Crystal and Molecular Structure of Uranyl Diperchlorate Heptahydrate

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The crystal and molecular structure of uranyl diperchlorate heptahydrate, $UO_2[ClO_4]_2 \cdot 7H_2O$, has been determined by single-crystal *X*-ray methods. The crystals are orthorhombic, space group $Pca2_1$, with unit-cell dimensions a = 9.302(4), b = 14.692(6), and c = 10.842(5) Å, Z = 4. 493 Reflections have been measured by a diffractometer and the structure solved by heavy-atom methods to R 0.046. The crystal contains $[UO_2(OH_2)_5]^{2+}$, $2[ClO_4]^-$, and $2H_2O$ in each asymmetric unit, held together by hydrogen bonds. The uranium has pentagonal-bipyramidal co-ordination with U–O(uranyl) of 1.71 Å (average), U–O(aqua) of 2.45 Å (average), and O · · · O contacts of 2.88 Å.

ALTHOUGH the structures of a number of uranyl complexes have been determined in recent years,[1] very few have identical unidentate ligands. In particular, the structure of the simple hydrated uranyl ion is unknown. This can only be examined in salts with anions of low co-ordinating power as, for example, $[NO_3]^-$ is co-ordinated to $[UO_2]^{2+}$ in preference to water, in aqueous solution and in the crystal.[2] The perchlorate salt is suitable, and the structure of hydrated $UO_2[ClO_4]_2$ (1) is reported here.

EXPERIMENTAL

The perchlorate (1) was obtained commercially as a slurry of crystals and solution. Suitable crystals were obtained by treating the complex on a vacuum line to remove most of the water, giving yellow crystals of irregular shape. Prolonged evaporation *in vacuo* produced a yellow powder. The crystals were deliquescent, and were mounted in a Lindemann glass capillary in a dry-box. No density measurements were made because of experimental difficulties.

Crystal Data.—$H_{14}Cl_2O_{17}U$, Orthorhombic, a = 9.302(4), b = 14.692(6), c = 10.842(5) Å, U = 1 481.7 Å^3, M = 594.9, D_c = 2.75 g cm^{-3}; Mo-K_α radiation, λ = 0.710 7 Å.

Data were collected with a Syntex $P2_1$ four-circle diffractometer in the θ—2θ mode with a graphite monochromator. Accurate cell constants were obtained by means of least-squares calculations based on the reflecting positions of 15 high-angle reflections. The maximum 2θ value was limited to 50° for the first 832 reflections and then increased to 55°. Of 1 118 reflections, 493 had $I > 2\sigma(I)$. Variable scan rates were employed, depending on the

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[1] L. Cattalini, U. Croatto, S. Degetto, and E. Tondello, *Inorg. Chim. Acta Rev.*, 1971, **5**, 19.

[2] J. C. Taylor and M. H. Mueller, *Acta Cryst.*, 1965, **19**, 536.

intensity of a pre-scan. For the first 832 reflections the speed varied between 1 and 29.3° min^{-1} in 2θ, and for the rest the minimum rate was 1.5° min^{-1}. Three standard reflections were measured at intervals of 100 reflections. Despite all the precautions taken against trace amounts of moisture, the crystal had a limited lifetime, and suddenly ceased to diffract. However, only a few high-order reflections were lost, most of which would probably have been classified as unobserved. No previous decomposition was observed and a rescaling of intensities was unnecessary.

TABLE 1

Atomic co-ordinates (× 10^3) and isotropic and anisotropic (× 10^3) * temperature factors, with standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	252.1(3)	251.5(5)	0	27.2(6)	33(1)	20.6(5)	5(2)	0(2)	−2(2)
Cl(1)	780.5	390.6	232.8	7(6)	23(12)	2(7)	6(4)	−13(6)	−1(5)
Cl(2)	706.8	110.3	261.8	260(48)	119(38)	126(38)	−114(37)	53(38)	−46(33)

Atom	x	y	z	U	Atom	x	y	z	U
O(1)	214(8)	210(4)	−134(7)	119(31)	O(11)	760.5	378.6	354.9	58(18)
O(2)	264(3)	329(2)	128(2)	7(7)	O(12)	872.6	320.9	186.8	69(18)
O(3)	47(3)	177(2)	85(3)	5(7)	O(13)	644.9	385.6	172.0	132(35)
O(4)	348(3)	129(3)	114(3)	15(8)	O(14)	843.9	477.2	210.2	92(25)
O(5)	518(3)	264(3)	−13(5)	26(9)	O(21)	715.6	117.8	130.9	72(22)
O(6)	314(5)	396(4)	−111(5)	53(16)	O(22)	830.2	151.2	316.3	147(38)
O(7)	27(7)	342(5)	−56(6)	103(24)	O(23)	580.6	155.5	304.3	153(39)
O(8)	504(4)	497(3)	515(3)	19(1)	O(24)	700.5	16.7	295.7	101(27)
O(9)	523(6)	7(3)	11(4)	42(17)					

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

The data were corrected for Lorentz and polarisation effects. An absorption correction was also applied (μ 138.7 cm^{-1}) at a late stage, but this yielded a significantly higher R factor and was therefore omitted. The reason for this may be the irregular shape of the crystal (a block *ca.* 0.03 cm in each direction) and the presence of mother liquor in the tube, and the consequent uncertainty in the determination of the faces.

Apparent systematic absences, $0kl$ ($l \neq 2n$), $h0l$ ($h \neq 2n$), and $hk0$ ($h + k \neq 2n$), indicated space group *Pcan* (no. 60 *Pbcn* rotated) with the uranium atom at a centre of symmetry. Structure solution in this space group by heavy-atom methods gave the relatively low R of 0.085, but the structure was obviously wrong with unreasonable bond lengths and angles. Program RLIST, which calculates R for groups of reflections, revealed that the weak reflections with l, $h + k$ and $h + k + l$ odd had very poor agreement between observed and calculated values, corresponding to R of *ca.* 0.5.

Thus other space groups were examined. The conditions for absences in group *Pcan* were relaxed, one at a time, to give 11 possible orthorhombic space groups. All of these were examined, and trial structures were set up based on the U and one Cl position as in *Pcan*; these were refined as far as possible and the same R-factor test was applied. Only for $Pca2_1$ did satisfactory values result, and this was therefore selected as the correct space group. The uranium-atom position deviates only slightly from $\frac{1}{4},\frac{1}{4},0$, which corresponds to the centre of symmetry position in *Pcan*. The lighter atoms were found from Fourier maps. There was some trouble in locating the perchlorate oxygens, and the distances and angles in the perchlorate groups showed great variations, no doubt because of thermal motion. These groups were therefore held fixed as regular tetrahedra, with Cl–O of 1.425 Å. The 'hand' of the crystal examined was found at a late stage by calculating with both + and − values. The accepted set gave a slightly lower R and substantially less spread in the U–O(1) and U–O(2) distances. Final full-matrix least-squares refinement with unit weights and with anisotropic temperature factors for the uranium and chlorine atoms gave an overall final R of 0.046, with satisfactory figures for the groups of weak reflections, and a final difference-Fourier synthesis showed no significant features. However, it should be noted that some of the light-atom positions have fairly high standard deviations.

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses

U–O(1)	1.62(7)	O(1)–U–O(2)	161(3)
U–O(2)	1.80(3)	O(1)–U–O(3)	90(3)
U–O(3)	2.35(4)	O(1)–U–O(4)	105(3)
U–O(4)	2.38(3)	O(1)–U–O(5)	101(3)
U–O(5)	2.48(2)	O(1)–U–O(6)	87(3)
U–O(6)	2.51(6)	O(1)–U–O(7)	79(3)
U–O(7)	2.55(6)	O(2)–U–O(3)	93(1)
O(1) · · · O(3)	2.88(8)	O(2)–U–O(4)	93(1)
O(1) · · · O(4)	3.19(8)	O(2)–U–O(5)	86(2)
O(1) · · · O(5)	3.22(8)	O(2)–U–O(6)	79(2)
O(1) · · · O(6)	2.91(9)	O(2)–U–O(7)	84(2)
O(1) · · · O(7)	2.74(10)	O(3)–U–O(4)	75(1)
O(2) · · · O(3)	3.05(4)	O(4)–U–O(5)	73(1)
O(2) · · · O(4)	3.05(5)	O(5)–U–O(6)	71(2)
O(2) · · · O(5)	2.97(5)	O(6)–U–O(7)	71(2)
O(2) · · · O(6)	2.80(6)	O(7)–U–O(3)	69(2)
O(2) · · · O(7)	3.00(7)		
O(3) · · · O(4)	2.89(4)		
O(4) · · · O(5)	2.88(6)		
O(5) · · · O(6)	2.92(7)		
O(6) · · · O(7)	2.85(8)		
O(7) · · · O(3)	2.87(8)		

TABLE 3

Equations of least-squares plane and line in orthogonal (Å) co-ordinates. Deviations (Å) are given in square brackets

Plane: U, O(3), O(4), O(5), O(6), O(7)

$$0.043\,9X + 0.533\,6Y + 0.844\,6Z = 2.16$$

[U 0.09, O(3) −0.05, O(4) 0.01, O(5) 0.01, O(6) −0.03, O(7) −0.03]

Line: U, O(1), O(2)

Direction cosines −0.141 6, −0.530 8, −0.835 6

[U 0.18, O(1) 0.09, O(2) 0.08]

Angle between plane normal and line: 5.6°

TABLE 4

Hydrogen-bonding interactions; lengths (Å) and angles (°) with standard deviations in parentheses. Symmetry transformations refer to the second atom listed. For atoms O(11)—O(24) only errors due to individual atoms are included

O(3)H · · · O(9) $(y - \frac{1}{2}, -x, z)$	2.82(6)	O(3)H · · · O(12) $(x - 1, y, z)$	2.89(3)	U–O(3)–O(9) U–O(3)–O(12) O(9)–O(3)–O(12)	113(2) 105(1) 140(2)
O(4)H · · · O(9)	2.67(6)	O(4)H · · · O(23)	3.01(3)	U–O(4)–O(9) U–O(4)–O(23) O(9)–O(4)–O(23)	122(2) 122(2) 86(1)
O(5)H · · · O(13)	2.93(5)	O(5)H · · · O(22) $(1\frac{1}{2} - x, y, z - \frac{1}{2})$	2.86(5)	U–O(5)–O(13) U–O(5)–O(22) O(13)–O(5)–O(22)	114(2) 119(2) 127(1)
O(6)H · · · O(8) $(1 - x, 1 - y, z - \frac{1}{2})$	2.68(6)	O(6)H · · · O(14) $(1 - x, 1 - y, z - \frac{1}{2})$	3.06(5)	U–O(6)–O(8) U–O(6)–O(14) O(8)–O(6)–O(14)	113(2) 135(2) 106(2)
O(7)H · · · O(8) $(\frac{1}{2} - x, y, z - \frac{1}{2})$	2.42(8)	O(7)H · · · O(12) $(x - 1, y, z)$	3.01(7)	U–O(7)–O(8) U–O(7)–O(12) O(8)–O(7)–O(12)	121(3) 98(2) 76(2)
O(8) · · · HO(6) O(8) · · · HO(7) } as above		O(8)H · · · O(13) $(\frac{1}{2} - x, y, \frac{1}{2} + z)$ O(8)H · · · O(14) $(1 - x, 1 - y, \frac{1}{2} + z)$	2.80(4) 2.56(3)	O(6)–O(8)–O(7) O(6)–O(8)–O(13) O(6)–O(8)–O(14) O(7)–O(8)–O(13) O(7)–O(8)–O(14) O(13)–O(8)–O(14)	118(2) 105(2) 98(2) 136(2) 103(2) 80(1)
O(9) · · · HO(3) O(9) · · · HO(4) } as above		O(9)H · · · O(21) O(9)H · · · O(24) $(1 - x, y, z - \frac{1}{2})$	2.74(5) 3.14(5)	O(3)–O(9)–O(4) O(3)–O(9)–O(21) O(3)–O(9)–O(24) O(4)–O(9)–O(21) O(4)–O(9)–O(24) O(21)–O(9)–O(24)	125(2) 112(2) 99(2) 78(1) 89(2) 148(2)

The atomic scattering-factor curves used were taken from ref. 3, using the analytical expressions. Those for uranium and chlorine were corrected for anomalous dispersion, using $\Delta f'$ and $\Delta f''$ values from ref. 3. Apart from the local initial processing program, all the computing was made with the '*X*-RAY' and '*X*-RAY '76' systems.[4] The final co-ordinates and temperature factors are in Table 1, bond lengths and angles in Table 2, and equations of least-squares planes in Table 3. Final structure factors are listed in Supplementary Publication No. SUP 22002 (5 pp., 1 microfiche).*

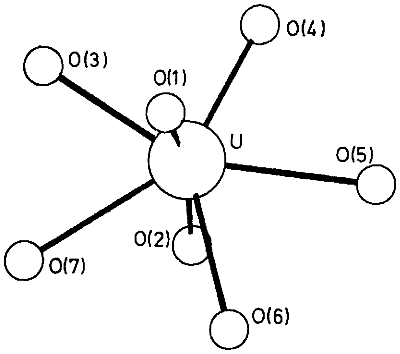

FIGURE 1 The $[UO_2(OH_2)_5]^{2+}$ ion showing the atomic numbering

DISCUSSION

The crystals contain discrete $[UO_2(OH_2)_5]^{2+}$ and $[ClO_4]^-$ ions, and the determination shows the presence of two molecules of water of solvation per uranium atom. This is unexpected, because the original preparation of the material[5] gave the formula $UO_2[ClO_4]_2\cdot6H_2O$; the error is certainly the result of the crystals both being deliquescent and losing water readily. The phase reported[5] to be formed at 80 °C with loss of two molecules of water is no doubt $[UO_2(OH_2)_5][ClO_4]_2$, rather than the supposed tetrahydrate.

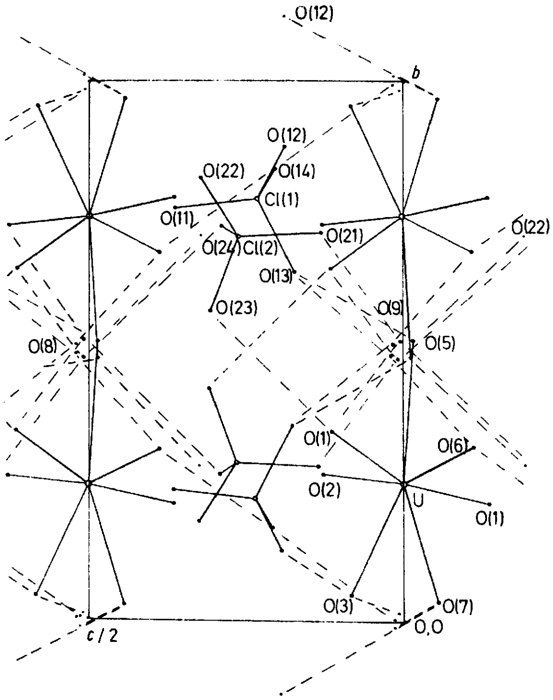

FIGURE 2 Packing diagram for $[UO_2(OH_2)_5][ClO_4]_2\cdot2H_2O$. Hydrogen bonds are shown as broken lines

The cation (Figure 1) has the characteristic pentagonal-bipyramidal geometry found for uranyl complexes if the

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* See Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[3] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[4] J. M. Stewart, Technical Report TR 192, University of Maryland, 1972, and unpublished work.

[5] R. Salvadori, *Chem.-Ztg.*, 1912, **36**, 513.

ligands do not include any chelating groups with short 'bites.' There are deviations from regularity in the lengths of the U–O (uranyl) bonds, in the O–U–O (uranyl) angle, in the inclination of the UO_2 group to the equatorial plane, and in the variable U–O(aqua) distances. Some of these may be due to different degrees of hydrogen bonding, but the fairly low quality of the data suggests that the averaged dimensions give the most reliable view of the complex, with U–O(uranyl) 1.71 Å and U–O(aqua) of 2.45 Å. This is quite similar to the results of the much more accurate study by neutron diffraction of the $[UO_2\{OC(NH_2)_2\}_4(OH_2)]^{2+}$ ion.[6] This ion again comprises a uranyl group with unidentate ligands only, arranged in a pentagon, and it has U–O(uranyl) of 1.78(2), U–O(urea) of 2.36(1), and U–O(aqua) of 2.46(2) Å (averaged distances). The controlling factor in all these complexes seems to be the non-bonded O · · · O contacts.[7] In $[UO_2(OH_2)_5]^{2+}$, these average 2.88 Å, slightly larger than in the urea complex, in agreement with the evidence from the U–O distances that the effective radius of the urea-oxygen atom is slightly smaller than that of the aqua-oxygen atoms. It is clear from many other examples [1,7] that 2.6—2.8 Å represents the minimum possible O · · · O contact distance, and it thus follows that $[UO_2(OH_2)_5]^{2+}$ has the maximum possible hydration number. The distances O(uranyl)–O(aqua) average 2.98 Å in the hydrate, again close to the expected contact distance.

The crystal is held together by an extensive network of hydrogen bonds (Figure 2, Table 4), with both crystal water molecules forming four bonds and each of the ligand water molecules forming two bonds; seven of the eight perchlorate oxygen atoms are also involved, although several of their interactions are long, consistent with their high thermal motion. There is a very short approach between O(7) and O(8) which probably does not indicate a strong hydrogen bond, but rather is due either to the effect of thermal motion or to the data quality.

We thank the S.R.C. for the award of a grant for the diffractometer (to N. W. A.).

[6/1691 *Received, 6th September, 1976*]

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[6] N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1972, **11**, 1840.

[7] N. W. Alcock, *J.C.S. Dalton*, 1973, 1616.