Taking into consideration the intermolecular distances only weak van der Waals interactions are expected to be found between pyridines (II) and (III) (Fig. 2). The shortest of these distances are 3·431 (12) [C(24)···N(3)] and 3·669 (18) Å [C(25)···C(31)]. The molecular packing is shown in the stereoscopic view of the unit cell (Fig. 2).

This study was supported by the Polish Academy of Sciences as part of the problems MR.I-9 and MR.I-4.

References

ACKERMAN, J. F., COLE, G. M. & HOLT, S. L. (1974). *Inorg. Chim. Acta*, **8**, 323.

ANDRÉ, J. J., BIEBER, A. & GAUTIER, F. (1976). *Ann. Phys.* **1**, 145–256.

CLEGG, W. (1979). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GOLDBERG, I. & SHMUELI, U. (1973). *Acta Cryst.* B**29**, 421–431, 432–440.

HALUT-DESPORTES, S. (1977). *Acta Cryst.* B**33**, 599–601.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JANUSZCZYK, M. (1982). PhD Thesis, A. Mickiewicz Univ., Poznań, Poland.

JANUSZCZYK, M., PIETRZAK, J. & STECKI, A. (1981). Proc. XXVII Meet. Pol. Phys. Soc. M. Curie-Sklodowska Univ., Lublin, Poland 109.

JASKÓLSKI, M. (1981). To be published.

LIND, M. D. (1967). *J. Chem. Phys.* **47**(3), 990–993.

PIETRZAK, J., JANUSZCZYK, M. & OBUSZKO, Z. (1979). Proc. Conf. *Kryształy Molekularne* – 79 Poznań, Poland.

SHCHEGOLEV, I. F. (1972). *Phys. Status Solidi A*, **12**, 9.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 1041–1043

The Structure of Indenyluranium Trichloride–Bis(tetrahydrofuran), $[U(C_9H_7)]Cl_3.2C_4H_8O$

BY J. REBIZANT

Commission of the European Communities, European Institute for Transuranium Elements, Postfach 2266, *D*-7500 *Karlsruhe, Federal Republic of Germany*

M. R. SPIRLET*

Laboratoire de Physique Expérimentale, Université de Liège au Sart Tilman, B-4000 *Liège, Belgium*

AND J. GOFFART†

Institut de Radiochimie, Université de Liège au Sart Tilman, B-4000 *Liège, Belgium*

(*Received* 18 *October* 1982; *accepted* 11 *May* 1983)

Abstract. $M_r = 603{\cdot}8$, monoclinic, $P2_1/c$, $a = 9{\cdot}137\,(3)$, $b = 15{\cdot}970\,(3)$, $c = 14{\cdot}318\,(5)$ Å, $\beta = 108{\cdot}17\,(3)°$, $V = 1985\,(2)$ Å^3, $D_x = 2{\cdot}020$ Mg m^{-3}, $Z = 4$, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0{\cdot}71073$ Å, $T = 295\,(1)$ K, $\mu = 82{\cdot}453$ cm^{-1}, $F(000) = 1136$. The crystal structure was solved by direct methods. Full-matrix least-squares refinement with all atoms, except H atoms, treated anisotropically gave an R value of 0·043. The coordination geometry about the uranium ion is pseudo-octahedral with one η^5-C_9H_7 ligand and one coordinated H_4f (THF) molecule occupying *trans* axial positions, and the other H_4f molecule and three Cl atoms occupying equatorial positions.

Introduction. The number of questions regarding the mode of bonding in organoactinide compounds has increased during the last ten years since actinide elements possess several unique features not found among transition elements. Actinides exhibit very sizable ionic radii that give rise to variable formal coordination numbers and unusual coordination geometries depending upon the ligand systems. The presence of 5*f* valence orbitals, whose involvement in the bonding may be important, is another characteristic of actinides that distinguishes them from the lanthanides and the *d*-block elements.

The largest proportion of organouranium complexes whose molecular structures have been described in the literature are complexes of the cyclopentadienide ligand (Atwood, Hains, Tsutsui & Gebala, 1973; Bombieri, De Paoli, Delpra & Bagnall, 1978; Burns, 1974; Eigenbrot & Raymond, 1981; Ernst, Kennelly, Day, Day & Marks, 1979; Fischer, Klahne & Kopf, 1978; Leong, Hodgson & Raymond, 1973; Perego, Cesari, Farina & Lugli, 1975, 1976; Wong, Yen & Lee, 1965). Only one structural determination has been reported for organouranium complexes of the indenide ligand (Burns & Laubereau, 1971).

---

* To whom correspondence should be addressed.

† Chercheur qualifié FNRS.

0108-2701/83/081041-03$01.50

The determination of the structure of the title compound was undertaken to provide further knowledge of the bonding (ionic, covalent or electrostatic) in uranium systems and to determine the coordination geometry of the uranium atom in a complex of the URX_3 type (R = indenyl, X = halide).

Experimental. Red, prismatic crystals by slow evaporation at room temperature from tetrahydrofuran solution; crystal 0·26 × 0·24 × 0·26 mm. Space group from Weissenberg photographs, cell dimensions by least squares from angle data for 25 reflections. Intensities of 3889 observed reflections [$I \geq 3\sigma(I)$, $\pm h$, k, $\pm l$], corresponding to 2618 independent reflections ($R_{\text{int}} = 0{\cdot}035$) collected, ω–2θ scan mode ($1 \leq \theta \leq 25°$), Enraf–Nonius CAD-4 diffractometer, using Mo $K\alpha$ radiation. Two reflections measured at 30 min intervals to check stability of crystal and diffractometer. Lorentz, polarization and absorption corrections (calculated transmission factors range from 14·82 to 27·42%). Direct-method and Fourier techniques; full-matrix least-squares refinement [minimizing $\sum w(\Delta F)^2$] on 1863 independent reflections with $F^2 \geq 3\sigma(F^2)$, including f' and f'' anomalous-dispersion terms for the U and Cl atoms; unit weights. All atoms, except hydrogens, treated anisotropically; H-atom positions calculated by assuming an appropriate geometry and C—H bond lengths of 1·087 Å. $R = 0{\cdot}043$, $R_w = 0{\cdot}050$, $S = 2{\cdot}30$, ratio of maximum least-squares shift to error 0·01, $\Delta\rho$ in final difference Fourier map $\leq 0{\cdot}42\,\text{e}\,\text{Å}^{-3}$ (not due to residual peaks around U atoms); atomic scattering factors from *International Tables for X-ray Crystallography* (1974); Enraf–Nonius (1981) *SDP* programs.

Discussion. The positional parameters from the final least-squares cycle and their associated standard deviations are listed in Table 1.*

Table 1. *Atomic positional and equivalent isotropic thermal parameters with standard deviations in indenyluranium trichloride–bis(tetrahydrofuran)*

$B_{\text{eq}} = \frac{1}{3}\,\text{trace}\,\tilde{\mathbf{B}}$.

	x	y	z	B_{eq}(Å^2)
U	0·30991 (7)	0·39202 (4)	0·22912 (4)	3·02 (2)
Cl(1)	0·0305 (5)	0·4003 (4)	0·1086 (3)	5·4 (2)
Cl(2)	0·2271 (5)	0·4596 (3)	0·3712 (3)	4·8 (2)
Cl(3)	0·3895 (6)	0·2754 (3)	0·1265 (3)	5·6 (2)
C(1)	0·362 (2)	0·559 (1)	0·228 (1)	5·8 (9)
C(2)	0·305 (2)	0·537 (1)	0·130 (2)	8·4 (9)
C(3)	0·398 (2)	0·480 (2)	0·093 (1)	6·8 (9)
C(4)	0·683 (2)	0·435 (2)	0·188 (2)	6·8 (9)
C(5)	0·793 (2)	0·448 (2)	0·277 (2)	6·5 (9)
C(6)	0·777 (2)	0·496 (2)	0·356 (2)	7 (1)
C(7)	0·642 (2)	0·535 (1)	0·348 (1)	6·1 (9)
C(8)	0·519 (2)	0·526 (1)	0·257 (1)	5·4 (8)
C(9)	0·538 (2)	0·475 (1)	0·176 (1)	5·0 (7)
O(1)	0·524 (1)	0·3363 (7)	0·3675 (8)	3·8 (5)
C(11)	0·563 (2)	0·365 (1)	0·470 (1)	4·1 (8)
C(12)	0·710 (3)	0·316 (2)	0·521 (2)	7 (1)
C(13)	0·715 (4)	0·248 (2)	0·461 (2)	10 (1)
C(14)	0·615 (2)	0·262 (1)	0·359 (2)	7 (1)
O(2)	0·198 (1)	0·2687 (7)	0·2821 (9)	4·8 (5)
C(21)	0·202 (3)	0·247 (2)	0·379 (1)	10 (1)
C(22)	0·126 (3)	0·161 (2)	0·368 (2)	12 (2)
C(23)	0·023 (3)	0·160 (2)	0·275 (2)	10 (2)
C(24)	0·106 (3)	0·205 (2)	0·210 (2)	9 (1)

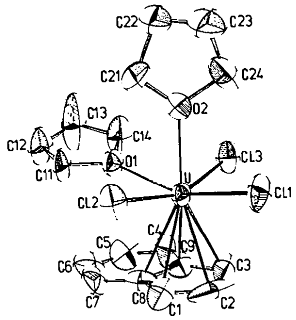

Fig. 1. The molecule of $(C_9H_7)UCl_3.(OC_4H_8)_2$.

The structure is illustrated in Fig. 1, which represents one molecule. The thermal motions of the U, Cl, C and O atoms are depicted by their 50% probability ellipsoids. To simplify the drawing H atoms are omitted.

The motion of the U atom is nearly isotropic. The C atoms exhibit large anisotropic thermal motion especially in the tetrahydrofuran molecules where their r.m.s. amplitudes of vibration along the major axes of the ellipsoids range from 0·123 to 0·668 Å.

The structure consists of discrete molecules of $(C_9H_7)UCl_3.(OC_4H_8)_2$ in which the uranium(IV) ion is octahedrally coordinated to three Cl atoms, to the five-membered-ring portion of one indenyl ligand, occupying a single coordination site, and to the O atoms of two tetrahydrofuran molecules, which occupy *cis* positions. The indenyl ligand is *trans* with respect to one H_4f molecule.

Bond distances and polyhedral edge lengths in the coordination group are reported in Table 2. The average U—Cl bond length of 2·609 (2) Å is quite close to the value of 2·638 (4) Å in UCl_4 (Taylor & Wilson, 1973) and is of the order of U—Cl distances observed in several formally ten-coordinate complexes: 2·559 (16) Å in $(C_5H_5)_3UCl$ (Wong *et al.*, 1965), 2·593 (3) Å in $U(C_9H_7)_3Cl$ (Burns & Laubereau, 1971), 2·627 (2) Å in $U(C_5H_5CH_2C_5H_4)_3Cl$ (Leong *et al.*, 1973) and 2·623 (3) Å in $(CH_3C_5H_4)UCl_3.(OC_4H_8)_2$ (Ernst *et al.*, 1979).

Examination of the U—C distances shows that the U atom is bonded in a pentahapto fashion to the five-membered ring portion of the indenyl. The two bridging carbons [C(8) and C(9)] are about 0·08 Å farther from the metal than are the remaining (non-bridging) C atoms [C(1), C(2), C(3)] in the five-

---

* Lists of structure factors, anisotropic thermal parameters, hydrogen coordinates, intramolecular bond lengths, atomic displacements from selected least-squares mean planes and shortest intramolecular and intermolecular distances, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38578 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances and polyhedral edge lengths* (Å) *in the coordination group of* $(C_9H_7)UCl_3.(OC_4H_8)_2$, *and bond angles* (°) *subtended at the* U^{IV} *atom*

Standard deviations are given in parentheses.

U–Cl(1)	2·601 (2)	Cl(1)···Cl(2)	3·749 (3)
U–Cl(2)	2·615 (2)	Cl(1)···Cl(3)	3·779 (3)
U–Cl(3)	2·612 (2)	Cl(1)···O(2)	3·251 (7)
U–O(1)	2·477 (5)	Cl(1)···Ind*	3·753 (6)
U–O(2)	2·444 (6)	Cl(2)···O(1)	3·369 (6)
U–C(1)	2·71 (1)	Cl(2)···O(2)	3·284 (6)
U–C(2)	2·705 (9)	Cl(2)···Ind*	3·883 (5)
U–C(3)	2·719 (9)	Cl(3)···O(1)	3·423 (6)
U–C(8)	2·814 (9)	Cl(3)···O(2)	3·233 (7)
U–C(9)	2·768 (7)	Cl(3)···Ind*	3·890 (5)
U–C(4)	3·701 (9)	O(1)···O(2)	3·043 (8)
U–C(5)	4·34 (1)	O(1)···Ind*	3·98 (1)
U–C(6)	4·41 (1)		
U–C(7)	3·76 (1)		
U···Ind*	2·4535 (6)		

Cl(1)–U–Cl(2)	91·90 (7)	O(1)–U–O(2)	76·4 (2)
Cl(1)–U–Cl(3)	92·92 (8)	O(1)–U–Ind	107·7 (3)
Cl(1)–U–O(2)	80·2 (2)	Cl(1)–U–O(1)	156·5 (1)
Cl(1)–U–Ind	95·8 (2)	Cl(2)–U–Cl(3)	158·57 (8)
Cl(2)–U–O(1)	82·8 (1)	O(2)–U–Ind	175·5 (2)
Cl(2)–U–O(2)	80·9 (2)		
Cl(2)–U–Ind	100·0 (3)		
Cl(3)–U–O(1)	84·5 (1)		
Cl(3)–U–O(2)	79·4 (2)		
Cl(3)–U–Ind	100·3 (3)		

* Ind denotes the intersection of the perpendicular from the U atom to the indenyl plane.

membered ring. This slight displacement of the six-membered-ring portion of the indenyl away from the metal reflects electronic factors rather than steric factors since there are no short intra- or intermolecular non-bonded contacts involving the C atoms in the 8 and 9 positions.

The U–O distances average 2·460 (5) Å, in good agreement with the corresponding average value of 2·450 (8) Å in $(CH_3C_5H_4)UCl_3.(OC_4H_8)_2$ (Ernst *et al.*, 1979). They may be interpreted as evidence of an electronic interaction between the uranium and the oxygen donor H_4f ligands which stabilizes the uranium coordination sphere.

The indenyl ring is planar to within 0·04 Å. Bond distances and angles are all normal and within the range expected for five-and six-membered conjugated ring systems (Atwood, Burns & Laubereau, 1973; Atwood, Hunter, Hrncir, Samuel, Alt & Rausch, 1975; Burns & Laubereau, 1971; Webb & Marsh, 1967).

In the tetrahydrofuran rings, all bond lengths and angles are also close to expected values (Ernst, Kennelly, Day, Day & Marks, 1979; Sekutowski, Jungst & Stucky, 1978). Cl(1), Cl(2), Cl(3) and O(1) are coplanar to within 0·038 Å. Their mean plane corresponds to the equatorial plane of the coordination group of $(C_9H_7)UCl_3.(OC_4H_8)_2$ and is within 5·5° of being parallel to that of the C_9H_7 skeleton; the U atom is displaced by 0·48 Å from this four-atom mean plane toward the indenyl ligand.

Bond angles subtended at the U atom (Table 2) show the extent of distortion from the idealized octahedral coordination geometry about the uranium. Likewise the major deviations from the idealized octahedral value of 90° result from the displacement of the uranium out of the equatorial plane and not from steric effects between the bulky ligands. Indeed the interligand contacts corresponding to polyhedral edge lengths [Cl···Cl, Cl···O, O···O (Table 2)] are all larger than the sum of the appropriate van der Waals radii (Pauling, 1960). On the other hand, as several short Cl···C and C···C intra- and intermolecular contacts are observed, the positions of the ligands and their respective orientations on the coordination sphere seem to be dictated mainly by minimization of intramolecular ligand–ligand repulsion.

References

Atwood, J. L., Burns, J. H. & Laubereau, P. G. (1973). *J. Am. Chem. Soc.* **95**, 1830–1833.

Atwood, J. L., Hains, C. F., Tsutsui, M. & Gebala, A. E. (1973). *J. Chem. Soc. Chem. Commun.* pp. 452–453.

Atwood, J. L., Hunter, W. E., Hrncir, D. C., Samuel, E., Alt, H. & Rausch, M. D. (1975). *Inorg. Chem.* **14**(8), 1757–1762.

Bombieri, G., De Paoli, G., Delpra, A. & Bagnall, K. W. (1978). *Inorg. Nucl. Chem. Lett.* **14**, 359–361.

Burns, J. H. (1974). *J. Org. Chem.* **69**, 225–233.

Burns, J. H. & Laubereau, P. G. (1971). *Inorg. Chem.* **10**, 2789–2792.

Eigenbrot, C. W. & Raymond, K. N. (1981). *Inorg. Chem.* **20** (5), 1553–1556.

Enraf–Nonius (1981). *Structure Determination Package.* Version 18. Enraf–Nonius, Delft.

Ernst, R. D., Kennelly, W. J., Day, S. C., Day, V. W. & Marks, T. J. (1979). *J. Am. Chem. Soc.* **101**(10), 2656–2664.

Fischer, R. D., Klahne, E. & Kopf, J. (1978). *Z. Naturforsch. Teil B*, **33**, 1393–1399.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Leong, J., Hodgson, K. O. & Raymond, K. N. (1973). *Inorg. Chem.* **12**(6), 1329–1335.

Pauling, L. (1960). *The Nature of the Chemical Bond,* 3rd ed. Ithaca: Cornell Univ. Press.

Perego, G., Cesari, M., Farina, F. & Lugli, G. (1975). *Gazz. Chim. Ital.* **105**, 643–646.

Perego, G., Cesari, M., Farina, F. & Lugli, G. (1976). *Acta Cryst.* B**32**, 3034–3039.

Sekutowski, D., Jungst, R. & Stucky, G. D. (1978). *Inorg. Chem.* **17** (7), 1848–1855.

Taylor, J. C. & Wilson, P. W. (1973). *Acta Cryst.* B**29**, 1942–1944.

Webb, N. C. & Marsh R. E. (1967). *Acta Cryst.* **22**, 382–387.

Wong, C. H., Yen, Y. M. & Lee, T. Y. (1965). *Acta Cryst.* **18**, 340–345.