

On the Structures of the Predominant Hydrolysis Products of Uranyl(VI) in Solution

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The X-ray scattering from concentrated hydrolyzed and acid solutions of uranyl(VI) chloride has been measured. The uranium concentration has been kept constant at 3 M but the OH:U ratio has been varied from 0 to 1.11. The coordination number of the uranyl ion in solution is close to values found in crystal structures. In the hydrolyzed solutions polynuclear complexes are formed in which the U—U distance is 3.86 Å and the uranium atoms are probably joined by double oxygen bridges. The scattering data, the results from emf measurements and geometrical considerations lead to the conclusion that the predominant polynuclear complexes can contain only two or three uranium atoms. The dinuclear complex has a structure similar to that found for the discrete dinuclear complex $[(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4]$ occurring in crystals of a solid uranyl(VI) hydroxo compound. In the trinuclear complex the uranium atoms form an equilateral or almost equilateral triangle.

The hydrolysis of the uranyl(VI) ion, UO_2^{2+} , has been investigated by a large number of workers during the last 25 years. Different techniques, e.g., emf, optical absorption, and ultracentrifugation measurements have been used. For an almost complete list of papers published before 1964 the reader is referred to the *Tables of Stability Constants*.¹ Most authors agree on the presence of a dinuclear complex with the formula $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and several of them also propose trimers with different numbers of OH groups, most frequently four or five. Additional complexes, both monomers and polymers, have been suggested, but their compositions depend to some extent on the ionic medium selected for the studies.

Very little is known about the structures of the polynuclear hydrolysis complexes of UO_2^{2+} but Evans² has suggested some models on the basis of what is known about the coordination of uranyl(VI) in crystals. Since a rather high value of n_{OH} ($n_{\text{OH}}^{\text{max}}=1.11$, where n_{OH} is the average number of OH groups per U atom) could be obtained for hydrolyzed 3 M uranyl(VI) chloride solutions without precipitation, it seemed likely that X-ray scattering data could give information on the structures of the hydrolysis products.

The interpretation of the scattering curves could most probably be facilitated by considering the interatomic distances obtained from a crystal structure determination of the uranyl(VI) hydroxo compound $[(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4]^{3-}$.³ Three solutions with different n_{OH} values (0, 0.58, and 1.11) but with a constant uranium concentration of 3.1 M were investigated.

EXPERIMENTAL

Preparation of solutions. A stock solution of approximately 3 M uranyl(VI) chloride was prepared by dissolving spectroscopically pure UO_3 obtained from AB Atomenergi, Stockholm, in a slight excess of concentrated hydrochloric acid (*p.a.*), evaporating under an infrared lamp until the excess had been removed and dissolving the residue in water. The most hydrolyzed solution was prepared by shaking a portion of the stock solution with an OH^- -saturated anion exchanger (Dowex 2-X8). The acid solution was obtained by adding concentrated hydrochloric acid to part of the stock solution. A solution with an intermediate value of n_{OH} was made by mixing approximately equal amounts of the other two solutions.

Analysis. The uranium concentration was determined by precipitation with 8-hydroxyquinoline according to a method described by Hecht and Donau.⁴ The amount of chloride was determined by passing a portion of the solution through an H^+ -saturated cation exchanger (Dowex 50W-X8) and titrating the eluate with NaOH. The densities were determined with a pycnometer.

The compositions of the different solutions are given in Table 1.

Table 1. Compositions of the solutions in gatoms/l. (n_{OH} = average number of OH groups per U atom).

n_{OH}	U	Cl	O	H
0	3.10 ₁	6.42	52.3	92.4
0.58 ₄	3.13 ₀	4.43	55.2	96.0
1.11 ₀	3.13 ₀	2.79	57.5	99.0

X-Ray measurements. The X-ray scattering was measured in a diffractometer described in previous papers from this institute.^{5,6} $\text{AgK}\alpha$ -radiation ($\lambda = 0.5608 \text{ \AA}$) was used. The range of θ (2θ = the scattering angle) was 0.7 to 70° corresponding to a range in $s = 4\pi \sin \theta / \lambda$ from 0.3 to 21. Opening slits of 1/12°, 1/4° and 1° were used to limit the primary X-ray beam. Points were measured at intervals in θ of 0.1° up to $\theta = 6^\circ$ and 0.25° to $\theta = 70^\circ$. For each point 40 000 counts were usually taken which corresponds to a statistical error of about 0.5 %. Scaling factors for converting all measured data to the same opening slit were obtained from measurements in overlapping regions. Within each region the measurements were repeated at larger intervals in order to detect and enable correction for any long-time variations in the X-ray and the counting equipment. These variations were practically always less than 1 % of the measured intensity.

TREATMENT OF THE DATA

The measured intensities were corrected for polarization by dividing by the factor $(1 + \cos^2 2\alpha \cos^2 2\theta) / (1 + \cos^2 2\alpha)$, where 2α is the diffraction angle at the monochromator. They were put on an absolute scale by comparing the

high-angle region ($\theta > 45^\circ$) of the scattering curves with the sum of the independent coherent scattering ($\sum n_i f_i^2$) and the incoherent scattering. The atomic scattering factors (f_i) used were those given by Cromer and Waber⁷ for the neutral U, Cl and O atoms and were taken from the *International Tables*⁸ for H. Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) according to Cromer⁹ were applied to U and Cl. The amount of incoherent radiation was obtained from the *International Tables*⁸ for O and Cl, was calculated according to the formula given by Bewilogua¹⁰ for U, and was obtained from the values given by Compton and Allison¹¹ for H. The amount of incoherent radiation reaching the counter was estimated in a semi-empirical way from the spectrum of the X-ray tube and the resolving power of the monochromator.

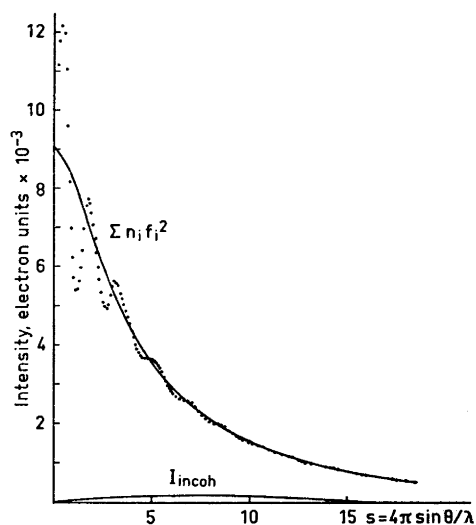


Fig. 1. Scattering curves for the solution with $n_{\text{OH}}=1.11$. Observed intensity values after scaling, corrections for incoherent and fluorescent radiation and addition of $i_{\text{corr}}(s)$ values are indicated by dots.

Fig. 1 shows the scaled experimental values as a function of s for the solution with $n_{\text{OH}}=1.11$. Fig. 2a (curve A) gives the function $s \cdot i(s)$ for the same solution. The reduced intensity $i(s)$ is the difference between the scaled intensity values after subtraction of the incoherent radiation and the sum of the squares of the scattering factors, $\sum n_i f_i^2$, for a stoichiometric unit of solution chosen to be the volume containing one uranium atom.

Curve A in Fig. 2a shows that nearly all points have negative $s \cdot i(s)$ values. This depends on the scaling factor for transforming the experimental data to absolute values being too low which may be explained by the presence of an additional constant intensity term causing all measured data to be too high. When considering the positions of the absorption edges of uranium ($\lambda(K)=0.108 \text{ \AA}$, $\lambda(L_I)=0.569 \text{ \AA}$, $\lambda(L_{II})=0.592 \text{ \AA}$, $\lambda(L_{III})=0.722 \text{ \AA}$),¹² it is highly probable that this extra radiation is due to fluorescence of a wave-length so close to the $K\alpha$ -radiation of the X-ray tube that it cannot be eliminated by the monochromator. This is supported by the fact that the effect is much more pronounced when $\text{Mo}K\alpha$ -radiation ($\lambda=0.7107 \text{ \AA}$) is used.

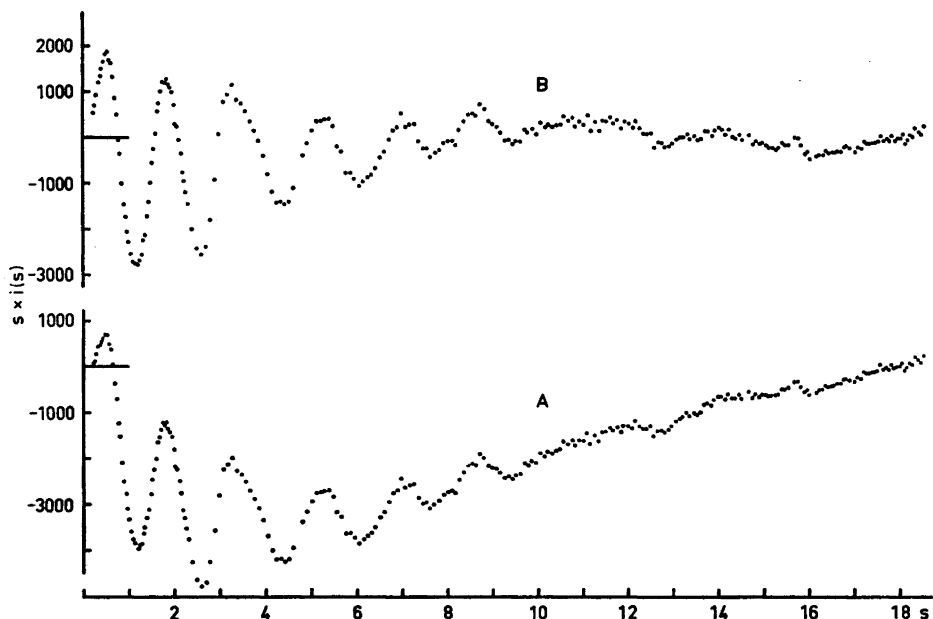


Fig. 2a. Reduced intensity function, $i(s)$, multiplied by s for the solution with $n_{\text{OH}}=1.11$. Curve A gives the uncorrected experimental values and curve B the values after correction for fluorescence.

In order to get correct scaling factors, the amount of fluorescence had to be estimated. This was done in the following way. The fluorescent radiation was assumed to be independent of angle. In a series of calculations, different values of a constant correction term were subtracted from the measured intensity values. The new data were corrected for polarization and were put on an absolute scale both by means of the method described above, which uses only intensity values for $\theta > 45^\circ$, and by a method suggested by Norman¹³ and Krogh-Moe¹⁴ which also includes the low-angle region of the scattering curve. The correction term that gave the best agreement between the two scaling factors was chosen. In this way the fluorescence was found to be about 20 % of the intensity at the largest diffraction angles when $\text{AgK}\alpha$ -radiation was used. For $\text{MoK}\alpha$ -radiation the amount was more than 80 %.

In Fig. 2a (curve B) the function $s \cdot i(s)$ for the solution with $n_{\text{OH}}=1.11$ is shown when the correction for fluorescence has been made. The effect of this fluorescence correction on the $D(r)$ curve is an increase in the sizes of the interaction peaks due to the higher value of the scaling factor. The U-U interaction peak is about 9 % larger after the correction has been applied to the data than before.

Radial distribution functions, $D(r)$, were calculated according to the formula

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\text{max}}} s \cdot i(s) \cdot f(s) \cdot \sin(sr) \cdot ds$$

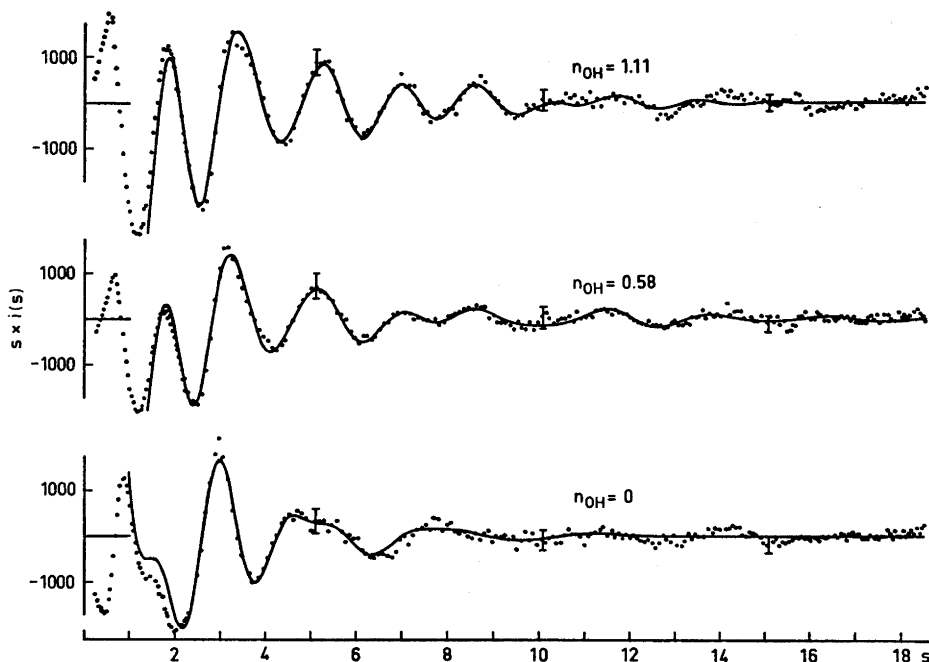


Fig. 2b. Observed values $s \cdot i(s)$. The full curves are calculated with the parameters given in Table 2. Vertical bars give the magnitude of three times the standard deviation in the intensity measurements.

where ρ_0 , the average scattering density, is given by the square of the number of electrons per unit volume. The modification function is $f(s) = (f_U^0/f_U(s))^2 \cdot \exp(-ks^2)$, where f_U^0 is the scattering factor of U at $s=0$. For k a value of 0.016 was chosen. The cut-off limit was $s_{\max} = 17$. The observed $i(s)$ values were used for the integration and no attempt was made to draw a smooth curve through the experimental points. A small number of $i(s)$ values, at most 10 values out of about 300 for each solution, which seemed to be definitely outside the estimated limits of error, were, however, excluded from the calculations. All calculations were carried out on the computer Trask by means of programs written by Johansson.¹⁵

The $D(r)$ curves calculated directly from the experimental $i(s)$ values showed some spurious peaks for $r < 1 \text{ \AA}$, which is a region where no interatomic distances can occur. The shortest distance between atoms in the solutions is the O-H distance within the water molecule which is about 1 \AA . These spurious peaks are the Fourier inversion of a slowly varying function of s superposed on the $i(s)$ values. They must be eliminated in order to make least squares refinements of the $i(s)$ values feasible. The corrections were made by addition of the function

$$i_{\text{corr}}(s) = 1/f(s) \int_0^{r_{\max}} (D'(r) - 4\pi r^2 \rho_0) \cdot [\sin(sr)/(sr)] \cdot dr$$

to the experimental $i(s)$ data. The upper integration limit was set to $r_{\max} = 1.5 \text{ \AA}$. The $D'(r)$ values were taken from the preliminary $D(r)$ curves, were reversed in sign and were finally corrected for the calculated contributions to the radial distribution functions from the O–H interaction at about 1 \AA and the uranyl U–O interaction at about 1.8 \AA in the region $r \leq 1.5 \text{ \AA}$. The $i_{\text{corr}}(s)$ values so obtained were added to the experimental $i(s)$ data and new radial distribution curves were calculated. These calculations were made on the computer by means of a specially written correction program closely related to the main program.

Fig. 2b gives the $s \cdot i(s)$ curves for the three solutions after correction for fluorescence and addition of the $i_{\text{corr}}(s)$ values. Radial distribution functions, $D(r)$, and functions $D(r) - 4\pi r^2 \rho_0$ obtained by Fourier inversion of the corrected $i(s)$ values are shown in Figs. 3 and 4, respectively.

Theoretical pair interaction functions were calculated from

$$i_{nm}(s) = f_n f_m \exp(-bs^2) \cdot \sin(sr_{nm}) / sr_{nm}$$

where r_{nm} is the distance between the atoms n and m , f_n and f_m are the scattering factors and b is a temperature factor. The Fourier inversion of $i_{nm}(s)$ was made with the same modification function, $f(s)$, and the same cut-off limit as were used for the experimental values.

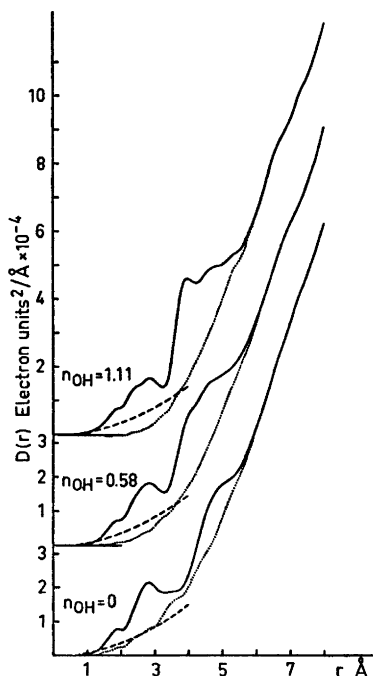


Fig. 3. Radial distribution functions $D(r)$. The dotted curves are the difference between the experimental and calculated distribution functions. The dashed lines are $4\pi r^2 \rho_0$ functions with only light atoms included.

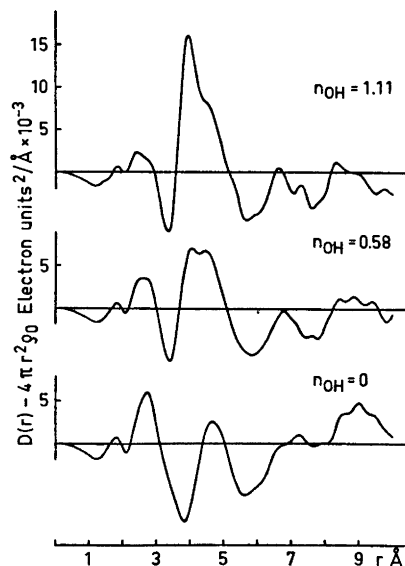


Fig. 4. Functions $D(r) - 4\pi r^2 \rho_0$.

ANALYSIS OF THE RADIAL DISTRIBUTION CURVES

The main change in the radial distribution curves when the value of n_{OH} is increased is the appearance of a peak at 3.9 Å (Figs. 3 and 4). The unresolved peak in the region 2–3 Å is the sum of two peaks, one at about 2.8 Å which becomes smaller with increasing hydrolysis and one at about 2.4 Å which is more pronounced in the hydrolyzed solutions. The peak at 1.8 Å seems to be independent of n_{OH} .

These peaks in the radial distribution curves correspond closely to the interatomic distances in the hydroxo compound $[(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4]$ which crystallizes by evaporation of solutions with $n_{\text{OH}} \approx 0.6$. According to the crystal structure determination of this compound, it is built up from discrete dinuclear complexes with a U–U distance of 3.944 Å (Fig. 5).³ The two uranium atoms are joined by a double OH bridge. Each uranium atom is surrounded by seven light atoms: one chlorine atom at 2.75 Å, four oxygen atoms at an average distance of 2.40 Å and two oxygen atoms at an average distance of 1.79 Å. The latter atoms form together with the uranium atom the linear uranyl group which is perpendicular to the plane pentagon formed by the other five atoms. The two uranyl groups in a complex are parallel and the two pentagons are coplanar.

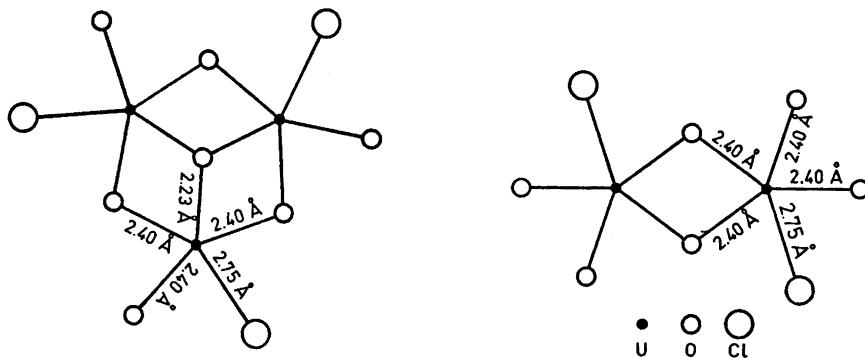


Fig. 5. Simplified pictures of the di- and trinuclear complexes. All atoms shown in the pictures lie approximately in the same plane. The uranyl oxygen atoms are left out but these U–O bonds are perpendicular to the plane.

By a comparison with the distances in the hydroxo compound, the following identification of the peaks in the radial distribution curves can be made.

The peak at 1.8 Å is due to the U–O interaction in the UO_2^{2+} group. It appears at a distance found in all crystals of uranyl salts. Its size is nearly the same in all the curves, *i.e.* is independent of n_{OH} , and corresponds approximately to two U–O distances per U atom.

The 2.4 Å peak corresponds to a U–O distance and the 2.8 Å peak to a U–Cl distance within the first coordination sphere of the uranium atom. The decrease of the U–Cl peak and the corresponding increase in the U–O

peak with increasing n_{OH} support this identification. Although the two peaks are only partly resolved and interactions between light atoms occur in the same region, an approximate estimate of the areas under the peaks has been made and shows that each U atom is in contact with 4–6 light atoms at these distances including both oxygen and at most two chlorine atoms. These coordination numbers are in agreement with values found in crystal structures.

The 3.9 Å peak represents U–U interactions. The value is in good agreement with the U–U distance found in the hydroxo compound in which the uranium atoms are joined by double OH bridges. The size of the peak increases with n_{OH} and it does not occur in the $D(r)$ curve for the acid solution.

A second coordination sphere of mainly water molecules around the uranium atom is also clearly indicated, although somewhat obscured by the appearance of the 3.9 Å peak in the hydrolyzed solutions. It occurs at about 4.7 Å which is approximately the distance one would expect from packing considerations and atomic radii. Whether its size is dependent of n_{OH} or not cannot be ascertained by inspecting the radial distribution curves. The peak seems, however, to occur at a somewhat lower r value in the hydrolyzed solutions.

LEAST SQUARES REFINEMENTS OF THE INTENSITY FUNCTIONS

In order to discuss what kind of complexes are present in the solutions, it is necessary to estimate quantitatively the number of U–U interactions at 3.9 Å. This can be done in two different ways: by a comparison of the size of the peak in the experimental $D(r)$ curves with calculated peak shapes or by a direct analysis of the $i(s)$ curves for the larger s values.

The comparison of the size of the peak in the radial distribution curves with calculated peak shapes is uncertain because one does not know where to draw the base line of the peak. The main contributions to the 4 Å region of the $D(r)$ curves come from light atom interactions which cannot easily be determined. An estimate of the number of U–U interactions may, however, be obtained by subtracting the $D(r) - 4\pi r^2 \rho_0$ curve for the acid solution from each of those for the hydrolyzed solutions. The inherent assumption in this procedure is that the variation around the average distribution function $4\pi r^2 \rho_0$ is the same for the three solutions except for the U–U interaction. This subtraction procedure gives 0.82 and 0.51 as the average numbers of U–U distances per U atom at 3.9 Å for the solutions with $n_{\text{OH}} = 1.11$ and 0.58, respectively, which means that the numbers of nearest U neighbours around each U atom are about 1.6 and 1.0.

If U–U interactions occur, they give the largest contributions to the $i(s)$ curves for the higher s values compared with contributions from U–Cl, U–O, and light atom interactions. This is due to the slower decrease of the scattering factors of the U atom than of those of the Cl, O, and H atoms and to the particularly well-defined U–U distance. The first step in the analysis of the experimental $i(s)$ curves for estimating the U–U interaction parameters can thus be to compare the data for s values in the high angle region, e.g. $s > 5 \text{ \AA}^{-1}$, with calculated intensity curves, $i_{\text{calc}}(s)$, for a simplified model of the solution.

The comparison between the experimental $i(s)$ values and the calculated $i(s)$ curves for the model was made by means of a least squares refinement procedure taking into account only interactions involving U atoms. For each interaction, three parameters were introduced: the distance, the number of interactions per U atom and a temperature factor. In addition to the U-U interaction, a constant assumed background correction was included consisting of 2 U-O distances at 1.8 Å, n_{Cl} U-Cl distances at 2.8 Å (n_{Cl} is the analytical number of Cl atoms per U atom), and $5-n_{\text{Cl}}$ U-O distances at 2.4 Å. The parameters of the U-U interaction were varied until a minimum for the function $\sum w(|i(s)| - |i_{\text{calc}}(s)|)^2$ was reached. The weighting function $w=s^2$ was chosen. The calculations were carried out by means of a computer program based on Sillén's Letagrop program.¹⁶

The refinement gave U-U distances of 3.88 Å and 3.84 Å for the solutions with $n_{\text{OH}}=0.58$ and 1.11, respectively. The numbers of U-U distances per U atom were 0.26 ($n_{\text{OH}}=0.58$) and 0.63 ($n_{\text{OH}}=1.11$) (Table 2). This means that on an average each U atom is surrounded by about 0.5 and 1.3 nearest U neighbours, respectively. For the temperature factor of the U-U interaction a value of 0.009 ($\sigma=0.001$) was obtained.

Table 2. Results of the least squares refinements of the $i(s)$ curves. n_{OH} =average number of OH groups per U atom, r =distance in Å, n_r =number of distances per U atom. The standard deviations given in parentheses are those calculated by the least squares refinements.

		n_{OH}	0	0.58	1.11
First coordination sphere around the uranyl(VI) ion	1st U-O distance	r	1.77 (0.02)	1.77 (0.01)	1.76 (0.01)
		n_r	1.6 (0.1)	1.9 (0.1)	2.1 (0.2)
	2nd U-O distance	r	2.50 (0.01)	2.39 (0.01)	2.40 (0.01)
		n_r	2.5 (0.1)	3.0 (0.1)	4.3 (0.2)
	U-Cl distance	r	2.81 (0.02)	2.79 (0.01)	2.89 (0.02)
		n_r	1.3 (0.1)	1.3 (0.1)	0.8 (0.1)
U-U distance	r	—	3.88 (0.01)	3.84 (0.01)	
	n_r	—	0.26 (0.03)	0.63 (0.06)	
Second coordination sphere	3rd U-O distance	r	4.64 (0.01)	4.37 (0.01)	4.37 (0.01)
		n_r	8.0 (0.6)	15.2 (1.2)	15.3 (1.3)

In the next step of the refinement, an attempt was made to refine the parameters of the three uranium-light atom interactions in the first coordination sphere around uranium although the U–O and U–Cl interactions in the region 2–3 Å could not be separated. The contribution to the calculated $i(s)$ values from the U–U interaction was kept constant. All intensity data were used except values for $s < 2 \text{ \AA}^{-1}$ because the main contributions to the first peak come from the highly damped intermolecular interactions which were not included in the model. The refinement was carried out in cycles: the distance, the number of interactions per U atom and a temperature factor were refined for one uranium-light atom interaction at a time and the procedure was repeated until no better agreement between observed and calculated intensity values could be obtained. The final results of the refinements are given in Table 2. The U–O distance in the UO_2^{2+} group was 1.76–1.77 Å with a frequency of 1.6–2.1. For the distances within the first coordination sphere around the uranyl ion the values 2.39–2.50 Å and 2.79–2.89 Å were obtained for U–O and U–Cl, respectively. The total frequency was 3.8–5.1 and the temperature factors varied between 0.00 and 0.02. The standard deviations given in the table are those calculated by the least squares refinements and are of limited value because of the systematic errors that are present. These systematic errors have, however, more influence on the sizes of the interaction peaks than on their positions.

The second coordination sphere around the uranium atom was included in the model in a separate step of the refinement. It was treated as if it contained only oxygen atoms and was assumed to be represented by a single peak in the $D(r)$ curves. All other parameters of the model were kept constant during this refinement. The average U–O distances obtained were 4.64 Å ($n_{\text{OH}}=0$) and 4.37 Å ($n_{\text{OH}}=0.58$ and 1.11). The numbers of oxygen neighbours per U atom given in Table 2 are insignificant mainly because there is a distribution of uranium-light atom distances in this region as well as large contributions from light atom interactions.

The agreement between the final calculated and the observed $s \cdot i(s)$ curves is shown in Fig. 2b.

The significance of the values of the U–U interaction parameters obtained in the first step of the refinement was tested in the following way. With the new values of the parameters of the first and second coordination spheres kept constant, the parameters of the U–U interaction were refined using $s = 5 \text{ \AA}^{-1}$ as the lower limit for the $i(s)$ data. No significant difference was obtained. Nor did the parameter values change outside the limits of error when the second coordination sphere was excluded from the model.

The $i(s)$ values calculated from the parameters in Table 2 were used for a Fourier inversion to give the calculated peak shapes. When these are subtracted from the radial distribution curves obtained from the experimental $i(s)$ values, the result is an approximate correction curve for the light atom interactions not included in the model and for variations in the electron density outside the first coordination sphere. This difference curve is shown in Fig. 3 for the three solutions together with $4\pi r^2 \rho_0$ functions including only light atoms. It can be said to constitute an essentially even background curve with no pronounced unexplained peaks.

DISCUSSION

The coordination of uranium(VI). For the shortest U–O distance, which is that within the UO_2^{2+} group, an average value of 1.77 Å was obtained. This value is in agreement with the corresponding U–O distance of 1.79 Å found in the uranyl(VI) hydroxo compound.³ The number of O neighbours per U atom does not differ significantly from 2.

As has been mentioned previously, both chlorine and oxygen atoms are coordinated in the first coordination sphere around uranium. The total coordination number of UO_2^{2+} is 3.8 ($n_{\text{OH}}=0$), 4.3 ($n_{\text{OH}}=0.58$) and 5.1 ($n_{\text{OH}}=1.11$) (Table 2). Because of the uncertainty of the experimental data mainly due to fluorescence and because of the nearly complete overlap of the U–O and U–Cl interaction peaks in the region 2–3 Å, the main conclusion that can be drawn from these figures is that the coordination number of UO_2^{2+} in solution varies between 4 and 5 which values are the most common ones in crystal structures.^{2,3} From the results of the present investigation nothing can be said with certainty about how these 4–5 distances are distributed between U–O and U–Cl distances. The maximum number of U–Cl distances per U atom in the first coordination sphere is, however, limited by the composition of the solutions. The analytical number of chlorine atoms per U atom is 2.1 ($n_{\text{OH}}=0$), 1.4 ($n_{\text{OH}}=0.58$) and 0.9 ($n_{\text{OH}}=1.11$).

The polynuclear hydrolysis complexes. The U–U distance in the polynuclear complexes was found to be 3.88 Å and 3.84 Å in the solutions with $n_{\text{OH}}=0.58$ and 1.11, respectively. The difference between the values is hardly significant. As the average distance 3.86 Å is close to the U–U distance of 3.944 Å found in the solid hydroxo compound,³ the uranium atoms are likely to be joined by double oxygen bridges (Fig. 5) in the solution.

For the average number of nearest U neighbours per U atom at 3.86 Å in the most hydrolyzed solution, values >1.0 have been obtained by both described methods. This means that complexes with more than two uranium atoms have to be present to explain the experimental data. From the radial distribution curves it is clear that there are no U–U interactions of high frequency at larger distances than 3.86 Å.

There are also a number of geometrical restrictions on the structures of the polynuclear complexes if the coordination characteristics are assumed to be the same as for the dinuclear complex in the solid state. The uranyl groups are linear and perpendicular to the equatorial plane. The coordination numbers of the uranyl(VI) ion are four, five, or six.² Four atoms form a plane quadrangle, five atoms form a plane pentagon and six atoms form either a plane or a puckered hexagon of which the plane arrangement is the most common one.

Considering the geometrical restrictions and the information from the radial distribution curves, the following can be said about the structures of the predominant polynuclear hydrolysis products of uranyl(VI). The absence of a second U–U interaction of high frequency excludes chain formations of all kinds and also, *e.g.*, a square arrangement of U atoms. The necessity of a plane or nearly plane grouping of U atoms due to the presence of the uranyl oxygen atoms excludes tetrahedral and all other nonplanar arrangements.

The only complexes without a second U—U distance which can explain the experimental data are dinuclear complexes of the type found in the hydroxo compound (Fig. 5) and trinuclear complexes (Fig. 5). In a trinuclear complex the U atoms should form an equilateral triangle with a U—U distance of 3.86 Å as no broadening of the peak in the $D(r)$ curves due to non-equal U—U distances is indicated ($b=0.009$). This leads to a central U—O distance of 2.23 Å which is somewhat, although not unacceptably, shorter than the average distance 2.40 Å in the hydroxo compound. The uranyl groups must be perpendicular or very nearly perpendicular to the plane grouping of light atoms around the uranium atoms in order not to give too short distances between the uranyl oxygen atoms and other light atoms within the same pentagonal bipyramid.

The presence of a second U—U distance with low frequency cannot be definitely excluded by the experimental data and four uranium atoms at the corners of two coplanar equilateral triangles sharing one edge may be in agreement with the present results. The longer U—U distance of $3.86\sqrt{3}=6.69$ Å would have a frequency of 20 % of that of the main peak if all uranium atoms are bonded in tetranuclear complexes of this type. If, *e.g.*, di- and tetranuclear complexes are present in comparable amounts, the frequency would be less than 20 % of that of the 3.86 Å peak and this peak might not be distinguished from the interaction peaks of the second coordination sphere around the uranium atom which also appear in this region (*cf.* Fig. 6b).

A tetranuclear complex with approximately this quadrangular arrangement of the uranium atoms has been found in crystals which are obtained in small yield from solutions with $n_{\text{OH}} \approx 1$. The crystals probably have the composition $[(\text{UO}_2)_4\text{O}_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$ with $x=4$.¹⁷

Thus it seems that the predominant hydrolyzed species in the solutions can be dinuclear, triangular trinuclear and possibly quadrangular tetranuclear complexes of uranyl(VI). The presence of the latter complexes may explain the shorter U—U distance in solution as compared with that in the crystal where there are only dimers. Other complexes may also be present but must have so low concentrations that the characteristic second U—U interaction peak cannot be found in the radial distribution curves.

The hydrolysis of uranyl(VI) in several ionic media has been studied in this laboratory by means of precise emf measurements covering broad U concentration ranges. The investigations for a 3 M chloride medium have been performed by Dunsmore and Sillén^{18,19} for U concentrations between 0.625 and 80 mM. With the use of the stability constants they obtained, the complex concentrations have been calculated for a 3.1 M uranyl(VI) solution. The results are shown in Fig. 7. Provided that these constants are valid for the concentrated solutions used here, a trinuclear complex should be dominating for $n_{\text{OH}}=1.11$ and about equal amounts of di- and trinuclear complexes should be present in the solution with $n_{\text{OH}}=0.58$.

Thus, if the results from this investigation and from the emf measurements are compared, the conclusion is that the predominant polynuclear complexes in solution can contain only two or three uranium atoms and that they have structures similar to those shown in Fig. 5. Obviously, formation of di- and tetranuclear complexes is favoured in the crystallization process.

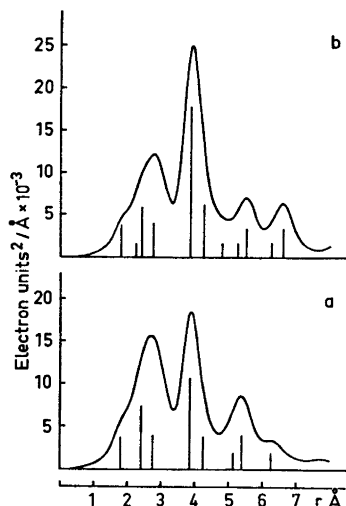


Fig. 6. Calculated radial distribution functions for the solution with $n_{\text{OH}}=1.11$. a. 100 % dinuclear complexes; b. 84 % trinuclear complexes, 16 % mononuclear complexes. The heights of the columns are proportional to the sizes of the different atomic interactions in the complexes in which uranium atoms are involved.

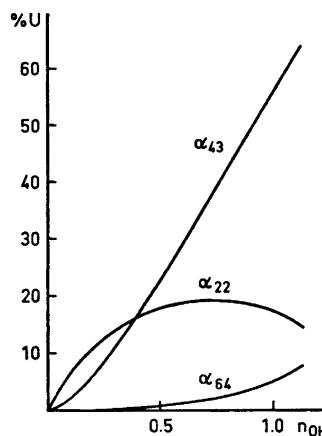


Fig. 7. Survey of the percentage of uranium(VI) bonded in the different hydrolysis complexes $(\text{UO}_2)_q(\text{OH})_p$ (α_{pq}) in a 3.1 M uranyl solution as a function of n_{OH} , calculated from the stability constants given by Dunsmore and Sillén.¹⁸

In order to make a final test of the proposed model for the solution with $n_{\text{OH}}=1.11$, all uranium atoms were assumed to be present as dinuclear complexes of the type shown in Fig. 5, where the nonbridging oxygen atoms may belong to H_2O or OH groups. Keeping all interatomic distances constant and the temperature factor of the U–U interaction constant at 0.009, an overall temperature factor for the uranium-light atom interactions in the model was refined in a least squares procedure with $s_{\text{min}}=2 \text{ \AA}^{-1}$. A value of 0.015 ($\sigma=0.006$) was obtained. The Fourier inversion of the calculated $i(s)$ values for this model is shown in Fig. 6a. The difference between the radial distribution functions obtained from experimental and calculated $i(s)$ values shows that a dinuclear complex alone is not sufficient to explain the experimental results. Next the uranium atoms were assumed to be present as only triangular trinuclear complexes of the type shown in Fig. 5 in addition to unhydrolyzed uranyl ions. The percentage of uranium bonded in the trinuclear complex was refined using experimental data for $s > 2 \text{ \AA}^{-1}$. A value of 84 % ($\sigma=3$) was obtained. This is higher than the value 63 % ($\sigma=6$) obtained previously. The Fourier inversion of the calculated $i(s)$ values for this model is shown in Fig. 6b.

The heights of the columns in Fig. 6 which have been calculated with the formula for theoretical pair interactions given previously are proportional to the sizes of the different atomic interactions in the di- and trinuclear complexes

in which uranium atoms are involved. This figure may explain the second coordination sphere being at 4.3, Å in the hydrolyzed solutions as compared with 4.6₄ Å in the acid solution (Table 2). The distance from one uranium atom to a uranyl oxygen atom bonded to another uranium atom in the same polynuclear complex has been calculated to 4.25 Å. It has a comparatively high frequency (Fig 6) and does not appear in the unhydrolyzed solution.

The numerical results for the average number of U–U distances per U atom in the solution with $n_{\text{OH}} = 1.11$ can now be summarized. In the least squares refinement of experimental $i(s)$ data for $s > 5 \text{ \AA}^{-1}$ a value of 0.63 has been obtained regardless of whether or not corrections for a second coordination sphere have been included. This result shows that uranium-light atom interactions have very little influence on the $i(s)$ data for these higher s values. From the subtraction of the differential radial distribution curve for the acid solution from that for the hydrolyzed solution a value of 0.82 was obtained. This greater value is mainly explained by the contributions from the U–O interaction at 4.25 Å within the polynuclear complexes. From the refinement of the concentration of the trinuclear complex a value of 0.84 was obtained. Here $i(s)$ data for $s > 2 \text{ \AA}^{-1}$ were used and the second coordination sphere at about 4.7 Å outside the trinuclear complex which was not included may explain the high frequency. The most probable value lies between 0.63 and 0.84 which can be regarded as minimum and maximum values, respectively.

Some years ago, Evans² proposed that the dinuclear complex, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, found in hydrolyzed solutions would have the structure later determined for $[(\text{UO}_2)_2(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_4]^{3-}$ and that the trinuclear complex, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, would have a triangular arrangement similar to the one described above. Here a structure has also been proposed for the tetranuclear complex which, according to the emf measurements, should be present in small amounts in the solution with $n_{\text{OH}} = 1.11$ (Fig. 7). It will be proved by a complete crystal structure determination.

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