

## Structure of the Hydrated Dioxouranium(VI) Ion in Aqueous Solution. An X-ray Diffraction and $^1\text{H}$ NMR Study

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X-ray diffraction data on a 1 M aqueous solution of dioxouranium(VI) (uranyl) perchlorate are consistent with the hydrated uranyl ion having a pentagonal-bipyramidal geometry with the U-O distances 1.702 (5) Å within the  $\text{UO}_2^{2+}$  ion and 2.421 (5) Å between the uranium atom and the water of hydration. This structure is not significantly different from the one found in crystals of  $\text{UO}_2(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ . From proton magnetic resonance data in water-acetone mixtures at about  $-80^\circ\text{C}$ , the hydration number of the uranyl ion has been determined to be 4.9 ( $\pm 0.2$ ) in 1 M  $\text{UO}_2(\text{ClO}_4)_2$  solution. In more concentrated solutions, with lower  $\text{H}_2\text{O}/\text{UO}_2^{2+}$  mole ratios, the hydration number decreases. It is shown that these results are not dependent on the acetone concentration. Agreement with previous results is discussed.

### Introduction

Very little is known about the hydration of the dioxouranium(VI) (uranyl) ion in solution. X-ray diffraction studies,<sup>1</sup>  $^1\text{H}$  NMR measurements,<sup>2</sup> and other investigations<sup>3</sup> indicate that water molecules in the first hydration shell may be displaced by  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , or  $\text{Br}^-$  ions. The  $\log K_1$  values are  $\sim 0$ .<sup>3</sup> In the presence of  $\text{ClO}_4^-$  ions, no complex formation seems to occur, and  $^1\text{H}$  NMR data are explained by assuming a hydration number of 4,<sup>2a</sup> indicating a rare octahedral coordination geometry for uranium(VI).<sup>4</sup> A hydration number of 6 is deduced from thermochemical measurements<sup>5</sup> and from another  $^1\text{H}$  NMR investigation.<sup>2b</sup> A hydration number of 5 is found in the crystal structure of  $\text{UO}_2(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ , where each uranyl ion is equatorially surrounded by five water molecules.<sup>6</sup> This pentagonal-bipyramidal geometry is the most common one for uranyl complexes in the solid state.<sup>5b</sup>

The present X-ray and  $^1\text{H}$  NMR investigations of acidic uranyl perchlorate solutions have been carried out in order to determine the structure of the hydrated uranyl ion in aqueous solution.

### Experimental Section

**Materials.** Uranyl perchlorate solutions were prepared and analyzed as described elsewhere.<sup>7</sup> A small amount of standardized  $\text{HClO}_4$  was added in order to avoid hydrolysis. The densities of the solutions were determined with an Anton Paar digital densitometer, DMA35. Acetone and acetone- $d_6$  (99.5%), reagent grade, were used as received, but it was controlled that they did not contain measurable amounts of water. The compositions of the investigated solutions are given in Table I.

**Measurements.** The X-ray-scattering experiments and the treatment of the diffraction data were performed in the same way as described in the previous paper.<sup>8</sup>

The proton magnetic resonance spectra were recorded at 200 MHz (Bruker WP200 spectrometer) by using 5-mm (outer diameter) nonspinning sample tubes. The sample temperature, about  $-80^\circ\text{C}$ ,

was chosen individually for each solution in order to give well-resolved, narrow signals. The variable-temperature accessory (Bruker VT1000) was calibrated with the methanol thermometer.<sup>9</sup> Internal acetone- $d_6$  was used as the field lock. The chemical shifts are given in ppm toward higher frequency with respect to the acetone signal. Its position was practically constant throughout the measurements ( $\pm 0.02$  ppm). It was controlled so that no changes occurred in the integrals of the water peaks when the pulse repetition time ( $\sim 1.5$  s for  $\sim 15^\circ$  pulses) was increased. The spectra were recorded within 24 h after mixing the aqueous solutions with acetone.

### Results and Discussion

**X-ray Diffraction Data.** A 1 M aqueous solution of  $\text{UO}_2(\text{ClO}_4)_2$  was investigated (solution 3, Table I). The reduced intensity data in the form  $s[i(s)]$  are shown in Figure 1. The radial distribution curve,  $D(r)$ , is given in Figure 2, and the  $D(r) - 4\pi r^2 \rho_0$  function is shown in Figure 3. The radial distribution curve shows peaks at 1.6, 2.45, 2.8, 4.5, and 6.75 Å. The first peak at 1.6 Å corresponds to the Cl-O interactions within the tetrahedral  $\text{ClO}_4^-$  ion and the U-O interactions within the linear  $\text{UO}_2^{2+}$  group. These interactions are not resolved. The second peak at 2.45 Å corresponds mainly to the U-O interactions within the hydrated  $\text{UO}_2^{2+}$  group, but the O-O interactions within the  $\text{ClO}_4^-$  ion are also present. O-O interactions within the water structure and the hydrated  $\text{UO}_2^{2+}$  group are expected at about 2.9 Å, where the radial distribution curve has a shoulder. The broad peak at 4.5 Å probably includes U-O interactions from the second hydration shell, light-atom interactions within the hydrated  $\text{UO}_2^{2+}$  group, and also interactions within the remaining water structure.

A structural model for the solution was constructed from tetrahedral  $\text{ClO}_4^-$  ions, tetrahedral  $\text{H}_2\text{O}(\text{H}_2\text{O})_4$  groups, and pentagonal-bipyramidal  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  complexes.

Least-squares refinements were performed as described previously.<sup>8</sup> Experimental data for  $7 \text{ \AA}^{-1} < s < 17 \text{ \AA}^{-1}$  were used. The U-O distance within the  $\text{UO}_2^{2+}$  group and the first U-OH<sub>2</sub> distance were varied in addition to the temperature factors. The results are shown in Table II and Figure 4.

The refined  $r$  values for the first coordination sphere around uranium are in good agreement with the corresponding distances in the crystal structure of  $\text{UO}_2(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ .<sup>6</sup> The average U-O distance within the  $\text{UO}_2^{2+}$  group in the solid perchlorate is 1.71 Å, and the average U-OH<sub>2</sub> distance is 2.45 Å.

The difference curve in Figure 3b has a pronounced peak at 4.4 Å, where U-OH<sub>2</sub> interactions within a second hydration shell are expected to occur. Least-squares refinements of the parameters of these interactions were performed. They converged, and the obtained values ( $r = 4.37 \text{ \AA}$ ,  $b = 0.05 \text{ \AA}^2$ ,  $n$

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Table I. Compositions of the Solutions and Results of the 200-MHz  $^1\text{H}$  NMR Investigations<sup>a</sup>

no.	initial aqueous solution	mole ratios		$\delta^B$ ( $\pm 0.02$ )	$\Delta\nu_{1/2}^B$ , Hz	$\delta^C$ ( $\pm 0.02$ )	$\Delta\nu_{1/2}^C$ , Hz	$\nu^B - \nu^C$ , Hz	$\text{UO}_2^{2+}$ hydration no. ( $\pm 0.2$ )
		$\text{H}_2\text{O}/\text{UO}_2^{2+}$	acetone/ $\text{H}_2\text{O}$						
1	2.945 M $\text{UO}_2(\text{ClO}_4)_2$ ; $[\text{H}^+] \leq 0.09$ M	12.7	0						
1a			3.3 <sup>b</sup>	3.27	37	9.44	57	1235	(4.3) <sup>b</sup>
1b			2	3.38	42	9.45	74	1216	4.6
1c			3	3.35	37	9.48	52	1228	4.6
1d			5	3.23	36	9.51	47	1257	4.6
1e			10	2.99	36	9.53	51	1308	4.5
2	2.222 M $\text{UO}_2(\text{ClO}_4)_2$ ; $[\text{H}^+] < 0.07$ M	19.0	0						
2a			2.2 <sup>b</sup>	3.26	30	9.44	75	1238	(4.5) <sup>b</sup>
2b			2	3.32	36	9.47	64	1231	4.6
2c			5	3.13	32	9.52	42	1287	4.6
2d			10	2.81	29	9.52	48	1343	4.5
3	1.014 M $\text{UO}_2(\text{ClO}_4)_2$ ; $[\text{H}^+] = 0.09$ M	48.6	0						
3a			3.3 <sup>b</sup>	3.02	26	9.47	54	1289	(4.5) <sup>b,c</sup>
3b			3	3.15	31	9.50	51	1271	4.9
3c			10	2.76	30	9.53	40	1355	4.9

<sup>a</sup> Acetone- $d_6$  was used unless stated otherwise. The chemical shifts  $\delta$  are toward higher frequency with respect to the acetone signal. Superscript B represents the bulk water signal and C the solvation water signal.  $\Delta\nu_{1/2}$  is the width at half-height. <sup>b</sup> Contained 90% acetone + 10% acetone- $d_6$ . <sup>c</sup>  $\pm 0.3$ .

Table II. Parameter Values for the Hydrated Uranyl Ion in the 1 M Perchlorate Solution As Obtained from the Least-Squares Refinements (Estimated Standard Deviations in Parentheses)

interaction	$r$ , Å	$b$ , Å <sup>2</sup>	$n$
U-O(uranyl)	1.702 (5)	0.0004 (4)	2
U-O(water)	2.421 (5)	0.0008 (4)	5

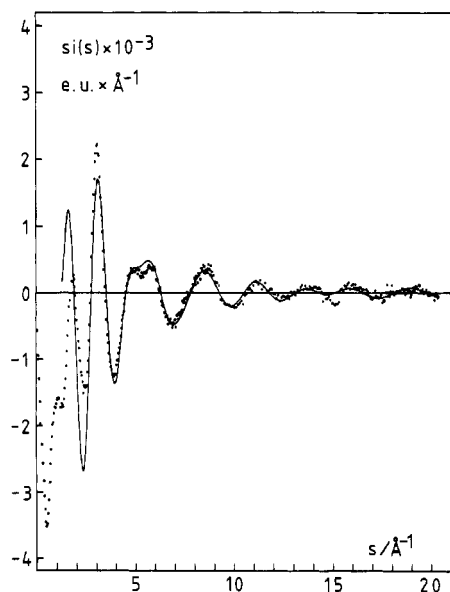


Figure 1. Reduced intensity function,  $i(s)$ , multiplied by  $s$  for the 1 M perchlorate solution (solution 3, Table I). The experimental values are given as dots. The full-drawn curve represents the intramolecular interactions calculated with the use of the parameter values given in Tables II and III.

= 14) gave a significant decrease in the error-squares sum for each  $s$  interval studied.

After the subtraction of the calculated peak shape for the second hydration shell (see Figure 3c), the difference curve for  $r < 5$  Å is rather smooth with a broad peak in a region where light-atom interactions not included in the model are expected to occur (Figure 3d).

With the refined parameter values, theoretical curves were calculated. The parameter values used are given in Table III, and the calculated curves are shown in Figures 1–3.

In a separate series of least-squares refinements, the uranyl group was assumed to be surrounded by four water molecules

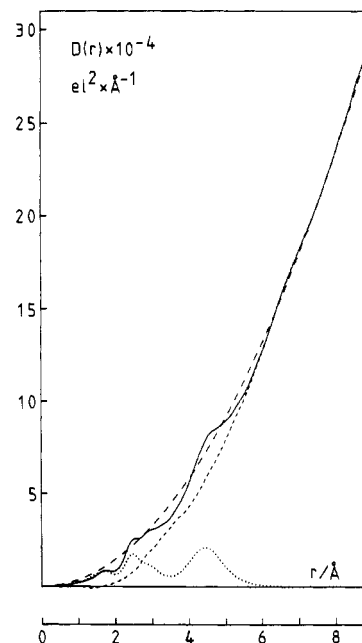


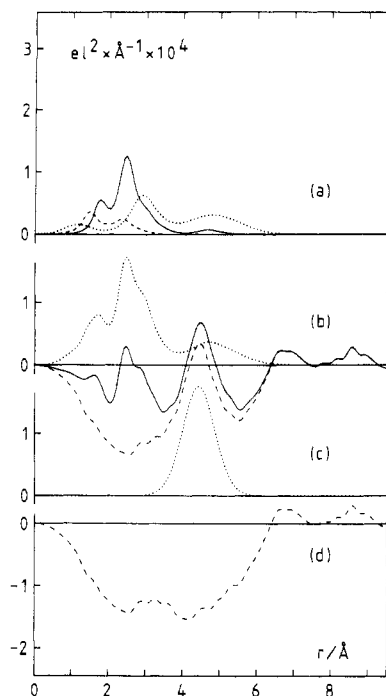
Figure 2. Radial distribution curve,  $D(r)$ , for the 1 M perchlorate solution (solution 3, Table I). The experimental function is shown as a solid line, and the function calculated with the use of the parameter values given in Tables II and III is represented by a dotted curve. The difference between them is marked by short dashes, and the function  $4\pi r^2 \rho_0$  is indicated by long dashes.

Table III. Parameter Values Used for the Calculation of Theoretical Curves for the 1 M Perchlorate Solution

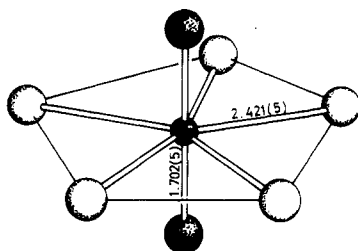
complex <sup>a</sup>	intramolecular dist $r$ , Å	temp factors $b$ , Å <sup>2</sup>
$\text{ClO}_4^-$ tetrahedron	Cl-O 1.43	Cl-O 0.00072, O-O 0.00164
$\text{H}_2\text{O}$	O-H 1.0	O-H 0.004
$\text{H}_2\text{O}^I(\text{H}_2\text{O}^{II})_4$ tetrahedron	$\text{O}^I\text{-O}^{II}$ 2.86	$\text{O}^I\text{-O}^{II}$ 0.015, $\text{O}^{II}\text{-O}^{II}$ 0.2

<sup>a</sup> For  $\text{UO}_2(\text{H}_2\text{O})_5(\text{H}_2\text{O})_{14}^{2+}$  values, see Table II and the text.

in the equatorial plane. The refinements converged properly, and reasonable parameter values were obtained. The error-squares sum values were, however, generally somewhat higher than for the pentagonal model. Coordination of six water molecules at the U-O distance of 2.42 Å would result in too



**Figure 3.**  $D(r) - 4\pi r^2 \rho_0$  function and calculated peak shapes for the 1 M perchlorate solution (solution 3, Table I). In (a) peak shapes calculated separately for the complexes  $\text{ClO}_4^-$  (dashes),  $\text{H}_2\text{O}(\text{H}_2\text{O})_4$  (dots), and  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  (solid line) are shown. In (b) the full-drawn curve is the experimental function and the dotted curve represents the function calculated from the parameter values given in Tables II and III with the second hydration shell excluded. The difference between them is given as dashes. When the calculated peak shape for the second hydration shell, which is shown in (c), is also subtracted, the difference curve in (d) is obtained.

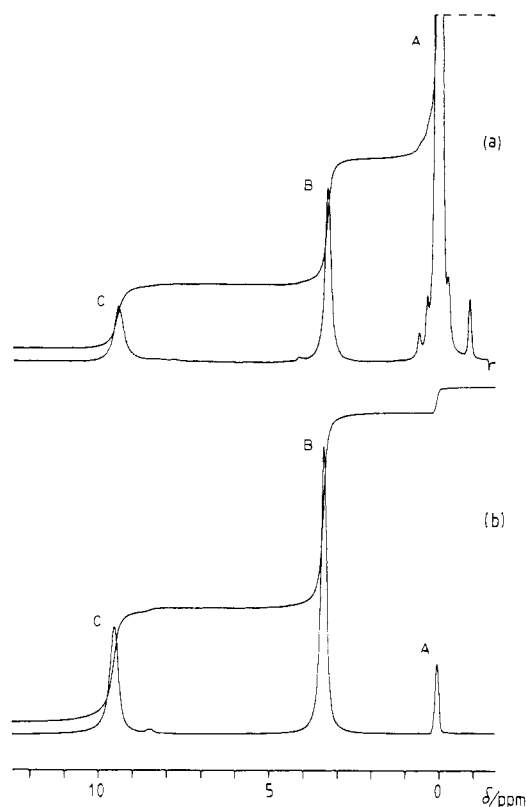


**Figure 4.** Model for the hydrated  $\text{UO}_2^{2+}$  ion. The small filled circle represents uranium, the large filled circles are the uranyl oxygens, and the open circles are the water oxygens. Refined bond lengths with estimated standard deviations in parentheses are given.

short oxygen–oxygen distances within the hydrated  $\text{UO}_2^{2+}$  ion.

Thus, the scattering data alone cannot be used to distinguish between the hydration numbers 4 and 5 for the first coordination sphere around  $\text{UO}_2^{2+}$ . But, as the coordination number of 5 is preferred in the solid state,<sup>5b,6</sup> the  $\text{U}-\text{OH}_2$  distance in  $\text{UO}_2(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}(\text{s})$  is in good agreement with that obtained for the solution and the calculated  $i(s)$  values for the pentagonal model fit the experimental data somewhat better, this model has been chosen as the most likely one (see also Conclusions).

**<sup>1</sup>H NMR Data.** The X-ray diffraction data gave accurate information about the  $\text{U}-\text{O}$  distances but were less sensitive with respect to the number of water molecules surrounding the uranyl ion. Hence, it was decided to determine the hydration number by an independent method, nuclear magnetic resonance, by repeating and extending the <sup>1</sup>H NMR measurements of Fratiello et al.<sup>2a</sup> The method is based on the fact that separate signals can be observed for the bound water and for the bulk water, provided that the chemical exchange is slowed by cooling the sample to low temperature.<sup>10</sup> By in-



**Figure 5.** <sup>1</sup>H NMR spectra of a  $\text{UO}_2(\text{ClO}_4)_2$  solution in water–acetone mixture, recorded at 200 MHz: (a) solution 1a (cf. Table I); (b) solution 1c, where acetone- $d_6$  was used instead of ordinary acetone. The signals arising from acetone (A), bulk water (B), and water molecules in the  $\text{UO}_2^{2+}$  ion solvation shell (C) are labeled.

tegration of the peak areas, the number of the coordinated water molecules can be calculated, if the composition and the density of the solution are known.

The use of an improved spectrometer in connection with a higher magnetic field ought to provide more accurate hydration numbers than those obtained by previous investigators.<sup>2</sup> A comparison of data at two different magnetic fields could also reveal possible systematic errors. We have investigated uranyl perchlorate solutions with three different  $\text{H}_2\text{O}/\text{UO}_2^{2+}$  ratios, varying the amounts of acetone added. (It was not possible to obtain separate peaks for the bound and the free water in the pure aqueous solutions.) The compositions of the solutions as well as the determined hydration numbers are given in Table I. Two representative spectra are shown in Figure 5.

The spectrum of solution 1a, which was chosen to have approximately the same composition as that investigated by Fratiello et al.,<sup>2a</sup> gives a hydration number of  $4.3 \pm 0.2$ , i.e. in agreement with Fratiello's value of  $4.0 \pm 0.4$ . The low-field tail of the acetone peak may partially overlap the peak from the bulk water, resulting in a too low value of the number of coordinated water molecules. We investigated this possible source of systematic error by using acetone- $d_6$  instead of ordinary acetone. The results in Table I show that a higher solvation number is obtained when acetone- $d_6$  is used. This type of systematic error will be larger in the study of Fratiello et al.,<sup>2a</sup> due to the lower magnetic field used by them. Thus, it seems advisable to use acetone- $d_6$  in this type of determination of hydration numbers.

In order to check whether acetone can compete with water as a ligand, we made a series of measurements where the ratio  $\text{H}_2\text{O}/\text{UO}_2^{2+}$  was kept constant, while the ratio acetone/ $\text{H}_2\text{O}$

(10) In several cases acetone has to be added in order to avoid freezing and to keep the viscosity reasonably low.

varied from 2 to 10. The hydration number is 4.6 and is constant within the precision of the measurement ( $\pm 0.2$ ) for  $\text{H}_2\text{O}/\text{UO}_2^{2+}$  ratios equal to 13 and 19, but it increases significantly when the ratio is 49 and approaches the value of 5. It is not possible to investigate the hydration number at higher ratios because of loss of precision in the method. We are not able to explain the discrepancy between the result of Shcherbakov et al. ( $n = 6.0 \pm 0.15$ )<sup>2b</sup> and our result ( $n = 4.9 \pm 0.2$ ) because they do not give experimental details. However, the low magnetic field (60 MHz) used in the previous investigation may be one of the reasons.

The  $^1\text{H}$  NMR measurements indicate a hydration number of 5 for the  $\text{UO}_2^{2+}$  ion at low temperature for a relatively concentrated solution in a mixed  $\text{H}_2\text{O}$ -acetone solvent. We feel that these results are valid also at room temperature, even for dilute solutions and for a pure  $\text{H}_2\text{O}$ -solvent. The reasons are the following:

(1) The hydration number seems to be independent of the temperature as indicated by measurements of the hydration numbers of  $\text{Be}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Ga}^{3+}$  over a 40 °C interval.<sup>11</sup> For  $\text{UO}_2^{2+}$ , we have only been able to confirm a constant hydration number over the 20 °C interval, where precise measurements could be made. A great many studies, e.g. large-angle X-ray and neutron diffraction, NMR, IR, and Raman spectroscopy, indicate that the structures of discrete complexes are very nearly the same in the solid state and in solution. Hence, it seems less probable that a change in solution temperature would cause a change in the geometry of the complex.

(2) The  $^1\text{H}$  NMR measurements have to be made in fairly concentrated solutions in order to be able to measure the concentrations of bulk and bound water with sufficient precision. It can be argued that the hydration number for the ion may be higher when the water/ion ratio is increasing to very high values. However, earlier  $^1\text{H}$  NMR studies as well as numerous X-ray and neutron diffraction investigations reveal that this, in general, is not the case (however, cf. the following section).

(3) Chemical effects of acetone on the coordination of water have previously been observed for  $\text{Mg}^{2+}$  at  $\text{H}_2\text{O}/\text{Mg}^{2+} < 8$ .<sup>12</sup> The present data do not indicate a coordination of acetone to  $\text{UO}_2^{2+}$ . However, the variation of the chemical shifts of the bulk water with increasing concentration of acetone may indicate the presence of hydrogen bonds between the carbonyl oxygens in acetone and water. The hydration number 4.6 may indicate the presence of some inner-sphere coordination of  $\text{ClO}_4^-$ . However, we have not been able to obtain an independent confirmation of this possibility.

All of the recorded spectra showed the presence of a small peak at about 8.5 ppm (cf. Figure 5). Since the integral value of this peak agreed approximately with the concentration of the excess  $\text{H}^+$  (hydrated by some water molecules) and since this integral value was approximately constant for different

acetone concentrations, the peak was assumed to originate from the hydrated proton. No attempt was made to investigate this peak in detail, since this was outside the scope of the present work. It has been shown by Fratiello et al.<sup>2a</sup> that the concentration of excess  $\text{H}^+$  has no influence on the hydration number of  $\text{UO}_2^{2+}$ .

### Conclusions

Two independent experimental methods indicate a hydration number of 5 for  $\text{UO}_2^{2+}$  in 1 M aqueous solution. The solution X-ray diffraction data give a  $\text{U}-\text{OH}_2$  distance of 2.421 (5) Å, which is in good agreement with the value for  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  in the solid state.<sup>6</sup> The corresponding distance is expected to be about 2.35 Å for four-coordination and about 2.49 Å for six-coordination.<sup>13</sup> Four-coordination in the equatorial plane of  $\text{UO}_2^{2+}$  is relatively rare.<sup>4,5b</sup>

$^1\text{H}$  NMR data indicate a coordination number of 5 in the mixed  $\text{H}_2\text{O}$ -acetone solvent at  $\sim -80$  °C. In view of the arguments presented in the previous section, it seems likely that this value is true also in dilute aqueous solution at room temperature.

The recent EXAFS measurements,<sup>14</sup> performed on less concentrated solutions (0.2 and 0.02 M, respectively), are in agreement with our results, even if the accuracy of the EXAFS method is comparably low.

The average hydration number of the uranyl ion (and probably of other ions) decreases when the  $\text{H}_2\text{O}/\text{UO}_2^{2+}$  ratio reaches low values and the concentration of water is much below the value for the pure solvent ( $\sim 55$  M). A similar effect has been observed by Shcherbakov<sup>2b</sup> for  $\text{UO}_2^{2+}$  and by Hewish et al.<sup>15</sup> in their neutron diffraction investigation of the  $\text{Ca}^{2+}$  ion in aqueous solution. The hydration number of  $\text{Ca}^{2+}$  increased from  $\sim 6$  to  $\sim 10$  as the molality decreased from 4.5 to 1.<sup>15</sup> The coordination number of the metal ion is probably still constant. This may be achieved either by sharing of one water molecule between two metal ions or by inner-sphere coordination of the counterions. The dependence of the hydration number on the solute concentration should be taken into account in all experimental determinations of hydration numbers.

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**Registry No.**  $\text{UO}_2(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ , 63815-02-1.

**Supplementary Material Available:** A listing of primary experimental data in the form of  $i(s)$  for the solution investigated by X-ray diffraction (7 pages). Ordering information is given on any current masthead page.

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