

R_3 space), and (b) in terms of coordinates \bar{x} , \bar{y} and \bar{z} and the functions $u(\tau)$, $v(\tau)$ and $w(\tau)$. The origin is chosen as a symmetry center in R_4 . A possible symbol for this group might be $R_{3v2}\bar{3}^+e$.

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An X-ray Diffraction Study of Sodium Thiosulphate Pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

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A three-dimensional X-ray diffraction study of sodium thiosulphate pentahydrate was based on densitometer-measured photographic data. The structure was refined by full-matrix least squares to an R (excluding zero-weight data) of 0.082 for 1301 reflexions and an R (including zero-weight data) of 0.089 for 1359 reflexions. The Na–O distances range from 2.386 (6)–2.439 (7) Å for Na(1) octahedra and 2.331 (6)–2.418 (6) Å for Na(2) octahedra. In the tetrahedral $\text{S}_2\text{O}_3^{2-}$ anion the S–S and S–O bond lengths are 2.015 (3) and 1.455 (5)–1.490 (4) Å respectively. The hydrogen-bonding scheme described by previous workers is basically confirmed. The controversy over the O(8)–H(9) \cdots S(1*) bond seems to be clarified in this work.

Introduction

The crystal structure of sodium thiosulphate pentahydrate has been determined by Taylor & Beevers (1952) using two-dimensional X-ray diffraction intensity data. El Saffar (1968) has reported the positional parameters of H atoms deduced from his NMR studies. Padmanabhan *et al.* (1971) refined the above-mentioned crystal structure from two-dimensional neutron diffraction data and they basically confirmed the hydrogen-bonding scheme as proposed by Taylor & Beevers (1952) and El Saffar (1968), with the exception of atom H(9). Baur (1972) suggests that this disagreement needs clarification. Manojlović-Muir (1975) has claimed that the differences in bond distances in $\text{S}_2\text{O}_3^{2-}$ ions may be attributed to the thermal vibrations of the atoms in the ion.

In view of this, we have undertaken this three-dimensional work as part of a project in which the effects of the environment and thermal vibration on bonding in the $\text{S}_2\text{O}_3^{2-}$ ion in several ionic thiosulphates are being examined.

Experimental

A crystal of hexagonal prismatic habit was cut and ground into a cylinder 0.135 mm in diameter and 0.6 mm in length, so that the cylinder axis corresponded to the [100] axis. All the X-ray data were collected with this crystal.

Crystal data

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, FW 248.2. Monoclinic, space group $P2_1/c$, $a = 5.941$, $b = 21.570$, $c = 7.525$ Å, $\beta = 103^\circ 55'$, $Z = 4$ (Taylor & Beevers, 1952; Padmanabhan *et al.*, 1971). The linear absorption coefficient for Cu $K\alpha$ radiation was found to be 59.7 cm^{-1} .

Intensity measurement

With Cu $K\alpha$ radiation and Weissenberg equi-inclination techniques, multiple-film exposures were taken of the layers $0 \leq h \leq 5$. The intensities of all the reflexions were measured photometrically with a Joyce–Loebl microdensitometer. Of the possible 1764 reflexions, 1359 were classified as observed, and about

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350 were discarded because they were on or near white-radiation streaks and had a very low intensity level. The remaining reflexions (~50) were already systematically absent.

The intensities were corrected for Lorentz, polarization (Zalkin, 1967) and absorption (Alcock, 1975) effects with the IBM 360/40 computer.

Refinement of the structure

The initial structural model involving the non-hydrogen atoms only was that of Taylor & Beevers. The structure was refined by full-matrix least squares with *LALS* (Zalkin, 1968). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. A weighting scheme of the form $w = 1/(A + B|F_o| + C|F_o|^2)$ (Cruickshank, 1965) was used. *A*, *B* and *C* were varied slightly during the refinement in order to give a satisfactory constancy to $\sum w\Delta^2$ for the amplitudes in various groups. In the last cycle of the refinement, *A*, *B* and *C* were 0.358, -0.327 and 0.0030 respectively. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Table 1. Coordinates ($\times 10^3$) and isotropic temperature factors ($\times 10$) with standard deviations for hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	496 (4)	216 (2)	94 (3)	33 (3)
H(2)	738 (4)	208 (2)	153 (2)	26 (3)
H(3)	100 (4)	276 (3)	235 (3)	23 (3)
H(4)	100 (4)	300 (2)	401 (3)	38 (3)
H(5)	630 (4)	330 (2)	390 (3)	37 (3)
H(6)	768 (4)	395 (2)	439 (3)	42 (4)
H(7)	875 (4)	491 (2)	202 (3)	41 (4)
H(8)	830 (4)	460 (2)	10 (3)	29 (2)
H(9)	760 (4)	48 (2)	218 (3)	26 (2)
H(10)	486 (4)	42 (2)	197 (3)	36 (3)

Starting positional and individual isotropic thermal parameters of all atoms, except H, led to an *R* (including zero-weight data) of 0.32 and an *R_w* of 0.19, where $R = \sum w\Delta/\sum |F_o|$ and $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$.

Eight cycles of refinement, with positional parameters and isotropic thermal parameters for the non-hydrogen atoms, reduced *R* to 0.13 and *R_w* to 0.13. At this stage, unlike Padmanabhan *et al.* (1971), we found evidence of extinction and the 25 severely extinction-affected reflexions were corrected for extinction effects (Aydin Uraz & Armağan, 1975) as described by Zachariasen (1967) and Killean, Lawrence & Sharma (1972). With these extinction-corrected structure amplitudes in two cycles of isotropic refinement, *R* and *R_w* reduced to 0.10 and 0.11 respectively.

A three-dimensional difference Fourier synthesis with structure factors not including the contributions of the H atoms was calculated at the end of this refinement and all the H atoms were found in plausible positions (Table 1). The standard deviations of the H atom positional parameters were calculated on the basis of a Fourier synthesis (Stout & Jensen, 1968). Further refinement cycles with anisotropic temperature factors for non-hydrogen atoms and isotropic for H atoms reduced *R* (excluding zero-weight data) to 0.082 for 1301 reflexions, *R* (including zero-weight data) to 0.089 for 1359 reflexions and *R_w* to 0.097. For these last cycles, all the atoms except H were included in the refinement. The positional parameters of the H atoms were those found from a three-dimensional difference synthesis. The individual isotropic thermal parameters of Padmanabhan *et al.* were assigned to the H atoms. The final coordinates and thermal parameters and their estimated standard deviations for the non-hydrogen atoms are given in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32245 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final coordinates ($\times 10^5$) and anisotropic thermal parameters ($\times 10^6$) with standard deviations for non-hydrogen atoms

Thermal parameters are of the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	10178 (23)	6814 (5)	10662 (16)	141 (5)	7 (1)	76 (3)	-2 (1)	28 (4)	-3 (1)
S(2)	14786 (20)	14142 (5)	27772 (15)	73 (1)	7 (1)	54 (2)	-1 (1)	22 (4)	1 (1)
Na(1)	72384 (38)	34131 (9)	7478 (29)	97 (7)	11 (1)	92 (4)	-1 (2)	41 (8)	1 (2)
Na(2)	25429 (38)	40849 (9)	21526 (32)	122 (8)	10 (1)	131 (5)	-1 (2)	18 (8)	3 (2)
O(1)	33656 (75)	12729 (19)	43600 (54)	139 (15)	16 (1)	78 (8)	-3 (5)	64 (15)	7 (4)
O(2)	93402 (72)	15324 (19)	33392 (56)	118 (15)	17 (1)	98 (8)	15 (5)	98 (15)	9 (4)
O(3)	20221 (69)	19585 (16)	17342 (52)	181 (15)	7 (1)	96 (8)	-11 (5)	80 (15)	2 (3)
O(4)	62227 (72)	23495 (18)	9812 (60)	156 (15)	11 (1)	142 (9)	-7 (5)	24 (17)	14 (4)
O(5)	9200 (71)	31383 (16)	27783 (52)	165 (14)	9 (1)	92 (8)	16 (5)	49 (15)	-4 (3)
O(6)	61606 (71)	36777 (18)	35740 (55)	131 (15)	13 (1)	99 (8)	3 (5)	3 (15)	7 (4)
O(7)	86410 (74)	44796 (18)	10971 (56)	181 (15)	10 (1)	104 (8)	12 (5)	38 (15)	2 (4)
O(8)	64610 (74)	1518 (18)	24596 (61)	124 (14)	12 (1)	145 (9)	-1 (5)	66 (16)	12 (4)

Discussion of the structure

The crystal structure, built of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions and water molecules, was discussed in some detail by Taylor & Beevers, and Padmanabhan *et al.* The coordinates of the non-hydrogen atoms of the present work differed at most by 0.27 and 0.28 Å from those of the previous X-ray and neutron work respectively.

Environment of the Na atoms

As shown by previous workers, coordination polyhedra for Na atoms can be described as distorted octahedra. Interatomic distances in these coordination octahedra (Table 3) reveal all the expected features, but the spread in the distances of the present coordination groups is found to be considerably less than those reported. In the Na(1) case, O—Na distances lie between 2.386 (6) and 2.439 (7) Å, whereas the same distances, in the earlier X-ray and neutron works, were 2.38 to 2.53 Å and 2.25 to 2.64 Å respectively. Na—O distances lie between 2.331 (6) and 2.418 (6) Å in the Na(2) coordination group and are in close agreement with those obtained by Taylor & Beevers and considerably different from those obtained by Padmanabhan *et al.* The Na octahedra are linked by edge-sharing, and thus form continuous columns along the [100] axis. Such edge-sharing octahedral columns are found in the structures of other hydrated Na salts, *e.g.* sodium sulphate decahydrate (Ruben, Templeton, Rosenstein & Olovsson, 1961), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Morimoto, 1956), and sodium chlorite trihydrate (Tarimci, Schempp & Chang, 1975). Average Na—O distances in these structures are 2.43, 2.42 and 2.409 (1) Å respectively. In the present work, the average Na—O distance for the Na(1) octahedron is 2.418 (6) Å, which is in excellent agreement with those mentioned above. For the Na(2) case, agreement is poor, perhaps because of the presence of S in the group.

The structure of the thiosulphate ion

The geometry and bonding in the $\text{S}_2\text{O}_3^{2-}$ ion (Table 4) are similar to those observed in two other ionic thiosulphates: $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Manojlović-Muir, 1975) and

Table 4. *Geometry of the thiosulphate group*

S(1)—S(2)	2.015 (3) Å	O(1)—S(2)—O(3)	111.9 (3)°
S(2)—O(1)	1.458 (5)	O(1)—S(2)—O(2)	110.7 (3)
S(2)—O(2)	1.455 (5)	O(2)—S(2)—O(3)	109.3 (2)
S(2)—O(3)	1.490 (4)	S(1)—S(2)—O(1)	108.5 (2)
		S(1)—S(2)—O(2)	109.2 (2)
		S(1)—S(2)—O(3)	107.2 (2)

$\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (Baggio, Amzel & Becka, 1969). The bond angles at the central S vary from 107.2 (2) to 111.9 (3)°, and reveal only slight distortions from ideal tetrahedral symmetry, which is the striking feature of previous work on $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. As pointed out by Manojlović-Muir, bond lengths indicate considerable π -bonding character in both S—O and S—S bonds. The S—O distances [1.455 (5)–1.490 (4) Å] are in agreement with those in the Ba [1.472 (3)–1.483 (3) Å] and Mg [1.465 (5)–1.471 (5) Å] salts. The S—S distance of 2.015 (3) Å is the second striking feature in comparison with earlier work on the same compound. This bond length is significantly greater than that of 1.979 (3) Å in the Ba salt; on the other hand, it is in excellent agreement with the value of 2.013 (3) Å in the Mg salt.

The hydrogen bonding

The hydrogen-bonding scheme described by Taylor & Beevers, Padmanabhan *et al.* and El Saffar is basically confirmed in this three-dimensional work, within the limits mentioned by Baur (1972). The O—H distances in O—H...O bonds are between 0.77 (3) and 0.96 (3) Å; on the other hand O—H distances in O—H...S bonds are 1.04 (3)–1.15 (4) Å. The first type of O—H distance can be considered as normal because the observed O—H distances from X-ray determinations tend to be 0.1 to 0.2 Å shorter than those from neutron diffraction. An explanation of the observed longer O—H and shorter H—S distances of the O—H...S hydrogen bonds with respect to those obtained by neutron work awaits further work. Within the limitations of X-ray studies, the H—O—H angles [94 (3)–109 (3)°] can be considered as normal. The controversy over the O(8)—H(9)...S(1*) bond seems to be clarified. The parameters obtained in this work revealed values of 3.333 (6) and 2.42 (2) Å for O(8)—S(1*) and H(9)—S(1*) respectively; these are in excellent agreement with those calculated by Baur [3.25 and 2.42 Å]. The reason for this may not be the new atomic site for H(9) as predicted by Baur, but the high accuracy of the atomic parameters for S(1) and O(8) found in this three-dimensional work. The reasonable value of 147 (3)° for the angle O(8)—H(9)...S(1*) also supports the claim that H(9) takes part in hydrogen bonding.

Table 3. *Interatomic distances in the coordination groups around sodium atoms*

Na(1)—O(1)	2.386 (6) Å	Na(2)—S(1)	3.322 (5) Å
Na(1)—O(2)	2.439 (5)	Na(2)—O(1)	2.397 (5)
Na(1)—O(4)	2.390 (7)	Na(2)—O(5)	2.354 (6)
Na(1)—O(5)	2.422 (6)	Na(2)—O(6)	2.331 (6)
Na(1)—O(6)	2.432 (5)	Na(2)—O(7)	2.418 (6)
Na(1)—O(7)	2.439 (7)	Na(2)—O(8)	2.377 (7)

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The Crystal Structure of Chromium Thiophosphate, CrPS₄

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Chromium thiophosphate, CrPS₄, is monoclinic with $a = 10.871(2)$, $b = 7.254(2)$, $c = 6.140(2)$ Å, $\beta = 91.88(4)^\circ$, $V = 483.9(4)$ Å³, space group $C2$ and $Z = 4$. The crystal structure has been determined by Fourier methods from the X-ray intensities of 911 independent reflexions measured on a four-circle automatic single-crystal diffractometer, and refined to $R = 0.019$. It is characterized by puckered hexagonally close-packed sulphur layers stacked parallel to (100) with Cr in octahedral and P in tetrahedral interstices. CrPS₄ is the first metal thiophosphate with the metal atom in octahedral sulphur coordination.

Introduction

Metal phosphorus sulphides of compositional type M_xPS_4 (x values so far known are 1.0, 1.5, 3.0) must be looked upon as thiophosphates. The determinations of the crystal structures of BPS₄ (Weiss & Schaefer, 1963), AlPS₄ (Weiss & Schaefer, 1960), GaPS₄ (Buck & Carpentier, 1973), InPS₄ (Carpentier, Diehl & Nitsche, 1970), BiPS₄ (Zimmerman, Carpentier & Nitsche, 1975), Pd₃(PS₄)₂ (Bither, Donohue & Young, 1971) and Cu₃PS₄ (Ferrari & Cavalca, 1948) have shown that the tetrahedral PS₄ group is a common feature of all M_xPS_4 compounds so far studied. This class of compounds has gained interest not only because of its manifold crystal chemistry but also for potential

applications in solid-state devices since many of the compounds crystallize in non-centrosymmetric space groups.

A new metal thiophosphate with $M = Cr$ and $x = 1.0$ has recently been synthesized. To obtain further information on the crystal chemistry of thiophosphates the crystal structure of CrPS₄ has been investigated by X-ray diffraction methods.

Experimental

CrPS₄ was synthesized from powdered stoichiometric amounts of the elements in evacuated quartz ampoules at a temperature of 700°C. Reaction velocity was enhanced by adding 5 mg of iodine per cm³ of the tube volume. Black, lustrous single crystals were obtained by chemical transport in a temperature gradient from

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