Structure of Chlorotris(1,2,4,5,6,7-hexamethylindenyl)uranium(IV)

By M. R. Spirlet* and J. Rebizant

Commission of the European Communities Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe, Germany

and S. Bettonville† and J. Goffart‡

Laboratoire de Chimie Analytique et Radiochimie, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

Abstract. [U(C$_{15}$H$_{19}$)$_3$Cl], M_r = 871.44, triclinic, $P\bar{1}$, a = 10.081 (4), b = 13.339 (4), c = 15.083 (3) Å, α = 85.24 (4), β = 82.673 (5), γ = 67.37 (4)°, V = 1856 (1) Å^3, Z = 2. D_x = 1.560 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 42.491 cm^{-1}, $F(000)$ = 872, T = 295 (1) K, R = 0.027 for 4364 reflections [$I > 3\sigma(I)$]. The coordination polyhedron of the U atom is a regular tetrahedron. Geometrical molecular features indicate a tendency for a monohapto mode of bonding of the hexamethylindenyl ligands. This type of bonding has never before been observed in σ-indenyl complexes of uranium or thorium.

Introduction. Molecular and crystal structures of a number of organouranium or organothorium complexes of the indenyl ligand have been reported. In these compounds, the indenyl rings are σ-linked to the actinide atom through C atoms of the five-membered-ring portion. In the tetrahedral trisindenyl derivatives, An—C distances suggest a trihapto covalent mode of bonding of the indenyl rings (Burns & Laubereau, 1971; Spirlet, Rebizant & Goffart, 1982; Meunier-Piret & Van Meerssche, 1984; Rebizant, Spirlet, Kanellakopulos & Dornberger, 1986; Spirlet, Rebizant & Goffart, 1987; Rebizant, Spirlet, Van den Bossche & Goffart, 1988; Spirlet, Rebizant, Bettonville & Goffart, 1990).

The title compound is the first ever observed where the uranium(IV) is monohapto σ-bonded to the indenyl rings and exhibits a regular tetrahedral coordination polyhedron. Its characterization and structure analysis by single-crystal X-ray diffraction are reported here.

Experimental. The title compound was synthesized by reaction of hexamethylindenylpotassium with uranium tetrachloride in tetrahydrofuran at room temperature. Recrystallization from pentane yielded single crystals suitable for X-ray analysis. A specimen (0.25 × 0.15 × 0.15 mm) was selected and sealed in a thin-walled glass capillary under an inert atmosphere. Intensity data were recorded on an Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation using ω–2θ scans. Cell parameters were refined by least squares from angular data of 25 reflections in the range $10 < 2\theta < 22°$. No systematic absences were detected. 4847 unique observed [$I > 1\sigma(I)$] reflections were collected in the range $4 < 2\theta < 45°$ (h 10→0, k 14→ − 13, l 16 → − 16). Intensities of three standard reflections were measured at 30 min intervals and linear decay corrections were applied to the data (the total decay was 3.91%). The intensities were corrected for Lorentz-polarization effects. Empirical absorption corrections, based on a method which uses a set of scans of reflections with χ values close to 90° (North, Phillips & Mathews, 1968), gave transmission factors ranging from 55.45 to 99.98%. The structure was solved by direct methods in the two possible space groups $P1$ and $P\bar{1}$. The procedure revealed the structure to be centrosymmetric. Refinement was carried out by full-matrix least-squares techniques which minimized $\Sigma w(\Delta F)^2$; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I) + (0.06I)^2]^{1/2}$/Lp. All non-H atoms were refined anisotropically. A secondary-extinction coefficient was refined to g = 1.2491 (1) × 10^{-7} {F_c = F_c/[1 + $g(F_c)^2$Lp]}. The agreement factors in least-squares refinement for 4364 reflections with $I > 3\sigma(I)$ and 425 variables were R = 0.031 and wR = 0.046; S = 1.410. Final $(\Delta/\sigma)_{max}$ < 0.01. Most H atoms could be located on a difference Fourier map. Only the positions of some methyl H atoms (8) were calculated in fixed positions with C—H = 0.95 Å. All H atoms were included in a final structure-factor calculation with isotropic thermal parameters fixed at 1.3B_{eq} of the bonded C atom. The final agreement

* On secondment from University of Liège, Belgium.
† Research Assistant, FNRS, Brussels.
‡ Research Associate, IISN, Brussels.

factors dropped to $R = 0.027$ and $wR = 0.036$; $S = 1.148$. Maximum and minimum heights in $\Delta\rho$ map are 0.896 and -1.727 e Å^{-3}, near the U-atom positions. The atomic scattering factors and anomalous-dispersion terms were from *International Tables for X-ray Crystallography*. (1974, Vol. IV). All calculations were performed with Enraf–Nonius (1986) *SDP* programs.

Discussion. The molecular structure is illustrated in Fig. 1. To clarify the drawing we did not include H atoms. Final atomic coordinates are given in Table 1; intramolecular bond lengths and angles are listed in Table 2.* As previously observed in indenyl complexes (Spirlet, Rebizant & Goffart, 1982; Rebizant, Spirlet & Goffart, 1983, 1985), the idenyl and methyl C atoms exhibit relatively large anisotropic thermal motion. The indenyl C atoms show a preferential oscillation about their respective pseudo fivefold and sixfold axes. The r.m.s. amplitudes of vibration along the major axes of the ellipsoids range from 0.136 to 0.298 Å. For the methyl C atoms, corresponding values range from 0.137 to 0.368 Å.

As expected, the coordination of the uranium is tetrahedral, each indenyl ligand occupying one

---

* Lists of structure amplitudes, anisotropic displacement parameters, H-atom coordinates, shortest intra- and intermolecular non-bonded distances and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54962 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0235]
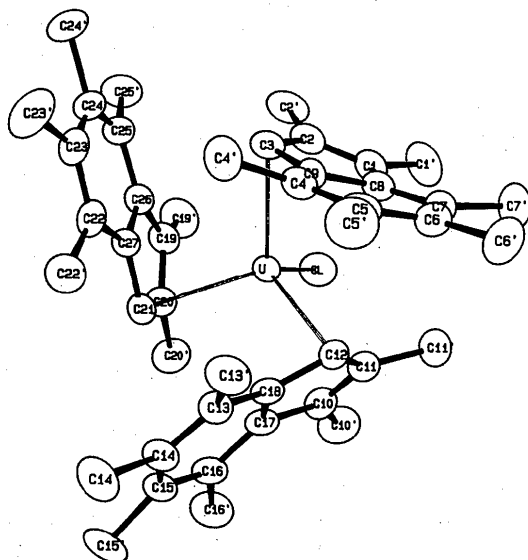

Fig. 1. The molecular structure with the atoms represented by their 50% probability spheres for thermal motion (Johnson, 1965).

Table 1. *Fractional atomic coordinates and isotropic temperature factors*

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

Numbering system:
Indenyl I: C(1)→C(9), C(1')→C(7')
Indenyl II: C(10)→C(18), C(10')→C(16')
Indenyl III: C(19)→C(27), C(19')→C(25')

	x	y	z	B_{eq}(Å^2)
U	0.12116 (2)	0.23678 (2)	0.22214 (1)	2.135 (5)
Cl	-0.1256 (2)	0.2109 (1)	0.2348 (1)	3.90 (4)
C(1)	-0.0265 (7)	0.3629 (5)	0.0715 (5)	3.2 (1)
C(2)	-0.0435 (6)	0.4283 (5)	0.1422 (5)	3.2 (2)
C(3)	0.0942 (7)	0.4280 (5)	0.1547 (5)	3.0 (1)
C(4)	0.3416 (7)	0.3550 (5)	0.0595 (5)	2.9 (1)
C(5)	0.4124 (7)	0.2998 (5)	-0.0189 (5)	3.3 (2)
C(6)	0.3356 (7)	0.2627 (5)	-0.0733 (5)	3.3 (2)
C(7)	0.1922 (8)	0.2773 (5)	-0.0511 (5)	3.5 (2)
C(8)	0.1188 (7)	0.3282 (5)	0.0327 (5)	3.0 (1)
C(9)	0.1941 (6)	0.3680 (4)	0.0845 (4)	2.4 (1)
C(1')	-0.1556 (8)	0.3491 (7)	0.0363 (6)	5.0 (2)
C(2')	-0.1865 (8)	0.4930 (6)	0.1933 (6)	4.5 (2)
C(4')	0.4085 (7)	0.4114 (6)	0.1121 (5)	3.9 (2)
C(5')	0.5683 (8)	0.2844 (6)	-0.0483 (6)	4.9 (2)
C(6')	0.416 (1)	0.2147 (6)	-0.1611 (6)	5.2 (2)
C(7')	0.1048 (9)	0.2531 (6)	-0.1178 (6)	5.2 (2)
C(10)	0.1941 (6)	0.0020 (5)	0.2102 (5)	3.0 (1)
C(11)	0.2070 (7)	0.0519 (5)	0.1265 (5)	3.1 (2)
C(12)	0.3221 (6)	0.0900 (5)	0.1197 (4)	2.8 (1)
C(13)	0.5183 (6)	0.0591 (5)	0.2255 (5)	2.6 (1)
C(14)	0.5709 (6)	0.0059 (5)	0.3027 (5)	2.9 (1)
C(15)	0.4973 (7)	-0.0546 (5)	0.3580 (5)	3.1 (2)
C(16)	0.3694 (7)	-0.0592 (5)	0.3363 (5)	2.9 (1)
C(17)	0.3094 (7)	0.0004 (5)	0.2577 (5)	2.8 (1)
C(18)	0.3876 (6)	0.0570 (4)	0.2015 (4)	2.3 (1)
C(10')	0.0881 (7)	-0.0533 (5)	0.2364 (6)	4.7 (2)
C(11')	0.1207 (8)	0.0537 (6)	0.0502 (5)	4.4 (2)
C(13')	0.6020 (7)	0.1109 (5)	0.1583 (5)	3.8 (2)
C(14')	0.7128 (7)	0.0044 (6)	0.3301 (6)	4.6 (2)
C(15')	0.5701 (9)	-0.1250 (6)	0.4376 (6)	5.0 (2)
C(16')	0.3081 (8)	-0.1360 (5)	0.3871 (6)	4.6 (2)
C(19)	-0.0283 (7)	0.3222 (5)	0.3967 (5)	3.1 (2)
C(20)	0.0735 (7)	0.2168 (5)	0.4063 (5)	2.9 (1)
C(21)	0.2158 (7)	0.2163 (5)	0.3801 (4)	2.7 (1)
C(22)	0.3058 (7)	0.3740 (5)	0.3467 (5)	3.2 (1)
C(23)	0.2604 (8)	0.4858 (5)	0.3405 (5)	3.8 (2)
C(24)	0.1097 (9)	0.5510 (5)	0.3536 (5)	4.1 (2)
C(25)	0.0037 (8)	0.5104 (5)	0.3723 (5)	3.5 (2)
C(26)	0.0482 (7)	0.3937 (5)	0.3743 (4)	3.0 (2)
C(27)	0.1984 (6)	0.3268 (5)	0.3623 (4)	2.6 (1)
C(19')	-0.1901 (8)	0.3518 (7)	0.4219 (6)	4.9 (2)
C(20')	0.0412 (8)	0.1188 (6)	0.4441 (5)	4.4 (2)
C(22')	0.4664 (7)	0.2997 (6)	0.3469 (6)	4.0 (2)
C(23')	0.3741 (9)	0.5385 (6)	0.3245 (6)	5.7 (2)
C(24')	0.063 (1)	0.6792 (6)	0.3479 (7)	6.2 (2)
C(25')	-0.1516 (9)	0.5825 (6)	0.4001 (6)	5.0 (2)

Table 2. *Selected distances (Å) and angles (°) with e.s.d.'s in parentheses*

U—Cl   2.621 (1)

Indenyl I		Indenyl II		Indenyl III	
U—C(1)	2.918 (6)	U—C(10)	2.945 (6)	U—C(19)	2.944 (6)
U—C(2)	2.733 (6)	U—C(11)	2.747 (6)	U—C(20)	2.767 (6)
U—C(3)	2.592 (5)	U—C(12)	2.641 (6)	U—C(21)	2.633 (6)
U—C(8)	3.011 (6)	U—C(17)	3.035 (5)	U—C(26)	3.061 (6)
U—C(9)	2.812 (5)	U—C(18)	2.831 (5)	U—C(27)	2.843 (6)
U—I*	2.548 (6)	U—II	2.572 (6)	U—III	2.584 (6)

Cl—U—C(1)	74.4 (1)	Cl—U—C(10)	73.8 (1)	Cl—U—C(19)	74.7 (1)
Cl—U—C(2)	80.3 (1)	Cl—U—C(11)	80.8 (1)	Cl—U—C(20)	80.8 (1)
Cl—U—C(3)	110.8 (1)	Cl—U—C(12)	111.2 (1)	Cl—U—C(21)	111.2 (1)
Cl—U—C(8)	97.7 (1)	Cl—U—C(17)	96.9 (1)	Cl—U—C(26)	98.2 (1)
Cl—U—C(9)	121.4 (1)	Cl—U—C(18)	121.2 (1)	Cl—U—C(27)	121.5 (1)

C(3)—U—C(12)   108.3 (2)
C(3)—U—C(21)   107.9 (2)
C(12)—U—C(21)   107.3 (2)

I–U–II†   118.8 (2)
I–U–III   118.4 (2)
II–U–III   118.3 (2)

* Distances to the five-membered-ring centroids.
† Ring-centroid–U–ring-centroid angles.

coordination site. The U—Cl bond length of 2.621 (1) Å is in agreement with U—Cl distances observed in other chloroindenyl complexes {2.593 (3) Å in [U(C₉H₇)₃Cl] (Burns & Laubereau, 1971), 2.609 (2) Å in [U(C₉H₇)Cl₃].2C₄H₈O (Rebizant, Spirlet & Goffart, 1983), 2.601 (3) Å in [U(C₁₂H₁₃)₃Cl] (Meunier-Piret & Van Meerssche, 1984)}. Significant differences in U—C distances are observed to each indenyl ligand. The shortest distances correspond in each case to the bond towards the non-methyl-substituted C atom [C(3), C(12) and C(21)]. Moreover, the angles subtended at the U atoms (Table 2) show that the non-methyl-substituted C atoms occupy, with the Cl atom, the sites of a regular tetrahedron. These geometrical features would indicate a monohapto mode of bonding of the indenyl rings. This mode of bonding would probably result from both electronic and steric factors. Indeed, most short intramolecular contacts* involve the methyl-substituted C atoms of the five-membered portion of the indenyl rings. The results of least-squares-plane calculations* show that the five- and six-membered portions of the indenyl rings are almost planar (within 6 e.s.d.'s), although each indenyl ring as a whole exhibits significant deviations from planarity. Bendings of 7.0 (12), 9.8 (9) and 7.2 (7)°, respectively, for the three indenyl ligands are

* See deposition footnote.

observed between the five- and six-membered-ring portions. These bendings are probably induced by steric crowding on the coordination sphere of the U atom. Moreover, some of the methyl groups are planar with the rings to which they belong, some are not; the largest displacement is 0.265 (8) Å for C(7').

References

BURNS, J. H. & LAUBEREAU, P. G. (1971). *Inorg. Chem.* **10**, 2789–2792.
ENRAF-NONIUS (1986). *Structure Determination Package.* Version 18. Enraf-Nonius, Delft, The Netherlands.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
MEUNIER-PIRET, J. & VAN MEERSSCHE, M. (1984). *Bull. Soc. Chim. Belg.* **93**, 299–301.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
REBIZANT, J., SPIRLET, M. R. & GOFFART, J. (1983). *Acta Cryst.* C**39**, 1041–1043.
REBIZANT, J., SPIRLET, M. R. & GOFFART, J. (1985). *Acta Cryst.* C**41**, 334–336.
REBIZANT, J., SPIRLET, M. R., KANELLAKOPULOS, B. & DORNBERGER, E. (1986). *Acta Cryst.* C**42**, 1497–1500.
REBIZANT, J., SPIRLET, M. R., VAN DEN BOSSCHE, G. & GOFFART, J. (1988). *Acta Cryst.* C**44**, 1710–1712.
SPIRLET, M. R., REBIZANT, J., BETTONVILLE, J. & GOFFART, J. (1990). *Acta Cryst.* C**46**, 1234–1236.
SPIRLET, M. R., REBIZANT, J. & GOFFART, J. (1982). *Acta Cryst.* B**38**, 2400–2404.
SPIRLET, M. R., REBIZANT, J. & GOFFART, J. (1987). *Acta Cryst.* C**43**, 354–357.

Structure of Barium Guanosine 5'-Monophosphate

BY MAIR E. A. CHURCHILL

MRC Laboratory of Molecular Biology, Hills Road, Cambridge CB2 2QH, England

ROBIN G. PRITCHARD

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England

AND MADELEINE HELLIWELL

Department of Chemistry, University of Manchester, Manchester M13 9PL, England

Abstract. $2Ba^{2+}.2C_{10}H_{10}N_5O_8P^{2-}.12H_2O$, $M_r = 1209.22$, orthorhombic, $P2_12_12_1$, $a = 21.37$ (2), $b = 22.04$ (1), $c = 8.66$ (1) Å, $V = 4076$ (1) Å³, $Z = 4$, $D_x = 1.970$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 21.01$ cm⁻¹, $F(000) = 2400$, $T = 296$ K, $R = 0.061$ for 2602 observed reflections $[I > 3.0\sigma(I)]$. Two each of barium and guanosine 5'-monophosphate make up the asymmetric unit. Each Ba ion has nine ligands which include the N(7) of each guanosine, sugar hydroxyls, a phosphate O atom, water molecules and bridging water molecules. The guanosines have *anti* glycosidic torsional angles and C(2')-*endo* sugar