

## The structure of strontium dithionate tetrahydrate

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### Auszug

Die Kristallstruktur des Strontiumdithionat-Tetrahydrats wurde mittels Patterson- und Fourier-Methoden und dem Minimumrest-Verfahren an einem Zwillingskristall bestimmt und aus den Reflexen unter  $2\theta \leq 40^\circ$  bis zu  $R = 0,119$  verfeinert. Die Struktur von  $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$  hat die Raumgruppe  $P6_2$ , die Gitterkonstanten  $a = 6,32 \pm 0,02 \text{ \AA}$ ,  $c = 19,29 \pm 0,03 \text{ \AA}$  und  $Z = 3$ . Die Atomabstände sind: S—S =  $2,15 \pm 0,03 \text{ \AA}$  und, im Mittel, S—O =  $1,41 \text{ \AA}$ . Die Sr-Atome sind von acht O-Atomen im mittleren Abstand von  $2,58 \pm 0,04 \text{ \AA}$  umgeben; an dieser Umgebung sind nur jeweils zwei der drei Atome der  $\text{SO}_3$ -Gruppen beteiligt. Es sind keine Wasserstoffbindungen vorhanden.

### Abstract

The crystal structure of strontium dithionate tetrahydrate, space group  $P6_2$ ,  $a = 6.32 \pm 0.02 \text{ \AA}$ ,  $c = 19.29 \pm 0.03 \text{ \AA}$ ,  $Z = 3$ , has been determined by Patterson, Fourier, and minimum residual refinement methods. The intensity measurements were recorded on a Picker automatic four-circle x-ray diffractometer using  $\text{MoK}\alpha$  radiation, and a twinned crystal. The S—S bond length is  $2.15 \pm 0.03 \text{ \AA}$  and the mean S—O bond length is  $1.41 \text{ \AA}$ . Each strontium ion is bound to eight oxygen atoms at a mean distance of  $2.58 \pm 0.04 \text{ \AA}$ . Only two of the three independent oxygen atoms of the dithionate ion are coordinated. There appears to be no hydrogen bonding. The value of the residual for all reflections having  $2\theta \leq 40^\circ$ ,  $R = 0.119$ .

### Introduction

$\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$  was assigned to the class 32 by SLIKER (1964) as a preliminary to linear electro-optic studies on certain non-centrosymmetric crystals. [This assignment was based on the morphology of the crystals, which have trigonal symmetry, and are hemimorphic and optically active (SLIKER private communication)].

A previous crystallographic investigation by FERRARI, CAVALCA, and NARDELLI (1946) on calcium, strontium and lead dithionates suggested possible space groups  $P6/mmm$ ,  $P6_122$ ,  $P6_222$ , and their enantiomorphs and  $P6_322$ ,  $P6mm$ ,  $P\bar{6}m2$  and  $P\bar{6}2m$  based on the Laue symmetry and the observed reflection condition:  $000l$  only when  $l = 6n$ . Preliminary photographs showed reflections  $000l$  when  $l = 3n$  to be present, though extremely weak. The overall reflection condition then becomes  $000l$  only when  $l = 3n$ . This, together with the Laue symmetry  $6/mmm$ , points to the space groups  $P6_222$  and its enantiomorph  $P6_422$  as the most likely. Unfortunately these space groups can be ruled out because the only threefold positions, required to accommodate the three  $S_2O_6$  ions, have symmetry  $222$ , which is not a possible symmetry of the dithionate ion. The morphological evidence for the threefold axis is not especially strong; the existence of a  $6_2$  or  $6_4$  axis always leads to an apparent threefold symmetry in the external form (DONNAY and HARKER, 1937).

#### Preliminary measurements

The unit-cell dimensions were determined from diffractometer measurements as:

$$a = 6.32 \pm 0.02 \text{ \AA}, \quad c = 19.29 \pm 0.03 \text{ \AA}.$$

The density is  $2.373 \text{ g} \cdot \text{cm}^{-3}$  (*Handbook of Chemistry and Physics*) giving a unit cell containing three molecules of  $SrS_2O_6 \cdot 4H_2O$ .

An approximately spherical crystal was used for the measurement of the intensity data on a Picker four-circle diffractometer using  $2\theta$  scan. Equivalent reflections  $hki\bar{l}$ ,  $ihkl$ , and  $kihl$ , were measured independently and their observed intensities averaged. The Lorentz and polarization factors were applied, but no correction was made for absorption effects. During the course of prolonged exposure to x-rays the crystal become strongly purple in colour; no change in x-ray diffracted intensity was observed.

The Laue symmetry,  $6/mmm$ , was confirmed in the intensity relationship:

$$I(hk\bar{i}l) = I(kh\bar{i}l) = I(hk\bar{i}\bar{l}).$$

Since the space group  $P6_222$  cannot accommodate the dithionate ions, it was assumed that the space group was  $P6_2$  which can accommodate

the unit-cell contents. The Laue symmetry would be  $6/m$ ; the extra symmetry has been assumed to arise from twinning.

507 unique observations with  $2\theta \leq 40^\circ$  were recorded.

### Structure determination

The effect of twinning is to give rise to additional mirror symmetry in the reciprocal lattice and Patterson function. Recognition of this, was sufficient to permit the interpretation of the Patterson function. It was not necessary to separate the contributions of the two parts of the crystal, to the observed intensity, prior to the refinement stage.

Symmetry requirements of the space group  $P6_2$  demand that the strontium ion lies on either the  $6_2$  axis or the twofold axis. The  $(hki0)$  and  $(0kil)$  Patterson projections were calculated and showed the former possibility to be the most likely. The dithionate ion was located lying on the twofold axis. The origin was placed at the strontium position. A three-dimensional Fourier synthesis of electron density was calculated using the phases of the reflections calculated from the positions of the atoms located in the Patterson synthesis and amplitudes  $F_{o,1} = \sqrt{\{F_{c,1}^2/(F_{c,1}^2 + F_{c,2}^2)\}} I_0$  where  $F_{c,1}$  and  $F_{c,2}$  are the contributions from the two halves of the twin. This synthesis enabled the two unique water molecules to be located.

### Refinement of the structure

Refinement of the positional and isotropic thermal parameters of the structure was carried out using the minimum residual method of BHUIYA and STANLEY (1963). The minimizing of some function of the difference between the observed and calculated intensities, with respect to the structural parameters, is complicated by the effect of twinning. The contributions of the two parts of the crystal to the calculated intensity must be combined prior to any such calculations. In the case of  $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ , structure factors were calculated for both halves of the twin and a composite structure factor was calculated

$${}_cF_c = [rI_1 + (1 - r) I_2]^{1/2}.$$

Initially  $r$  was set equal to 0.5.  ${}_cF_c$  was then compared with the square root of the observed corrected intensity  $I_0$ .

The function minimized was:

$$R = \frac{\sum ||I_0|^{1/2} - |cF_c||}{\sum |I_0|^{1/2}} .$$

Refinement was continued until the predicted shifts of all coordinates were less than 0.005 Å, at which point refinement was considered complete. The value of the parameter  $r$ , which controls the contribution from each part of the twin, was then refined using the minimum residual method in which  $R$  was calculated for a series of values around the value  $r = 0.50$ . The best value of  $r$  was 0.46 implying that (within experimental error) the two parts of the twin contributed equally to the reflections. The final value of  $R$  for all reflections up to the limit  $2\theta \leq 40^\circ$  was 0.119. The scattering curves for all atoms were calculated by use of the constants given by FORSYTH and WELLS (1959).

Table 1. *Final fractional coordinates and Debye temperature factors*

Atom	Number	$x$	$y$	$z$	$B$
Sr	3	0.000	0.000	0.000	0.6 Å <sup>2</sup>
S	6	0.692	0.065	0.162	1.6
O(1)	6	0.747	0.004	0.097	3.4
O(2)	6	0.752	0.985	0.223	5.5
O(3)	6	0.808	0.319	0.166	3.5
O(4)	6	0.188	0.448	0.038	4.4
O(5)	6	0.449	0.199	0.952	2.6

An estimated error for a coordinate and temperature factor of each atom type was calculated from the statistics of the refinement, using the equation of CRUICKSHANK (1960). The final values of the coordinates and isotropic temperature factors are given in Table 1. The observed and calculated structure factors are given in Table 2.

### Discussion of the structure

A sketch of the structure is shown in Fig. 1 and the projection on (001) in Fig. 2. The dimensions of the dithionate ion are given in Table 3 and are compared with other determinations; they are in good agreement with the published values for other dithionates.

Coordination of the dithionate ion to the strontium ion, takes place via two of the three independent oxygen atoms. The third



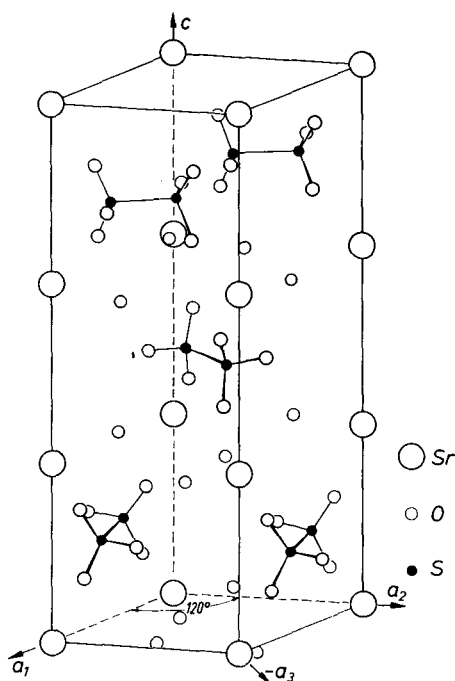


Fig. 1. Sketch of the structure of the unit cell of  $\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

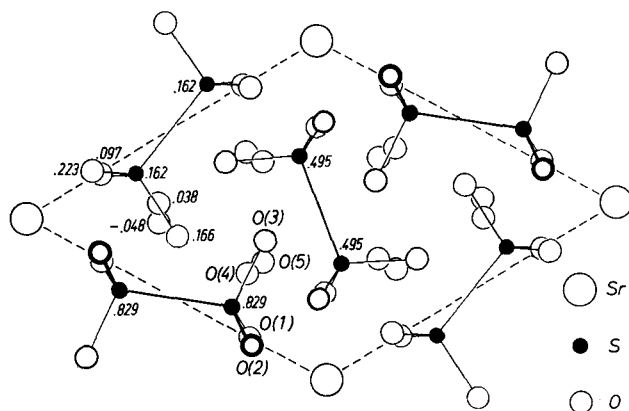


Fig. 2. Projection of the unit-cell content on (001)

oxygen atom, O(3), is uncoordinated, and lies at  $z = \frac{1}{6}$ , equidistant from the two nearest strontium ions at  $z = 0$  and  $z = \frac{1}{3}$ . This Sr—O(3) distance is  $4.28 \pm 0.03 \text{ \AA}$ .

Table 3a. *Dimensions of the dithionate ion*

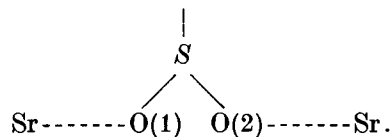
Bond	Length	Bonds	Angle
S—S	2.15 — 0.02 Å	S—S—O(1)	107 ± 1°
S—O(1)	2.41 ± 0.04	S—S—O(2)	109 ± 1
S—O(2)	2.41 ± 0.04	S—S—O(3)	107 ± 1
S—O(3)	2.40 ± 0.04	O(1)—S—O(2)	120 ± 1
		O(1)—S—O(3)	108 ± 1
		O(2)—S—O(3)	107 ± 1

Table 3b. *Comparison with other determinations*

Salt	S—S	S—O
(1) Rb <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	2.08	1.50
(2) NaK <sub>5</sub> Cl <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	2.08	1.48
(3) NaK <sub>2</sub> ClS <sub>2</sub> O <sub>6</sub>	2.08	1.48
(4) BaS <sub>2</sub> O <sub>6</sub> · 2H <sub>2</sub> O	2.17	1.47
(5) Na <sub>2</sub> S <sub>2</sub> O <sub>6</sub> · 2H <sub>2</sub> O	2.16	1.45
(6) K <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	2.15, 2.14	1.43, 1.42
(7) (NH <sub>4</sub> ) <sub>3</sub> ClS <sub>2</sub> O <sub>6</sub>	2.13, 2.16	1.41, 1.44
(8) NiS <sub>2</sub> O <sub>6</sub> · 6H <sub>2</sub> O	2.12	1.46
(9) SrS <sub>2</sub> O <sub>6</sub> · 4H <sub>2</sub> O	2.15	1.41

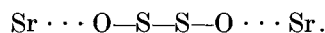
- (1) BARNES and WENDLING (1938).  
 (2) (3) STANLEY (1953).  
 (4) GARCIA-BLANCO *et al.* (1953).  
 (5) MARTINEZ *et al.* (1956).  
 (6) STANLEY (1956).  
 (7) GUTTORMSON and STANLEY (1969).  
 (8) CHAN and STANLEY (1970).  
 (9) Present work.

The dithionate ion performs two separate bridging functions in the structure. Along the *z* direction, the strontium ions are bridged by one end of the dithionate ion:



The O(1)—S—O(2) angle is 120°, a large value probably resulting from the coordination of atoms O(1) and O(2) to the metal ion,

In the *xy* plane, the bridging mechanism involves both sulfur atoms:



The mean value of the S—S—O angles is  $108^\circ$ , in good agreement with published values, e.g.  $105^\circ$  in  $\text{K}_2\text{S}_2\text{O}_6$  (STANLEY, 1956). The mean S—O bond length is  $1.41 \pm 0.04 \text{ \AA}$  which is shorter than that usually found in the dithionate ion.

Table 4. *Coordination of the strontium ion*

Bond	Length
Sr—O(1)	$2.48 \pm 0.03 \text{ \AA}$
Sr—O(2)	$2.62 \pm 0.03$
Sr—O(4)	$2.58 \pm 0.03$
Sr—O(5)	$2.64 \pm 0.03$
[Sr—O(3)]	$4.28 \pm 0.03]$

There is no evidence of any significant hydrogen bonding. The closest approach of any oxygen atoms to those of the water molecules is  $3.03 \text{ \AA}$ , a value greater than twice the van der Waals radius of oxygen ( $1.40 \text{ \AA}$ ).

The Sr—O bond distances are given in Table 4. Each strontium ion is associated with eight oxygen atoms of which four are crystallographically unique. Both water molecules are coordinated together with two of the oxygen atoms from the dithionate ion. The mean Sr—O bond length is  $2.56 \text{ \AA}$ .

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