

# The Crystal Structure of Hexaaqua-tri- $\mu$ -hydroxo- $\mu_3$ -oxo-triuranyl(VI) Nitrate Tetrahydrate, $[(\text{UO}_2)_3\text{O}(\text{OH})_3(\text{H}_2\text{O})_6]\text{NO}_3 \cdot 4\text{H}_2\text{O}$

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The title compound crystallizes in the triclinic space group  $P\bar{1}$  (No. 2) with  $a=8.026(2)$  Å,  $b=11.276(2)$  Å,  $c=12.346(4)$  Å,  $\alpha=109.65(2)^\circ$ ,  $\beta=99.39(2)^\circ$ ,  $\gamma=88.62(2)^\circ$ , and  $Z=2$ . The crystal structure determination was based on 2513 independent reflections collected with a computer-controlled Syntex P2<sub>1</sub> four-circle diffractometer. The structural parameters were refined by least squares methods to a conventional  $R$  value of 0.074.

The structure is built up from hexaaqua-tri-hydroxo-oxo-triuranyl(VI) ions, nitrate ions, and water molecules of crystallization. The three U atoms form an equilateral triangle with an average U–U distance of 3.809 Å. They are linked through double bridges containing one O atom and one HO group. Each uranyl group is surrounded by five O atoms at the corners of an irregular planar pentagon. The mean bond lengths are: U–O (uranyl) = 1.78 Å, U–O(oxo) = 2.21 Å, and U–O (aqua or hydroxo) = 2.44 Å.

Polynuclear complexes are formed when aqueous uranyl(VI) salt solutions are hydrolyzed.<sup>1</sup> According to, e.g., emf data, a dinuclear complex is predominant in all ionic media, but tri- and tetranuclear complexes are also of importance, at least in more strongly hydrolyzed solutions.<sup>1</sup> X-Ray diffraction investigations of concentrated hydrolyzed and acidic uranyl(VI) chloride solutions indicate that dinuclear and triangular trinuclear complexes are the predominant species.<sup>2</sup> From the hydrolyzed solutions two different solid phases have been crystallized. One of these phases is built up from dinuclear<sup>3</sup> and the second phase from tetranuclear uranyl(VI) complexes.<sup>4</sup> On studying the system  $\text{UO}_3 - \text{HCl} - \text{H}_2\text{O}$  at 25 °C Prins and Cordfunke<sup>5</sup> found a third meta-

stable hydrolyzed solid phase, of which it has not been possible to obtain crystals by evaporation at room temperature. In the system  $\text{UO}_2(\text{NO}_3)_2 - \text{UO}_3 - \text{H}_2\text{O}$  at 25 °C one hydrolyzed phase,  $\text{UO}_2(\text{NO}_3)_2 \cdot 5\text{UO}_3 \cdot 25\text{H}_2\text{O}$ , has been found.<sup>6</sup> This compound is metastable, but crystals can easily be prepared. As  $n_{\text{HO}}$  (bound HO/U) = 5/3 for this solid as compared to 1 for the dinuclear and 3/2 for the tetranuclear hydrolyzed complex in the  $\text{UO}_3 - \text{HCl} - \text{H}_2\text{O}$  system, a crystal structure determination has been carried out.

## EXPERIMENTAL

*Preparation of crystals.* According to the phase diagram<sup>6</sup> the hydrolyzed solid nitrate is in equilibrium with a solution with the mol ratio  $1.4 < \text{NO}_3^-/\text{UO}_2^{2+} < 1.5$ . Amorphous ("active")  $\text{UO}_3$ <sup>7</sup> was dissolved in an aqueous solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (*p.a.*) until  $\text{NO}_3^-/\text{UO}_2^{2+} = 1.45$ . From this solution prismatic crystals were obtained by evaporation at room temperature.

*Analysis.* A powder photograph was taken in a Guinier focusing camera using  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54051$  Å). The diffraction pattern was found to be identical to that reported by Woodhead *et al.*<sup>8</sup> for a polynuclear uranyl(VI) nitrate with the suggested formula  $[(\text{UO}_2)_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}\text{H}_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Obviously the empirical formula is the same as that found by Cordfunke for the hydrolyzed nitrate in the  $\text{UO}_2(\text{NO}_3)_2 - \text{UO}_3 - \text{H}_2\text{O}$  system.<sup>6</sup>

The density of the crystals was determined by benzene displacement to  $3.50(4)$  g cm<sup>-3</sup>. Woodhead *et al.*<sup>8</sup> obtained a value of  $3.65$  g cm<sup>-3</sup>. The calculated density is  $3.64$  g cm<sup>-3</sup> for  $[(\text{UO}_2)_3\text{O}(\text{OH})_3(\text{H}_2\text{O})_6]\text{NO}_3 \cdot 5\text{H}_2\text{O}$  and  $3.58$  g cm<sup>-3</sup> for the tetrahydrate. The present density determination does not

give any clear indication whether there are five or four water molecules of crystallization. But when the crystal structure was solved only four were found.

*X-Ray data collection.* The intensity data were collected with a computer-controlled Syntex P2<sub>1</sub> four-circle diffractometer using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). The lattice parameters and the orientation matrix were determined as described previously using 16 reflections from an oscillation photograph.<sup>9</sup>

Crystal data for [(UO<sub>2</sub>)<sub>3</sub>O(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>3</sub>NO<sub>3</sub>·4H<sub>2</sub>O are:

$a = 8.026(2)$ Å	$V = 1037.6(5)$ Å <sup>3</sup>
$b = 11.276(2)$ Å	$Z = 2$
$c = 12.346(4)$ Å	$D_m = 3.50(4)$ g cm <sup>-3</sup>
$\alpha = 109.65(2)^\circ$	$D_x = 3.58$ g cm <sup>-3</sup>
$\beta = 99.39(2)^\circ$	$\mu(\text{MoK}\alpha) = 222.2$ cm <sup>-1</sup>
$\gamma = 88.62(2)^\circ$	Space group $P\bar{1}$ (No. 2)

The  $\omega$  scan mode was used for the intensity data collection. The scan speed was variable, but most reflections were so weak that they were measured with the minimum scan speed of  $2^\circ \text{ min}^{-1}$ . Background counts were taken at half the scan time on either side of the peak. The intensity,  $I$ , and its standard deviation,  $\sigma(I)$ , were calculated as previously.<sup>9</sup> 3640 reflections with  $2\theta < 50^\circ$  were processed in total. 2513 of these had intensities greater than  $1.96\sigma(I)$  and were used in the data treatment. The intensities of four check reflections were measured after every 62th reflection. They remained constant to within  $\pm 6\%$ .

The intensity data were corrected for the Lorentz and polarization factors and for absorption. The crystal used was prismatic  $a$  with dimensions  $0.123 \text{ mm} \times 0.068 \text{ mm} \times 0.052 \text{ mm}$  along  $a$ ,  $b$ , and  $[01\bar{1}]$  and had seven boundary planes. The transmission factors varied between 0.133 and 0.321. A semi-empirical absorption correction method was also tried for comparison.<sup>9,10</sup> The maximum measured intensity variation ratio was then 1.000 to 0.313.

*Computer programs.* The computer program system supplied by Syntex (XTL version 2)<sup>11</sup> for a NOVA 24K computer with a disk memory unit was used for the calculations. In addition the program DATAPU was used for the absorption correction using the Gaussian integration method and the plot program ORTEP 2 for the crystal structure illustrations. The originally written programs<sup>12</sup> have been modified for IBM 360/75 in Stockholm.

## STRUCTURE DETERMINATION

A three-dimensional Patterson map was calculated. From the peak listing six U–U vectors with a multiplicity of two and three with a multi-

plicity of one could be identified. Therefore the space group was assumed to be the centrosymmetrical  $P\bar{1}$  (No. 2).

The positions of the three U atoms in the asymmetric unit were determined. These parameters in addition to individual isotropic temperature factors and a scale factor were refined using the block-diagonal least squares method to a conventional  $R$  value of 0.139.

The positions of all light atoms were found from subsequent difference Fourier maps. Block-diagonal followed by full-matrix least squares refinements with U anisotropic gave an  $R$  value of 0.074 (0.078 with the semi-empirical absorption corrections). The weighted  $R$  value according to Hamilton<sup>13</sup> was then 0.102 (0.105). In the last cycle of the refinements no parameter shifts were greater than 0.5% of the calculated standard deviations. The weighting scheme was based on the counter statistics,  $1/w = \sigma^2(F_o) + 0.0016F_o^2$ . The function minimized was  $\sum w(|F_o| - k|F_c|)^2$ . Final difference Fourier maps revealed an essentially smooth background of 2–3 electrons Å<sup>-3</sup>. All of the residual peaks were too close to the atoms already found to be interpreted as the O atom in a fifth water of crystallization.

When no absorption corrections were applied to the intensity data the final conventional  $R$  value was 0.100 and the weighted  $R$  value 0.128. The difference Fourier map then showed sharp peaks of 5–7 electrons Å<sup>-3</sup> within 1 Å from the U atoms in addition to the essentially smooth background of 2–3 electrons Å<sup>-3</sup>. The structural parameters were not changed significantly on introducing the absorption corrections but the standard deviations were slightly reduced.

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. All these values are based on data where the Gaussian integration absorption correction method has been applied.

An attempt to introduce anisotropic thermal parameters for the light atoms was not successful. One of the  $U(ii)$  elements for three of the O atoms came out slightly negative. The remaining errors in the data are thus too large to make such refinements physically meaningful.

As a test, refinements were also performed in the space group  $P1$  (No. 1). Then the  $R$  value only decreased by 0.001 to 0.073 and some of the O atoms obtained negative  $U$  values.

Table 1. Final positional and isotropic thermal parameters ( $\text{\AA}^2$ ) in the form  $\exp[-8\pi^2 U(\sin^2 \theta/\lambda^2)]$ . The positional parameters of U(1) to O(16) are referred to atoms in the same trinuclear complex and those of N(1) to O(3N) to atoms in the same nitrate ion. O(N)=nitrate O atoms, O(W)=O atoms in water molecules of crystallization.

Atom	x	y	z	U
U(1)	0.42446(17)	0.24136(13)	0.48431(14)	
U(2)	0.30968(17)	0.04145(13)	0.16582(14)	
U(3)	0.09907(17)	0.35650(13)	0.28310(14)	
O(1)	0.2558(42)	0.1585(31)	0.5078(31)	0.049(9)
O(2)	0.6040(30)	0.3211(23)	0.4682(23)	0.021(6)
O(3)	0.1456(32)	-0.0410(24)	0.2005(24)	0.025(6)
O(4)	0.4833(34)	0.1129(25)	0.1204(25)	0.030(7)
O(5)	-0.0526(42)	0.2870(30)	0.3240(31)	0.048(9)
O(6)	0.2407(34)	0.4384(25)	0.2388(25)	0.028(6)
O(7)	0.2955(32)	0.2227(24)	0.3103(24)	0.026(6)
O(8)	0.4862(33)	0.0450(25)	0.3450(25)	0.027(6)
O(9)	0.2407(31)	0.4174(23)	0.4843(23)	0.022(6)
O(10)	0.0948(39)	0.1706(29)	0.1097(29)	0.043(8)
O(11)	0.6215(32)	0.1463(23)	0.5979(24)	0.023(6)
O(12)	0.4595(36)	0.3762(26)	0.6925(27)	0.035(7)
O(13)	0.4549(32)	-0.1514(24)	0.1105(24)	0.026(6)
O(14)	0.1993(32)	-0.0638(23)	-0.0462(24)	0.023(6)
O(15)	-0.0197(43)	0.5609(32)	0.3811(32)	0.052(9)
O(16)	-0.1154(41)	0.3930(30)	0.1316(30)	0.047(9)
N(1)	0.2121(44)	0.3379(32)	0.9260(32)	0.030(8)
O(1N)	0.2157(47)	0.2268(36)	0.9137(35)	0.062(10)
O(2N)	0.0714(61)	0.3788(44)	0.8945(45)	0.092(15)
O(3N)	0.3355(48)	0.4018(35)	0.9723(35)	0.062(10)
O(1W)	0.2966(35)	0.6468(26)	0.1303(26)	0.032(7)
O(2W)	0.0332(52)	0.8026(38)	0.3652(39)	0.076(12)
O(3W)	0.8296(48)	0.0375(36)	0.3195(36)	0.065(11)
O(4W)	0.5851(52)	0.3628(38)	0.2111(38)	0.076(12)

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

Atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
U(1)	0.0161(7)	0.0185(7)	0.0212(9)	-0.0003(6)	0.0014(6)	0.0071(7)
U(2)	0.0170(7)	0.0165(7)	0.0221(9)	0.0013(6)	0.0038(6)	0.0042(7)
U(3)	0.0154(7)	0.0199(7)	0.0212(9)	0.0032(6)	0.0046(6)	0.0073(7)

The scattering factors used were those given in the International Tables, Vol. IV,<sup>14</sup> for neutral atoms. Corrections for anomalous dispersion for U were applied.

## DESCRIPTION OF THE STRUCTURE

The structure is shown in Fig. 1. It is built up from discrete charged triangular trinuclear com-

plexes, nitrate ions, and water molecules of crystallization. One trinuclear complex is drawn separately in Fig. 2. Some important distances and angles are given in Table 3.

Each U atom in a trinuclear complex is surrounded by seven O atoms. The coordination polyhedron is a distorted pentagonal bipyramid. Two of these seven O atoms are the uranyl O atoms. The corresponding U—O bond lengths vary from 1.69

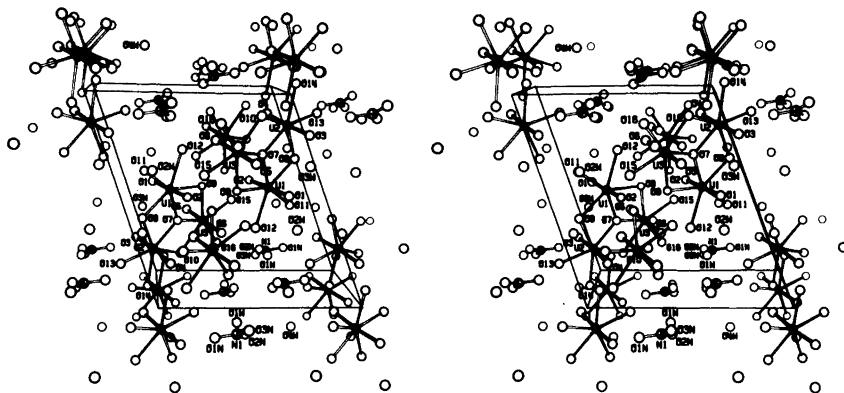


Fig. 1. A stereogram showing the unit-cell contents of  $[(UO_2)_3O(OH)_3(H_2O)_6]NO_3 \cdot 4H_2O$ . The view is parallel to the  $a^*$  axis.

to 1.88 Å with an average value of 1.78 Å. One O atom, O(7), is shared between all three U atoms and is probably an  $O^{2-}$  oxygen atom. The corresponding U–O bond lengths are 2.17, 2.22 and 2.23 Å, the average value being 2.21 Å. Two O atoms within each pentagonal bipyramid are shared between two U atoms and are probably  $HO^-$  oxygens. The remaining two O atoms are coordinated to only one U atom and they are probably water O atoms. There are no significant differences in the U–O bond lengths for the  $HO^-$  and the water O atoms. The average value is 2.44 Å and the variation is from 2.39 to 2.50 Å. The formula of the complex ion can thus be written as  $[(UO_2)_3O(OH)_3(H_2O)_6]^+$ .

The U atoms are joined through double bridges

containing one O atom and one HO group. The U–U distances are 3.788, 3.816 and 3.824 Å. The three U atoms in a trinuclear complex are at the corners of an equilateral triangle with an average edge length of 3.809 Å.

As the pentagons around the uranyl groups are roughly planar, least squares planes have been calculated through: (1) all three pentagons U(1), U(2), U(3), (2) the U(1) pentagon, (3) the U(2) pentagon, (4) the U(3) pentagon, (5) the uranyl groups of U(1) and U(2), (6) the uranyl groups of U(1) and U(3), (7) the uranyl groups of U(2) and U(3). A least squares plane through the nitrate group has also been calculated (8). The results are shown in Table 4. The deviations of atoms from the

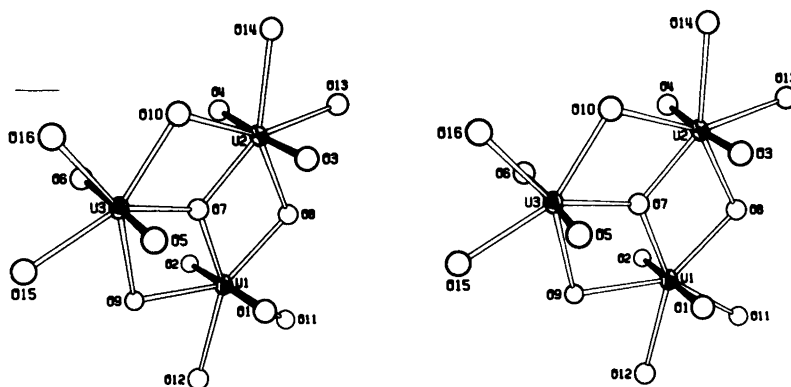


Fig. 2. A stereoscopic pair of perspective projections showing one trinuclear complex  $[(UO_2)_3O(OH)_3(H_2O)_6]^+$ . The thermal ellipsoids for U(1), U(2), U(3), O(2), O(3), O(9), O(11), and O(14) are scaled to include 50% probability. For the other atoms U has been reduced to  $0.025 \text{ \AA}^2$  for clarity.

Table 3. Some important interatomic distances (Å) and angles (°).

U(1)–U(2)	3.788(2)							
U(1)–U(3)	3.816(2)	U(2)–U(3)	3.824(2)					
U(1)–O(1)	1.78(3)	U(2)–O(3)	1.81(3)	U(3)–O(5)	1.69(3)			
U(1)–O(2)	1.79(3)	U(2)–O(4)	1.88(3)	U(3)–O(6)	1.74(3)			
U(1)–O(7)	2.17(3)	U(2)–O(7)	2.23(3)	U(3)–O(7)	2.22(3)			
U(1)–O(8)	2.40(3)	U(2)–O(8)	2.41(3)	U(3)–O(9)	2.43(3)			
U(1)–O(9)	2.44(3)	U(2)–O(10)	2.40(3)	U(3)–O(10)	2.44(3)	O(7)–O(8)	2.60(4)	
U(1)–O(11)	2.41(3)	U(2)–O(13)	2.39(3)	U(3)–O(15)	2.46(4)	O(7)–O(9)	2.59(4)	
U(1)–O(12)	2.48(3)	U(2)–O(14)	2.50(3)	U(3)–O(16)	2.46(3)	O(7)–O(10)	2.61(4)	
O(7)–U(1)–O(8)	69.1(10)	O(7)–U(2)–O(8)	68.0(10)	O(7)–U(3)–O(9)	67.6(9)			
O(8)–U(1)–O(11)	76.0(9)	O(8)–U(2)–O(13)	76.5(9)	O(9)–U(3)–O(15)	75.4(10)			
O(11)–U(1)–O(12)	71.0(9)	O(13)–U(2)–O(14)	74.0(9)	O(15)–U(3)–O(16)	75.2(12)			
O(12)–U(1)–O(9)	76.0(9)	O(14)–U(2)–O(10)	72.5(10)	O(16)–U(3)–O(10)	74.0(11)			
O(9)–U(1)–O(7)	68.0(10)	O(10)–U(2)–O(7)	68.7(11)	O(10)–U(3)–O(7)	68.1(11)			
O(1)–U(1)–O(2)	175.9(14)	O(3)–U(2)–O(4)	174.9(12)	O(5)–U(3)–O(6)	174.4(15)			
U(1)–O(7)–U(2)	118.8(12)	U(1)–O(7)–U(3)	120.7(13)	U(2)–O(7)–U(3)	118.5(12)			
U(1)–O(8)–U(2)	103.7(11)	U(1)–O(9)–U(3)	103.1(10)	U(2)–O(10)–U(3)	104.6(12)			
N(1)–O(1N)	1.21(6)			O(1N)–N(1)–O(2N)	117(4)			
N(1)–O(2N)	1.26(6)			O(2N)–N(1)–O(3N)	124(4)			
N(1)–O(3N)	1.18(5)			O(3N)–N(1)–O(1N)	119(4)			

Table 4. Deviations (Å) of atoms from the calculated least squares planes.

Plane 1: U(1) 0.001(1), U(2) 0.000(1), U(3) 0.000(1), O(7) 0.18(3), O(8) –0.01(3), O(9) 0.00(2), O(10) –0.14(3), O(11) –0.11(3), O(12) –0.22(3), O(13) 0.00(3), O(14) –0.03(3), O(15) –0.03(3), O(16) –0.14(3)
Plane 2: U(1) 0.000(1), O(7) 0.02(3), O(8) –0.10(3), O(9) –0.04(2), O(11) 0.02(3), O(12) –0.07(3)
Plane 3: U(2) 0.000(1), O(7) 0.12(3), O(8) –0.07(3), O(10) –0.13(3), O(13) 0.02(3), O(14) 0.04(3)
Plane 4: U(3) 0.000(1), O(7) 0.08(3), O(9) –0.09(2), O(10) –0.13(3), O(15) 0.02(3), O(16) –0.01(3)
Plane 5: U(1) 0.000(1), U(2) 0.000(1), O(1) –0.02(3), O(2) –0.08(3), O(3) –0.08(3), O(4) –0.01(3)
Plane 6: U(1) 0.000(1), U(3) 0.000(1), O(1) 0.06(3), O(2) –0.06(3), O(5) –0.11(3), O(6) 0.04(3)
Plane 7: U(2) 0.000(1), U(3) 0.000(1), O(3) 0.07(3), O(4) –0.01(3), O(5) –0.01(3), O(6) 0.10(3)
Plane 8: N(1) 0.02(3), O(1N) –0.01(4), O(2N) –0.01(5), O(3N) –0.01(4)

planes are of the same magnitude as or smaller than those obtained for the tetranuclear complex  $[(\text{UO}_2)_4\text{Cl}_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ .<sup>4</sup> The maximum deviation of the dihedral angles from the ideal values 0 and 90° is 7° (between plane 2 and 4 and between plane 2 and 7).

As there are 23 H atoms in the asymmetric unit, hydrogen bonds are most probably holding the different complexes in the structure together. Table 5 gives a survey of the suggested hydrogen bond system.

## DISCUSSION

According to statistical tests,<sup>14</sup> the absorption corrections based on the Gaussian integration method only marginally improved the intensity data in comparison with the semi-empirical absorption corrections. They are thus nearly equally good. The rather high final *R* value of 0.074 (0.078 with the semi-empirical absorption corrections) indicates that there are still systematic errors in the data. One reason for this is that there are very few strong reflections but many weak ones which were measured using the comparatively high minimum scan speed of 2° min<sup>-1</sup>. Therefore it is not meaning-

Table 5. Intermolecular O—O distances (Å) for the suggested hydrogen bond system. The symmetry codes are:

(a) $1-x, 1-y, 1-z$		(g) $-x, 1-y, 1-z$	
(b) $x, y, -1+z$		(h) $-1+x, y, z$	
(c) $1-x, -y, 1-z$		(i) $-1+x, 1+y, z$	
(d) $x, -1+y, z$		(j) $1+x, y, z$	
(e) $1-x, -y, -z$			
(f) $-x, -y, -z$			
O(8)—O(3W)	2.82(5)	O(1W)—O(2Ng)	2.93(6)
O(9)—O(2a)	3.06(4)	O(1W)—O(3Nb)	2.84(5)
O(10)—O(1Nb)	3.00(5)	O(2W)—O(1g)	2.95(5)
O(11)—O(8c)	2.68(4)	O(2W)—O(3Wi)	3.24(6)
O(11)—O(2Wa)	2.78(5)	O(3W)—O(3j)	3.10(5)
O(12)—O(1Wa)	2.76(4)	O(3W)—O(5j)	2.97(6)
O(12)—O(4Wa)	2.82(5)	O(4W)—O(4)	2.75(5)
O(13)—O(1Nc)	2.79(5)	O(4W)—O(6)	2.91(5)
O(13)—O(1Wd)	2.73(4)		
O(14)—O(4e)	2.83(4)		
O(14)—O(10f)	2.56(4)		
O(15)—O(9g)	2.58(4)		
O(15)—O(2W)	2.84(6)		
O(16)—O(2Ng)	2.74(6)		
O(16)—O(4Wh)	2.81(5)		

ful to discuss the hydrogen bond system in full detail.

The most remarkable aspect of the present structure as compared to those of other solids containing  $\text{UO}_2^{2+}$  and  $\text{NO}_3^-$  groups is that the nitrate ion is not coordinated to the U atom neither as a monodentate nor as a bidentate ligand. In  $[\text{UO}_2(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ <sup>15,16</sup> and  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ <sup>17</sup> each uranyl group is surrounded by two nitrate ions acting as bidentate ligands and by two water molecules. In  $\text{Rb}[\text{UO}_2(\text{NO}_3)_3]$ <sup>18</sup> and the isomorphous  $\text{Cs}[\text{UO}_2(\text{NO}_3)_3]$ <sup>19</sup>  $\text{UO}_2^{2+}$  is bidentately coordinated by three nitrate ions. In  $\text{M}_2[\text{UO}_2(\text{NO}_3)_4]$  ( $\text{M} = \text{NH}_4^+, \text{Rb}^+, \text{Cs}^+$ )<sup>20</sup> the uranyl group is also hexa-coordinated. In these compounds, however, two nitrate ions act as monodentate and the other two as bidentate ligands.

Recently the crystal structure of  $[(\text{UO}_2)_2(\text{NO}_3)_2(\text{OH})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  has been reported.<sup>21</sup> This phase was not found by Cordfunke during the investigation of the system  $\text{UO}_2(\text{NO}_3)_2 - \text{UO}_3 - \text{H}_2\text{O}$  at 25 °C.<sup>6</sup> It is built up from dinuclear complexes. The two U atoms are joined through a double HO bridge. The nitrate ions are bidentately coordinated to the same U atom. Three of the water molecules are coordinated to the second U atom. The structure of  $[(\text{UO}_2)_2(\text{NO}_3)_2(\text{OH})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  ( $n_{\text{HO}} = 1$ ) is

thus different from that of the more hydrolyzed  $[(\text{UO}_2)_3\text{O}(\text{OH})_3(\text{H}_2\text{O})_6] \cdot \text{NO}_3 \cdot 4\text{H}_2\text{O}$  ( $n_{\text{HO}} = 5/3$ ). Furthermore it is different from that of  $[(\text{UO}_2)_2\text{Cl}_2(\text{OH})_2(\text{H}_2\text{O})_4]$  ( $n_{\text{HO}} = 1$ ), which is also built up from dinuclear complexes with double HO bridges, but the Cl atoms are here coordinated to different U atoms.<sup>3</sup>

The U—O bond lengths obtained in the present investigation are in good agreement with those in the tetranuclear complex.<sup>4</sup> The shortest U—U distance, 3.788 Å, is nearly identical to the corresponding distance in the tetranuclear complex, *i.e.* the U—U distance within the HO/O bridge. The other two U—U distances, 3.816 and 3.824 Å, are significantly longer if only the standard deviations are considered. But because of the systematic errors, these differences may not be real. There might, however, be a chemical reason why the U(1)—U(3) and U(2)—U(3) distances are longer than the U(1)—U(2) distance. The  $\text{HO}^-$  oxygen atoms O(9) and O(10) bonded to U(3) seem to be more strongly hydrogen-bonded (2.58 and 2.56 Å, respectively) than the  $\text{HO}^-$  oxygen atom O(8) joining U(1) and U(2) (Table 5).

The nitrate ion is planar but slightly distorted. This distortion may be only apparent, but as O(2N) seems to be the most strongly hydrogen-bonded of

the three nitrogen-coordinated O atoms, it is reasonable that the N(1)–O(2N) bond is longer than the other two N–O bonds.

## CONCLUSION

In the  $\text{UO}_2^{2+} - \text{HO}^- - \text{Cl}^-$  as well as in the  $\text{UO}_2^{2+} - \text{HO}^- - \text{NO}_3^-$  system discrete polynuclear hydrolyzed complexes are formed as solids. The dinuclear complex  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  has been isolated in both systems. Two anions and a number of water molecules are also coordinated. The structure of  $[(\text{UO}_2)_2\text{Cl}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{3+}$  is, however, different from that of  $[(\text{UO}_2)_2(\text{NO}_3)_2(\text{OH})_2(\text{H}_2\text{O})_3]^{2+}$ .<sup>21</sup> The trinuclear complex  $(\text{UO}_2)_3\text{O}(\text{OH})_3^{4+}$  has been found in the nitrate system only. It does not coordinate any anions, only six water molecules. The tetranuclear complex  $(\text{UO}_2)_4\text{O}_2(\text{OH})_2^{2+}$  seems to be formed only in the presence of  $\text{Cl}^-$  ions, which act as bridges between the U atoms. Two  $\text{Cl}^-$  ions and six water molecules are coordinated.<sup>4</sup>

In hydrolyzed and acidic uranyl chloride solutions  $\text{Cl}^-$  ions are coordinated to  $\text{U}^{2+}$ . No X-ray diffraction investigations of uranyl nitrate solutions have been performed. Unfortunately, the system  $\text{UO}_2(\text{NO}_3)_2 - \text{UO}_3 - \text{H}_2\text{O}$  is less favourable for such measurements than the corresponding  $\text{Cl}^-$  system. From the phase diagram<sup>6</sup> it can be estimated that  $n_{\text{H}_2\text{O}} \approx 0.5$  for the region of highest solubility. The maximum value of  $n_{\text{H}_2\text{O}}$  is only about 0.7 and then the solubility is probably too low for an X-ray diffraction investigation. For the system  $\text{UO}_3 - \text{HCl} - \text{H}_2\text{O}$  the maximum  $n_{\text{H}_2\text{O}}$  obtainable was 1.11 when the solubility was about 3.1 M.<sup>2</sup>

*Acknowledgements.* I wish to thank Dr. Georg Johansson for his interest in this work and for valuable advice and Prof. Ingmar Grenthe for criticism of the manuscript. The work has been financially supported by the Swedish Natural Science Research Council. Through a generous grant from the "Knut and Alice Wallenberg's Foundation" it has been possible to buy the computer-controlled four-circle diffractometer with a complete program system for crystal structure determinations.

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Received August 30, 1977.