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Sodium Thiosulfate Pentahydrate: A Redetermination by Neutron Diffraction*

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Abstract. $Na_2S_2O_3.5H_2O$, monoclinic, $P2_1/c$, $Z = 4$. Cell parameters at 25 ± 2°C, $a = 5{\cdot}9522\,(9)$, $b = 21{\cdot}618\,(6)$, $c = 7{\cdot}543\,(3)$ Å, $\beta = 103{\cdot}804\,(24)°$, were determined by least-squares refinement from the first moments of 40 neutron diffraction Bragg reflections; $\lambda = 1{\cdot}0155$ Å based on NaCl $a_0 = 5{\cdot}64037$ Å. The structure was refined from 2109 symmetry-independent structure-factor squares. All H atom positions and anisotropic thermal parameters were precisely determined. Conclusions of a recent X-ray study [Uraz & Armağan (1977). *Acta Cryst.* B**33**, 1396–1399] are confirmed.

Introduction. Single-crystal neutron diffraction measurements were collected from an 11 mm^3 specimen on the Oak Ridge automatic neutron diffractometer by means of 2θ scans for which backgrounds were measured at the end points of the scans. Neutrons with $\lambda = 1{\cdot}0155$ Å were selected by reflection from the (110) planes of a single crystal of beryllium at a scattering angle of 52·5°. The data set of 2283 integrated reflections (152 of which were reference measurements repeated periodically) was reduced after averaging replicates and equivalents to 2109 symmetry-independent structure factors and standard errors in the usual manner. The absences of space group $P2_1/c$ ($h0l$ with l odd, $0k0$ with k odd) were confirmed. Absorption corrections computed by Gaussian integration, $\mu = 0{\cdot}1879$ mm^{-1}, ranged between 1·43 and 1·33. The structure parameters were refined by the full-matrix least-squares procedure starting with the parameters given by Padmanabhan *et al.* (1971). Final discrepancy indices were as follows:

	Reflections	R_F	R_{F^2}	R_{wF^2}	σ_1
All data	2109	0·087	0·061	0·085	1·05
$F^2 > \sigma(F^2)$	1655	0·055	0·054	0·072	1·01.

The parameters adjusted numbered 200 and included positional and anisotropic thermal parameters for all atoms, one scale multiplier for F_c and one isotropic extinction coefficient (Coppens & Hamilton, 1970).

Table 1. *Fractional positional parameters* ($\times 10^4$) *for sodium thiosulfate pentahydrate*

	x	y	z
S(1)	1013 (5)	680 (1)	1070 (4)
S(2)	1476 (4)	1416 (1)	2779 (3)
Na(1)	7232 (4)	3412 (1)	743 (3)
Na(2)	2546 (4)	4084 (1)	2157 (3)
O(1)	3378 (3)	1278 (1)	4346 (2)
O(2)	9329 (3)	1532 (1)	3339 (2)
O(3)	2026 (3)	1953 (1)	1740 (2)
O(4)	6225 (3)	2345 (1)	988 (2)
O(5)	907 (3)	3136 (1)	2786 (2)
O(6)	6161 (3)	3678 (1)	3565 (2)
O(7)	8636 (3)	4480 (1)	1096 (2)
O(8)	6455 (3)	151 (1)	2459 (2)
H(1)	4817 (5)	2239 (1)	1339 (4)
H(2)	7410 (5)	2133 (1)	1871 (4)
H(3)	1364 (5)	2734 (1)	2453 (4)
H(4)	1078 (5)	3117 (1)	4087 (4)
H(5)	6100 (5)	3313 (2)	4287 (4)
H(6)	7498 (5)	3899 (2)	4222 (4)
H(7)	8499 (6)	4821 (2)	1879 (4)
H(8)	7912 (6)	4618 (1)	9874 (4)
H(9)	7491 (6)	367 (2)	1885 (5)
H(10)	4964 (6)	336 (2)	2039 (5)

For the most severe case the extinction multiplier for F_c^2 was 0·9465. Table 1 lists the atomic positional parameters.‡ Scattering lengths used, in cm $\times 10^{-13}$, were 2·847 for S, 3·620 for Na, 5·803 for O, and −3·74 for H.

Discussion. This work was completed before the appearance of the report of a three-dimensional X-ray study by Uraz & Armağan (1977), with which our results are in excellent agreement. In particular, pronounced disagreements with the earlier neutron diffraction study of Padmanabhan *et al.* (1971) are confirmed.

The H atoms have now been precisely located. Characteristics of the water molecules and the hydrogen bonds are presented in Table 2. Every H atom participates in hydrogen bonding, four of them binding

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33431 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Characteristics of hydrogen bonds and water molecules in sodium thiosulfate pentahydrate*

		Distances (Å)			Angles (°)		
O–H···*A*		O–H*	H···*A*	O···*A*	O–H···*A*	H–O–H	*A*···O···*A*
O(4)	H(1)···O(3)	0·965 (4)	1·864 (4)	2·822 (2)	171·7 (3)	103·7 (3)	99·44 (7)
	H(2)···O(2)	0·963 (4)	1·900 (4)	2·843 (2)	165·3 (3)		
O(5)	H(3)···O(3)	0·962 (3)	1·843 (3)	2·803 (2)	176·0 (3)	105·0 (3)	102·52 (6)
	H(4)···O(3)	0·963 (3)	1·951 (3)	2·903 (2)	169·4 (3)		
O(6)	H(5)···O(4)	0·964 (4)	1·905 (4)	2·863 (2)	172·1 (3)	104·8 (3)	94·67 (7)
	H(6)···S(1)	0·958 (4)	2·399 (4)	3·351 (3)	172·1 (3)		
O(7)	H(7)···S(1)	0·960 (4)	2·390 (4)	3·337 (3)	168·4 (3)	105·4 (3)	110·05 (7)
	H(8)···O(8)	0·967 (4)	1·889 (4)	2·855 (2)	177·4 (3)		
O(8)	H(9)···S(1)	0·956 (4)	2·418 (5)	3·336 (3)	160·8 (3)	107·1 (3)	125·52 (9)
	H(10)···S(1′)	0·956 (4)	2·408 (4)	3·359 (3)	172·8 (3)		

* Uncorrected for thermal motion effects.

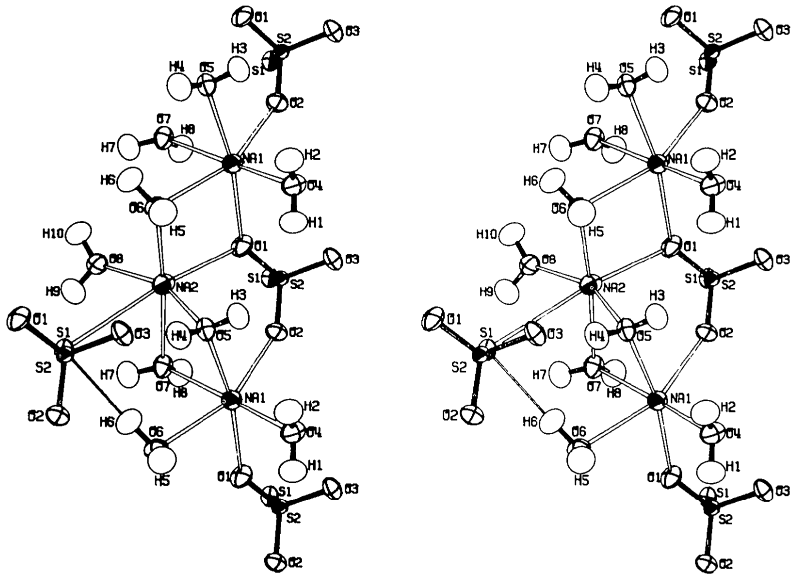

Fig. 1. A portion of a chain of hydrated sodium ions. **a** is vertical, positive upward.

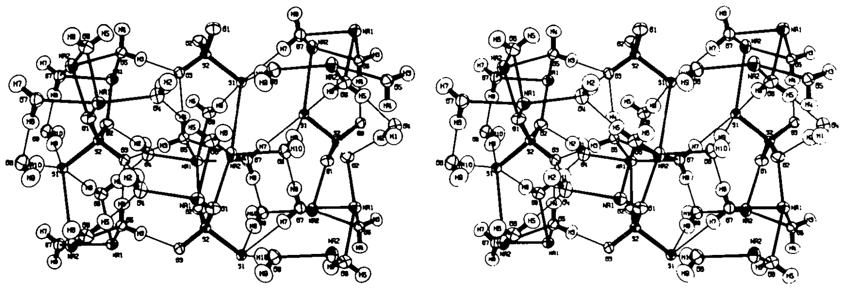

Fig. 2. A portion of the structure viewed approximately along the chain direction. **b** is horizontal, positive to the right, and **c** is vertical, positive upward.

to the peripheral S(1) of the thiosulfate group. The O—H distances for the hydroxyl groups bonded to S are the shortest in the structure; they average 0·958 Å, a value identical with the bond length in the gaseous water molecule. The remaining hydrogen atoms have O—H distances averaging 0·964 Å, the slightly longer link reflecting a stronger hydrogen bond to acceptor O than to S.

Table 3. *Distances* (Å) *and angles* (°) *in the coordination polyhedra of the sodium ions*

Na(1)–O(1)	2·380 (3)	Na(2)–O(1)	2·420 (3)
Na(1)–O(2)	2·437 (3)	Na(2)–O(5)	2·366 (3)
Na(1)–O(4)	2·402 (3)	Na(2)–O(6)	2·332 (3)
Na(1)–O(5)	2·430 (3)	Na(2)–O(7)	2·429 (3)
Na(1)–O(6)	2·432 (3)	Na(2)–O(8)	2·381 (3)
Na(1)–O(7)	2·448 (3)	Na(2)–S(1)	3·330 (4)
O(1)–Na(1)–O(2)	105·5 (1)	O(1)–Na(2)–O(5)	94·3 (1)
O(1)–Na(1)–O(4)	94·1 (1)	O(1)–Na(2)–O(6)	85·3 (1)
O(1)–Na(1)–O(5)	167·4 (1)	O(1)–Na(2)–O(7)	101·9 (1)
O(1)–Na(1)–O(6)	84·0 (1)	O(1)–Na(2)–O(8)	108·8 (1)
O(1)–Na(1)–O(7)	92·9 (1)	O(1)–Na(2)–S(1)	169·3 (1)
O(2)–Na(1)–O(4)	106·6 (1)	O(5)–Na(2)–O(6)	87·8 (1)
O(2)–Na(1)–O(5)	86·6 (1)	O(5)–Na(2)–O(7)	87·9 (1)
O(2)–Na(1)–O(6)	158·0 (1)	O(5)–Na(2)–O(8)	156·5 (1)
O(2)–Na(1)–O(7)	79·2 (1)	O(5)–Na(2)–S(1)	75·0 (1)
O(4)–Na(1)–O(5)	85·3 (1)	O(6)–Na(2)–O(7)	171·9 (1)
O(4)–Na(1)–O(6)	92·1 (1)	O(6)–Na(2)–O(8)	97·6 (1)
O(4)–Na(1)–O(7)	169·2 (1)	O(6)–Na(2)–S(1)	94·1 (1)
O(5)–Na(1)–O(6)	83·5 (1)	O(7)–Na(2)–O(8)	83·7 (1)
O(5)–Na(1)–O(7)	86·0 (1)	O(7)–Na(2)–S(1)	78·1 (1)
O(6)–Na(1)–O(7)	80·6 (1)	O(8)–Na(2)–S(1)	81·8 (1)

Table 4. *Distances* (Å) *and angles* (°) *in the thiosulfate ion*

S(2)–S(1)	2·024 (4)	S(1)–S(2)–O(1)	108·5 (2)
S(2)–O(1)	1·459 (3)	S(1)–S(2)–O(2)	108·9 (2)
S(2)–O(2)	1·461 (3)	S(1)–S(2)–O(3)	107·0 (2)
S(2)–O(3)	1·481 (3)	O(1)–S(2)–O(2)	111·4 (2)
		O(1)–S(2)–O(3)	111·2 (2)
		O(2)–S(2)–O(3)	109·7 (2)

A chain of edge-sharing octahedra around Na ions extending along **a** is illustrated in Fig. 1. The cross-linking to neighboring chains, through thiosulfate ion coordination and water molecule hydrogen bonding, is shown in Fig. 2. Tables 3 and 4 present distances and angles in the coordination octahedra about the Na ions and in the thiosulfate tetrahedron respectively. All are in good agreement with the recent X-ray study (Uraz & Armağan, 1977).

The differences in parameter values between this study and the X-ray refinement were analyzed by means of normal probability plots (*International Tables for X-ray Crystallography*, 1974). For the 36 position parameters for the non-hydrogen atoms only, the weighted differences fit very well a straight line of slope 1·18 passing nearly through the origin, indicating that, although the combined standard errors were estimated too small by 18%, there was no evidence of other significant systematic discrepancies. For the 36 diagonal elements of the anisotropic temperature-factor coefficients, the values from the X-ray study are clearly smaller than those of the neutron study. Multiplying factors k estimated by the method of least squares to minimize $\sum(\beta_N - k\beta_X)^2$ are 1·22 for the coefficients β_{11}, 1·17 for β_{22}, and 1·09 for β_{33}. After the X-ray values had been thus adjusted, the normal probability plot indicated no further disagreement. The non-diagonal coefficients were not included in this comparison; however, the only evident discrepancy is the apparent omission of a minus sign on β_{13} for atom O(1).

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