Table 3. Na—O *distances* (Å) *within* 3·0 Å

Na(1)—Aq(1^{i})	2·44 (3)	Na(2)—Aq(2)	2·48 (3)
Aq(4)	2·41 (3)	Aq(3^{iii})	2·39 (3)
Aq(8)	2·42 (3)	Aq(5)	2·37 (3)
Aq(9)	2·49 (3)	Aq(6^{iv})	2·43 (2)
O_t(1^{i})	2·36 (2)	Aq(10)	2·40 (2)
O_t(6^{i})	2·51 (2)	O_t(4^{ii})	2·42 (2)
Na(3)—Aq(6)	2·46 (2)		
Aq(6^{iv})	2·46 (2)		
Aq(7)	2·42 (2)		
Aq(7^{iv})	2·42 (2)		
Aq(10)	2·42 (2)		
Aq(10^{iv})	2·42 (2)		

Superscripts refer to the following symmetry operations: (i)x, y, $z-1$; (ii)$1+x, y, z$; (iii)x, $1+y$, z; (iv)$-x$, $1-y$, $-z$.

Table 4. *Probable hydrogen-bond distances* (<3·1 Å)

Aq(1)—O_t(1)	3·06 (4)	Aq(5)—O_b(8)	2·72 (4)
Aq(3)	2·79 (3)	Aq(7)	2·98 (3)
O_b(9^{ii})	2·86 (4)	O_t(2^{vi})	2·80 (3)
Aq(8^{i})	2·90 (3)	O_t(4^{iv})	3·02 (4)
Aq(2)—O_t(4^{iv})	2·89 (3)	Aq(6)—O_t(6^{vii})	2·93 (2)
Aq(2^{iii})	2·73 (7)	O_t(5^{viii})	2·85 (3)
O_b(9^{v})	2·88 (2)		
		Aq(7)—O_c(11)	2·66 (3)
Aq(3)—O_b(7^{i})	2·74 (3)	Aq(8)	2·70 (3)
Aq(4)—O_c(10^{i})	2·82 (4)	Aq(8)—O_c(12^{i})	2·68 (3)
O_t(2^{vi})	2·85 (4)	O_t(6^{vii})	3·02 (2)
		Aq(9)—Aq(10)	2·94 (2)
		O_t(1^{vi})	2·98 (2)
		Aq(10)—O_t(3^{viii})	2·79 (3)

Superscripts refer to the following symmetry operations: (i)x, y, $-z$; (ii)$-x$, $-y$, $1-z$; (iii)$1-x$, $1-y$, $1-z$; (iv)$1+x, y, z$; (v)$-x$, $1-y$, $1-z$; (vi)$1-x$, $-y$, $-z$; (vii)$x, y, -1+z$; (viii)$-x$, $1-y$, $-z$.

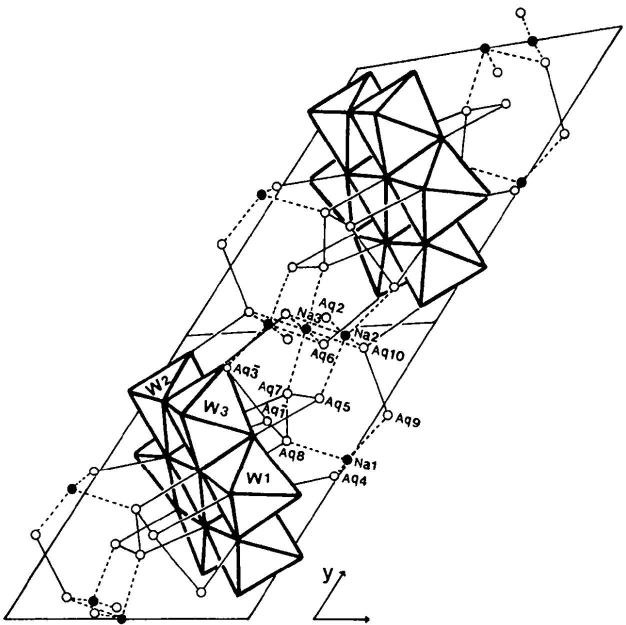

Fig. 2. Projection of the structure on the xy plane.

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Pentapotassium Disulfite Tris(hydrogensulfite), $K_5(HSO_3)_3(S_2O_5)$

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Abstract. $M_r = 582{\cdot}82$, monoclinic, $C2/m$, $a = 20{\cdot}3475\,(11)$, $b = 5{\cdot}9114\,(6)$, $c = 14{\cdot}7733\,(9)$ Å, $\beta = 104{\cdot}380\,(5)°$, $V = 1721{\cdot}3\,(2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}249\,(1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}90$ mm^{-1}, $T = 298$ K, $F(000) = 1160$; $R = 0{\cdot}039$ was obtained for 1751 observed reflections. The disulfite ion has m (C_s) symmetry and consists of a thionite and a thionate group linked by an S—S bond of 2·226 (2) Å. The S—O distances are 1·489 (3) Å in the thionite group and 1·462 (4)–1·463 (3) Å in the thionate group. There are three crystallographically different HSO_3^- ions in the cell, with average S—O distances of 1·419 (3), 1·451 (2), and 1·445 (2) Å, respectively. The H atom is bonded to the S atom in all three HSO_3^- ions, with H—S distances of 1·31 (6), 1·16 (7), and 1·16 (5) Å, respectively.

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Introduction. The system SO_2–H_2O is of great importance in atmospheric chemistry. One of the equilibria in this system involves the disulfite ion and the hydrogensulfite ion: $S_2O_5^{2-} + H_2O \rightleftharpoons 2HSO_3^-$. In connection with research on the chemistry of sulfur dioxide in the environment, our interest has been directed towards the structural chemistry of these two ions. Two disulfite structures, $K_2S_2O_5$ (Lindqvist & Mörtsell, 1957) and $(NH_4)_2S_2O_5$ (Baggio, 1971), have so far been determined. In the case of the hydrogensulfite ion, only one crystallographic determination, that of $CsHSO_3$ (Johansson, Lindqvist & Vannerberg, 1980), has been reported. Further investigations of the two ions are desirable in order to obtain a reliable picture of their structural chemistry. The compound reported as $K_2S_2O_5.4KHSO_3$ (Foerster, Brosche & Norberg-Schulz, 1924) seemed to be an ideal phase for this purpose, since it contains both ions of interest.

Experimental. The crystals, initially assumed to be $K_2S_2O_5.4KHSO_3$ $[K_6(HSO_3)_4(S_2O_5)]$, were prepared from a potassium disulfite solution under N_2 at 273 K according to Foerster, Brosche & Norberg-Schulz (1924). To obtain useful single crystals the supersaturation of the solution had to be very slight. The presence of two different kinds of sulfur oxo-anions was verified by IR spectroscopy.

Three different space groups (Cm, $C2$, and $C2/m$) are consistent with the systematic absences: $h + k = 2n + 1$, determined from Weissenberg photographs. Intensities from a lanceolate single crystal (0·51 × 0·13 × 0·05 mm), Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan technique, variable scan rate 3–29° min^{-1}. 2394 reflections measured with $h \geq 0$, $k \geq 0$, $h + k = 2n$, and $\sin\theta \leq 0{\cdot}50$; of these, 1751 had $I > 3\sigma(I)$ and were used in the subsequent calculations. Two standard reflections, $\bar{5}\bar{1}0$ and 312, were measured periodically, average intensities: 635 800(30 700) counts for $\bar{5}\bar{1}0$ and 308 200(8500) counts for 312; the difference between maximum and minimum intensity was $3{\cdot}6\sigma(I)$ for both reflections. Integrated intensities obtained using a profile-analysis procedure (Lindqvist & Ljungström, 1979; originally from Lehmann & Larsen, 1974); Lorentz and polarization corrections applied as well as an empirical absorption correction based on ψ scans from five reflections with 2θ values from 13 to 46° (Syntex, 1973) (transmission factors 0·56–0·84); six very strong reflections with low values of 2θ excluded in the final cycles of refinement due to secondary extinction. Space group Cm chosen in initial stages of structure determination. Direct methods (Main, Lessinger, Woolfson, Germain & Declercq, 1977) revealed the positions of the K and S atoms; full-matrix least-squares refinement (Coppens & Hamilton, 1970) based on F values and weighted according to $w = (35{\cdot}0 + F + 0{\cdot}005F^2)^{-1}$; electron density ($\rho$) calculations gave the positions of the remaining atoms; a twofold axis could easily be detected in the ρ calculations. Significance tests based on trial refinements (Hamilton, 1965) showed that the space group was $C2/m$ and not $C2$ or Cm. Final $wR = 0{\cdot}053$, $S = 0{\cdot}253$ with anisotropic thermal parameters for K, S, and O, and isotropic for H. Average shift-to-error ratio $4{\cdot}2 \times 10^{-4}$ with a maximum of $5{\cdot}9 \times 10^{-3}$ for $B_{\rm iso}$ of H(4). The final $\Delta\rho$ showed a maximum of 0·7 e Å^{-3} and a minimum of −1·0 e Å^{-3} less than 0·4 Å from a K or an S atom. Scattering factors for K^0, S^0, O^0, and H^0 were used (*International Tables for X-ray Crystallography,* 1974). Cell parameters were refined from powder diffractometer data with $Pb(NO_3)_2$ as internal standard ($a = 7{\cdot}8566$ Å at 294 K; *International Tables for X-ray Crystallography,* 1962).* The least-squares refinement of the unit-cell parameters was based on 53 single-indexed reflections (*POWDER*; Lindqvist & Wengelin, 1967).

Discussion. The compound is most likely the phase described by Foerster, Brosche & Norberg-Schulz (1924). They proposed the formula $K_2S_2O_5.4KHSO_3$ [*i.e.* $K_6(HSO_3)_4(S_2O_5)$], which would theoretically give K and S contents of 40·25 and 54·63%, calculated as K_2O and SO_2 respectively. The corresponding values for the formula found in the present structure determination, $K_5(HSO_3)_3(S_2O_5)$, are 40·41 and 54·99%.

The refined atomic positions and thermal parameters are given in Table 1. The high temperature factors of O(31) and O(32) are probably due to a certain freedom of rotation of the HSO_3^- group to which they belong.

The structure is built up of K^+, $S_2O_5^{2-}$, and HSO_3^- ions. Fig. 1 shows a stereoscopic picture of the packing in the unit cell. For clarity, the K···O contacts have not been drawn. Interatomic distances and angles are given in Table 2, and Fig. 2 shows the labeling of the atoms.

There are six crystallographically different K atoms in the unit cell with coordination numbers varying from six to nine. The K—O distances range from 2·667 (4) to 3·274 (2) Å, which is normal for K—O coordination and comparable with what is found in other structures, *e.g.* in $K_2S_2O_5$ (Lindqvist & Mörtsell, 1957).

The structure of the disulfite ion agrees well with that found in $K_2S_2O_5$ (Lindqvist & Mörtsell, 1957) and $(NH_4)_2S_2O_5$ (Baggio, 1971). The S—S bond length is 2·226 (2) Å in the present structure, 2·21 Å in $K_2S_2O_5$ and 2·170 (4) Å in $(NH_4)_2S_2O_5$. The $S_2O_5^{2-}$ ion has m (C_s) symmetry in all three structures and the eclipsed thionite and thionate parts of the ion have significantly different S—O distances. The structure of the $S_2O_5^{2-}$ ion has also been determined in aqueous solution (Yamaguchi & Lindqvist, 1982) with an S—S bond length of 2·22 (1) Å.

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* Powder data and lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38467 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *calculated according to Hamilton* (1959)

For the H atoms the isotropic temperature factor (Å^2) is given. The e.s.d.'s are given in parentheses.

	x	y	z	$B_{eq}(B_{iso})$
K(1)	0·5	0·0	0·5	2·21 (3)
K(2)	0·5	0·0	0·0	2·03 (3)
K(3)	0·22212 (6)	0·5	0·11352 (9)	2·46 (2)
K(4)	0·42421 (6)	0·5	0·30303 (8)	2·07 (2)
K(5)	0·08491 (6)	0·0	0·21539 (8)	2·02 (2)
K(6)	0·29319 (6)	0·0	0·37140 (9)	2·59 (2)
S(1)	0·34200 (6)	0·0	0·15683 (8)	1·79 (2)
S(2)	0·45423 (6)	0·0	0·21191 (8)	1·55 (2)
S(3)	0·17764 (7)	0·5	0·34926 (9)	2·11 (2)
S(4)	0·12917 (6)	0·0	0·01224 (9)	1·88 (2)
S(5)	0·10890 (6)	0·0	0·48213 (8)	1·79 (2)
O(11)	0·3259 (1)	0·2069 (5)	0·2046 (2)	2·77 (5)
O(21)	0·4793 (1)	0·2055 (5)	0·1767 (2)	2·62 (5)
O(22)	0·4660 (2)	0·0	0·3136 (3)	3·08 (8)
O(31)	0·1834 (2)	0·3001 (7)	0·2982 (3)	6·34 (11)
O(32)	0·2214 (3)	0·5	0·4400 (4)	7·70 (20)
O(41)	0·1080 (1)	0·2041 (5)	0·0525 (2)	3·08 (6)
O(42)	0·2004 (2)	0·0	0·0152 (3)	3·96 (10)
O(51)	0·1060 (1)	0·2027 (5)	0·5361 (2)	3·20 (6)
O(52)	0·0603 (2)	0·0	0·3929 (3)	4·34 (11)
H(3)	0·114 (3)	0·5	0·355 (4)	2·8 (11)
H(4)	0·097 (4)	0·0	−0·064 (5)	4·6 (12)
H(5)	0·162 (3)	0·0	0·467 (3)	1·2 (10)

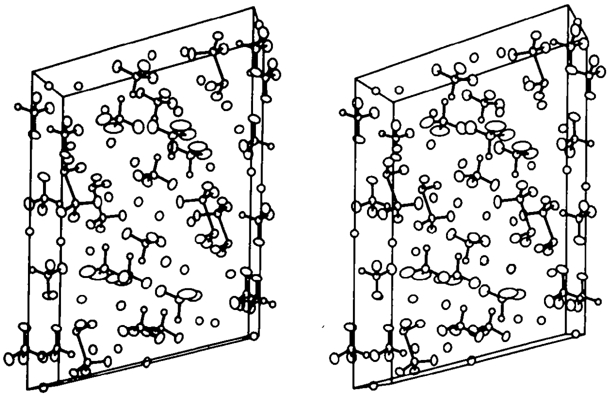

Fig. 1. A stereoscopic view of the structure (*ORTEP*; Johnson, 1965).

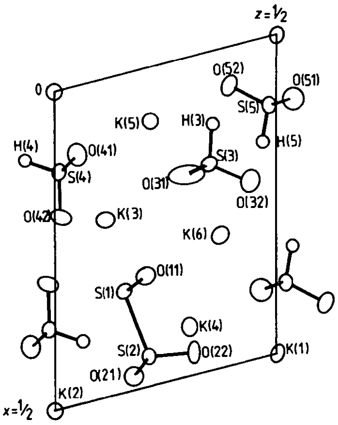

Fig. 2. Projection of the structure down the b axis. The atom labels agree with those given in Table 1.

Table 2. *Some interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code: (i) $x, -y, z$; (ii) $x, 1-y, z$.

The disulfite ion

S(1)–S(2)	2·226 (2)	O(11)–S(1)–O(11$^{\mathrm{i}}$)	110·5 (1)
S(1)–2O(11)	1·489 (3)	O(11)–S(1)–S(2)	98·9 (1)
S(2)–2O(21)	1·463 (3)	O(21)–S(2)–O(21$^{\mathrm{i}}$)	112·3 (1)
S(2)–O(22)	1·462 (4)	O(21)–S(2)–O(22)	112·5 (1)
		O(21)–S(2)–S(1)	106·7 (1)
		O(22)–S(2)–S(1)	105·5 (2)

The hydrogensulfite ions

	Uncorrected	Riding-motion model		
S(3)–2O(31)	1·422 (4)	1·476 (4)	H(3)–S(3)–O(31)	104·3 (13)
S(3)–O(32)	1·413 (6)	1·487 (6)	H(3)–S(3)–O(32)	109·6 (26)
S(3)–H(3)	1·31 (6)		O(31)–S(3)–O(31$^{\mathrm{ii}}$)	112·4 (1)
O(31)–O(31$^{\mathrm{ii}}$)	2·363		O(31)–S(3)–O(32)	112·8 (2)
O(31)–O(32)	2·362 (7)			
S(4)–2O(41)	1·457 (3)	1·472 (3)	H(4)–S(4)–O(41)	104·1 (19)
S(4)–O(42)	1·439 (5)	1·467 (5)	H(4)–S(4)–O(42)	110·8 (37)
S(4)–H(4)	1·16 (7)		O(41)–S(4)–O(41$^{\mathrm{i}}$)	111·8 (1)
O(41)–O(41$^{\mathrm{i}}$)	2·413		O(41)–S(4)–O(42)	112·7 (2)
O(41)–O(42)	2·410 (5)			
S(5)–2O(51)	1·448 (3)	1·465 (3)	H(5)–S(5)–O(51)	105·9 (13)
S(5)–O(52)	1·439 (5)	1·473 (5)	H(5)–S(5)–O(52)	106·6 (25)
S(5)–H(5)	1·16 (5)		O(51)–S(5)–O(51$^{\mathrm{i}}$)	111·7 (1)
O(51)–O(51$^{\mathrm{i}}$)	2·396		O(51)–S(5)–O(52)	113·0 (2)
O(51)–O(52)	2·408 (5)			

Coordination around K

K(1)–2O(22)	2·667 (4)	K(2)–4O(41)	2·765 (3)
K(1)–4O(51)	2·730 (3)	K(2)–4O(21)	3·002 (3)
K(3)–O(42)	2·755 (5)	K(4)–O(52)	2·757 (5)
K(3)–2O(11)	2·803 (3)	K(4)–2O(11)	2·771 (3)
K(3)–2O(41)	2·868 (3)	K(4)–2O(51)	2·862 (3)
K(3)–2O(31)	3·245 (5)	K(4)–2O(21)	2·969 (3)
K(3)–2O(42)	3·274 (2)	K(4)–2O(22)	3·069 (1)
K(5)–2O(21)	2·714 (3)	K(6)–2O(51)	2·788 (3)
K(5)–2O(31)	2·728 (4)	K(6)–2O(31)	2·848 (4)
K(5)–O(52)	2·789 (4)	K(6)–O(32)	2·874 (6)
K(5)–2O(41)	2·833 (3)	K(6)–2O(11)	2·971 (3)

The hydrogensulfite ion HSO_3^- has previously only been determined crystallographically in $CsHSO_3$ (Johansson, Lindqvist & Vannerberg, 1980), in which the HSO_3^- ion has $3m$ (C_{3v}) symmetry. *Ab initio* calculations on the HSO_3^- ion in the $CsHSO_3$ crystal (Strömberg, Gropen, Wahlgren & Lindqvist, 1983) show good agreement with the expermental data. A detailed discussion of the bonding within the HSO_3^- ion is given in this publication.

The three crystallographically different HSO_3^- ions in the present structure are located on the mirror plane. The average S—O distances for the three ions are 1·419 (3), 1·451 (2), and 1·445 (2) Å, respectively, compared with the 1·454 (2) Å found in $CsHSO_3$ (Johansson, Lindqvist & Vannerberg, 1980). One of the HSO_3^- ions exhibits significantly shortened S—O bonds as a result of the large thermal motion of O(31) and O(32). The distances were corrected using the riding-motion model (Busing & Levy, 1964; Busing, Martin &

Levy, 1964). The values so obtained are presented in Table 2 together with the uncorrected values. The differences between the groups did not persist after the correction, but the new values seem somewhat overcorrected. Minimum corrections, based on the individual atomic motions only, gave average S—O distances of 1·440 (4), 1·455 (4), and 1·450 (4) Å for the three groups respectively. Also, this correction cancels the differences, and thus it may be concluded that the short S—O distances in one of the HSO_3^- ions are vibration artefacts.

The three H—S bond lengths are not significantly different according to the significance test of Hamilton (1964). As expected the values refined in this X-ray study are less than that of 1·345 (11) Å found in the neutron diffraction work on $CsHSO_3$ (Johansson & Lindqvist, 1980). The three H atoms in $K_5(HSO_3)_3(S_2O_5)$ have O neighbors at distances H(3)—O(22) 2·92 (6), H(4)—O(21) 2·63 (6), and H(5)—O(32) 2·43 (5) Å, with corresponding S—H—O angles of 165 (4), 136 (2), and 136 (3)°. This implies that only very weak or no hydrogen bonding at all exists in the structure.

The authors are indebted to Dr Rita Hazell at the Division of Inorganic Chemistry of Aarhus University, Denmark for performing the calculations on the thermal motion corrections of the distances.

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Structure de l'Octasulfure de Pentaindium et de Potassium, In_5KS_8

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(*Reçu le* 21 *juin* 1982, *accepté le* 3 *février* 1983)

Abstract. $M_r = 869{\cdot}7$, monoclinic, $B2/m$, $a = 19{\cdot}054\ (4)$, $b = 9{\cdot}213\ (2)$, $c = 3{\cdot}8463\ (4)$ Å, $\gamma = 103{\cdot}27\ (2)°$, $V = 657{\cdot}2\ (3)$ Å^3, $Z = 2$, $D_m = 4{\cdot}3$, $D_x = 4{\cdot}4$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}0$ mm^{-1}, $F(000) = 784$, $T = 293$ K, $R = 0{\cdot}027$ for 1214 reflexions. The In atoms are in fourfold or sixfold coordination. The K atom is in sixfold prismatic coordination.

Introduction. Un mélange d'oxyde d'indium et de carbonate acide de potassium dans la proportion de cinq molécules de In_2O_3 pour deux molécules de $KHCO_3$ est sulfuré à 1073 K par un courant de sulfure d'hydrogène. Les monocristaux ainsi formés se présentent sous la forme de parallélipipèdes allongés de couleur jaune.

Partie expérimentale. L'étude a été effectué sur un monocristal ayant la forme d'une aiguille allongée parallèlement à **c**, 25 × 30 × 100 µm. Les extinctions systématiques correspondent aux groupes d'espace $B2$, Bm, ou $B2/m$. Le mode de préparation des mono-

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