

Neutron 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 single-crystal neutron-diffraction investigation of sodium thiosulphate pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, has been made with three sets of zonal data. The structure was refined by least-squares techniques, with individual temperature factors, to an R value of 8.2%. The geometry of the S_2O_3 group and sodium-oxygen framework agree with those of X-ray studies. The positional parameters of some of the atoms differ from those postulated from the X-ray and nuclear magnetic resonance studies. The O-H and H-H bond distances and the H-O-H valence angle of all the five water molecules were found to be normal. The hydrogen-bond scheme falls into four classes: two strong water-thiosulphate oxygen, two weak water-thiosulphate oxygen, two water-water, and three water-sulphur hydrogen bonds. From the geometry of its surroundings one of the hydrogen atoms H(9) may be regarded as not participating in hydrogen bonding.

Introduction

The crystal structure of sodium thiosulphate pentahydrate has been determined by Taylor & Beevers (1952) using X-ray diffraction techniques. Large differences in the S-O distances were reported and these were ascribed to the possible errors in the positional parameters of the oxygen atoms. From nuclear magnetic resonance studies El Saffar (1968) has reported the parameters of the hydrogen atoms. These atomic parameters support the hydrogen bonding scheme suggested earlier by Taylor & Beevers. The present study by neutron diffraction techniques was undertaken to check the discrepancy in the S-O distances and the hydrogen bonding scheme in the crystal.

Experimental

Crystals of sodium thiosulphate pentahydrate can be grown easily by slow evaporation from solution. The space group $P2_1/c$, and unit-cell dimensions $a=5.941$, $b=21.570$, $c=7.530$ Å, $\beta=103^\circ 58'$, $Z=4$, which were determined by X-ray and neutron diffraction are in agreement with previous X-ray results. For each of the three zones a crystal was cut and ground into a cylinder of about 1.5 mm diameter and approximately 5 mm in length, so that the axis of the cylinder corresponded to the zone axis. The integrated intensities of 350 $h0l$, $hk0$ and $0kl$ reflexions were measured on the instruments at the Cirrus reactor, Trombay, and Diliman city. The crystal angles were set by hand and the intensity recorded by step scanning through the peak in the $\theta-2\theta$ mode. There was no evidence of extinction effects.

The intensities were corrected for absorption, and a set of observed structure factors with weights for each reflexion was obtained as described in an earlier paper (Padmanabhan, Mehdi Ali & Srikanta, 1965).

Analysis of data

The pattern of hydrogen bonding has been indicated by Taylor & Beevers. In this pattern, since every hydrogen atom is involved in a hydrogen bond, it was easy to calculate the approximate coordinates for the hydrogen atoms. Thus the structure of Taylor & Beevers and the n.m.r. work of El Saffar provided a complete set of coordinates. Structure factors were calculated with these parameters and nuclear scattering amplitudes 0.35, 0.28, 0.58 and -0.38 (10^{-12}cm) for Na, S, O and H respectively. Using these signs and observed structure amplitudes, nuclear density projections were drawn on the (100) and (001) planes to locate the positions of the hydrogen atoms. These parameters together with individual isotropic temperature factors were refined by the method of least-squares with the CDC 3600 computer using the program of Busing & Levy (1962). The R index based on F was 0.086 and the weighted R was 0.082. The values of the refined parameters and their standard deviations are compared with those obtained by X-ray and n.m.r. methods in Table 1.

Discussion

From the point of view of molecular geometry, the description of the S_2O_3 group and the sodium-oxygen framework are in reasonable agreement with those of Taylor & Beevers. From the point of view of parameter statistics there are significant differences between our coordinates and those of the X-ray and n.m.r.

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Table 1. *Atomic parameters and temperature factors*

		Taylor & Beavers	El Saffar	This work	Standard deviation	Temperature factor
S(1)	x	0.104	—	0.089	0.001	1.62 ± 0.13
	y	0.069	—	0.065	0.001	
	z	0.109	—	0.102	0.002	
S(2)	x	0.145	—	0.148	0.002	1.26 ± 0.14
	y	0.142	—	0.137	0.001	
	z	0.275	—	0.261	0.002	
Na(1)	x	0.695	—	0.703	0.002	1.23 ± 0.13
	y	0.342	—	0.339	0.001	
	z	0.074	—	0.078	0.002	
Na(2)	x	0.242	—	0.236	0.002	1.81 ± 0.13
	y	0.409	—	0.399	0.001	
	z	0.209	—	0.191	0.002	
O(1)	x	0.323	—	0.337	0.002	2.20 ± 0.13
	y	0.122	—	0.140	0.002	
	z	0.433	—	0.425	0.001	
O(2)	x	0.889	—	0.946	0.001	1.93 ± 0.14
	y	0.153	—	0.151	0.002	
	z	0.342	—	0.329	0.002	
O(3)	x	0.194	—	0.201	0.002	1.62 ± 0.14
	y	0.195	—	0.195	0.001	
	z	0.183	—	0.178	0.001	
O(4)	x	0.597	—	0.605	0.002	1.82 ± 0.16
	y	0.234	—	0.233	0.002	
	z	0.117	—	0.094	0.001	
O(5)	x	0.099	—	0.079	0.001	1.90 ± 0.14
	y	0.311	—	0.310	0.002	
	z	0.284	—	0.294	0.001	
O(6)	x	0.606	—	0.624	0.002	2.21 ± 0.13
	y	0.369	—	0.365	0.002	
	z	0.358	—	0.362	0.001	
O(7)	x	0.838	—	0.863	0.002	1.92 ± 0.13
	y	0.445	—	0.453	0.001	
	z	0.117	—	0.113	0.001	
O(8)	x	0.629	—	0.648	0.001	1.62 ± 0.13
	y	0.014	—	0.017	0.001	
	z	0.250	—	0.250	0.002	
H(1)	x	—	0.446	0.462	0.003	3.31 ± 0.32
	y	—	0.220	0.224	0.002	
	z	—	0.135	0.135	0.003	
H(2)	x	—	0.715	0.733	0.003	2.62 ± 0.26
	y	—	0.207	0.206	0.002	
	z	—	0.198	0.156	0.003	
H(3)	x	—	0.148	0.127	0.003	2.31 ± 0.25
	y	—	0.271	0.271	0.002	
	z	—	0.247	0.253	0.003	
H(4)	x	—	0.114	0.104	0.003	3.81 ± 0.34
	y	—	0.310	0.311	0.002	
	z	—	0.416	0.420	0.003	
H(5)	x	—	0.592	0.613	0.003	3.72 ± 0.33
	y	—	0.335	0.325	0.003	
	z	—	0.432	0.408	0.003	
H(6)	x	—	0.746	0.694	0.004	4.21 ± 0.38
	y	—	0.392	0.397	0.003	
	z	—	0.421	0.434	0.002	
H(7)	x	—	0.848	0.802	0.003	4.10 ± 0.40
	y	—	0.482	0.478	0.002	
	z	—	0.194	0.191	0.003	

Table 1 (*cont.*)

		Taylor & Beevers	El Saffar	This work	Standard deviation	Temperature factor
H(8)	<i>x</i>	—	0.771	0.794	0.002	2.94 ± 0.22
	<i>y</i>	—	0.463	0.454	0.002	
	<i>z</i>	—	0.995	0.993	0.003	
H(9)	<i>x</i>	—	0.752	0.768	0.002	2.62 ± 0.22
	<i>y</i>	—	0.019	0.046	0.002	
	<i>z</i>	—	0.203	0.291	0.003	
H(10)	<i>x</i>	—	0.480	0.495	0.004	3.61 ± 0.32
	<i>y</i>	—	0.019	0.031	0.002	
	<i>z</i>	—	0.195	0.190	0.003	

work. A difference of about 0.38 Å was observed between the X-ray and neutron coordinates of one of the oxygen atoms of the S₂O₃ group, namely O(2). The S–O distances in the X-ray work showed large differences of 1.40 to 1.56 Å and these large variations were attributed by Taylor & Beevers to the possible errors in the positional parameters of the oxygen atoms. In the neutron study the S–O distances are 1.45–1.47 Å and compare well with the S–O distances, 1.465–1.471 Å, observed in MgS₂O₃ · 6H₂O by Baggio, Amzel & Becka (1969). Taylor & Beevers reported *R* values of 0.31, 0.29 and 0.26 for the three axial zones. In our case, the final *R* value was 0.086 and hence we think our coordinates are correct. The final parameter shift was less than one tenth of the standard error for every parameter. The goodness of fit, $\sum \omega(F_o^2 - F_c^2)^2 / np$ (where ω is the weight of an observation F_o , n is the total number of observations, p is the number of parameters), which should be unity when observational errors are randomly distributed and correctly estimated and the model is correct, was 1.16. The two sodium atoms have a distorted octahedral coordination. In the case of Na(1) this consists of four water and two thiosulphate oxygen atoms at distances of 2.25 to 2.64 Å and bond angles at the sodium atom ranging from 79.2 to 104.4° (Table 2). The other sodium atom is surrounded by a group of one thiosulphate oxygen atom, four water oxygen atoms and the external sulphur atom of the thiosulphate group, with sodium to oxygen distances of 2.34 to 2.62 Å and with a sodium to sulphur distance of 3.49 Å. The bond angles at this

sodium atom range from 74.3 to 102.1°. These octahedra form continuous linked chains parallel to the *a* axis by sharing edges. A projection of the structure along the *a* axis is shown in Fig. 1.

Hydrogen bonding

The bond lengths and bond angles of the five water molecules are listed in Table 3. The distances in the water molecules of 0.92 to 0.98 Å (uncorrected for thermal vibration) and angles of 106.2 to 109.8°, appear to be normal. The mean H–H distance is 1.58 Å, but the individual values are more widely scattered from 1.51 to 1.67 Å. The hydrogen bonding is nearly symmetrical on the two sides of the water molecules H(1)–O(4)–H(2), H(3)–O(5)–H(4) and H(9)–O(8)–H(10). Following the classification scheme of Chidambaram, Sequeira & Sikka (1964), the lone-pair coordination is of type *A*, for the water molecules H(3)–O(5)–H(4), H(5)–O(6)–H(6) and H(7)–O(7)–H(8) (the two electron lone-pairs are directed towards two monovalent metal ions), type *G* for the water molecule H(1)–O(4)–H(2) (one of the lone pairs of electrons is directed towards a monovalent metal ion and the other pair towards a monovalent bond donor group), and type *E* for the water molecule H(9)–O(8)–H(10) (the two lone pairs directed toward two H-bond donor groups). Associated angles for each water oxygen atom are listed in the last column of Table 3. There seems to be no correlation between the magnitude of the angles H–O–H and associated angles.

Table 2. *Interatomic distances and angles*

S ₂ O ₃ group			
S(1)–S(2)	1.95 (0.02) Å	O(1)–S(2)–O(3)	102.2 (1.5)°
S(2)–O(1)	1.46	O(1)–S(2)–O(2)	112.1
S(2)–O(2)	1.45	O(2)–S(2)–O(3)	106.5
S(2)–O(3)	1.47	S(1)–S(2)–O(1)	116.3
		S(1)–S(2)–O(2)	109.3
		S(1)–S(2)–O(3)	114.1
Environment of the sodium atoms			
Na(1)–O(1)	2.25 (0.02) Å	Na(2)–S(1)	3.49 (0.02) Å
Na(1)–O(2)	2.64	Na(2)–O(1)	2.37
Na(1)–O(4)	2.45	Na(2)–O(5)	2.34
Na(1)–O(5)	2.51	Na(2)–O(6)	2.46
Na(1)–O(6)	2.36	Na(2)–O(7)	2.44
Na(1)–O(7)	2.62	Na(2)–O(8)	2.64

Table 3. Distances and angles in the water molecules

O-H...X	O-H	H...X	O...X	Angle O---H...X	H-H	Angle H-O-H-	Associated angle A...O(W)...B
O(4) H(1)···O(3)	0.98 Å (1.00)	1.76 Å	2.73 Å	171.0°	1.63 Å	107.5°	101.8°
O(4) H(2)···O(2)	0.98 (1.00)	1.97	2.94	173.0			
O(5) H(3)···O(3)	0.96 (0.98)	1.82	2.77	171.2	1.57	106.2	105.7
O(5) H(4)···O(3*)	0.95 (0.98)	1.90	2.81	162.6			
O(6) H(5)···O(4*)	0.94 (0.96)	1.88	2.73	159.3	1.56	107.6	103.4
O(6) H(6)···S(1*)	0.92 (0.95)	2.52	3.30	143.2			
O(7) H(7)···S(1*)	0.93 (0.96)	2.38	3.13	142.8	1.51	108.2	112.9
O(7) H(8)···O(8*)	0.93 (0.95)	1.88	2.79	166.5			
O(8) H(9)	0.95 (0.96)				1.65	109.8	
O(8) H(10)···S(1)	0.96 (0.98)	2.59	3.40	145.2			

The bond lengths given in brackets are corrected values assuming a riding model. The atoms marked with asterisks indicate atoms related to the atoms in the asymmetric unit by symmetry transformations. The standard deviation in the bond distances is 0.02 Å and in the bond angles, 1.2°.

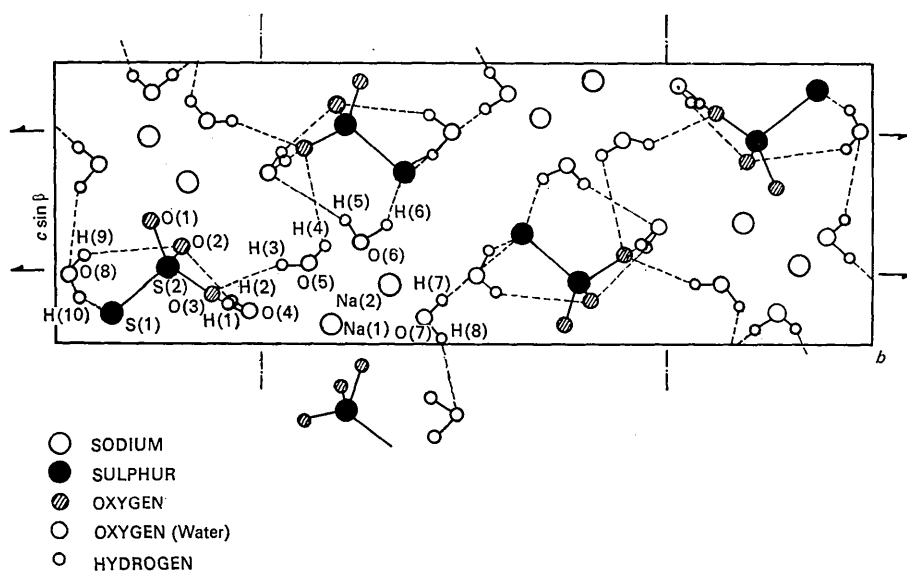


Fig. 1. Projection of the structure along the a axis. Dashed lines represent hydrogen bonds.

The hydrogen bond system may be divided into four types:

- (i) two strong water-thiosulphate oxygen hydrogen bonds, O(4)–H(1)···O(3) (2.73 Å) and O(5)–H(3)···O(3) (2.77 Å),
- (ii) two weak water-thiosulphate oxygen hydrogen bonds, O(4)–H(2)···O(2) (2.94 Å) and O(5)–H(4)···O(3*) (2.81 Å),
- (iii) two water–water oxygen hydrogen bonds O(6)–H(5)···O(4*) (2.73 Å) and O(7)–H(8)···O(8*) (2.79 Å),
- (iv) three water–sulphur hydrogen bonds, O(6)–H(6)···S(1*) (3.30 Å) O(7)–H(7)···S(1*) (3.13 Å) and O(8)–H(10)···S(1) (3.40 Å).

In the case of the water molecule H(9)–O(8)–H(10), Taylor & Beevers have suggested that both the hydrogen atoms are bonded to the sulphur atom. As revealed by the neutron study, the existence of a hydrogen bond between the atom H(9) and the sulphur atom is doubtful, since the distance H(9)···S(1*) is 2.68 Å and the angle O(8)–H(9)···S(1*) is 119°, a considerable deviation from linearity. Apart from the sulphur atom, the nearest atom is O(2) which makes an angle O(8)–H(9)···O(2) of 163°, but in this case H(9)···O(2) is 2.48 Å and O(8)···O(2) is 3.39 Å. Hence it is reasonable to assume that the atom H(9) does not participate in any meaningful hydrogen bonding. The hydrogen atoms H(6), H(7) and H(10)

may be regarded as being involved in hydrogen bonding to the sulphur atom. In these cases the H···S distances range from 2.38 to 2.59 Å and the O···S distances from 3.13 to 3.40 Å. The O–H···S angles are in the region 142.8 to 145.2°. Recently Muir (1969) has reported an O–H···S bond in BaS₂O₃ · H₂O with O···S, 3.298, H···S, 2.367 Å and an O–H···S angle of 163°. These are the first reports of hydrogen bonding to a sulphur atom revealed by neutron diffraction.

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The Crystal Structure of NbCoB

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The crystal structure of NbCoB has been determined by single-crystal X-ray analysis. The lattice constants are $a = 3.266$ (1), $b = 17.177$ (3), $c = 5.947$ (3) Å, the unit cell contains 30 atoms, and the space group is $Pm\bar{m}n$ (D_{2h}^{13}). The atomic parameters have been refined by least-squares analysis to a final R value of 0.086, based on the 265 observed reflections. The NbCoB structure is a combination of the TiNiSi- and ZrAlNi-type structures (isostructural with Cl₂Pb and Fe₂P respectively): the slightly deformed trigonal prisms [BM₆] form columns of three types – isolated, connected by two, and by three edges. The nets (two per cell) perpendicular to the x axis are built of pentagons, quadrangles and triangles. The coordination numbers are 17 (Nb), 12 (Co) and 9 (B); the coordination polyhedra are derived from pentagonal, tetragonal and trigonal prisms respectively.

Introduction

The ternary compound NbCoB was revealed in the course of an X-ray investigation of the Nb–Co–B

system; at 800°C it exists in equilibrium with Co, NbCo₂, NbB and Nb₂Co₂₁B₆. The following dimensions of the orthorhombic NbCoB cell were found: 3.26, 5.93 and 17.08 Å (Kuz'ma, Ciolkovsky & Baburova, 1968). Stadelmaier & Schöbel (1966) ascribe the composition NbCo₂B, rather than NbCoB, to the second ternary compound in this system.

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