

# Sodium sulfite heptahydrate and its relation to sodium carbonate heptahydrate

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The monoclinic crystal structure of  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$  is characterized by an alternating stacking of (100) cationic sodium–water layers and anionic sulfite layers along [100]. The cationic layers are made up from two types of  $[\text{Na}(\text{H}_2\text{O})_6]$  octahedra that form linear  ${}^1_\infty[\text{Na}(\text{H}_2\text{O})_{4/2}(\text{H}_2\text{O})_{2/1}]$  chains linked by dimeric  $[\text{Na}(\text{H}_2\text{O})_{2/2}(\text{H}_2\text{O})_{4/1}]_2$  units on both sides of the chains. The isolated trigonal–pyramidal sulfite anions are connected to the cationic layers through an intricate network of O—H...O hydrogen bonds, together with a remarkable O—H...S hydrogen bond, with an O...S donor–acceptor distance of 3.2582 (6) Å, which is about 0.05 Å shorter than the average for O—H...S hydrogen bonds in thiosalt hydrates and organic sulfur compounds of the type Y—S—Z (Y/Z = C, N, O or S). Structural relationships between monoclinic  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$  and orthorhombic  $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_7$  are discussed in detail.

## 1. Introduction

Sodium sulfite is used extensively in industrial processes, for example, as an antioxidant and preservative in food industries (E number for food additives E221), as a corrosion inhibitor in aqueous media, as a bleaching agent, as a solubilizing agent for cellulose, straw and wood in the pulp and paper industry, or as an additive in dyeing processes. In the USA alone, the production of sodium sulfite reached 150 000 tons in 2002 (Weil *et al.*, 2007). Solid sodium sulfite is stable in its anhydrous form and as the heptahydrate. Despite its use at industrial scales, structural details are known only for anhydrous  $\text{Na}_2\text{SO}_3$  that crystallizes with two formula units in the trigonal system in the space group  $P\bar{3}$  (Larsson & Kierkegaard, 1969). Bond lengths and near-neighbour distances of sodium sulfite in aqueous solution have been calculated by *ab initio* quantum mechanical charge field molecular dynamics (QMCF MD) studies and determined experimentally by large-angle X-ray scattering (LAXS) by Eklund *et al.* (2012). For crystalline  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$ , lattice parameters and the space group ( $P2_1/n$ ) have previously been determined from Weissenberg photographs without providing further structural details, except for a close metrical resemblance with orthorhombic  $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_7$  (Dunsmore & Speakman, 1963). To obtain a more detailed picture of the relationship between the heptahydrates of  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{CO}_3$ , we grew single crystals of  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$  and determined its crystal structure. Indeed, the two heptahydrates show not only a close metrical relationship (Table 1), but also structural similarities, though they belong to different crystal systems and contain differently shaped divalent anions, *viz.* trigonal–pyramidal  $\text{SO}_3^{2-}$  and trigonal–planar  $\text{CO}_3^{2-}$ .

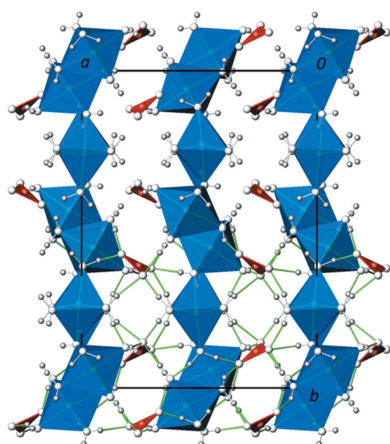


Table 1

Comparison of lattice parameters (Å, °) for Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> (this work) and Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> (Betzel *et al.*, 1982).

	Na <sub>2</sub> SO <sub>3</sub> (H <sub>2</sub> O) <sub>7</sub>	Na <sub>2</sub> CO <sub>3</sub> (H <sub>2</sub> O) <sub>7</sub>
<i>a</i>	14.6563 (8)	14.492 (7)
<i>b</i>	19.7180 (9)	19.490 (5)
<i>c</i>	7.2197 (5)	7.017 (3)
$\alpha$	90	90
$\beta$	90	90
$\gamma$	94.0997 (17)	90
<i>V</i> (Å <sup>3</sup> )	2081.1 (2)	1981.95
<i>T</i> (K)	100	RT
Space group	C112 <sub>1</sub> / <i>a</i>	<i>Pbca</i>

## 2. Experimental

### 2.1. Crystallization

Colourless prismatic crystals of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> were grown by recrystallization of a commercial anhydrous sample (Merck, p.A. grade) from an aqueous solution at room temperature by slow evaporation over the course of several days. In order to remove adherent mother liquor, the crystals were placed on filter paper and subsequently immersed in Paratone oil. The crystal under investigation was cleaved from a larger specimen.

### 2.2. Crystallography and refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal structure of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> was originally solved and refined in the space group *P*12<sub>1</sub>/*n*1 (No. 14), with lattice parameters *a* = 11.8576 (8), *b* = 7.2197 (5), *c* = 12.6965 (9) Å and  $\beta$  = 106.7938 (17)° at 100 K (full crystal data in the setting *P*12<sub>1</sub>/*n*1 are available in CIF format as supporting information). The values for the lattice parameters at 100 K are in good agreement with the previous study, with values of *a* = 11.922, *b* = 7.260, *c* = 12.765 Å and  $\beta$  = 107.22° obtained at room temperature from Weissenberg film data (note that *a* and *c* are interchanged in the original description; Dunsmore & Speakman, 1963). For a better comparison with the reported crystal structure of  $\beta$ -Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> (Betzel *et al.*, 1982), the nonconventional setting C112<sub>1</sub>/*a* was chosen for the final structural description of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>, using the matrix (101, 10 $\bar{1}$ , 010) for transformation of the primitive cell to the *C*-centred cell with *c* as the unique axis; moreover, the atomic coordinates and the origin of the unit cell were chosen to ensure a similar packing of structural building blocks in the two unit cells of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> and  $\beta$ -Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>. All H atoms present in the crystal structure of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> were located in a difference Fourier map and were refined freely.

## 3. Results and discussion

### 3.1. Crystal structure

In the crystal structure of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>, all atoms (2 Na, 1 S, 10 O and 14 H) are located on general sites. The two sodium cations are surrounded by six water molecules, defining a distorted octahedral coordination polyhedron in each case.

Table 2

Experimental details.

Crystal data	Na <sub>2</sub> SO <sub>3</sub> (H <sub>2</sub> O) <sub>7</sub>
Chemical formula	Na <sub>2</sub> SO <sub>3</sub> (H <sub>2</sub> O) <sub>7</sub>
<i>M<sub>r</sub></i>	252.15
Crystal system, space group	Monoclinic, C112 <sub>1</sub> / <i>a</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.6563 (8), 19.7180 (9), 7.2197 (5)
$\gamma$ (°)	94.0997 (17)
<i>V</i> (Å <sup>3</sup> )	2081.1 (2)
<i>Z</i>	8
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.42
Crystal size (mm)	0.15 × 0.13 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.675, 0.747
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	16909, 4845, 4222
<i>R<sub>int</sub></i>	0.021
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.827
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.023, 0.063, 1.06
No. of reflections	4845
No. of parameters	174
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.89, -0.33

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ATOMS* (Dowty, 2006), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

The Na—O distances range from 2.3690 (6) to 2.4952 (6) Å (Table 3), with mean values of 2.42 (4) Å for Na1 and 2.43 (6) Å for Na2, in fairly good agreement with the mean value for Na<sup>[6]</sup>—O of 2.44 (11) Å calculated for 5520 individual bonds (Gagné & Hawthorne, 2016). The bond valence sums (Brown, 2002) for the sodium cations, as calculated with parameters provided by Brese & O'Keeffe (1991), are 1.15 valence units (v.u.) for Na1 and 1.13 v.u. for Na2, and thus in the expected range for monovalent Na<sup>+</sup>. The O—Na—O angles deviate clearly from ideal values, with values for *trans* O atoms in the range 172.149 (16)–176.42 (2)° for Na1 and 165.81 (2)–174.23 (2)° for Na2, and for *cis* O atoms in the range 81.464 (19)–101.74 (2)° for Na1 and 81.51 (2)–103.23 (2)° for Na2. The two types of [Na(H<sub>2</sub>O)<sub>6</sub>] octahedra show a different linkage pattern. Octahedra centred by Na1 share common edges (O8/O10 and O8<sup>ii</sup>/O10<sup>i</sup>; see Table 3 for symmetry codes) to form infinite linear  $\infty$ [Na1(H<sub>2</sub>O)<sub>4/2</sub>(H<sub>2</sub>O)<sub>2/1</sub>] chains running parallel to [001], whereas octahedra centred by Na2 make up dimeric [Na2(H<sub>2</sub>O)<sub>2/2</sub>(H<sub>2</sub>O)<sub>4/1</sub>]<sub>2</sub> units by sharing an edge (O5 and O5<sup>iii</sup>). In both cases, the corresponding Na—O bonds to the shared O atoms at the edges are the shortest in the respective octahedron. The dimeric units connect adjacent chains by sharing the terminal water molecules (O9 and O7) on both sides of the chains (corner-sharing links). This way, the sodium–water octahedra are assembled by edge- and corner-sharing into an infinite layer extending parallel to (100) (Fig. 1a).

The sulfite anion has the characteristic trigonal–pyramidal configuration, with the S<sup>IV</sup> atom occupying the pyramidal

position. Atom S1 is 0.5912 (4) Å above the basal plane formed by atoms O1, O2 and O3. The S–O bond lengths are in a narrow range 1.5224 (5)–1.5338 (5) Å [mean 1.527 (6) Å], just like the O–S–O angles [105.85 (3)–106.07 (3)°; mean 105.93 (16)°]. Again, these values are in good agreement with the grand mean  $S^{IV}$ –O bond length of 1.529 (15) Å calculated for 90 bonds and with the O– $S^{IV}$ –O angles in the range ~99–107° with a mean value of ~104° (Gagné & Hawthorne, 2018). The bond valence sum for atom S1 is 4.12 v.u., using the parameters of Brese & O’Keeffe (1991) for calculation. The sulfite anions are isolated from the sodium–water layer, lying alternately on both sides outside of an individual layer. In this way, cationic sodium–water layers at  $x \simeq 0, \frac{1}{2}$  are sandwiched by sulfite layers at  $x \simeq \frac{1}{4}, \frac{3}{4}$  and stacked along [100], with the sulfite anions situated approximately at the height in  $y$  where the  $[Na_2O_{2/2}O_{4/1}]_2$  dimers are linked to the  ${}^1[Na-(H_2O)_{4/2}(H_2O)_{2/1}]$  chains (Fig. 2a).

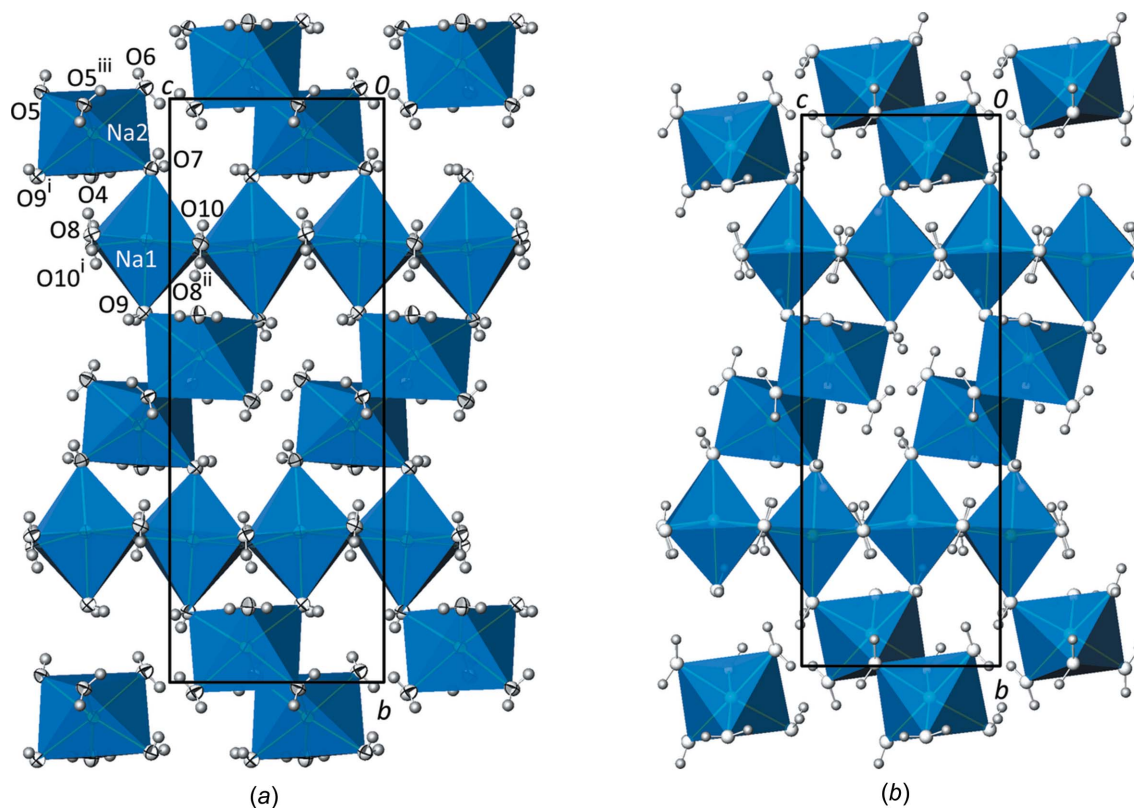
The seven independent water molecules possess approximately tetrahedral coordination arrangements (including hydrogen bonds), except for O9, and five of them each bridge two sodium cations (O5, O7, O8, O9 and O10), whereas two are each bonded to only one sodium cation (O4 and O6). An intricate network of O–H···O hydrogen bonds between the water molecules and the sulfite O atoms link the anionic layers to adjacent cationic layers, thus establishing a three-dimensional hydrogen-bonded network structure (Fig. 2a). Based on

**Table 3**  
Selected geometric parameters (Å, °).

Na1–O10	2.3690 (6)	Na2–O4	2.3939 (6)
Na1–O8	2.3785 (6)	Na2–O7	2.4093 (6)
Na1–O10 <sup>i</sup>	2.4199 (6)	Na2–O6	2.4928 (6)
Na1–O7	2.4199 (6)	Na2–O9 <sup>i</sup>	2.4952 (6)
Na1–O8 <sup>ii</sup>	2.4436 (6)	S1–O3	1.5224 (5)
Na1–O9	2.4599 (6)	S1–O1	1.5234 (5)
Na2–O5 <sup>iii</sup>	2.3787 (6)	S1–O2	1.5338 (5)
Na2–O5	2.3805 (6)		
O3–S1–O1	105.85 (3)	O1–S1–O2	105.87 (3)
O3–S1–O2	106.07 (3)		

Symmetry codes: (i)  $-x+1, -y+\frac{1}{2}, z+\frac{1}{2}$ ; (ii)  $-x+1, -y+\frac{1}{2}, z-\frac{1}{2}$ ; (iii)  $-x+1, -y, -z+3$ .

the donor–acceptor distances between 2.7204 (7) and 2.9110 (8) Å (Table 4), the hydrogen-bonding strength is moderate according to the classification of Jeffrey (1997). Most of these hydrogen bonds are donated to sulfite atoms O1, O2 and O3 (Fig. 3a). Thereby, atom O1 is the acceptor of three, O2 of four and O3 of three hydrogen bonds. It is worth noting that the S–O bond lengths reflect this situation nicely, with S1–O2 = 1.5338 (5) Å being about 0.01 Å longer than the remaining two. The O9 water molecule, bonded to Na1, Na2 and *via* H9A to O2, lacks a clearcut hydrogen bond for its second H atom (H9B), which points to H6B of the O6–H6B···O3 hydrogen bond  $[H9B(x, y - \frac{1}{2}, z + \frac{5}{2}) \cdots H6B =$



**Figure 1**

(a) View along  $[100]$  onto the cationic water–sodium (100) layer in the crystal structure of  $Na_2SO_3(H_2O)_7$  made up from edge- and corner-sharing  $[Na(H_2O)_6]$  octahedra (turquoise). Anisotropic displacement ellipsoids are drawn at the 90% probability level and H atoms are shown as grey spheres of arbitrary radii. Symmetry codes refer to Table 3. (b) The same type of layer in the crystal structure of  $Na_2CO_3(H_2O)_7$ , with atoms as spheres of arbitrary radii.

2.49 Å], while distances from O9( $x, y - \frac{1}{2}, z + \frac{5}{2}$ ) to O6 and O3 exceed 3.3 Å.

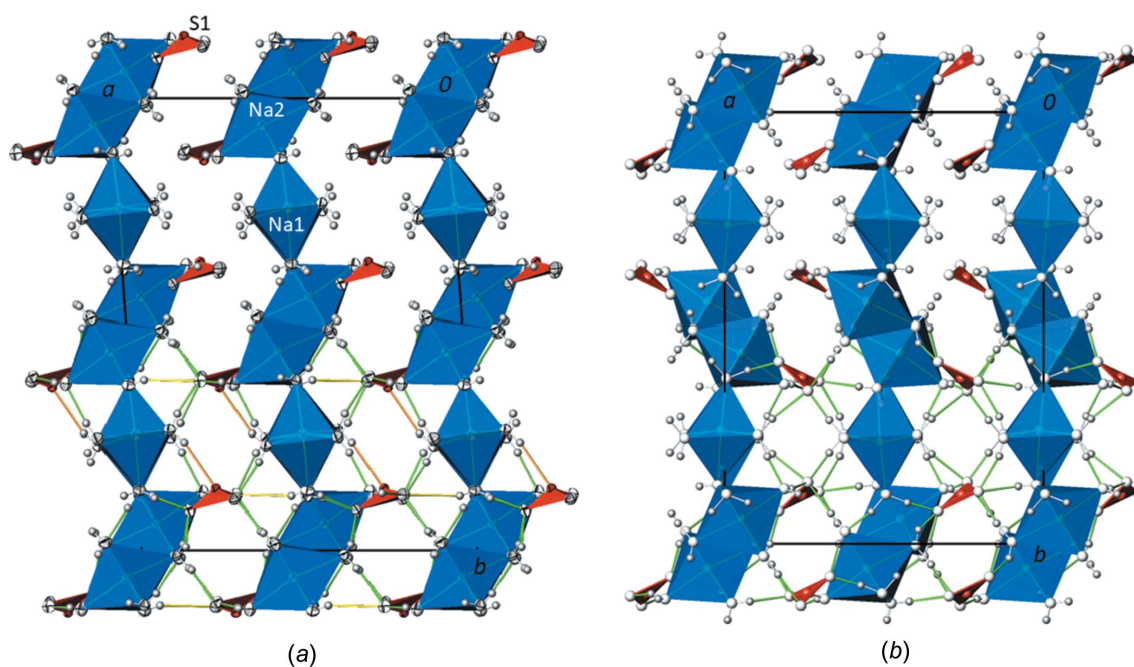
In addition to the interactions between water molecules and sulfite O atoms, there are two hydrogen bonds between water molecules only (O7···O6<sup>vi</sup> and O10···O4<sup>ii</sup>; symmetry codes refer to Table 4), and, as a peculiarity, an O—H···S hydrogen bond between O8 and S1<sup>vii</sup>. In general, S···H interactions involving divalent S atoms are considered as weak hydrogen bonds (Allen *et al.*, 1997). The H···S hydrogen-bonding strength becomes even weaker for H···SO<sub>3</sub><sup>2-</sup> contacts because the S atom is positively polarized in an SO<sub>3</sub><sup>2-</sup> anion with partial double-bond character for the S—O bonds (Nyberg & Larsson, 1973). The hydrogen-bond acceptor ability of divalent sulfur was evaluated some time ago from 1811 substructures of mostly organic compounds, *i.e.* Y—S—Z systems (Y/Z = C, N, O or S) as acceptor groups retrieved from the Cambridge Structural Database, giving a mean intermolecular >S···H distance of 2.67 (5) Å for O—H donors and a mean S···O distance of 3.39 (4) Å (Allen *et al.*, 1997; Groom *et al.*, 2016). In comparison, the first ever reported crystal structure determination of an inorganic compound with an O—H···S hydrogen bond and a clear location of the H atoms, *viz.* BaS<sub>2</sub>O<sub>3</sub>(H<sub>2</sub>O) from neutron single-crystal diffraction data (Manojlović-Muir, 1969), revealed a considerably shorter S···H distance of 2.367 (4) Å and a likewise shorter S···O distance of 3.298 (4) Å. The O—H···S angle in BaS<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O was determined as 163 (3)°. Corresponding values of the O—H···S hydrogen bond in the crystal structure of Na<sub>2</sub>SO<sub>3</sub>·(H<sub>2</sub>O)<sub>7</sub> are somewhat larger at 2.455 (14) Å for H8B···S1<sup>vii</sup> (X-ray data), slightly shorter at 3.2582 (6) Å for O8···S1<sup>vii</sup> and

**Table 4**  
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3 <sup>iv</sup>	0.800 (15)	2.031 (16)	2.8216 (8)	169.7 (15)
O4—H4B···O1 <sup>v</sup>	0.821 (16)	1.983 (16)	2.7904 (7)	167.8 (15)
O5—H5A···O1	0.804 (13)	1.947 (13)	2.7503 (7)	175.9 (13)
O5—H5B···O2 <sup>iv</sup>	0.798 (15)	1.994 (15)	2.7694 (7)	163.9 (15)
O6—H6A···O2 <sup>v</sup>	0.777 (14)	2.072 (14)	2.8206 (7)	161.8 (14)
O6—H6B···O3	0.774 (15)	1.962 (15)	2.7204 (7)	166.5 (15)
O7—H7A···O2 <sup>v</sup>	0.810 (13)	1.976 (14)	2.7761 (7)	169.3 (13)
O7—H7B···O6 <sup>vi</sup>	0.773 (14)	2.171 (14)	2.9110 (8)	160.7 (15)
O8—H8A···O1 <sup>iii</sup>	0.792 (15)	2.009 (15)	2.7900 (7)	168.9 (13)
O8—H8B···S1 <sup>vii</sup>	0.825 (14)	2.455 (14)	3.2582 (6)	164.5 (13)
O9—H9A···O2 <sup>vii</sup>	0.807 (14)	2.106 (14)	2.9096 (7)	174.0 (14)
O10—H10A···O4 <sup>ii</sup>	0.839 (15)	1.962 (15)	2.7908 (8)	169.5 (14)
O10—H10B···O3 <sup>vi</sup>	0.762 (14)	2.069 (14)	2.8210 (7)	169.1 (14)

Symmetry codes: (ii)  $-x + 1, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + 1, -y, -z + 3$ ; (iv)  $-x + \frac{3}{2}, -y, z + \frac{1}{2}$ ; (v)  $-x + \frac{3}{2}, -y, z - \frac{1}{2}$ ; (vi)  $-x + 1, -y, -z + 2$ ; (vii)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ .

similar at 164.5 (13)° for the O8—H8B···S1<sup>vii</sup> angle. A comparable O···S distance of 3.326 Å was found as the mean value for 86 hydrogen-bonding interactions between water molecules and S atoms in a variety of thiosalt hydrates, such as Schlippe's salt, Na<sub>3</sub>SbS<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub> (Mikenda *et al.*, 1989). A literature search indicated that the O—H···S hydrogen bond in the title compound appears to be unprecedented thus far among hydrated sulfites. This suggests that in sulfite hydrates, O—H···O hydrogen bonding is clearly preferred over O—H···S hydrogen bonding and that a certain structural motif is needed to induce O—H···S hydrogen bonding like in the title compound. Invoking the results of an electron deformation density study of MgSO<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub> (Bats *et al.*, 1986), the coor-



**Figure 2**  
(a) The crystal structure of Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> in a projection along [001], showing the layered character with cationic water–sodium layers at  $x \approx 0, \frac{1}{2}$  alternating with sulfite layers (red polyhedra) at  $x \approx \frac{1}{4}, \frac{3}{4}$ . (b) The crystal structure of Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> in a projection along [00 $\bar{1}$ ], showing the same type of layer stacking but a different orientation of the dimeric groups and adjacent carbonate anions at  $y \approx \frac{1}{2}$ . For clarity, hydrogen bonds are displayed only in the lower half of the figures, with moderate O—H···O hydrogen bonds shown as green lines, weak O—H···O bonds as yellow lines and O—H···S hydrogen bonds as orange lines.

dination capability of the sulfite S atom *via* its electron lone-pair lobe at the apex of the SO<sub>3</sub> pyramid is not unexpected, but this capability seems to be weak in the context of hydrogen bonding because otherwise more examples with features comparable to the title compound would have been encountered already. As soon as covalent bonding comes into play, the coordination capability of the sulfite S atom is well documented by transition-metal complexes like K<sub>2</sub>[Pd(SO<sub>3</sub>)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (Messer *et al.*, 1979) or K<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>] $\cdot$ 2.25H<sub>2</sub>O (Weil *et al.*, 2010), with metal–sulfur bonds, or by hydrogen sulfites like CsHSO<sub>3</sub> (Johansson *et al.*, 1980) or K<sub>5</sub>(HSO<sub>3</sub>)(S<sub>2</sub>O<sub>5</sub>) (Magnusson *et al.*, 1983) that contain HSO<sub>3</sub><sup>−</sup> anions with hydrogen covalently bonded to sulfur.

The numerical values of the atomic distances for crystalline Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> (Tables 3 and 4) are in good agreement with those of aqueous Na<sub>2</sub>SO<sub>3</sub> solutions determined from LAXS studies, with S–O = 1.53 Å for the sulfite group and Na–O = 2.41 Å for the sodium–water distances (Eklund *et al.*, 2012). In the latter study, the S $\cdots$ O<sub>water</sub> distance in solution was determined as 3.68 Å, which is considerably longer than in the solid state, giving further evidence for a weak but existing O–H $\cdots$ S hydrogen bond in the crystalline material.

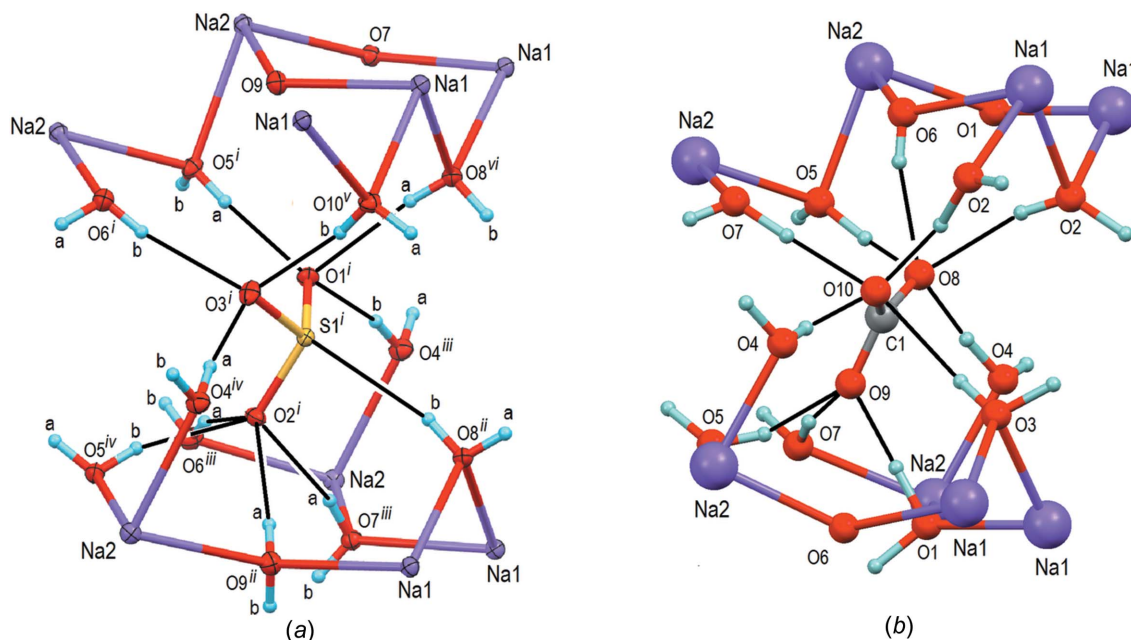
### 3.2. Comparison with Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>

The close structural relationship between monoclinic Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> and orthorhombic Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> (Table 1) becomes evident from the similar arrangement of the principal building units in the crystal structures. The same type of

cationic sodium–water layers made up from edge- and corner-sharing [Na(H<sub>2</sub>O)<sub>6</sub>] octahedra [mean Na–O distance = 2.43 (4) Å and O–Na–O angles = 81–102 and 164–180°; Fig. 1*b*] is present in the carbonate, likewise situated at  $x \simeq 0, \frac{1}{2}$  in the unit cell (Fig. 2*b*). The carbonate groups do not show pyramidalization (Zemann, 1981) and occupy the same space as the sulfite groups between adjacent layers close to the [Na(H<sub>2</sub>O)<sub>2/2</sub>(H<sub>2</sub>O)<sub>4/1</sub>]<sub>2</sub> dimers.

The main difference between the two structures is related to the orientation of the [Na(H<sub>2</sub>O)<sub>2/2</sub>(H<sub>2</sub>O)<sub>4/1</sub>]<sub>2</sub> dimers in the layers. Whereas in the sulfite structure, the dimers at  $y \simeq 0$  and  $\frac{1}{2}$  in one layer and also the accompanying anions close to them have the same orientation relative to (100), in the carbonate structure, the orientation of every second dimer (at  $y \simeq \frac{1}{2}$ ) and the accompanying anions in a layer is reversed due to the presence of the *c*-glide plane (Fig. 2).

The hydrogen-bonding schemes in the two heptahydrates are similar (Fig. 3). In the carbonate structure, the anions are likewise hydrogen bonded to water molecules through medium–strong hydrogen bonds [O $\cdots$ O = 2.690 (5)–3.060 (4) Å, with an additional weak interaction of 3.223 (5) Å]. In analogy, two water–water O–H $\cdots$ O interactions with donor–acceptor distances of 2.827 (5) and 2.766 (5) Å are also observed. However, in contrast to the central sulfite S atom with its free electron lone pair, the central C atom of the carbonate anion cannot act as a hydrogen-bond acceptor, and thus this interaction is missing in the carbonate structure.



**Figure 3**

Comparison of the hydrogen bonding to the anion in (a) Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>, with displacement ellipsoids drawn at the 50% probability level, and (b) Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>, with atoms as arbitrary spheres; hydrogen bonds are shown as thin solid lines. Atoms O1 and O3 in the sulfite structure accept three hydrogen bonds each, whereas O8 and O10 in the carbonate structure accept four each. Likewise, O2 in the sulfite structure accepts four hydrogen bonds, whereas the corresponding O9 atom in the carbonate accepts three. Note that the arrangement of the hydrogen-bonded water molecules around SO<sub>3</sub><sup>2−</sup> is approximately mirror-symmetric (e.g. O5<sup>i</sup> and O6<sup>i</sup>), whereas it is less symmetric for the carbonate. Symmetry codes for atoms in Na<sub>2</sub>SO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub> involved in hydrogen bonding with the SO<sub>3</sub><sup>2−</sup> anion are: (i)  $x, y, z$ ; (ii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (iii)  $-x + \frac{3}{2}, -y, z + \frac{1}{2}$ ; (iv)  $-x + \frac{3}{2}, -y, z - \frac{1}{2}$ ; (v)  $-x + 1, -y, -z + 2$ ; (vi)  $-x + 1, -y, -z + 3$ .

### 3.3. Comparison with related compounds

Crystal structures with sulfite groups anchored exclusively by hydrogen bonds are at present restricted to the title compound  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$ , to  $\text{NH}_4\text{SO}_3(\text{H}_2\text{O})$  (Battelle & Trueblood, 1965; Durand *et al.*, 1977) and to  $\text{MgSO}_3(\text{H}_2\text{O})_6$  (Andersen & Lindqvist, 1984; Bats *et al.*, 1986). In  $\text{MgSO}_3(\text{H}_2\text{O})_6$ , which is built up from  $[\text{Mg}(\text{H}_2\text{O})_6]$  octahedra and isolated  $\text{SO}_3$  pyramids within a lattice of the space group type  $R\bar{3}$ , and with Mg and S atoms both located on threefold rotation axes, there are two independent water molecules that donate, apart from one water–water hydrogen bond, three water– $\text{O}_{\text{sulfite}}$  hydrogen bonds to each sulfite O atom, comparable to O1 and O3 in  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$ , but with shorter O...O distances [2.687 (3), 2.701 (3) and 2.726 (3) Å] than in the latter. An electron deformation density study of  $\text{MgSO}_3(\text{H}_2\text{O})_6$  (Bats *et al.*, 1986) proved the presence of an extended lone-pair lobe at the apex of the  $\text{SO}_3$  pyramid, but neither  $\text{MgSO}_3(\text{H}_2\text{O})_6$  nor  $\text{NH}_4\text{SO}_3(\text{H}_2\text{O})$  contain O–H...S or N–H...S hydrogen bonds.

A further comparison with other hydrated sodium compounds comprised of related oxo anions shows no close structural relationship to the title heptahydrate. For example,  $\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_7$  (Oswald *et al.*, 2008) ( $I4_1/amd$ ,  $Z = 4$ ) has a completely different arrangement of the principal building units. Its crystal structure is comprised of  $[\text{Na}(\text{H}_2\text{O})_6]$  octahedra concatenated by edge- and corner-sharing into a three-dimensional network with isolated tetrahedral sulfate anions hydrogen bonded to the chains. Also, for sodium compounds with analogous trigonal–pyramidal oxoanions and the same charge, *i.e.*  $\text{XO}_3^{2-}$ , with  $X = \text{Se}$  and  $\text{Te}$ , no phases related structurally or compositionally to  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$  are known. For  $\text{Na}_2\text{SeO}_3$ , the anhydrous form ( $P2_1/c$ ,  $Z = 4$ ) is made up from  $[\text{NaO}_6]$  octahedra and trigonal–pyramidal  $\text{SeO}_3^{2-}$  anions (Wickleder, 2002), and is isotypic with  $\text{Na}_2\text{TeO}_3$  (Masse *et al.*, 1980). Hydrated forms are known only for the pentahydrates  $\text{Na}_2\text{SeO}_3(\text{H}_2\text{O})_5$  (Mereiter, 2013) and  $\text{Na}_2\text{TeO}_3(\text{H}_2\text{O})_5$  (Philippot *et al.*, 1979) that are, surprisingly, not isotypic ( $Pbcm$ , with  $Z = 8$ , and  $C2/c$ , with  $Z = 8$ , respectively). These structures are based on two- or three-dimensional assemblies of  $[\text{NaO}_5]$  polyhedra (Se) and  $[\text{NaO}_6]$  octahedra (Se and Te), to which  $\text{SeO}_3/\text{TeO}_3$  groups are bonded *via* two (Se) or one (Te) O atom. The  $[\text{NaO}_6]$  octahedra in these two salts share common faces and edges but no vertices. As pointed out by Philippot *et al.* (1979) for  $\text{Na}_2\text{TeO}_3(\text{H}_2\text{O})_5$  and confirmed also for  $\text{Na}_2\text{SeO}_3(\text{H}_2\text{O})_5$  (Mereiter, 2013), the electron lone pair of Se and Te in these structures shows no attracting interactions with neighbouring H atoms. This might be one reason why hydrates of  $\text{Na}_2\text{SeO}_3$  and  $\text{Na}_2\text{TeO}_3$  do not crystallize in the  $\text{Na}_2\text{SO}_3(\text{H}_2\text{O})_7$  structure and *vice versa*.

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## supporting information

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## Sodium sulfite heptahydrate and its relation to sodium carbonate heptahydrate

Matthias Weil and Kurt Mereiter

## Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ATOMS* (Dowty, 2006) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## Sodium sulfite heptahydrate

## Crystal data

$\text{H}_{14}\text{Na}_2\text{O}_{10}\text{S}$

$M_r = 252.15$

Monoclinic,  $C112_1/a$

Hall symbol:  $-C_2ac$

$a = 14.6563$  (8) Å

$b = 19.7180$  (9) Å

$c = 7.2197$  (5) Å

$\beta = 90^\circ$

$V = 2081.1$  (2) Å<sup>3</sup>

$Z = 8$

$F(000) = 1056$

$D_x = 1.610$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8292 reflections

$\theta = 2.8\text{--}36.0^\circ$

$\mu = 0.42$  mm<sup>-1</sup>

$T = 100$  K

Fragment, colourless

$0.15 \times 0.13 \times 0.12$  mm

## Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

$\omega$ - and  $\phi$ -scan

Absorption correction: multi-scan  
(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.675$ ,  $T_{\max} = 0.747$

16909 measured reflections

4845 independent reflections

4222 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 36.0^\circ$ ,  $\theta_{\min} = 2.8^\circ$

$h = -24 \rightarrow 23$

$k = -32 \rightarrow 30$

$l = -11 \rightarrow 11$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.063$

$S = 1.06$

4845 reflections

174 parameters

0 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.806P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.89$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.33$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Na1	0.49508 (2)	0.24227 (2)	1.10868 (4)	0.00970 (6)
Na2	0.55111 (2)	0.06011 (2)	1.35665 (4)	0.01015 (6)
S1	0.76676 (2)	-0.13751 (2)	1.37190 (2)	0.00782 (4)
O1	0.71232 (3)	-0.11448 (2)	1.53732 (7)	0.01115 (8)
O2	0.85230 (3)	-0.08810 (3)	1.36082 (6)	0.01132 (8)
O3	0.70978 (4)	-0.12350 (3)	1.20165 (7)	0.01248 (9)
O4	0.69179 (4)	0.12961 (3)	1.36691 (7)	0.01302 (9)
O5	0.60016 (4)	-0.01074 (3)	1.59875 (7)	0.01119 (8)
O6	0.60771 (4)	-0.01777 (3)	1.11731 (7)	0.01330 (9)
O7	0.50388 (4)	0.12044 (3)	1.08692 (7)	0.01129 (8)
O8	0.39237 (4)	0.23269 (3)	1.36393 (7)	0.01119 (8)
O9	0.49463 (4)	0.36695 (3)	1.11835 (7)	0.01244 (9)
O10	0.39308 (4)	0.24819 (3)	0.85559 (7)	0.01182 (9)
H4A	0.7253 (10)	0.1272 (7)	1.454 (2)	0.040 (4)*
H4B	0.7270 (10)	0.1258 (7)	1.280 (2)	0.043 (4)*
H5A	0.6351 (9)	-0.0397 (7)	1.5804 (18)	0.026 (3)*
H5B	0.6230 (10)	0.0138 (7)	1.6763 (19)	0.036 (4)*
H6A	0.6299 (9)	0.0083 (7)	1.047 (2)	0.035 (4)*
H6B	0.6429 (10)	-0.0432 (8)	1.1470 (18)	0.033 (4)*
H7A	0.5492 (9)	0.1157 (6)	1.0255 (19)	0.030 (3)*
H7B	0.4660 (10)	0.0941 (7)	1.053 (2)	0.034 (4)*
H8A	0.3667 (10)	0.1966 (7)	1.3816 (17)	0.032 (4)*
H8B	0.3519 (10)	0.2597 (7)	1.3636 (16)	0.026 (3)*
H9A	0.4574 (10)	0.3785 (7)	1.192 (2)	0.030 (3)*
H9B	0.5427 (11)	0.3788 (7)	1.1579 (19)	0.034 (4)*
H10A	0.3612 (10)	0.2819 (8)	0.8574 (17)	0.032 (4)*
H10B	0.3596 (10)	0.2171 (7)	0.8447 (17)	0.026 (3)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Na1	0.01001 (12)	0.01018 (12)	0.00894 (11)	0.00089 (9)	-0.00002 (8)	0.00018 (8)
Na2	0.01087 (13)	0.01032 (12)	0.00923 (11)	0.00053 (9)	-0.00029 (8)	0.00100 (8)
S1	0.00777 (6)	0.00762 (6)	0.00812 (6)	0.00102 (4)	-0.00010 (4)	0.00042 (4)
O1	0.0113 (2)	0.0120 (2)	0.01032 (18)	0.00238 (16)	0.00291 (14)	-0.00012 (14)
O2	0.0090 (2)	0.0124 (2)	0.01216 (19)	-0.00153 (16)	0.00037 (14)	0.00118 (15)
O3	0.0144 (2)	0.0131 (2)	0.01010 (19)	0.00150 (17)	-0.00474 (15)	0.00016 (15)
O4	0.0119 (2)	0.0158 (2)	0.0114 (2)	0.00138 (17)	0.00043 (16)	0.00018 (16)
O5	0.0113 (2)	0.0101 (2)	0.01232 (19)	0.00204 (16)	-0.00185 (15)	-0.00181 (15)



O6	0.0132 (2)	0.0122 (2)	0.0147 (2)	0.00227 (17)	0.00056 (16)	0.00217 (16)
O7	0.0112 (2)	0.0112 (2)	0.01143 (19)	0.00058 (16)	0.00061 (15)	-0.00022 (15)
O8	0.0099 (2)	0.0104 (2)	0.01337 (19)	0.00126 (16)	0.00133 (15)	0.00157 (15)
O9	0.0139 (2)	0.0117 (2)	0.01171 (19)	0.00068 (17)	0.00033 (16)	-0.00053 (15)
O10	0.0101 (2)	0.0117 (2)	0.0136 (2)	0.00013 (17)	-0.00087 (15)	-0.00148 (15)

*Geometric parameters (Å, °)*

Na1—O10	2.3690 (6)	Na2—O4	2.3939 (6)
Na1—O8	2.3785 (6)	Na2—O7	2.4093 (6)
Na1—O10 <sup>i</sup>	2.4199 (6)	Na2—O6	2.4928 (6)
Na1—O7	2.4199 (6)	Na2—O9 <sup>i</sup>	2.4952 (6)
Na1—O8 <sup>ii</sup>	2.4436 (6)	S1—O3	1.5224 (5)
Na1—O9	2.4599 (6)	S1—O1	1.5234 (5)
Na2—O5 <sup>iii</sup>	2.3787 (6)	S1—O2	1.5338 (5)
Na2—O5	2.3805 (6)		
O5 <sup>iii</sup> —Na2—O5	88.41 (2)	H4A—O4—H4B	101.7 (15)
O5 <sup>iii</sup> —Na2—O4	165.81 (2)	Na2 <sup>iii</sup> —O5—Na2	91.59 (2)
O5—Na2—O4	91.68 (2)	Na2 <sup>iii</sup> —O5—H5A	110.7 (9)
O5 <sup>iii</sup> —Na2—O7	91.10 (2)	Na2—O5—H5A	122.0 (9)
O5—Na2—O7	173.08 (2)	Na2 <sup>iii</sup> —O5—H5B	119.4 (10)
O4—Na2—O7	90.48 (2)	Na2—O5—H5B	106.9 (10)
O5 <sup>iii</sup> —Na2—O6	100.56 (2)	H5A—O5—H5B	106.6 (14)
O5—Na2—O6	91.13 (2)	Na2—O6—H6A	100.9 (10)
O4—Na2—O6	93.62 (2)	Na2—O6—H6B	118.2 (10)
O7—Na2—O6	82.177 (19)	H6A—O6—H6B	110.0 (14)
O5 <sup>iii</sup> —Na2—O9 <sup>i</sup>	81.51 (2)	Na2—O7—Na2	118.38 (2)
O5—Na2—O9 <sup>i</sup>	83.523 (19)	Na2—O7—H7A	96.9 (9)
O4—Na2—O9 <sup>i</sup>	84.40 (2)	Na1—O7—H7A	104.6 (9)
O7—Na2—O9 <sup>i</sup>	103.23 (2)	Na2—O7—H7B	98.3 (10)
O6—Na2—O9 <sup>i</sup>	174.23 (2)	Na1—O7—H7B	127.0 (10)
O10—Na1—O8	101.74 (2)	H7A—O7—H7B	107.6 (13)
O10—Na1—O10 <sup>i</sup>	172.170 (15)	Na1—O8—Na1 <sup>i</sup>	97.465 (19)
O8—Na1—O10 <sup>i</sup>	81.77 (2)	Na1—O8—H8A	117.0 (9)
O10—Na1—O7	94.44 (2)	Na1 <sup>i</sup> —O8—H8A	109.6 (9)
O8—Na1—O7	92.86 (2)	Na1—O8—H8B	115.3 (8)
O10 <sup>i</sup> —Na1—O7	92.36 (2)	Na1 <sup>i</sup> —O8—H8B	112.2 (9)
O10—Na1—O8 <sup>ii</sup>	81.464 (19)	H8A—O8—H8B	105.3 (14)
O8—Na1—O8 <sup>ii</sup>	172.149 (16)	Na1—O9—Na2 <sup>ii</sup>	125.08 (2)
O10 <sup>i</sup> —Na1—O8 <sup>ii</sup>	94.20 (2)	Na1—O9—H9A	110.5 (10)
O7—Na1—O8 <sup>ii</sup>	94.04 (2)	Na2 <sup>ii</sup> —O9—H9A	97.1 (10)
O10—Na1—O9	85.75 (2)	Na1—O9—H9B	104.1 (11)
O8—Na1—O9	90.60 (2)	Na2 <sup>ii</sup> —O9—H9B	112.2 (11)
O10 <sup>i</sup> —Na1—O9	87.22 (2)	H9A—O9—H9B	106.7 (14)
O7—Na1—O9	176.42 (2)	Na1—O10—Na1 <sup>ii</sup>	98.38 (2)
O8 <sup>ii</sup> —Na1—O9	82.451 (19)	Na1—O10—H10A	114.6 (9)
O3—S1—O1	105.85 (3)	Na1 <sup>ii</sup> —O10—H10A	111.2 (9)

O3—S1—O2	106.07 (3)	Na1—O10—H10B	114.4 (10)
O1—S1—O2	105.87 (3)	Na1 <sup>ii</sup> —O10—H10B	112.4 (9)
Na2—O4—H4A	119.9 (11)	H10A—O10—H10B	106.0 (14)
Na2—O4—H4B	116.4 (11)		

Symmetry codes: (i)  $-x+1, -y+1/2, z+1/2$ ; (ii)  $-x+1, -y+1/2, z-1/2$ ; (iii)  $-x+1, -y, -z+3$ .

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O4—H4A $\cdots$ O3 <sup>iv</sup>	0.800 (15)	2.031 (16)	2.8216 (8)	169.7 (15)
O4—H4B $\cdots$ O1 <sup>v</sup>	0.821 (16)	1.983 (16)	2.7904 (7)	167.8 (15)
O5—H5A $\cdots$ O1	0.804 (13)	1.947 (13)	2.7503 (7)	175.9 (13)
O5—H5B $\cdots$ O2 <sup>iv</sup>	0.798 (15)	1.994 (15)	2.7694 (7)	163.9 (15)
O6—H6A $\cdots$ O2 <sup>v</sup>	0.777 (14)	2.072 (14)	2.8206 (7)	161.8 (14)
O6—H6B $\cdots$ O3	0.774 (15)	1.962 (15)	2.7204 (7)	166.5 (15)
O7—H7A $\cdots$ O2 <sup>v</sup>	0.810 (13)	1.976 (14)	2.7761 (7)	169.3 (13)
O7—H7B $\cdots$ O6 <sup>vi</sup>	0.773 (14)	2.171 (14)	2.9110 (8)	160.7 (15)
O8—H8A $\cdots$ O1 <sup>iii</sup>	0.792 (15)	2.009 (15)	2.7900 (7)	168.9 (13)
O8—H8B $\cdots$ S1 <sup>vii</sup>	0.825 (14)	2.455 (14)	3.2582 (6)	164.5 (13)
O9—H9A $\cdots$ O2 <sup>vii</sup>	0.807 (14)	2.106 (14)	2.9096 (7)	174.0 (14)
O10—H10A $\cdots$ O4 <sup>ii</sup>	0.839 (15)	1.962 (15)	2.7908 (8)	169.5 (14)
O10—H10B $\cdots$ O3 <sup>vi</sup>	0.762 (14)	2.069 (14)	2.8210 (7)	169.1 (14)

Symmetry codes: (ii)  $-x+1, -y+1/2, z-1/2$ ; (iii)  $-x+1, -y, -z+3$ ; (iv)  $-x+3/2, -y, z+1/2$ ; (v)  $-x+3/2, -y, z-1/2$ ; (vi)  $-x+1, -y, -z+2$ ; (vii)  $x-1/2, y+1/2, z$ .