PPh)$_2${P(OMe)$_3$}$_2$] (Richmond & Kochi, 1986). Finally, no significant steric interactions are observed within the cluster framework and the similarities between the two phosphite clusters suggest that thermodynamic product control directs the incoming [P(OEt)$_3$] groups to their respective locations.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Nicolet Instrument Corporation (1986). *SHELXTL* for Desktop 30 (Microeclipse). Report PN-269-1040340. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

PITTMAN, C. U. JR, RICHMOND, M. G., WILEMON, G. M. & ABSI-HALIBI, M. (1984). *Catalysis of Organic Reactions*, edited by J. R. KOSAK, pp. 101–128. New York: Marcel Dekker.

PITTMAN, C. U. JR & RYAN, R. C. (1978). *CHEMTECH*, pp. 170–175.

PITTMAN, C. U. JR, WILEMON, G. M., WILSON, W. D. & RYAN, R. C. (1980). *Agnew. Chem. Int. Ed. Engl.* **19**, 478–488.

RICHMOND, M. G. & KOCHI, J. K. (1986). *Inorg. Chem.* **25**, 1334–1345.

RICHMOND, M. G. & KOCHI, J. K. (1987a). *Organometallics*, **6**, 254–265.

RICHMOND, M. G. & KOCHI, J. K. (1987b). *Inorg. Chim. Acta*, **126**, 83–90.

RICHMOND, M. G., KORP, J. D. & KOCHI, J. K. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1102–1103.

RYAN, R. C. & DAHL, L. F. (1975). *J. Am. Chem. Soc.* **97**, 6904–6906.

RYAN, R. C., PITTMAN, C. U. JR & O'CONNOR, J. P. (1977). *J. Am. Chem. Soc.* **99**, 1986–1988.

RYAN, R. C., PITTMAN, C. U. JR, O'CONNOR, J. P. & DAHL, L. F. (1980). *J. Organomet. Chem.* **193**, 247–269.

WHYMAN, R. (1980). *Transition Metal Clusters*, edited by B. F. G. Johnson, pp. 564–566. New York: John Wiley.

Structure of Tris(cyclopentadienyl)uranium Bromide

BY M. R. SPIRLET*

Physique Expérimentale, B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

J. REBIZANT AND C. APOSTOLIDIS

Commission of the European Communities, J. R. C. Karlsruhe, Postfach 2340, D-7500 Karlsruhe, Federal Republic of Germany

G. D. ANDREETTI

Instituto di Strutturistica Chimica, Università di Parma, I-43100 Parma, Italy

AND B. KANELLAKOPULOS

Institut für Heisse Chemie, Kernforschungszentrum, Karlsruhe, Postfach 3640, D-7500 Karlsruhe, Federal Republic of Germany

Abstract. |U(C$_5$H$_5$)$_3$|Br, $M_r = 513.23$, monoclinic, $P2_1/n$, $a = 14.138$ (4), $b = 8.233$ (2), $c = 24.743$ (4) Å, $\beta = 90.90$ (4)°, $V = 2879$ (2) Å^3, $Z = 8$, $D_x = 2.367$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 134.180$ cm^{-1}, $F(000) = 1856$, $T = 295$ (1) K, $R = 0.023$ for 2642 observed reflections. The three cyclopentadienyl rings are η^5-covalently bonded to the uranium atom to form a distorted tetrahedron with the bromine atom. Although geometrically equivalent, |U(C$_5$H$_5$)$_3$| Br is not isostructural with |U(C$_5$H$_5$)$_3$|Cl.

Introduction. As part of our investigation on the bonding and coordination geometry in organoactinide complexes, we recently reported the structure of tris(indenyl)uranium bromide, |U(C$_9$H$_7$)$_3$|Br (Spirlet, Rebizant & Goffart, 1987). It was found to be isostructural with the corresponding chloride derivative, |U(C$_9$H$_7$)$_3$|Cl (Burns & Laubereau, 1971). Undertaking the crystal structure analysis of the title complex, we expected to verify its isomorphism with |U(C$_5$H$_5$)$_3$|Cl (Wong, Yen & Lee, 1965).

Experimental. |U(C$_5$H$_5$)$_3$|Br was prepared from uranium bromide and potassium cyclopentadienide in

---

Table 1. *Atomic positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}* or B_{iso}(Å^2)
U(1)	0·22632 (3)	0·30522 (5)	0·50453 (2)	2·762 (9)
U(2)	0·00105 (3)	0·15644 (5)	−0·23770 (2)	2·017 (8)
Br(1)	0·0766 (1)	0·2613 (3)	0·57709 (6)	6·68 (4)
Br(2)	−0·0404 (1)	0·1424 (2)	−0·12670 (6)	5·29 (4)
C(1)	0·0818 (9)	0·169 (2)	0·4463 (6)	5·0 (3)
C(2)	0·101 (1)	0·313 (2)	0·4186 (5)	5·6 (4)
C(3)	0·195 (1)	0·295 (2)	0·3969 (5)	4·7 (3)
C(4)	0·230 (1)	0·141 (2)	0·4094 (5)	5·3 (3)
C(5)	0·157 (1)	0·058 (2)	0·4407 (5)	5·2 (3)
C(6)	0·167 (1)	0·619 (2)	0·4950 (9)	10·6 (5)
C(7)	0·198 (1)	0·611 (2)	0·5444 (9)	9·6 (6)
C(8)	0·291 (1)	0·589 (2)	0·5450 (8)	7·4 (4)
C(9)	0·320 (1)	0·586 (2)	0·4922 (8)	8·8 (5)
C(10)	0·246 (2)	0·608 (2)	0·4620 (9)	13·9 (9)
C(11)	0·396 (1)	0·262 (2)	0·5564 (7)	6·5 (4)
C(12)	0·400 (1)	0·158 (2)	0·5108 (7)	7·8 (4)
C(13)	0·340 (1)	0·034 (2)	0·5176 (8)	9·2 (5)
C(14)	0·294 (1)	0·057 (2)	0·5656 (8)	9·5 (5)
C(15)	0·326 (1)	0·192 (2)	0·5901 (6)	8·6 (5)
C(16)	0·1470 (9)	0·314 (2)	−0·1863 (6)	4·8 (3)
C(17)	0·1879 (9)	0·182 (2)	−0·2110 (6)	5·6 (4)
C(18)	0·1843 (9)	0·202 (2)	−0·2628 (7)	7·0 (4)
C(19)	0·139 (1)	0·347 (2)	−0·2771 (6)	7·4 (4)
C(20)	0·1163 (9)	0·422 (2)	−0·2258 (7)	6·2 (4)
C(21)	−0·1723 (9)	0·191 (2)	−0·2860 (7)	6·7 (4)
C(22)	−0·180 (1)	0·253 (3)	−0·2385 (7)	12·5 (5)
C(23)	−0·135 (1)	0·384 (2)	−0·2350 (6)	9·3 (4)
C(24)	−0·093 (1)	0·415 (2)	−0·2816 (8)	8·4 (4)
C(25)	−0·1116 (9)	0·289 (2)	−0·3144 (5)	6·3 (4)
C(26)	0·050 (2)	−0·104 (2)	−0·2956 (8)	12·7 (6)
C(27)	−0·048 (1)	−0·114 (2)	−0·2932 (8)	9·2 (5)
C(28)	−0·074 (1)	−0·142 (2)	−0·2449 (9)	8·1 (5)
C(29)	0·003 (1)	−0·164 (2)	−0·2127 (8)	7·2 (5)
C(30)	0·081 (1)	−0·144 (2)	−0·2431 (9)	8·7 (6)

$$* B_{eq} = (4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + abcos\gamma B(1,2) + accos\beta B(1,3) + bccos\alpha B(2,3)].$$

tetrahydrofuran, as described by Fischer, von Ammon & Kanellakopulos (1970). Extraction with n-pentane followed by recrystallization from acetonitrile solution yield brown prismatic single crystals.

Selected specimen (0·30 × 0·20 × 0·20 mm) sealed in a thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated radiation. Unit cell determined from 25 reflections, $2 < 2\theta < 30°$. Space group established from systematic absences. Data collected (θ–2θ scans) in range $4° \le 2\theta \le 50°$, h 0→15, k 0→8, l −26→26, 4083 unique reflections [$I \ge 1\sigma(I)$] collected, 2642 with $I \ge 3\sigma(I)$ used in refinement. Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Lorentz–polarization and empirical absorption corrections (transmission factors range from 65·53 to 99·95%). Structure solved by direct methods and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$. Anisotropic thermal parameters for non-H atoms. A secondary-extinction coefficient refined to $g = 5·3 \times 10^{-8}$ $\{F_c = F_c/[1 + g(F_c)^2 Lp]\}$. $R = 0·023$, $wR = 0·042$, $S = 1·24$. Number of variables refined in least squares 308, final $(\Delta/\sigma)_{max} = 0·01$. H atoms included in final structure factor calculation in idealized positions with B_{iso} equal to B_{eq} of the attached C atom. Maximum and minium heights in final difference Fourier map +0·67 and −0·79 e Å^{-3}. Weighting

Table 2. *Selected bond distances (Å) and angles (°), e.s.d.'s are given in parentheses*

(a) Bond distances

U(1)–Br(1)	2·820 (2)		U(2)–Br(2)	2·819 (1)	
U(1)–C(1)	2·72 (1)		U(2)–C(16)	2·73 (1)	
U(1)–C(2)	2·75 (1)		U(2)–C(17)	2·72 (1)	
U(1)–C(3)	2·69 (1)		U(2)–C(18)	2·70 (1)	
U(1)–C(4)	2·72 (1)		U(2)–C(19)	2·70 (1)	
U(1)–C(5)	2·75 (1)		U(2)–C(20)	2·74 (1)	
U(1)–C(6)	2·73 (2)		U(2)–C(21)	2·73 (1)	
U(1)–C(7)	2·74 (2)		U(2)–C(22)	2·68 (2)	
U(1)–C(8)	2·70 (1)		U(2)–C(23)	2·69 (2)	
U(1)–C(9)	2·68 (2)		U(2)–C(24)	2·72 (1)	
U(1)–C(10)	2·72 (2)		U(2)–C(25)	2·69 (1)	
U(1)–C(11)	2·72 (1)		U(2)–C(26)	2·67 (2)	
U(1)–C(12)	2·74 (2)		U(2)–C(27)	2·70 (2)	
U(1)–C(13)	2·76 (2)		U(2)–C(28)	2·68 (2)	
U(1)–C(14)	2·71 (2)		U(2)–C(29)	2·71 (1)	
U(1)–C(15)	2·69 (1)		U(2)–C(30)	2·72 (1)	
U(1)–Cp.I*	2·44 (2)		U(2)–Cp.IV	2·45 (2)	
U(1)–Cp.II	2·46 (2)		U(2)–Cp.V	2·46 (2)	
U(1)–Cp.III	2·46 (2)		U(2)–Cp.VI	2·44 (2)	

(b) Bond angles

Br(1)–U(1)–Cp.I	99·7 (4)		Br(4)–U(2)–Cp.IV	99·6 (5)
Br(1)–U(1)–Cp.II	101 (1)		Br(2)–U(2)–Cp.V	99·8 (7)
Br(1)–U(1)–Cp.III	101·0 (8)		Br(2)–U(2)–Cp.VI	99·3 (8)
Cp.I–U(1)–Cp.II	116 (1)		Cp.IV–U(2)–Cp.V	120 (1)
Cp.I–U(1)–Cp.III	116·9 (8)		Cp.IV–U(2)–Cp.VI	117 (1)
Cp.II–U(1)–Cp.III	117 (1)		Cp.V–U(2)–Cp.VI	116 (1)

(c) Short interligand contacts

Br···C contacts (< 3·65 Å)

Br(1)···C(1)	3·33 (1)		Br(2)···C(16)	3·36 (1)
Br(1)···C(7)	3·46 (2)		Br(2)···C(22)	3·49 (3)
Br(1)···C(14)	3·52 (2)		Br(2)···C(23)	3·58 (2)
Br(1)···C(15)	3·58 (2)		Br(2)···C(29)	3·36 (2)

C···C contacts (< 3·4 Å)

C(2)···C(6)	3·28 (3)		C(17)···C(30)	3·18 (2)
C(2)···C(10)	3·35 (4)		C(18)···C(26)	3·25 (4)
C(3)···C(10)	3·12 (3)		C(18)···C(30)	3·24 (3)
C(4)···C(13)	3·20 (3)		C(19)···C(24)	3·33 (3)
C(5)···C(13)	3·20 (3)		C(21)···C(27)	3·07 (3)
C(8)···C(11)	3·08 (2)		C(21)···C(28)	3·24 (2)
C(9)···C(11)	3·27 (3)			

* Cp.I denotes centroid of cyclopentadienyl ring I, *etc.*

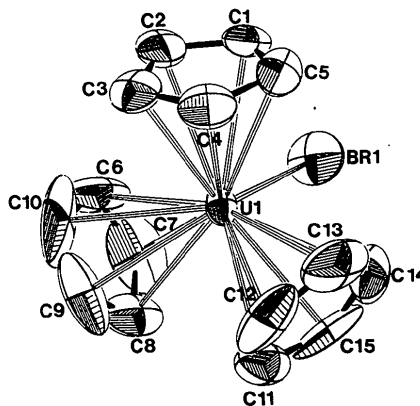Fig. 1. The molecule of [U(C$_5$H$_5$)$_3$]Br. Thermal ellipsoids are at the 50% probability level.

scheme based on counting statistics: $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (PI)^2]^{1/2}/Lp$, P (ignorance factor used to downweight intense reflections) $= 0·06$. Atomic factors and anomalous-dispersion terms from *International Tables for X-ray*

Crystallography (1974). Enraf–Nonius (1981) *SDP* programs.

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are listed in Table 2. The structure is illustrated in Fig. 1. H atoms are omitted to simplify the drawing. The structure analysis shows that the title compound is not isostructural with the corresponding chloride derivative [U(C₅H₅)₃]Cl (Wong *et al.*, 1965), although the pseudo-tetrahedral coordination geometry about the U atom is identical in the two compounds. In the [U(C₅H₅)₃]Br structure there are two crystallographically independent molecules in the asymmetric unit of the cell. These are geometrically equivalent as shown by comparison of bond distances and angles (Table 2).

The average U–C bond lengths are 2·72 (1) and 2·71 (1) Å, respectively, for the two crystallographically indepedent molecules, in agreement with the

---

* Lists of structures amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51640 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

value of 2·74 Å observed in [U(C₅H₅)₃]Cl (Wong *et al.*, 1965). The angles subtended at the U atom (Table 2) also compare favourably with the corresponding angles in the chlorine compound. The U–Br bond length is significantly longer than that observed in [U(C₉H₇)₃]Br (Spirlet *et al.*, 1987). This lengthening may result from steric hindrance on the coordination sphere of the uranium. Indeed, there are several short intramolecular Br···C distances (Table 2) in the two independent molecules. Such short contacts have not been observed in the indenide derivative.

References

BURNS, J. H. & LAUBEREAU, P. G. (1971). *Inorg. Chem.* **10**(12), 2789–2792.
Enraf–Nonius (1981). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
FISCHER, R. D., VON AMMON, R. & KANELLAKOPULOS, B. (1970). *J. Organomet. Chem.* **25**, 123–128.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
SPIRLET, M. R., REBIZANT, J. & GOFFART, J. (1987). *Acta Cryst.* C43, 354–355.
WONG, C. H., YEN, T. M. & LEE, T. Y. (1965). *Acta Cryst.* **18**, 340–345.

The Solution and Solid-State Structure of a Macrocyclic Silver(I) Complex with 6,9,12-Trioxa-3,15-dithia-21-azabicyclo[15.3.1]henicosa-1(21),17,19-triene

By George Ferguson

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Canada N1G 2W1

and Andrew Craig, David Parker and Karen E. Matthes

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

Abstract. $C_{30}H_{46}Ag_2N_2O_6S_4^{2+}.2PF_6^-$, $M_r = 1164\cdot6$, monoclinic, $P2_1/n$, $a = 23\cdot678$ (3), $b = 18\cdot721$ (4), $c = 9\cdot690$ (3) Å, $\beta = 96\cdot31$ (1)°, $V = 4269$ (2) Å³, $Z = 4$, $D_x = 1\cdot81$ g cm⁻³, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu = 12\cdot7$ cm⁻¹, $F(000) = 2336$, $T = 294$ K, $R = 0\cdot045$ for 3688 observed reflections. In the solid state the cation is dimeric, with the two Ag ions in different coordination environments. One Ag ion is bound strongly to a pyridine N atom [Ag–N 2·368 (6) Å], to three O atoms in a polyether chain [Ag–O 2·397 (6) to 2·604 (8) Å] and to one S atom [Ag–S 2·501 (3) Å]. The other S atom is directed away from the macro-cyclic cavity and is bound to the second Ag ion. This Ag ion is bound more weakly to a pyridine N atom [Ag–N 2·528 (8) Å], to three S atoms [Ag–S 2·545 (2) to 2·611 (3) Å]; there is also a weak interaction with an ether O atom [Ag–O 2·883 (7) Å]. The solution NMR data are interpreted in terms of a monomeric structure in which either the pyridine N and two S atoms are not bound simultaneously or in which the polyether chain is conformationally mobile.

Introduction. During the course of studies directed towards an examination of the binding properties of