

Structure of Thorium Sulphate Octahydrate, $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$

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Abstract. $M_r = 568.3$, monoclinic, $P2_1/n$, $a = 8.51$ (2), $b = 11.86$ (2), $c = 13.46$ (2) Å, $\beta = 92.65$ (1)°, $U = 1357$ (7) Å³, $Z = 4$, $D_x = 2.778$, $D_m = 2.78$ g cm⁻³ (by flotation in iodobenzene/diiodomethane), Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 137.95$ cm⁻¹. Non-hydrogen atoms refined anisotropically to a final R of 0.1022. The thorium is ten-coordinate, both the sulphate groups being chelate, and six of the water oxygens being coordinated to thorium. The resulting complexes are linked together *via* hydrogen bonds. The thorium coordination polyhedron approximates closely to the bicapped square antiprism (1.4/4.1) of D_{4d} symmetry and with $\theta = 63^\circ$.

Introduction. Thorium sulphate was first prepared by Berzelius (1829), who observed that the degree of hydration varied with the temperature of crystallization. Anhydrous thorium sulphate and hydrates containing 2, 4, 7.5, 8, and 9 water molecules are known (Molodkin & Arutyunyan, 1965). The octahydrate is obtained by crystallization from neutral aqueous solution at 293–298 K (Cleve, 1874). Lower hydrates may be obtained by drying at 373–383 K, and the anhydrous salt is formed at 673 K (Bagnall, 1972). The compound exists in solution as the neutral complex $[\text{Th}(\text{SO}_4)_2]^0$ (Zebroski, Alter & Heumann, 1951).

Experimental. Plate-shaped crystals from slow evaporation of thorium sulphate at room temperature; chemical analysis: found: Th 40.79; S 11.21; H 2.78; calc. for $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$: Th 40.85; S 11.27; H 2.82%; Th determined gravimetrically by precipitation as oxalate and ignition to the dioxide, S and H by standard microanalytical techniques; $0.04 \times 0.19 \times 0.27$ mm, Stoe 2-circle diffractometer, ω -scan, Mo $K\alpha$ (graphite monochromator), unit-cell parameters by least squares from 60 reflexions, hkl and $h\bar{k}l$ up to $2\theta = 60^\circ$, counting time for $(h+k)$ odd twice that for $(h+k)$ even, because of systematic weakness of odd layers; crystal mounted along $[110]$, absences $h0l$ with $h+l$ odd, $0k0$ with k odd, non-standard setting of $P2_1/c$. 2639 independent with $I > 3\sigma(I)$, standard reflexion every 50, no signs of decay; absorption correction by

Gaussian interpolation (Busing & Levy, 1957), $6 \times 8 \times 10$ Gaussian points; $\mu = 137.95$ cm⁻¹, absorption coefficient of Th from Roof (1959), others from *International Tables for X-ray Crystallography* (1962); scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); anomalous dispersion corrections for Th from Roof (1961) ($f' = -12.0$, $f'' = 14.4$ electrons); heavy-atom method, block-diagonal isotropic, full matrix anisotropic, H not located; final difference synthesis showed no peak interpretable as an atom. High final R (0.1022) attributed to incomplete absorption correction because of irregular crystal shape. The residual absorption errors are also reflected in the negative values of six of the b_{ii} 's, two of which are more negative than -2.5σ (and the low values of B_{eq}).

Discussion. Positional parameters are listed in Table 1 and interatomic distances and angles in Table 2.† The Th coordination polyhedron is a bicapped square

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38105 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters ($\times 10^4$) for the non-hydrogen atoms with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters (Å²)

	x	y	z	B_{eq}
Th	9993 (1)	1083 (1)	2523 (1)	1.24
S(1)	8037 (7)	2107 (5)	654 (4)	0.54
S(2)	13749 (6)	1083 (5)	2605 (4)	0.62
O(1)	11987 (29)	3924 (31)	318 (22)	3.52
O(2)	8130 (36)	4072 (22)	4597 (21)	2.93
O(3)	7529 (20)	1270 (16)	1351 (13)	0.81
O(4)	7816 (20)	-144 (19)	2987 (15)	1.22
O(5)	7103 (23)	3117 (17)	729 (13)	1.00
O(6)	9714 (20)	2343 (17)	1011 (14)	0.93
O(7)	12634 (20)	1123 (20)	1699 (14)	1.21
O(8)	10907 (25)	-836 (16)	3059 (15)	1.01
O(9)	14683 (15)	62 (15)	2574 (18)	1.30
O(10)	14668 (19)	2111 (16)	2673 (17)	1.20
O(11)	11092 (20)	2958 (15)	2975 (14)	0.71
O(12)	7910 (19)	2451 (18)	3067 (15)	1.18
O(13)	12716 (19)	994 (16)	3445 (13)	0.71
O(14)	9906 (21)	-315 (18)	1138 (14)	0.97
O(15)	9903 (19)	1127 (17)	4347 (12)	0.78
O(16)	7975 (24)	1655 (19)	-335 (12)	1.21

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

Thorium coordination polyhedron

Th—O(3)*	2.57 (2)
Th—O(4)	2.46 (2)
Th—O(6)*	2.53 (2)
Th—O(7)*	2.55 (2)
Th—O(8)	2.50 (2)
Th—O(11)	2.48 (2)
Th—O(12)	2.54 (2)
Th—O(13)*	2.58 (2)
Th—O(14)	2.49 (2)
Th—O(15)	2.46 (2)

Square edges

O(4)—Th—O(12)	76.1 (6)
O(12)—Th—O(6)	79.3 (6)
O(6)—Th—O(14)	78.0 (6)
O(14)—Th—O(4)	78.5 (6)
O(7)—Th—O(8)	82.7 (6)
O(8)—Th—O(15)	75.8 (6)
O(15)—Th—O(11)	76.4 (6)
O(11)—Th—O(7)	76.1 (6)
Mean	77.86

Pyramid edges

O(3)—Th—O(4)	66.7 (6)
O(3)—Th—O(6)	54.0 (6)
O(3)—Th—O(12)	64.0 (6)
O(3)—Th—O(14)	66.7 (6)
O(13)—Th—O(7)	54.5 (5)
O(13)—Th—O(8)	64.1 (6)
O(13)—Th—O(11)	66.3 (6)
O(13)—Th—O(15)	65.8 (6)
Mean	62.76 (6)

Equatorial (zigzag) edges

O(12)—Th—O(11)	67.5 (6)
O(11)—Th—O(6)	71.8 (6)
O(6)—Th—O(7)	72.0 (6)
O(7)—Th—O(14)	71.6 (6)
O(14)—Th—O(8)	67.0 (6)
O(8)—Th—O(4)	67.5 (6)
O(4)—Th—O(15)	72.5 (6)
O(15)—Th—O(12)	69.1 (6)
Mean	69.88 (6)

Axial angle

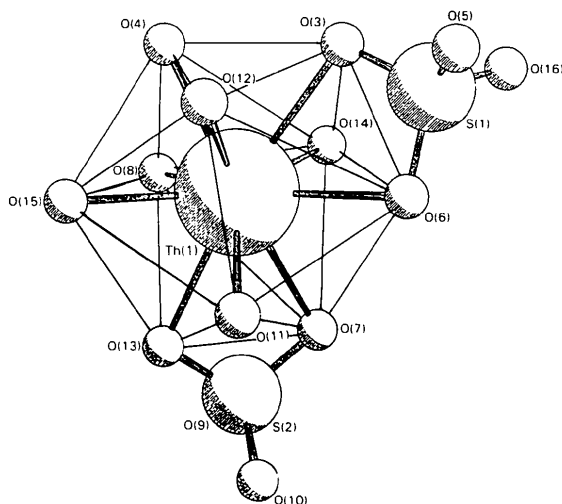
O(3)—Th—O(13)	170.5 (6)
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Sulphate groups

S(1)—O(3)	1.45 (2)
S(1)—O(5)	1.44 (2)
S(1)—O(6)	1.51 (2)
S(1)—O(16)	1.43 (2)
S(2)—O(7)	1.51 (2)
S(2)—O(9)	1.45 (2)
S(2)—O(10)	1.45 (2)
S(2)—O(13)	1.46 (2)
O(3)—S(1)—O(5)	110.5 (11)
O(3)—S(1)—O(6)	103.2 (11)
O(3)—S(1)—O(16)	110.3 (11)
O(5)—S(1)—O(6)	109.8 (11)
O(5)—S(1)—O(16)	112.2 (12)
O(6)—S(1)—O(16)	111.0 (11)
O(7)—S(2)—O(9)	109.1 (11)
O(7)—S(2)—O(10)	109.9 (11)
O(7)—S(2)—O(13)	104.3 (11)
O(9)—S(2)—O(10)	114.1 (11)
O(9)—S(2)—O(13)	108.2 (11)
O(10)—S(2)—O(13)	110.6 (11)
Mean	109.43
Mean (chelating)	103.75
Mean (nonchelating)	110.57

Probable hydrogen bonds

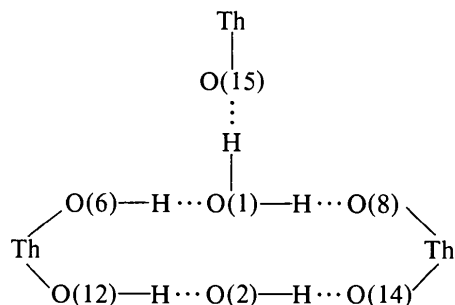
O(1)—H...O(6)	2.88 (4)
O(1)—H...O(8)	2.77 (4)
O(1)—H...O(15)	2.86 (4)
O(2)—H...O(12)	2.82 (3)
O(2)—H...O(14)	2.83 (3)
O(4)—H...O(5)	2.69 (3)
O(4)—H...O(9)	2.71 (3)
O(8)—H...O(10)	2.66 (3)
O(8)—H...O(13)	2.70 (3)
O(11)—H...O(9)	2.67 (3)
O(11)—H...O(13)	2.77 (3)
O(11)—H...O(16)	2.76 (3)
O(12)—H...O(3)	2.71 (3)
O(12)—H...O(10)	2.81 (3)
O(12)—H...O(11)	2.78 (3)
O(14)—H...O(3)	2.78 (3)
O(14)—H...O(8)	2.75 (3)
O(14)—H...O(16)	2.67 (3)
O(15)—H...O(5)	2.73 (3)
O(15)—H...O(13)	2.74 (3)

Fig. 1. Environment of the thorium atom in $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$.

The Th—O distances vary from 2.46 (2) to 2.58 (2) Å [mean 2.52 (2) Å]. The average Th—O (sulphate) and Th—O (water) are 2.56 (2) and 2.49 (2) Å respectively. The mean S—O (coordinated) bonds are longer than the terminal ones. Their mean values are 1.48 (2) and 1.44 (2) Å respectively. The former is entirely typical for SO_4^{2-} ions.

The water molecules represented by O(1), O(2), O(4), O(8), O(11), O(12), O(14) and O(15) form hydrogen bonds among themselves and with the oxygens of the sulphate groups. The hydrogen-bond distances vary from 2.66 (3) to 2.88 (4) Å.

The water molecules O(1) and O(2) are not coordinated to thorium; they are bonded only *via* hydrogen bonds to symmetry-related molecules to hold the structure together. Therefore, it is possible to represent the chain of attachment through different Th atoms in the following simple scheme.



The coordinated water molecules also form hydrogen bonds as is shown by their short O...O distances, and these cross link the structure in a more complex manner. The probable hydrogen bonds are listed in Table 2. There are twenty such bonds although the formula shows only sixteen H atoms. This fact is attributed to either (i) disorder (static or dynamic) of a

antiprism with 1.4/4.1 geometry and approximate D_{4d} symmetry, as predicted for ten-coordination by Muetterties & Wright (1967), and observed in the complex oxalate $\text{K}_4\text{Th}(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$ (Akhtar & Smith, 1975). The coordination sphere of the thorium contains the four O atoms (3,6,7, and 13) from two chelate sulphate groups and six water molecules (O atoms 4, 8, 11, 12, 14, and 15). A least-squares fit of the idealized to the observed polyhedron was carried out as described by Akhtar & Smith (1975) and yielded a r.m.s. deviation of 3.7°. The shape parameters of the idealized polyhedron are $\theta = 62.6^\circ$ and the ratio of metal—ligand distances for axial and antiprism positions = 1.030. It is noteworthy that the two sulphate groups in this structure both span pyramid (*p*) edges. Fig. 1 represents the attachment of groups around Th.

* Sulphate oxygen.

single H atom between two alternative acceptors, or (ii), if the alternative acceptors are close enough together, a bifurcated hydrogen bond.

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Mo₆Br₆S₃: Nouveau Composé Bidimensionnel à Clusters Octaédriques Mo₆

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Abstract. $M_r = 1151.3$, orthorhombic, $Cmcm$, $a = 17.250$ (7), $b = 6.600$ (4), $c = 11.929$ (7) Å, $Z = 4$, $V = 1358$ Å³, $D_m = 5.51$, $D_x = 5.63$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 24.34$ mm⁻¹, $F(000) = 2040$. The structure has been solved by direct methods and refined by least squares to $R = 0.062$ ($R_w = 0.052$) for 423 independent reflections. The structure can be described as a layer structure of [Mo₆L₈] units. Along **c**, these units are bonded by their apices to build up chains. Along **b**, these chains are linked by Mo–S bonds. Along **a**, the cohesion is made only by contacts between Br atoms, leading to a two-dimensional character for this compound.

Introduction. La chimie du molybdène de degré II se caractérise principalement par la présence de composés comportant des motifs [Mo₆L₈] ($L = \text{halogène ou chalcogène}$) à clusters octaédriques Mo₆ (Kepert, 1972). Récemment, nous avons isolé de nouveaux chalcologénures du Mo^{II}: Mo₆X₁₀Y ($X = \text{Cl, Br, I}$; $Y = \text{S, Se, Te}$) dans lesquels les motifs [Mo₆L₈] sont reliés entre eux par six atomes d'halogène en pont (Perrin, Sergent & Prigent, 1973; Perrin, Sergent, Le Traon & Le Traon, 1978), et Mo₆S₆X₂ ($X = \text{Br, I}$) où les motifs [Mo₆L₈] sont directement reliés entre eux (Sergent, Fischer, Decroux, Perrin & Chevrel, 1977; Perrin, Chevrel, Sergent & Fischer, 1979).

Nous décrivons ici un nouveau thiobromure du molybdène(II) présentant un type d'empilement original des motifs [Mo₆L₈].

Partie expérimentale. Mo₆Br₆S₃ a été préparé à partir d'un mélange de 3MoBr₂ + 3Mo + 3S comprimé, puis chauffé en tube de silice scellé sous vide à une température de 1473 K pendant 24 h, suivi d'un ou deux recuits. Des monocristaux en forme de plaquettes noires brillantes croissent par recuit prolongé à 1523 K.

L'étude cristallographique préliminaire effectuée sur chambre photographique de Weissenberg et de précession conduit aux groupes spatiaux possibles $Cmcm$, $Cmc2_1$, $C2cm$. Les paramètres de maille ont été affinés sur poudre selon la méthode des moindres carrés en utilisant le silicium comme étalon interne. L'enregistrement des intensités diffractées par un monocristal a été effectué à l'aide d'un diffractomètre automatique CAD-4 Nonius. Dimensions du cristal utilisé: 0,01 × 0,028 × 0,17 mm; radiation: Mo $K\alpha$; monochromateur: lame de graphite; distance cristal–détecteur: 173 mm; $\theta \leq 30^\circ$; balayage: $\omega - 2\theta$; amplitude de balayage: $(1,20 + 0,35 \text{ tg } \theta)^\circ$; ouverture: $(2 + 0,50 \text{ tg } \theta)$ mm; nombre de réflexions non nulles indépendantes: 493. Les intensités mesurées, exploitées par le programme MAXE (Le Marouille, 1972) sont corrigées du facteur de Lorentz–polarisation.

Des corrections d'absorption ont été effectuées en utilisant la méthode analytique décrite par de Meulenaer & Tompa (1965); les faces latérales du cristal en forme de parallépipède rectangle s'indexent selon les plans (100) et (010) et les faces extrêmes selon (001). Le facteur de transmission varie de 0,51 à 0,78 avec une valeur moyenne de 0,70. Seules les 423