

## SHORT STRUCTURAL PAPERS

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## Refinement of Disodium Dithionate Dihydrate\*

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**Abstract.**  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ : orthorhombic, *Pnma*,  $a = 6.411$  (5),  $b = 10.761$  (7),  $c = 10.675$  (8) Å;  $Z = 4$ ,  $D_o = 2.19$ ,  $D_c = 2.18$  g cm<sup>-3</sup>;  $R = 0.045$  for 2717 independent reflexions. The compound crystallizes as a three-dimensional network with short O...Na distances and O—H...O hydrogen bonds. The  $\text{S}_2\text{O}_6^{2-}$  ion has  $D_{3d}$  ( $\bar{3}m$ ) symmetry, to a good approximation, with S—S = 2.141 (1), S—O = 1.452 (1) Å,  $\langle \text{S—S—O} \rangle = 104.6$  and  $\langle \text{O—S—O} \rangle = 114.1^\circ$ .

**Introduction.** The present paper is part of a series of papers in which the variations in bond lengths and valence angles in groups or ions of type  $-(\text{SO}_x)_y$  with  $x, y = 1-3$ , are studied (for part III, see Kiers & Vos, 1978). For the dithionate ion S—S values varying between 2.08 and 2.19 Å have been reported in the literature. To determine the geometry of this ion accurately, the structure of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ , found earlier by Martínez, García-Blanco & Rivoir (1956) from two-dimensional X-ray data, has been refined.

$\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  is commercially available (Merck). Crystals of good quality were obtained by recrystallization from water. The crystals were mounted on a glass fibre with Tixo glue. Accurate cell dimensions were determined from Weissenberg photographs calibrated with NaCl reflexion spots. By least-squares refinement  $a$ ,  $b$  and  $c$  were adjusted to  $80 \sin^2 \theta / \lambda^2$  values of  $\alpha_1$  and  $\alpha_2$   $0kl$  and  $h0l$  reflexions [ $\lambda(\text{Cu } K\alpha_1) = 1.54051$ ,  $\lambda(\text{Cu } K\alpha_2) = 1.54434$  Å,  $a(\text{NaCl}) = 5.64006$  Å]. The length of the  $c$  axis, which deviates significantly from the value of 10.62 (1) Å reported by Martínez *et al.* (1956), was confirmed by an accurate measurement of the  $\theta$  values of the  $00l$  reflexions on a Nonius CAD-3 diffractometer (Mo radiation). The intensities of 3912 independent reflexions with  $\sin \theta / \lambda \leq 1.08$  Å<sup>-1</sup> were collected at room temperature on the Nonius diffractometer [Zr-filtered Mo radiation,  $\theta/2\theta$  scan, scan angle  $(0.80 + 0.50 \tan \theta)^\circ$ , counter width  $1.0^\circ$ , crystal size

$0.50 \times 0.30 \times 0.22$  mm]. Deviations from linearity of the scintillation counting equipment were kept below 1% by the use of attenuation filters. The intensities of the three reference reflexions 260, 013 and 134 did not deviate more than 2% from their respective average values. Corrections for Lorentz and polarization effects and for absorption were made. The absorption factors for the intensities, calculated according to the Busing & Levy (1957) scheme with the crystal divided into  $6 \times 6 \times 6$  volume elements, varied from 1.094 to 1.149. Of the 3912 reflexions 2717 had a positive nett intensity. For the latter reflexions the standard deviations  $\sigma_c(|F_o|)$  due to counting statistics and the errors in the filter factors were calculated. Starting from the 'heavy' atom coordinates of Martínez *et al.* (1956) and from the positions of the H atoms as found from difference maps, a least-squares refinement was carried out. For H, isotropic temperature factors, and for the heavy atoms anisotropic temperature factors, were used. Scattering factors were taken from Cromer & Mann (1968) for the heavy atoms, and from Stewart, Davidson & Simpson (1965) for H. The weighting scheme  $w = [\sigma_c^2(|F_o|) + (0.016)^2 |F_o|^2]^{-1}$  was applied. The residuals  $R = \sum |F_o - k^{-1}F_c| / \sum |F_o|$  and  $R_w = [\sum w(F_o - k^{-1}F_c)^2 / \sum wF_o^2]^{1/2}$  decreased to 0.045 and 0.046 respectively for the 2717 reflexions. The goodness of fit  $G = [\sum w(F_o - k^{-1}F_c)^2 / (N - N_v)]^{1/2} = 1.53$ .

The final difference map showed maxima at the centres of the S—S and S—O bonds, varying in height between 2.5 and  $4.0\sigma$  ( $\sigma = 0.14$  e Å<sup>-3</sup>). The atomic coordinates are given in Table 1.† Calculations were made with the set of programs of the XRAY system (1973).

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33102 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

\* The Nature of the S—S bonds in Different Compounds. IV.

Table 1. Fractional atomic coordinates ( $\times 10^5$ ; for H  $\times 10^3$ )

Standard deviations as calculated by the least-squares program are given in parentheses in units of the last digit.

	x	y	z
S(1)	24952 (5)	25000	45862 (3)
S(2)	-172 (5)	25000	59078 (3)
O(1)	36469 (13)	13654 (9)	48293 (8)
O(2)	14272 (20)	25000	33809 (10)
O(3)	-11403 (14)	13621 (9)	56327 (9)
O(4)	9540 (20)	25000	71368 (11)
O(5)	25162 (16)	4448 (9)	18906 (9)
Na	6863 (8)	6191 (5)	84712 (5)
H(1)	316 (4)	55 (3)	129 (3)
H(2)	235 (4)	111 (3)	223 (3)

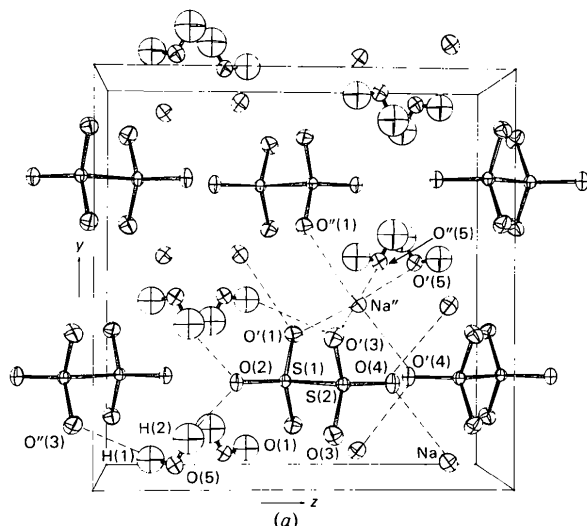


Fig. 1. Packing of the  $\text{Na}^+$  and  $\text{S}_2\text{O}_6^{2-}$  ions and the water molecules in the crystal structure of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ . (a) Numbering scheme.

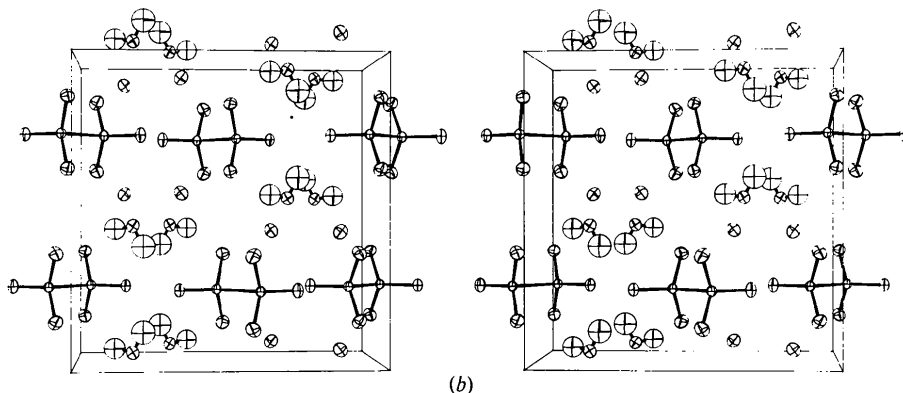


Fig. 1 (cont.). (b) Stereoview along x.

**Discussion.** The packing of the molecules with the numbering scheme is given in Fig. 1. Bond lengths and angles and short atomic distances are given in Table 2. The atomic parameters obtained by the present refinement differ significantly from the less accurate parameters of Martinez *et al.* (1956). This causes large changes in some of the atomic distances (up to 0.10 Å) and bond angles.

In the structure there are short  $\text{Na} \cdots \text{O}$  distances and nearly linear hydrogen bonds  $\text{O}(5)-\text{H} \cdots \text{O}$  in which the  $\text{O}(5)-\text{H}$  bonds of the water molecule are involved. Each O atom takes part in two short  $\text{O} \cdots \text{Na}$  or  $\text{O} \cdots \text{H}$  distances. The oxygen atoms  $\text{O}(1)$ ,  $\text{O}(4)$  and  $\text{O}(5)$  are each coordinated to two  $\text{Na}^+$  ions,  $\text{O}(3)$  is involved in one short  $\text{Na} \cdots \text{O}$  and one short  $\text{O} \cdots \text{H}$  distance and  $\text{O}(2)$  has two short  $\text{O}(2) \cdots \text{H}$  distances. In this way each water molecule forms two  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds and each Na atom is pseudo octahedrally surrounded by six O atoms.

Because of its location at a special position, the  $\text{S}_2\text{O}_6^{2-}$  ion contains a crystallographic mirror plane. In good approximation the ion has  $D_{3d}$  ( $3m$ ) symmetry. Average values for bond lengths and angles are  $\text{S}-\text{S} = 2.141$  (1),  $\text{S}-\text{O} = 1.452$  (1) Å,  $\text{S}-\text{S}-\text{O} = 104.6$  and  $\text{O}-\text{S}-\text{O} = 114.1^\circ$ . The  $\text{S}-\text{S}$  bond of 2.141 (1) Å in the dithionite ion is longer than the  $\text{S}-\text{S}$  bonds in  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$  [2.03 (1) Å (Lee & Bryant, 1969)],  $p\text{-BrC}_6\text{H}_4(\text{SO}_2)\text{SC}_6\text{H}_4\text{Br}$ - $p$  [2.09 (1) Å (Noordik & Vos, 1967)] and  $p\text{-CH}_3\text{C}_6\text{H}_4\text{S}(\text{SO})\text{C}_6\text{H}_4\text{CH}_3$ - $p$  [2.105 (3) Å (Kiers & Vos, 1978)], but shorter than the  $\text{S}-\text{S}$  bond in  $\text{C}_6\text{H}_5(\text{SO}_2)(\text{SO}_2)\text{C}_6\text{H}_5$  [2.193 (1) Å (Kiers & Vos, 1972)] and in the  $\text{S}_2\text{O}_5^{2-}$  ion in  $(\text{NH}_4)_2\text{S}_2\text{O}_5$  [2.170 (4) Å (Baggio, 1971)], whereas for the  $\text{S}_2\text{O}_4^{2-}$  ion in  $\text{Na}_2\text{S}_2\text{O}_4$  (Dunitz, 1956) a very large value of 2.389 (2) Å has been found. The mean value of the  $\text{S}-\text{O}$  bonds in our  $\text{S}_2\text{O}_6^{2-}$  ion [1.452 (1) Å] is equal to that in the  $-\text{SO}_3^-$  part of the  $\text{S}_2\text{O}_5^{2-}$  ion in  $(\text{NH}_4)_2\text{S}_2\text{O}_5$  [1.454 (7) Å], but slightly larger than the  $\text{S}-\text{O}$  bond lengths of 1.446 (11) and 1.428 (1) Å reported for the sulphones  $p\text{-BrC}_6\text{H}_4$ -

Table 2. Bond lengths, short non-bonded distances (Å) and valence angles (°)

For numbering see Fig. 1. Standard deviations calculated from the standard deviations in Table 1 are given in parentheses in units of the last digit.

S(1)—S(2)	2.141 (1)	Na''...O'(4)	2.481 (2)
S(1)—O(1)	1.450 (1)	Na''...O'(1)	2.376 (2)
S(1)—O(2)	1.457 (2)	Na''...O''(1)	2.342 (2)
S(2)—O(3)	1.451 (1)	Na''...O'(5)	2.382 (2)
S(2)—O(4)	1.452 (2)	Na''...O''(5)	2.342 (2)
O(5)—H(1)	0.77 (3)	Na''...O'''(3)*	2.386 (2)
O(5)—H(2)	0.80 (3)		
O(1)...O'(1)	2.442 (2)	S(2)—S(1)—O(1)	105.37 (5)
O(1)...O(2)	2.430 (2)	S(2)—S(1)—O(2)	103.19 (8)
O(3)...O'(3)	2.449 (2)	S(1)—S(2)—O(3)	103.89 (5)
O(3)...O(4)	2.425 (2)	S(1)—S(2)—O(4)	105.83 (8)
H(1)...O''(3)	2.28 (3)	O(1)—S(1)—O'(1)	114.68 (7)
H(2)...O(2)	2.03 (3)	O(1)—S(1)—O(2)	113.40 (5)
O(5)...O''(3)	2.995 (2)	O(3)—S(2)—O'(3)	115.16 (8)
O(5)...O(2)	2.812 (2)	O(3)—S(2)—O(4)	113.31 (5)
O(1)—S(1)—S(2)—O'(3)	179.6		
O(2)—S(1)—S(2)—O(4)	180		
S(2)—S(1) ^ O(1)—S(1)—O'(1)	119.4		
S(2)—S(1) ^ O(1)—S(1)—O(2)	116.7		
S(1)—S(2) ^ O(3)—S(2)—O'(3)	116.6		
S(1)—S(2) ^ O(3)—S(2)—O(4)	117.8		

\*  $x[O'''(3)], y[O'''(3)], z[O'''(3)] = x[O'(3)] + 1, y[O'(3)], z[O'(3)]$ .

(SO<sub>2</sub>)SC<sub>6</sub>H<sub>4</sub>Br-*p* and C<sub>6</sub>H<sub>5</sub>(SO<sub>2</sub>)(SO<sub>2</sub>)C<sub>6</sub>H<sub>5</sub>, respectively. All S—O bonds mentioned above are considerably shorter than the value of 1.70 Å assumed for the single S—O bond (Gillespie & Robinson, 1963) and have thus a partly double-bond character. In agreement with the rule that the repulsion force is larger for a double than for a single bond (Gillespie, 1972), the angles S—S—O (104.6°) in our S<sub>2</sub>O<sub>6</sub><sup>2-</sup> ion are smaller

than the angles O—S—O (114.1°). A more extensive comparison of the bond lengths and angles in the S<sub>2</sub>O<sub>6</sub><sup>2-</sup> ion with those in other —(SO<sub>x</sub>)—(SO<sub>y</sub>) groups and a theoretical discussion of the observed variations has been given by Kiers (1976).

The computations were done at the Computing Center of the University of Groningen.

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