H2(*W*1) to both O2(P1) and O3(P1) of another symmetry-related molecule with O to O distances of 3·139 and 3·033 Å, respectively. The second pair involves weaker but symmetric hydrogen bonds between H3(N1) and both O1(P1) and O2(P1) of a neighboring phosphate with equal N to O distances of 3·333 Å.

The relatively flat six-membered chelate rings in both structures result in an increased distance between the ammonia ligands on the Cr atom and the phosphate anionic O atoms when compared to the distance for a more sharply puckered chelate ring. This increased distance prevents the formation of any intramolecular hydrogen bonds between the metal ligands and the pyrophosphate O atoms of the type previously observed for several metal–pyrophosphate chelate complexes (Sundaralingam & Haromy, 1985).

Crystal packing. Packing diagrams of both structures are shown in Fig. 4. In both structures, water molecules fill the void between symmetry-related molecules in both the **b** and **c** directions. The centrosymmetric facial dimer complexes sit at the corners and at the center of the unit cell.

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References

Cornelius, R. D. & Cleland, W. W. (1978). *Biochemistry*, **17**, 3279–3285.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Dunaway-Mariano, D. & Cleland, W. W. (1980). *Biochemistry*, **19**, 1506–1515.

Harmoy, T. P. (1982). PhD Thesis. Univ. of Wisconsin–Madison, WI, USA.

Haromy, T. P., Knight, W. B., Dunaway-Mariano, D. & Sundaralingam, M. (1983). *Biochemistry*, **22**, 5015–5021.

Haromy, T. P., Knight, W. B., Dunaway-Mariano, D. & Sundaralingam, M. (1984). *Acta Cryst.* C**40**, 223–226.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 148–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Janson, C. A. & Cleland, W. W. (1974). *J. Biol. Chem.* **249**, 2572–2574.

Jeffrey, G. A. & Mitra, J. (1984). *J. Am. Chem. Soc.* **106**, 5546–5553.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Knight, W. B., Ting, S.-J., Chuang, S., Dunaway-Mariano, D., Haromy, T. & Sundaralingam, M. (1983). *Arch. Biochem. Biophys.* **227**, 302–309.

McLaren, E. H. & Helmholtz, L. (1959). *J. Phys. Chem.* **63**, 1279–1283.

Merritt, E. A. & Sundaralingam, M. (1980). *Acta Cryst.* B**36**, 2576–2584.

Merritt, E. A., Sundaralingam, M. & Dunaway-Mariano, D. (1981). *J. Am. Chem. Soc.* **103**, 3565–3567.

Pecoraro, V. L., Rawlings, J. & Cleland, W. W. (1984). *Biochemistry*, **23**, 153–158.

Shorter, A. L., Haromy, T. P., Scalzo-Brush, T., Knight, W. B., Dunaway-Mariano, D. & Sundaralingam, M. (1987). *Biochemistry*, **26**, 2060–2066.

Speckhard, D. C., Rawlings, J., Pecoraro, V. L. & Cleland, W. W. (1989). In preparation.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sundaralingam, M. & Haromy, T. P. (1985). In *Mechanisms of Enzymatic Reactions: Stereochemistry*. Proceedings of the Fifteenth Steenbock Symposium, edited by P. A. Frey, pp. 249–265. New York: Elsevier.

Werner, A. (1906). *Ber. Dtsch. Chem. Ges.* **39**, 2656–2667.

Acta Cryst. (1990). C**46**, 957–960

Structure of Disodium Triaquatri-μ-sulfato-thorate(IV) Trihydrate

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Abstract. $Na_2[Th(SO_4)_3(H_2O)_3].3H_2O$, $M_r = 674{\cdot}290$, monoclinic, $P2_1/c$, $a = 5{\cdot}567\ (2)$, $b = 16{\cdot}81\ (2)$, $c = 15{\cdot}76\ (2)$ Å, $\beta = 91{\cdot}925\ (4)°$, $V = 1474{\cdot}0$ Å^3, $Z = 4$, $D_m = 2{\cdot}99$, $D_x = 3{\cdot}036$ g cm^{-3}, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0{\cdot}71069$ Å), $\mu = 129{\cdot}25$ cm^{-1}, $F(000) = 1264$, room temperature, final $R = 0{\cdot}043$ for 2618 unique observed X-ray reflexions. The thorium is nine-coordinate; all the three sulfates are bidentate and bridging and link the Th atoms into infinite chains parallel to [100]. Three of the six water molecules are coordinated to the thorium. The thorium coordination polyhedron is a slightly distorted tricapped trigonal prism (3/3/3) (idealized symmetry D_{3h}) with $\theta = 46{\cdot}8°$ (angle between princi-

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pal symmetry axis and a non-equatorial metal—ligand bond). The sodium ions are coordinated in rather irregular octahedra.

Introduction. This substance was first prepared by Cleve (1874) by the evaporation of a mixed solution of the component sulfates. Later the corresponding tetrahydrate and dodecahydrate were isolated. The ternary system thorium sulfate–sodium sulfate–water was studied by Huang-Pang & Fedorov (1961).

Molodkin, Skotnikova & Ivanova (1965) could not determine precisely the number of inner-sphere water molecules in this compound. They describe two different methods of obtaining $Na_2Th(SO_4)_3.6H_2O$, from thorium sulfate and from thorium nitrate respectively.

Experimental. Prismatic crystals, elongated along [100], were obtained by slow evaporation of a solution containing $Th(SO_4)_2.9H_2O$ and anhydrous sodium sulfate, Na_2SO_4, in a molar ratio of 1:2, at room temperature. Chemical analysis confirmed the formula {found: Th 34·22, S 14·13, H 1·70; calculated for $Na_2[Th(SO_4)_3(H_2O)_3].3H_2O$: Th 34·42, S 14·24, H 1·78}. Thorium was determined gravimetrically by precipitation as oxalate and ignition to the dioxide; sulfur and hydrogen were estimated by standard microanalytical techniques.

X-ray reflexion data from a small (approximately 0·35 × 0·15 × 0·04 mm) crystal, mounted parallel to [100], were collected on a Stoe two-circle diffractometer operating in the ω-scan mode and using molybdenum $K\alpha$ radiation. The unit-cell parameters were determined by least squares from ω measurements of 39 carefully chosen reflexions. Two octants of reciprocal space, hkl and $hk\bar{l}$, were explored up to $2\theta = 48°$. 3017 measurements were made on 2774 reflexions.

The density was measured by flotation in a mixture of iodobenzene and diiodomethane. After corrections, intensities of 2618 independent reflexions greater than $3\sigma(I)$ above background were obtained and used for the structure determination. A standard reflexion was monitored every 50 reflexions and showed no sign of decay.

Correction for absorption was carried out by means of a Gaussian integration method based on Busing & Levy (1957) with a grid of 10 × 8 × 8 Gaussian points and $\mu = 129{\cdot}25\ \text{cm}^{-1}$. The absorption coefficient used for thorium was that measured by Roof (1959) and the other coefficients were taken from *International Tables for X-ray Crystallography* (1962). Throughout the analysis, the scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974) were used. Anomalous-dispersion corrections for thorium were those measured by Roof (1961) ($f' = -12{\cdot}0, f'' = 14{\cdot}4$ e).

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

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Th	1994 (1)	799 (< 1)	2515 (< 1)	0·93
S(1)	2985 (5)	4343 (2)	3015 (2)	0·67
S(2)	6904 (5)	1978 (2)	1491 (2)	0·62
S(3)	7094 (5)	806 (2)	4136 (2)	0·61
Na(1)	4576 (10)	2541 (4)	4394 (3)	1·76
Na(2)	4711 (9)	3880 (3)	1061 (3)	1·37
O(1)	1040 (15)	4953 (5)	3060 (6)	1·16
O(2)	1684 (18)	2953 (6)	387 (7)	2·03
O(3)	2303 (16)	3748 (5)	2366 (6)	1·25
O(4)	2518 (16)	4992 (5)	568 (6)	1·35
O(5)	2540 (17)	631 (6)	930 (6)	1·61
O(6)	3340 (17)	3980 (6)	3857 (6)	1·49
O(7)	1924 (16)	2235 (5)	3147 (6)	1·17
O(8)	5219 (15)	4746 (5)	2743 (6)	1·54
O(9)	8496 (16)	4566 (5)	1491 (6)	1·26
O(10)	8726 (18)	4174 (6)	4548 (6)	2·04
O(11)	8934 (15)	1019 (5)	3511 (5)	1·04
O(12)	6208 (16)	1780 (6)	613 (5)	1·31
O(13)	5241 (16)	1571 (5)	2068 (6)	1·26
O(14)	6826 (18)	2836 (5)	1640 (6)	1·65
O(15)	7648 (17)	2929 (6)	3445 (6)	1·66
O(16)	9380 (14)	1685 (5)	1683 (6)	1·23
O(17)	4686 (15)	876 (6)	3711 (5)	1·32
O(18)	7190 (16)	1381 (5)	4832 (5)	1·30

The structure was solved by the heavy-atom method and the positions of all the non-H atoms were refined, initially with isotropic thermal factors by block-diagonal, and finally with anisotropic thermal vibration parameters (217 refined parameters) by full-matrix least squares [function minimized $w(|F_o| - |F_c|)^2$]. H atoms were not located. Unit weights were used throughout.

All calculations were carried out using the Sheffield suite of crystallographic programs on an ICL 1906S computer.

Refinement converged at $R = 0{\cdot}043$; maximum shifts on the final cycle were 0·04 and 0·5 times the corresponding e.s.d.'s for positional and vibrational parameters respectively. A final difference Fourier synthesis showed no peak higher than 1·1 e Å^{-3} and none which could be interpreted as an atom. Analysis of the final output showed no unusual variation of R with $|F_o|$ or with $(\sin\theta)/\lambda$. The atomic positional parameters are listed in Table 1 and the principal interatomic distances and angles are quoted in Table 2.*

Discussion. Each Th atom is coordinated to nine O atoms, six from sulfate groups and three from water molecules. The conclusion of Molodkin, Skotnikova

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52297 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Thorium coordination polyhedron		Probable hydrogen bonds	
Th—O(1)*	2·36 (1)	O(2)—H···O(18)	2·85 (1)
Th—O(5)	2·54 (1)	O(5)—H···O(10)	2·65 (1)
Th—O(7)	2·61 (1)	O(5)—H···O(12)	2·87 (1)
Th—O(8)*	2·40 (1)	O(5)—H···O(16)	2·79 (1)
Th—O(9)	2·62 (1)	O(7)—H···O(3)	2·84 (1)
Th—O(11)*	2·38 (1)	O(7)—H···O(11)	2·71 (1)
Th—O(13)*	2·35 (1)	O(7)—H···O(15)	2·71 (1)
Th—O(16)*	2·43 (1)	O(9)—H···O(1)	2·88 (1)
Th—O(17)*	2·37 (1)	O(9)—H···O(8)	2·75 (1)
		O(9)—H···O(17)	2·84 (1)
		O(10)—H···O(6)	2·84 (1)
Sulfate groups			
S(1)—O(1)	1·50 (1)	Sodium coordination	
S(1)—O(3)	1·47 (1)	Na(1)···O(2)	2·43 (1)
S(1)—O(6)	1·47 (1)	Na(1)···O(6)	2·65 (1)
S(1)—O(8)	1·49 (1)	Na(1)···O(7)	2·47 (1)
S(2)—O(12)	1·46 (1)	Na(1)···O(12)	2·39 (1)
S(2)—O(13)	1·49 (1)	Na(1)···O(15)	2·40 (1)
S(2)—O(14)	1·46 (1)	Na(1)···O(18)	2·52 (1)
S(2)—O(16)	1·49 (1)	Na(2)···O(2)	2·50 (1)
S(3)—O(4)	1·46 (1)	Na(2)···O(3)	2·50 (1)
S(3)—O(11)	1·49 (1)	Na(2)···O(4)	2·35 (1)
S(3)—O(17)	1·48 (1)	Na(2)···O(9)	2·48 (1)
S(3)—O(18)	1·46 (1)	Na(2)···O(14)	2·29 (1)
		Na(2)···O(18)	2·45 (1)
Pyramid edges		Equatorial angles	
O(5)—Th—O(1)	70·4 (3)	O(5)—Th—O(7)	118·8 (3)
O(5)—Th—O(8)	69·6 (3)	O(7)—Th—O(9)	120·0 (3)
O(5)—Th—O(13)	69·4 (3)	O(9)—Th—O(5)	121·2 (3)
O(5)—Th—O(16)	68·1 (3)	Mean	120·00
O(7)—Th—O(11)	65·5 (3)		
O(7)—Th—O(13)	68·1 (3)	Sulfate groups	
O(7)—Th—O(16)	67·9 (3)	O(1)—S(1)—O(3)	109·2 (5)
O(7)—Th—O(17)	70·4 (3)	O(1)—S(1)—O(6)	108·6 (5)
O(9)—Th—O(1)	70·5 (3)	O(1)—S(1)—O(8)	108·3 (5)
O(9)—Th—O(8)	66·3 (3)	O(3)—S(1)—O(6)	111·7 (5)
O(9)—Th—O(11)	68·8 (3)	O(3)—S(1)—O(8)	107·8 (5)
O(9)—Th—O(17)	69·1 (3)	O(6)—S(1)—O(8)	111·2 (5)
Mean	68·733	O(12)—S(2)—O(13)	108·9 (5)
		O(12)—S(2)—O(14)	111·6 (5)
Prism edges		O(12)—S(2)—O(15)	109·4 (5)
O(1)—Th—O(8)	87·1 (3)	O(13)—S(2)—O(14)	109·5 (5)
O(11)—Th—O(17)	85·1 (3)	O(13)—S(2)—O(16)	108·3 (5)
O(13)—Th—O(16)	87·3 (3)	O(14)—S(2)—O(16)	109·1 (5)
Mean	86·503	O(4)—S(3)—O(11)	109·8 (5)
		O(4)—S(3)—O(17)	109·9 (5)
Triangle edges		O(4)—S(3)—O(18)	112·3 (5)
O(1)—Th—O(11)	80·1 (3)	O(11)—S(3)—O(17)	108·3 (5)
O(11)—Th—O(16)	80·4 (3)	O(11)—S(3)—O(18)	109·2 (5)
O(16)—Th—O(1)	75·8 (3)	O(17)—S(3)—O(18)	107·3 (5)
O(8)—Th—O(13)	81·3 (3)	Mean	109·46
O(13)—Th—O(17)	74·7 (3)	Mean (bridging)	108·29
O(17)—Th—O(8)	77·3 (3)	Mean (non-bridging)	109·69
Mean	78·257		

* Sulfate oxygen.

& Ivanova (1965) concerning the number of inner-sphere water molecules is thus confirmed. Each sulfate group links a pair of adjacent Th atoms in a chain parallel to [100]. The thorium coordination polyhedron is a trigonal prism with three centred rectangular faces (symmetrically tricapped trigonal prism). The coordinated water molecules occupy the equatorial (capping) positions. This (3/3/3) polyhedron, which approximates to D_{3h} symmetry, is the most frequently observed one in nine coordination. It has also been reported in the structure of $K_4Th(SO_4)_4.2H_2O$ (Molodkin & Arutyunyan, 1965) in which the thorium is coordinated by seven O atoms from six sulfate groups and two O atoms from water molecules.

A least-squares fit of the idealized polyhedron to the observed one was carried out (Akhtar & Smith, 1975) and yielded a shape parameter of $\theta = 46{\cdot}8°$ with an r.m.s. deviation of 2·0°. θ is the angle between the principal symmetry axis and a metal—ligand bond (in this case a non-equatorial one). Fig. 1 represents the Th atom with its coordination polyhedron of nine atoms. Fig. 2 shows the sulfate

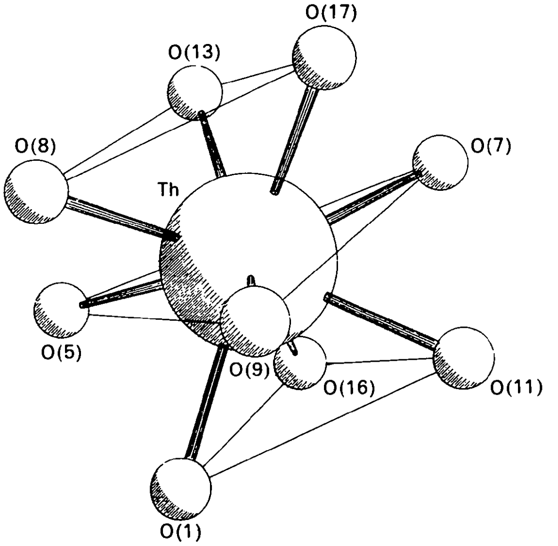

Fig. 1. Environment of the Th atom in $Na_2[Th(SO_4)_3(H_2O)_3].3H_2O$ showing the coordination polyhedron.

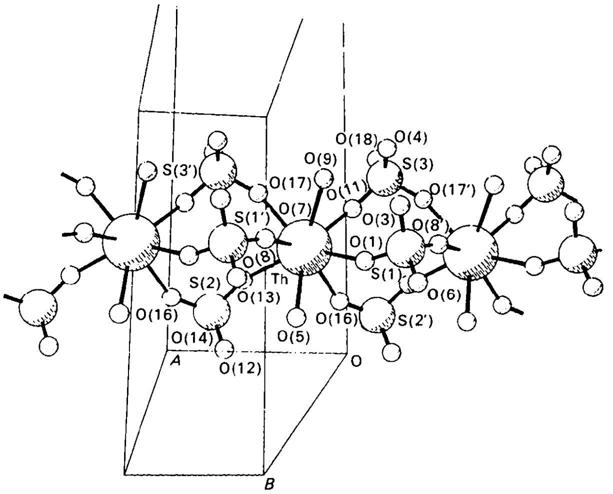

Fig. 2. The chains in $Na_2[Th(SO_4)_3(H_2O)_3].3H_2O$ showing the bridging sulfate groups.

groups around the Th atoms and the structure of the bridged chains parallel to [100].

The Th—O bond distances range from 2·35 (1) to 2·61 (1) Å with a mean of 2·45 (10) Å. The Th—O(water) distances are, on average, longer than the Th—O(sulfate) ones, the mean values being 2·59 (4) and 2·38 (3) Å respectively. This difference may perhaps be correlated with the relatively easy removal of water from the coordination sphere and/or with the fact that the waters occupy the equatorial positions.

The S—O bonds to coordinated oxygen are, as expected, longer than those to terminal oxygen. The mean values are 1·49 (1) and 1·46 (1) Å respectively.

The water molecules [represented by O(2), O(5), O(7), O(9), O(10), and O(15)] form hydrogen bonds among themselves and with the O atoms of the sulfate groups, though, without a neutron diffraction study, these hydrogen bonds cannot be positively located. The hydrogen-bond distances range from 2·56 to 2·88 Å and, as in the structure of Th(SO_4).8H_2O (Habash & Smith, 1983), some of them appear to be either disordered or bifurcated.

The sodium ions are each surrounded by six O atoms in the form of a distorted octahedron. The Na···O distances range from 2·29 to 2·65 Å with a mean of 2·45 Å.

References

Akhtar, M. N. & Smith, A. J. (1975). *Acta Cryst.* **B31**, 1361–1366.
Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180–182.
Cleve, P. T. (1874). *Bull. Soc. Chim. Fr.* [2], **21**, 115–123.
Habash, J. & Smith, A. J. (1983). *Acta Cryst.* **C39**, 413–415.
Huang-Pang, C. & Fedorov, P. I. (1961). *Russ. J. Inorg. Chem.* **6**, 494–497.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dodrecht.)
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Molodkin, A. K. & Arutyunyan, E. G. (1965). *Russ. J. Inorg. Chem.* **10**, 189–195.
Molodkin, A. K., Skotnikova, G. A. & Ivanova, O. M. (1965). *Russ. J. Inorg. Chem.* **10**, 1220–1225.
Roof, R. B. (1959). *Phys. Rev.* **113**, 820–825.
Roof, R. B. (1961). *Acta Cryst.* **14**, 934–940.

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Structure of Hexaaquadichloroyttrium(III) Chloride

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Abstract. $[YCl_2(H_2O)_6]Cl$, $M_r = 303{\cdot}356$, monoclinic, $P2/n$, $a = 7{\cdot}8346\,(25)$, $b = 6{\cdot}4729\,(26)$, $c = 9{\cdot}5817\,(50)$ Å, $\beta = 93{\cdot}768\,(35)^\circ$, $V = 484{\cdot}86$ Å^3, $Z = 2$, $D_x = 2{\cdot}0776$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 68{\cdot}66$ cm^{-1}, $F(000) = 300$, room temperature, final $R = 0{\cdot}0449$ for 940 unique observed reflexions. The yttrium is coordinated, as expected, by two chlorines and six water molecules in a square antiprismatic arrangement.

Introduction. In the course of attempts to prepare other yttrium compounds we obtained good crystals of $[YCl_2(H_2O)_6]Cl$. Although this compound is a member of a well known isomorphous series, its structure parameters have not previously been reported. Dicke & Crossthwaite (1956) have reported a β value of 92° for this compound.

Experimental. Y_2O_3 was heated with excess solid NH_4Cl and the product (mostly YOCl) was dissolved in 2*M* HCl. Crystals were obtained on evaporation.

X-ray reflexion data from a small (approximately 0·2 × 0·2 × 0·4 mm) crystal were collected on a Nicolet *R*3*M* four-circle automatic diffractometer operating in the ω-scan mode and using Mo $K\alpha$ radiation. The unit-cell parameters were determined from a least-squares fit of the setting angles of 25 well centred and well distributed reflexions in the range $4 < \theta < 14^\circ$. Reflexions in the range $3{\cdot}5 < \theta < 55^\circ$ and having h, k, and l in the ranges -10 to 10, 0 to 8, and 0 to 12, respectively, were surveyed. Two check reflexions were monitored every 50 reflexions and showed no evidence of decay. 1359 measurements were made giving 1307 unique reflexions, of which 940 were accepted as observed $[|F_o| > 3\sigma(F)]$. $R_{\rm int}$ was 0·0096. The structure was solved by Patterson and difference Fourier methods and refined by cascade blocked-diagonal least squares [function minimized $w(F_o - F_c)^2$] with weights $w =$

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