X-Ray Crystal and Molecular Structure of $UCl_4,3Me_2SO$: Dichlorohexakis-(dimethyl sulphoxide)uranium Hexachlorouranate $[UCl_2(Me_2SO)_6][UCl_6]$

By GABRIELLA BOMBIERI
(*Laboratorio di Chimica e Technologia dei Radioelementi del C.N.R., Padova, Italy*)
and KENNETH W. BAGNALL*
(*Chemistry Department, University of Manchester, Manchester* M13 9PL)

Summary In the title compound the uranium atom in the cation is dodecahedrally co-ordinated and that in the anion is octahedrally co-ordinated.

THE u.v.–visible spectrum of $UCl_4,3Me_2SO$ in non-aqueous solvents has recently been interpreted on the basis of ionised species of the form $[UCl_3(Me_2SO)_5][UCl_5(Me_2SO)]$[1,2] or $[UCl_2(Me_2SO)_6][UCl_6]$,[2] with the latter favoured[2] on the grounds of higher lattice energy. Complexes of the type $[UCl_3(Me_2SO)_5]ClO_4$ and $[UCl_2(Me_2SO)_6](ClO_4)_2$ have also been isolated[2], but attempts to isolate salts of the type $[UCl_5L]^-$ have been unsuccessful.[3] Since spectrophotometric and conductivity data are inadequate to distinguish between the two possible structures of $UCl_4,3Me_2SO$, the structure of the solid complex has been determined. This shows the $[UCl_2L_6]^{2+}[UCl_6]^{2-}$ proposal to be correct. It can be deduced from this that the other known similar actinoid complexes of stoicheiometry MCl_43L and $MCl_42{\cdot}5L$ may also be ionic. Crystals of the compound were obtained by the published method.[4]

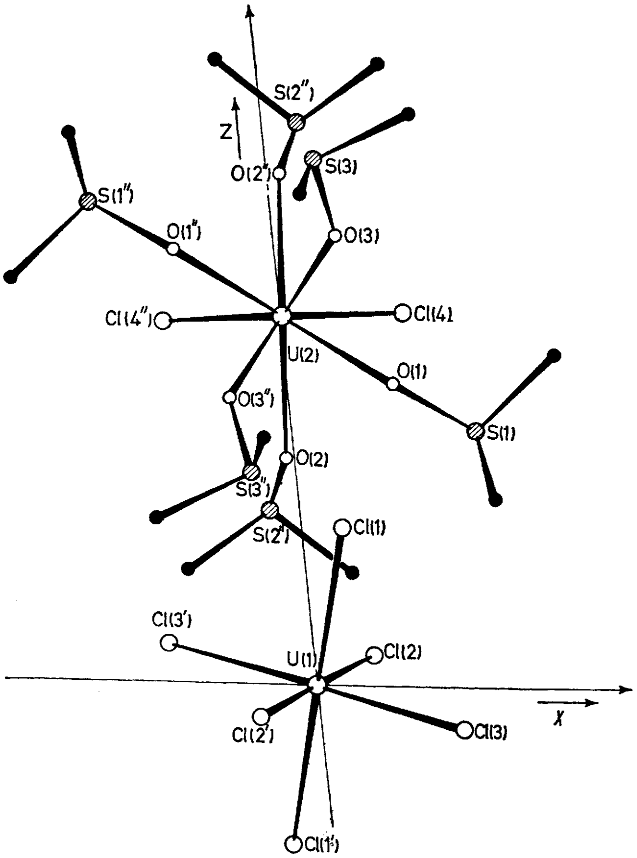

FIGURE. Structure of $[UCl_2(Me_2SO)_6][UCl_6]$. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses. Cation sphere (dodecahedron): U(2)–O(1), 2·27(4); U(2)–O(2), 2·34(4); U(2)–O(3), 2·36(4); U(2)–Cl(4), 2·70(2); O–S av. value, 1·52(5); ∠O(1)–U(2)–O(1″), 128(1); O(3)–U(2)–O(3″), 83(1); O(2)–U(2)–O(2″), 148(1); Cl(4)–U(2)–Cl(4″), 91(1), U(2)–O–S av. value 138(2). Anion sphere (octahedron): U(1)–Cl(1), 2·60(2); U(2)–Cl(2), 2·62(2); U(3)–Cl(3), 2·58(2); ∠Cl(1)–U(1)–Cl(2), 90·3(5); Cl(1)–U(1)–Cl(3), 91·1 (5); Cl(2)–U(1)–Cl(3), 89·5 (5); (key for symmetry: unprimed atoms x, y, z; primed $-x$, $1 - y$, $-z$; double primed $-x$, y, $1/2 - z$).

Crystal data: $[UCl_2(Me_2SO)_6][UCl_6]$; $M = 1228{\cdot}5$, grey-green prismatic crystals; monoclinic: $a = 12{\cdot}247(3)$, $b = 13{\cdot}670(3)$, $c = 23{\cdot}340(7)$ Å, $\beta = 95{\cdot}31°(8)$, $U = 3891{\cdot}05$ Å^3, $D_c = 2{\cdot}10$ g cm^{-3}, $Z = 4$, F (000) = 2228; space group $C2/c$, Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å).

Intensity data were collected by the ω scan method on an automated Philips PW 1100 four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation. Scan width 0·6°, scan speed 4·8° per min and two 4 s background counts were chosen. The intensities of 2380 reflections between $\theta = 3°$ and $\theta = 20°$ were collected.

The high scan speed and relatively low angle limit were used in order to minimise decomposition of the crystals under X-ray irradiation. The 1268 reflections having a net intensity greater than 3 σ (I) were used in the structure refinement [σ (I) based on counting statistics].

The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure using unitary weight factors to a conventional R factor of 0·087. Anisotropic temperature factors have been introduced for U, Cl, S, and O atoms, and the C atoms have been refined isotropically. All computations were performed on a C.D.C. 6600 computer using the 'X-RAY 70' programme system.[5]

The structure consists of the cation $[UCl_2(Me_2SO)_6]^{2+}$, which has crystallographic twofold symmetry with the uranium atom lying on the axis, and the anion $[UCl_6]^{2-}$ in which the uranium atom lies at a crystallographic inversion centre. The co-ordination geometry around the two non-equivalent uranium atoms is respectively distorted dodecahedral and octahedral.

The Figure shows the projection of the cationic and anionic units down the b axis, together with the most significant bond lengths and angles.

The average value of the U–Cl bond length in the cation, 2·70(2) Å, is significantly greater than that in the anion, 2·60(2) Å, a lengthening which could be due to the mutual repulsion of the ligands in the 8-co-ordinate cation. The bond length in the anion is close to those reported for the octahedral species UCl_4,2(tppo)[6] [2·609(4), 2·626(3)] and UCl_4,2(hmpa)[7] [2·58(1), 2·60(1) Å], whilst the longer U–Cl bond length in the cation lies between the values reported[8] for the two sets of U–Cl distances [2·638(4) and 2·869(3) Å] for the dodecahedral arrangement in UCl_4. The average U–O bond length in the cation [2·32(4) Å] is also longer than those reported for UCl_4,2(tppo)[6] and UCl_4,2(hmpa)[7] (2·24 Å).

The authors thank Professor A. Immirzi of the Istituto di Chimica delle Macromolecole C.N.R., Milano for facilities for the measurement of the intensity data on a Philips PW 1100 diffractometer and Dr. B. Whittaker (Chemistry Division, A.E.R.E., Harwell) for the crystals.

(*Received*, 15*th January* 1975; *Com.* 045.)

---

[1] P. J. Alvey, K. W. Bagnall, D. Brown, and J. Edwards, *J.C.S. Dalton*, 1973, 2308.
[2] J. G. H. du Preez and M. L. Gibson, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1795.
[3] J. G. H. du Preez, R. A. Edge, M. L. Gibson, H. E. Rohwer, and C. P. J. van Vuuren, *Inorg. Chim. Acta*, 1974, **10**, 27.
[4] K. W. Bagnall, D. Brown, D. G. Holah, and F. Lux, *J. Chem. Soc.* (*A*), 1968, 465.
[5] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-RAY 70' system, version of July 1970, University of Maryland.
[6] G. Bombieri, D. Brown, and R. Graziani, *J.C.S. Dalton*, in the press.
[7] J. F. de Wet and S. F. Darlow, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1041.
[8] J. C. Taylor and P. W. Wilson, *Acta Cryst.*, 1973, **B29**, 1942.