Notes

Crystal Structure of Pentakis(dimethyl sulphoxide-*O*)dioxouranium(VI) Bis(perchlorate) *

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The crystal structure of the title compound $[UO_2(OSMe_2)_5][ClO_4]_2$ has been determined by single-crystal *X*-ray diffraction methods at 295 K and refined by least squares to a residual of 0.064 for 1 768 ' observed ' reflections. Crystals are monoclinic, space group *Cc*, with a = 22.196(6), b = 12.140(4), c = 11.954(4) Å, β = 113.68(2)°, and Z = 4. The dioxouranium(VI) group is surrounded in the equatorial plane by five oxygen atoms from the dimethyl sulphoxide groups (mean U–O 2.38 Å).

In dioxouranium(VI) species the co-ordination sphere about the uranium atom invariably comprises a linear O=U=O moiety as its axis, with an equatorial plane comprised of the other ligating species. Where the latter consists of identical oxygen ligand atoms, we find that the maximum co-ordination number in the equatorial plane is six; those examples for which this in-plane co-ordination number has been well defined crystallographically have the common feature that the six equivalent atoms are drawn from a tris(symmetrical bidentate) situation, in which the bidentate ligand has a small ' bite ' {$Na[UO_2(O_2CMe)_3]$,[1a] $Rb[UO_2(NO_3)_3]$ (neutron-diffraction study),[1b] $[NH_4]_4[UO_2(CO_3)_3]$,[1c] and $Ba[NpO_2(O_2CMe)_3]$ [2]}.

Whilst the co-ordination of five identical oxygen-donor solvent (solv) molecules in the equatorial plane of dioxouranium(VI) has been established by n.m.r. spectroscopy for a wide range of solvents, and a number of complexes of stoicheiometry $[UO_2(solv)_5][ClO_4]_2$ have been isolated,[3] only two systems, $[UO_2\{OC(NH_2)_2\}_5][NO_3]_2$ [4] and $[UO_2(H_2O)_5][ClO_4]_2{\cdot}2H_2O$,[5] have been established structurally. In the last complex there is evidence of extensive hydrogen bonding in the solid state which may give added stability to $[UO_2(H_2O)_5]^{2+}$, whereas it has been shown that in aqueous acetone solution dioxouranium(VI) exists as $[UO_2(H_2O)_4]^{2+}$.[6-8] Thus there is no reported structural study in the solid state of a $[UO_2(solv)_5]^{2+}$ complex which is known to co-ordinate five identical oxygen-donor ligands in solution. Clearly the existence of such complexes for oxygen-donor solvents other than water in the solid state remains to be firmly established.

Dimethyl sulphoxide, Me_2SO, is an almost ubiquitous co-ordinating agent for which it has been well established that both sulphur and oxygen may act as donor sites,[9] and for which there is spectroscopic evidence that it may also, after deprotonation, act as a stable carbon-donor ligand.[10] In numerous instances, dimethyl sulphoxide ' adducts ' of metal salts are readily isolated as stable crystalline solids which are highly convenient sources of the anhydrous metal ion in preparations.[9,11,12] These and other complexes have been widely used in detailed kinetic and mechanistic studies of metal-ion substitution processes [3,12-15] and have been the basis of an examination of co-ordination stereochemistry in the lanthanoid series.[16,17] Although it seems that oxygen co-ordination is generally preferred over sulphur co-ordination [12,18,‡] and, in fact, is the only co-ordination mode known for the lanthanoid ions,[16] no structural data unambiguously establishing the mode of co-ordination to an actinoid ion have yet been reported.

Since the solid adduct formed with dioxouranium(VI), isolated as the perchlorate, has the stoicheiometry $[UO_2(OSMe_2)_5][ClO_4]_2$, and since the n.m.r. evidence is indicative of five-co-ordination of the solvent oxygen atoms in the equatorial plane in dimethyl sulphoxide solution, it seemed appropriate to carry out a single-crystal structure determination in order to establish the co-ordination number and mode of co-ordination. The preparation of the complex is described in the literature.[6]

Experimental

Crystallography.—General details are given in ref. 19.

Crystal data. $[UO_2(OSMe_2)_5][ClO_4]_2$, $C_{10}H_{30}Cl_2O_{15}S_5U$, M = 849.6, Monoclinic, space group *Cc* (C_s^4, no. 9), a = 22.196(6), b = 12.140(4), c = 11.954(4) Å, β = 113.68(2)°, U = 2 950(2) Å^3, D_m = 1.89(1), Z = 4, D_c = 1.91 g cm^{-3}, $F(000)$ = 1 664, prism size 0.28 × 0.23 × 0.18 mm, μ_{Mo} = 58 cm^{-1}, $2\theta_{max.}$ = 50°, N = 2 616, N_o = 1 768, R = 0.064, R' = 0.076.

Abnormal features. Solution of this structure presented considerable difficulty because of the location of the uranium atom at a position of the type $(\frac{1}{4}, y, \frac{1}{4})$. The data were eventually successfully phased by progressive introduction of sulphur atoms into the refinement. Refinement proceeded employing anisotropic thermal parameters for uranium and sulphur atoms, with ' symmetry-related ' parameters blocked together; no hydrogen atoms were considered.

The material slowly degrades in the atmosphere and the specimen employed was enclosed in a capillary.

Discussion

The unit-cell contents are shown in projection down b (Figure 1); the structure determination defines the stoicheiometry and mode of co-ordination as that of $[UO_2(OSMe_2)_5][ClO_4]_2$, the dimethyl sulphoxide acting as a donor ligand. As noted above, the unit-cell array very closely approximates

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* *Supplementary data available* (No. SUP 23433, 13 pp.): thermal parameters, anion and ligand geometries, structure-factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ Even with Hg^{II}, well known to interact strongly with S-donor ligands, Me_2SO is bound *via* O.

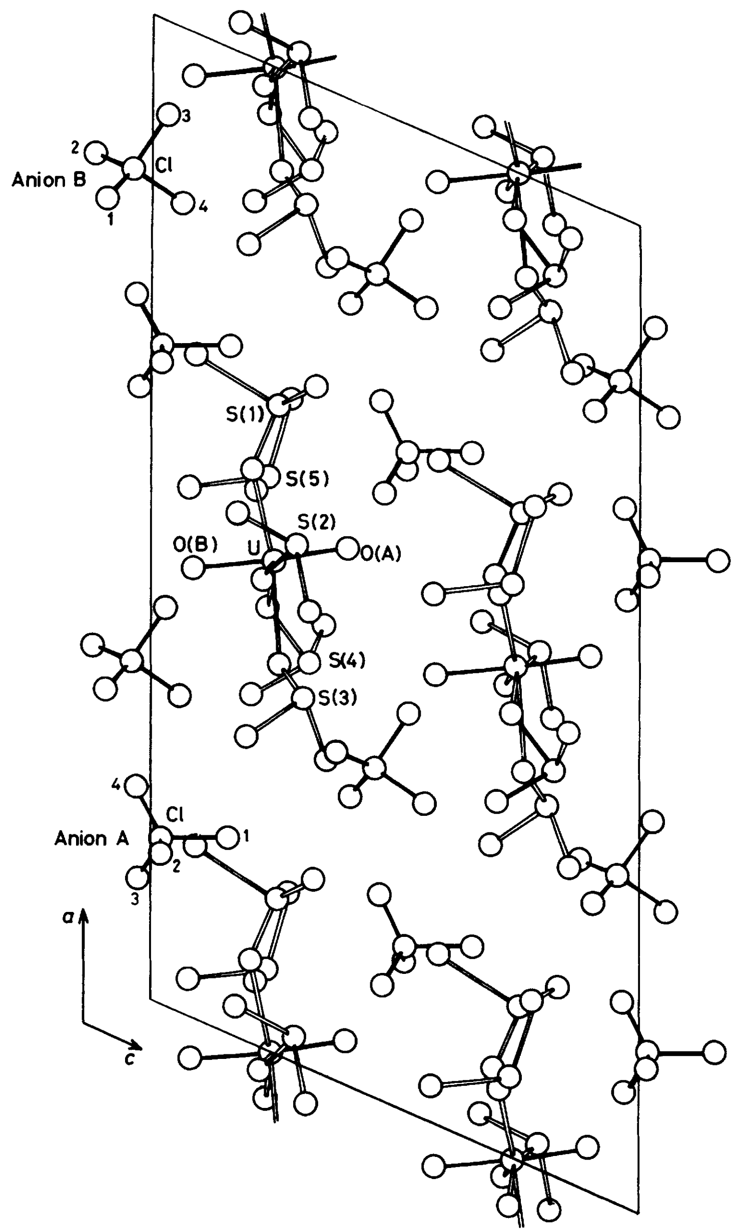

Figure 1. Unit-cell contents of $[UO_2(OSMe_2)_5][ClO_4]_2$ projected down *b*

to $C2/c$ in symmetry, the only major perturbation of this, and of a local point symmetry of 2 for the cation, being the five-fold co-ordination array of dimethyl sulphoxide ligands in the equatorial plane. In consequence of the pseudo-symmetry and consequent refinement problems, the precision of the geometrical parameters is less than might reasonably otherwise be expected. Thus we note that the light-atom geometries cannot be considered to differ notably from their usual values; likewise the irregularities in the uranium co-ordination sphere cannot be considered significant (see Figure 2 and Tables 1 and 2).

Of those dioxouranium(VI) species with six oxygen atoms co-ordinated in the equatorial plane, the most precisely defined are the tricarbonate (mean U–O 2.45 Å) and the trinitrate (mean U–O 2.48 Å),[1] both of which have three bidentate ligands. In species with five unidentate median ligands we find $U–OH_2$ to be 2.4_5,[5] 2.436(8),[20] and 2.46(2) Å,[21] while $U–OC(NH_2)_2$ is 2.3_6 [21] and 2.38 Å [4] and $U–OCHN(CH_2)_5$ is 2.38_7 Å,[20] more nearly comparable with the present mean value of 2.3_8 Å, suggesting that urea, *N*-formylpiperidine, and dimethyl sulphoxide may be more strongly bound than water. For the (in-plane) four-co-ordinate system $[UO_2\{O=P(NMe_2)_3\}_4]^{2+}$, mean $U–OP(NMe_2)_3$ is 2.27 Å. The above results thus suggest a systematic shortening of the equatorial metal–oxygen distance as the co-ordination number diminishes, but superimposed on this effect is another relating bond length to donor strength.

The tendency of $(Me_2N)_3PO$ for four-co-ordination in the equatorial plane relative to five-co-ordination for Me_2SO is presumably a reflection of size and/or donor stability. A convenient measure of the latter is the Gutmann donor number [22] which is 38.8 for $(Me_2N)_3PO$ and 29.8 for the (smaller) Me_2SO. A larger bond length for water *vis-à-vis* Me_2SO may be further understood in terms of a donor number of 18 (in spite of its

Table 1. Atomic co-ordinates for the complex $[UO_2(OSMe_2)_5][ClO_4]_2$

Atom	*x*	*y*	*z*
(*a*) Cation			
Dioxouranium(VI)			
U	0.500 000(—)	0.046 11(7)	0.250 00(—)
O(A)	0.545(2)	0.046(2)	0.403(3)
O(B)	0.457(2)	0.046(2)	0.086(3)
Ligand 1			
O	0.583(1)	0.146(2)	0.207(2)
S	0.658 8(4)	0.103 3(9)	0.260 1(1)
C(A)	0.695(2)	0.234(9)	0.338(3)
C(B)	0.675(2)	0.113(4)	0.093(4)
Ligand 2			
O	0.477(1)	0.238(2)	0.227(2)
S	0.526 6(4)	0.327 8(7)	0.299 0(8)
C(A)	0.464(2)	0.404(4)	0.325(4)
C(B)	0.532(3)	0.431(4)	0.180(5)
Ligand 3			
O	0.398(1)	0.073(2)	0.267(2)
S	0.374 9(4)	0.168 2(9)	0.316 0(10)
C(A)	0.309(2)	0.234(3)	0.198(3)
C(B)	0.321(2)	0.098(3)	0.361(3)
Ligand 4			
O	0.451(1)	−0.131(3)	0.241(3)
S	0.413 1(7)	−0.170 2(11)	0.327 1(11)
C(A)	0.457(3)	−0.298(5)	0.358(5)
C(B)	0.355(3)	−0.271(4)	0.211(4)
Ligand 5			
O	0.565(2)	−0.090(3)	0.217(3)
S	0.582 5(5)	−0.209 5(9)	0.241 9(12)
C(A)	0.670(2)	−0.214(3)	0.286(3)
C(B)	0.538(2)	−0.261(3)	0.080(4)
(*b*) Anion A			
Cl	0.168 4(4)	0.971 1(6)	0.022 6(7)
O(1)	0.198(3)	0.950(3)	0.161(4)
O(2)	0.151(2)	1.083(4)	0.021(4)
O(3)	0.117(2)	0.900(3)	−0.025(3)
O(4)	0.209(2)	0.965(3)	−0.029(4)
(*c*) Anion B			
Cl	0.834 9(5)	0.027 5(10)	−0.040 0(12)
O(1)	0.795(2)	0.111(4)	−0.092(4)
O(2)	0.835(3)	−0.064(4)	−0.118(5)
O(3)	0.905(2)	0.052(3)	0.031(4)
O(4)	0.822(3)	−0.031(4)	0.063(5)

Table 2. Uranium environment. *r* Is the U–O distance in Å; the other entries in the matrix are the angles (°) subtended at U by the oxygen in question

	r	O(B)	O(1)	O(2)	O(3)	O(4)	O(5)
O(A)	1.70(3)	176(2)	93(2)	98(1)	95(2)	96(1)	92(1)
O(B)	1.81(4)		83(2)	83(1)	89(2)	85(1)	85(1)
O(1)	2.43(2)			68(1)	141(1)	144(1)	75(1)
O(2)	2.38(2)				73(1)	143(1)	143(1)
O(3)	2.38(3)					72(1)	142(1)
O(4)	2.39(3)						70(1)
O(5)	2.33(4)						

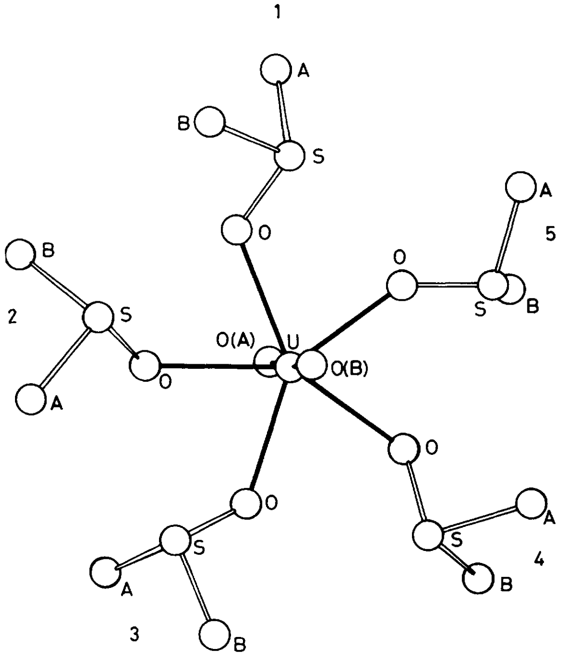

Figure 2. A projection of a single $[UO_2(OSMe_2)_5]^{2+}$ cation

small size), although later authors have suggested that a more probable value is 33.[23]

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Received 1*st March* 1982; *Paper* 2/365