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The Crystal Structure of $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6].4H_2O$, a Compound Containing a Tetranuclear Aquachlorohydroxooxo Complex of Uranyl(VI)

MÄRTHA ÅBERG

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

The title compound crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 11.645(1)$ Å, $b = 10.101(1)$ Å, $c = 10.206(1)$ Å, $\beta = 105.77(1)°$, and $Z = 2$. The crystal structure determination was based on 1900 independent reflections collected by the Weissenberg multiple film method. The structural parameters were refined by least squares methods to a conventional R value of 0.12.

The structure is built up from discrete uncharged molecules containing four U atoms at the corners of two approximately coplanar equilateral triangles sharing one edge. Each uranyl group is surrounded by one Cl and four O atoms, the uranium coordination polyhedron being a pentagonal bipyramid. The four U atoms are linked through double bridges of three types: one double O bridge, two HO/O bridges, and two Cl/O bridges. The corresponding U–U distances are 3.693(2), 3.787(2), and 4.036(2) Å, respectively. The mean bond lengths are: U–O(uranyl) = 1.77 Å, U–O(oxo) = 2.23 Å, U–O(aqua or hydroxo) = 2.42 Å, and U–Cl = 2.89 Å.

Hydrolysis of aqueous uranyl salt solutions leads to the formation of polynuclear complexes. Different suggestions have been made as to the compositions of these complexes.[1] Most investigators seem to agree that the dinuclear complex $(UO_2)_2(OH)_2^{2+}$ is present in all solutions regardless of the ionic medium. Additional complexes have also been suggested, *e.g.*, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^{+}$, and $(UO_2)_4(OH)_6^{2+}$.

Clarification of the structures involved in the hydrolysis was carried out using X-ray diffraction studies of concentrated hydrolyzed and acidic uranyl(VI) chloride solutions.[2] The results indicate that the predominant species are dinuclear and triangular trinuclear complexes. Two solid phases have been isolated as single crystals from the hydrolyzed solutions. Knowledge of the structures of these phases, especially the coordination of the uranyl group and the type of bridging between the U atoms in the polynuclear complexes, has been valuable for the interpretation of the X-ray scattering data from the solutions. The crystal structure of $[(UO_2)_2Cl_2(OH)_2(H_2O)_4]$, containing a dinuclear aquachlorohydroxo complex of uranyl(VI), has been reported.[3] The crystal structure of the second phase, built up from tetranuclear aquachlorohydroxooxo uranyl(VI) complexes and previously published in a short communication,[4] will be fully described in the present paper.

EXPERIMENTAL

Preparation of crystals. One of the uranyl(VI) chloride solutions studied by X-ray diffraction was hydrolyzed to the maximum extent (bound HO/U = 1.11 for [U(VI)] = 3.1 M). When this solution crystallized, small amounts of a new phase were obtained in addition to large quantities of the already known compound $[(UO_2)_2Cl_2(OH)_2(H_2O)_4]$.[3] The separation of the two phases was possible as the new one was found to be insoluble in ethanol.

Analysis. A weighed amount of the compound was dissolved in hydrochloric acid of known concentration. The uranium content was determined by precipitation with 8-hydroxyquinoline.[5] The amount of chloride was obtained by passing a portion of the solution through an H^+-saturated cation exchanger and titrating the eluate (dilute HCl) with standardized NaOH. The density of the crystals was cal-

culated from the apparent loss of weight in benzene. Found: UO_3 80.4; HCl 5.0; H_2O 14.6 (difference). Calc. for $(UO_3)_4(HCl)_2(H_2O)_{10}$: UO_3 81.9; HCl 5.2; H_2O 12.9.

From a preliminary structure determination it was known that some of the water molecules were not coordinated to U. An attempt to determine this part of the water content was made by heating the substance at 105 °C to constant weight. The weight loss was 5.1 %. The theoretical value was 1.3 % per water molecule in $(UO_3)_4(HCl)_2(H_2O)_{10}$.

After the heating the crystals were soluble in pyridine-methanol, and a Karl Fischer titration [6] was carried out to estimate the total number of non-uranyl O atoms, *i.e.*, O^{2-} and HO^- as well as water O atoms. The titrations gave an average value of 2.6 such O atoms per uranyl group. Thus the crystals with the stoichiometric composition $(UO_3)_4(HCl)_2(H_2O)_{10}$ have four water molecules of crystallization and ten uranyl-coordinated O atoms in each formula unit. It will be shown that the crystal structure determination indicates that the formula should be written as $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6].4H_2O$.

Crystal data. Weissenberg photographs taken around *b* and *c* showed that the symmetry was monoclinic. Systematically absent reflections were $h0l$ for $h+l=2n+1$ and $0k0$ for $k=2n+1$. This is characteristic of the space group $P2_1/n$.

Values of the lattice parameters were obtained by a least squares refinement (unit weights) using the line positions on a powder photograph taken in a Guinier focusing camera. Cu$K\alpha_1$ radiation ($\lambda=1.54051$ Å) was used with KCl as internal standard ($a=6.2929$ Å at 25 °C). Crystal data for $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6].4H_2O$ are:

a = 11.645(1) Å	Z = 2
b = 10.101(1) Å	D_m = 4.02(2) g cm^{-3}
c = 10.206(1) Å	D_x = 4.02 g cm^{-3}
β = 105.77(1)°	μ(Cu$K\alpha$) = 871 cm^{-1}
V = 1155.3 Å^3	Space group $P2_1/n$ (No.14)

Intensity data. Intensity data were collected in a Weissenberg camera with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). Photographs were taken around *b* ($h0l$ to $h8l$) and *c* ($hk0$ to $hk8$) using the multiple film technique. Intensities were estimated visually by comparison with a calibrated intensity scale and were corrected for Lorentz and polarization factors as well as for absorption, but not for secondary extinction effects. About 1650 and 1850 independent reflections were collected around *b* and *c*, respectively.

The crystals used were roughly prismatic *c* with the maximum dimensions (along a^*, *b*, and *c*) 0.060 mm × 0.054 mm × 0.176 mm ($V=2.28\times10^{-4}$ mm^3) for the data taken around *b*, and 0.153 mm × 0.124 mm × 0.166 mm ($V=1.14\times10^{-3}$ mm^3) for the data taken around *c*. The number of faces needed to describe the shapes of the crystals was 14 and 8, respectively. The maximum ratio between the calculated transmission factors, A_{max}/A_{min}, was approximately 10.

Computer programs. The following programs, written or modified for a CDC 3600 computer and briefly described previously,[3] were used for the calculations: CELSIUS, DATAP2, DRF, LALS, DISTAN, PLANE (called PLNJO on IBM 370/155 in Uppsala).

For IBM 360/75 modified versions of DRF, LALS, and DISTAN (B. G. Brandt and A. G. Nord, Stockholm, Sweden) were also used.

Two additional programs were used on IBM 360/75: LIST, Listing of structure factor data. Written by I. Carlbom and modified by A. G. Nord, Stockholm, Sweden; ORTEP2, Thermal-ellipsoid plot program for crystal structure illustrations. Written by C. K. Johnson, ORNL, USA and modified for IBM 360/75 and a CALCOMP 835 micro film plotter by A. G. Nord and B. G. Brandt, Stockholm, Sweden.

STRUCTURE DETERMINATION

Patterson maps $P(u,p,w)$ and $P(u,v,p)$ showed that the eight U atoms in the unit cell must 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 the space group $P2_1/n$. Two possible sets of parameter values for the U atoms were deduced, and one of these led to a reasonably low conventional R value (0.22).

The positions for all light atoms coordinated to U were found from a subsequent difference map. Least squares refinement of the parameters of all atoms gave an R value of 0.184 before and 0.152 after absorption corrections had been applied to the data taken around *b*. Individual scale factors and isotropic temperature factors were included in the refinement. A further least squares refinement series using an overall scale factor and anisotropic temperature factors for the U atoms lowered R to 0.143.

The data taken around *c* were treated similarly, and the following R values were obtained: 0.211 before and 0.185 after absorption corrections, and 0.167 when the overall scale factor and anisotropic temperature factors for U had been refined. The two sets of data were then analyzed simultaneously in a new series of refinements to an R value of 0.163.

Table 1. Final positional parameters and isotropic thermal parameters (Å²) in the form exp $[-8\pi^2 U(\sin^2\theta/\lambda^2)]$. The positional parameters given are referred to atoms in the same tetranuclear complex. The other half of the complex is obtained from the centre of symmetry at $(0,0,\frac{1}{2})$. O(10) and O(11) are oxygen atoms in water molecules of crystallization.

Atom	x	y	z	U
U(1)	0.12337(12)	0.06018(13)	0.64236(14)	
U(2)	0.11325(13)	0.13620(13)	0.25114(15)	
Cl(1)	0.2735(11)	0.2085(12)	0.5136(13)	0.052(3)
O(1)	0.0414(37)	0.1968(41)	0.6598(44)	0.066(10)
O(2)	0.2187(30)	−0.0772(33)	0.6326(36)	0.050(8)
O(3)	0.0632(38)	0.2929(42)	0.2644(45)	0.069(10)
O(4)	0.1799(32)	−0.0246(38)	0.2315(39)	0.058(9)
O(5)	0.0426(21)	0.0630(22)	0.4147(26)	0.027(5)
O(6)	0.0788(21)	−0.0283(24)	0.8392(26)	0.029(5)
O(7)	0.2839(40)	0.1400(43)	0.8282(48)	0.073(11)
O(8)	0.0675(28)	0.1582(31)	0.0085(34)	0.046(7)
O(9)	0.3026(40)	0.2097(46)	0.2102(47)	0.076(11)
O(10)	0.4501(45)	−0.0810(49)	0.5847(54)	0.083(13)
O(11)	0.0636(81)	0.5313(92)	0.4366(91)	0.16(3)

Table 2. Final anisotropic thermal parameters (Å²) in the form exp $[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)	0.0364(8)	0.0291(7)	0.0292(8)	−0.0059(10)	0.0172(11)	−0.0015(10)
U(2)	0.0430(9)	0.0272(7)	0.0328(8)	−0.0056(10)	0.0301(13)	−0.0032(10)

On comparing the two sets of F_o's with each other and with F_c, it was noticed that the intensities of some weak reflections were overestimated by more than 100 %. Such reflections were discarded when they had been observed on only one film and for just one setting. It was also noticed that the intensities of some reflections at $\sin\theta/\lambda$ values > 0.6 Å^{-1} were underestimated by more than 100 %, mainly due to spot deformation which was not corrected for in this region. These reflections were also discarded. For all other reflections the arithmetic mean of F_o for the two settings was taken. Thus 1900 independent reflections out of 2100 remained. These were used in a least squares refinement of the positional and thermal parameters of the 12 atoms (two U, one Cl, and nine O atoms). An overall scale factor and anisotropic temperature factors for the U atoms were included, and the R value dropped to 0.132. A new difference map was calculated, and two peaks there could be interpreted as the water molecules of crystallization. The positional and thermal parameters of all the 14 atoms were then refined, and an R value of 0.129 was obtained. In a final series of least squares refinements 21 strong low order reflections assumed to be affected by secondary extinction were given zero weight. R then dropped to 0.120. In the last cycle all parameter shifts were less than 0.1 % of the calculated standard deviations. A final difference map was then calculated. No peaks there were larger than about 4 electrons Å^{-3}. None of the residual peaks could be interpreted as remaining O atoms owing to improbable O – U, O – Cl, or O – O distances.

The final parameter values are given in Tables 1 and 2. A listing of the observed and calculated structure factors is available from the author on request.

The scattering factors used were those given by Cromer and Waber [7] for neutral atoms. The real part of the anomalous dispersion correc-

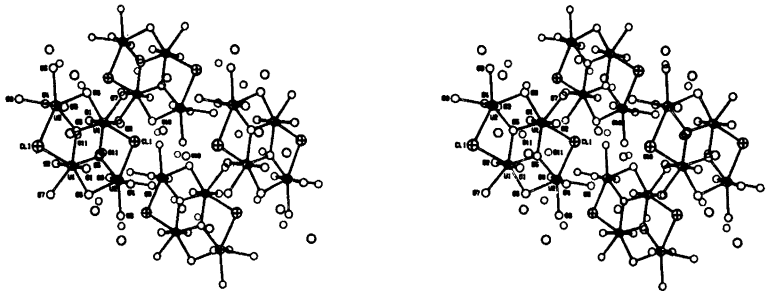

Fig. 1. Stereoscopic perspective projection of the structure parallel to the *b* axis.

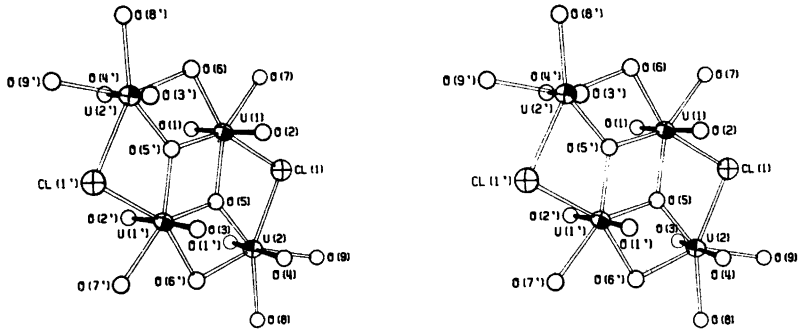

Fig. 2. Stereoscopic perspective picture of one tetranuclear complex as viewed parallel to the *b* axis. The numbering of the atoms is shown. The molecule has a centre of symmetry. The thermal ellipsoids for U(1), U(2), Cl(1), O(5), and O(6) are scaled to include 50 % probability. For the other atoms $U = 0.025$ Å^2 has been chosen arbitrarily for clarity.

tions for U and Cl, according to Cromer,[8] was included. The weighting scheme for the refinements was that suggested by Hughes.[9] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $\sqrt{w} = 1$ for $|F_o| \leq 72$ and $\sqrt{w} = 72/|F_o|$ for $|F_o| \geq 72$.

DESCRIPTION OF THE STRUCTURE

A stereoscopic perspective projection of the structure parallel to the *b* axis of the unit cell is shown in Fig. 1. The structure may be regarded as being built up from discrete tetranuclear complexes, one of which is drawn separately in Fig. 2. Some important distances and angles within a tetranuclear complex are given in Table 3.

Each U atom in a tetranuclear complex is surrounded by one Cl and six O atoms at the vertices of a pentagonal bipyramid. The coordination of U is thus similar to that found in the dinuclear complex $[(UO_2)_2Cl_2(OH)_2(H_2O)_4]$.[3]

Two O atoms, O(5) and O(5′), are shared between three U atoms and they are probably O^{2-} oxygens. Two O atoms, O(6) and O(6′), are shared between two U atoms and are probably HO^- oxygens. The Cl atoms, Cl(1) and Cl(1′), are also shared between two U atoms. The remaining O atoms are coordinated to only one U atom: O(7), O(7′), O(8), O(8′), O(9), O(9′) as water O atoms and O(1), O(1′), O(2), O(2′), O(3), O(3′), O(4), O(4′) as uranyl O atoms. Thus the formula of the tetranuclear complex can be written as $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]$.

The U atoms are joined through bridges of three types. Between U(1) and U(1′) there is a double O bridge with a U–U distance of 3.693 Å. U(1) and U(2′) as well as U(1′) and U(2) are joined through an HO/O bridge with a U–U distance of 3.787 Å. Between U(1)

Table 3. Some important interatomic distances (Å) and angles (°). An atom marked with a prime (′) is related by the centre of symmetry at $(0,0,\frac{1}{2})$ to the corresponding atom without the prime (Table 1).

U(1)–U(1′)	3.693(2)		
U(1)–U(2)	4.036(2)		
U(1)–U(2′)	3.787(2)	U(2)–U(2′)	6.902(2)
U(1)–Cl(1)	2.88(1)	U(2)–Cl(1)	2.91(1)
U(1)–O(1)	1.72(4)	U(2)–O(3)	1.71(4)
U(1)–O(2)	1.80(3)	U(2)–O(4)	1.84(4)
U(1)–O(5)	2.26(2)	U(2)–O(5)	2.18(2)
U(1)–O(5′)	2.24(2)	U(2)–O(6′)	2.43(2)
U(1)–O(6)	2.38(2)	U(2)–O(8)	2.40(3)
U(1)–O(7)	2.41(4)	U(2)–O(9)	2.47(4)
Cl(1)–O(1)	3.43(4)		
Cl(1)–O(2)	3.26(3)		
Cl(1)–O(3)	3.13(4)		
Cl(1)–O(4)	3.65(4)		
Cl(1)–O(5)	2.99(2)		
Cl(1)–O(7)	3.25(5)		
Cl(1)–O(9)	3.21(5)		
O(1)–O(5)	2.85(5)	O(3)–O(5)	2.83(5)
O(1)–O(5′)	2.83(5)	O(3)–O(6′)	3.17(5)
O(1)–O(6)	2.88(5)	O(3)–O(8)	2.96(6)
O(1)–O(7)	2.94(6)	O(3)–O(9)	3.10(6)
O(2)–O(5)	2.95(4)	O(4)–O(5)	2.91(4)
O(2)–O(5′)	2.95(4)	O(4)–O(6′)	2.95(4)
O(2)–O(6)	3.03(4)	O(4)–O(8)	2.95(5)
O(2)–O(7)	2.92(6)	O(4)–O(9)	2.80(6)
O(5)–O(5′)	2.56(5)	O(6)–O(7)	2.96(5)
O(5)–O(6′)	2.62(4)	O(6)–O(8′)	2.91(4)
O(8)–O(9)	2.99(6)		
Cl(1)–U(1)–O(5)	70.0(6)	Cl(1)–U(2)–O(5)	70.2(7)
O(5)–U(1)–O(5′)	70(1)	O(5)–U(2)–O(6′)	68.8(9)
O(5′)–U(1)–O(6)	68.9(9)	O(6′)–U(2)–O(8)	74(1)
O(6)–U(1)–O(7)	76(1)	O(8)–U(2)–O(9)	76(1)
O(7)–U(1)–Cl(1)	75(1)	O(9)–U(2)–Cl(1)	73(1)
O(1)–U(1)–O(2)	176(2)	O(3)–U(2)–O(4)	174(2)
U(1)–O(5)–U(1′)	110(1)		
U(1′)–O(5)–U(2)	118(1)		
U(2)–O(5)–U(1)	131(1)		

and U(2) as well as between U(1′) and U(2′) there is a Cl/O bridge with a U–U distance of 4.036 Å. In the dinuclear complex, where the U atoms are joined through a double HO bridge, the U–U distance is 3.944 Å.

The shortest U–O bond lengths are naturally those within the uranyl group. They vary from 1.71 to 1.84 Å but do not differ significantly from the average value 1.77 Å. In the dinuclear complex the mean U–O bond length within the uranyl group is 1.79 Å. The angles O(1)–U(1)–O(2) and O(3)–U(2)–O(4) are 176 and 174°, respectively. The deviation from 180° is not significant.

The U–O bond lengths within the bridges formed by O(5) and O(5′) are 2.18, 2.24 and 2.26 Å with an average value of 2.23 Å. The remaining U–O bond lengths within the pentagonal bipyramids vary from 2.38 to 2.47 Å, mean value 2.42 Å, with no significant difference between O(6) (HO^-) on the one hand and O(7), O(8), and O(9) (H_2O) on the other hand.

Table 4. Least squares planes $Ax+By+Cz+D=0$. For each plane values of A, B, C, and D are given, and, within square brackets, deviations (Å) of atoms from the planes.

Plane 1: 6.254, −8.514, −1.816, 0.908
[U(1) 0.001(2), U(1′) −0.001(2), U(2) 0.001(2), U(2′) −0.001(2), Cl(1) −0.09(1), Cl(1′) 0.09(1), O(5) −0.12(2), O(5′) 0.12(2), O(6) 0.12(2), O(6′) −0.12(2), O(7) −0.01(4), O(7′) 0.01(4), O(8) −0.03(3), O(8′) 0.03(3), O(9) 0.63(5), O(9′) −0.63(5)]

Plane 2: 6.507, −8.351, −2.191, 1.107
[U(1) −0.001(2), Cl(1) 0.02(1), O(5) −0.05(2), O(5′) 0.07(2), O(6) 0.02(2), O(7) −0.03(5)]

Plane 3: −5.586, 8.860, 1.104, −0.852
[U(2) −0.001(2), Cl(1) 0.04(1), O(5) −0.07(2), O(6′) 0.02(2), O(8) 0.18(3), O(9) −0.45(5)]

Plane 4: −9.580, −4.858, −0.696, 1.921
[U(1) 0.001(2), U(2) 0.001(2), O(1) 0.11(4), O(2) −0.24(4), O(3) −0.29(5), O(4) 0.16(4)]

The angles between the planes are: 2.4° (1 and 2), 5.0° (1 and 3), 88.5° (1 and 4), 7.4° (2 and 3), 87.6° (2 and 4), 88.8° (3 and 4).

The U−Cl bond lengths are 2.88 and 2.91 Å. The average value 2.89 Å is greater than the U−Cl bond length of 2.75 Å in the dinuclear complex. In the dinuclear complex, however, the Cl atoms are coordinated to only one U atom.

The four pentagonal bipyramids in a tetranuclear complex are linked together by sharing edges. The U(1) bipyramid shares the edge Cl(1)−O(5) of 2.99 Å with the U(2) bipyramid, the edge O(5)−O(5′) of 2.56 Å with the U(1′) bipyramid, and the edge O(5′)−O(6) of 2.62 Å with the U(2′) bipyramid. The U(2) bipyramid shares only two edges with neighbouring bipyramids: Cl(1)−O(5) with U(1) and O(5)−O(6′) with U(1′).

The pentagons around the uranyl groups are roughly planar. The degree of planarity has been tested by fitting least squares planes to selected atoms within a $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]$ molecule. The results are shown in Table 4. Four least squares planes have been tried: (1) through all four pentagons U(1), U(1′), U(2), and U(2′), (2) through the U(1) pentagon, (3) through the U(2) pentagon, and (4) through the uranyl groups of U(1) and U(2). The weights which have been used are based on the calculated standard deviations of the positional parameters in Table 1. The largest deviations from the least squares planes occur for atom O(9) (planes 1 and 3 in Table 4). The angles between the planes have also been calculated, and they are given in Table 4. Here the largest deviation from the expected values 0 or 90° occurs for the angle between the planes through the U(1) and U(2) pentagons.

As all the Cl atoms are included in the uncharged tetranuclear complex, only hydrogen and van der Waals bonds hold the different complexes together. The water molecules of crystallization, O(10) and O(11), situated in the holes of the structure, are most probably an important part of the hydrogen bond system. Several intermolecular O−O distances are short enough to be hydrogen bond distances (Table 5). However, a more detailed discussion is not meaningful due to the comparatively high standard deviations, especially for distances involving O(11).

Table 5. Short (<3 Å) intermolecular oxygen-oxygen distances (Å). The symmetry codes are: $(\frac{1}{2}-x,\frac{1}{2}+y-1,\frac{1}{2}-z+1)$ (*a*); $(\frac{1}{2}-x,\frac{1}{2}+y-1,\frac{1}{2}-z)$ (*b*); $(x,y,z-1)$ (*c*); $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ (*d*); $(-x+1,-y,-z+1)$ (*e*); $(-x,-y+1,-z+1)$ (*f*).

O(2)−O(7*a*)	2.88(5)	O(7)−O(11*a*)	2.79(10)
O(2)−O(10)	2.87(6)	O(8)−O(10*d*)	2.79(6)
O(3)−O(11)	2.98(10)	O(10)−O(10*e*)	2.85(10)
O(4)−O(9*b*)	2.74(6)	O(11)−O(11*f*)	2.31(18)
O(6)−O(8*c*)	2.58(4)		

DISCUSSION

The peak of O(11), about 4 electrons Å^{-3}, is indistinguishable from the background peaks in the difference Fourier map calculated with F_c based on all the atoms except O(10) and O(11). The atom O(10), however, is easily located, even in the difference map where the F_c values are calculated from the U atom positions only. Its peak height does not differ from those of the O atoms coordinated to U. The standard deviations of the atomic parameters of O(10) are only slightly higher than those of the coordinated water oxygens O(7) and O(9). The uncertainty in the position of O(11) has not been considered too important, as the main purpose of the structure determination has been to establish unambiguously the arrangement of atoms within the tetranuclear complex. The high temperature factor of O(11) might indicate an occupation number < 1.0 (statistically distributed water molecules).

As already mentioned, the structures of the dinuclear and the tetranuclear complexes are closely related. They are built up from pentagonal bipyramids, UO_2ClO_4, sharing edges. The uncharged polynuclear complexes are linked to each other through hydrogen bonds and van der Waals forces. Differences in U – Cl and in some U – O bond lengths have been noticed. They are explained by the different types of bridges between the U atoms in the two complexes.

The structure of $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]4H_2O$ is also closely related to that of $Cs_x(UO_2)OCl_x$ ($x \approx 0.9$).[10] This compound is built up from double chains with Cl/O bridges along the chain direction and double O bridges holding the two chains together. Each uranyl group is surrounded by three O and two Cl atoms and has four U neighbours, two at 3.704 Å and two at 4.118 Å. These U – U distances are in good agreement with those obtained in the present work. The arrangement of U atoms at the corners of two approximately equilateral triangles sharing one edge can be recognized as a building element of the double chain in $Cs_x(UO_2)OCl_x$. One O atom inside each triangle is also found, and the Cl atoms act as bridges between the U atoms.

Precise emf titrations covering a broad uranyl(VI) concentration range have been carried out in this institute using many different ionic media.[1] The percentage of uranium bound in the different hydrolysis complexes as a function of n_{HO} (= bound HO/U) is dependent on the ionic medium. In, *e.g.*, 3 M (Mg)ClO_4 the maximum value of n_{HO} is 0.55 for the highest uranyl(VI) concentration studied (1.2 M).[11] Then 51 % of the total amount of uranium in the solution is bound in dinuclear complexes and only 6 % in higher complexes. In 3 M (Na)Cl the maximum total uranyl(VI) concentration has been 0.080 M.[12] For that concentration about 10, 70, and 14 % of the total uranium amount is bound in dinuclear, trinuclear, and tetranuclear complexes, respectively, at the maximum degree of hydrolysis, $n_{HO} = 1.26$. Provided the stability constants are valid also for a 3.1 M uranyl(VI) chloride solution, the corresponding values are 15, 63, and 7 % for $n_{HO} = 1.11$, *i.e.*, for the solution used to prepare crystals of $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6].4H_2O$. Thus it seems that although the emf titration results indicate that trinuclear complexes are by far predominating in strongly hydrolyzed uranyl(VI) chloride solutions, tetranuclear, and above all dinuclear complexes, are more easily crystallized. An anion like Cl^- can be coordinated to one U atom as in $[(UO_2)_2Cl_2(OH)_2(H_2O)_4]$ or, probably more important, bridge two U atoms as in $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]$, and its presence can probably explain why trinuclear complexes are much more stable in hydrolyzed uranyl(VI) chloride than in perchlorate solutions.

On analyzing the X-ray scattering data from hydrolyzed uranyl(VI) chloride solutions, it was suggested that the trinuclear complex was built up from three U atoms joined through double HO/O bridges and with one Cl atom coordinated to each uranyl group.[2] Now, on the basis of the knowledge of the structure of the tetranuclear complex, it seems more likely to assume a structure with double HO(O) or Cl/HO(O) bridges between the U atoms. The average Cl/U ratio and the positions of the Cl atoms cannot be given unambiguously. But if the U – U distances are the same in the trinuclear complex in solution as in the tetranuclear complex in the solid, the average U – U distance of 3.86 Å obtained by analysis of the X-ray scattering data indicates that, on an average, the trinuclear complexes do not contain more than one Cl/HO(O) bridge.

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REFERENCES

1. Sillén, L. G. and Martell, A. (compilers) *Stability Constants of Metal-Ion Complexes*, Chem. Soc. Spec. Publ. No. 17 (1964); Suppl. No. 1, Spec. Publ. No. 25 (1971).
2. Åberg, M. *Acta Chem. Scand. 24* (1970) 2901.
3. Åberg, M. *Acta Chem. Scand. 23* (1969) 791.
4. Åberg, M. *Acta Chem. Scand. 25* (1971) 368.
5. Hecht, F. and Donau, J. *Anorganische Mikrogewichtsanalyse*, Springer, Wien 1940, p. 205.
6. Fischer, K. *Angew. Chem. 48* (1935) 394.
7. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
8. Cromer, D. T. *Acta Crystallogr. 18* (1965) 17.
9. Hughes, E. W. *J. Am. Chem. Soc. 63* (1941) 1737.
10. Allpress, J. G. and Wadsley, A. D. *Acta Crystallogr. 17* (1964) 41.
11. Hietanen, S., Row, B. R. L. and Sillén, L. G. *Acta Chem. Scand. 17* (1963) 2735.
12. Dunsmore, H. S. and Sillén, L. G. *Acta Chem. Scand. 17* (1963) 2657.

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