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Molecular structure and charge distribution in organometallics of the 4f and 5f elements
V*: crystal and molecular structure of tetrakis(η^5-cyclopentadienyl)-thorium(IV) and the temperature dependence of its electrical dipole moment

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Abstract

The crystal and molecular structure of $Th(C_5H_5)_4$ was investigated by single crystal X-ray diffraction. The compound crystallizes tetragonal with $a = 868.3(1)$, $c = 1064.4(3)$ pm with two molecules per unit cell. The average Th–Cp distance of 260.6 pm is in good agreement with the predicted distance of 258.8 pm, and is larger than the corresponding distance of the uranium compound (253.8 pm). The temperature dependence of the dipole moment of the title compound, of thorium tetramethylcyclopentadienide (Cp'_4Th), and of the homologous uranium compound in benzene solution is discussed with respect to their molecular structure.

1. Introduction

Recently we reported on the dipole moment of the tetracyclopentadienides of the lighter tetravalent actinides with quasi T_d-molecular symmetry [1]. In this paper predictions have also been made concerning the distances and angles in homologous compounds for which crystallographic investigations have not yet been carried out. We report here on the crystal and molecular structure of thorium tetracyclopentadienide, $ThCp_4$, and on the charge distribution within the molecule as it can be experimentally obtained from dipole moment measurements.

2. Experimental details

All investigated compounds of thorium and uranium were synthesized by reaction of the pure tetrachlorides and an excess of potassium cyclopentadienide in tetrahydrofuran under reflux, followed by extraction of the dried crude product with pentane. Recrystallization in pentane yielded crystalline compound of high purity. The characterization and investigation of the compounds was carried out as reported in ref. 1. In addition to that, the diamagnetic susceptibility of $Th(C_5H_5)_4$ was measured in a Faraday magnetic balance [2]. Between 77 and 300 K the molar diamagnetic susceptibility of $Th(C_5H_5)_4$ is $-(188 \pm 2) \cdot 10^{-6}$ emu. Single crystals suitable for X-ray investigation were grown by gentle sublimation of the crystalline powder in a sealed glass tube (200 °C, 10 Torr). All manipulations were carried out in a dried argon atmosphere.

3. Results and discussion

3.1. *The crystal and molecular structure*

The selected specimen ($0.1 \times 0.35 \times 0.50$ mm) of the transparent single crystal was sealed in thin-walled quartz capillary under argon atmosphere. X-ray diffraction data were collected with an Enraf-Nonius CAd4-X-ray diffractometer using graphite monochromated Mo K_α radiation and θ–2θ scans. 1095 unique reflections were collected, 300 of which were observed $[I \geqslant 2\sigma(I)]$ and used in the refinement. The intensities

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*Part IV is detailed in ref. 6.

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of three standard reflections measured at one hour intervals showed no deviation from the mean; every 100 measurements orientation control was performed. Lattice constants were obtained from least-squares fit to 25 reflexes at the range $5^\circ < \theta < 15^\circ$, calculated density 2.038 g cm^{-3}, space group $I\bar{4}2m$, $\theta/2\theta$-scans, $\theta_{max} = 22.5^\circ$. Empirical absorption corrections were applied, with min/max transmission factors 0.705/0.999. The structure was solved by direct methods and Fourier synthesis. The values were refined by full-matrix least-squares techniques with minimized $\Sigma w(Fo)^2$: $w = 1/[\sigma(Fo)]^2$ with $\sigma(Fo) = \sigma(Fo)^2/2Fo$ and $\sigma(Fo^2) = [\sigma(I) + (AI)^2]^{1/2}$ Lp, $Goof = \Sigma w[(|Fo| - |Fc|)^2/(No - Nv)]^{1/2} = 1.027$. The refinement converged to $R = 0.019$, $Rw = 0.024$ with $Goof = 1.031$. Residual electron density in a final Fourier map were smaller than 0.76 e$^-$ Å^{-3}. Anisotropic thermal parameters were used for the Th and C atoms. The positions of the hydrogen atoms were calculated with $d_{C-H} = 95$ pm with an isotropic thermal factor of 1.3 times the B_{iso} of the C atoms. All calculations were carried out with programs from the Enraf-Nonius SDP system [3]. The crystal data of the isostructural tetracyclopentadienides of thorium and uranium [4] are summarized in Table 1.

As in the case of the isostructural uranium compound [4] the thorium atom is tetrahedrally surrounded by four pentahapto-bonded C_5H_5 rings as shown in Fig. 1.

The mean values of C–C and Th–C distances in $Th(C_5H_5)_4$ are 1.43(2) and 2.87(2) respectively. These values are larger than the corresponding values 1.39(3) and 2.81(2) Å in the uranium compound [4]. The mean distance Th–Cp_i between Th and the center of the cyclopentadienyl ring is 2.606(1) Å, a value which is slightly larger than the corresponding value in the uranium compound (2.588 Å) as is expected for the ionic radius [5] of the Th^{4+} (94.0 pm), which is larger than the radius of U^{4+} (89.0 pm). The experimental value for the Th–Cp_i distance is in very good agreement with the predicted value of 2.588 Å [1]. The positional parameters are summarized in Table 2, bond lengths and angles are listed in Table 3.

TABLE 1. Summary of the crystal data

	$Th(C_5H_5)_4$	$U(C_5H_5)_4$ [4]
Formula	$ThC_{20}H_{20}$	$UC_{20}H_{20}$
Molecular weight	492.420	498.412
Colour	Colourless	Brown–red
Crystal system	Tetragonal	Tetragonal
Space group (*No*)	$I\bar{4}2m$ (121)	$I\bar{4}2m$ (121)
Z	2	2
Calc. density ρ (g cm^{-3})	2.038	2.10
a (Å)	8.683 (1)	8.635 (2)
c (Å)	10.644 (3)	10.542 (3)

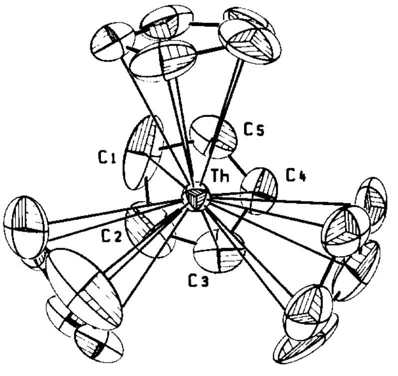

Fig. 1. The $(C_5H_5)_4Th$ molecule without hydrogen atoms (50% probability thermal ellipsoids).

TABLE 2. Positional parameters and their standard deviations

Atom	*x*	*y*	*z*	B(Å^2)
Th	1.000	1.000	1.000	1.860(5)
C1	0.734(2)	0.812(2)	1.046(1)	3.9(3)[a]
C2	0.861(2)	0.719(2)	1.090(2)	4.7(3)[a]
C3	0.942(2)	0.787(3)	1.200(2)	5.0(3)[a]
C4	0.841(2)	0.913(2)	1.226(1)	4.4(3)[a]
C5	0.726(2)	0.928(2)	1.140(1)	3.4(2)[a]
H1	0.617	0.7985	0.9732	5.1[b]
H2	0.8902	0.6242	1.0518	6.2[b]
H3	1.0336	0.7551	1.2414	6.5[b]
H4	0.8530	0.9793	1.2963	5.7[b]
H5	0.6503	1.0063	1.1423	4.4[b]

[a] Atoms were refined isotropically;
[b] $B(H) = 1.3 \cdot B(C)$; anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as: $(4/3) \cdot \{a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ab(\cos\gamma) \cdot B(1,2) + ac(\cos\beta) \cdot B(1,3) + bc(\cos\alpha) \cdot B(2,3)$.

TABLE 3. Bond distances (Å) and bond angles (°)

Distances (Å)		Angles (°)	
Th–C1	2.87(2)	C2–C1–C5	102(1)
Th–C2	2.88(2)	C1–C2–C3	113(2)
Th–C3	2.87(2)	C1–C5–C4	112(1)
Th–C4	2.88(2)		
Th–C5	2.87(2)	Cp_1–$ThCp_2$	110.23
		Cp_1–$ThCp_3$	109.9
$ThCp_i$[a]	2.606(1)	Cp_1–Th–Cp_4	109.9
		Cp_3–Th–Cp_4	110.23
C1–C2	1.44(3)		
C1–C5	1.42(2)	C3–C4–C5	113(2)
C2–C3	1.49(3)	C2–C3–C4	100(2)
C3–C4	1.43(3)		
C4–C5	1.36(2)		

[a] Cp_i denotes the centre of the *i*th cyclopentadienyl ring.

3.2. *The electrical dipole moment of $ThCp_4$*

From the tetrahedral arrangement of the four Cp-rings around the Th atom a quasi T_d molecular symmetry for the $ThCp_4$ results. The electrical dipole moment of a molecule with T_d symmetry, dissolved in a non-polar organic solvent, must be zero [1]. Nevertheless the tetracyclopentadienides of the tetravalent lighter actinoids show in solution an electrical dipole moment [1], which has its origin in a deviation from the ideal T_d symmetry. As discussed in ref. 1 the induced electrical dipole moment arises through an asymmetrical vibration of the AnCp$_3$ unity perpendicular to the C$_3$-axis of the molecule, so that this group is flattened. The Cp$_i$–Th–Cp$_j$ angle then becomes larger, and the C$_3$ axis–Th–Cp$_i$ angle ϕ smaller than the tetrahedral angle (109.5°). Recently we measured an induced, temperature-dependent dipole moment also in the 1:2 adducts of uranylnitrate with trialkylphosphates [6]. In this class the electrical dipole moment results through a small deviation of the (P)O–U–O(P) axis from linearity.

At 20° the measured dipole moment for ThCp$_4$C is 1.18 ± 0.05 D. This value can be calculated according to eqn. (5) in ref. 1 for a Th–Cp$_i$ distance of 260.1 pm (as found from the crystallographic analysis) and a Cp$_i$–Th–Cp$_j$ angle of 110.6°, which corresponds to a C$_3$ axis–Th–Cp$_i$ ($=\phi$) angle of 108.0°. Both values are in excellent agreement with the predicted values for ThCp$_4$ in ref. 1 (258.8 pm and 107.6°).

The deviation from ideal tetrahedral symmetry yields an induced electrical dipole moment, which is temperature dependent (Fig. 2). In contrast to that, the tris(cyclopentadienyl) halides of the tetravalent actinoids, Cp$_3$An^{IV}Hal, exhibit a static permanent dipole moment of 3.0 to 3.6 D [7], which is temperature independent. A comparison between the crystal structures of An^{IV}Cp$_4$ (T_d) and Cp$_3$An^{IV}Hal (C_{3v}) shows that the AnCp$_3$ group in the halides is flattened [7]. For example, the angle Cp$_i$–U–Cp$_j$ in Cp$_3$UCl is about 116.2° and the angle C$_3$ axis–U–Cp$_i$ ($=\phi$) is about 101.3° [8, 9]. Figure 2 shows the temperature-dependent electrical dipole moments of cyclopentadienyl (Cp) and methylcyclopentadienyl (Cp′) compounds of thorium and uranium with T_d and C_{3v} molecular symmetries.

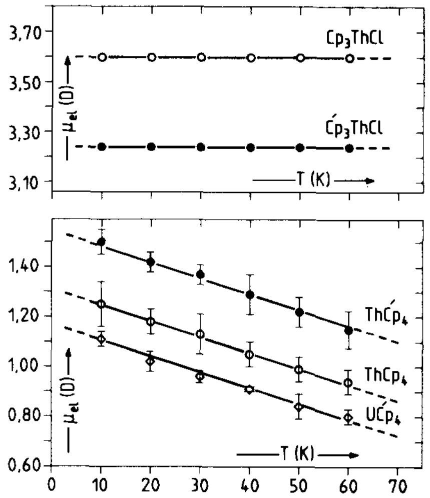

Fig. 2. The dipole moments of cyclopentadienyl complexes of the tetravalent thorium and uranium (Cp = C$_5$H$_5^-$, Cp′ = CH$_3$C$_5$H$_4^-$).

4. Conclusions

As denoted elsewhere [1], precise measurements of the charge distribution in molecules can give exact information on distances and angles in homologous molecules. This has been demonstrated in the present paper for Th(C$_5$H$_5$)$_4$.

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