

## A Very Short, and Asymmetrical, Hydrogen Bond in the Structure of $\text{Na}_3\text{H}(\text{SO}_4)_2$ and S—OH vs O—H...O Correlation

BY MICHELE CATTI, GIOVANNI FERRARIS AND GABRIELLA IVALDI

*Istituto di Mineralogia, Cristallografia e Geochimica 'G. Spezia' dell'Università di Torino, via San Massimo 24, 10123 Torino, Italy*

(Received 7 June 1978; accepted 16 November 1978)

### Abstract

$\text{Na}_3\text{H}(\text{SO}_4)_2$  crystallizes in space group  $P2_1/c$  with  $a = 8.648$  (1),  $b = 9.648$  (1),  $c = 9.143$  (1) Å,  $\beta = 108.77$  (1)°,  $Z = 4$ . The structure was anisotropically (except the H atom) refined to  $R = 0.034$  for 1403 counter reflexions. An indexed X-ray powder spectrum is given. The structure is dominated by a framework of Na coordination polyhedra built up by the intersection of two non-coplanar systems of chains and, to some extent, condensed into (010) layers. The S tetrahedra are approximately close packed in (010) layers and form  $(\text{SO}_4\text{H}.\text{SO}_4)^{3-}$  dimers *via* a very short asymmetrical hydrogen bond with  $\text{O}\cdots\text{O} = 2.434$  (4),  $\text{O—H} = 1.03$  (6) Å and  $\angle\text{O—H}\cdots\text{O} = 177$  (4)°. Through the analysis of published data, a linear correlation between the length of S—OH and that of the corresponding  $\text{O}\cdots\text{O}$  hydrogen bond is found. Empirical correlations concerning the geometry and the bond valence in the S tetrahedra are applied and discussed.

### Introduction

Trisodium hydrogen disulphate was accidentally obtained at about 353 K during the preparation of  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  (matteuccite) (Catti, Ferraris & Franchini-Angela, 1975), and was later prepared according to Faust & Esselmann (1926). Its structural study seemed worthwhile as a part of the research on hydrogen bonding (Catti, Ferraris & Ivaldi, 1978), in order to extend our investigation to simple inorganic salts containing oxyanions with different acidity. In fact, by analogy with the acid salts of carboxylic acids studied by J. C. Speakman and co-workers (McGregor, Speakman & Lehmann, 1977), this type of salt could be particularly inclined to display unusual behaviour of the acidic H atoms, such as involvement in very short or disordered bonds.

Among the small group of such inorganic compounds hitherto studied, a series of six ferroelectric alkali trihydrogenselenites (Chomnilpan, Tellgren & Liminga, 1978) and the ferroelectric  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$

(Suzuki & Makita, 1978) show disordered and/or apparently symmetrical hydrogen bonds.  $\text{KH}_2(\text{PO}_4)_2$  (Philippot, Richard, Roudault & Maurin, 1972) was one of the first examples found to show quasi-symmetrical hydrogen bonds (Catti & Ferraris, 1974a), and the  $\text{H}(\text{NO}_3)_2^-$  anion was found to be involved in hydrogen bonds of quite different lengths (Williams, Dowling, Gunde, Hadži & Orel, 1976). Salts of the same type, but with a more complex composition, appear without special features, *e.g.*  $(\text{NH}_3)_5\text{CoO}_2 \cdot \text{Co}(\text{NH}_3)_5\text{SO}_4(\text{HSO}_4)_3$  (Schaefer & Marsh, 1966),  $[\text{Ag}(\text{C}_6\text{H}_{16}\text{N}_{10})]\text{SO}_4\text{HSO}_4 \cdot \text{H}_2\text{O}$  (Coghi & Pelizzi, 1975),  $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2$  tetra- (Ferraris & Abbona, 1972) and nona-hydrated (Catti & Ferraris, 1974b).

### Experimental

$\text{Na}_3\text{H}(\text{SO}_4)_2$  was identified by comparison with the un-indexed X-ray powder spectrum reported on card 2-0294 of the ASTM X-ray Powder Data File, 1950. Weissenberg photographs and single-crystal diffraction showed a monoclinic  $P2_1/c$  symmetry with the least-squares-refined cell parameters given in the *Abstract* ( $\lambda = 0.71069$  Å). A powder spectrum obtained from a Guinier camera was indexed with the reported cell parameters, taking into account the single-crystal intensities (Table 1). Well-developed crystals are {001} prismatic and the following forms were detected: {100}, {110}, {010}, {011} and  $\{\bar{1}11\}$ ; ( $\bar{1}01$ ) swallow-tail twins were found.

Other data:  $M_r = 267.101$ ,  $V = 722.3$  Å<sup>3</sup>,  $D_m = 2.423$  (Pascal, 1966),  $D_c = 2.410$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 520$ ,  $\mu(\text{Mo } K\alpha) = 0.92$  mm<sup>-1</sup>.

Intensities were collected on a Philips PW 1100 automatic four-circle diffractometer from a [001] needle crystal (0.54 × 0.14 × 0.10 mm). The measurement conditions were: Mo  $K\alpha$  radiation; graphite monochromator,  $\omega \leq 28^\circ$ ,  $\omega/2\theta$  scan,  $\Delta\omega = 2^\circ$ , scanning speed 0.035° s<sup>-1</sup>, background time 5 s on both sides of each peak, attenuating filter inserted for intensities higher than 60 000 counts s<sup>-1</sup>, three

Table 1. Observed and calculated *d* spacings, indices and intensities (on an arbitrary scale) of the reflexions of the powder spectrum of Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>

Guinier camera, 4 mm = 1°  $\theta$ ; Cu K $\alpha$  radiation.

<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i> <sub>obs</sub>
8.15	8.19	1 0 0	50	1.963	1.965	1 3 3	10
6.44	6.44	0 1 1	45	1.947	1.950	2 4 1	5
6.23	6.24	1 1 0	40	1.895	1.899	2 2 3	35
4.81	4.82	0 2 0	60	1.864	1.861	1 3 4	55
4.46	4.47	1 0 2	20	1.855	1.851	0 4 3	10
4.32	4.33	0 0 2	5	1.850	1.850	3 4 1	10
4.22	4.21	0 2 1	45	1.847	1.848	4 2 3	10
4.15	4.16	1 2 0	5	1.831	1.834	2 3 4	5
4.09	4.09	2 0 0	5	1.829	1.829	4 1 1	5
4.01	4.01	1 2 1	95	1.809	1.811	3 4 2	10
3.95	3.95	0 1 2	100	1.802	1.805	4 0 4	45
3.77	3.77	2 1 0	95	1.785	1.787	2 1 5	40
3.61	3.61	2 0 2	80	1.774	1.774	4 1 4	5
3.52	3.53	1 2 1	25	1.761	1.762	0 5 2	30
3.401	3.401	1 0 2	40	1.741	1.745	2 5 0	5
3.266	3.277	1 2 2	25	1.741	1.738	2 3 3	5
3.203	3.208	1 1 2	75	1.734	1.737	4 2 1	25
3.110	3.121	2 2 0	10	1.723	1.727	5 0 2	20
3.010	3.015	0 3 1	45	1.723	1.726	3 3 4	20
3.000	2.993	1 3 0	5	1.697	1.700	5 1 2	40
2.903	2.905	1 1 3	95	1.697	1.698	3 1 3	40
2.891	2.890	2 2 2	100	1.676	1.678	1 5 2	10
2.769	2.780	1 2 2	5	1.649	1.649	5 1 3	5
2.763	2.765	0 1 3	75	1.635	1.638	5 0 0	5
2.730	2.732	1 3 1	100	1.627	1.630	0 2 5	40
2.635	2.636	3 1 2	40	1.603	1.608	0 6 0	40
2.627	2.626	3 1 0	10	1.591	1.593	2 5 3	5
2.605	2.610	1 3 2	5	1.568	1.569	2 4 3	30
2.583	2.588	2 0 2	70	1.557	1.560	3 4 4	25
2.571	2.576	1 2 3	10	1.549	1.551	5 1 4	20
2.434	2.438	2 2 3	15	1.549	1.551	5 2 0	20
2.411	2.412	0 4 0	45	1.524	1.528	3 3 5	25
2.380	2.383	3 2 2	30	1.520	1.523	2 0 6	25
2.318	2.314	1 4 0	40	1.501	1.503	2 3 4	30
2.301	2.307	2 3 1	10	1.483	1.485	5 3 3	15
2.284	2.288	1 4 1	15	1.469	1.471	3 1 6	10
2.204	2.282	1 0 4	15	1.469	1.469	2 6 2	10
2.204	2.207	1 2 3	50	1.449	1.452	5 2 1	20
2.186	2.186	1 4 1	5	1.449	1.451	1 4 5	20
2.171	2.176	2 1 4	45	1.438			10
2.161	2.164	0 0 4	20	1.429			5
2.151	2.154	3 2 3	20	1.424			5
2.144	2.143	3 2 1	20	1.402			5
2.117	2.112	0 1 4	10	1.394			5
2.097	2.102	4 1 1	50	1.374			5
2.097	2.100	2 4 1	50	1.363			15
2.077	2.078	2 4 0	15	1.353			5
2.058	2.063	1 2 4	30	1.348			15
2.044	2.046	3 0 4	20	1.333			15
2.004	2.006	2 4 2	50	1.310			10
1.972	1.975	0 2 4	60	1.298			5

reference reflexions. After removal of 341 reflexions with  $|F_o| \leq 3\sigma(|F_o|)$  1403 independent observations were left.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33981 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## Solution and refinement of the structure

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) revealed the two independent S atoms, four O and two Na atoms, which were then used to phase a difference map which showed all the non-hydrogen atoms. After a least-squares anisotropic refinement, the H atom was found on a difference map and then refined isotropically. At the last stage of the refinement the following weighting scheme was used,  $w = (1.096 - 0.0128|F_o| + 0.0004|F_o|^2)^{-1}$ , which produced 0.09 and 1.00 minimum and maximum weights, respectively, and satisfactorily constant values of  $\Delta^2$  for groups of reflexions vs  $|F_o|$  and  $\sin \theta$ . An analysis of the function  $I_c/I_o = k(1 + gI_c)$  for secondary extinction showed no effects except for the weakest reflexions which showed  $|F_o| < |F_c|$  systematically, as already observed for other structures (Catti, Ferraris & Franchini-Angela, 1977). To the factors there listed as possible sources of this effect, one could add the omission of corrections for anomalous scattering and TDS and, in general, for any physical effect which is likely to have a higher per cent influence on the weak reflexions.

The refinement converged to  $R = 0.034$  with the atomic parameters listed in Table 2. Scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1962) and the XRAY system (Stewart, Kundell & Baldwin, 1970) were used.

## Discussion

### Description of the structure

The structure is dominated by a framework of Na coordination polyhedra (Table 3) built up by the intersection of two non-coplanar systems of chains. A system is confined within (010) layers at  $y = 0$  and  $\frac{1}{2}$

Table 2. Fractional atomic coordinates with significant figures of the e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0.13929 (8)	0.30906 (7)	0.85771 (7)
S(2)	0.63436 (8)	0.31874 (7)	0.40524 (8)
Na(1)	0	0	0
Na(2)	$\frac{1}{2}$	0	$\frac{1}{2}$
Na(3)	0.7453 (2)	-0.0060 (1)	0.2774 (1)
Na(4)	0.3869 (1)	0.1559 (1)	0.1279 (1)
O(1)	0.1547 (3)	0.1578 (2)	0.8752 (2)
O(2)	0.2554 (3)	0.3765 (2)	0.9916 (2)
O(3)	-0.0324 (3)	0.3496 (2)	0.8547 (3)
O(4)	0.1596 (3)	0.3568 (3)	0.7146 (3)
O(5)	0.6162 (3)	0.3648 (3)	0.5503 (3)
O(6)	0.8095 (3)	0.3375 (2)	0.4152 (3)
O(7)	0.5926 (3)	0.1718 (2)	0.3752 (2)
O(8)	0.5334 (3)	0.4044 (2)	0.2778 (3)
H(1)	-0.102 (7)	0.270 (6)	0.877 (6)

and consists of equivalent chains formed by blocks of three octahedra  $\text{Na}(3)\text{--Na}(2)\text{--Na}(3,2)^*$  which are intraconnected through the face  $\text{O}(2,4)^{\text{i}}\text{--O}(8,4)\text{--O}(7,2)^{\text{vi}}$  and its centrosymmetric  $\text{O}(2,3)^{\text{vii}}\text{--O}(8,3)^{\text{iv}}\text{--O}(7)$ ; the blocks are bridged by the  $\text{Na}(1)$  octahedron *via* the  $\text{O}(1)^{\text{i}}$  and  $\text{O}(1,2)^{\text{ii}}$  vertices (Fig. 1). The second system of chains zig-zags along  $[010]$  and consists of  $\text{Na}(4)$  polyhedra interlinked through the  $\text{O}(8)$  and  $\text{O}(8,3)^{\text{iv}}$  vertices. This type of chain is tied to the previous one both along  $[010]$ , *via*  $\text{O}(8)$  which belongs to four Na polyhedra, and, within  $(010)$ , by sharing (i) the face  $\text{O}(5,4)^{\text{i}}\text{--O}(8,3)^{\text{iv}}\text{--O}(7)$  with  $\text{Na}(3)$  and the edge  $\text{O}(7)\text{--O}(8,3)^{\text{iv}}$  with  $\text{Na}(2)$  of one chain; (ii) the

\* A single figure in parentheses denotes an atom of the asymmetric unit; a second figure, ranging from 2 to 4, is included for atoms in the positions  $\bar{x}, \bar{y}, \bar{z}$  and  $\pm(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$ . Roman numerals represent the following translations: (i)  $-c$ ; (ii)  $c$ ; (iii)  $-b$ ; (iv)  $a - b$ ; (v)  $-a - c$ ; (vi)  $a + c$ ; (vii)  $a - b + c$ ; (viii)  $a - c$ ; (ix)  $-a$ .

Table 3. *Interatomic distances* (Å) *in the Na polyhedra; e.s.d.'s are 0.002 Å*

$\text{Na}(1)\text{--O}(1)^{\text{i}}$	2.528	$\text{Na}(2)\text{--O}(2,3)^{\text{vii}}$	2.408
$\text{Na}(1)\text{--O}(1,2)^{\text{ii}}$		$\text{Na}(2)\text{--O}(2,4)^{\text{i}}$	
$\text{Na}(1)\text{--O}(4,3)^{\text{iii}}$	2.433	$\text{Na}(2)\text{--O}(7)$	2.297
$\text{Na}(1)\text{--O}(4,4)^{\text{j}}$		$\text{Na}(2)\text{--O}(7,2)^{\text{vi}}$	
$\text{Na}(1)\text{--O}(6,3)^{\text{iv}}$	2.225	$\text{Na}(2)\text{--O}(8,3)^{\text{iv}}$	2.629
$\text{Na}(1)\text{--O}(6,4)^{\text{v}}$		$\text{Na}(2)\text{--O}(8,4)$	
Average	2.395	Average	2.445
$\text{Na}(3)\text{--O}(1,2)^{\text{vi}}$	2.370	$\text{Na}(4)\text{--O}(1)^{\text{j}}$	2.527
$\text{Na}(3)\text{--O}(2,3)^{\text{vii}}$	2.399	$\text{Na}(4)\text{--O}(2)^{\text{i}}$	2.542
$\text{Na}(3)\text{--O}(3,4)^{\text{viii}}$	2.366	$\text{Na}(4)\text{--O}(4,4)^{\text{j}}$	2.348
$\text{Na}(3)\text{--O}(5,4)^{\text{i}}$	2.433	$\text{Na}(4)\text{--O}(5,4)^{\text{j}}$	2.319
$\text{Na}(3)\text{--O}(7)$	2.499	$\text{Na}(4)\text{--O}(7)$	2.391
$\text{Na}(3)\text{--O}(8,3)^{\text{iv}}$	2.455	$\text{Na}(4)\text{--O}(8)$	2.849
Average	2.420	$\text{Na}(4)\text{--O}(8,3)^{\text{iv}}$	2.593
		Average	2.510

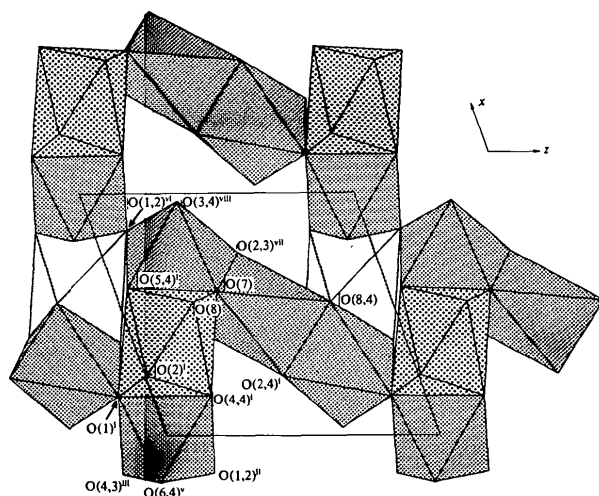


Fig. 1. *Orthogonal projection onto the plane (010) of the Na coordination polyhedra in the structure of  $\text{Na}_3\text{H}(\text{SO}_4)_2$ . The  $\text{Na}(4)$  polyhedra lie above (large dots) and below (small dots) the layer at  $y = 0$  occupied by the  $\text{Na}(1)$ ,  $\text{Na}(2)$  and  $\text{Na}(3)$  polyhedra which are filled with dots of medium size.*

edge  $\text{O}(1)^{\text{i}}\text{--O}(4,4)$  with  $\text{Na}(1)$  and the corner  $\text{O}(1)^{\text{i}}$  with  $\text{Na}(3)$  of another chain.

The two independent S tetrahedra (Table 4) are arranged within cavities in the Na framework and form close packed but corrugated  $(010)$  layers at about  $y = \frac{1}{4}$  and  $\frac{3}{4}$  (Fig. 2). The tetrahedra are connected to the Na polyhedra by sharing all their corners with them and the edges  $\text{O}(1)\text{--O}(2)$  and  $\text{O}(7)\text{--O}(8)$  with the  $\text{Na}(4)$  polyhedra.

#### Hydrogen bonding

The S tetrahedra are grouped in  $(\text{SO}_4\text{H}\cdot\text{SO}_4)^{3-}$  dimers *via* the very short hydrogen bond  $\text{O}(3)\text{--H}\cdots\text{O}(6,4)^{\text{ix}} = 2.434(4)$  Å with  $\text{O}(3)\text{--H} = 1.03(6)$ ,  $\text{H}\cdots\text{O}(6,4)^{\text{ix}} = 1.40(6)$  Å and  $\angle\text{O}(3)\text{--H}\cdots\text{O}(6,4)^{\text{ix}} = 177(4)^\circ$ . This is one of the shortest symmetry-free (Catti & Ferraris, 1974a) or type B (Currie & Speakman, 1970) hydrogen bonds ever found; its role in the building of the structure seems, however, definitely minor because of the framework of Na polyhedra. Presumably the dimer is already present in solution and the hydrogen bond acts as an intramolecular bond, as it does in all the cases of very short hydrogen bonds found in molecular compounds.

Table 4. *Interatomic distances* (Å) *and O--S--O angles* ( $^\circ$ ) *in the S tetrahedra*

Columns B, C and D show S--O values calculated according to Baur (1970), Ferraris & Catti (1973) and Louisnathan, Hill & Gibbs (1977), respectively (see text). E.s.d.'s are 0.002, 0.003 Å and  $0.1^\circ$  for S--O, O--O and angles, respectively.

	A	B	C	D
$\text{S}(1)\text{--O}(1)$	1.470	1.478	1.470	1.457
$\text{S}(1)\text{--O}(2)$	1.462	1.478	1.470	1.468
$\text{S}(1)\text{--O}(3)$	1.527	1.522	1.514	1.511
$\text{S}(1)\text{--O}(4)$	1.450	1.457	1.449	1.450
Average	1.477	1.484	1.476	1.472
$\text{O}(1)\text{--O}(2)$	2.397	109.7		
$\text{O}(1)\text{--O}(3)$	2.425	108.1		
$\text{O}(1)\text{--O}(4)$	2.426	112.4		
$\text{O}(2)\text{--O}(3)$	2.413	107.6		
$\text{O}(2)\text{--O}(4)$	2.406	111.4		
$\text{O}(3)\text{--O}(4)$	2.402	107.5		
Average	2.412	109.5		
	A	B	C	D
$\text{S}(2)\text{--O}(5)$	1.455	1.457	1.449	1.459
$\text{S}(2)\text{--O}(6)$	1.498	1.484	1.477	1.501
$\text{S}(2)\text{--O}(7)$	1.467	1.457	1.449	1.456
$\text{S}(2)\text{--O}(8)$	1.466	1.475	1.467	1.469
Average	1.472	1.468	1.461	1.471
$\text{O}(5)\text{--O}(6)$	2.391	108.1		
$\text{O}(5)\text{--O}(7)$	2.421	111.9		
$\text{O}(5)\text{--O}(8)$	2.392	110.0		
$\text{O}(6)\text{--O}(7)$	2.401	108.1		
$\text{O}(6)\text{--O}(8)$	2.401	108.2		
$\text{O}(7)\text{--O}(8)$	2.408	110.4		
Average	2.402	109.5		

It is well known that in oxyanions  $X\text{—OH}$  bonds are longer than  $X\text{—O}$  (Cruickshank, 1961), and individual values have been explained in the context of empirical theories of bond valence or bond strength (Baur, 1970; Brown & Shannon, 1973). The examination of structures containing  $\text{HSO}_4^-$  oxyanions has revealed that the length of the  $\text{S—OH}$  bond is in strong linear correlation ( $r = 0.79$ , mean square error = 0.00017) with the length of the corresponding  $\text{O}\cdots\text{O}$  hydrogen bond (Fig. 3). The effect is due to the well documented

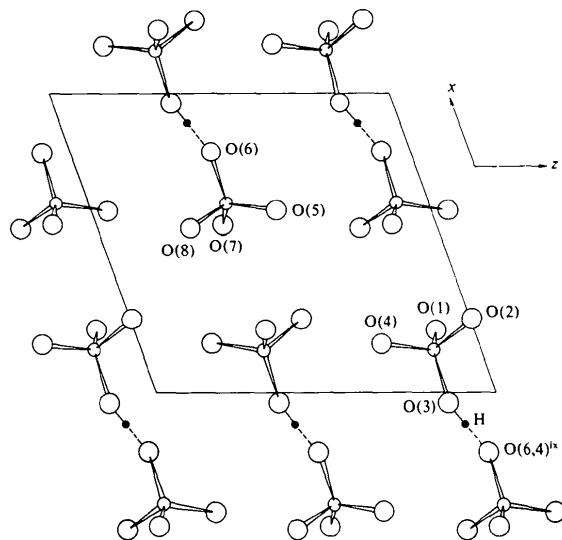


Fig. 2. Orthogonal projection onto the plane (010) of one layer of  $\text{SO}_4\cdot\text{H}\cdot\text{SO}_4$  groups in the structure of  $\text{Na}_3\text{H}(\text{SO}_4)_2$ . Dashed lines represent the hydrogen bonds.

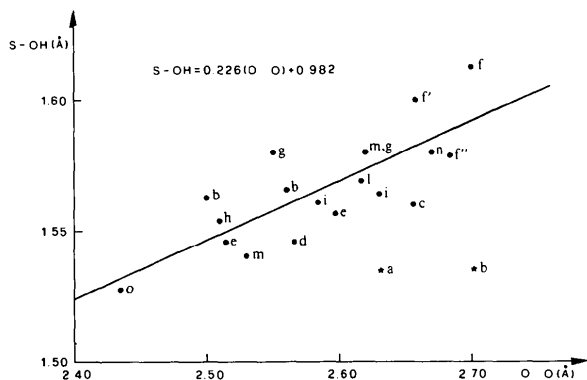


Fig. 3. Scatter diagram of the observed values of the bond length  $\text{S—OH}$  vs the  $\text{O}\cdots\text{O}$  distance observed for the corresponding hydrogen bond. The equation of the regression line is calculated without the two stars (see text). (a)  $\text{H}_2\text{SO}_4$  (Pascard-Billy, 1965); (b)  $(\text{NH}_3)_3\text{CoO}_2\text{Co}(\text{NH}_3)_3\text{SO}_4(\text{HSO}_4)_3$  (Schaefer & Marsh, 1966); (c)  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$  (Taesler & Olovsson, 1968); (d)  $\text{CH}_3\text{COOH}\cdot\text{H}_2\text{SO}_4$  (Jönsson & Olovsson, 1968); (e)  $\text{NH}_4\text{HSO}_4$  (Nelmes, 1971); (f)  $\text{NaHSO}_4\cdot\text{H}_2\text{O}$  (Pringle & Broadbent, 1965); (f')  $\text{NaHSO}_4\cdot\text{H}_2\text{O}$  (Grimvall, 1971); (f'')  $\text{NaHSO}_4\cdot\text{H}_2\text{O}$  (Catti, Ferraris & Franchini-Angela, 1975); (g)  $\text{K}_{0.55}\text{Rb}_{0.45}\text{HSO}_4$  (Mumme, 1973); (h)  $[\text{Ag}(\text{C}_6\text{H}_{16}\text{N}_{10})]\text{SO}_4\text{HSO}_4\cdot\text{H}_2\text{O}$  (Coghi & Pelizzi, 1975); (i)  $\text{KHSO}_4$  (Cotton, Frenz & Hunter, 1975); (l)  $\text{trans-}[\text{CoCl}_2(\text{NH}_3)_4]\text{HSO}_4$  (Bonapace & Mandel, 1975); (m)  $\text{RbHSO}_4$  (Ashmore & Petch, 1975); (n)  $\beta\text{-NaHSO}_4$  (Sonneveld & Visser, 1978); (o) this paper.

attraction of the H atom towards the acceptor with the consequent weakening of the  $\text{O—H}$  bond, so that the donor is forced to strengthen other bonds. In Fig. 3, structures with disorder are not reported and the regression line has been obtained without the two bonds shown as stars; they refer to earlier structures and, at least for (a), their positions in the diagram could reflect uncertainties in the structural model.

The exceptional shortness of the hydrogen bond not only makes  $\text{S(1)—O(3)}$  the shortest  $\text{S—OH}$  bond ever observed, in agreement with the trend in Fig. 3, but also forces the acceptor  $\text{O(6)}$  to form the longest  $\text{S—O}$  bond in sulphates. This represents the reverse effect of Fig. 3 and should clearly indicate that H is nearer to  $\text{O(6)}$  than shown by the X-ray results. In fact, the  $\text{O(3)—H}$  length is shorter than that expected from the  $\text{O—H vs O}\cdots\text{O}$  correlation deduced from neutron diffraction results (Olovsson & Jönsson, 1976); it is quite long for an X-ray solution (in which  $\text{O—H}$  bonds are notoriously shortened), and is likely to be actually of the expected length, as a neutron diffraction study now in progress should clarify.

#### Coordination polyhedra

In spite of the unusual  $\text{S—O}$  bond lengths where the O atoms are involved in hydrogen bonds, the two S tetrahedra (Table 4) are remarkably regular as far as the  $\text{O}\cdots\text{O}$  edges are concerned. A maximum  $\text{O—O}$  deviation of 0.6 and 0.5% ( $\text{S—O}$ , 3.4 and 1.8%;  $\text{O—S—O}$  angles, 3.7 and 2.3%) is observed for  $\text{S(1)}$  and  $\text{S(2)}$ , respectively, which is in agreement with Baur's (1970) hypothesis of a central tetrahedral atom moving within a rigid framework of O atoms.

The predictive power of correlations of the  $\text{S—O}$  bond length vs the bond strength  $p$  [ $\text{S—O} = 1.225 + 0.128p$  (Baur, 1970);  $\text{S—O} = 1.473 + 1.128(p - 2)$  (Ferraris & Catti, 1973)] and vs the average value of the three  $\text{O—S—O}$  angles contiguous to  $\text{S—O}$  [ $\text{S—O} = 1.035 - 0.145/\cos(\langle\text{O—S—O}\rangle_3)$  (Louisnathan, Hill & Gibbs, 1977)] has been tested. With the bond strength of the hydrogen bond distributed between  $\text{O(3)}$  and  $\text{O(6)}$  as shown in Table 5 (Lippincot-Schroeder values), the three correlations appear practically equivalent, with an average difference  $|(\text{S—O})_{\text{calc}} - (\text{S—O})_{\text{obs}}|$  of 0.008, 0.008 and 0.007 Å (columns B, C and D in Table 4).

The large stoichiometric Na/O ratio requires high sharing of the oxygen atoms between coordination polyhedra; in particular,  $\text{Na(2)}$  and  $\text{Na(3)}$  polyhedra share two faces each,  $\text{Na(4)}$  one, and the edge  $\text{O(7)—O(8,3)^{\text{iv}}}$  is common to three Na polyhedra. The complete participation of the O atoms is shown in Table 5, where the bond valence, calculated according to Brown & Wu (1976) and to the Lippincot-Schroeder curve (Brown, 1976) for the hydrogen bond, is reported. The fourfold coordination of  $\text{O(8)}$  with

Table 5. Bond valence (see text)

	S(1)	S(2)	Na(1)	Na(2)	Na(3)	Na(4)	H	$\Sigma$
O(1)	1.52		0.15		0.20	0.15		2.02
O(2)	1.56			0.18	0.19	0.15		2.08
O(3)	1.30				0.20		0.65	2.15
O(4)	1.62		0.18			0.20		2.00
O(5)		1.59			0.18	0.22		1.99
O(6)		1.41	0.26				0.35	2.02
O(7)		1.54		0.22	0.16	0.19		2.11
O(8)		1.54		0.13	0.17	0.09 0.13		2.06
$\Sigma$	6.00	6.08	0.59 $\times$ 2 = 1.18	0.53 $\times$ 2 = 1.06	1.10	1.13	1.00	

respect to Na is certainly unusual, and the consequent very long Na—O(8) bonds are the major causes of the distortions observed, not only in the Na(4) seven-cornered polyhedron but also in the Na(1), Na(2) and Na(3) octahedra.

### Twinning

The small difference between *a* and *b* values is the reticular basis for ( $\bar{1}01$ ) twinning by pseudomerohedry or twin-lattice quasi-symmetry (Donnay & Donnay, 1974) with obliquity  $\omega = 3.39^\circ$ . Structurally the twinning is supported by the fact that ( $\bar{1}01$ ) is a pseudo mirror plane, at least for Na and S atoms within their respective layers (Figs. 1, 2).

The X-ray intensities were measured at the Centro di Studio del CNR per la Cristallografia Strutturale, Pavia. Research was supported by the Consiglio Nazionale delle Ricerche, Roma.

### References

- ASHMORE, J. P. & PETCH, H. E. (1975). *Can. J. Phys.* **53**, 2694–2702.
- BAUR, W. H. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 129–155.
- BONAPACE, J. A. & MANDEL, N. S. (1975). *Acta Cryst.* **B31**, 2540–2542.
- BROWN, I. D. (1976). *Acta Cryst.* **A32**, 24–31.
- BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* **A29**, 266–282.
- BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
- CATTI, M. & FERRARIS, G. (1974a). *Acta Cryst.* **B30**, 1–6.
- CATTI, M. & FERRARIS, G. (1974b). *Acta Cryst.* **B30**, 1789–1794.
- CATTI, M., FERRARIS, G. & FRANCHINI-ANGELA, M. (1975). *Atti Accad. Sci. Torino*, **109**, 531–545.
- CATTI, M., FERRARIS, G. & FRANCHINI-ANGELA, M. (1977). *Acta Cryst.* **B33**, 3449–3452.
- CATTI, M., FERRARIS, G. & IVALDI, G. (1978). *Acta Cryst.* **B34**, 369–373.
- CHOMNILPAN, S., TELLGREN, R. & LIMINGA, R. (1978). *Acta Cryst.* **B34**, 373–377.
- COGHI, L. & PELIZZI, G. (1975). *Acta Cryst.* **B31**, 131–134.
- COTTON, F. A., FRENZ, B. A. & HUNTER, D. C. (1975). *Acta Cryst.* **B31**, 302–304.
- CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
- CURRIE, N. A. & SPEAKMAN, J. C. (1970). *J. Chem. Soc. A*, pp. 1923–1925.
- DONNAY, G. & DONNAY, J. D. H. (1974). *Can. Mineral.* **12**, 422–425.
- FAUST, O. & ESSELMANN, P. (1926). *Z. Anorg. Chem.* **157**, 290–298.
- FERRARIS, G. & ABBONA, F. (1972). *Bull. Soc. Fr. Minéral. Cristallogr.* **95**, 33–41.
- FERRARIS, G. & CATTI, M. (1973). *Acta Cryst.* **B29**, 2006–2009.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GRIMVALL, S. (1971). *Acta Chem. Scand.* **25**, 3213–3219.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JÖNSSON, P. G. & OLOVSSON, I. (1968). *Acta Cryst.* **B24**, 559–564.
- LOUISNATHAN, S. J., HILL, R. J. & GIBBS, G. V. (1977). *Phys. Chem. Miner.* **1**, 53–69.
- MCGREGOR, D. R., SPEAKMAN, J. C. & LEHMANN, M. S. (1977). *J. Chem. Soc. Perkin Trans. 2*, pp. 1740–1746.
- MUMME, W. G. (1973). *Acta Cryst.* **B29**, 1076–1083.
- NELMES, R. J. (1971). *Acta Cryst.* **B27**, 272–281.
- OLOVSSON, I. & JÖNSSON, P. G. (1976). *The Hydrogen Bond*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORF, pp. 395–456. Amsterdam: North Holland.
- PASCAL, P. (1966). *Nouveau Traité de Chimie Minérale*. Vol. II. Paris: Masson.
- PASCARD-BILLY, C. (1965). *Acta Cryst.* **18**, 827–829.
- PHILIPPOT, E., RICHARD, P., ROUDAULT, R. & MAURIN, M. (1972). *Rev. Chim. Minér.* **9**, 825–835.
- PRINGLE, G. E. & BROADBENT, T. A. (1965). *Acta Cryst.* **19**, 426–432.
- SCHAEFER, W. P. & MARSH, R. E. (1966). *Acta Cryst.* **21**, 735–743.
- SONNEVELD, E. J. & VISSER, J. W. (1978). *Acta Cryst.* **B34**, 643–645.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- SUZUKI, S. & MAKITA, Y. (1978). *Acta Cryst.* **B34**, 732–735.
- TAESLER, I. & OLOVSSON, I. (1968). *Acta Cryst.* **B24**, 299–304.
- WILLIAMS, J. M., DOWLING, N., GUNDE, R., HADŽI, D. & OREL, B. (1976). *J. Am. Chem. Soc.* **98**, 1581–1582.