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An X-Ray Investigation of the Coordination and the Hydrolysis of the Uranium(IV) Ion in Aqueous Perchlorate Solutions

STEVAN POCEV* and GEORG JOHANSSON

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

The coordination of the uranium(IV) ion in acid and hydrolyzed water solutions of uranium(IV) perchlorate has been investigated by means of X-ray scattering measurements. Analysis of the scattering data indicates a well-defined inner coordination sphere around the uranium(IV) ion with a coordination number which is not significantly different from eight. The perchlorate groups do not enter the inner coordination sphere but seem to form outer-sphere complexes. In hydrolyzed solutions polynuclear hydrolysis complexes are formed with a shortest U–U distance within the complexes of 4.0 Å. This is indicative of the formation of a double hydroxo bridge between the uranium atoms.

An X-ray investigation of the structures of the hydrolysis products of thorium(IV) in aqueous nitrate solutions has been reported in a previous paper.[1] The polynuclear hydrolysis complexes were found to be built up from thorium atoms joined by double hydroxo bridges and the nitrate groups were bonded to the thorium atoms as bidentate ligands in inner-sphere complexes. A similar investigation of uranium(IV) perchlorate solutions is reported in the present paper. Polynuclear hydrolysis complexes are formed in this case also, and the metal-metal distances within the complexes indicate the same type of bridging as for thorium. The perchlorate ions, however, do not seem to enter the first coordination sphere.

Because of its high charge the U^{4+} ion hydrolyzes easily. Several investigators have found evidence for the ion $U(OH)^{3+}$.[2] An early investigation by emf methods by Hietanen,[3] carried out in a 3 M perchlorate medium with U(IV) concentrations between 2 mM and 40 mM, showed that polynuclear complexes are also formed. The results were interpreted in terms of the "core +

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* Permanent address: University of "Kiril and Methodi", Faculty of Technology and Metallurgy, Skoplje, Yugoslavia.

link" hypothesis, assuming the formation of an infinite series of complexes with the general formula $U[(OH)_3U]_n^{(n+4)+}$.

In the present work the X-ray scattering from three different uranium(IV) perchlorate solutions has been measured.The uranium concentration was kept constant at about 2 M in all of the solutions, but the acidity was varied. Because of precipitation the hydrolysis could not be carried as far as was possible for Th^{4+}. For the most hydrolyzed of the solutions investigated, however, it was found that polynuclear complexes are formed and the shortest metal-metal distances within the complexes could be determined.

EXPERIMENTAL

Preparation of solutions. Uranium(IV) perchlorate was prepared by cathodic reduction of uranyl(VI) perchlorate. The uranyl perchlorate was prepared from uranyl nitrate (Merck, *p.a.*) in the following way: Hydrogen peroxide was added to an aqueous solution of the uranyl nitrate. The precipitate of uranium peroxide was filtered off and was ignited at 850°C. The U_3O_8, which was thus formed, was dissolved in an excess of perchloric acid, H_2O_2 being added simultaneously. The resulting uranyl perchlorate solution was evaporated until crystallization occurred. The crystals were dissolved in doubly-distilled water, and the uranium concentration and the acidity were adjusted to give suitable starting solutions for the reduction to uranium(IV) perchlorate.

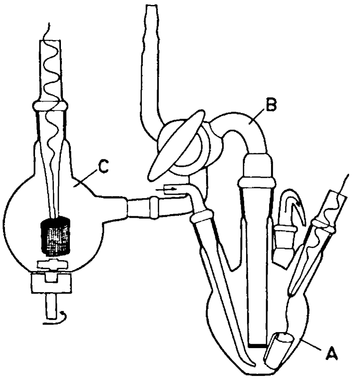

Fig. 1. The apparatus used for the reduction of the uranyl(VI) perchlorate solutions.

Cathodic reduction. The apparatus used for the reduction is illustrated in Fig. 1. The uranyl perchlorate solution was introduced into the vessel A. The anode compartment, C, was filled with a solution of ferrous perchlorate. The bridge, B, which contained 1 M perchloric acid, was separated from the anode compartment by a sintered glass disc (G-3). A gold cathode and a platinum net anode were used. A Regatron power supply (C633CMK) was used to obtain a 100 mA constant current, corresponding to a current density of about 7 mA/cm² and a voltage of about 30 V. A stream of oxygen-free nitrogen was bubbled through the cathode compartment before and during the reduction. Any residual traces of oxygen were removed from the nitrogen by passing the gas through a column of dispersed metallic copper at 200°C. The nitrogen gas was saturated with water vapor before being passed into the cathode compartment. The solution at the anode was stirred with a magnetic stirrer in order to decrease the concentration polarization.

The time needed for the reduction was estimated from the constant current used and from the amount of uranyl perchlorate. Hydrolyzed solutions were prepared by decreasing the concentration of $HClO_4$ in the starting solution. If this decrease was carried too far a black precipitate, probably UO_2, appeared at the cathode. This limit, which determines the maximum degree of hydrolysis that can be obtained by this method, was found by trial and error.

Analysis of the solutions. The solutions were analyzed for U(IV), U(VI), and ClO_4^- both before and after the X-ray measurements. The hydrogen ion excess, H, was obtained from the material balance. No significant change in composition was caused by the X-ray irradiation.

Uranium(VI) was determined gravimetrically by precipitation as uranium peroxide, igniting at 850°C and weighing as U_3O_8. Uranium(IV) was determined, after acidifying the solution with 1 M H_2SO_4, by titration with $KMnO_4$ under nitrogen atmosphere. The $KMnO_4$ solution was standardized against sodium oxalate.

Perchlorate was determined with a cation exchange resin (Dowex 50W-X8). The uranium(IV) perchlorate was oxidized by a stream of oxygen and was then passed through a column of the H^+ saturated ion exchanger. The eluate was titrated with a sodium hydroxide solution.

The compositions of the solutions are given in Table 1. About 2 % of the uranium in the solutions investigated was present as uranium(VI), but this amount is too small to have any noticeable effect on the results.

Table 1. Composition of the solutions investigated.

Solution	A		B		C	
Concentration	g atom/l	atom/V	g atom/l	atom/V	g atom/l	atom/V
U(IV)	2.044	1	2.130	1	2.283	1
U(VI)	0.035	0.017	0.032	0.015	0.061	0.027
Cl	8.95	4.38	8.82	4.14	7.69	3.37
O	72.9	35.7	71.6	33.6	71.1	31.2
H	74.8	36.6	72.8	34.2	79.0	34.6
Hydrogen ion excess	0.71	0.35	0.23	0.11	−1.57	−0.69
Stoichiometric volume, V Å^3	812.4		779.6		727.4	

X-Ray measurements. The diffractometer used for the X-ray measurements has been described in previous papers.[5] During the irradiation the solutions were kept in a nitrogen atmosphere to prevent oxidation of the uranium(IV).

Because of the presence of strong fluorescence radiation when Mo$K\alpha$ radiation is used, the measurements were made with Ag$K\alpha$ radiation ($\lambda = 0.5608$ Å). Even then, some fluorescence radiation seemed to be present, as was also found in a previous investigation of uranium(VI).[6] Opening slits of 1°, 1/4°, and 1/12° were used. A recalculation of the measured data to a common slit width was made from measurements in overlapping regions. Measurements were made at intervals of 0.25° except in the low angle region ($\theta < \sim 4°$) where 0.1° intervals were used. About 40 000 counts were measured for each point, corresponding to a statistical accuracy of 0.5 %. Long-time variations in the X-ray source and the counting equipment were checked by measurements at larger intervals. No significant variations were observed.

DATA TREATMENT

The measured data were corrected in the usual way for polarization in the sample and in the monochromator. The incoherent part of the scattering was estimated from the spectrum of the X-ray tube. The final correction curve used was adjusted by a comparison with results obtained for a concentrated mercury(II) iodide solution, which does not give fluorescence radiation and which was measured with both Ag$K\alpha$ and Mo$K\alpha$ radiation. The amount of fluorescence radiation was estimated in the way described in a previous paper.[6] It amounted to about 10 % of the intensity measured at the largest scattering angles, roughly corresponding to an intensity of 2 cps. No corrections were made for multiple scattering ($\mu \approx 60$ cm^{-1}), as it could be assumed to be negligible.

The scattering factors used were those given by Cromer and Waber [7] for U and Cl. For O and H the values were taken from the International Tables.[8] They were corrected for the real and the imaginary part of the anomalous dispersion according to Cromer.[9] The incoherent radiation was taken from Cromer [10] for U, O, and Cl and from Compton and Allison [11] for H and was corrected for the Breit-Dirac factor.

The scaling constant, K, was estimated from the high-angle portion ($\theta > 45°$) of the measured data according to the formula:

$$KI_{\mathrm{obs}} = \sum_{\mathrm{i}} n_{\mathrm{i}} f_{\mathrm{i}}^2 + \sum_{\mathrm{i}} n_{\mathrm{i}} I_{\mathrm{inc}}$$

Here, I_{obs} are observed data corrected for fluorescence radiation and for polarization, f_{i} are the scattering factors corrected for the real and imaginary part of the anomalous dispersion,[12] I_{inc} the incoherent radiation reaching the counter, and n_{i} the number of atoms "i" in the stoichiometric volume chosen.

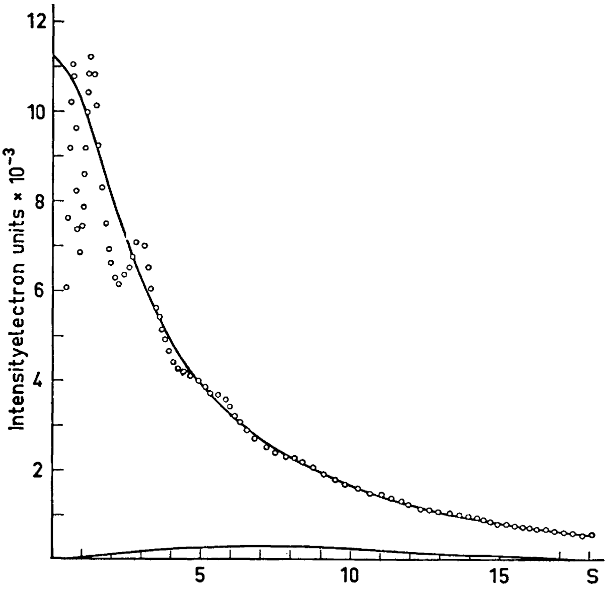

Fig. 2. Survey of the X-ray scattering measurements for solution A. Some of the observed normalized intensities, marked by dots, are compared with the corresponding calculated independent coherent scattering. The lower full-drawn curve gives the estimated amount of incoherent radiation reaching the counter.

Table 2. Observed intensity values, $I(s)$, after scaling and subtraction of incoherent radiation, and reduced intensity values, $i(s)$, given as functions of $s = 4\pi \sin \theta/\lambda$ for the three solutions investigated.

	A		B		C	
s	I	i	I	i	I	i
0.403	4304	-7292.0	-	-	9444	-1663.6
0.442	5095	-6459.1	5977	-5546.3	10163	-903.9
0.481	6639	-4870.4	-	-	11290	265.0
0.520	8183	-3277.9	-	-	12604	1624.9
0.559	8245	-3163.4	8614	-2766.1	14232	3300.6
0.598	9748	-1607.3	9440	-1885.6	15908	5026.3
0.637	10750	-548.3	10399	- 870.6	15471	4645.2
0.676	11638	399.1	10829	- 380.7	12150	1387.7
0.715	11351	176.5	10068	-1076.0	10430	-269.9
0.755	10206	-901.9	8745	-2330.9	9537	-1099.2
0.794	8785	-2252.8	7981	-3024.9	8048	-2521.6
0.833	7890	-3076.4	7206	-3723.0	7688	-2815.9
0.872	7552	-3342.6	6976	-3886.7	7687	-2748.7
0.911	7408	-3413.4	7011	-3778.9	7907	-2460.7
0.950	7666	-3081.6	7216	-3499.0	8299	-1998.8
0.989	8004	-2667.9	7605	-3035.4	8644	-1582.5
1.028	8407	-2187.8	8193	-2371.3	9131	-1023.7
1.067	9124	-1393.0	8687	-1799.8	9713	- 369.2
1.106	9698	- 741.0	9100	-1308.6	10153	145.7
1.145	10499	140.0	10138	- 192.3	10343	410.9
1.184	10959	681.1	10787	535.9	10422	567.2
1.223	11371	1174.4	11084	915.3	10360	582.9
1.262	11689	1575.6	10953	867.1	10425	725.4
1.301	11647	1617.3	11147	1145.0	10190	569.8
1.340	11641	1696.1	11153	1235.3	9971	430.6
1.379	11320	1460.5	10934	1100.7	9663	401.9
1.419	11030	1255.7	10719	971.9	9514	133.8
1.458	10577	889.1	10267	606.9	9268	- 31.3
1.497	10019	418.2	9978	403.9	9053	-165.4
1.536	9681	156.4	9617	129.3	8951	-186.4
1.575	9431	3.4	9360	- 40.6	8720	-336.2
1.614	9139	-202.3	9059	-255.1	8713	-263 0
1.653	8729	- 525.2	8652	-574.7	8476	-418.3
1.692	8559	-608.9	8417	-723.1	8342	-471.1
1.731	8242	-839.6	8113	-940.9	8216	-516.1
1.770	7923	-1071.5	7847	-1120.5	7989	-662.9
1.809	7752	-1156.9	7631	-1250.3	7844	-726.9
1.848	7560	-1262.9	7468	-1327.8	7742	-748.4
1.886	7335	-1402.5	7193	-1517.9	7620	-790.6
1.925	7180	-1472.7	7177	-1449 3	7463	-868.6
1.964	6988	-1579.7	6988	-1553.5	-	-
2.003	6860	-1624.1	6823	-1534.1	7129	-1044.1
2.042	6768	-1632.3	6702	-1671.4	7009	-1085.1
2.081	6677	-1640.0	6615	-1675.6	6780	-1235.3
2.120	6603	-1631.3	6551	-1657.4	6655	-1283.4
2.159	6555	-1596.5	6447	-1679.0	6518	-1342.9
2.198	6485	-1585.6	6416	-1628.1	6441	-1342.9
2.237	6509	-1480.1	-	-	6394	-1313.9
2.276	6556	-1352.4	6465	-1418.6	6423	-1210.2
2.315	6582	-1247.5	6527	-1278.1	6366	-1192.4
2.354	6570	-1180.3	6488	-1237.6	6335	-1148.3
2.392	6628	-1043.1	6523	-1125.2	6349	-1061.0
2.431	6684	- 910.2	6585	- 984.9	6354	- 982.9
2.470	6710	-806.9	6917	-577.2	6404	-860.2
2.509	6726	-714.2	6767	-650.8	6383	-809.9
2.548	6736	-627.8	6817	-525.0	6379	-742.1
2.587	6854	-434.9	6872	-395.6	6459	-592.2
2.626	6922	-292.7	6937	-256.3	6502	-478.5
2.664	6965	-176.5	6991	-129.0	6629	-283.2
2.703	7067	- 1.4	7057	9.6	6695	-147.9
2.742	7202	205.8	7223	247.2	6759	- 16.0
2.781	7252	326.8	7298	392.8	6921	212.9
2.820	7353	499.1	7441	606.1	7009	367.2
2.858	7428	643.2	7483	717.6	7131	555.4
2.897	7471	755.5	7551	853.7	7222	711.0
2.936	7480	833.3	7581	951.8	7257	810.5
2.975	7492	912.5	7551	989.8	7306	923.6
3.014	7474	961.4	7474	979.1	7327	1007.5
3.052	7405	958.4	7380	951.3	7234	977.0
3.091	7239	858.4	7277	913.2	7194	999.0
3.130	7111	795.6	7126	826.6	7100	966.0
3.168	6893	641.6	6986	750.7	7036	962.1
3.207	6751	562.8	-	-	6835	819.4
3.246	6591	465.0	6648	538.1	6678	723.5
3.285	6376	312.0	6457	409.1	6531	634.3
3.323	6251	248.2	-	-	6397	557.7
3.362	6111	167.6	6166	238.3	6245	462.6
3.401	5929	45.5	6025	157.2	6097	371.7
3.439	5835	10.5	5917	107.0	59[illegible]	307.2
3.478	5777	9.6	5808	49.8	5855	241.0
3.516	5691	-19.2	5675	-20.0	5743	182.1
3.555	5610	-44.4	5585	-54.5	5642	134.0
3.594	5527	-71.2	5471	-112.7	5518	63.5
3.632	5409	-134.0	5424	-105.6	5408	5.3
3.671	5335	-154.4	5299	-176.9	5248	-103.0
3.709	5253	-183.5	5223	-200.3	5139	-162.1
3.748	5164	-220.1	5148	-222.3	5068	-182.6
3.787	5082	-249.9	5038	-280.8	4945	-257.1
3.825	4985	-295.7	4933	-334.6	4875	-278.4
3.864	4889	-341.5	4881	-337.1	4711	-394.4
3.902	4832	-348.0	4785	-382.6	4666	-391.4
3.941	4731	-400.5	4699	-421.2	4607	-403.6
3.979	4652	-430.4	4646	-426.2	-	-
4.018	4643	-392.3	4581	-443.6	4452	-467.2
4.056	4572	-416.5	4529	-448.5	4404	-470.7
4.094	4502	-439.9	4499	-433.0	-	-
4.130	4472	-423.6	-	-	-	-
4.133	-	-	4451	-435.4	4314	472.7
4.171	4450	-401.1	4408	-433.5	4308	-436.0
4.210	4408	-398.9	4391	-406.4	4276	-426.0
4.248	4377	-385.8	4348	-405.5	4240	-419.7
4.287	4369	-350.3	4324	-387.1	4192	-426.6
4.325	4347	-330.3	4340	-329.8	4201	-377.7
4.363	4329	-306.1	4328	-299.6	4167	-370.9
4.402	4308	-285.9	4263	-323.1	4176	-322.4
4.440	4296	-257.0	4255	-281.3	4166	-293.9
4.478	4277	-235.3	4243	-263.0	4135	-288.6
4.517	4269	-203.3	4210	-257.0	4125	-258.7
4.555	4250	-183.7	4220	-208.0	4107	-238.5
4.593	4233	-161.9	4207	-182.4	4142	-167.2
4.631	4227	-129.9	4202	-150.3	-	-
4.670	4204	-115.3	4176	-138.0	4105	-130.9
4.708	4168	-113.5	4185	- 92.6	-	-
4.746	4186	- 58.7	4179	- 62.8	-	-
4.784	4192	- 17.6	4135	- 71.1	-	-
4.823	4126	- 47.0	4134	- 36.9	-	-
4.861	4118	- 20.0	4109	- 26.7	4077	13.1
4.899	4117	13.3	4061	- 40.7	-	-
4.937	4074	4.9	4083	15.0	-	-
4.956	-	-	-	-	4043	67.1
4.975	4073	37.6	4050	16.3	-	-
5.013	4033	31.2	4032	0.9	-	-
5.051	4009	39.6	4019	50.6	4015	113.1
5.089	3978	41.4	3979	41.9	-	-
5.128	-	-	3991	86.5	-	-
5.147	3953	63.7	-	-	3964	138.8
5.166	3923	50.1	3935	61.5	-	-
5.204	3895	52.8	3942	99.4	-	-
5.242	3861	50.1	-	-	3884	153.4
5.280	-	-	3881	98.6	-	-
5.318	-	-	3858	105.6	-	-
5.337	3821	85.3	-	-	3810	132.3
5.356	3805	84.0	3865	141.6	-	-
5.394	-	-	3812	117.5	-	-
5.432	3779	116.1	3818	152.2	3764	156.4
5.470	-	-	3794	156.5	-	-
5.507	-	-	3773	163.4	-	-
5.526	3783	190.3	-	-	3681	141.2
5.545	-	-	3782	199.5	-	-
5.563	-	-	3750	194.5	-	-
5.621	3725	201.0	3714	185.3	3643	168.1
5.659	3701	203.3	3678	175.7	-	-
5.697	-	-	3694	218.4	-	-
5.716	3704	245.9	-	-	3554	142.8
5.735	-	-	3680	229.5	-	-
5.772	-	-	3628	202.8	-	-
5.810	3642	248.3	3601	201.0	3461	112.7
5.848	3610	241.1	3571	196.4	-	-
5.886	3555	211.5	3551	200.6	-	-
5.904	3552	220.4	-	-	3409	120.4
5.923	3546	226.3	3524	197.8	-	-
5.961	3511	215.4	3491	189.5	-	-
5.999	3466	194.9	3423	144.8	3308	77.8
6.036	-	-	3415	160.1	-	-
6.039	3406	158.1	-	-	-	-
6.074	-	-	3384	151.9	-	-
6.093	3364	151.7	-	-	3274	99.7
6.112	-	-	3339	130.7	-	-
6.149	3299	120.5	3268	82.6	-	-
6.187	3250	94.3	-	-	3208	89.1
6.224	3252	118.7	-	-	-	-
6.262	3196	84.9	3212	92.7	-	-
6.281	3159	58.1	-	-	3103	37.6
6.300	-	-	3147	49.3	-	-
6.337	3107	39.1	3107	30.7	-	-
6.375	3057	10.0	3058	2.4	3064	50.2
6.412	3020	-6.0	3055	20.6	-	-
6.468	2969	-26.2	-	-	2987	23.0
6.487	-	-	2988	-5.6	-	-
6.521	2928	-36.3	2951	-22.5	-	-
6.562	2900	-44.3	2922	-31.1	2906	-8.3
6.599	-	-	2903	-30.1	-	-
6.655	2812	-83.7	-	-	2833	-34.3
6.674	-	-	2832	-63.0	-	-
6.711	-	-	2813	-57.7	-	-
6.748	2756	-91.2	2781	-75.0	2782	-38.5
6.786	-	-	2758	80.0	-	-
6.823	-	-	2750	-69.4	-	-
6.842	2700	-100.8	-	-	2717	-57.6
6.860	-	-	2728	-72.6	-	-
6.897	-	-	2681	-101.0	-	-
6.935	2661	-94.4	2622	-142.5	-	-
6.990	-	-	2615	-122.5	-	-
7.027	2631	-79.8	-	-	2608	-79.5
7.083	-	-	2569	-125.1	-	-
7.120	2561	-106.9	-	-	2538	-107.8
7.213	2525	-100.0	2541	- 92.9	2499	-104.9
7.305	2498	- 86.0	2502	- 90.8	2451	-112.2

Table 2. Continued.

	A		B		C	
s	I	i	I	i	I	i
7.342	2483	- 84.2	-	-	-	-
7.379	2470	- 81.7	-	-	-	-
7.398	2448	- 96.0	2476	-76.1	2434	-90.4
7.490	2416	-88.1	-	-	2405	-80.7
7.582	2412	-52.8	2405	-67.3	2371	-75.9
7.674	2353	-73.3	-	-	2343	-66.9
7.766	2362	-26.8	2337	-58.9	2326	-46.6
7.857	2319	-32.9	2327	-32.1	2320	-16.6
7.949	2318	2.0	2310	-12.4	2324	22.3
8.040	2301	20.0	2290	3.8	2284	17.0
8.131	2260	14.1	2267	15.4	2254	21.6
8.222	2214	2.5	2260	42.7	2222	22.9
8.313	2209	30.0	2200	17.0	2216	49.7
8.404	2192	46.2	2171	21.1	2178	44.5
8.494	2139	25.0	2144	26.3	2135	33.2
8.585	2100	17.2	2126	40.9	2099	27.9
8.675	2098	46.2	2099	45.4	2069	28.6
8.765	2048	26.7	2044	20.9	2018	7.1
8.855	2018	26.3	-	-	1991	9.4
8.945	1997	32.9	1981	16.6	1954	0.5
9.034	1956	20.6	1956	20.5	1916	-9.4
9.124	1910	1.6	1907	-0.9	1888	-10.3
9.213	1864	-0.7	1876	-4.0	1850	-21.7
9.302	1842	-12.9	1847	-6.2	1824	-20.6
9.391	1806	-23.8	1821	-6.4	1800	-18.6
9.479	-	-	1797	-4.3	1775	-19.1
9.568	-	-	1755	-20.7	1765	4.3
9.656	1735	-19.8	1737	-13.4	1731	-13.9
9.744	1714	-17.7	1700	-27.0	1706	-14.6
9.832	1692	-16.0	1691	-11.7	1685	-12.1
9.920	1672	-13.5	1651	-28.6	1673	- 1.0
10.007	-	-	1646	-10.2	1648	- 3.8
10.095	1623	-17.8	1601	-32.9	1625	- 4.9
10.182	1613	- 5.5	1603	- 9.4	1598	-10.0
10.269	1595	- 3.3	1582	- 8.6	1597	10.8
10.356	1578	0.8	-	-	1570	4.0
10.425	-	-	1556	3.7	-	-
10.442	1571	14.0	-	-	1548	3.5
10.529	1546	9.1	1523	-5.5	1520	-3.7
10.615	1534	16.9	-	-	1510	5.5
10.701	1505	7.4	1496	7.7	1478	-6.4
10.787	1486	7.3	1482	12.3	1484	18.4
10.872	1479	19.4	1468	17.4	1449	3.0
10.958	1450	8.0	1452	19.9	1444	15.4
11.043	1471	47.7	1422	8.0	1441	31.0
11.111	-	-	-	-	1412	16.9
11.123	1432	25.7	1414	18.5	-	-
11.213	1408	20.3	1395	16.5	1392	17.3
11.297	1377	5.1	1359	-2.2	1364	6.9
11.381	1353	-1.5	1337	-6.9	1344	4.1
11.465	1341	2.3	1322	-6.2	1326	2.2
11.549	1324	2.0	1307	-4.2	1302	-5.3
11.633	1301	-5.3	1273	-22.7	1298	6.3
11.716	1284	-6.9	1263	-16.8	1264	-12.0
11.800	1262	-13.9	1259	- 6.2	1242	-18.0
11.883	1252	- 8.6	1238	-12.5	-	-
11.916	-	-	-	-	1232	-7.6
11.965	1221	-25.4	1208	-27.0	1217	-13.3
12.048	1209	-22.6	1194	-26.6	1203	-12.7
12.130	1189	-28.0	1180	-26.5	1173	-23.4
12.212	1175	-28.6	1164	-29.3	1175	-12.6
12.294	1170	-20.4	1153	-25.9	1156	-17.3
12.376	1163	-13.0	-	-	1152	- 8.4
12.457	1140	-23.0	1127	-25.4	1130	-17.1
12.538	1136	-15.0	1133	-7.5	1123	-10.8
12.619	-	-	1106	-21.6	-	-
12.700	1104	-21.9	1101	-13.5	1105	-3.6
12.780	1103	-10.1	1096	- 6.9	1084	-12.6
12.860	1094	-7.0	1089	- 1.8	1087	2.0
12.940	1085	-4.1	1083	3.2	1071	-2.1
13.020	1070	-7.6	-	-	1063	1.4
13.099	-	-	1054	-2.8	1041	+9.6
13.179	1064	8.7	1064	17.9	1044	5.5
13.258	1050	5.2	1047	12.0	1034	6.0
13.336	1048	14.1	1043	18.8	1023	5.1
13.415	1041	17.6	1023	9.0	1014	6.9
13.493	1021	8.5	-	-	1014	17.0
13.571	1008	5.1	1002	8.7	1000	13.1
13.648	1006	13.1	988	4.4	979	2.4
13.726	1000	17.1	989	15.4	980	12.8
13.803	987	13.9	984	20.2	-	-
13.880	974	10.6	959	4.2	945	-2.7
13.956	961	6.1	951	6.0	945	6.1
14.033	949	4.2	944	8.2	927	-2.9
14.109	940	3.8	945	17.5	932	11.0
14.185	925	-2.2	922	3.8	909	-3.8
14.260	925	6.6	915	5.3	909	4.7
14.335	905	-5.3	-	-	898	1.9
14.410	899	-3.1	887	-6.1	882	-5.6
14.485	889	-4.2	874	-10.5	882	2.7
14.560	884	-1.5	872	- 4.7	869	-2.2
14.634	870	-7.4	859	- 9.4	861	-2.6
14.708	858	-11.8	849	-12.1	849	-7.4
14.781	845	-16.5	837	-16.3	844	-4.0
14.855	838	-16.2	842	- 4.1	830	-10.9
14.928	836	-10.2	833	- 4.7	827	-6.3
15.000	837	- 2.1	811	-19.7	826	-0.8
15.073	825	- 7.2	812	-12.2	815	-4.1
15.145	814	-10.7	799	-17.8	809	-3.9
15.217	813	- 4.5	802	- 7.2	798	-7.4
15.289	810	- 0.9	794	- 8.4	-	-
15.360	797	-6.7	783	-12.9	790	-2.3
15.431	795	-2.1	780	-9.3	780	-5.9
15.502	788	-2.7	776	-7.0	777	-2.5
15.572	777	-7.1	778	1.9	767	-5.8
15.642	771	-6.4	765	-5.3	764	-3.0
15.712	762	-9.0	763	-0.4	756	-4.5
15.782	765	0.0	760	2.4	748	-6.7
15.851	-	-	753	1.8	737	11.4
15.920	752	-0.3	741	-4.1	743	0.6
15.988	748	1.4	738	-1.4	735	-2.0
16.057	733	-7.1	733	-0.4	730	-1.4
16.125	738	3.7	731	3.0	729	3.4
16.192	728	-0.7	721	-0.8	722	2.4
16.260	723	0.1	-	-	-	-
16.271	-	-	-	-	711	2.4
16.327	726	8.6	716	5.5	714	4.9
16.394	714	1.8	710	4.4	711	7.2
16.460	707	0.2	707	7.2	697	-0.8
16.526	710	8.6	693	-1.6	694	1.4
16.592	701	5.0	697	6.9	692	4.2
16.658	700	9.6	680	-3.9	693	10.1
16.723	689	4.4	669	-9.9	672	-5.8
16.788	686	6.3	678	3.3	675	3.1
16.853	677	1.5	669	-0.4	671	3.2
16.917	676	5.6	660	-4.7	668	4.9
16.981	668	2.7	661	1.8	658	0.2
17.044	661	1.1	652	-2.9	657	4.2
17.108	658	2.4	646	-3.9	-	-
17.171	653	2.4	-	-	644	0.3
17.233	647	1.1	643	1.4	644	4.5
17.296	639	-1.9	637	0.7	632	-2.8
17.357	637	0.6	631	-1.0	627	-2.9
17.419	636	4.0	629	1.7	623	-2.8
17.480	626	-2.3	622	-1.3	618	-3.2
17.541	624	0.5	618	-0.8	616	-0.8
17.602	615	-3.5	614	-1.2	613	0.7
17.662	609	-5.7	612	1.7	607	-1.5
17.722	608	-2.5	609	3.0	603	-1.0
17.782	599	-7.5	602	-0.2	602	1.6
17.841	596	-5.7	603	5.1	597	0.5
17.900	595	-3.0	596	1.7	590	-2.4
17.959	589	-4.6	587	-2.9	592	4.0
18.017	598	8.2	589	2.5	582	-2.3
18.075	592	6.3	-	-	580	-0.3
18.133	587	5.0	-	-	575	-1.5
18.190	583	5.0	579	3.5	575	2.7
18.247	584	10.2	578	6.3	569	0.2
18.303	578	7.2	576	8.2	569	3.9
18.360	565	-1.4	566	2.4	568	7.0
18.415	568	4.5	569	9.3	559	1.3
18.471	554	-5.5	562	5.1	555	0.3
18.526	567	10.8	560	7.0	552	1.5
18.581	568	15.3	-	-	549	1.9
18.635	559	9.6	551	5.1	547	3.0
18.689	556	10.2	550	7.4	539	-0.9
18.743	543	0.7	546	6.6	530	-6.9
18.797	557	17.8	540	3.8	530	-3.7
18.850	542	6.3	542	8.5	529	-1.6
18.902	538	5.3	539	9.2	529	2.0
18.955	532	3.3	540	13.1	523	-1.5
19.007	532	6.5	529	5.2	523	1.6
19.058	531	7.6	523	2.7	512	-5.8

The scaled intensity values were corrected for the incoherent part of the radiation and from the resulting intensity values, $I(s)$, the reduced intensities, $i(s)$, were calculated according to the expression[12]

$$i = I - \sum n_i f_i^2$$

All calculations were normalized to correspond to a stoichiometric volume of solution, V Å^3, containing one uranium(IV) atom. The I values are given in Table 2 as a function of $s = 4\pi \sin \theta/\lambda$. The reduced intensity values were corrected for spurious peaks below 1 Å in the radial distribution curves, as described in previous papers,[5,6] and the resulting $i(s)$ values are given in Table 2 as a function of s. Observed and reduced intensities are also shown in Figs. 2 and 3.

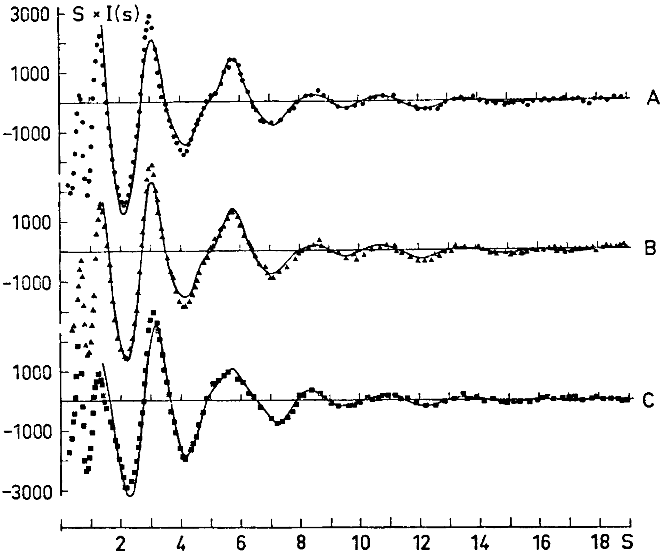

Fig. 3. Reduced intensity values, $i(s)$, multiplied by s, given as a function of $s = 4\pi \sin \theta/\lambda$. Between one half and one third of the observed intensities are given as dots. The full-drawn curves represent $si(s)$ values calculated with parameters from the least squares refinements.

Electronic radial distribution curves, $D(r)$, were calculated from the reduced intensities using the expression:[12]

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi}\int_0^{s_{\max}} si(s)\{f_U^2(0)/f_U^2(s) \exp(-ks^2)\} \sin(rs) \mathrm{d}s$$

In the sharpening factor, given within brackets, the first part compensates for the electron distribution within the atoms. The sharpening effect obtained in this way is reduced by the exponential part, in which the constant k for the following calculations has been chosen to be 0.01.

Theoretical intensity curves were calculated from [12]

$$i(s) = \sum_m \sum_n f_m f_n \frac{\sin(rs)}{rs} \exp(-b_{mn} s^2)$$

All calculations were carried out on an IBM 360/75 computer with the KURVLR program, which is an extended version,[12] written in Fortran, of the previously used Algol programs.[13]

ANALYSIS OF THE DATA

The radial distribution curves. Radial distribution curves, $D(r)$, for the solutions investigated are shown in Fig. 4. The variation of the $D(r)$ functions around the average, $4\pi r^2\varrho_0$, are given in Fig. 5.

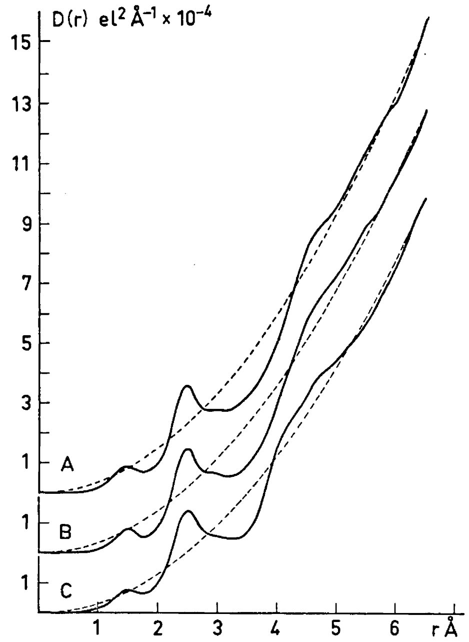

Fig. 4. Radial distribution curves, $D(r)$, for the solutions investigated. Broken lines are the corresponding $4\pi r^2\varrho_0$ functions.

The Cl – O peak at 1.4 Å in the perchlorate group is easily recognized. The first coordination sphere around the U^{4+} ion is represented by the peak at 2.5 Å. The broad peak at about 4.5 Å can probably be taken to indicate distances between the U^{4+} ion and atoms in a second coordination sphere. This peak is the only one that is noticeably different for the acid and the hydrolyzed solutions.

Polynuclear complexes. The changes in the distribution curves, when the hydrolysis is increased, are best brought out by taking the difference between the curves. The differences were calculated after subtracting the $4\pi r^2\varrho_0$ functions, including the light atoms only, from the $D(r)$ functions, and are given in Fig. 6. The significant differences are limited to the region around 4 Å and, possibly, around 5.5 Å. The changes in the region corresponding to the first coordination sphere of the uranium atom are too small to allow any quantitative analysis.

The peak at 4.0 Å in Fig. 6 is close to the corresponding position of the Th – Th peak in the polynyclear complexes found in the thorium nitrate solutions previously investigated which occurred at 3.95 Å. Thus it seems likely that the 4 Å peak indicates the formation of polynuclear complexes in solution

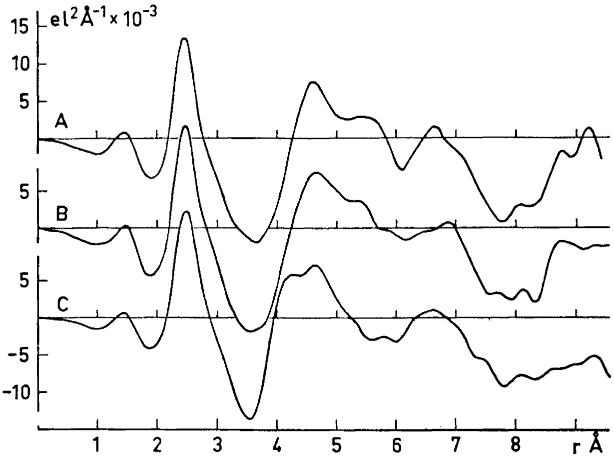

Fig. 5. $[D(r)-4\pi r^2\varrho_0]$ functions for the three solutions investigated.

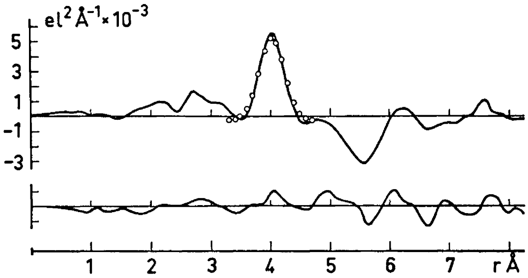

Fig. 6. Differences between distribution functions. The upper curve gives the difference between the solutions C and A and the lower curve that between the solutions B and A. Calculated values for an U–U interaction, assuming 0.34 U–U distances per U atom and a temperature factor of 0.013, are indicated on the upper curve.

C. By analogy with the Th^{4+} results this would indicate that the uranium atoms in the complexes are joined by double hydroxo bridges.

Comparison with calculated peak shapes for U–U interactions (Fig. 6) indicates that the average number of U atoms bound to each other U atom in solution C is about 0.7. In solution B no significant peak occurs at 4.0 Å (Fig. 6) indicating that no significant amount of polynuclear complexes has formed in this solution.

Coordination of the U^{4+} ion. The radial distribution curve for the acid solution, A, and to a somewhat lesser extent, the corresponding curves for solutions B and C, show irregularities in the region of the broad peak between about 4 and 6 Å, interpreted as indicating a concentration of distances corresponding to a second coordination sphere around the U^{4+} ion. This is particularly evident when these results are compared with the results from the thorium nitrate solutions previously investigated, for which no pronounced peaks were found corresponding to those at 5.5 Å and 6.7 Å (Fig. 5) in the uranium(IV) solutions. On the other hand, the peak at 2.5 Å representing the first coordination sphere of the U^{4+} ion, is more regular than the corresponding peak for the acid thorium nitrate solution.

For the thorium nitrate solutions it was concluded that inner-sphere complexes are formed with the nitrate groups bound as bidentate ligands. The resulting Th – N distances were clearly indicated in the radial distribution curves. If the perchlorate groups form similar complexes with the U^{4+} ion, the corresponding U – Cl distances should be even more pronounced, because of the higher atomic number of the chlorine atom. The effects to be expected are illustrated in Fig. 7, where calculated peak shapes are given for an eight-coordinated uranium atom with perchlorate groups bound either as bidentate or as monodentate ligands. A comparison with the observed distribution curves gives no support for a formation of any significant amount of these types of complexes.

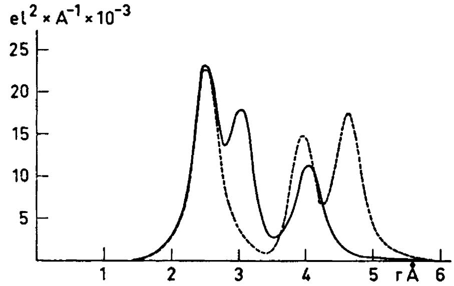

Fig. 7. Calculated peak shapes for uranium-light atom interactions within a U – ClO_4 complex. The U atom is assumed to be 8-coordinated (U – O distance 2.4 Å) with two perchlorate groups bound either as monodentate (broken curve) or as bidentate ligands (solid curve).

If, on the other hand, formation of an outer-sphere complex is assumed, the peaks at 5.5 Å and 6.7 Å are easily explained. A perchlorate group orientated as a bidentate ligand would give U – O contributions to the peaks at 4.6 Å and 6.7 Å and U – Cl contributions to the peak at 5.5 Å. As the peaks at these comparatively large distances correspond only to small variations in the very large number of background interactions in this region (Fig. 5), this conclusion is not, of course, very firmly based. Some support for it, in addition to that obtained from the comparison with the results for the thorium nitrate solutions, is obtained from the observation that the supposed U – Cl peak at 5.5 Å, decreases when the perchlorate concentration is decreased (Fig. 6).

Least-squares refinement of the intensity curves. The dominant frequencies in the observed intensity curves (Fig. 3) were further analyzed by a least squares method with which a comparison was made with calculated intensity curves, obtained by including the Cl – O and O – O interactions of the perchlorate groups and interactions involving the uranium atoms. For each type of interaction the distance, d, a temperature factor, b, and a frequency factor, n, were introduced. A minimum was sought for the function $\sum[si(s)_{\text{obs}} - si(s)_{\text{calc}}]^2$, the summation being taken over the observed points. For the ClO_4 interactions the parameters obtained in a previous investigation of tin(II) perchlorate solutions [14] were used. The low-angle part of the intensity curves, where other types of interactions are the main contributors, was not included in the refinement. In order to check the constancy of the frequencies the refinement was carried out using different values for the lower s limit.

Table 3. Results of the least squares refinement for solutions A and B, when two different U – O interactions are included. The longer U – O distance has significant contributions only for the two lower s limits.

		$(U-O)_1$			$(U-O)_2$		
s_{min}	sol.	d	b	n	d	b	n
1.9	A	2.519[6]	0.012[2]	9.5[3]	4.57[2]	0.018[7]	6.0[6]
	B	2.530[5]	0.016[2]	10.5[3]	4.55[2]	0.038[8]	7.7[7]
3.5	A	2.472[5]	0.003[1]	7.0[3]	4.43[1]	0.019[6]	7.0[9]
	B	2.480[5]	0.003[1]	6.9[3]	4.42[2]	0.046[12]	9.8[23]
6.6	A	2.432[6]	0.003[1]	7.2[7]			
	B	2.430[5]	0.001[1]	6.4[7]			
7.8	A	2.425[6]	0.004[1]	8.9[13]			
	B	2.427[5]	0.003[1]	7.7[10]			
8.8	A	2.419[6]	0.005[2]	10.1[24]			
	B	2.426[6]	0.002[1]	7.0[12]			
10.3	A	2.423[9]	0.002[2]	5.9[6]			
	B	2.426[6]	0.002[1]	7.0[12]			

Table 3 gives the results of the first part of this refinement. The number of U – O interactions corresponding to the 2.5 Å peak in the distribution curve does not differ significantly from eight. The introduction of a second U – O interaction at about 4.5 Å, as an approximation of a second coordination sphere, does not affect this result. Thus the coordination of the uranium atom does not differ significantly from that which has been found in crystal structures.[15]

Table 4. Results of the least squares refinements for solutions A and B, when U – ClO_4 interactions are included in addition to the two U – O and the intramolecular ClO_4 interactions.

	sol.	$(U-O)_1$			$(U-O)_2$			$U-ClO_4$		
s_{min}		d	b	n	d	b	n	d	b	n
1.9	A	2.495[4]	0.005[1]	7.9[2]	4.46[1]	0.021[5]	8.5[5]	5.74[3]	0.031[5]	3.3[4]
	B	2.510[4]	0.009[2]	9.2[3]	4.47[2]	0.038[7]	9.6[9]	5.77[5]	0.036[9]	2.5[6]
3.5	A	2.457[4]	0.004[1]	7.8[3]	4.40[1]	0.045[8]	16 [3]	5.69[2]	0.07[1]	8.2[12]
	B	2.472[4]	0.005[1]	8.0[4]	4.38	0.046[6]	13 [2]	5.67[4]	0.06[1]	4.3[7]

In the second part of the refinement an attempt was made to include interactions between a U atom and an outer-sphere perchlorate group. This refinement converged but significant parameter values were obtained only for the lower s limit where systematic errors can be expected to be large. The results are given in Table 4.

Introduction of O – O interactions within the first coordination sphere of the uranium atom, assuming an antiprismatic arrangement of the oxygen atoms, did not affect the results of the refinements, although it led to a small decrease in the least squares error sum. A parameter introduced to allow a change in the orientation of the ClO_4 group did not show any significant deviation of the ClO_4 group from the assumed bidentate orientation.

The final agreement between observed and calculated intensity curves is shown in Fig. 3. The contributions of the various interactions to the intensity curves and the distribution functions are shown in Figs. 8 and 9.

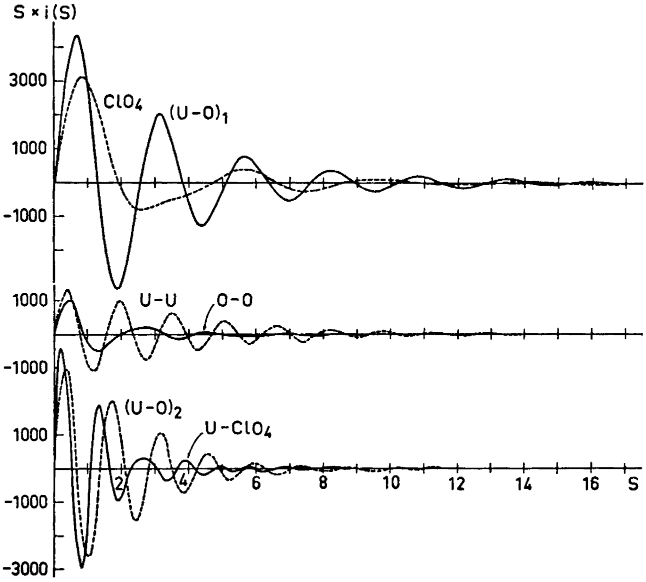

Fig. 8. The contributions from the separate interactions used to calculate $si(s)$ values for solution C. The following parameters were used: ClO_4: $d=2.43$ Å (Cl – O), $b=0.003$ (Cl – O) (broken line); $(U-O)_1$: $d=2.46$ Å, $b=0.005$, n = 8.0 (solid line); U – U: $d=4.00$ Å, $b=0.013$, $n=0.34$ (broken line); O – O: an Archimedean antiprism surrounding the U atom (solid line); $(U-O)_2$: $d=4.46$ Å, $b=0.03$, $n=9.6$ (broken line); U – ClO_4; $d=5.75$ Å (U – Cl), $b=0.034$, $n=2.5$ (solid line).

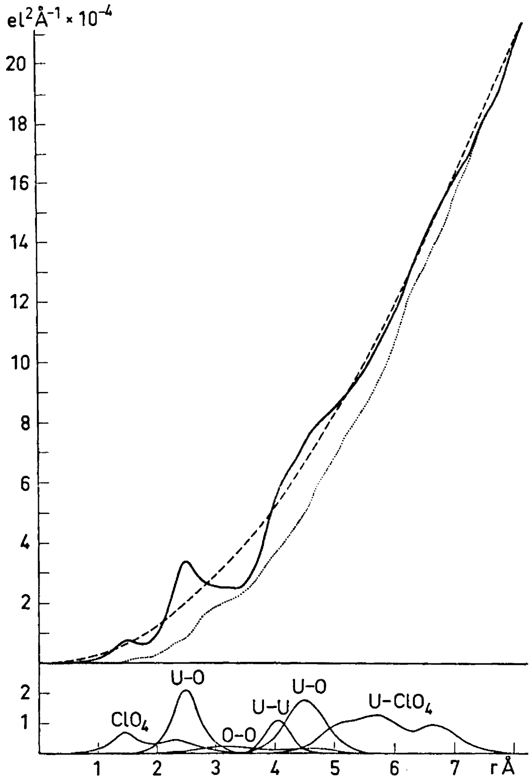

Fig. 9. A comparison between the $D(r)$ function for solution C and the peak shapes for the separate interactions calculated with the parameters given in Fig. 8. The dotted line shows the difference between observed and calculated curves. The broken line shows the $4\pi r^2\varrho_0$ function.

DISCUSSION OF THE RESULTS

The analysis of the scattering data shows the uranium(IV) ion to have a well-defined first coordination sphere with a coordination number which is not significantly different from eight. The least-squares analysis with the use of the high-angle parts of the intensity curves, which should be the least affected by systematic errors, gives a value of 2.43 Å for the corresponding U – O distance (Table 3). Similar distances have been reported for crystals of uranium(IV) compounds.[15] In UO_2, which has the fluorite structure, the U – O bonding distance has been found to be 2.37 Å.[16] In several other crystals, such as $U(OH)_2SO_4$,[17] $U_6O_4(OH)_4(SO_4)_6$,[18] and $U(SO_4)_2(H_2O)_4$,[19] the uranium(IV) ion has also been found to be eight-coordinated, but with the oxygen atoms arranged at the corners of an Archimedean antiprism. The U – O distances in these crystals are close to those found in the UO_2 structure, but the oxygen positions were derived from mainly geometrical reasoning.

It has not been possible to deduce from the solution scattering data the arrangement of oxygen atoms in the inner sphere, as the contributions from the corresponding O – O distances to the scattered intensities are too small (Figs. 8 and 9). No evidence is, however, found for inner-sphere complex formation with the perchlorate ions.

Well-defined distances, which can be related to a second coordination sphere, are found in the analysis of the scattering data. Water molecules at a distance of 4.4_6 Å from the uranium ion and ClO_4 groups with a U – Cl distance of 5.7_2 Å seem to form a relatively well-defined second coordination sphere around the uranium ion. If the water molecules in the inner coordination sphere are assumed to form a cube or a square antiprism around the uranium atom as has been found in crystals, the distances between the water molecules in the first and the second sphere can be estimated. If the water molecules in the second sphere are assumed to be situated outside an edge of the cube or the antiprism, the shortest distances to the two water molecules of the inner sphere, which define that edge, will be about 2.9 Å. Such a position seems likely as it would allow the formation of hydrogen bonds from the two water molecules in the inner sphere. For a perchlorate group in a similar position, that is with an edge of the ClO_4 tetrahedron parallel to an edge of the cube or the antiprism the O – O distances would be about the same, when the U – Cl distance is 5.7 Å. Thus, the distances derived from the X-ray scattering data and assigned to atoms in a second coordination sphere of the uranium atom lead to reasonable O – O contact distances, which supports our interpretation. Other positions for the oxygens than those now discussed lead either to too long or to too short O – O distances. We have found no crystal structure determinations of uranium(IV) perchlorates reported in the literature with which a comparison can be made. A crystal structure determination of the compound $U(OH)(ClO_4)_3(H_2O)_6$ has therefore been started.

Although only relatively weakly hydrolyzed solutions of the uranium(IV) perchlorate could be prepared, the formation of polynuclear hydrolysis complexes in the most hydrolyzed of the solutions investigated, is clearly indicated (Fig. 6). The shortest U – U distance within the complexes is 4.00 Å, which is close to the distance 3.95 Å found for the Th – Th distance in the polynuclear hydrolysis complexes of thorium,[1] where the thorium atoms are joined by two hydroxo bridges. A similar distance, 3.90 Å, has been found by Lundgren[17] in a crystal structure investigation of $U(OH)_2SO_4$ in which the uranium atoms are joined by double hydroxo bridges into infinite chains. In crystals of $U_6O_4(OH)_4(SO_4)_6$,[18] which contain discrete complexes in which the uranium atoms are octahedrally arranged with each uranium atom sharing two oxygens with a neighboring uranium atom, the U – U distances have been reported to be 3.85 Å. Thus it seems likely that the uranium atoms in the polynuclear complexes formed in hydrolyzed solutions are joined by double hydroxo bridges. A dinuclear complex should therefore have a structure analogous to the one previously found for thorium.[1] The formation of larger complexes cannot be excluded on the basis of the scattering data only, as longer interactions in such complexes would probably be too weak to be distinguished in the distribution curves.

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REFERENCES

1. Johansson, G. *Acta Chem. Scand.* **22** (1968) 399.
2. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-Ion Complexes,* Special Publication No. 17, The Chemical Society, London 1964, and Supplement No. 1, London 1970.
3. Hietanen, S. *Acta Chem. Scand.* **10** (1956) 1531.
4. El-Shamy, H. K. and El-Dinzayan, S. *J. Chem. Soc.* **1953** 384.
5. Johansson, G. *Acta Chem. Scand.* **20** (1966) 553; **25** (1971) 2787.
6. Åberg, M. *Acta Chem. Scand.* **24** (1970) 2931.
7. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
8. *International Tables for X-Ray Crystallography,* The Kynoch Press 1962, Vol. III.
9. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
10. Cromer, D. T. *J. Chem. Phys.* **50** (1969) 4857.
11. Compton, A. H. and Allison, S. K. *X-Rays in Theory and Experiment,* Van Nostrand, New York 1935.
12. Johansson, G. and Sandström, M. *Chemica Scripta. In press.*
13. Johansson, G. Programs with accession Nos. 6037 and 6038 in *IUCr World List of Crystallographic Computer Programs,* 2nd Ed. 1966.
14. Johansson, G. and Ohtaki, H. *Acta Chem. Scand.* **27** (1973) 643.
15. Chernyaev, I. I., Ed., *Complex Compounds of Uranium.* Israel Program for Scientific Translations, Jerusalem 1966.
16. Zachariasen, W. H. *Phys. Rev.* **78** (1948) 1104.
17. Lundgren, G. *Arkiv Kemi* **2** (1950) 535.
18. Lundgren, G. *Arkiv Kemi* **5** (1953) 349.
19. Kierkegaard, P. *Acta Chem. Scand.* **10** (1956) 599.

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