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Structure of Aquabis(sulfato)tetrakis(urea)thorium(IV) Dihydrate

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Abstract. [Th(SO$_4$)$_2$(CH$_4$N$_2$O)$_4$(H$_2$O)].2H$_2$O, $M_r = 718\cdot42$, monoclinic, $C2/c$, $a = 16\cdot17$ (1), $b = 8\cdot15$ (1), $c = 32\cdot01$ (1) Å, $\beta = 93\cdot52$ (4)°, $V = 4210$ (6) Å^3, $Z = 8$, $D_m = 2\cdot255$, $D_x = 2\cdot267$ g cm^{-3}, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0\cdot71069$ Å), $\mu = 76$ cm^{-1}, $F(000) = 2752$, room temperature, final $R = 0\cdot023$ for 4011 unique observed X-ray reflections. The thorium atom is bonded to nine oxygen atoms: four of these are contributed by two bidentate sulfato ligands and a further four by urea ligands. A water oxygen atom completes the tricapped trigonal prismatic (3/3/3) thorium coordination polyhedron (idealized symmetry D_{3h}).

Introduction. Thorium has extensive coordinating power and chiefly exhibits nine- or ten-coordination (Habash & Smith, 1983, 1990). A series of sulfato-aqua compounds of thorium were prepared and studied by Evstaféva, Molodkin, Dvoryantseva, Ivanova & Struchkova (1966). The infrared absorption spectra of urea-containing nitrato and halogeno complexes of thorium were interpreted by Petrov, Molodkin, Ivanova & Saralidze (1969) who concluded that the thorium is bonded to urea through oxygen atoms. The aim of the present work was to establish whether urea-sulfato complexes of thorium contain O- or N-bonded urea.

Experimental. Colourless prismatic crystals, elongated along [010], were obtained by slow evaporation

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of a solution containing Th(SO$_4$)$_2$.4H$_2$O and urea, CO(NH$_2$)$_2$, in a molar ration of 1:8, at room temperature. Chemical analysis confirmed the formula {found: Th 32·10, S 8·27, N 15·98, C 6·74, H 3·07%; calculated for [Th(SO$_4$)$_2$.[CO(NH$_2$)$_2$]$_4$.H$_2$O].2H$_2$O: Th 32·29, S 8·92, N 15·59, C 6·69, H 3·08%}. Thorium was determined gravimetrically by precipitation as oxalate and ignition to the dioxide. Sulfur, nitrogen, carbon and hydrogen were estimated by standard microanalytical techniques. X-ray data from a small (approximately 0·11 × 0·08 × 0·29 mm) crystal, mounted parallel to [010], were collected on a Rigaku AFC6S diffractometer operating in the ω-scan mode using monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by least squares from ω measurements of 25 carefully centred reflections in the range $9\cdot56 < 2\theta < 19\cdot22°$. Two octants of reciprocal space, hkl and $hk\bar{l}$ (h 0 to 19, k 0 to 9 and l -38 to 37), were explored up to $2\theta = 50°$. 4169 measurements were made on 4011 reflections. The density was measured by flotation in a mixture of iodobenzene and diiodomethane. After corrections, intensities of 3085 independent reflections greater than $3\sigma(I)$ above background were obtained for structure determination. Three standard reflections were monitored every 150 measured reflections and showed no sign of decay. Corrections for Lorentz–polarization effects, secondary extinction and absorption were carried out (transmission range 76 to 100%). Neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol.

Table 1. Atomic positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

The equivalent isotropic temperature factor is defined as

$$B_{eq} = 8\pi^2/3 \; \Sigma_{i=1}^{3}\Sigma_{j=1}^{3} U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Th	0·23449 (1)	0·07784 (2)	0·121332 (6)	1·60 (1)
S1	0·33676 (8)	−0·0298 (2)	0·20504 (4)	2·04 (5)
S2	0·12978 (9)	0·1968 (2)	0·04052 (4)	2·48 (6)
O1	0·3450 (2)	−0·0834 (5)	0·1604 (1)	2·5 (2)
O2	0·2648 (2)	0·0826 (5)	0·2020 (1)	2·6 (2)
O3	0·3197 (2)	−0·1718 (5)	0·2310 (1)	3·1 (2)
O4	0·4129 (2)	0·0535 (5)	0·2200 (1)	2·7 (2)
O5	0·1100 (3)	0·0627 (5)	0·0701 (1)	3·4 (2)
O6	0·2112 (2)	0·2576 (5)	0·0587 (1)	3·0 (2)
O7	0·1350 (3)	0·1376 (6)	−0·0015 (1)	4·4 (2)
O8	0·0694 (3)	0·3296 (6)	0·0422 (1)	3·6 (2)
O9	0·1387 (3)	−0·1107 (5)	0·1491 (1)	3·2 (2)
O10	0·2516 (3)	−0·1581 (5)	0·0812 (1)	3·1 (2)
O11	0·1402 (2)	0·2610 (5)	0·1481 (1)	3·0 (2)
O12	0·3164 (2)	0·3115 (5)	0·1391 (1)	2·7 (2)
O13	0·3671 (3)	0·0856 (5)	0·0825 (2)	3·9 (2)
O14	0·4636 (3)	0·3930 (7)	0·0747 (2)	5·0 (3)
O15	0·4065 (3)	−0·1188 (8)	0·0166 (2)	5·4 (3)
N1	0·1296 (4)	−0·214 (1)	0·2133 (2)	4·7 (3)
N2	0·0208 (3)	−0·2299 (8)	0·1651 (2)	4·0 (3)
N3	0·1764 (5)	−0·3860 (8)	0·0859 (2)	5·2 (4)
N4	0·2828 (5)	−0·3754 (8)	0·0420 (2)	4·5 (3)
N5	0·0149 (4)	0·3647 (8)	0·1285 (2)	3·4 (2)
N6	0·0557 (4)	0·3361 (8)	0·1975 (2)	3·7 (3)
N7	0·3698 (4)	0·5627 (7)	0·1426 (2)	3·7 (3)
N8	0·2879 (5)	0·4723 (9)	0·1932 (2)	4·4 (3)
C1	0·0972 (3)	−0·1823 (7)	0·1760 (2)	2·6 (3)
C2	0·2371 (4)	−0·3053 (7)	0·0700 (2)	2·9 (3)
C3	0·0711 (3)	0·3184 (7)	0·1577 (2)	2·4 (2)
C4	0·3241 (4)	0·4459 (7)	0·1579 (2)	2·6 (3)

IV) and anomalous dispersion included in F_c (Ibers & Hamilton, 1964). Calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1985) and diagrams with *PLUTO* (Motherwell & Clegg, 1978).

The Th-atom position was obtained by the Patterson method (Calbrese, 1972) and those of lighter atoms by direct methods (Beurskens, 1984). Positions of all the non-hydrogen atoms and also of the urea hydrogen atoms were refined, as were the anisotropic thermal vibration parameters for non-hydrogen atoms, by full-matrix least squares (Busing, Martin & Levy, 1962) (320 refined parameters with reflection/parameter ratio of 9·64). Urea hydrogen atoms were initially located from a difference Fourier map in which the hydrogens of two water molecules were also just discernible. Hydrogens of the third water molecule were not located. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The factor w was based on counting statistics plus a dampening factor q for intense reflections: $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) \propto \sigma^2(\text{counts}) + (qF_o^2)^2$ and $q = 0·03$. The refinement converged at $R = 0·023$ ($wR = 0·028$); maximum shifts on the final cycle were < 0·06 e.s.d. A final difference Fourier synthesis showed no peak higher than 0·9 e Å^{-3} (minimum height −0·63 e Å^{-3}) and none which could be interpreted as an atom. There was no unusual variation of R with $|F_o|$ or with $(\sin\theta)/\lambda$. The atomic positional

Table 2. Bond lengths (Å) and principal angles (°)

Thorium coordination polyhedron

Th—O1*	2·491 (4)	Th—O10†	2·337 (4)
Th—O2*	2·599 (4)	Th—O11†	2·334 (4)
Th—O5*	2·520 (4)	Th—O12†	2·368 (4)
Th—O6*	2·492 (4)	Th—O13‡	2·544 (4)
Th—O9†	2·390 (4)		

Pyramid edges

O2—Th—O1	54·8 (1)	O5—Th—O10	73·7 (1)
O2—Th—O9	74·2 (1)	O5—Th—O11	75·9 (1)
O2—Th—O11	73·4 (1)	O13—Th—O1	70·0 (1)
O2—Th—O12	71·4 (1)	O13—Th—O6	71·6 (1)
O5—Th—O6	55·3 (1)	O13—Th—O10	67·7 (1)
O5—Th—O9	72·5 (1)	O13—Th—O12	67·7 (1)
Mean 68·97			

Prism edges

O1—Th—O12	86·0 (1)	O9—Th—O11	79·7 (2)
O6—Th—O10	93·4 (2)		
Mean 86·37			

Triangle edges

O1—Th—O9	86·3 (2)	O6—Th—O11	81·3 (1)
O1—Th—O10	74·7 (1)	O6—Th—O12	77·0 (1)
O9—Th—O10	77·1 (2)	O11—Th—O12	76·5 (2)
Mean 78·82			

Equatorial angles

O2—Th—O5	137·8 (1)	O5—Th—O13	110·4 (2)
O2—Th—O13	111·8 (1)		
Mean 120·0			

Sulfate groups

S1—O1	1·509 (4)	S2—O5	1·494 (4)
S1—O2	1·479 (4)	S2—O6	1·491 (4)
S1—O3	1·461 (4)	S2—O7	1·436 (4)
S1—O4	1·461 (4)	S2—O8	1·461 (4)
O1—S1—O2	103·4 (2)	O5—S2—O6	102·4 (2)
O1—S1—O3	109·9 (2)	O5—S2—O7	112·1 (3)
O1—S1—O4	108·9 (2)	O5—S2—O8	110·4 (3)
O2—S1—O3	110·6 (2)	O6—S2—O7	112·1 (3)
O2—S1—O4	112·2 (2)	O6—S2—O8	108·4 (3)
O3—S1—O4	111·5 (2)	O7—S2—O8	111·1 (3)
Mean 109·75			
Mean (chelating) 102·90			
Mean (nonchelating) 111·12			

Urea groups

C1—O9	1·267 (7)	C2—N3	1·309 (9)
C2—O10	1·270 (7)	C2—N4	1·326 (9)
C3—O11	1·267 (6)	C3—N5	1·317 (8)
C4—O12	1·252 (7)	C3—N6	1·320 (7)
C1—N1	1·301 (8)	C4—N7	1·318 (8)
C1—N2	1·321 (8)	C4—N8	1·322 (9)
N1—C1—N2	120·0 (6)	N5—C3—N6	119·3 (5)
N3—C2—N4	120·6 (6)	N7—C4—N8	119·2 (6)
Mean 119·78			

Probable hydrogen bonds

O13—H···O15	2·794 (7)	N1—H···O4	2·965 (7)
O13—H···O14	2·970 (7)	N6—H···O3	2·957 (7)
O14—H···O7	2·765 (6)	N7—H···O1	2·971 (8)
O15—H···O8	3·055 (8)		

* Sulfate oxygen atom.
† Urea oxygen atom.
‡ Water oxygen atom.

parameters for non-hydrogen atoms are listed in Table 1 and the principal interatomic distances and angles are quoted in Table 2.*

Discussion. Each thorium atom is coordinated to nine oxygen atoms, four from sulfate groups, four from urea molecules and one from a water molecule. The sulfate groups are bidentate. The thorium coordination polyhedron (Fig. 1) is a trigonal prism with three centred rectangular faces (symmetrically tricapped trigonal prism). The coordinated water molecule occupies one of the equatorial (capping)
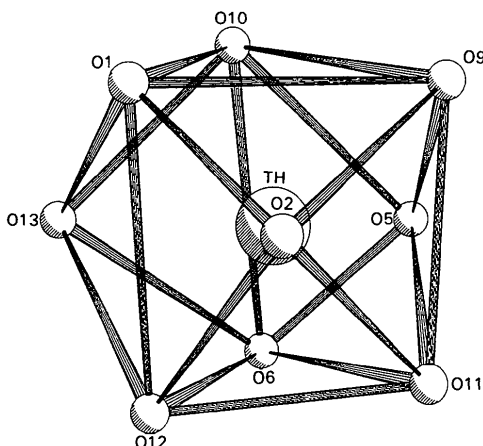

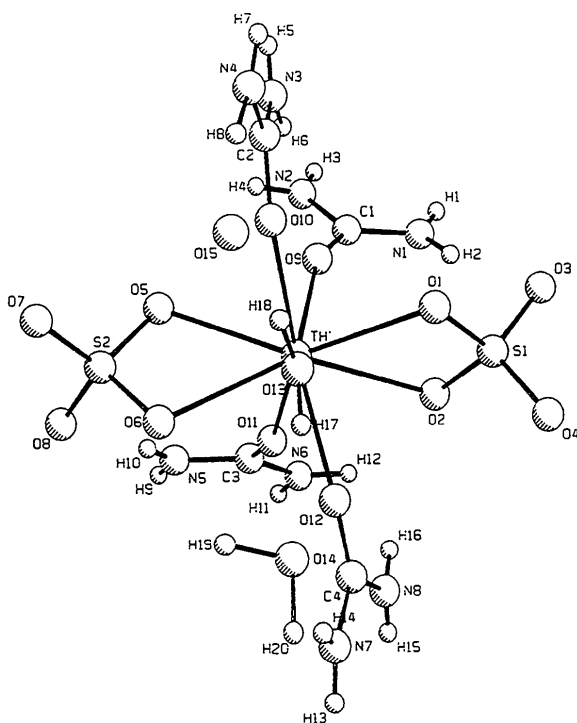Fig. 1. The thorium-atom coordination polyhedron.

positions. This 3/3/3 polyhedron, which approximates to D_{3h} symmetry, is the most frequently observed one in nine coordination (Habash & Smith, 1990; Molodkin, Skotnikova & Arutyunyan, 1964). The three donor oxygen triangles (1: O1,O9,O10; 2: O2,O5,O13; 3: O6,O11,O12) are nearly parallel, with the angles between planes 1 and 2, 1 and 3, and 2 and 3 of 11·4, 9·8 and 7·1° respectively. Fig. 2 shows the whole molecule. The Th—O bond distances range from 2·334 (4) to 2·599 (4) Å with a mean of 2·453 (4) Å. The Th—O(water) distance of 2·544 (4) Å is longer than both the mean Th—O(sulfate) and Th—O(urea) bond lengths of 2·526 (4) and 2·357 (4) Å respectively. This difference may perhaps be correlated with the relatively easy removal of the water from the coordination sphere. Urea molecules are strongly bonded to thorium. The S—O bonds to coordinated oxygen are, as expected, longer than those to terminal oxygen. The mean values are 1·493(4) and 1·455 (4) Å respectively. In the urea molecules the average C—O and C—N bond distances are 1·264 (7) and 1·317 (8) Å respectively. The water molecules represented by O13, O14 and O15 form hydrogen bonds among themselves and with the oxygens of the sulfate groups and N—H⋯O hydrogen bonds link urea and sulfate groups. The O⋯O and N⋯O distances vary from 2·765 (6) to 3·055 (8) Å.

Fig. 2. One molecule of the structure.

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