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On the Crystal Structure of a Tetranuclear Hydroxo Complex of Uranyl(VI)

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Hydrolyzed aqueous solutions of uranyl(VI) chloride have been found to contain polynuclear complexes.[1] X-Ray diffraction studies on such solutions have shown that the dominating species are probably dinuclear and triangular trinuclear complexes.[2] Crystals containing a dinuclear complex can easily be prepared from solutions with $0.3 \lesssim$ bound $OH/U \lesssim 1.0$. The crystal structure of this compound, $[(UO_2)_2(OH)_2Cl_2(H_2O)_4]$, has been solved.[3] An attempt to isolate the trinuclear complex from solutions with nearly maximum degree of hydrolysis (bound $OH/U \approx 1.0$ for $[UO_2^{2+}]_{total} = 3.1$ M) for a structure determination has resulted in the formation of crystals containing a tetranuclear complex. Tetranuclear hydroxo complexes are most probably present in rather small amounts even in strongly hydrolyzed solutions. It has, however, been considered worthwhile to carry out a complete crystal structure determination of this compound to clarify how the polynuclear complexes are formed.

The crystals have the composition $[(UO_2)_4O_2(OH)_2Cl_2(H_2O)_6].xH_2O$, where x is probably equal to four. The symmetry is monoclinic and the space group is No. 14: $P2_1/n$. The unit cell contains two formula units and has the dimensions: $a = 11.645$ Å, $b = 10.101$ Å, $c = 10.206$ Å ($3\sigma = 0.004$ Å) and $\beta = 105.77°$ ($3\sigma = 0.04°$). The calculated density is 3.91 g/cm³.

Using the multiple film technique, Weissenberg photographs were taken around the b axis ($h0l$ to $h8l$) and around the c axis ($hk0$) with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Intensities were estimated visually by comparison with a calibrated intensity scale and were corrected for Lorentz and polarization factors and for absorption. The number of observed reflections was 1633. Approximate positions of the uranium atoms were found from the Patterson projections $P(u,0,w)$ and $P(u,v,0)$. The eight uranium atoms in a unit cell occupy two of the general fourfold positions, $\pm(x,y,z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$; in space group $P2_1/n$. The parameters of the uranium atoms were refined in a least squares procedure using the three-dimensional data without absorption correction The positions of the light atoms were found from an electron density map based on $F_{obs} - F_{calc}^{U}$. The least squares refinement of the parameters of all atoms gave an R-value of 0.184 without absorption correction and 0.152 with absorption correction. Individual scale factors for the nine layers and isotropic temperature factors for all atoms were also refined. The positional and thermal parameters at this stage of the crystal structure determination are given in Table 1.

The structure of the tetramer is shown in Fig. 1. The four uranium atoms lie at the corners of two coplanar, approximately equilateral triangles sharing one edge. Each uranyl group is surrounded by one chlorine and four oxygen atoms exactly as in the dinuclear complex.[3] In the

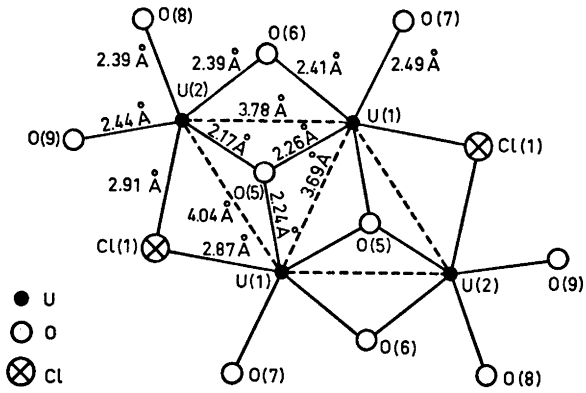

Fig. 1. Structure of the tetramer. All atoms lie approximately in the same plane. The uranyl oxygen atoms [O(1), O(2), O(3), and O(4)] are not shown. The linear O—U—O group is perpendicular to the plane.

Table 1. Positional and thermal parameters based on data collected around the *b* axis. The positional parameters given belong to atoms in the same tetramer. Standard deviations are given in parentheses. All atoms are in the positions 4(*e*) ($\pm(x,y,z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$;) in space group No. 14: $P2_1/n$.

Atom	*x*	*y*	*z*	*B*
U(1)	0.1233(2)	0.0600(2)	0.6423(2)	1.97(5)
U(2)	0.1133(2)	0.1362(2)	0.2513(2)	2.19(6)
Cl(1)	0.273(2)	0.209(2)	0.514(2)	3.8(3)
O(1)	0.037(3)	0.209(4)	0.658(4)	4.1(7)
O(2)	0.221(3)	−0.080(4)	0.635(3)	3.7(5)
O(3)	0.065(4)	0.298(4)	0.251(4)	5.1(7)
O(4)	0.180(6)	−0.026(7)	0.234(6)	3.7(1.3)
O(5)	0.043(4)	0.063(5)	0.414(5)	1.2(1.0)
O(6)	0.075(5)	−0.029(6)	0.840(5)	2.2(1.0)
O(7)	0.289(5)	0.143(5)	0.835(5)	4.7(1.0)
O(8)	0.062(5)	0.150(6)	0.009(6)	2.4(1.2)
O(9)	0.299(5)	0.219(6)	0.214(6)	4.5(1.1)

dinuclear complex, the uranium atoms are joined through a double OH bridge. In the tetranuclear complex, however, the oxygen atoms inside the quadrangle are most probably O atoms and the oxygen atoms coordinated to only two uranium atoms are most probably OH oxygen atoms. The chlorine atoms are shared between two uranium atoms. Thus the tetranuclear complex contains one double O bridge, two O/OH bridges and two O/Cl bridges giving three unequal U—U distances with lengths around 4 Å. The whole tetranuclear group is uncharged and the discrete groups in the structure are probably held together by hydrogen bonds in which water molecules of crystallization also take part.

A full report on this structure determination will be published when three-dimensional data around the *c* axis have been collected and the whole data set has been analyzed.

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