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## Structure, Deformation Density and Atomic Charges in Potassium Hydrogenperoxomonosulfate Monohydrate, $\text{KHSO}_5 \cdot \text{H}_2\text{O}$

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**Abstract.**  $M_r = 170.2$ , monoclinic,  $C2/c$ ,  $a = 18.226$  (3),  $b = 7.662$  (1),  $c = 7.420$  (5) Å,  $\beta = 90.83$  (2)°,  $V = 1036.1$  (8) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.182$  (1) g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 13.5$  cm<sup>-1</sup>,  $F(000) = 608$ ,  $T = 130$  (2) K,  $R = 0.023$ , 4144 independent reflections. Sulfur has tetrahedral coordination with the average sulfate-type S–O distance of 1.445 (5) Å, the peroxo S–O distance of 1.634 (1) Å, the peroxo O–O distance of 1.463 (1) Å and the S–O–O–H torsion angle of 87 (1)°. Electron deformation density maps reveal the expected bonding features and lone-pair density. Atomic charge calculations are presented and compared with theoretical calculations for  $\text{S}_2\text{O}_8^{2-}$ .

**Introduction.** Although potassium hydrogenperoxomonosulfate is sold in an impure form commercially, pure salts of peroxomonosulfate have not been previously available. We have developed a procedure involving hydrolysis of  $\text{K}_2\text{S}_2\text{O}_8$  that affords highly pure  $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ . This product yielded crystals suitable for the first determination of the structure of the  $\text{HSO}_5^-$  ion. An earlier X-ray study (Kyrki & Lappalainen, 1965) reported an orthorhombic unit cell but did not include a structure determination.

Because of the difference in chemistry of oxidation–reduction in comparison with  $\text{H}_2\text{O}_2$  [i.e. a tendency for peroxide-bond breakage in  $\text{HSO}_5^-$  upon oxidation (Thompson, 1981)], we were interested not only in comparison of the O–O distance with that in  $\text{S}_2\text{O}_8^{2-}$  and in  $\text{H}_2\text{O}_2$  but also a comparison of deformation density with that observed for  $\text{H}_2\text{O}_2$  (Savariault & Lehmann, 1980), for  $\text{SO}_4^{2-}$  (Kirfel & Will, 1980, 1981), and for  $\text{S}_2\text{O}_3^{2-}$  (Elerman, Bats & Fuess, 1983).

**Experimental.** Concentrated solution of sodium peroxodisulfate was converted to the acid by passage through a column of Dowex 50X8 cation-exchange resin in the hydrogen form. The solution was concentrated in a rotary evaporator and hydrolyzed by heating at 323 K until no peroxodisulfate was detected. The solution was then neutralized to pH 3.5 by addition of  $\text{KHCO}_3$  in an ice bath, filtered and freeze-dried. The residue was redissolved in a small quantity of water at room temperature and filtered. The filtrate was chilled in an ice bath and the crystals that formed were filtered, washed with a small quantity of absolute ethanol and dried between sheets of filter paper. Iodometric analysis indicated a bulk composition approximating  $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ . Plate-like crystal;  $\sim 0.07 \times 0.23 \times 0.27$  mm; Enraf–Nonius CAD-4 diffractometer;  $T$  maintained by constant flow of  $\text{N}_2$  gas; 24 reflections,  $\theta = 9$ – $15^\circ$ , used for cell dimensions; empirical  $\psi$ -scan absorption (range of transmission = 0.83–1.00, average = 0.95); graphite monochromator; max.  $2\theta = 89^\circ$ ;  $hkl$  and  $h\bar{k}l$  ( $2\theta = 3$ – $89^\circ$ ),  $\bar{h}kl$  and  $\bar{h}\bar{k}l$  ( $2\theta = 2$ – $27.5^\circ$ ); 3 standard reflections every 3600 s ( $\sim 1\%$  variation, no correction); 5842 reflections measured;  $\theta$ – $2\theta$  scan method; scan speed to obtain 2% statistics to a maximum scan time of 120 s; 4144 unique;  $R_{\text{int}} = 0.024$  (measures agreement of the lower-angle data); 933 reflections with  $F_o^2 < 2.0\sigma(F_o^2)$  considered unobserved; structure solved with *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier syntheses; refinement minimized  $\sum w(|F_o| - |F_c|)^2$ ; 85 variables (all positional parameters and anisotropic temperature factors except isotropic for hydrogen atoms);  $R = 0.023$ ;  $wR = 0.030$ ;  $S = 1.21$ ;  $w^{-1} = [\sigma_{\text{counting}}^2 + (0.03F_o^2)^2]/4F_o^2$ ; max.  $\Delta/\sigma$  in last cycle = 0.20; max. difference density

after refinement  $<0.5 \text{ e } \text{\AA}^{-3}$  (largely in bonding and lone-pair regions); no extinction correction;  $ff'$  and  $f''$  from *International Tables for X-ray Crystallography* (1974); Enraf-Nonius (1979) *SDP* programs used except for charge refinement (*RADIEL*; Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). Parameters from the final refinement with the complete data set are in Table 1.\*

To compare the effect of different methods of absorption correction an analytical correction (absolute transmission 0.74–0.91) was applied in place of the empirical  $\psi$  correction. Relative deviations between the two methods were much less than 1% for all reflections. In addition, the effect of inclusion of an isotropic extinction factor (Zachariasen, 1963) [ $g = 3.4 (1.0) \times 10^{-7}$ ] was examined. The final agreement factors were unchanged in the first two significant figures. However, since there was significant improvement in fit of the more intense reflections, deformation density maps and radial refinement (as described below) were done both with and without extinction correction. Again, agreement factors at all stages were the same with or without inclusion of extinction.

In addition to the above routine structural details, the following describes the deformation density mapping and atomic charge modeling. Atomic positions and thermal parameters were determined for nonhydrogen atoms from a high-order X-ray refinement with hydrogen atoms held with parameters from the full data-set refinement. This refinement used 1570 reflections with  $(\sin\theta/\lambda) > 0.75 \text{ \AA}^{-1}$  and with  $F_o^2 > 2\sigma(F_o^2)$  and converged with  $R = 0.026$ . These atomic parameters were then held, and the scale factor alone was refined using the 1965 data with  $F_o^2 > 2\sigma(F_o^2)$ ;  $(\sin\theta/\lambda) < 0.80 \text{ \AA}^{-1}$ . This refinement gave  $R = 0.022$ . Both of the above refinements used the spherical neutral-atom scattering factors. Deformation density maps were generated based on the  $F_c$ 's from the latter refinement. These maps are contoured at intervals of  $0.05 \text{ e } \text{\AA}^{-3}$  (negative contours are broken lines).

Individual atomic charges were derived by radial refinement (Coppens *et al.*, 1979) [separate core and valence contributions, refinement of occupancy of core and valence, inclusion of expansion/contraction parameter ( $\kappa$ ) for valence, only valence for hydrogen atoms, charge neutrality constrained, only core for K, all data with  $F_o^2 > 2\sigma(F_o^2)$ , positional and thermal parameters fixed at high-angle values]. This refinement converged with  $R = 0.023$ .

**Discussion.** The crystal structure consists of discrete potassium and hydrogenperoxomonosulfate ions and

Table 1. *Positional parameters and their e.s.d.'s*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> ( $\text{\AA}^2$ ) <sup>†</sup>
K	0.31924 (1)	0.12129 (2)	0.62293 (2)	0.741 (2)
S	0.84756 (1)	0.14091 (2)	0.64362 (2)	0.600 (2)
O(1)	0.90958 (3)	0.37680 (7)	0.46299 (9)	1.018 (8)
O(2)	0.86123 (3)	0.22525 (7)	0.44462 (8)	0.893 (7)
O(3)	0.91932 (3)	0.08789 (8)	0.71028 (7)	0.852 (7)
O(4)	0.81443 (3)	0.27560 (8)	0.75199 (8)	0.915 (7)
O(5)	0.79922 (3)	0.00021 (8)	0.59236 (9)	1.059 (8)
O(6)	1.04018 (3)	0.22983 (8)	0.45146 (8)	0.992 (8)
H(1)	0.9525 (9)	0.327 (2)	0.458 (2)	2.6 (3)*
H(2)	1.0458 (9)	0.139 (2)	0.390 (2)	2.4 (3)*
H(3)	1.0499 (9)	0.186 (2)	0.561 (2)	2.4 (3)*

\* Atoms were refined isotropically.

<sup>†</sup>  $B_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

waters of hydration. The  $\text{HSO}_5^-$  ion is shown in Fig. 1 and the unit-cell contents in Fig. 2. The potassium ion has coordination number ten with K–O 2.772 (1)–3.181 (1)  $\text{\AA}$  (see Table 2), which includes nine oxygen atoms from peroxomonosulfate ions and one water oxygen. One of the six peroxomonosulfate ions has both of the peroxide oxygen atoms coordinated to potassium. The  $\text{HSO}_5^-$  ion is surrounded by six potassium ions as well as three water molecules, which are involved in hydrogen bonds with sulfate-type oxygen O(3) as an acceptor of two hydrogen bonds and the peroxide hydrogen as a donor. The parameters for these hydrogen bonds are given in Table 3. The strongest hydrogen bond is from the peroxide hydrogen to the water oxygen.

The  $\text{HSO}_5^-$  ion (Fig. 1) has the expected tetrahedral sulfur coordination with three short (sulfate like) S–O bonds and one longer S–O bond to the peroxide group (Table 2 gives all distances and angles). In  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Sivertsen & Sørum, 1969) the peroxide S–O distances are 1.644 (5)  $\text{\AA}$  while the sulfate-type S–O distances average 1.427 (3)  $\text{\AA}$ . In  $\text{CaSO}_4$  (Kirfel & Will, 1980, 1981) the average S–O distance [1.475 (1)  $\text{\AA}$ ] is longer than for the sulfate-type distances in either of the above. In  $\text{HSO}_5^-$  there is very significant deviation from tetrahedral angles with angles involving the peroxide oxygen less than tetrahedral [av. 104 (3) $^\circ$ ] and those between sulfate oxygens greater than tetrahedral [av. 114 (1) $^\circ$ ]. The small but significant differences in S–O distances for the sulfate-type oxygen atoms can be correlated with their crystallographic environment. The longest of these, S–O(3), involves the oxygen atom that accepts two hydrogen bonds from water hydrogen atoms and the shortest, S–O(5), has the weakest interactions with potassium ions (Table 2).

Despite the crystallographic interactions (including hydrogen bonding of the peroxide hydrogen with the water oxygen), the S–O(2)–O(1)–H(1) torsion angle is very close to that [90.2 (4) $^\circ$ ] in solid hydrogen peroxide (Savariault & Lehmann, 1980). The O–O distance is also very close to their value [1.458 (4)  $\text{\AA}$ ] for hydrogen peroxide. Both of these are considerably

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39652 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shorter than the value of 1.497 (8) Å observed for (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Sivertsen & Sørum, 1969).

One might have expected the sulfur thermal parameters to be larger than those of potassium, but the reverse is observed. Both K and S should have fewer electrons than the number included in the neutral-atom form factors that were used. The valence electron for K is very diffuse, and therefore the potassium atom's loss in scattering power is small. However, sulfur loses a significant contribution to its overall scattering power. Therefore, one would expect an artificially large *B* for S because the model overestimates its scattering. Since its *B* is small, one might conclude that the thermal motion of the ion must involve only small translations of S and probably more low-frequency librations (as a rigid group). Such low-frequency motions would be the last to 'freeze out' on cooling.

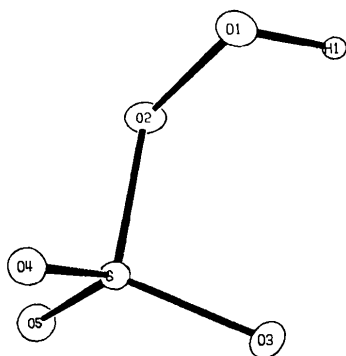


Fig. 1. A perspective view of the HSO<sub>5</sub><sup>-</sup> ion showing the atom numbering and the thermal ellipsoids (50% probability level).

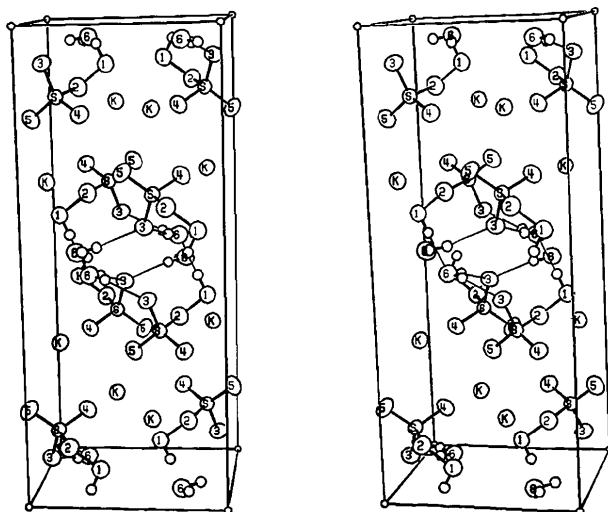


Fig. 2. A stereoscopic view of the unit-cell contents (97% probability level). The oxygen atoms are labeled by number only. Hydrogen atoms are unlabeled. Hydrogen bonds are the thinner lines between hydrogen and oxygen atoms.

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

Numbers in parentheses are e.s.d.'s in the least significant digits.

K—O(1)	2.772 (1)	S—O(2)	1.634 (1)
K—O(1)	2.993 (1)	S—O(3)	1.450 (1)
K—O(2)	2.759 (1)	S—O(4)	1.446 (1)
K—O(4)	2.818 (1)	S—O(5)	1.440 (1)
K—O(4)	2.874 (1)	O(1)—O(2)	1.463 (1)
K—O(4)	2.864 (1)	O(1)—H(1)	0.87 (2)
K—O(5)	2.825 (1)	O(6)—H(2)	0.84 (2)
K—O(5)	2.934 (1)	O(6)—H(3)	0.90 (2)
K—O(5)	3.181 (1)		
K—O(6)	2.866 (1)		
O(2)—S—O(3)	105.69 (3)	O(4)—S—O(5)	114.99 (3)
O(2)—S—O(4)	106.90 (3)	O(2)—O(1)—H(1)	101 (1)
O(2)—S—O(5)	99.09 (3)	S—O(2)—O(1)	109.22 (4)
O(3)—S—O(4)	113.09 (3)	H(2)—O(6)—H(3)	99 (1)
O(3)—S—O(5)	115.21 (3)		

Table 3. Hydrogen-bond parameters

	O...O (Å)	O—H (Å)	H...O (Å)	O—H...O (°)
O(1)—H(1)...O(6)	2.636 (1)	0.87 (2)	1.77 (2)	179 (1)
O(6)—H(2)...O(3)	2.817 (1)	0.84 (2)	2.00 (2)	165 (1)
O(6)—H(3)...O(3)	2.824 (1)	0.90 (2)	1.93 (2)	174 (1)

Deformation density maps are presented of the S,O(5),O(2),O(1) plane (Fig. 3) as well as the O(2),-S,O(4) (Fig. 4) and O(3),S,O(5) (Fig. 5) planes. These clearly show greater electron density in the sulfur-oxygen bonds involving the sulfate-type oxygens compared with the S—O(2) peroxide oxygen bond. They also show the depletion of electron density around the sulfur and 'lone pair' density on the oxygen atoms. In Fig. 6 the plane perpendicular to and bisecting the O(1)—O(2)—S angle is shown and reveals 'resolved' lone pairs on O(2). An interesting feature of Fig. 3 is the absence of excess electron density in the O(1)—O(2) peroxide bond. Apparently, the overlap of spherical neutral atoms is sufficient to account for the density in the peroxide bond. A nearly identical electron density was found by Savariault & Lehmann (1980) for the peroxide bond in H<sub>2</sub>O<sub>2</sub>. General features of the sulfur and sulfate oxygen regions are in agreement with those for CaSO<sub>4</sub> (Kirkel & Will, 1980, 1981) and MgS<sub>2</sub>O<sub>8</sub>·6H<sub>2</sub>O (Elerman, Bats & Fuess, 1983). These maps were generated from the refinement without extinction correction. Changes with extinction correction are generally quite small. The largest changes involved enhancements or depletions of ~0.10 e Å<sup>-3</sup> in certain regions (this is the estimated error level of the maps).

Atomic charge calculations using the radial refinement (see *Experimental*) gave the following individual atom charges.

	Charge		Charge
S	0.67 (12)	O(6)	-0.57 (9)
O(1)	-0.32 (8)	K	0.98 (1)
O(2)	-0.31 (8)	H(1)	0.55 (7)
O(3)	-0.57 (7)	H(2)	0.41 (8)
O(4)	-0.52 (8)	H(3)	0.23 (5)
O(5)	-0.54 (7)		

The largest change in the charge values with inclusion of the isotropic secondary extinction corrections was for H(3) [0.26 (5) with extinction]. All of the changes were much less than the corresponding e.s.d. Although this model for charge calculations is known to have

limitations, these results appear to be at least chemically reasonable. The sulfate-like oxygen atoms [O(3), O(4) and O(5)], which would be expected to be of nearly equal charge, have identical charges within one standard deviation and, as also might be expected, more negative charge than the peroxide oxygen atoms. The latter also have equal charge, which seems reasonable

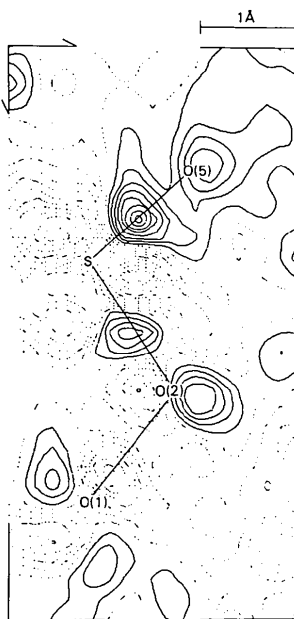


Fig. 3. The deformation density in the plane of the peroxide group [the O(5), S, O(2), O(1) plane]. Solid contours represent  $0.05 e \text{ \AA}^{-3}$  intervals. Negative contours are dashed.

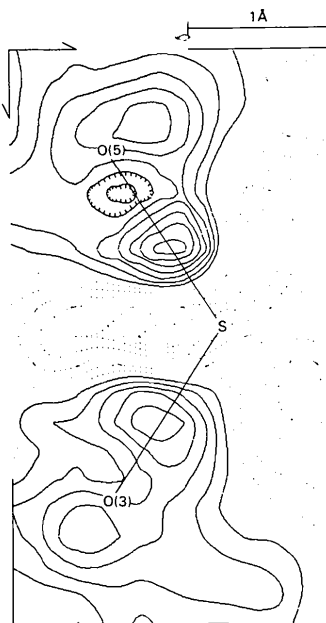


Fig. 5. The deformation density in the O(3), S, O(5) plane. Contours as in Fig. 3.

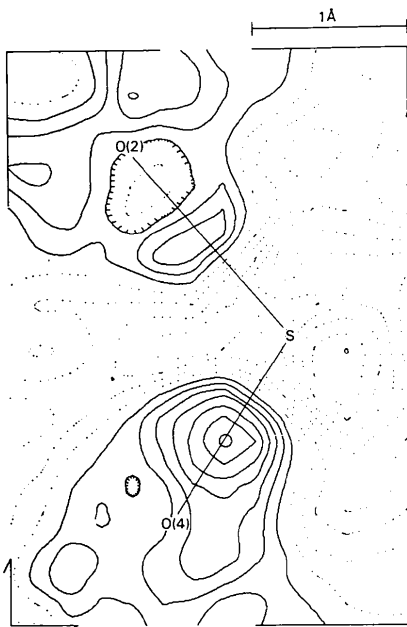


Fig. 4. The deformation density in the O(2), S, O(4) plane. Contours as in Fig. 3.

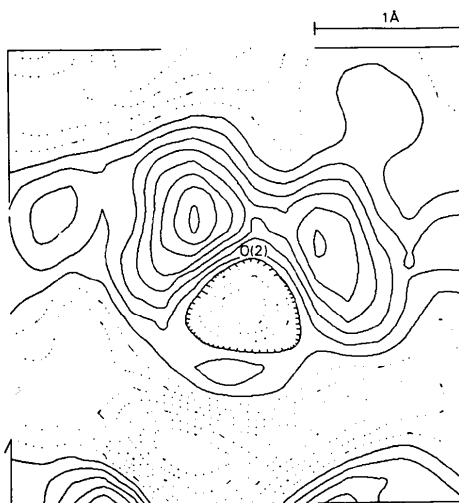


Fig. 6. The deformation density in the plane bisecting the S—O(2)—O(1) angle showing 'lone-pair' density. The plane of the S and two oxygens is perpendicular to the figure and vertical [projections of S and O(1) are below O(2)]. Contours as in Fig. 3.

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.