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Lanthanum Thallium Bis(sulphate) Dihydrate, TlLa(SO₄)₂.2H₂O

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Abstract. $M_r = 571.44$, monoclinic, $P2_1/n$, $a = 7.216$ (1), $b = 11.853$ (1), $c = 10.486$ (1) Å, $\beta = 92.05$ (1)°, $V = 896.31$ Å³, $Z = 4$, $D_x = 4.233$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 233.5$ cm⁻¹, $F(000) = 1016$, $T = 293$ K, final $R = 0.035$ for 1791 observed reflections. The La and Tl atoms are nine-coordinated by O atoms, La atoms in the form of a distorted monocapped square antiprism [La—O distances 2.404 (7)–2.637 (6) Å] and Tl atoms in the form of an irregular polyhedron [Tl—O distances 2.740 (6)–3.465 (8) Å]. The sulphate groups join La and Tl polyhedra into a three-dimensional framework.

Introduction. The crystal structure of the title compound was determined as a continuation of our research programme concerning double salts of the rare earths of the general formula $M^I\text{Ln}^{III}(\text{SO}_4)_2.x\text{H}_2\text{O}$ (Bukovec & Golič, 1975; Bukovec, Bukovec, Golič & Šiftar, 1977; Bukovec, Golič, Bukovec & Šiftar, 1978; Bukovec, Kaučič & Golič, 1980).

Experimental. Single crystals prepared by isothermal evaporation of aqueous solutions containing equivalent quantities of thallium and lanthanum sulphate.

D_m not determined. Single crystal *ca* $0.06 \times 0.08 \times 0.34$ mm. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters by least-squares refinement of setting angles of 60 centred reflections with $2\theta > 20°$. Intensities of reflections (h: 0→10; k: 0→16; l: −14→14) with $0.03 < \sin\theta/\lambda < 0.70$ Å⁻¹ measured at room temperature. ω–2θ scan mode, scan angle $\Delta\omega = (0.60 + 0.20 \tan\theta)°$. Three reflections ($\overline{3}22$, 314, 114) monitored after every 240 intensities measured; no significant variation in intensity. Of 2583 independent reflections measured, 1791 with $I_o > 3\sigma(I_o)$ considered as observed, 792 unobserved. Empirical absorption corrections applied (transmission factors from 0.163 to

0.301). Structure solved with direct methods, using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) to locate La and Tl atoms. Subsequent Fourier map revealed positions of the other non-H atoms. Refinement by full-matrix least squares on F of positional and anisotropic thermal parameters of all non-H atoms and an isotropic-extinction parameter (final value 0.53×10^{-3}) converged to final $R = 0.035$ and $wR = 0.036$. $(\Delta/\sigma)_{max} = 0.2$. 128 parameters. Weighting function $w = W_F W_S$ determined empirically from $W_F(|F_o| < 60) = (|F_o|/60)^2$, $W_F(|F_o| > 110) = (110/|F_o|)^2$, and $W_F(60 < |F_o| < 110) = 1.0$, and $W_S(\sin\theta < 0.30) = (\sin\theta/0.30)^2$, $W_S(\sin\theta > 0.38) = (0.38/\sin\theta)^2$, and $W_S(0.30 < \sin\theta < 0.38) = 1.0$.

Final difference Fourier map shows max. height of 1.08 e Å⁻³ close to La atom. We could locate two of the four H atoms in the map: 0.44 e Å⁻³ high maximum 1.06 Å from the water atom O(10) and 0.39 e Å⁻³ high maximum 0.76 Å from the water atom O(9). These atoms were not included in the refinement.

All calculations, except direct methods, carried out using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors for non-H atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion-correction factors for non-H atoms from Cromer & Liberman (1970).

Discussion. The final atomic coordinates, bond lengths and bond angles are given in Tables 1 and 2.* The atom-numbering scheme is shown in Fig. 1.

Table 1. *Final atomic coordinates* ($\times 10^5$ *for* Tl, La *and* S; $\times 10^4$ *for* O) *and* U_{eq} ($\text{Å}^2 \times 10^3$) (*Hamilton*, 1959) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}
Tl	23886 (5)	14282 (4)	33725 (4)	30·7 (2)
La	74781 (6)	40371 (4)	30573 (4)	12·9 (2)
S(1)	25119 (25)	44983 (18)	43646 (17)	13·9 (9)
S(2)	75253 (24)	9474 (18)	40775 (16)	13·6 (8)
O(1)	4167 (8)	4131 (7)	3713 (6)	26 (3)
O(2)	860 (8)	4031 (6)	3694 (6)	23 (3)
O(3)	2604 (9)	4083 (6)	5697 (6)	21 (3)
O(4)	2415 (10)	5743 (6)	4438 (6)	26 (3)
O(5)	7915 (11)	2135 (5)	3804 (7)	29 (3)
O(6)	9082 (8)	247 (6)	3655 (6)	21 (3)
O(7)	7279 (10)	829 (6)	5439 (6)	27 (3)
O(8)	5898 (8)	550 (6)	3315 (6)	21 (3)
O(9)	5248 (10)	2789 (6)	1632 (6)	28 (3)
O(10)	9217 (10)	3059 (8)	1260 (8)	39 (4)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

(*a*) SO$_4$ groups

S(1)–O(1)	1·463 (6)	S(2)–O(5)	1·466 (7)
S(1)–O(2)	1·470 (6)	S(2)–O(6)	1·477 (7)
S(1)–O(3)	1·481 (6)	S(2)–O(7)	1·452 (6)
S(1)–O(4)	1·479 (7)	S(2)–O(8)	1·474 (6)

O(1)–S(1)–O(2)	109·0 (4)	O(5)–S(2)–O(6)	109·1 (4)
O(1)–S(1)–O(3)	109·4 (4)	O(5)–S(2)–O(7)	108·4 (4)
O(1)–S(1)–O(4)	111·2 (4)	O(5)–S(2)–O(8)	110·8 (4)
O(2)–S(1)–O(3)	109·5 (4)	O(6)–S(2)–O(7)	111·2 (4)
O(2)–S(1)–O(4)	111·2 (4)	O(6)–S(2)–O(8)	104·9 (4)
O(3)–S(1)–O(4)	106·4 (4)	O(7)–S(2)–O(8)	112·3 (4)

(*b*) La and Tl polyhedra

La–O(1)	2·512 (6)	Tl–O(1)	3·465 (8)
La–O(5)	2·404 (7)	Tl–O(2)	3·297 (7)
La–O(9)	2·615 (7)	Tl–O(8)	2·740 (6)
La–O(10)	2·577 (8)	Tl–O(9)	3·234 (7)
La–O(2^i)	2·507 (6)	Tl–O(5^{iv})	3·381 (8)
La–O(3^{ii})	2·585 (7)	Tl–O(6^{iv})	2·792 (6)
La–O(4^{ii})	2·637 (6)	Tl–O(7^v)	2·957 (7)
La–O(6^{iii})	2·531 (6)	Tl–O(10^{vi})	3·316 (8)
La–O(8^{iii})	2·605 (7)	Tl–O(4^{vii})	3·066 (6)

(*c*) Hydrogen-bond contacts

O(9)···O(3^{viii})	2·982 (10) Å	O(10)···O(3^{viii})	2·846 (11) Å
O(9)···O(7^{ix})	2·940 (10)	O(10)···O(7^{viii})	2·738 (11)

Symmetry code: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $-1 + x, y, z$; (v) $1 - x, -y, 1 - z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ix) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

The dimensions of the sulphate groups are consistent with the values observed in other sulphate structures. There are only small variations in the S–O bond lengths. The average S–O distances for the two crystallographically nonequivalent SO$_4$ groups are 1·473 and 1·467 Å; the average O–S–O angle is 109·5° for both groups. Smaller angles O(3)–S(1)–O(4) and O(6)–S(2)–O(8) result from the bonding of the O atoms to the same La atom. Each S(1) sulphate group is bonded to three different La atoms, monodentate through O(1) and O(2) and bidentate through O(3) and O(4), while each S(2) sulphate group is bonded to two different La atoms, monodentate through O(5) and

bidentate through O(6) and O(8); O(7) is not coordinated to the La atoms.

The La atom is coordinated to nine O atoms, seven of these are sulphate O atoms and two are water O atoms. In the coordination sphere the nine La–O distances vary between 2·404 (7) and 2·637 (6) Å and the coordination polyhedron can be described as a distorted monocapped square antiprism (Fig. 2).

The Tl atom is also nine-coordinated with O atoms in the form of an irregular polyhedron. Tl–O distances are in the range 2·740 (6) to 3·465 (8) Å. The sulphate groups join La and Tl polyhedra into a three-dimensional framework (Fig. 1).

The two water molecules are coordinated to La and Tl atoms and they also form weak hydrogen bonds to O(3) and O(7) of the sulphate groups (Table 2). Around each of the water atoms O(9) and O(10) there are La, Tl, O(3) and O(7) atoms in the form of a distorted tetrahedron.
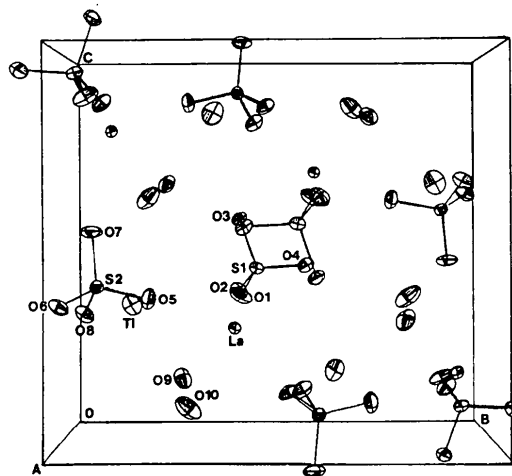
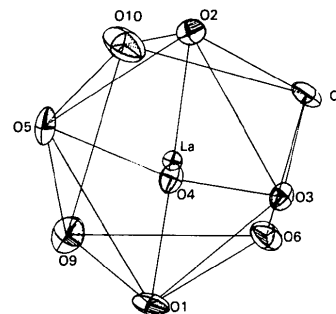Fig. 1. A view of the unit cell with the atom-numbering scheme.

Fig. 2. The coordination polyhedron of La.

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Location and Anisotropic Refinement of Hydrogen Atoms in Disodium Dihydrogen-silicate Tetrahydrate, Na₂H₂SiO₄.4H₂O, by Neutron Diffraction; Hydrogen Bonding at 173 K

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Abstract. $M_r = 212.14$, triclinic, $P\bar{1}$, $a = 7.916$ (2), $b = 9.558$ (2), $c = 6.643$ (1) Å, $\alpha = 70.13$ (2), $\beta = 104.83$ (2), $\gamma = 122.56$ (2)°, $V = 396.71$ Å³, $Z = 2$, $D_m = 1.74$, $D_x = 1.776$ Mg m⁻³, $\lambda = 0.7017$ Å, $\mu(n) = 0.204$ mm⁻¹, $F(000) = 4.09$, $T = 173$ K, $R = 0.028$ for 1498 independent reflections. Anisotropic structure refinement including absorption and secondary-extinction correction. The crystal structure of Na₂H₂SiO₄.4H₂O consists of linear chains of hydrogen-bonded [H₂SiO₄]²⁻ tetrahedra running along [110] and columns of edge-linked Na—O polyhedra running parallel to the c axis. The [H₂SiO₄]²⁻ tetrahedron shows the smallest HO—Si—OH angle observed in the series of Na₂H₂SiO₄.nH₂O ($n = 8, 7, 5, 4$) hydrates which is due to the arrangement of the hydroxyl H atoms. All Na atoms have coordination number (CN) 5 with short Na—O bonds [mean Na—O = 2.37 (2) Å]. CN = 4 with tetrahedral geometry is observed for the coordination polyhedra of the O atoms of all hydrate water molecules.

Introduction. Two series of crystalline hydrate phases exist in the alkali-rich section of the system Na₂O–SiO₂–H₂O: Na₃HSiO₄.nH₂O ($n = 5,2,1,0$) with an Na₂O:SiO₂ ratio of 3:2; and Na₂H₂SiO₄.nH₂O ($n = 8, 7, 5, 4$) with an Na₂O:SiO₂ ratio of 1:1. Members of the first series are built up of isolated [HSiO₄]³⁻ anions, as shown by the X-ray single-crystal structure analyses for Na₃HSiO₄.5H₂O (Smolin, Shepelev & Butikova, 1973)

and Na₃HSiO₄.2H₂O (Schmid, Huttner & Felsche, 1979; Schmid, Szolnay, Felsche & Huttner, 1981). The members of the second series are built up of isolated [H₂SiO₄]²⁻ anions as has been shown by X-ray and neutron single-crystal structure analyses: Na₂H₂SiO₄.-8H₂O [Jamieson & Dent-Glasser, 1966a,b (X-ray); Schmid, Felsche & McIntyre, 1984 (neutron)], Na₂H₂-SiO₄.7H₂O [Dent-Glasser & Jamieson, 1976 (X-ray)], Na₂H₂SiO₄.5H₂O [Jamieson & Dent-Glasser, 1967 (X-ray); Williams & Dent-Glasser, 1971 (neutron)] and Na₂H₂SiO₄.4H₂O [Jost & Hilmer, 1966 (X-ray)].

Na₂H₂SiO₄.4H₂O shows the most pronounced thermal stability within the 1:1 series of sodium silicate hydrates which all melt congruently at temperatures between 313 and 343 K (Felsche, Ketterer & Schmid, 1984). A distinct tendency to form supercooled melts has been observed for all four hydrate phases existing within this series. Glass-points at temperatures between 223 and 273 K have been observed by means of differential scanning calorimetry (Felsche, Ketterer & Schmid, 1984). In order to provide a better understanding of these thermal properties which are unique in oxosalt–hydrate crystal chemistry we will elaborate correlations with hydrogen bonding in the structures of all four hydrate phases based on neutron diffraction.

In this paper we will report on a single-crystal neutron diffraction study of Na₂H₂SiO₄.4H₂O at 173 K. The results of a 296 K experiment will be published separately.