



# Crystal structure of sodium (1*S*)-*D*-mannit-1-yl-sulfonate

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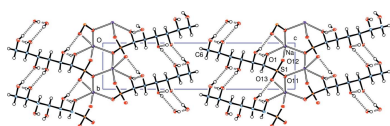
**Keywords:** crystal structure; *D*-mannose bisulfite adduct; sodium hydrogen sulfite; sodium meta-bisulfite.**CCDC reference:** 1862155**Supporting information:** this article has supporting information at journals.iucr.org/e

The title salt, Na<sup>+</sup>·C<sub>6</sub>H<sub>13</sub>O<sub>9</sub>S<sup>-</sup> [systematic name: sodium (1*S*,2*S*,3*S*,4*R*,5*R*)-1,2,3,4,5,6-hexahydroxyhexane-1-sulfonate], is formed by reaction of *D*-mannose with sodium bisulfite (sodium hydrogen sulfite) in water. The anion has an open-chain structure with the S atom and the C atoms of the carbohydrate chain forming an essentially planar zigzag chain in which the absolute values of the torsion angles lie between 173.6 (2) and 179.9 (3)°. The sodium cations are penta-coordinated by O atoms, with one link to a carbohydrate O atom and four to O atoms of sulfonate residues in separate anions, thus creating a three-dimensional network. The carbohydrate anions are arranged in a head (–SO<sub>3</sub><sup>-</sup>) to head (–SO<sub>3</sub><sup>-</sup>) arrangement, thereby forming two parallel sheets linked through coordination to sodium ions, with each sheet containing intermolecular hydrogen bonds between the anionic residues. Unusually, the double sheets are not connected to neighbouring sets of double sheets, either by ion coordination or intermolecular hydrogen bonding.

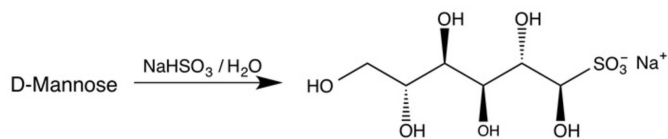
## 1. Chemical context

Adducts formed by the reaction of aldehydes and bisulfite anions have long been used for aldehyde purification since they are often crystalline, whereas the parent aldehydes are often liquids with varying stabilities on storage. The addition reaction is reversible, which makes the bisulfite compounds useful intermediates in the synthesis of other adducts from aldehydes, such as cyanohydrins. Further, bisulfite adducts are useful since they are soluble in water, which can be important if the compounds need to be compatible with aqueous, biological systems, for example to aid delivery of medicinal drugs insoluble in water. Such considerations are important since aldehydes are involved in many synthetic processes for the production of commercially relevant compounds, including pharmaceuticals, and the relative advantages of using different counter-ions (*e.g.* stability, hygroscopicity, ease of filtration of the adduct) are of interest (Kissane *et al.*, 2013).

The bisulfite addition products of aldoses are unusual in that they are acyclic compounds despite the fact that the parent carbohydrates exist predominantly in the cyclic, hemiacetal form. Although such adducts were synthesised many years ago, unequivocal proof of their acyclic nature awaited X-ray structure determination, firstly on the potassium adducts of *D*-glucose and *D*-mannose (Cole *et al.*, 2001), of *D*-galactose (Haines & Hughes, 2010), *D*-ribose (Haines & Hughes, 2014), *D*-lyxose (Haines & Hughes, 2015), and of the sodium adducts of *D*-glucose (Haines & Hughes, 2012) and *D*-lyxose (Haines & Hughes, 2016).



We now report the preparation, properties, and crystal structure of the sodium bisulfite adduct of D-mannose, and comment on its significant structural difference from that of the corresponding potassium adduct.



Mixing concentrated, equimolar solutions of D-mannose and sodium bisulfite (sodium hydrogen sulfite formed by the *in situ* hydrolysis of sodium metabisulfite) in water led to immediate precipitation of the adduct in high yield; this was purified by recrystallization from water, giving material stable in air but which melted over a large temperature range (413–444 K) with extended and continual decomposition.

Obtaining suitable crystals for X-ray analysis was challenging since there was a tendency for formation of thin, rough, multiple crystals, but slow crystallization at approximately 283–286 K and careful selection from the crop so-produced afforded the crystal for examination. The newly formed chiral centre at C1 had the *S*-configuration and in solution in water:acetic acid (9:1) the adduct gave a positive rotation which remained stable over an extended period, suggesting that hydrolysis to its component parts was hindered under the acidic conditions.

## 2. Structural commentary

The newly formed chiral centre at C1 has the *S*-configuration (as shown in Fig. 1) and the systematic name for the salt is sodium (1*S*,2*S*,3*S*,4*R*,5*R*)-1,2,3,4,5,6-hexahydroxyhexane-1-sulfonate. The anion has an open-chain structure in which the S atom and the C atoms of the sugar chain form an essentially planar zigzag (*all-trans*) chain with the corresponding torsion angles lying between the absolute values of 173.6 (2) and 179.9 (3)°. The hydrogen atoms of the hydroxyl groups on C1 to C6 of the carbon chain form hydrogen bonds with oxygen atoms O2, O13, O5, O3, O6 and O4, respectively, of neighbouring chains (Fig. 1 and Table 1) and all the hydroxyl O atoms except O1 are acceptors of hydrogen bonds; O1 is bonded to a sodium ion. We note that all the hydrogen bonds are arranged in cyclic systems, some comprising four O—H...O bonds, others with two O—H...O bonds plus two Na—O coordination bonds.

Unusually, the sodium atom has a coordination sphere of five rather than six oxygen atoms, hexa-coordination having been observed in related adducts from D-glucose (Haines & Hughes, 2012) and D-lyxose (Haines & Hughes, 2016). Further, coordination of a sodium ion by O1 of the carbohydrate chain and oxygen atoms O11, O12 and O13 of four different sulfonate groups leads to a sheet of Na ions coordinated to the ‘heads’ of the anions, Fig. 2.

**Table 1**  
Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1O...O2 <sup>ii</sup>	0.81 (3)	1.92 (4)	2.693 (4)	160 (8)
O2—H2O...O1	0.81 (3)	2.36 (5)	2.828 (3)	118 (5)
O2—H2O...O13 <sup>i</sup>	0.81 (3)	2.08 (4)	2.745 (4)	140 (5)
O3—H3O...O4	0.81 (3)	2.32 (7)	2.838 (3)	123 (7)
O3—H3O...O5 <sup>v</sup>	0.81 (3)	2.11 (6)	2.743 (4)	136 (7)
O4—H4O...O3 <sup>vi</sup>	0.82 (3)	1.87 (3)	2.692 (3)	179 (8)
O5—H5O...O6 <sup>ii</sup>	0.80 (3)	1.91 (3)	2.704 (4)	169 (6)
O6—H6O...O4 <sup>i</sup>	0.81 (3)	2.00 (4)	2.753 (4)	154 (6)
O6—H6O...O5	0.81 (3)	2.45 (6)	2.853 (4)	112 (5)

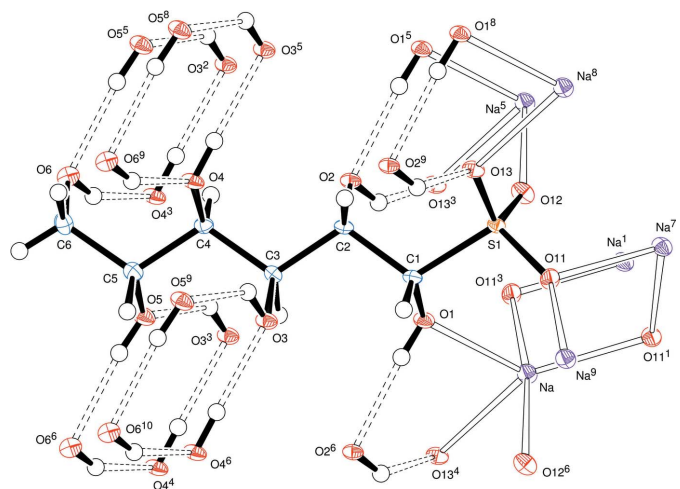
Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $x - 1, y, z$ ; (v)  $x, y + 1, z$ ; (vi)  $x + 1, y, z$ .

**Table 2**  
Selected bond lengths (Å).

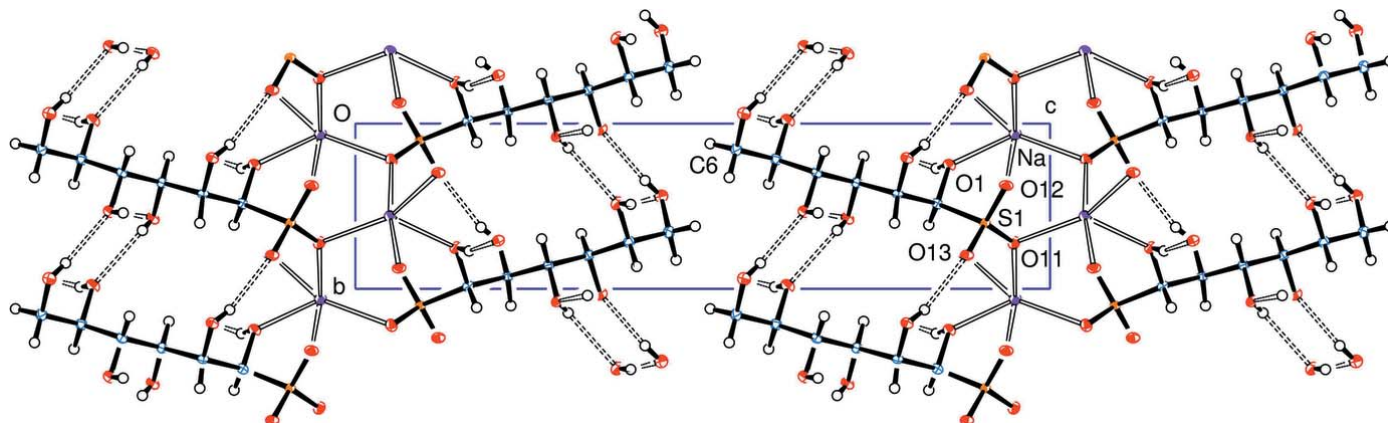
Na—O1 <sup>i</sup>	2.293 (3)	Na—O1	2.386 (3)
Na—O12 <sup>ii</sup>	2.328 (3)	Na—O13 <sup>iv</sup>	2.421 (3)
Na—O11 <sup>iii</sup>	2.370 (3)	Na—O12 <sup>iii</sup>	2.757 (3)

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

The Na—O bonds have lengths in the range 2.293 (3) to 2.421 (3) Å (Table 2) and form a distorted square pyramidal shape with O1 in the apical site. The next shortest Na—O contact distance is 2.757 Å to O12<sup>iii</sup>, which would provide a rather distorted octahedral coordination. Twofold screw axes of symmetry (parallel to the *b* axis) relate the sodium ions in the sheet close to the *ab* plane at  $z = 0$  and 1, and the zigzag  $C_6$  chains lie approximately normal to this plane and nearly parallel to the *c* axis. The ‘tails’ of these chains, around the C6, O6 groups, lie close to the  $z = \frac{1}{2}$  plane where the screw axes relate them to the tails of adjacent molecules. But, whereas the heads are linked through the sodium atoms across the  $z = 0$



**Figure 1**  
View of the D-mannose–NaHSO<sub>3</sub> adduct, indicating the atom-numbering scheme. All sodium coordination contacts and hydrogen bonds involving the atoms of the sugar adduct are indicated. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (1)  $1 - x, y - \frac{1}{2}, 2 - z$ ; (2)  $1 + x, y - 1, z$ ; (3)  $x, y - 1, z$ ; (4)  $x - 1, y - 1, z$ ; (5)  $1 + x, y, z$ ; (6)  $x - 1, y, z$ ; (7)  $1 - x, \frac{1}{2} + y, 2 - z$ ; (8)  $1 + x, 1 + y, z$ ; (9)  $x, 1 + y, z$ ; (10)  $x - 1, 1 + y, z$ .



**Figure 2**  
View down the  $a$  axis of the crystal packing.

plane, there are no short intermolecular contacts across the  $z = \frac{1}{2}$  plane; the shortest contacts here are  $H61 \cdots H62^{11} = 2.57 \text{ \AA}$ ,  $H61 \cdots O6^{12} = 2.70 \text{ \AA}$ ,  $H62 \cdots H5^{13} = 2.60 \text{ \AA}$  and  $H62 \cdots C6^{13} = 2.95 \text{ \AA}$ , *i.e.* at normal van der Waals' distances; symmetry codes: (11)  $1 - x, y + \frac{1}{2}, 1 - z$ ; (12)  $2 - x, y + \frac{1}{2}, 1 - z$ ; (13)  $1 - x, y - \frac{1}{2}, 1 - z$ .

The neighbours of the zigzag  $C_6$  chains are related only by translation parallel to the  $a$  and  $b$  axes, Fig. 3; all the cations here are aligned in the same direction. Anions related across the Na coordination plane and about the  $z = \frac{1}{2}$  plane have the opposite alignment. Here, we observe a major difference between this sodium complex and the corresponding potassium *D*-mannose complex (Cole *et al.*, 2001) where each  $C_6$  chain is surrounded by four chains pointing in the opposite direction, as shown in Fig. 4. Hence the distances between the

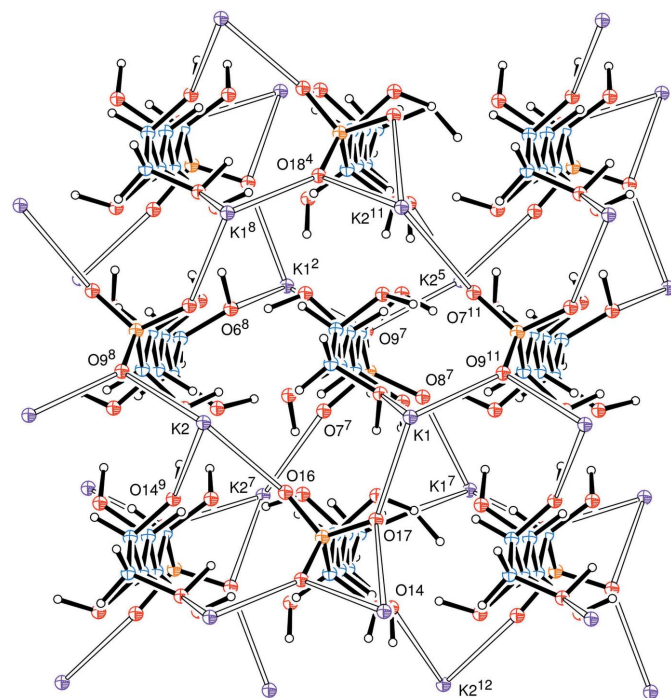


**Figure 3**  
View looking along the all-*trans* sugar chain and neighbouring chains, all pointing in the same direction. Displacement ellipsoids are shown at the 30% probability level. Symmetry codes are defined as for Fig. 1.

coordination planes are quite different, *viz*  $21.08 \text{ \AA}$  in the sodium complex, but  $11.55 \text{ \AA}$  for the potassium compound.

### 3. Supramolecular features

A three-dimensional bonding network exists in the crystal structure through (i) penta-coordination of a sodium cation with oxygens from five different mannose bisulfite residues, and (ii) intermolecular hydrogen bonds from each of the six hydroxyl groups to acceptor oxygen atoms in four different residues.



**Figure 4**  
View looking along the all-*trans* sugar chain and neighbouring chains in the *D*-mannose–potassium bisulfite adduct; adjacent chains point in opposite directions. Atom coordinates were taken from the CCDC deposition, code 172060 (Cole *et al.*, 2001). Atoms are represented by small spheres of arbitrary radii. Symmetry codes: (2)  $1 - x, \frac{1}{2} + y, -z$ ; (4)  $1 + x, y, z$ ; (5)  $1 - x, y - \frac{1}{2}, -z$ ; (7)  $x, y, z - 1$ ; (8)  $1 - x, \frac{1}{2} + y, 1 - z$ ; (9)  $-x, \frac{1}{2} + y, -z$ ; (11)  $1 - x, y - \frac{1}{2}, 1 - z$ ; (12)  $-x, y - \frac{1}{2}, -z$ .



#### 4. Spectroscopic results

High resolution mass spectrometry in negative ion mode showed, as the base peak in the spectrum, a peak for  $[\text{C}_6\text{H}_{13}\text{O}_9\text{S}_1]^-$  at  $m/z$  261.0287 and a significant peak was observed at  $m/z$  243.0182  $[\text{C}_6\text{H}_{13}\text{O}_9\text{S}_1-\text{H}_2\text{O}]^-$ . A minor peak observed at  $m/z$  359.1194  $[\text{C}_{12}\text{H}_{23}\text{O}_{12}]^-$  was assigned to a dimer ion  $([2M - \text{H}]^-)$  produced by association of a D-mannose molecule ( $M = \text{C}_6\text{H}_{12}\text{O}_6$ ) with the mono-anion of D-mannose  $[\text{C}_6\text{H}_{11}\text{O}_6]^-$  under the electrospray ionization conditions of the mass spectrometric measurement.

The  $^1\text{H}$  NMR spectrum of the adduct in  $\text{D}_2\text{O}$  indicated the presence of the  $\alpha$ - and  $\beta$ -pyranose forms of D-mannose and the major and minor forms of the acyclic sulfonate in the % ratios 25.24:13.14:55.00:6.62, respectively. Clearly, the *R*-stereoisomer at C1 is present in solution but only the *S*-isomer crystallizes. Further, some hydrolysis of the adduct to afford the parent sugar occurs during the NMR measurement.

The  $^{13}\text{C}$  NMR spectrum showed signals for C1 nuclei at  $\delta_{\text{C}}$  94.70, 94.31, 84.43 and 82.34 arising, respectively, from the  $\alpha$ - and  $\beta$ -pyranose forms of D-mannose, the minor adduct and the major adduct, in the % ratios of 32.73:15.00:3.64:48.63.

#### 5. Synthesis and crystallization

D-Mannose (0.9 g) was dissolved in water (2 ml), sodium metabisulfite (0.475 g) was added, and the solution was then warmed to achieve complete solution. On cooling to room temperature, precipitation occurred within 3 min (see scheme). The product was collected by filtration, and dried to give the adduct (1.42 g, 84%), a portion of which was recrystallized to afford the analytical sample, m.p. 413–444 K (with extended and continual decomposition);  $[\alpha]_{\text{D}}^{20} +8.2$  (15 min.) (*c*, 0.79 in 9:1  $\text{H}_2\text{O}$ : HOAc).  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 400 MHz, reference  $\text{Me}_3\text{COH}$  at  $\delta_{\text{H}}$  1.24):  $\delta_{\text{H}}$  5.17 (*d*,  $J_{1,2} = 1.5$  Hz, H-1 of  $\alpha$ -pyranose), 4.89 (*d*,  $J_{1,2} = 0.8$  Hz, H-1 of  $\beta$ -pyranose); signals for the major acyclic sulfonate:  $\delta_{\text{H}}$  4.64 (*s*, H-1), 4.20 (*d*,  $J_{2,3} = 9.5$  Hz, H-2); for the minor acyclic sulfonate:  $\delta_{\text{H}}$  4.64 (*d*,  $J_{1,2} = 5.2$  Hz, H-1), 4.07 (*d*,  $J_{2,3} = 7.8$  Hz, H-2); ratio of major to minor sulfonate = 8.3:1.  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ , 100 MHz, reference  $\text{Me}_3\text{COH}$  at  $\delta_{\text{C}}$  30.29):  $\delta_{\text{C}}$  94.70 (C1,  $\alpha$ -pyranose), 94.31 (C1,  $\beta$ -pyranose); signals for the major acyclic sulfonate:  $\delta_{\text{C}}$  82.34 (C1), 71.48, 69.46, 69.18\*, 68.91\* (C2, C3, C4, C5), 63.96 (C6); the minor acyclic sulfonate showed a peak at  $\delta_{\text{C}}$  84.43 (C1). Each of the signals marked with \* is the average value of two closely spaced singlets of equal intensity separated by 4 Hz. The reasons for these small separations in the proton decoupled  $^{13}\text{C}$  spectrum are not clear.

Integration of the various signals for H-1 in the  $^1\text{H}$  NMR spectrum indicated that the species  $\alpha$ -pyranose,  $\beta$ -pyranose, major acyclic sulfonate and minor acyclic sulfonate were present in the % ratios of 25.24: 13.14: 55.00: 6.62, respectively. In the  $^{13}\text{C}$  NMR spectrum, based on peak heights, the corresponding ratios were: 32.73: 15.00: 48.63: 3.64.

HRESMS (negative ion mode, measured in an  $\text{H}_2\text{O}/\text{MeOH}$ , solution) gave a base peak at  $m/z$  261.0287  $[\text{C}_6\text{H}_{13}\text{O}_9\text{S}_1]^-$ , and a significant peak at 243.0182  $[\text{C}_6\text{H}_{13}\text{O}_9\text{S}_1-\text{H}_2\text{O}]^-$ .

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	$\text{Na}^+ \cdot \text{C}_6\text{H}_{13}\text{NaO}_9\text{S}^-$
$M_r$	284.21
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	140
$a, b, c$ (Å)	4.8744 (2), 5.0042 (2), 21.0759 (10)
$\beta$ (°)	93.867 (4)
$V$ (Å <sup>3</sup> )	512.92 (4)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.40
Crystal size (mm)	0.52 × 0.20 × 0.04
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3/ Sapphire3 CCD
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)
$T_{\text{min}}, T_{\text{max}}$	0.618, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	9424, 2972, 2926
$R_{\text{int}}$ ( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.030 0.703
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.093, 1.16
No. of reflections	2972
No. of parameters	206
No. of restraints	7
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.49, -0.45
Absolute structure	Flack $x$ determined using 1240 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.04 (4)

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b), *ORTEP* (Johnson, 1976) and *ORTEP-3 for Windows and WinGX* (Farrugia, 2012).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All the hydrogen atoms were located in difference maps and were refined with isotropic thermal parameters; the hydroxyl hydrogen atoms were refined with constrained O–H distances.

#### Acknowledgements

We thank the EPSRC UK National Mass Spectrometry Facility (NMSF) at Swansea University for determination of the low and high resolution mass spectra, Dr Sergey Nepogodiev of the John Innes Centre, Norwich and Dr Ryan Tinson of the University of East Anglia for measurement of the NMR spectra, and Dr James Orton of the UK National Crystallographic Service for preliminary measurements.

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## supporting information

*Acta Cryst.* (2018). E74, 1314-1318 [https://doi.org/10.1107/S2056989018011556]

## Crystal structure of sodium (1S)-D-mannit-1-ylsulfonate

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## Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *ORTEP* (Johnson, 1976) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014/7* (Sheldrick, 2015b) and *WinGX* (Farrugia, 2012).

## Sodium (1S,2S,3S,4R,5R)-1,2,3,4,5,6- hexahydroxyhexane-1-sulfonate

## Crystal data

Na<sup>+</sup>·C<sub>6</sub>H<sub>13</sub>NaO<sub>9</sub>S<sup>-</sup>

$M_r = 284.21$

Monoclinic,  $P2_1$

$a = 4.8744$  (2) Å

$b = 5.0042$  (2) Å

$c = 21.0759$  (10) Å

$\beta = 93.867$  (4)°

$V = 512.92$  (4) Å<sup>3</sup>

$Z = 2$

$F(000) = 296$

$D_x = 1.840$  Mg m<sup>-3</sup>

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

Cell parameters from 4715 reflections

$\theta = 3.9$ – $32.5$ °

$\mu = 0.40$  mm<sup>-1</sup>

$T = 140$  K

Plate, colourless

$0.52 \times 0.20 \times 0.04$  mm

## Data collection

Oxford Diffraction Xcalibur 3/Sapphire3 CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source  
Graphite monochromator

Detector resolution: 16.0050 pixels mm<sup>-1</sup>

Thin slice  $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.618$ ,  $T_{\max} = 1.000$

9424 measured reflections

2972 independent reflections

2926 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 30.0$ °,  $\theta_{\min} = 3.9$ °

$h = -6$ → $6$

$k = -7$ → $7$

$l = -29$ → $29$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.093$

$S = 1.16$

2972 reflections

206 parameters

7 restraints

Primary atom site location: dual

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 0.694P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.49$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.44$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

1240 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)

Absolute structure parameter: 0.04 (4)

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5658 (7)	0.4844 (7)	0.83763 (16)	0.0099 (6)
O1	0.4257 (5)	0.2507 (5)	0.85501 (12)	0.0124 (5)
C2	0.7379 (7)	0.4250 (7)	0.78081 (16)	0.0092 (6)
O2	0.9236 (5)	0.2083 (5)	0.79422 (12)	0.0112 (5)
C3	0.5507 (7)	0.3570 (7)	0.72169 (16)	0.0103 (6)
O3	0.3628 (5)	0.5738 (6)	0.70848 (11)	0.0124 (5)
C4	0.7176 (7)	0.2973 (7)	0.66432 (16)	0.0106 (6)
O4	0.8619 (5)	0.5330 (5)	0.64719 (12)	0.0132 (5)
C5	0.5343 (7)	0.2160 (7)	0.60581 (16)	0.0121 (6)
O5	0.3884 (5)	−0.0177 (5)	0.62226 (13)	0.0149 (5)
C6	0.6989 (8)	0.1565 (7)	0.54832 (17)	0.0142 (7)
O6	0.8875 (5)	−0.0609 (5)	0.55969 (13)	0.0150 (5)
S1	0.77100 (15)	0.60171 (15)	0.90636 (4)	0.00914 (16)
O11	0.5782 (5)	0.7211 (6)	0.94817 (12)	0.0139 (5)
O12	0.9110 (5)	0.3741 (5)	0.93700 (12)	0.0142 (5)
O13	0.9575 (5)	0.7966 (5)	0.88046 (12)	0.0125 (5)
Na	0.2652 (3)	0.0627 (3)	0.94976 (6)	0.0129 (3)
H1	0.436 (10)	0.615 (13)	0.825 (2)	0.024 (13)*
H2	0.832 (11)	0.605 (16)	0.776 (3)	0.037 (15)*
H3	0.412 (9)	0.198 (9)	0.732 (2)	0.007 (10)*
H4	0.839 (8)	0.167 (8)	0.6749 (19)	0.002 (9)*
H5	0.377 (10)	0.363 (11)	0.595 (2)	0.020 (13)*
H61	0.800 (9)	0.326 (9)	0.5382 (19)	0.004 (10)*
H62	0.588 (9)	0.122 (11)	0.511 (2)	0.015 (11)*
H1O	0.281 (8)	0.275 (15)	0.834 (3)	0.045 (18)*
H2O	0.857 (10)	0.118 (11)	0.821 (2)	0.025 (13)*
H3O	0.458 (14)	0.672 (14)	0.689 (3)	0.08 (3)*
H4O	1.016 (7)	0.543 (16)	0.666 (3)	0.05 (2)*
H5O	0.246 (8)	−0.013 (12)	0.601 (2)	0.037 (17)*
H6O	0.829 (11)	−0.166 (10)	0.585 (2)	0.033 (16)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0066 (14)	0.0104 (15)	0.0125 (15)	−0.0002 (11)	−0.0005 (11)	0.0021 (11)
O1	0.0092 (11)	0.0132 (12)	0.0146 (12)	−0.0038 (9)	0.0000 (9)	0.0016 (9)
C2	0.0068 (13)	0.0078 (14)	0.0130 (14)	−0.0009 (11)	−0.0001 (11)	0.0005 (11)
O2	0.0077 (11)	0.0113 (11)	0.0145 (11)	0.0026 (9)	−0.0005 (9)	0.0014 (9)
C3	0.0094 (14)	0.0106 (15)	0.0108 (14)	−0.0007 (11)	−0.0013 (11)	−0.0001 (11)

O3	0.0094 (10)	0.0124 (12)	0.0152 (11)	0.0009 (10)	-0.0010 (8)	0.0033 (10)
C4	0.0090 (14)	0.0105 (15)	0.0122 (14)	0.0013 (12)	0.0005 (11)	0.0017 (11)
O4	0.0086 (11)	0.0134 (12)	0.0173 (12)	-0.0033 (9)	-0.0019 (9)	0.0022 (9)
C5	0.0120 (15)	0.0113 (15)	0.0129 (15)	-0.0011 (12)	-0.0006 (12)	0.0012 (12)
O5	0.0117 (12)	0.0154 (13)	0.0171 (12)	-0.0043 (10)	-0.0023 (9)	0.0032 (10)
C6	0.0164 (16)	0.0139 (18)	0.0118 (14)	0.0017 (12)	-0.0016 (12)	0.0001 (11)
O6	0.0133 (12)	0.0151 (14)	0.0167 (13)	0.0004 (10)	0.0024 (9)	0.0002 (10)
S1	0.0081 (3)	0.0080 (3)	0.0112 (3)	0.0010 (3)	-0.0003 (2)	-0.0002 (3)
O11	0.0138 (12)	0.0150 (12)	0.0128 (11)	0.0059 (10)	0.0007 (9)	-0.0018 (10)
O12	0.0150 (12)	0.0093 (11)	0.0176 (12)	0.0038 (9)	-0.0033 (9)	0.0012 (9)
O13	0.0104 (11)	0.0100 (11)	0.0171 (12)	-0.0031 (9)	-0.0002 (9)	0.0000 (9)
Na	0.0122 (6)	0.0123 (7)	0.0138 (6)	0.0036 (5)	-0.0006 (5)	-0.0009 (5)

*Geometric parameters (Å, °)*

Na—O11 <sup>i</sup>	2.293 (3)	O4—H4O	0.82 (3)
Na—O12 <sup>ii</sup>	2.328 (3)	C5—O5	1.424 (4)
Na—O11 <sup>iii</sup>	2.370 (3)	C5—C6	1.527 (5)
Na—O1	2.386 (3)	C5—H5	1.08 (5)
Na—O13 <sup>iv</sup>	2.421 (3)	O5—H5O	0.80 (3)
Na—O12 <sup>iii</sup>	2.757 (3)	C6—O6	1.434 (4)
C1—O1	1.415 (4)	C6—H61	1.01 (4)
C1—C2	1.537 (5)	C6—H62	0.94 (4)
C1—S1	1.802 (3)	O6—H6O	0.81 (3)
C1—H1	0.94 (6)	S1—O12	1.456 (3)
O1—Na	2.386 (3)	S1—O11	1.459 (3)
O1—H1O	0.81 (3)	S1—O13	1.464 (3)
C2—O2	1.429 (4)	S1—Na <sup>v</sup>	3.0557 (16)
C2—C3	1.532 (4)	O11—Na <sup>vi</sup>	2.293 (3)
C2—H2	1.02 (8)	O11—Na <sup>v</sup>	2.370 (3)
O2—H2O	0.81 (3)	O12—Na <sup>vii</sup>	2.328 (3)
C3—O3	1.435 (4)	O12—Na <sup>v</sup>	2.757 (3)
C3—C4	1.532 (5)	O13—Na <sup>viii</sup>	2.421 (3)
C3—H3	1.08 (4)	Na—S1 <sup>iii</sup>	3.0557 (16)
O3—H3O	0.81 (3)	Na—Na <sup>v</sup>	3.915 (2)
C4—O4	1.432 (4)	Na—Na <sup>iii</sup>	3.915 (2)
C4—C5	1.529 (5)	Na—H1O	2.66 (6)
C4—H4	0.90 (4)		
O1—C1—C2	109.9 (3)	C1—S1—Na <sup>v</sup>	135.30 (11)
O1—C1—S1	108.2 (2)	S1—O11—Na <sup>vi</sup>	140.39 (16)
C2—C1—S1	112.8 (2)	S1—O11—Na <sup>v</sup>	103.31 (14)
O1—C1—H1	109 (3)	Na <sup>vi</sup> —O11—Na <sup>v</sup>	114.20 (11)
C2—C1—H1	109 (3)	S1—O12—Na <sup>vii</sup>	153.71 (18)
S1—C1—H1	109 (3)	S1—O12—Na <sup>v</sup>	87.25 (12)
C1—O1—Na	137.2 (2)	Na <sup>vii</sup> —O12—Na <sup>v</sup>	113.65 (10)
C1—O1—H1O	99 (5)	S1—O13—Na <sup>viii</sup>	121.11 (15)
Na—O1—H1O	101 (5)	O11 <sup>i</sup> —Na—O12 <sup>ii</sup>	170.53 (12)



O2—C2—C3	109.1 (3)	O11 <sup>i</sup> —Na—O11 <sup>iii</sup>	95.09 (8)
O2—C2—C1	111.4 (3)	O12 <sup>ii</sup> —Na—O11 <sup>iii</sup>	94.13 (11)
C3—C2—C1	110.5 (3)	O11 <sup>i</sup> —Na—O1	91.47 (10)
O2—C2—H2	114 (3)	O12 <sup>ii</sup> —Na—O1	85.52 (10)
C3—C2—H2	111 (3)	O11 <sup>iii</sup> —Na—O1	121.61 (11)
C1—C2—H2	101 (3)	O11 <sup>i</sup> —Na—O13 <sup>iv</sup>	88.09 (10)
C2—O2—H2O	106 (4)	O12 <sup>ii</sup> —Na—O13 <sup>iv</sup>	82.76 (10)
O3—C3—C4	111.1 (3)	O11 <sup>iii</sup> —Na—O13 <sup>iv</sup>	151.65 (11)
O3—C3—C2	109.1 (3)	O1—Na—O13 <sup>iv</sup>	86.37 (10)
C4—C3—C2	111.5 (3)	O11 <sup>i</sup> —Na—O12 <sup>iii</sup>	90.22 (10)
O3—C3—H3	101 (2)	O12 <sup>ii</sup> —Na—O12 <sup>iii</sup>	93.28 (8)
C4—C3—H3	113 (2)	O11 <sup>iii</sup> —Na—O12 <sup>iii</sup>	55.17 (9)
C2—C3—H3	111 (2)	O1—Na—O12 <sup>iii</sup>	176.51 (11)
C3—O3—H3O	100 (6)	O13 <sup>iv</sup> —Na—O12 <sup>iii</sup>	96.74 (10)
O4—C4—C5	106.6 (3)	O11 <sup>i</sup> —Na—S1 <sup>iii</sup>	98.35 (8)
O4—C4—C3	109.5 (3)	O12 <sup>ii</sup> —Na—S1 <sup>iii</sup>	88.84 (8)
C5—C4—C3	112.1 (3)	O11 <sup>iii</sup> —Na—S1 <sup>iii</sup>	27.68 (7)
O4—C4—H4	109 (3)	O1—Na—S1 <sup>iii</sup>	148.15 (9)
C5—C4—H4	110 (3)	O13 <sup>iv</sup> —Na—S1 <sup>iii</sup>	123.98 (8)
C3—C4—H4	109 (3)	O12 <sup>iii</sup> —Na—S1 <sup>iii</sup>	28.43 (6)
C4—O4—H4O	112 (5)	O11 <sup>i</sup> —Na—Na <sup>v</sup>	96.85 (9)
O5—C5—C6	109.3 (3)	O12 <sup>ii</sup> —Na—Na <sup>v</sup>	92.10 (7)
O5—C5—C4	107.3 (3)	O11 <sup>iii</sup> —Na—Na <sup>v</sup>	32.29 (7)
C6—C5—C4	112.5 (3)	O1—Na—Na <sup>v</sup>	89.32 (8)
O5—C5—H5	105 (3)	O13 <sup>iv</sup> —Na—Na <sup>v</sup>	173.53 (8)
C6—C5—H5	112 (3)	O12 <sup>iii</sup> —Na—Na <sup>v</sup>	87.45 (8)
C4—C5—H5	111 (3)	S1 <sup>iii</sup> —Na—Na <sup>v</sup>	59.55 (4)
C5—O5—H5O	105 (4)	O11 <sup>i</sup> —Na—Na <sup>iii</sup>	33.52 (6)
O6—C6—C5	112.4 (3)	O12 <sup>ii</sup> —Na—Na <sup>iii</sup>	153.15 (10)
O6—C6—H61	111 (2)	O11 <sup>iii</sup> —Na—Na <sup>iii</sup>	65.29 (9)
C5—C6—H61	107 (2)	O1—Na—Na <sup>iii</sup>	119.46 (9)
O6—C6—H62	109 (3)	O13 <sup>iv</sup> —Na—Na <sup>iii</sup>	106.89 (7)
C5—C6—H62	114 (3)	O12 <sup>iii</sup> —Na—Na <sup>iii</sup>	61.18 (7)
H61—C6—H62	104 (4)	S1 <sup>iii</sup> —Na—Na <sup>iii</sup>	64.84 (4)
C6—O6—H6O	111 (4)	Na <sup>v</sup> —Na—Na <sup>iii</sup>	79.45 (5)
O12—S1—O11	110.74 (16)	O11 <sup>i</sup> —Na—H1O	102.9 (13)
O12—S1—O13	113.71 (16)	O12 <sup>ii</sup> —Na—H1O	72.2 (12)
O11—S1—O13	113.22 (16)	O11 <sup>iii</sup> —Na—H1O	132.0 (16)
O12—S1—C1	108.65 (16)	O1—Na—H1O	17.4 (8)
O11—S1—C1	105.88 (16)	O13 <sup>iv</sup> —Na—H1O	74.0 (14)
O13—S1—C1	104.03 (15)	O12 <sup>iii</sup> —Na—H1O	163.4 (9)
O12—S1—Na <sup>v</sup>	64.32 (11)	S1 <sup>iii</sup> —Na—H1O	152.7 (17)
O11—S1—Na <sup>v</sup>	49.00 (11)	Na <sup>v</sup> —Na—H1O	100.8 (14)
O13—S1—Na <sup>v</sup>	119.44 (11)	Na <sup>iii</sup> —Na—H1O	134.2 (11)
C2—C1—O1—Na	150.0 (2)	C2—C1—S1—O11	163.8 (2)
S1—C1—O1—Na	26.4 (4)	O1—C1—S1—O13	166.0 (2)
O1—C1—C2—O2	-55.8 (3)	C2—C1—S1—O13	44.2 (3)

S1—C1—C2—O2	65.0 (3)	O1—C1—S1—Na <sup>v</sup>	-27.4 (3)
O1—C1—C2—C3	65.6 (3)	C2—C1—S1—Na <sup>v</sup>	-149.19 (18)
S1—C1—C2—C3	-173.6 (2)	O12—S1—O11—Na <sup>vi</sup>	-179.4 (2)
O2—C2—C3—O3	179.6 (3)	O13—S1—O11—Na <sup>vi</sup>	51.6 (3)
C1—C2—C3—O3	56.8 (3)	C1—S1—O11—Na <sup>vi</sup>	-61.8 (3)
O2—C2—C3—C4	-57.3 (3)	Na <sup>v</sup> —S1—O11—Na <sup>vi</sup>	161.2 (3)
C1—C2—C3—C4	179.9 (3)	O12—S1—O11—Na <sup>v</sup>	19.44 (19)
O3—C3—C4—O4	57.3 (3)	O13—S1—O11—Na <sup>v</sup>	-109.62 (15)
C2—C3—C4—O4	-64.6 (3)	C1—S1—O11—Na <sup>v</sup>	137.03 (14)
O3—C3—C4—C5	-60.8 (4)	O11—S1—O12—Na <sup>vii</sup>	-160.2 (4)
C2—C3—C4—C5	177.2 (3)	O13—S1—O12—Na <sup>vii</sup>	-31.4 (4)
O4—C4—C5—O5	-179.7 (3)	C1—S1—O12—Na <sup>vii</sup>	83.9 (4)
C3—C4—C5—O5	-59.9 (4)	Na <sup>v</sup> —S1—O12—Na <sup>vii</sup>	-144.0 (4)
O4—C4—C5—C6	60.0 (4)	O11—S1—O12—Na <sup>v</sup>	-16.19 (16)
C3—C4—C5—C6	179.9 (3)	O13—S1—O12—Na <sup>v</sup>	112.62 (14)
O5—C5—C6—O6	-57.8 (4)	C1—S1—O12—Na <sup>v</sup>	-132.07 (12)
C4—C5—C6—O6	61.2 (4)	O12—S1—O13—Na <sup>viii</sup>	-67.7 (2)
O1—C1—S1—O12	44.6 (3)	O11—S1—O13—Na <sup>viii</sup>	59.9 (2)
C2—C1—S1—O12	-77.2 (3)	C1—S1—O13—Na <sup>viii</sup>	174.31 (16)
O1—C1—S1—O11	-74.4 (3)	Na <sup>v</sup> —S1—O13—Na <sup>viii</sup>	5.1 (2)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O $\cdots$ O2 <sup>ii</sup>	0.81 (3)	1.92 (4)	2.693 (4)	160 (8)
O2—H2O $\cdots$ O1	0.81 (3)	2.36 (5)	2.828 (3)	118 (5)
O2—H2O $\cdots$ O13 <sup>i</sup>	0.81 (3)	2.08 (4)	2.745 (4)	140 (5)
O3—H3O $\cdots$ O4	0.81 (3)	2.32 (7)	2.838 (3)	123 (7)
O3—H3O $\cdots$ O5 <sup>vi</sup>	0.81 (3)	2.11 (6)	2.743 (4)	136 (7)
O4—H4O $\cdots$ O3 <sup>vii</sup>	0.82 (3)	1.87 (3)	2.692 (3)	179 (8)
O5—H5O $\cdots$ O6 <sup>ii</sup>	0.80 (3)	1.91 (3)	2.704 (4)	169 (6)
O6—H6O $\cdots$ O4 <sup>i</sup>	0.81 (3)	2.00 (4)	2.753 (4)	154 (6)
O6—H6O $\cdots$ O5	0.81 (3)	2.45 (6)	2.853 (4)	112 (5)

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $x-1, y, z$ ; (vi)  $x, y+1, z$ ; (vii)  $x+1, y, z$ .