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On the Structure of the Hydrolysis Products of Thorium

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An X-ray investigation has been made of solutions prepared by dissolving aqueous thorium oxide in thorium nitrate solutions. The variation of the scattering curves with the hydroxyl number at a total constant thorium concentration = 2 M has been measured. The coordination number found for thorium in solution is close to the values found in crystal structures. The nitrate group is coordinated to thorium as a bidentate ligand. A dominating dinuclear complex is consistent with the data for low hydroxyl numbers but for more than about 2 OH per Th the average nuclearity is four or larger. The shortest distance between the thorium atoms in the polynuclear hydrolysis products is 3.94 Å, which is close to values found in basic thorium salts. Some structural models consistent with the scattering data are discussed.

As part of a work on the structure of the hydrolysis products of thorium, an X-ray investigation has been made of solutions prepared by dissolving aqueous thorium oxide in thorium nitrate solutions. The X-ray scattering data can give information on heavy atom bonding distances within the dissolved complexes. It can also be used to estimate the number of such distances and the coordination number of the heavy atoms. In special cases, when very concentrated solutions containing only one complex can be prepared, the information may be sufficient for a unique interpretation of the structure of the complex. In most other cases it can be used to limit the number of conceivable structures for the main complexes.

Several suggestions have been made about the polynuclear hydroxo complexes of thorium believed to exist in solution. Literature surveys have recently been made[1,2] and will not be repeated here. Most investigators seem to agree, however, that a dinuclear complex is first formed, which is then followed by complexes of higher nuclearity. Complexes containing 3, 4, 5, 6, 7 and up to an indefinite number of metal atoms have been suggested.

In the present work, solutions were investigated in which the thorium concentration was kept constant at 2 M but the hydroxyl number, n_{OH}, *i.e.* the number of hydroxyl groups per thorium atom, was varied. Nitrate was

used as the anion as it does not contain any atom heavier than oxygen, and thus contributes to a levelling off of background peaks from light atom interactions.

PREPARATION OF SOLUTIONS

Aqueous thorium oxide was precipitated by NH_3 from a nitrate solution, washed by decantation and immediately dissolved in a thorium nitrate solution. After evaporation to the desired concentration, the amount of thorium was determined by igniting to ThO_2 either directly or after precipitation with NH_3. The analytical hydrogen ion excess, H, was determined by passing a portion of the solution through a cation exchanger and titrating the eluate with NaOH. The result was checked by precipitating a known amount of the solution by a known excess of NaOH and titrating the remaining hydroxide with $HClO_4$. The amount of nitrate was calculated from the value of H and the thorium concentration. In most instances it was known also from the way the solution was prepared. The densities were determined with a pycnometer.

The concentrations of the various solutions are given in Table 1. All of the solutions were visibly clear and stable for an indefinite period of time. For lower values of H, that is for larger hydroxyl numbers, a weak Tyndall effect was apparent and was clearly observable for solutions with n_{OH} larger than about 2.

Table 1. Concentrations of solutions in gatoms/l. (n_{OH} = number of hydroxyl groups per Th atom).

n_{OH}	0	0.69	0.94	1.24	1.57	1.95	2.11	2.44	2.79	3.00
Th	1.93_7	1.94_0	1.95_0	1.94_5	1.94_8	1.95_7	1.96_6	1.93_5	1.94_7	1.93_9
O	67.8	67.7	66.8	65.6	64.7	63.3	62.8	62.3	61.0	60.6
N	8.23	6.43	5.97	5.36	4.74	4.01	3.71	3.01	2.35	1.94
H	86.7	95.4	95.9	96.6	97.9	98.7	99.1	101.9	102.4	103.8

On evaporation of the solutions with the larger H values ($H \approx -0.5$) crystals of a basic nitrate $Th_4(OH)_2(NO_3)_6(H_2O)_8$ were formed, which, according to a crystal structure determination,[3] contain discrete dinuclear complexes with two Th atoms joined by a double hydroxo bridge. For smaller H values ($H \approx -1$) crystals of another basic nitrate, $Th(OH)_2(NO_3)_2(H_2O)_x$, containing infinite one-dimensional thorium hydroxo complexes are formed.[4] For still lower H values the solutions solidify to a clear glass-like substance without the formation of crystals. From the solutions with $H \approx 0$ or larger the neutral thorium nitrate pentahydrate, which is built up from $Th(NO_3)_4(H_2O)_3$ molecules,[5,6] crystallizes.

X-RAY MEASUREMENTS

The X-ray scattering was measured in a diffractometer described in a previous paper[7]. Ag$K\lambda$-radiation ($\lambda = 0.5594$ Å) was used. The range in θ (2θ = the scattering angle) covered 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, 1, and 2° were used. Measurements were made at discrete points at intervals of 0.2° up to $\theta = 5°$, 0.25° to $\theta = 20°$, and 0.5° to $\theta = 70°$. About 40 000 counts were usually taken for each point, which corresponds to a statistical error of about 0.5 %. All data were recalculated to the same slit width by means of measurements in overlapping regions. Within each region the measurements were repeated once at larger intervals in order to detect and correct for long-time variations in the X-ray and the counting equipment. These variations were practically always less than 1 % of the measured intensity.

The measured data were corrected for polarization in the solution and in the monochromator. The amount of incoherent radiation reaching the counter was estimated in a

half-empirical way from the spectrum of the X-ray tube and the resolving power of the monochromator.

After correction for polarization, the observed intensity values were scaled by comparison with the sum of the independent coherent scattering ($\sum n_i f_i^2$) and the incoherent scattering in the high-angle region ($\theta > 45°$) of the scattering curves. The form factors given by Cromer and Waber [8] for the neutral atoms were used. Anomalous dispersion corrections according to Cromer [9] were applied to thorium ($\Delta f' = -3.95$, $\Delta f'' = 10.29$). The amount of incoherent radiation was obtained from the *International Tables* [10] for O and N, and was calculated from the formulas, given by Bewilogua [11] for Th and by Compton and Allison [12] for H.

Because of the short wavelength of Ag$K\alpha$-radiation the first peak in the scattering curves appears at a rather low θ-value, about 1.3°, for the most hydrolyzed solutions. In order to get a confirmation of this peak and also to get an independent check of the Ag$K\alpha$-data, particularly of the amount of incoherent radiation reaching the counter, the X-ray scattering from some of the solutions was also measured by Mo$K\alpha$ or by Cu$K\alpha$-radiation in combination with a focusing quartz monochromator. No significant differences were found, but the scaling factors obtained for the Ag$K\alpha$-data, when the high-angle region was used for the scaling, seemed to be slightly too low to judge from the overall fit to the $\sum n_i f_i^2$ curves. In order to assure a fit over the whole θ-range a correction was introduced. The final scaling factors obtained in this way were about 3 % higher than those originally determined. This uncertainty in the scaling factors may introduce a systematic error towards too large values in the estimate of the number of pair interactions for a particular distance. The maximal errors, however, will not exceed the standard deviations given in Table 2.

Table 2. Results of the least squares refinements of the $i(s)$ curves. n_{OH} = hydroxyl number, x_N = fraction of nitrate bonded to Th, d = distance in Å, n_d = number of interactions per Th atom. Standard deviations are given in parentheses.

	n_{OH}	0	0.69	0.94	1.24	1.57	1.95	2.11	2.44
	x_N	1	1	1.11	1.10	1.11	0.7	0.7	0.4
				(0.10)	(0.10)	(0.10)	(0.2)	(0.2)	(0.3)
1st Th—O distance	d	2.51	2.54	2.50	2.47	2.47	2.55	2.57	2.53
		(0.03)	(0.03)	(0.03)	(0.04)	(0.02)	(0.02)	(0.02)	(0.02)
	n_d	3.6	5.7	4.7	4.4	5.6	7.6	6.9	8.3
		(0.4)	(0.5)	(0.6)	(0.7)	(0.5)	(0.8)	(0.9)	(0.9)
2nd Th—O distance	d	4.70	4.78	4.77	4.77	4.77	4.72	4.67	4.52
		(0.04)	(0.03)	(0.03)	(0.04)	(0.03)	(0.04)	(0.03)	(0.04)
	n_d	7.9	10.6	11.6	10.9	12.1	11.5	12.2	17.6
		(0.8)	(1.1)	(1.4)	(1.2)	(1.4)	(0.8)	(0.9)	(2.2)
3rd Th—O distance	d	6.85	6.61	6.50	6.56	6.54	6.50	6.54	6.59
		(0.30)	(0.13)	(0.13)	(0.09)	(0.06)	(0.07)	(0.04)	(0.04)
	n_d	0.8	3.2	2.8	4.2	5.9	6.2	7.3	7.5
		(0.9)	(1.0)	(1.1)	(1.2)	(1.0)	(0.8)	(0.8)	(1.0)
Th—Th distance	d	—	3.99	3.935	3.943	3.935	3.918	3.922	3.925
			(0.05)	(0.024)	(0.019)	(0.011)	(0.008)	(0.007)	(0.007)
	n_d	—	0.44	0.56	0.75	1.11	1.33	1.47	1.52
			(0.07)	(0.08)	(0.07)	(0.06)	(0.05)	(0.05)	(0.06)
Calculated from above values:									
Number of NO_3 bonded per Th		4.2	3.3	3.4	3.0	2.7	1.4	1.3	0.6
		(—)	(—)	(0.4)	(0.3)	(0.3)	(0.4)	(0.4)	(0.3)
Coordination number of Th		12.1	12.4	11.4	10.5	10.5	10.3	9.5	9.5
		(0.9)	(0.9)	(0.9)	(1.0)	(0.8)	(1.1)	(1.1)	(1.0)

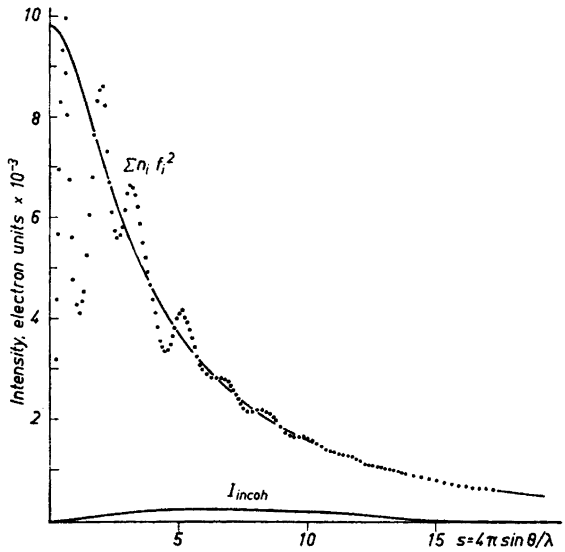

Fig. 1. Survey of measurements on the solution with $n_{OH} = 2.11$. Observed intensity values, after scaling and correction for incoherent radiation, are indicated by dots.

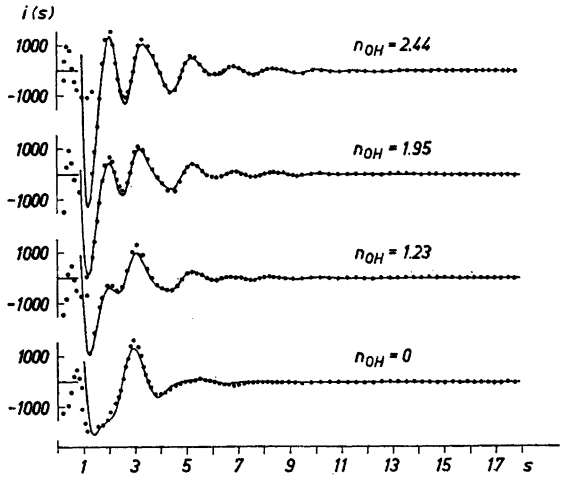

Fig. 2. Reduced intensity functions $i(s)$. Only every second experimental point has been marked. The full-drawn curves are calculated with the parameters given in Table 2. For $s < \sim 1.5$ the values have been reduced by a factor of 5 in the drawing.

TREATMENT OF THE DATA

The reduced intensity function $i(s) = I_{obs} - \sum n_i f_i^2$ was calculated by taking the difference between the scaled experimental intensity values, I_{obs}, after correction for incoherent radiation, and the sum of the squares of the form factors, $\sum n_i f_i^2$, for a stoichiometric unit chosen to be the unit containing one thorium atom. The procedure is illustrated for one of the solutions in Fig. 1. Some of the $i(s)$ curves are given in Fig. 2.

The radial distribution functions, $D(r)$, were calculated from:

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi} \int_0^{s_{max}} s \cdot i(s) \cdot f(s) \cdot ds$$

Here $s = 4\pi \sin\theta/\lambda$ and the modification function $f(s) = f_{Th}^{\circ}/f_{Th}(s) \cdot \exp(-ks^2)$ with f_{Th}° the scattering factor of Th at $s = 0$. For k a value of 0.01 was used. The average scattering density ϱ_0 is given by the square of the number of electrons per unit volume. Radial distribution functions, $D(r)$, and functions $D(r) - 4\pi r^2 \varrho_0$ are shown in Figs. 3 and 4, respectively.

All calculations were made on a computer. The experimental values were read into the computer and, after corrections, were scaled and compared with the calculated $\sum n_i f_i^2$ values obtained for each experimental point by interpolation in the scattering factor tables with the use of the five values nearest to the experimental s value. The resulting reduced intensity values were stored in the computer for later calculations of radial distribution functions and least squares refinements. The experimental values were thus kept

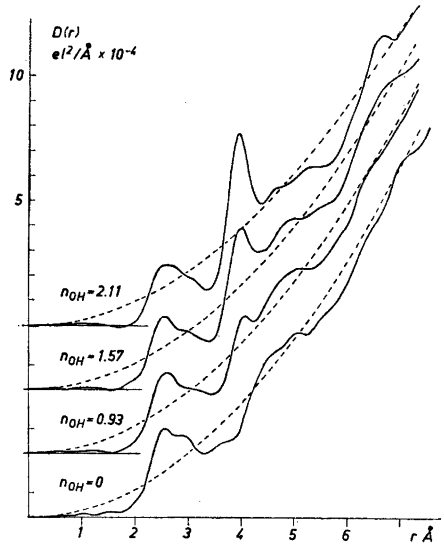

Fig. 3. Radial distribution functions $D(r)$.

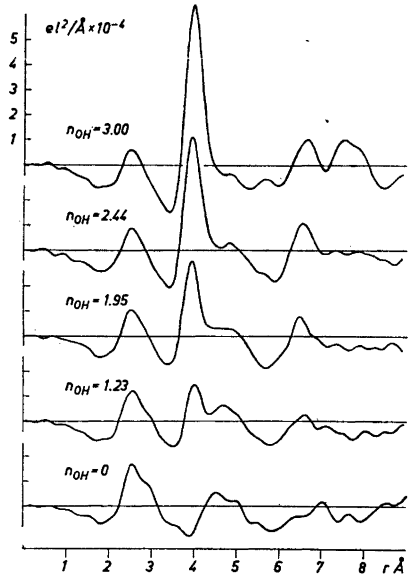

Fig. 4. Functions $D(r) - 4\pi r^2 \varrho_0$.

unchanged in all the following calculations and no smoothing out of the statistical variations was made.[13]

Theoretical pair interaction functions $f_i f_j \sin sr_{ij}/sr_{ij}$ were calculated in an analogous way with the use of the same modification function, $f(s)$, and the same cut-off limit for the Fourier inversion. A temperature factor $\exp(-bs^2)$ was introduced.

The least squares refinement used to fit a theoretical model to the experimentally determined intensity values was carried out by means of a computer program based on Sillén's Letagrop program.[14] Minimum was sought for the function $\sum(s \cdot I_{obs} - s \cdot I_{calc})^2$.

ANALYSIS OF THE RADIAL DISTRIBUTION CURVES

The main change in the radial distribution curves when the hydroxyl number is increased (Figs. 3 and 4) is the appearance of a sharp peak at 4.0 Å. A much smaller peak at 6.5 Å also is related to the hydrolysis process and increases slightly with increasing hydroxyl number. The peak at 2.6 Å becomes sharper and slightly smaller with increasing hydrolysis, reflecting changes in the first coordination sphere around the thorium atom.

In the more hydrolyzed solutions the 4 Å peak appears very sharp and can be fitted closely to a calculated curve for a single Th—Th interaction. Thus it represents a single Th—Th bond and it has a length which is very nearly the same as that found in crystals of basic thorium salts in which two Th atoms are bonded by a double hydroxo bridge.[3]

The peak at 2.6 Å represents interactions between a Th atom and the light atoms in the first coordination sphere. In crystals this distance is generally found to be about 2.5 to 2.7 Å.[3,5,6] For low hydroxyl numbers the peak has a hump at about three Å which disappears when hydrolysis is increased. Interactions between light atoms, the average distances of which are about 3 Å, may give some contribution to this peak, but this contribution should be fairly independent of the degree of hydrolysis. Therefore the asymmetry of the peak is probably to be explained by complex formation between nitrate and thorium. In the solid thorium nitrates the nitrate group has been found to act as a bidentate ligand with a Th—N distance of 3.0 to 3.1 Å.[3,5,6] This is consistent with the appearance of the peak in the radial distribution curves and thus indicates a similar bidentate complexing in the solution. The disappearance of the asymmetry and the reduction of the peak size with increasing hydrolysis, i.e. decreasing nitrate concentrations, are in agreement with this assumption.

A second coordination sphere around the thorium atom is also clearly indicated, although somewhat obscured by the appearance of the 4 Å peak in the more hydrolyzed solutions. It occurs at about 4.7 Å which is approximately the distance one would expect from packing considerations and atomic radii. There are also indications of a third coordination sphere in the region around 6 to 7 Å.

LEAST SQUARES REFINEMENT OF THE INTENSITY FUNCTIONS

In order to get a more quantitative evaluation of the changes in the scattering curves with the changes in hydroxyl number, theoretical intensity curves were calculated for a simplified model of the solution. The parameters in the model were refined by means of a least squares procedure until the best fit to the experimental $i(s)$ curves was obtained.

The model was composed of a number of pair interactions involving thorium atoms. For each, three parameters were introduced and refined: the distance, the number of interactions per Th atom and a temperature factor. Th—O distances representing first, second, and third coordination spheres (at about 2.5 Å, 4.5 Å, and 6.5 Å) of thorium were included as well as a Th—Th distance of about 4 Å. The nitrate complexing was represented by interactions between a Th atom and a nitrate group bonded as a bidentate ligand with a Th—N distance of 3.1 Å, the same as that found in crystal structures. The Th—N and the corresponding three Th—O distances were kept constant in the refinement and only the fraction of the total amount of nitrate bonded to thorium ($= x_N$ in Table 2) and a temperature factor were refined.

The first part of the intensity curves ($s < 1.5$ Å^{-1}) was excluded, both because it is more difficult to determine experimentally and because the main contributions to the first peak come from the highly damped intermolecular interactions, which were not included in the model. The outermost part of the curves ($s > 15$ Å^{-1}) in which peaks can no longer be observed was also not included.

The refinement of this simplified structural model led, for all solutions, to values for the fraction of nitrate bonded to thorium, which did not differ from $x_N = 1$ by more than the value of the corresponding standard deviation. Thus the number of nitrates bonded to thorium decreased from about 4 in the non-hydrolyzed solution to about 1.5 for $n_{OH} = 2.4$. According to stability constants given in the literature for thorium nitrate complexes [15] one would expect about 3.5 nitrate groups per thorium in the non-hydrolyzed solution.

Because of these results a slight modification in the model was made with the following refinements. All nitrate groups were assumed to be coordinated to thorium, *i.e.* $x_N = 1$, for the solutions with $n_{OH} = 0$ and 0.7. An O—O pair interaction at 3 Å, the average light atom distance in the solu-

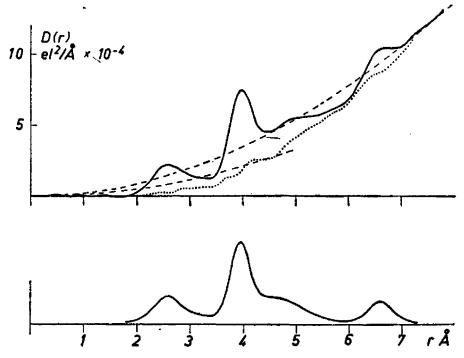

Fig. 5. The Fourier inversions of the experimental $i(s)$ curve (upper drawing) and the calculated $i(s)$ curve (lower drawing) for the solution with $n_{OH} = 2.4$. The difference between the two curves is given by the dotted line. The two dashed lines are $4\pi r^2 \varrho_0$ functions, the upper line includes all atoms, the lower line only light atoms.

tions, was introduced and the number of such distances was refined. The value found was 0.5 ($\sigma = 0.3$), which thus represents the number of O—O interactions per O atom beyond an average value at this distance. This was introduced as a constant correction for light atom interactions for all the other solutions. The introduction of this correction has no significant influence on the other parameters in the model but it leads to somewhat lower least squares error sums.

The final results of the refinements are given in Table 2. The temperature factors were about 0.009 ($\sigma = 0.002$) for the Th—Th bond and 0.01 to 0.04 for the Th—O interactions. The agreement between some calculated and observed $i(s)$ curves is shown in Fig. 2. The corresponding Fourier inversions for one of the solutions is shown in Fig. 5.

DISCUSSION

The coordination of thorium. The parameters given in Table 2 lead to coordination numbers of the thorium atom varying from 12 in the acid solution to 9.5 in the most hydrolyzed solution, with estimated standard deviations of about 1 oxygen atom. To the errors given by the standard deviations should be added the systematic errors caused by the unknown light atom interactions for which only an approximate correction could be introduced in the refinement. However, even the most unfavorable assumption about these will not affect the coordination numbers to any large extent, since the Th—O peak occurs at a distance of 2.6 Å (Fig. 3), which is considerably shorter than the expected first light atom distance of about 3 Å. The estimated standard deviations are therefore probably realistic but the deduced coordination numbers are likely to be maximum numbers.

In crystals of thorium nitrate pentahydrate [5,6] and in the basic nitrate $Th_2(OH)_2(NO_3)_6(H_2O)_8$[3] each Th atom is in contact with 11 oxygen atoms.

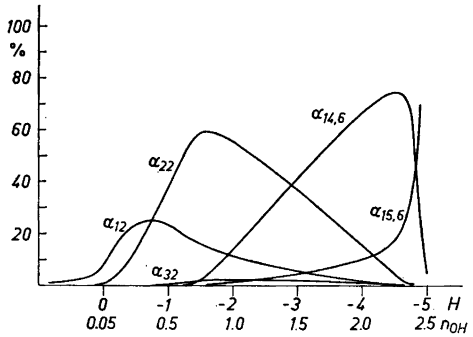

Fig. 6. Survey of the percentage of thorium bonded in the different hydrolysis complexes $Th_q(OH)_p$ (α_{pq}) in a 2 M thorium solution as a function of H and n_{OH}, calculated from the stability constants given by Hietanen and Sillén.[16]

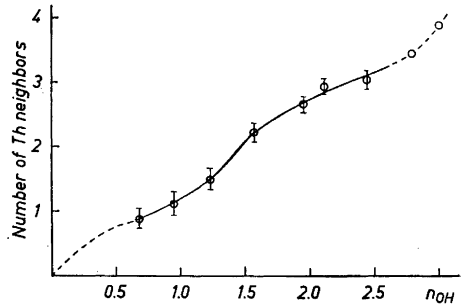

Fig. 7. Average number of nearest Th neighbors around each thorium atom as a function of n_{OH}. The vertical lines indicate the standard deviations. For the two solutions with the largest n_{OH} values the numbers have been estimated from the radial distribution curves.

In thorium salts without a ligand with the short O—O distance of the nitrate group, the coordination number is generally found to be 8.

The polynuclear hydrolysis complexes. The average shortest Th—Th distance in the polynuclear complexes is 3.94 Å with no significant deviations between the different solutions (Table 2). The average number of nearest Th neighbors around each Th atom is given in Fig. 7 as a function of the hydroxyl number.

With the use of the stability constants given by Hietanen and Sillén [16] for the hydrolysis complexes of thorium in a 3 M chloride medium, the complex concentrations have been calculated for a 2 M thorium solution. The results are shown in Fig. 6. Provided that these constants are valid for the concentrated solutions used here, dinuclear complexes should be dominating for $n_{OH} \approx 0.7$, which corresponds to the second solution in Table 1. In this solution each Th is bonded to approximately one other Th atom (Fig. 7) as expected for a dinuclear complex. Moreover, crystals containing dinuclear complexes can be obtained from such a solution.[3] The Th—Th distance within the complexes is 3.988 Å ($\sigma = 0.002$ Å) in the crystals. In the solution it is 3.99 Å ($\sigma = 0.05$ Å). It seems likely, therefore, that dinuclear complexes, with a structure similar to that found in the crystals, occur in the solution, although the interpretation of the scattering curves is not, of course, unique in this respect.

For $n_{OH} \approx 2.4$ the average number of neighbors at the distance 3.94 Å has increased to about 3.0 ($\sigma = 0.2$). The temperature factor calculated for the corresponding Th—Th interaction corresponds to a root mean square variation of the distance of about 0.1 Å, which indicates that it is probably a single distance with no structure dependent deviations between the different distances within the complexes.

The radial distribution curves (Fig. 4) and the results of the least squares refinements (Table 2) show that the only other peak which increases significantly with increasing hydrolysis up to $n_{OH} = 2.4$ is the one at 6.5 Å. It is therefore directly related to the hydrolysis process and may represent Th—O interactions, as assumed in Table 2, or Th—Th interactions. In the latter case it would correspond to somewhat more than 0.5 Th—Th interactions per Th atom for the solution with $n_{OH} = 2.4$.

A possible interpretation of the data would be to assume, beside the dinuclear complex, the formation of a tetrahedral complex. A model can easily be made by a combination of two of the dinuclear complexes found in the $Th_2(OH)_2(NO_3)_6(H_2O)_8$ structure.[3] Each of the tetrahedrally arranged thorium atoms would then be joined to its three neighbors by double bridges of oxygens and each of the four bridging oxygens would be common to three thorium atoms.

The combination of a dinuclear and a four-nuclear complex would quantitatively explain the size of the 3.94 Å peak for all the solutions with $n_{OH} < 2.4$. The longest Th—O distances within the complexes would be about 6.5 Å and would thus contribute to and explain the increase of the corresponding peaks in the distribution curves.

There are, however, a number of indications of an alternative interpretation, which would give equal or better agreement with the scattering data. The 6.5 Å peak seems somewhat too large and too sharp to be caused only

by Th—O interactions. The apparent levelling off of the curve in Fig. 7 at the limiting value of three nearest neighbors expected for a tetrahedral complex does not continue when the hydroxyl number is increased beyond about 2.4. The two solutions with $n_{OH} > 2.4$, which were investigated (see Table 1) also show a new peak at 7.6 Å, which is obviously caused by Th—Th interactions (Fig. 4). The results from the measurements on these two solutions were not used for a least squares refinement because here apparently larger complexes are formed and the simplified model used for the other solutions is no longer sufficient. Also, the solutions showed a rather strong Tyndall effect. However, there is hardly any reason to expect that the complexes at these large hydroxyl numbers should differ basically from those in the less hydrolyzed solutions, and if a Th—Th interaction occurs at 7.6 Å, which is about twice the primary distance of 3.94 Å, an intermediate Th—Th distance must also occur, as each Th atom has more than two nearest neighbors. This would indicate that the 6.5 Å peak at least in part is caused by Th—Th interactions.

The scattering data alone are obviously not sufficient for a unique interpretation of the structure of the complexes. The Th atoms could be positioned in a slightly puckered layer at the corners of regular triangles sharing edges, an arrangement which for complexes of low nuclearity would lead to the three distances assumed to represent Th—Th interactions. Another possibility, which would explain the Th—Th peaks at 3.94 Å and 6.5 Å, would be an arrangement in which the Th atoms occupied the corners of tetrahedra sharing faces. More crystal structure determinations of strongly basic thorium salts are probably necessary to obtain more conclusive evidence about the structure of the hydrolysis products. In any case the solution X-ray data seem to indicate that the number of Th atoms in the complexes is rather low and probably does not exceed five or six in solutions with hydroxyl numbers smaller than about 2.4.

Although the scattering data are not sufficient for a unique interpretation of the structures some structural models, which for other reasons would seem likely, can be eliminated as they are not in agreement with the data.

The linear complexes $Th(Th(OH)_2)_n$ found in the basic thorium salts for which crystal structures have been determined, do not seem to occur in the hydrolyzed solutions, with the exception of the dinuclear complex which is the first member of the series. The size of the 3.94 Å peak and the absence of a sufficiently large second peak show that a condensation to linear complexes of this kind does not take place.

A regular octahedral complex of the type found for example in crystals of $U_6O_4(OH)_4(SO_4)_6$[17] would have a second distance at $\sqrt{2} \times 3.94 = 5.57$ Å, which is not present in the radial distribution curves.

Although the Th—Th distance of 3.94 Å is close to that found in the cubic ThO_2 structure, 3.96 Å, it is not related to this structure in which the Th atoms have a face-centered arrangement.

CONCLUSIONS

The scattering data show that when thorium nitrate solutions are hydrolyzed the hydrated thorium ions are condensed to polynuclear hydrolysis products in which the shortest Th—Th distance is 3.94 Å. This distance

is close to corresponding distances in solid hydroxo salts of thorium in which the Th atoms are joined by double oxygen bridges and it seems likely that a similar type of bridging occurs in solution.

The scattering data are consistent with the occurrence of a dominating dinuclear complex at low hydroxyl numbers. For larger hydroxyl numbers up to $n_{OH} \approx 2.4$ the average nuclearity still seems to be rather low and does not exceed 5 or 6, but for $n_{OH} > 2.4$ the condensation increases further.

In order to explain the scattering data over the whole range of hydroxyl numbers investigated it seems to be necessary to assume the occurrence of more than one dominating complex beside the dinuclear one. The scattering data are not, however, sufficient for a unique interpretation of the structures of these complexes since more than one structural model can be shown to be in approximate agreement with the data.

Preliminary X-ray measurements on hydrolyzed perchlorate and chloride solutions have shown that the condensation process is not noticeably influenced by the anion present, at least for the small distances considered here. Both the 3.94 Å and the 6.5 Å peaks occur in the radial distribution curves with approximately the same frequencies as for the nitrate solutions. Thus the same types of complexes should occur.

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