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The Structure of a Dinuclear Hydroxo Complex of Thorium

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A crystal structure determination of $Th_2(OH)_2(NO_3)_6(H_2O)_8$ based on three-dimensional X-ray data has shown that the crystals contain discrete dinuclear complexes $Th_2(OH)_2(NO_3)_6(H_2O)_8$. The thorium atoms within a complex are joined by a double hydroxo bridge, with a Th—Th distance of 3.98_3 Å. Three nitrate groups, acting as bidentate ligands, three water molecules and two hydroxo groups are coordinated to each Th atom, which results in a coordination number of 11 for thorium.

Hydrolysis of an aqueous thorium salt solution leads to the formation of polynuclear complexes. Different suggestions have been made as to the complexes really formed,[1–3] but most investigators seem to agree that the first step is the formation of a dinuclear complex. As shown in a previous paper [4] crystals of the composition $Th_2(OH)_2(NO_3)_6(H_2O)_8$ containing discrete dinuclear complexes can be obtained from weakly hydrolyzed thorium nitrate solutions. As these complexes are likely to be similar to those believed to exist in solution a complete crystal structure determination is of interest for the clarification of the hydrolysis processes in solution.

UNIT CELL AND SPACE GROUP

The preparation and analysis of the crystals were described in a previous paper.[4] Weissenberg and precession photographs along the three axes of the unit cell indicated a monoclinic symmetry and gave preliminary unit cell dimensions. A powder photograph taken with Cu$K\alpha$-radiation ($\lambda = 1.5405$ Å) in a Guinier camera with KCl ($a = 6.2929$ Å) as internal standard was used for the calculation of more accurate unit cell dimensions. A least squares refinement led to the following values (the errors given correspond to three times the standard deviations):

$$a = 6.772 \pm 0.002 \text{ Å}$$
$$b = 11.693 \pm 0.005 \text{ Å}$$
$$c = 13.769 \pm 0.005 \text{ Å}$$
$$\beta = 102.63° \pm 0.02°$$

The first lines of the powder photograph are given in Table 1.

Systematically absent reflections are $h0l$ with l odd and $0k0$ with k odd, which is characteristic of the centrosymmetric space group No. 14: $P2_1/c$.

For four formula weights in the unit cell the calculated density is 3.209. That observed was 3.20 as determined from a comparison of the weight of a sample in benzene and in air.

INTENSITY DATA

The crystals are rod-shaped and extended along the a axis. A crystal 0.043 × 0.043 mm² in cross section and 0.10 mm in length was used to record the intensities with Cu$K\alpha$-radiation in a Weissenberg camera. Six layer lines around the a axis ($0kl$ to $5kl$) and three layer lines around the c axis ($hk0$ to $hk2$) were used. Intensities were estimated by comparison with an intensity scale prepared by timed exposures of one of the reflections of the same crystal. The intensity values were corrected for absorption (linear absorption coefficient $\mu = 480$ cm^{-1}). The number of observable independent reflections was about 1750. Of these 1384 had intensities larger than the minimum observable value.

All calculations were made on a Facit EDB or a CD3600 computer. Absorption and Lorentz-polarization corrections, Fourier summations, least squares refinements (block-diagonal approximation), and calculations of interatomic distances were carried out by means of programs with the accession numbers 6014, 6015, 6016, 6019, and 6023 in the *World List of Crystallographic Programs*.[5] The final full-matrix, anisotropic least-squares refinement was made with a program written by Gantzel, Sparks and Trueblood and modified by Zalkin and by Lundgren and Liminga.

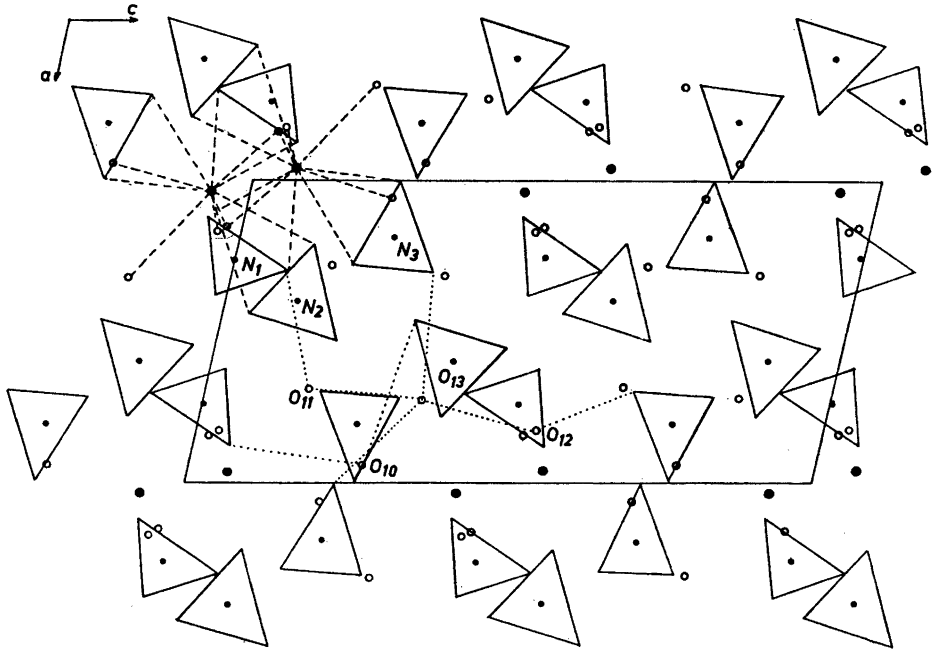

Fig. 1. A projection of the structure of $Th_2(OH)_2(NO_3)_6(H_2O)_8$ along the b axis. All Th—O contacts within one of the dinuclear complexes are marked by dashed lines. The dotted lines indicate some of the hydrogen bonds.

STRUCTURE DETERMINATION

From Patterson projections along the three axes of the unit cell the four thorium atoms were found to occupy the four-fold position 4(*e*) in the space group $P2_1/c$. The parameters found from the projections were refined by a least squares process with the use of all observed values. The resulting R factor ($\sum||F_{obs}|-|F_{calc}||/\sum|F_{obs}|$) was 0.22, which confirms the deduced Th positions.

A three-dimensional electron density map based on the thorium positions but with the contributions from the thorium atoms subtracted was used to locate the light atoms. All atoms present in the unit cell, according to the chemical analysis, were clearly indicated and no difficulties were encountered

Table 1. Comparison between calculated and observed $\sin^2\theta$ values for the first lines of a Guinier powder photograph of $Th_2(OH)_2(NO_3)_6(H_2O)_8$.

$h\,k\,l$	$(\sin^2\theta)_{calc}$	$(\sin^2\theta)_{obs}$	I_{obs}
0 1 $\bar{1}$	0.00763	0.00761	vs
0 0 2	0.01315	0.01313	s
1 0 0	0.01358	0.01356	m
0 1 2	0.01748	0.01747	m
1 1 $\bar{1}$	0.01829	0.01824	vs
1 0 $\bar{2}$	0.02089	0.02080	w
1 1 1	0.02413	0.02409	m
1 1 $\bar{2}$	0.02523	0.02519	vs
0 2 $\bar{2}$	0.03050	0.03048	vw
1 2 $\bar{1}$	0.03131	0.03124	s
1 0 2	0.03257	0.03253	m
1 1 2	0.03691	0.03685	m
0 3 1	0.04234	0.04224	m
0 2 3	0.04693	0.04686	m
1 2 $\bar{3}$	0.05175	0.05194	s
2 0 0	0.05434	0.05422	vw
2 1 $\bar{1}$	0.05612	0.05609	m
1 1 3	0.05627		
0 1 4	0.05692	0.05684	m
1 3 1	0.05884	0.05876	vs
1 1 $\bar{4}$	0.05882		
2 1 $\bar{2}$	0.06014	0.06018	m
2 1 1	0.06781	0.06776	m
1 2 3	0.06928	0.06919	m
2 2 0	0.07169	0.07166	vvw
1 3 $\bar{3}$	0.07345	0.07340	vvw
2 0 2	0.07917	0.07911	m
1 1 4	0.08219	0.08220	w
0 4 2	0.08257	0.08261	vw
1 4 $\bar{1}$	0.08338	0.08358	s
2 0 $\bar{4}$	0.08355		
2 2 $\bar{3}$	0.08373		
2 1 $\bar{4}$	0.08789	0.08777	w
1 2 $\bar{5}$	0.09849	0.09843	vw
0 2 5	0.09952	0.09951	vw
1 4 2	0.10200	0.10183	w
2 3 1	0.10252	0.10243	vw
1 4 $\bar{3}$	0.10382	0.10353	vw
1 0 $\bar{6}$	0.11437	0.11431	m

in determining their positions. A new least squares refinement, using the block-diagonal approximation, with all atoms included with individual isotropic temperature factors, reduced the R factor to 0.126. Hughes' weighting scheme was used.

The scattering factors were those given by Cromer and Waber [6] for the neutral atoms. The scattering factors of the thorium atoms were corrected for the real part of the anomalous dispersion ($\Delta f' = -4.61$) according to Cromer.[7] In the final cycle of this least squares refinement all shifts in positional and temperature parameters were less than 1/20 of the calculated standard deviations.

The atomic positions obtained in the least squares refinement were used to calculate a difference map and an electron density map with the thorium atoms subtracted. The difference map indicated a rather large anisotropic movement of the thorium atom. Except for the immediate vicinity of the thorium atoms, all peaks in the difference map were within $\pm$ 1.9 el/Å^3. The heights of the light atoms in the electron density maps were all within 8 to 10 el/Å^3. Thus no atoms other than those assumed to be present on the basis of the chemical analysis were indicated by the density maps.

At this stage the refinement was continued with the use of a full matrix least squares program after introducing anisotropic temperature factors ($\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$) for the thorium atom. This lowered the R factor to 0.094 when all observed reflections were included. In the final cycle all parameters shifts were less than 0.1 % of the calculated standard deviations.

The final difference map was correspondingly improved in comparison with the previously calculated one.

Table 2. Final parameters for $Th_2(OH)_2(NO_3)_6(H_2O)_8$. All atoms are in position 4(*e*) in space group No. 14: $P2_1/c$. Standard deviations, given within brackets, are multiplied by 10^4.

Th	0.9608 (2)	0.1490 (1)	0.0636 (1)
N_1	0.2655 (43)	0.1873 (20)	0.5002 (19)
O_1	0.2939 (36)	0.2341 (19)	0.5860 (16)
O_2	0.1164 (42)	0.2197 (21)	0.4391 (18)
O_3	0.3798 (45)	0.1178 (23)	0.4833 (21)
N_2	0.5957 (46)	0.1621 (20)	0.8799 (20)
O_4	0.7806 (40)	0.1719 (18)	0.8786 (18)
O_5	0.5606 (38)	0.1406 (19)	0.9640 (18)
O_6	0.4624 (53)	0.1723 (25)	0.8074 (24)
N_3	0.1964 (43)	0.0190 (19)	0.2485 (18)
O_7	0.2839 (41)	0.0733 (21)	0.1870 (19)
O_8	0.0042 (40)	0.0231 (19)	0.2292 (17)
O_9	0.6994 (40)	0.0343 (19)	0.6832 (18)
O_{10}	0.0553 (37)	0.2337 (19)	0.7252 (17)
O_{11}	0.6870 (45)	0.1638 (20)	0.1618 (20)
O_{12}	0.8289 (44)	0.1522 (21)	0.5344 (20)
O_{13}	0.7188 (43)	0.0533 (24)	0.3473 (20)
O_{14}	0.1599 (34)	0.0349 (17)	0.9771 (15)

A further refinement in which the imaginary part of the anomalous dispersion correction for the thorium atom ($\Delta f'' = 11.95$) [7] was taken into account had a very small effect on the R factor and did not lead to any significant changes in the parameter values.

The final parameters and their standard deviations are given in Tables 2 and 3. A comparison between observed and calculated structure factors is shown in Table 4.

DISCUSSION OF THE STRUCTURE

A projection of the structure along the b axis is shown in Fig. 1. Some bond lengths are listed in Table 5. Estimated standard deviations are about 0.002 Å for Th—Th, 0.02_5 Å for Th—O and Th—N distances, and about 0.04 Å for distances between light atoms.

Table 3. Temperature factors. Standard deviations, given within brackets, are multiplied by 10. The anisotropic thermal parameters for thorium ($\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-\beta_{23}kl)$) are listed as B_{ij} ($4\beta_{ij} = a_i^x \cdot a_j^x \cdot B_{ij}$) analogous to the isotropic Debye B.[13]

Th:	B_{11}: 2.3 (2)	B_{12}: 0.1 (1)
	B_{22}: 4.0 (1)	B_{13}: 0.6 (1)
	B_{33}: 2.3 (1)	B_{23}: −0.2 (1)
N_1 : 2.9 (4)	N_2 : 3.1 (5)	N_3 : 2.8 (4)
O_1 : 3.6 (4)	O_4 : 3.7 (6)	O_7 : 4.5 (5)
O_2 : 4.2 (4)	O_5 : 3.7 (4)	O_8 : 3.8 (4)
O_3 : 4.8 (4)	O_6 : 5.6 (5)	O_9 : 4.0 (4)
O_{10}: 3.7 (4)	O_{11}: 4.6 (5)	O_{12}: 4.5 (5)
O_{13}: 5.2 (5)	O_{14}: 3.2 (4)	

Coordination of thorium. The structure is built up from discrete complexes (Fig. 2) each containing two Th atoms joined by two bridging oxygens, O_{14}. The Th—Th distance within a complex is 3.988 Å whereas the shortest distance between Th atoms belonging to different complexes is 6.77 Å.

Three nitrate groups, acting as bidentate ligands, and three more oxygens, O_{10} to O_{12}, probably water molecules, are coordinated to each thorium atom. The coordination number of thorium is thus eleven and is larger than the value of eight usually found in thorium compounds. The large coordination number is possible because of the short O—O distances within the nitrate groups and between the two bridging oxygens, O_{14}. The same coordination number, eleven, has been found in thorium nitrate pentahydrate,[8,9] with four nitrate groups bonded to each Th, and a still higher value, twelve, in $MgTh(NO_3)_6(H_2O)_8$, where each thorium atom is coordinated to six nitrate groups.[10]

The coordination around thorium is rather irregular. If each nitrate group is considered as a single ligand, however, the coordination polyhedron may be described as a somewhat distorted dodecahedron.

Table 4. Observed and calculated structure factors.

h	k	l	F_o	F_c
0	0	2	247	234
0	0	4	62	57
0	0	6	155	142
0	0	8	219	199
0	0	10	130	114
0	0	12	<22	13
0	0	14	69	75
0	0	16	75	85
0	1	1	202	191
0	1	2	180	159
0	1	3	48	39
0	1	4	215	192
0	1	5	65	59
0	1	6	178	149
0	1	7	168	142
0	1	8	54	28
0	1	9	86	95
0	1	10	105	118
0	1	11	35	38
0	1	12	121	116
0	1	13	24	27
0	1	14	27	42
0	1	15	29	49
0	1	16	<15	6
0	1	17	27	38
0	2	0	114	120
0	2	1	97	108
0	2	2	141	138
0	2	3	214	210
0	2	4	36	40
0	2	5	226	198
0	2	6	96	80
0	2	7	77	73
0	2	8	70	66
0	2	9	90	85
0	2	10	27	23
0	2	11	180	160
0	2	12	<21	4
0	2	13	117	97
0	2	14	39	33
0	2	15	21	19
0	2	16	24	24
0	2	17	22	33
0	3	1	204	242
0	3	2	52	57
0	3	3	46	41
0	3	4	49	52
0	3	5	110	127
0	3	6	54	52
0	3	7	156	165
0	3	8	<18	9
0	3	9	158	166
0	3	10	59	58
0	3	11	46	41
0	3	12	34	41
0	3	13	38	34
0	3	14	35	32
0	3	15	75	81
0	4	0	169	196
0	4	1	17	22
0	4	2	182	211
0	4	3	120	136
0	4	4	20	28
0	4	5	107	118
0	4	6	72	75
0	4	7	58	58
0	4	8	145	143
0	4	9	43	47
0	4	10	73	76
0	4	11	85	81
0	4	12	<20	5
0	4	13	62	52
0	4	14	55	55
0	4	15	24	10
0	4	16	41	59
0	5	1	<13	11
0	5	2	118	127
0	5	3	18	15
0	5	4	216	237
0	5	5	<16	2
0	5	6	102	118
0	5	7	35	22
0	5	8	21	29
0	5	9	22	14
0	5	10	107	109
0	5	11	<21	9
0	5	12	144	115
0	5	13	<20	11
0	5	14	54	50
0	6	0	201	218
0	6	1	41	40
0	6	2	105	115
0	6	3	100	113
0	6	4	<16	2
0	6	5	78	88
0	6	6	68	81
0	6	7	32	37
0	6	8	82	92
0	6	9	45	47
0	6	10	70	68
0	6	11	50	53
0	6	12	<19	0
0	6	13	36	41
0	6	14	47	40
0	7	1	157	188
0	7	2	21	14
0	7	3	49	49
0	7	4	34	36
0	7	5	68	72
0	7	6	42	43
0	7	7	121	130
0	7	8	<20	8
0	7	9	87	98
0	7	10	36	29
0	7	11	41	37
0	7	12	35	26
0	7	13	49	41
0	7	14	<14	11
0	7	15	49	56
0	8	0	51	49
0	8	1	53	55
0	8	2	43	44
0	8	3	95	93
0	8	4	<20	20
0	8	5	111	113
0	8	6	47	59
0	8	7	<21	11
0	8	8	42	38
0	8	9	58	44
0	8	10	31	27
0	8	11	106	92
0	8	12	<18	4
0	8	13	61	57
0	9	1	83	90
0	9	2	77	83
0	9	3	25	15
0	9	4	87	90
0	9	5	29	28
0	9	6	61	61
0	9	7	54	56
0	9	8	24	19
0	9	9	40	39
0	9	10	60	54
0	9	11	23	14
0	9	12	70	61
0	10	0	123	132
0	10	1	<20	4
0	10	2	79	74
0	10	3	<20	5
0	10	4	<20	19
0	10	5	<20	10
0	10	6	67	62
0	10	7	<20	14
0	10	8	107	83
0	10	9	<19	4
0	10	10	57	47
0	11	1	58	46
0	11	2	47	46
0	11	3	35	39
0	11	4	67	70
0	11	5	24	17
0	11	6	63	48
0	11	7	37	55
0	11	8	<18	4
0	11	9	47	33
0	11	10	39	35
0	12	0	56	21
0	12	1	<21	21
0	12	2	<20	4
0	12	3	79	66
0	12	4	<19	9
0	12	5	45	43
0	12	6	<18	13
0	12	7	33	26
0	12	8	19	10
0	12	9	31	27
0	13	1	65	49
0	13	2	<18	14
0	13	3	<17	13
0	13	4	22	20
0	13	5	25	16
0	13	6	20	7
0	13	7	45	35
0	14	0	41	33
0	14	1	<14	7
0	14	2	33	27
0	14	3	21	14
0	14	4	<13	2
0	14	5	27	22
1	0	-16	76	76
1	0	-14	102	101
1	0	-12	52	38
1	0	-10	94	92
1	0	-8	254	229
1	0	-6	373	341
1	0	-4	51	41
1	0	-2	181	164
1	0	0	257	298
1	0	2	182	197
1	0	4	148	123
1	0	6	131	127
1	1	-17	36	37
1	1	-16	20	19
1	1	-15	40	45
1	1	-14	48	46
1	1	-13	68	62
1	1	-12	114	117
1	1	-11	<15	0
1	1	-10	123	117
1	1	-9	102	77
1	1	-8	39	39
1	1	-7	137	132
1	1	-6	173	147
1	1	-5	58	55
1	1	-4	165	139
1	1	-3	13	12
1	1	-2	244	208
1	1	-1	190	200
1	1	0	55	48
1	1	1	162	133
1	1	2	216	175
1	1	3	171	127
1	1	4	298	245
1	1	5	41	33
1	1	6	185	166
1	1	7	110	102
1	1	8	19	20
1	1	9	92	86
1	2	-17	42	51
1	2	-16	25	26
1	2	-15	<12	6
1	2	-14	38	35
1	2	-13	88	85
1	2	-12	25	22
1	2	-11	153	143
1	2	-10	21	16
1	2	-9	96	102
1	2	-8	49	90
1	2	-7	39	37
1	2	-6	79	84
1	2	-5	189	169
1	2	-4	< 7	9
1	2	-3	309	292
1	2	-2	55	65
1	2	-1	237	234
1	2	0	78	68
1	2	1	40	33
1	2	2	71	70
1	2	3	243	199
1	2	4	17	13
1	2	5	286	259
1	2	6	35	34
1	2	7	92	88
1	2	8	50	53
1	2	9	56	57
1	2	10	45	50
1	2	11	38	46
1	2	12	<10	8
1	2	13	91	92
1	2	14	<13	8
1	2	15	66	70
1	2	16	36	36
1	2	17	27	26
1	3	-10	54	53
1	3	-9	104	99
1	3	-8	17	20
1	3	-7	163	174
1	3	-6	21	21
1	3	-5	173	157
1	3	-4	93	90
1	3	-3	145	134
1	3	-2	104	103
1	3	-1	131	129
1	3	0	64	61
1	3	1	211	219
1	3	2	58	50
1	3	3	92	95
1	3	4	130	138
1	3	5	82	82
1	3	6	77	72
1	3	7	132	145
1	3	8	29	28
1	3	9	175	174
1	3	10	23	26
1	3	11	66	76
1	4	-16	54	57
1	4	-15	<11	2
1	4	-14	65	63
1	4	-13	48	45
1	4	-12	40	41
1	4	-11	61	61
1	4	-10	50	48
1	4	-9	62	62
1	4	-8	137	146
1	4	-7	49	49
1	4	-6	142	146
1	4	-5	115	115
1	4	-4	103	105
1	4	-3	121	109
1	4	-2	99	109
1	4	-1	175	176
1	4	0	111	115
1	4	1	59	56
1	4	2	179	181
1	4	3	200	183
1	4	4	<10	5
1	4	5	91	100
1	4	6	70	84
1	4	7	46	54
1	4	8	137	148
1	4	9	17	21
1	4	10	87	90
1	4	11	69	61
1	5	-16	22	24
1	5	-15	15	12
1	5	-14	59	50
1	5	-13	<13	7
1	5	-12	90	96
1	5	-11	<14	9
1	5	-10	117	126
1	5	-9	16	12
1	5	-8	25	24
1	5	-7	15	13
1	5	-6	80	85
1	5	-5	<10	4
1	5	-4	270	236
1	5	-3	<10	0
1	5	-2	231	242
1	5	-1	12	11
1	5	0	146	125
1	5	1	20	24
1	5	2	118	121
1	5	3	<10	0
1	5	4	206	226
1	5	5	<11	0
1	5	6	157	183
1	5	7	20	22
1	5	8	37	43
1	5	9	<14	1
1	5	10	67	68
1	5	11	<14	5
1	5	12	85	85
1	6	-16	34	44
1	6	-15	<9	3
1	6	-14	53	49
1	6	-13	48	45
1	6	-12	28	27
1	6	-11	60	62
1	6	-10	32	34
1	6	-9	57	55
1	6	-8	107	111
1	6	-7	29	25
1	6	-6	126	144
1	6	-5	98	104
1	6	-4	<11	11
1	6	-3	96	104
1	6	-2	58	67
1	6	-1	68	73
1	6	0	120	135
1	6	1	<10	0
1	6	2	151	156
1	6	3	119	116
1	6	4	24	22
1	6	5	65	76
1	6	6	49	54
1	6	7	36	42
1	6	8	95	96
1	6	9	<14	7
1	6	10	82	88
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2	9	-5	42	40	3	1	5	29	27	3	6	1	41	41	3	12	-6	22	14	4	4	1	87	82	4	10	-12	24	41
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2	10	-8	66	66	3	2	0	38	45	3	7	-4	36	36	3	13	2	<13	2	4	5	-4	81	74	4	11	-5	42	36
2	10	-7	<17	5	3	2	1	61	66	3	7	-3	58	60	3	13	3	39	35	4	5	-3	<17	5	4	11	-4	29	22
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2	10	2	86	97	3	2	10	15	19	3	7	6	40	40	4	0	2	149	154	4	5	6	111	119	4	11	5	21	25
2	10	3	<18	11	3	3	-16	20	19	3	7	7	52	52	4	0	4	149	141	4	5	7	<22	17	4	11	6	33	33
2	10	4	52	56	3	3	-15	71	66	3	7	8	<19	13	4	1	-16	48	54	4	5	8	103	95	4	12	-7	29	29
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2	12	-9	35	39	3	3	9	138	137	3	8	9	25	26	4	2-17		32	57	4	6	8	45	44	5	0	2	151	127
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Table 4. Continued.

5	1-15	25	24	5	3-15	34	42	5	5-14	31	35	5	6 8	32	24	5	9 -6	<21	22
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5	1-13	60	58	5	3-13	72	73	5	5-12	<20	17	5	7-12	<17	13	5	9 -4	<21	21
5	1-12	37	33	5	3-12	<22	12	5	5-11	<22	0	5	7-11	54	52	5	9 -3	30	31
5	1-11	53	52	5	3-11	72	72	5	5-10	87	92	5	7-10	27	21	5	9 -2	56	65
5	1-10	109	94	5	3-10	25	28	5	5 -9	<22	9	5	7 -9	<22	18	5	9 -1	<21	5
5	1 -9	39	20	5	3 -9	27	23	5	5 -8	110	108	5	7 -8	<22	25	5	9 0	65	68
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5	1 -7	64	52	5	3 -7	94	87	5	5 -6	60	55	5	7 -6	<22	9	5	9 2	28	36
5	1 -6	61	49	5	3 -6	37	30	5	5 -5	<21	4	5	7 -5	92	93	5	9 3	30	37
5	1 -5	108	93	5	3 -5	180	174	5	5 -4	45	38	5	7 -4	<22	11	5	9 4	<16	14
5	1 -4	34	34	5	3 -4	37	29					5	7 -3	81	81	5	9 5	23	23
5	1 -3	67	81	5	3 -3	97	90	5	5 -3	<20	8	5	7 -2	<22	18	5	9 6	38	43
5	1 -2	77	117	5	3 -2	49	48	5	5 -2	103	106	5	7 -1	<22	8	5	10-10	18	29
5	1 -1	<11	8	5	3 -1	<16	8	5	5 -1	<20	13					5	10 -9	<14	5
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5	1 3	93	78	5	3 3	134	134	5	5 3	<22	7	5	7 3	88	86	5	10 -5	<19	1
5	1 4	60	51	5	3 4	<22	9	5	5 4	41	42	5	7 4	<22	14	5	10 -4	61	60
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5	2-14	<19	17	5	4-14	48	49	5	5 8	72	78	5	8-11	35	43	5	10 0	23	21
5	2-13	<21	12	5	4-13	<20	8	5	6-14	31	38	5	8-10	<18	14	5	10 1	<18	7
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5	2 -3	101	104	5	4 -3	60	51	5	6 -4	85	81	5	8 0	<21	17	5	11 -2	27	33
5	2 -2	<15	20	5	4 -2	41	32	5	6 -3	55	50	5	8 1	72	68	5	11 -1	<16	5
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5	2 1	156	133	5	4 1	85	76	5	6 0	55	52	5	8 4	32	33	5	11 2	18	21
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5	2 3	44	32	5	4 3	<21	6	5	6 2	84	78	5	8 6	<18	10				
				5	4 4	86	83	5	6 3	<22	9	5	8 7	51	60	5	12 -4	13	15
5	2 4	<22	22	5	4 5	51	43	5	6 4	64	68	5	9-11	20	22	5	12 -3	18	31
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5	2 6	34	29	5	4 7	62	59	5	6 6	25	22	5	9 -9	<17	9	5	12 -1	27	38
5	2 7	107	104	5	4 8	42	39	5	6 7	57	60	5	9 -8	45	54	5	12 0	<10	6
												5	9 -7	<20	18	5	12 1	18	36

6	0 0	<17	13	6	7 0	34	24				
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6	4 0	<19	0	7	5 0	98	88				
6	5 0	107	109	8	1 0	99	56				
6	6 0	<17	11	8	5 0	57	61				
6	7 0	34	24	6	1 1	33	33				
6	8 0	<16	4	6	2 1	88	104				
6	9 0	62	45	6	3 1	44	42				
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8	1 0	99	56	6	7 1	37	26				
8	5 0	57	61	6	8 1	70	60				
6	1 1	33	33	7	2 1	77	81				
6	2 1	88	104	7	3 1	32	28				
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6	6 1	57	54	7	8 1	45	51				
6	7 1	37	26	8	2 1	65	69				
6	8 1	70	60	8	4 1	36	42				
7	2 1	77	81	6	0 2	78	88				
7	3 1	32	28	6	1 2	57	60				
7	4 1	52	46	6	4 2	70	69				
7	6 1	51	49	6	5 2	46	46				
7	8 1	45	51	6	6 2	44	41				
8	2 1	65	69	6	8 2	25	22				
8	4 1	36	42	6	9 2	37	34				
6	0 2	78	88	6	10 2	42	43				
6	1 2	57	60	7	0 2	73	69				
6	4 2	70	69	7	1 2	68	69				
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6	6 2	44	41	7	3 2	24	23				
6	8 2	25	22	7	4 2	44	43				
6	9 2	37	34	7	5 2	69	66				
6	10 2	42	43	7	6 2	46	41				
7	0 2	73	69	8	0 2	29	30				
7	1 2	68	69	8	1 2	52	56				

Table 5. Interatomic distances.

Distances within a $Th_2(OH)_2(NO_3)_6(H_2O)_6$ group:

Th—Th: 3.988 Å

Distances within the first coordination sphere of a Th atom:

	Th—O_1: 2.60 Å		Th—O_{10}: 2.57 Å
	—O_2: 2.68	water oxygens	—O_{11}: 2.53
nitrate oxygens	—O_4: 2.59		—O_{12}: 2.49
	—O_5: 2.76		Th—O_{14}: 2.39
	—O_7: 2.61	hydroxo oxygens	—O_{14}: 2.33
	—O_8: 2.68		O_{14}—O_{14}: 2.52

Other distances involving thorium atoms:

Th—N_1: 3.08 Å	Th—O_1: 5.40 Å	Th—O_{10}: 6.26 Å
—N_2: 3.13	—O_2: 5.05	—O_{11}: 5.65
—N_3: 3.09	—O_4: 4.15	—O_{12}: 6.20
—O_3: 4.25	—O_5: 4.76	
—O_6: 4.32	—O_7: 4.35	
—O_9: 4.31	—O_8: 4.56	

Distances within the nitrate groups:

N_1—O_1: 1.28 Å	N_2—O_4: 1.26 Å	N_3—O_7: 1.30 Å
—O_2: 1.23	—O_5: 1.26	—O_8: 1.27
—O_3: 1.18	—O_6: 1.20	—O_9: 1.22
O_1—O_2: 2.12 Å	O_4—O_5: 2.12 Å	O_7—O_8: 2.18 Å
—O_3: 2.13	—O_6: 2.16	—O_9: 2.17
O_2—O_3: 2.12	O_5—O_6: 2.15	O_8—O_9: 2.21

Possible hydrogen bond distances:

O_{10}—O_2: 2.93 Å	O_{11}—O_1: 2.90 Å	O_{12}—O_9: 2.77 Å	O_{13}—O_8: 2.81 Å
—O_6: 2.84	—O_{13}: 2.83	—O_{13}: 2.77	—O_9: 2.96
			—O_{11}: 2.83
			—O_{12}: 2.77

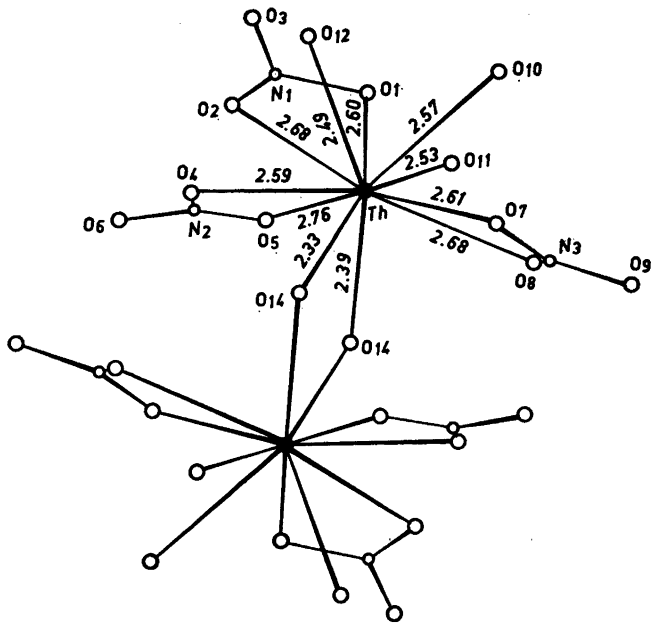

Fig. 2. The atomic arrangement in the $Th_2(OH)_2(NO_3)_6(H_2O)_6$ complex as viewed down [100], with [010] vertical.

The shortest Th—O distances, 2.36 Å, are those involving the bridging oxygens, O_{14}. The average value for the Th—O (nitrate) distances is 2.65 Å, which is somewhat larger than the corresponding value for the Th—O (water) distances, 2.53 Å.

The nitrate groups. In each of the three crystallographically non-equivalent nitrate groups the non-coordinated oxygen atom is closer to the nitrogen than are the other two. The difference, although hardly significant in view of the standard deviations, is probably real, as the same effect has been found in other structures. A literature survey has been made by Taylor *et al.*[9] The average values, which they give for the two non-equivalent distances, 1.263 and 1.215 Å, agree well with those found in the present structure which are 1.26_5 and 1.20 Å.

Hydrogen bonds. The oxygen atoms O_{10} to O_{12} bonded to thorium and the non-bonded O_{13} are probably water molecules. They are all involved in short O—O distances indicative of hydrogen bonding (Table 5). These distances, the number of which is equal to the number of hydrogen atoms, lead to an apparently satisfactory hydrogen bonding scheme (Fig. 1). The water of crystallization, O_{13}, forms two bonds to nitrogen oxygens, O_8 and O_9, and two bonds to the water molecules O_{11} and O_{12}, which are also bonded to thorium. The remaining hydrogen bonds occur between the thorium bonded water molecules and nitrate oxygens.

Some of the bonds are directed towards nitrate oxygens which are also bonded to thorium. A similar phenomenon has, however, been found to occur in other structures including the thorium nitrate pentahydrate.[9] The two bridging oxygens, O_{14}, which should be hydroxo groups according to the suggested hydrogen arrangement, do not seem to be involved in any hydrogen bonding.

The dinuclear thorium hydroxo complexes. The discrete units building up the structure can be described by the formula $Th_2(OH)_2(NO_3)_6(H_2O)_6$. Each group is bound to other groups only by means of hydrogen bonds and van der Waals contacts and different groups have no oxygen atoms in common. The charge is zero.

Other basic salts of thorium, for which structure determinations have been carried out, are $Th(OH)_2SO_4$ [11] and $Th(OH)_2CrO_4H_2O$,[12] both being built up from infinite chains, $(Th(OH)_2)_n$, with the shortest Th—Th distances 3.97 Å and 4.09 Å, respectively. Another basic nitrate, $Th(OH)_2(NO_3)_2(H_2O)_x$, is similarly built with a shortest Th—Th distance of 4.0_6 Å.[4] The Th—Th distance within the dinuclear complex as found here is 3.988 Å.

X-Ray investigations of hydrolyzed thorium salt solutions [14] have shown that the shortest Th—Th distance in the polynuclear complexes is close to 4.0 Å and is independent of the anion present. Therefore the first polynuclear complex formed in solution, *i.e.* the dinuclear one, is likely to have the same structure as that found in the present structure determination, apart, of course, from the amount of complexing with the anion.

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