

in view of the relative electronegativities of hydrogen and sulfur. Charges on the hydrogen atoms are the most suspect because the hydrogen-atom positions used were those obtained in the X-ray refinement, where the hydrogen position is shifted into the bonding region by a significant amount. These charge values can be compared with a recent INDO/2 calculation (Piroumian, Frigovan & Beylerian, 1983) for  $S_2O_8^{2-}$ , where the peroxide O—O distance was set as 1.5 Å. In that calculation, the resulting charges were  $-0.17$  on the peroxide oxygens,  $-0.51$  on the sulfate-type oxygens and  $0.70$  on the sulfur. These values are in remarkable agreement with our experimental values despite replacement of the  $SO_3$  group for the hydrogen in the theoretical treatment.

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## Refinement of Sodium Thiosulfate, $Na_2S_2O_3$ , at 120 K

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**Abstract.** The crystal structure of  $Na_2S_2O_3$  was refined at 120 K from X-ray and neutron diffraction data.  $M_r = 158.12$ , monoclinic,  $P2_1/a$ ,  $a = 6.401$  (1),  $b = 8.100$  (2),  $c = 8.474$  (2) Å,  $\beta = 96.88$  (2)°,  $V = 436.2$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.408$  (1) g cm<sup>-3</sup>. X-ray diffraction:  $F(000) = 312$ , Nb-filtered Mo K $\alpha$ ,  $\lambda = 0.71069$  Å,  $(\sin\theta/\lambda)_{\max} = 1.06$  Å<sup>-1</sup>,  $\mu = 12.55$  (1) cm<sup>-1</sup>,  $R_w(F) = 0.029$  for 3639 independent observed reflections; neutron diffraction:  $\lambda = 0.8400$  Å,  $(\sin\theta/\lambda)_{\max} = 0.95$  Å<sup>-1</sup>,  $\mu = 0.008$  cm<sup>-1</sup>,  $R_w(F) = 0.047$  for 2197 independent observed reflections. The positional parameters are similar for both data sets. The thermal parameters are on average 16% smaller in the neutron refinement. The average S—S and S—O bond lengths corrected for libration are 2.007 (1) and 1.479 (1) Å. They fall within the range for other thiosulfates.

**Introduction.** The present work is part of our study of the charge-density distribution in thiosulfates. Results on  $MgS_2O_3 \cdot 6H_2O$  have been reported (Elerman, Bats & Fuess, 1983). We have continued our study by an investigation of anhydrous  $Na_2S_2O_3$ . Its structure was determined from film data by Sándor & Csordás (1961), who reported an  $R(F)$  factor of 0.15. Thus a more accurate refinement seemed desirable. This paper presents a refinement of the structure of  $Na_2S_2O_3$  at 120 K. A detailed analysis of the charge distribution and a comparison with results on  $MgS_2O_3 \cdot 6H_2O$  are in progress.

**Experimental.** Single crystals from slow evaporation of an aqueous solution at 351 K, cell parameters at 120 K refined from setting angles of 15 reflections in the X-ray diffraction experiment.

*X-ray diffraction*

Crystal  $0.3 \times 0.4 \times 0.5$  mm, Syntex  $P2_1$  diffractometer,  $\omega/2\theta$  scan, Enraf–Nonius low-temperature device, temperature calibration using phase transition of  $\text{KH}_2\text{PO}_4$  at 122.8 K, three equivalent reflections up to  $2\theta = 65^\circ$ , two for  $65 < 2\theta \leq 90^\circ$ , one for  $90 < 2\theta \leq 98^\circ$ , 9449 reflections measured, range of  $hkl$ :  $0 \rightarrow 12$ ,  $0 \rightarrow 17$ ,  $-17 \rightarrow 17$ , 3798 unique; three standard reflections every 75 reflections fluctuated about 4%; data rescaling with respect to standards, background correction by profile analysis (Blessing, Coppens & Becker, 1974), transmission range for absorption: 0.612–0.710, weights assigned to individual reflections according to  $w(I) = [\sigma^2(I)_{\text{counting}} + (0.03I)^2]^{-1}$ , equivalent reflections averaged:  $R(I)_{\text{int}} = 0.028$ , 3639 reflections with  $I > 0$  used, calculations with XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), neutral-atom scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974), isotropic extinction coefficient  $g = 1.81$  (5) (Larson, 1969), refinement on  $F$  to  $R = 0.035$ ,  $R_w = 0.029$ ,  $S = 1.66$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$ , max. and min. height in final  $\Delta F$  map 0.37 and  $-0.49 \text{ e } \text{\AA}^{-3}$ .

*Neutron diffraction*

Irregular-shaped crystal, volume  $3.5 \text{ mm}^3$ ,  $\omega/2\theta$  scan, diffractometer D9 at ILL, Grenoble, Air Products Displex Cryostat, one quadrant measured up to  $(\sin\theta/\lambda) = 0.95 \text{ \AA}^{-1}$ , 2899 reflections measured, range of  $hkl$ :  $0 \rightarrow 12$ ,  $0 \rightarrow 15$ ,  $-16 \rightarrow 15$ , 2350 unique; three standard reflections every 50 reflections showed fluctuations up to 4.5%; data rescaling with respect to standards, background correction by profile analysis (Lehmann & Larsen, 1974), absorption negligible, averaging of equivalents:  $R(I)_{\text{int}} = 0.045$ , weights as for X-ray data, scattering lengths from Koester (1977). During the structure refinement it became apparent that a number of reflections contained contributions from multiple reflections, absorption by cables or scattering by a small satellite. 170 reflections with  $\Delta F > 4\sigma$  or  $F_o/F_c > 2.5$  were removed from the data set; remaining 2197 reflections refined on  $F$  to  $R = 0.050$ ,  $R_w = 0.047$  and  $S = 1.16$ , isotropic extinction coefficient  $g = 0.028$  (3),  $(\Delta/\sigma)_{\text{max}} < 0.001$ .

**Discussion.** The atomic parameters of the X-ray and neutron refinement are compared in Table 1.\* The present work confirms the structure described by Sándor & Csordás (1961), but gives considerably more accurate bond distances and angles (Table 2).

\* Lists of structure factors, anisotropic temperature factors and rigid-body thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39659 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent values of the anisotropic thermal parameters*

X: X-ray, N: neutron.  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

		x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Na(1)	X	0.29706 (6)	0.62396 (4)	0.08575 (4)	0.0114 (1)
	N	0.29709 (13)	0.62436 (10)	0.08551 (10)	0.0106 (3)
Na(2)	X	0.37673 (5)	0.30411 (4)	0.45416 (4)	0.0096 (1)
	N	0.37674 (12)	0.30413 (10)	0.45404 (9)	0.0087 (3)
S(1)	X	0.52324 (3)	0.10651 (2)	0.21126 (2)	0.00895 (7)
	N	0.52323 (15)	0.10630 (12)	0.21130 (11)	0.0075 (3)
S(2)	X	0.29660 (3)	-0.04671 (2)	0.26607 (2)	0.00594 (6)
	N	0.29693 (14)	-0.04686 (11)	0.26609 (10)	0.0045 (3)
O(1)	X	0.17577 (9)	0.03720 (7)	0.38049 (6)	0.0103 (2)
	N	0.17624 (8)	0.03711 (6)	0.38036 (6)	0.0090 (2)
O(2)	X	0.38604 (9)	-0.20144 (7)	0.33624 (6)	0.0096 (2)
	N	0.38592 (8)	-0.20143 (6)	0.33606 (6)	0.0083 (2)
O(3)	X	0.16248 (9)	-0.08546 (7)	0.11608 (6)	0.0101 (2)
	N	0.16250 (8)	-0.08550 (7)	0.11633 (6)	0.0088 (2)

Table 2. *Bond distances (Å) and angles (°)*

	X-ray	Neutron
S(1)–S(2)	2.0054 (4)	2.004 (1)
S(2)–O(1)	1.4765 (7)	1.475 (1)
S(2)–O(2)	1.4733 (6)	1.471 (1)
S(2)–O(3)	1.4797 (6)	1.479 (1)
S(1)–S(2)–O(1)	108.52 (3)	108.46 (6)
S(1)–S(2)–O(2)	111.29 (3)	111.39 (6)
S(1)–S(2)–O(3)	107.08 (3)	107.14 (6)
O(1)–S(2)–O(2)	109.59 (3)	109.62 (6)
O(1)–S(2)–O(3)	111.47 (4)	111.36 (6)
O(2)–S(2)–O(3)	108.88 (3)	108.86 (6)
Na(1)–S(2)	3.0744 (7)	3.072 (1)
Na(1)–O(2)	2.5575 (8)	2.556 (1)
Na(1)–O(3)	2.5301 (9)	2.527 (1)
Na(1)–O(3)	2.3432 (8)	2.344 (1)
Na(1)–S(1)	2.8522 (6)	2.854 (1)
Na(1)–S(1)	3.0532 (8)	3.052 (1)
Na(1)–O(3)	2.4445 (8)	2.447 (1)
Na(2)–S(1)	2.8531 (6)	2.853 (1)
Na(2)–O(1)	2.5546 (8)	2.554 (1)
Na(2)–O(2)	2.3465 (8)	2.349 (1)
Na(2)–O(1)	2.4479 (8)	2.451 (1)
Na(2)–S(1)	2.9605 (7)	2.960 (1)
Na(2)–S(2)	2.9904 (7)	2.992 (1)
Na(2)–O(1)	2.3987 (8)	2.400 (1)
Na(2)–O(2)	2.5888 (8)	2.590 (1)

The positional parameters of the X-ray and neutron investigation are very similar. No differences larger than  $4\sigma$  occur. Considerable differences are found in the thermal parameters of the two data sets. Those of the X-ray determination are on average 16% larger than those of the neutron determination. A temperature difference in the two experiments can be excluded as sole explanation as the discrepancies are considerably direction-dependent and larger along **b**. The direction dependence of the differences in thermal parameters can be calculated as

$$\Delta U_{ij} = \sum_{\text{atoms}} w[U_{ij}(X) - U_{ij}(N)] / \sum_{\text{atoms}}$$

and the values are  $\Delta U_{11} = 0.0008$  (1),  $\Delta U_{22} = 0.0020$  (1),  $\Delta U_{33} = 0.00088$  (9) and  $\Delta U_{13} = 0.00005$  (7)  $\text{\AA}^2$ . Similar discrepancies are generally

Table 3. Bond distances (Å) in thiosulfates, including libration corrections

	S—S	S—O(1)	S—O(2)	S—O(3)	⟨S—O⟩	Reference
BaS <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	1.987 (3)	1.493 (3)	1.482 (3)	1.483 (3)	1.486 (3)	(a)
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	2.031 (4)	1.465 (3)	1.468 (3)	1.487 (3)	1.473 (3)	(a)
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1.997 (2)	1.492 (3)	1.488 (4)	1.487 (3)	1.489 (3)	(a)
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2.007 (1)	1.479 (1)	1.474 (1)	1.483 (1)	1.479 (1)	(b)
MgS <sub>2</sub> O <sub>3</sub> ·6H <sub>2</sub> O	2.024 (2)	1.474 (1)	1.474 (1)	1.481 (2)	1.476 (1)	(c)

References: (a) Armağan (1983). (b) This work. (c) Elerman *et al.* (1983).

found in combined X-ray and neutron studies and have been attributed to diffuse scattering (Bats & Fuess, 1982; Elerman *et al.*, 1983).

A rigid-body analysis of the thermal parameters of the thiosulfate group with the method of Schomaker & Trueblood (1968) gave no significant differences in thermal parameters from the neutron refinement and the rigid-body model.\* Thus the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> group appears rigid in agreement with the observation by Armağan (1983) for other thiosulfates. Bond lengths corrected for libration are compared in Table 3 with similar values in other thiosulfates. From these data it is seen that there is some spread in bond distances among the various thiosulfates, resulting from the crystalline environment. The shortest S—S bond lengths correspond to the longer S—O lengths. The data for Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> coincide with the mean values of Table 3.

\* See deposition footnote.

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## Pb<sub>3</sub>Mn<sub>7</sub>O<sub>15</sub>: a Further Change in the Space Group of a Published Crystal Structure

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**Abstract.** It was recently pointed out that the structure of Pb<sub>3</sub>Mn<sub>7</sub>O<sub>15</sub> which had been previously described in space group *Cmc2*<sub>1</sub> is better described in *Cmcm* using the original diffractometer data. It is shown here that a description in *P6*<sub>3</sub>/*mcm* with the metrically hexagonal cell (**a**–**b**)/2, **b**, **c** discloses a new class of systematic absences. It gives a residual of 3.1% when refined with 29 parameters on 274 unique reflections averaged from the same data. The  $\sigma$ 's are improved, the distances, angles and thermal parameters are more regular and there is no indication of disorder. It is noted that quite accurate orientation is required to establish symmetry from Laue patterns and, in view of the hexagonal symmetry observed on Weissenberg photographs of Pb<sub>3</sub>Mn<sub>7</sub>O<sub>15</sub>, it is argued that the orthorhombic symmetry of this compound is not beyond question.

**Introduction.** The lattice of Pb<sub>3</sub>Mn<sub>7</sub>O<sub>15</sub>, described with the orthorhombic cell  $a_o = 17.28$  (1),  $b_o = 9.98$  (1),  $c_o = 13.55$  (1) Å by Marsh & Herbstein (1983) (MH) and Darriet, Devalette & Latourrette (1978) (DDL), is metrically hexagonal within the standard deviations with transformation matrix  $\mathbf{a}_h = [\frac{1}{2}, -\frac{1}{2}, 0/010/001] \mathbf{a}_o$ . The atomic coordinates in MH, transformed to this cell with the same origin, match within a few hundredths of an Å special positions in space group *P6*<sub>3</sub>/*mcm* except for one O atom which occupies a general position. The structure factor data from DDL transformed to intensities and averaged in this space group gave  $R_{\text{sym}} = \sum(I_{\text{obs}} - \bar{I}) / \sum I_{\text{obs}} = 12.9\%$ , the summations extending over the reflections for which multiple measurements could be found in the reported data. The 85 orthorhombic reflections *hhl*,  $h \neq 0$ ,  $l \neq 2n$  with Bragg