(3′)	0.115 (5)	0.101 (4)	0.377 (9)	16 (2)

Table 2. *Bond distances* (Å) *and angles* (°)

	U complex	Th complex
An—Cl	2.583 (6)	2.600 (5)
An—C (av.)	2.72 (2)	2.78 (2)
An—Cp*	2.47 (3)	2.53 (4)
Cl—An—Cl	97.9 (4)	100.1 (3)
Cl—An—Cp	105 (1)	106.3 (4)
Cp—An—Cp	132 (1)	128 (4)
C—C (av.)	1.37 (4)	1.34 (6)
C—C′ (av.)	1.52 (7)	1.52 (4)
C—C—C (av.)	108 (3)	108 (5)
C—C—C′ (av.)	126 (3)	126 (4)

* Cp denotes the centroid of the ring.

There are discrete molecules of [An{$C_5(CH_3)_5$}$_2$-Cl_2] with symmetry *mm*2 (C_{2v}). The An$^{\rm IV}$ ion is π-bonded to two [$(CH_3)_5C_5$]$^-$ ligands and σ-bonded to two Cl ligands, adopting the familiar pseudotetrahedral 'bent-sandwich' configuration (Marks & Ernst, 1982). The Th—Cl bond length of 2.600 (5) Å is similar to that of 2.664 (1) Å observed in [Th($C_{12}H_{13}$)$_3$Cl)] (Spirlet, Rebizant & Goffart, 1982), 2.673 (3) Å in [Th($C_{11}H_{11}$)$_3$Cl] (Spirlet, Rebizant, Bettonville & Goffart, 1990), and 2.672 (6) Å in [Th{$C_5(CH_3)_5$}$_2$Cl{$COCH_2C(CH_3)_3$}] (Fagan *et al.*, 1980). The U—Cl bond length, 2.583 (6) Å, is quite close to that of 2.638 (4) Å observed in UCl_4 (Taylor & Wilson, 1973), 2.559 (6) Å in [U(C_5H_5)$_3$Cl] (Wong, Yen & Lee, 1965), 2.593 (3) Å in [U(C_9H_7)$_3$Cl] (Burns & Laubereau, 1971), 2.627 (2) Å in [U(CH_3-C_5H_4)Cl_3](OC_4H_8)$_2$ (Ernst, Kennelly, Day, Day & Marks, 1979), 2.609 (2) Å in [U(C_9H_7)Cl_3](OC_4H_8)$_2$ (Rebizant, Spirlet & Goffart, 1983) and 2.601 (3) Å in [U($C_{12}H_{13}$)$_3$Cl] (Meunier-Piret & Van Meerssche,

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55337 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0097]

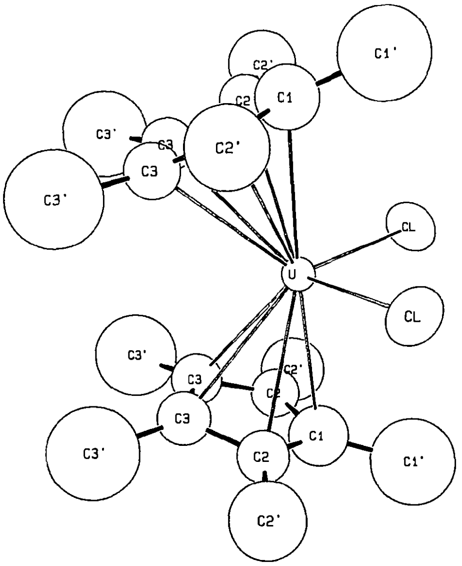

Fig. 1. The molecular structure of the U complex. The Th complex is isostructural. Thermal ellipsoids are drawn at the 50% probability level (Johnson, 1976).

1984). The An—C distances (Table 2) are comparable to the average value of 2.74 (2) Å in [U{$C_5(CH_3)_5$}$Cl_2(C_3H_4N_2)$] (Eigenbrot & Raymond, 1982), and 2.82 Å in [Th{$C_5(CH_3)_5$}Cl{$COCH_2C(CH_3)_3$}] (Fagan *et al.*, 1980). The angles Cp—An—Cp (where Cp = ring centroid) are in both cases much larger than the angle Cl—An—Cl, presumably as a result of intramolecular contact of methyl groups.

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Structures of Two Molybdenum Oxo Complexes [$MoOCl_3(OPPh_3)_2$] and [$MoOI(dmpe)_2$]I

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Abstract. Trichlorooxobis(triphenylphosphine oxide-*O*)molybdenum(V), [$MoOCl_3(C_{18}H_{15}OP)_2$], M_r = 774.88, monoclinic, $C2/c$, a = 14.041 (2), b = 13.126 (1), c = 19.210 (4) Å, β = 96.08 (1)°, V = 3521 (2) Å^3, Z = 4, D_x = 1.46 g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, μ = 64.06 cm^{-1}, $F(000)$ = 1572, T = 293 K, R = 0.064 for 2054 observed reflections. The compound was obtained by refluxing [$Cp_2Mo_2Cl_5$]$^-$ and $POPh_3$ in THF. Electron paramagnetic resonance (EPR) spectral parameters (X-band, room temperature, CH_2Cl_2): g = 1.938, a_{Mo} = 54.7 G. The compound adopts an octahedral geometry with *cis* phosphine oxide ligands and a meridional arrangement of the three Cl atoms. There is disorder

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