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## Structure Reports

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Poly[ $\mu_5$ -(4-methoxybenzenesulfonato)-sodium]Suchada Chantrapromma,<sup>a,\*</sup> Nawong Boonnak<sup>b</sup> and Hoong-Kun Fun<sup>c</sup>§

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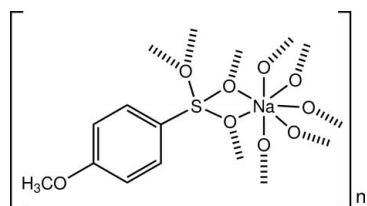
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.101; data-to-parameter ratio = 14.9.

In the title complex,  $[\text{Na}(\text{C}_7\text{H}_7\text{O}_4\text{S})]_n$ , the  $\text{Na}^{\text{I}}$  ion is coordinated in a slightly distorted pentagonal-bipyramidal environment by seven O atoms [ $\text{Na}-\text{O} = 2.3198$  (16)– $2.5585$  (17) Å]. The 4-methoxybenzenesulfonate anions act as bis-chelating and bridging ligands, forming a two-dimensional polymer parallel to (001), which is further linked into a three-dimensional network by weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the applications of aromatic sulfonic acids, see: Babu *et al.* (2003); Chanawanno *et al.* (2010); King (1991); Ruanwas *et al.* (2010); Schöngut *et al.* (2011); Siril *et al.* (2007); Taylor *et al.* (2006). For a related structure, see: Smith *et al.* (2004). For standard bond-lengths, see: Allen *et al.* (1987).



## Experimental

## Crystal data

[ $\text{Na}(\text{C}_7\text{H}_7\text{O}_4\text{S})$ ] $M_r = 210.19$ Orthorhombic,  $Pbca$  $a = 8.3121$  (8) Å $b = 6.0287$  (6) Å $c = 35.930$  (3) Å $V = 1800.5$  (3) Å<sup>3</sup> $Z = 8$ Mo  $K\alpha$  radiation $\mu = 0.38$  mm<sup>-1</sup> $T = 293$  K $0.54 \times 0.46 \times 0.22$  mm

## Data collection

Bruker APEXII CCD area detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2009)

 $T_{\text{min}} = 0.819$ ,  $T_{\text{max}} = 0.920$ 

8793 measured reflections

1769 independent reflections

1720 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.022$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$  $wR(F^2) = 0.101$  $S = 1.20$ 

1769 reflections

119 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.28$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.28$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                              | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C6}-\text{H6A}\cdots\text{O1}^{\text{i}}$  | 0.93         | 2.37               | 3.282 (3)   | 165                  |
| $\text{C7}-\text{H7A}\cdots\text{O4}^{\text{ii}}$ | 0.96         | 2.56               | 3.407 (4)   | 148                  |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL, PLATON (Spek, 2009), Mercury and publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5648).

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## supporting information

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**Poly[ $\mu_5$ -(4-methoxybenzenesulfonato)-sodium]****Suchada Chantrapromma, Nawong Boonnak and Hoong-Kun Fun****S1. Comment**

Aromatic sulfonic acids are one of several useful sulfonic acids which are frequently used as chemical reagents (King, 1991) such as reagents for phenol preparation. They are also widely used as acid catalysts in organic reactions (Siril *et al.*, 2007) such as for the deprotection of *O*-allylphenols (Babu *et al.*, 2003). Salts of benzenesulfonic acid exhibit pharmaceutical and biological activities (Chanawanno *et al.*, 2010; Taylor *et al.*, 2006), and are also used for nonlinear optical material preparations (Ruanwas *et al.*, 2010) and as raw materials in detergent manufacture (Schöngut *et al.*, 2011). Based on these significant roles played by aromatic sulfonic acids, we have synthesized the sodium salt of 4-methoxybenzenesulfonate and herein we report the crystal structure of the title compound (I).

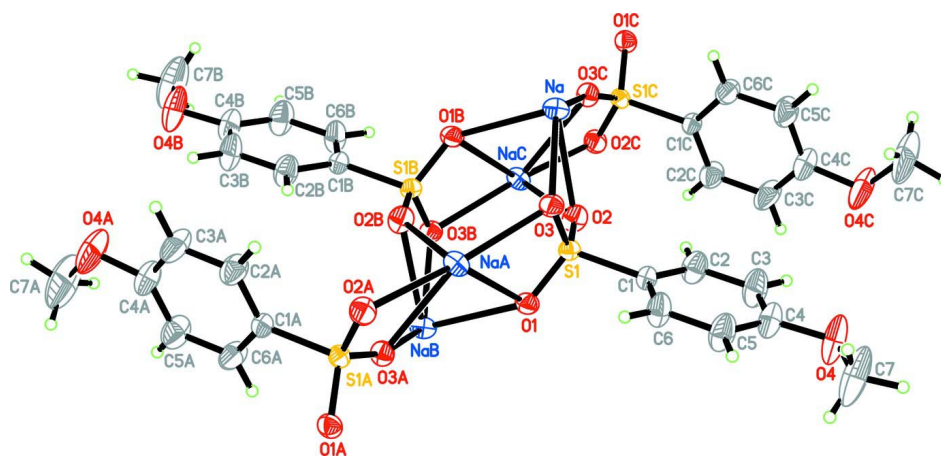
Within the title coordination polymer there are tetranuclear clusters containing four Na<sup>I</sup> ions and four 4-methoxybenzenesulfonate ligands (Fig. 1). All three O atoms of the 4-methoxybenzenesulfonate ligands are involved in coordination to the Na<sup>I</sup> ion. The coordination modes of the sulfonate unit are chelating bidentate and bridging monodentate linking two Na<sup>I</sup> ions. Each Na<sup>I</sup> is in a distorted pentagonal-bipyramidal geometry (Fig. 2) with three pairs of chelating O atoms from the three bidentate sulfonate groups and one bridging O atom from another monodentate sulfonate group which is also coordinated to a symmetry related Na<sup>I</sup> ion. The distance of the Na<sup>I</sup> ion from the mean plane of the O<sub>5</sub> equatorial atoms is 0.127 Å. Bond lengths (Allen *et al.*, 1987) and angles in the ligand are in normal ranges. The Na—O bond distances in the equatorial plane range from 2.3198 (16) - 2.5585 (17) Å, and the two axial Na—O bond distances are 2.3734 (17) and 2.4637 (16) Å. The O—Na—O bond angles in the equatorial plane are in the range 56.76 (5)–85.88 (6) ° and the axial angle is 158.12 (7)°. These values are comparable to those reported for another Na—O donor complex (Smith *et al.*, 2004). The overall structure is a two-dimensional polymer parallel to (001) (Fig. 3). In addition, weak C—H···O hydrogen bonds (Table 1) link the polymer into a three-dimensional network (Fig. 4).

**S2. Experimental**

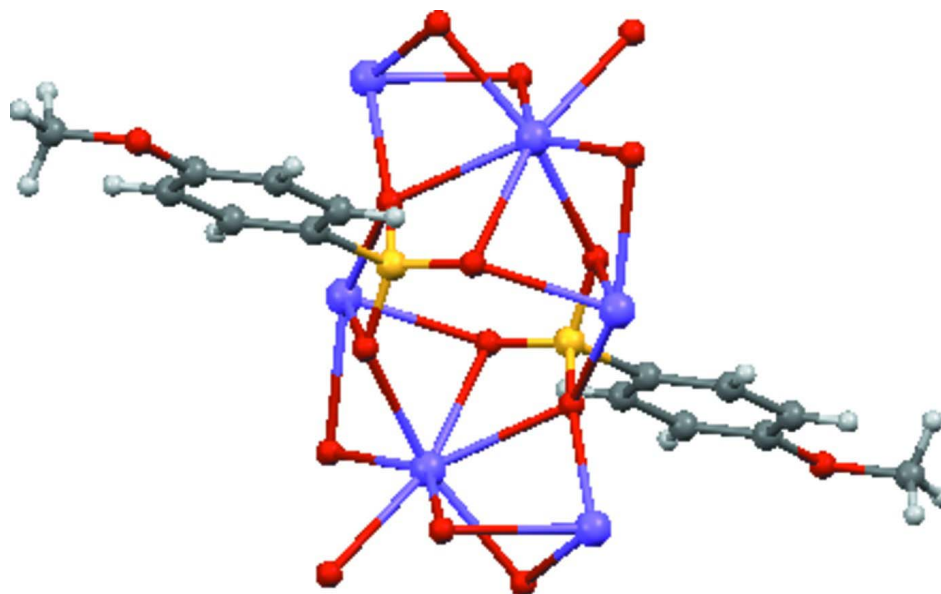
To a solution of 4-methoxybenzenesulfonyl chloride (3.00 g, 14.50 mmol) in hot methanol, sodium hydroxide (0.58 g, 14.50 mmol) was added. The suspension was stirred for 1 h. The reaction mixture was then cooled to the room temperature and the resulting white solid formed was filtered off and washed with CH<sub>3</sub>OH. Colorless needle-shaped single crystals suitable for X-ray structure determination were recrystallized from a solution of (I) in CH<sub>3</sub>OH by slow evaporation at room temperature over a few days.

**S3. Refinement**

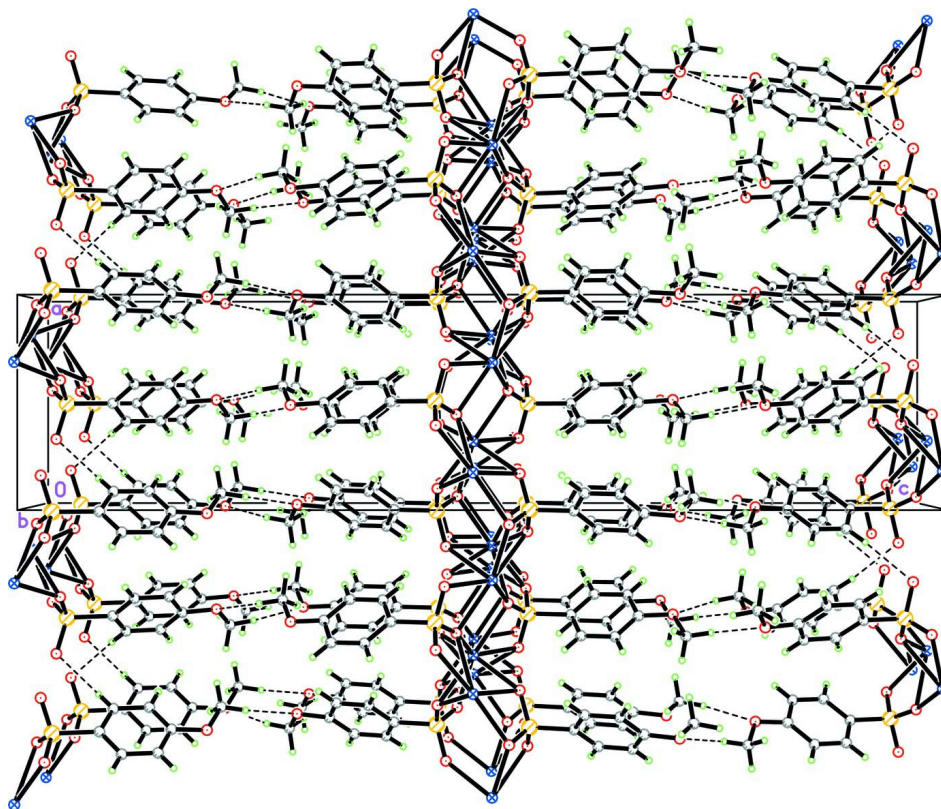
All H atoms were fixed geometrically and allowed to ride on their parent atoms, with  $d(\text{C—H}) = 0.93$  Å for aromatic and 0.96 for CH<sub>3</sub>. The  $U_{\text{iso}}$  values were constrained to be  $1.5U_{\text{eq}}$  of the carrier atom for methyl H atoms and  $1.2U_{\text{eq}}$  for the remaining H atoms. A rotating group model was used for the methyl groups.

**Figure 1**

Part of the polymeric structure of (I) showing a tetranuclear cluster with 50% probability displacement ellipsoids. Atoms labelled with the suffix A, B, and C are generated by the symmetry operations  $(x + 1/2, -y + 1/2, -z + 2)$ ,  $(-x + 1, -y, -z + 2)$  and  $(-x + 1/2, y + 1/2, z)$ , respectively.

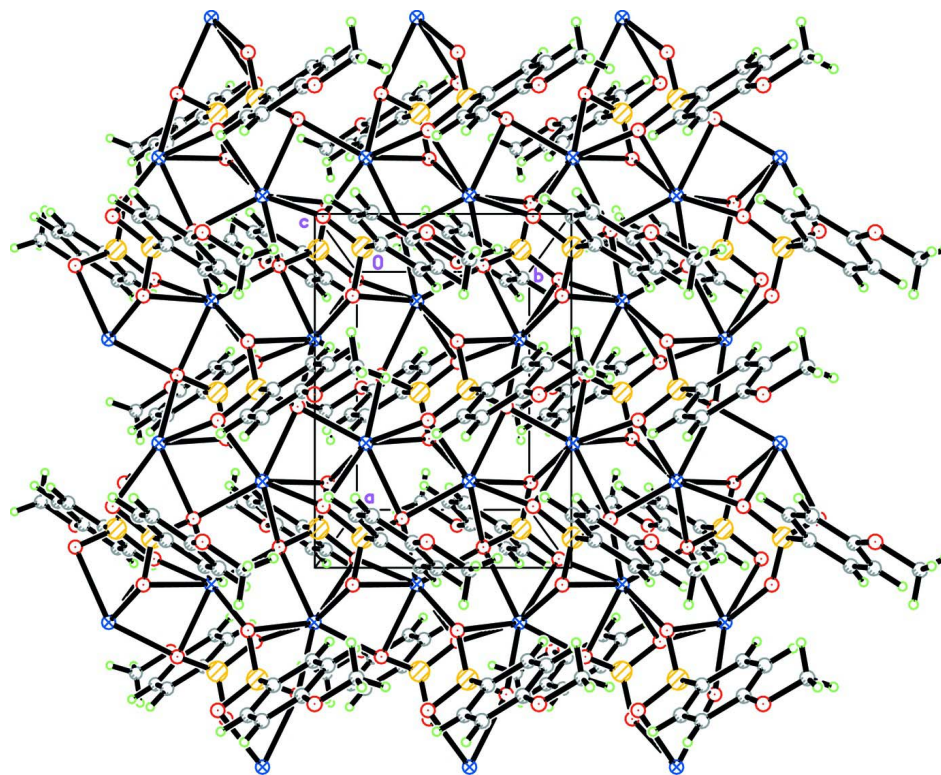
**Figure 2**

Part of the polymeric structure of (I) showing the coordination environment of  $\text{Na}^{\text{I}}$  ions in (I).



**Figure 3**

The two-dimensional polymer of (I) viewed along the *b* axis. Hydrogen bonds are drawn as dashed lines.

**Figure 4**

The crystal packing of (I), viewed along the *c* axis.

### Poly[ $\mu_5$ -(4-methoxybenzenesulfonato)-sodium]

#### Crystal data

[Na(C<sub>7</sub>H<sub>7</sub>O<sub>4</sub>S)]  
 $M_r = 210.19$   
 Orthorhombic, *Pbca*  
 Hall symbol: -P 2ac 2ab  
 $a = 8.3121$  (8) Å  
 $b = 6.0287$  (6) Å  
 $c = 35.930$  (3) Å  
 $V = 1800.5$  (3) Å<sup>3</sup>  
 $Z = 8$

$F(000) = 864$   
 $D_x = 1.551$  Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1769 reflections  
 $\theta = 2.3$ – $26.0^\circ$   
 $\mu = 0.38$  mm<sup>-1</sup>  
 $T = 293$  K  
 Needle, colorless  
 $0.54 \times 0.46 \times 0.22$  mm

#### Data collection

Bruker APEXII CCD area detector  
 diffractometer  
 Radiation source: sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2009)  
 $T_{\min} = 0.819$ ,  $T_{\max} = 0.920$

8793 measured reflections  
 1769 independent reflections  
 1720 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.3^\circ$   
 $h = -8 \rightarrow 10$   
 $k = -7 \rightarrow 7$   
 $l = -37 \rightarrow 44$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.037$  $wR(F^2) = 0.101$  $S = 1.20$ 

1769 reflections

119 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 1.6253P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$  $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$ Extinction correction: *SHELXL*, $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ 

Extinction coefficient: 0.042 (3)

*Special details*

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

|     | <i>x</i>     | <i>y</i>     | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| S1  | 0.50598 (6)  | 0.11687 (8)  | 0.950009 (13) | 0.0257 (2)                       |
| O1  | 0.67113 (17) | 0.0690 (2)   | 0.96029 (4)   | 0.0328 (4)                       |
| O2  | 0.39805 (19) | -0.0717 (3)  | 0.95165 (4)   | 0.0386 (4)                       |
| O3  | 0.44483 (18) | 0.3026 (2)   | 0.97215 (4)   | 0.0324 (4)                       |
| O4  | 0.4881 (4)   | 0.4270 (4)   | 0.79459 (6)   | 0.0843 (8)                       |
| C1  | 0.5047 (2)   | 0.2071 (4)   | 0.90315 (6)   | 0.0300 (5)                       |
| C2  | 0.4151 (4)   | 0.0971 (4)   | 0.87675 (7)   | 0.0483 (6)                       |
| H2A | 0.3570       | -0.0291      | 0.8831        | 0.058*                           |
| C3  | 0.4122 (4)   | 0.1762 (5)   | 0.84065 (7)   | 0.0603 (8)                       |
| H3A | 0.3511       | 0.1036       | 0.8227        | 0.072*                           |
| C4  | 0.4991 (4)   | 0.3615 (5)   | 0.83113 (7)   | 0.0526 (7)                       |
| C5  | 0.5888 (4)   | 0.4721 (5)   | 0.85733 (7)   | 0.0573 (8)                       |
| H5A | 0.6477       | 0.5974       | 0.8508        | 0.069*                           |
| C6  | 0.5902 (3)   | 0.3942 (4)   | 0.89371 (7)   | 0.0482 (7)                       |
| H6A | 0.6493       | 0.4688       | 0.9118        | 0.058*                           |
| C7  | 0.5762 (7)   | 0.6163 (7)   | 0.78319 (10)  | 0.1151 (19)                      |
| H7A | 0.5575       | 0.6431       | 0.7572        | 0.173*                           |
| H7B | 0.6888       | 0.5913       | 0.7873        | 0.173*                           |
| H7C | 0.5418       | 0.7428       | 0.7973        | 0.173*                           |
| Na  | 0.18295 (10) | 0.12772 (12) | 0.98998 (2)   | 0.0314 (3)                       |

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

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$      | $U^{13}$     | $U^{23}$     |
|----|-------------|-------------|-------------|---------------|--------------|--------------|
| S1 | 0.0260 (3)  | 0.0239 (3)  | 0.0273 (3)  | -0.00035 (18) | 0.00168 (17) | 0.00130 (18) |
| O1 | 0.0280 (7)  | 0.0355 (8)  | 0.0349 (8)  | 0.0061 (6)    | 0.0021 (6)   | 0.0032 (6)   |
| O2 | 0.0435 (9)  | 0.0347 (8)  | 0.0376 (8)  | -0.0131 (7)   | 0.0013 (7)   | 0.0018 (6)   |
| O3 | 0.0333 (8)  | 0.0311 (8)  | 0.0330 (8)  | 0.0078 (6)    | 0.0023 (6)   | -0.0011 (6)  |
| O4 | 0.143 (2)   | 0.0803 (16) | 0.0299 (10) | -0.0139 (15)  | -0.0124 (11) | 0.0134 (10)  |
| C1 | 0.0332 (11) | 0.0318 (11) | 0.0250 (10) | -0.0001 (8)   | -0.0003 (8)  | 0.0022 (8)   |
| C2 | 0.0630 (17) | 0.0453 (13) | 0.0367 (12) | -0.0158 (12)  | -0.0037 (11) | -0.0029 (10) |
| C3 | 0.086 (2)   | 0.0616 (17) | 0.0337 (13) | -0.0154 (16)  | -0.0139 (13) | -0.0076 (12) |
| C4 | 0.077 (2)   | 0.0512 (16) | 0.0294 (13) | 0.0020 (14)   | -0.0036 (11) | 0.0044 (11)  |
| C5 | 0.078 (2)   | 0.0531 (15) | 0.0404 (13) | -0.0231 (15)  | -0.0043 (13) | 0.0139 (12)  |
| C6 | 0.0598 (16) | 0.0497 (14) | 0.0351 (12) | -0.0218 (12)  | -0.0102 (11) | 0.0076 (10)  |
| C7 | 0.210 (6)   | 0.091 (3)   | 0.0443 (19) | -0.023 (3)    | -0.002 (3)   | 0.0328 (19)  |
| Na | 0.0295 (4)  | 0.0227 (4)  | 0.0420 (5)  | -0.0004 (3)   | 0.0039 (3)   | 0.0000 (3)   |

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|                       |             |                                       |             |
|-----------------------|-------------|---------------------------------------|-------------|
| S1—O2                 | 1.4495 (16) | C3—C4                                 | 1.374 (4)   |
| S1—O1                 | 1.4506 (15) | C3—H3A                                | 0.9300      |
| S1—O3                 | 1.4644 (15) | C4—C5                                 | 1.374 (4)   |
| S1—C1                 | 1.769 (2)   | C5—C6                                 | 1.389 (3)   |
| S1—Na <sup>i</sup>    | 3.0304 (10) | C5—H5A                                | 0.9300      |
| S1—Na                 | 3.0457 (10) | C6—H6A                                | 0.9300      |
| O1—Na <sup>ii</sup>   | 2.4637 (16) | C7—H7A                                | 0.9600      |
| O1—Na <sup>i</sup>    | 2.5585 (17) | C7—H7B                                | 0.9600      |
| O2—Na <sup>iii</sup>  | 2.3734 (17) | C7—H7C                                | 0.9600      |
| O2—Na                 | 2.5572 (18) | Na—O3 <sup>iii</sup>                  | 2.3198 (16) |
| O3—Na <sup>iv</sup>   | 2.3198 (16) | Na—O2 <sup>iv</sup>                   | 2.3734 (17) |
| O3—Na <sup>i</sup>    | 2.4384 (17) | Na—O3 <sup>v</sup>                    | 2.4384 (17) |
| O3—Na                 | 2.5021 (17) | Na—O1 <sup>ii</sup>                   | 2.4637 (16) |
| O4—C4                 | 1.374 (3)   | Na—O1 <sup>v</sup>                    | 2.5585 (17) |
| O4—C7                 | 1.416 (5)   | Na—S1 <sup>v</sup>                    | 3.0304 (9)  |
| C1—C6                 | 1.376 (3)   | Na—Na <sup>iv</sup>                   | 3.2138 (6)  |
| C1—C2                 | 1.377 (3)   | Na—Na <sup>iii</sup>                  | 3.2138 (6)  |
| C2—C3                 | 1.382 (4)   | Na—Na <sup>vi</sup>                   | 3.4843 (16) |
| C2—H2A                | 0.9300      |                                       |             |
| O2—S1—O1              | 114.78 (10) | O2 <sup>iv</sup> —Na—O3               | 77.09 (6)   |
| O2—S1—O3              | 111.27 (9)  | O3 <sup>v</sup> —Na—O3                | 140.94 (4)  |
| O1—S1—O3              | 110.02 (9)  | O1 <sup>ii</sup> —Na—O3               | 87.72 (6)   |
| O2—S1—C1              | 106.03 (10) | O3 <sup>iii</sup> —Na—O2              | 76.94 (6)   |
| O1—S1—C1              | 108.00 (9)  | O2 <sup>iv</sup> —Na—O2               | 104.17 (7)  |
| O3—S1—C1              | 106.25 (9)  | O3 <sup>v</sup> —Na—O2                | 161.64 (6)  |
| O2—S1—Na <sup>i</sup> | 132.07 (7)  | O1 <sup>ii</sup> —Na—O2               | 79.63 (5)   |
| O1—S1—Na <sup>i</sup> | 57.36 (6)   | O3—Na—O2                              | 56.76 (5)   |
| O3—S1—Na <sup>i</sup> | 52.67 (6)   | O3 <sup>iii</sup> —Na—O1 <sup>v</sup> | 141.19 (6)  |

|  |             |   |             |
|--|-------------|---|-------------|
| C1—S1—Na <sup>i</sup>                  | 121.58 (8)  | O2 <sup>iv</sup> —Na—O1 <sup>v</sup>    | 81.30 (6)   |
| O2—S1—Na                               | 56.77 (7)   | O3 <sup>v</sup> —Na—O1 <sup>v</sup>     | 57.04 (5)   |
| O1—S1—Na                               | 135.93 (6)  | O1 <sup>ii</sup> —Na—O1 <sup>v</sup>    | 81.74 (5)   |
| O3—S1—Na                               | 54.65 (6)   | O3—Na—O1 <sup>v</sup>                   | 84.91 (5)   |
| C1—S1—Na                               | 115.90 (7)  | O2—Na—O1 <sup>v</sup>                   | 137.65 (6)  |
| Na <sup>i</sup> —S1—Na                 | 94.675 (17) | O3 <sup>iii</sup> —Na—S1 <sup>v</sup>   | 113.81 (5)  |
| S1—O1—Na <sup>ii</sup>                 | 138.27 (9)  | O2 <sup>iv</sup> —Na—S1 <sup>v</sup>    | 83.53 (4)   |
| S1—O1—Na <sup>i</sup>                  | 94.12 (7)   | O3 <sup>v</sup> —Na—S1 <sup>v</sup>     | 28.52 (4)   |
| Na <sup>ii</sup> —O1—Na <sup>i</sup>   | 79.55 (5)   | O1 <sup>ii</sup> —Na—S1 <sup>v</sup>    | 88.14 (4)   |
| S1—O2—Na <sup>iii</sup>                | 142.94 (10) | O3—Na—S1 <sup>v</sup>                   | 112.98 (4)  |
| S1—O2—Na                               | 94.92 (8)   | O2—Na—S1 <sup>v</sup>                   | 164.05 (5)  |
| Na <sup>iii</sup> —O2—Na               | 81.26 (5)   | O1 <sup>v</sup> —Na—S1 <sup>v</sup>     | 28.52 (3)   |
| S1—O3—Na <sup>iv</sup>                 | 162.75 (9)  | O3 <sup>iii</sup> —Na—S1                | 104.79 (5)  |
| S1—O3—Na <sup>i</sup>                  | 98.81 (8)   | O2 <sup>iv</sup> —Na—S1                 | 89.59 (5)   |
| Na <sup>iv</sup> —O3—Na <sup>i</sup>   | 94.12 (6)   | O3 <sup>v</sup> —Na—S1                  | 169.25 (5)  |
| S1—O3—Na                               | 96.83 (8)   | O1 <sup>ii</sup> —Na—S1                 | 84.13 (4)   |
| Na <sup>iv</sup> —O3—Na                | 83.51 (5)   | O3—Na—S1                                | 28.52 (3)   |
| Na <sup>i</sup> —O3—Na                 | 129.48 (6)  | O2—Na—S1                                | 28.31 (4)   |
| C4—O4—C7                               | 118.3 (3)   | O1 <sup>v</sup> —Na—S1                  | 112.25 (4)  |
| C6—C1—C2                               | 120.3 (2)   | S1 <sup>v</sup> —Na—S1                  | 140.75 (3)  |
| C6—C1—S1                               | 118.91 (17) | O3 <sup>iii</sup> —Na—Na <sup>iv</sup>  | 162.05 (5)  |
| C2—C1—S1                               | 120.73 (18) | O2 <sup>iv</sup> —Na—Na <sup>iv</sup>   | 51.86 (4)   |
| C1—C2—C3                               | 119.3 (2)   | O3 <sup>v</sup> —Na—Na <sup>iv</sup>    | 96.89 (4)   |
| C1—C2—H2A                              | 120.3       | O1 <sup>ii</sup> —Na—Na <sup>iv</sup>   | 106.30 (5)  |
| C3—C2—H2A                              | 120.3       | O3—Na—Na <sup>iv</sup>                  | 45.82 (4)   |
| C4—C3—C2                               | 120.3 (2)   | O2—Na—Na <sup>iv</sup>                  | 101.45 (5)  |
| C4—C3—H3A                              | 119.8       | O1 <sup>v</sup> —Na—Na <sup>iv</sup>    | 48.93 (4)   |
| C2—C3—H3A                              | 119.8       | S1 <sup>v</sup> —Na—Na <sup>iv</sup>    | 72.048 (19) |
| C3—C4—C5                               | 120.6 (2)   | S1—Na—Na <sup>iv</sup>                  | 73.41 (3)   |
| C3—C4—O4                               | 115.9 (3)   | O3 <sup>iii</sup> —Na—Na <sup>iii</sup> | 50.67 (4)   |
| C5—C4—O4                               | 123.4 (3)   | O2 <sup>iv</sup> —Na—Na <sup>iii</sup>  | 144.53 (4)  |
| C4—C5—C6                               | 119.0 (2)   | O3 <sup>v</sup> —Na—Na <sup>iii</sup>   | 116.30 (4)  |
| C4—C5—H5A                              | 120.5       | O1 <sup>ii</sup> —Na—Na <sup>iii</sup>  | 51.52 (4)   |
| C6—C5—H5A                              | 120.5       | O3—Na—Na <sup>iii</sup>                 | 95.36 (5)   |
| C1—C6—C5                               | 120.3 (2)   | O2—Na—Na <sup>iii</sup>                 | 46.88 (4)   |
| C1—C6—H6A                              | 119.8       | O1 <sup>v</sup> —Na—Na <sup>iii</sup>   | 133.13 (4)  |
| C5—C6—H6A                              | 119.8       | S1 <sup>v</sup> —Na—Na <sup>iii</sup>   | 130.16 (2)  |
| O4—C7—H7A                              | 109.5       | S1—Na—Na <sup>iii</sup>                 | 70.98 (3)   |
| O4—C7—H7B                              | 109.5       | Na <sup>iv</sup> —Na—Na <sup>iii</sup>  | 139.42 (5)  |
| H7A—C7—H7B                             | 109.5       | O3 <sup>iii</sup> —Na—Na <sup>vi</sup>  | 44.27 (4)   |
| O4—C7—H7C                              | 109.5       | O2 <sup>iv</sup> —Na—Na <sup>vi</sup>   | 102.10 (6)  |
| H7A—C7—H7C                             | 109.5       | O3 <sup>v</sup> —Na—Na <sup>vi</sup>    | 41.61 (4)   |
| H7B—C7—H7C                             | 109.5       | O1 <sup>ii</sup> —Na—Na <sup>vi</sup>   | 93.85 (5)   |
| O3 <sup>iii</sup> —Na—O2 <sup>iv</sup> | 110.78 (7)  | O3—Na—Na <sup>vi</sup>                  | 176.92 (6)  |
| O3 <sup>iii</sup> —Na—O3 <sup>v</sup>  | 85.88 (6)   | O2—Na—Na <sup>vi</sup>                  | 120.91 (5)  |
| O2 <sup>iv</sup> —Na—O3 <sup>v</sup>   | 87.82 (6)   | O1 <sup>v</sup> —Na—Na <sup>vi</sup>    | 97.94 (5)   |
| O3 <sup>iii</sup> —Na—O1 <sup>ii</sup> | 91.09 (6)   | S1 <sup>v</sup> —Na—Na <sup>vi</sup>    | 69.75 (3)   |
| O2 <sup>iv</sup> —Na—O1 <sup>ii</sup>  | 158.12 (7)  | S1—Na—Na <sup>vi</sup>                  | 149.03 (4)  |



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| O3 <sup>v</sup> —Na—O1 <sup>ii</sup>     | 94.46 (6)    | Na <sup>iv</sup> —Na—Na <sup>vi</sup>      | 135.83 (4)   |
| O3 <sup>iii</sup> —Na—O3                 | 133.13 (7)   | Na <sup>iii</sup> —Na—Na <sup>vi</sup>     | 83.58 (3)    |
| O2—S1—O1—Na <sup>ii</sup>                | -46.59 (17)  | Na <sup>i</sup> —O3—Na—Na <sup>iv</sup>    | 90.00 (8)    |
| O3—S1—O1—Na <sup>ii</sup>                | 79.82 (15)   | S1—O3—Na—Na <sup>iii</sup>                 | 30.86 (7)    |
| C1—S1—O1—Na <sup>ii</sup>                | -164.62 (13) | Na <sup>iv</sup> —O3—Na—Na <sup>iii</sup>  | -166.50 (4)  |
| Na <sup>i</sup> —S1—O1—Na <sup>ii</sup>  | 78.90 (12)   | Na <sup>i</sup> —O3—Na—Na <sup>iii</sup>   | -76.51 (7)   |
| Na—S1—O1—Na <sup>ii</sup>                | 20.4 (2)     | S1—O2—Na—O3 <sup>iii</sup>                 | 169.52 (8)   |
| O2—S1—O1—Na <sup>i</sup>                 | -125.50 (8)  | Na <sup>iii</sup> —O2—Na—O3 <sup>iii</sup> | -47.62 (6)   |
| O3—S1—O1—Na <sup>i</sup>                 | 0.91 (9)     | S1—O2—Na—O2 <sup>iv</sup>                  | 61.03 (8)    |
| C1—S1—O1—Na <sup>i</sup>                 | 116.48 (9)   | Na <sup>iii</sup> —O2—Na—O2 <sup>iv</sup>  | -156.11 (6)  |
| Na—S1—O1—Na <sup>i</sup>                 | -58.50 (10)  | S1—O2—Na—O3 <sup>v</sup>                   | -169.45 (17) |
| O1—S1—O2—Na <sup>iii</sup>               | 48.05 (19)   | Na <sup>iii</sup> —O2—Na—O3 <sup>v</sup>   | -26.6 (2)    |
| O3—S1—O2—Na <sup>iii</sup>               | -77.71 (18)  | S1—O2—Na—O1 <sup>ii</sup>                  | -96.90 (8)   |
| C1—S1—O2—Na <sup>iii</sup>               | 167.19 (15)  | Na <sup>iii</sup> —O2—Na—O1 <sup>ii</sup>  | 45.95 (5)    |
| Na <sup>i</sup> —S1—O2—Na <sup>iii</sup> | -19.4 (2)    | S1—O2—Na—O3                                | -2.80 (6)    |
| Na—S1—O2—Na <sup>iii</sup>               | -82.01 (16)  | Na <sup>iii</sup> —O2—Na—O3                | 140.06 (7)   |
| O1—S1—O2—Na                              | 130.06 (8)   | S1—O2—Na—O1 <sup>v</sup>                   | -31.57 (12)  |
| O3—S1—O2—Na                              | 4.30 (10)    | Na <sup>iii</sup> —O2—Na—O1 <sup>v</sup>   | 111.29 (8)   |
| C1—S1—O2—Na                              | -110.81 (8)  | S1—O2—Na—S1 <sup>v</sup>                   | -56.4 (2)    |
| Na <sup>i</sup> —S1—O2—Na                | 62.61 (10)   | Na <sup>iii</sup> —O2—Na—S1 <sup>v</sup>   | 86.49 (17)   |
| O2—S1—O3—Na <sup>iv</sup>                | -94.5 (3)    | Na <sup>iii</sup> —O2—Na—S1                | 142.86 (10)  |
| O1—S1—O3—Na <sup>iv</sup>                | 137.1 (3)    | S1—O2—Na—Na <sup>iv</sup>                  | 7.82 (8)     |
| C1—S1—O3—Na <sup>iv</sup>                | 20.5 (4)     | Na <sup>iii</sup> —O2—Na—Na <sup>iv</sup>  | 150.67 (4)   |
| Na <sup>i</sup> —S1—O3—Na <sup>iv</sup>  | 138.1 (4)    | S1—O2—Na—Na <sup>iii</sup>                 | -142.86 (10) |
| Na—S1—O3—Na <sup>iv</sup>                | -90.1 (3)    | S1—O2—Na—Na <sup>vi</sup>                  | 174.81 (6)   |
| O2—S1—O3—Na <sup>i</sup>                 | 127.40 (8)   | Na <sup>iii</sup> —O2—Na—Na <sup>vi</sup>  | -42.33 (7)   |
| O1—S1—O3—Na <sup>i</sup>                 | -0.97 (10)   | O2—S1—Na—O3 <sup>iii</sup>                 | -10.56 (9)   |
| C1—S1—O3—Na <sup>i</sup>                 | -117.63 (8)  | O1—S1—Na—O3 <sup>iii</sup>                 | -103.07 (11) |
| Na—S1—O3—Na <sup>i</sup>                 | 131.81 (8)   | O3—S1—Na—O3 <sup>iii</sup>                 | 174.35 (10)  |
| O2—S1—O3—Na                              | -4.41 (10)   | C1—S1—Na—O3 <sup>iii</sup>                 | 82.24 (9)    |
| O1—S1—O3—Na                              | -132.77 (7)  | Na <sup>i</sup> —S1—Na—O3 <sup>iii</sup>   | -149.16 (5)  |
| C1—S1—O3—Na                              | 110.56 (8)   | O2—S1—Na—O2 <sup>iv</sup>                  | -121.97 (9)  |
| Na <sup>i</sup> —S1—O3—Na                | -131.81 (8)  | O1—S1—Na—O2 <sup>iv</sup>                  | 145.51 (10)  |
| O2—S1—C1—C6                              | 176.20 (19)  | O3—S1—Na—O2 <sup>iv</sup>                  | 62.94 (8)    |
| O1—S1—C1—C6                              | -60.3 (2)    | C1—S1—Na—O2 <sup>iv</sup>                  | -29.17 (9)   |
| O3—S1—C1—C6                              | 57.7 (2)     | Na <sup>i</sup> —S1—Na—O2 <sup>iv</sup>    | 99.43 (5)    |
| Na <sup>i</sup> —S1—C1—C6                | 1.9 (2)      | O2—S1—Na—O3 <sup>v</sup>                   | 162.0 (3)    |
| Na—S1—C1—C6                              | 115.82 (19)  | O1—S1—Na—O3 <sup>v</sup>                   | 69.5 (3)     |
| O2—S1—C1—C2                              | -1.4 (2)     | O3—S1—Na—O3 <sup>v</sup>                   | -13.1 (3)    |
| O1—S1—C1—C2                              | 122.1 (2)    | C1—S1—Na—O3 <sup>v</sup>                   | -105.2 (3)   |
| O3—S1—C1—C2                              | -119.9 (2)   | Na <sup>i</sup> —S1—Na—O3 <sup>v</sup>     | 23.4 (3)     |
| Na <sup>i</sup> —S1—C1—C2                | -175.71 (18) | O2—S1—Na—O1 <sup>ii</sup>                  | 79.02 (9)    |
| Na—S1—C1—C2                              | -61.8 (2)    | O1—S1—Na—O1 <sup>ii</sup>                  | -13.49 (13)  |
| C6—C1—C2—C3                              | 0.2 (4)      | O3—S1—Na—O1 <sup>ii</sup>                  | -96.07 (8)   |
| S1—C1—C2—C3                              | 177.8 (2)    | C1—S1—Na—O1 <sup>ii</sup>                  | 171.82 (9)   |
| C1—C2—C3—C4                              | 0.6 (5)      | Na <sup>i</sup> —S1—Na—O1 <sup>ii</sup>    | -59.58 (4)   |
| C2—C3—C4—C5                              | -0.6 (5)     | O2—S1—Na—O3                                | 175.09 (11)  |

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| C2—C3—C4—O4                               | -179.9 (3)   | O1—S1—Na—O3                              | 82.58 (12)    |
| C7—O4—C4—C3                               | -179.6 (4)   | C1—S1—Na—O3                              | -92.11 (11)   |
| C7—O4—C4—C5                               | 1.2 (5)      | Na <sup>i</sup> —S1—Na—O3                | 36.49 (7)     |
| C3—C4—C5—C6                               | -0.1 (5)     | O1—S1—Na—O2                              | -92.51 (12)   |
| O4—C4—C5—C6                               | 179.1 (3)    | O3—S1—Na—O2                              | -175.09 (11)  |
| C2—C1—C6—C5                               | -0.9 (4)     | C1—S1—Na—O2                              | 92.80 (11)    |
| S1—C1—C6—C5                               | -178.6 (2)   | Na <sup>i</sup> —S1—Na—O2                | -138.60 (8)   |
| C4—C5—C6—C1                               | 0.9 (5)      | O2—S1—Na—O1 <sup>v</sup>                 | 157.60 (9)    |
| S1—O3—Na—O3 <sup>iii</sup>                | -7.49 (14)   | O1—S1—Na—O1 <sup>v</sup>                 | 65.09 (12)    |
| Na <sup>iv</sup> —O3—Na—O3 <sup>iii</sup> | 155.15 (6)   | O3—S1—Na—O1 <sup>v</sup>                 | -17.49 (8)    |
| Na <sup>i</sup> —O3—Na—O3 <sup>iii</sup>  | -114.86 (10) | C1—S1—Na—O1 <sup>v</sup>                 | -109.60 (9)   |
| S1—O3—Na—O2 <sup>iv</sup>                 | -113.99 (8)  | Na <sup>i</sup> —S1—Na—O1 <sup>v</sup>   | 19.00 (4)     |
| Na <sup>iv</sup> —O3—Na—O2 <sup>iv</sup>  | 48.64 (6)    | O2—S1—Na—S1 <sup>v</sup>                 | 158.80 (9)    |
| Na <sup>i</sup> —O3—Na—O2 <sup>iv</sup>   | 138.64 (9)   | O1—S1—Na—S1 <sup>v</sup>                 | 66.29 (11)    |
| S1—O3—Na—O3 <sup>v</sup>                  | 176.15 (9)   | O3—S1—Na—S1 <sup>v</sup>                 | -16.29 (8)    |
| Na <sup>iv</sup> —O3—Na—O3 <sup>v</sup>   | -21.21 (9)   | C1—S1—Na—S1 <sup>v</sup>                 | -108.40 (9)   |
| Na <sup>i</sup> —O3—Na—O3 <sup>v</sup>    | 68.79 (11)   | Na <sup>i</sup> —S1—Na—S1 <sup>v</sup>   | 20.20 (4)     |
| S1—O3—Na—O1 <sup>ii</sup>                 | 81.88 (7)    | O2—S1—Na—Na <sup>iv</sup>                | -172.01 (8)   |
| Na <sup>iv</sup> —O3—Na—O1 <sup>ii</sup>  | -115.49 (5)  | O1—S1—Na—Na <sup>iv</sup>                | 95.48 (10)    |
| Na <sup>i</sup> —O3—Na—O1 <sup>ii</sup>   | -25.49 (8)   | O3—S1—Na—Na <sup>iv</sup>                | 12.91 (7)     |
| S1—O3—Na—O2                               | 2.78 (6)     | C1—S1—Na—Na <sup>iv</sup>                | -79.21 (8)    |
| Na <sup>iv</sup> —O3—Na—O2                | 165.42 (7)   | Na <sup>i</sup> —S1—Na—Na <sup>iv</sup>  | 49.40 (2)     |
| Na <sup>i</sup> —O3—Na—O2                 | -104.59 (9)  | O2—S1—Na—Na <sup>iii</sup>               | 27.79 (8)     |
| S1—O3—Na—O1 <sup>v</sup>                  | 163.79 (7)   | O1—S1—Na—Na <sup>iii</sup>               | -64.73 (10)   |
| Na <sup>iv</sup> —O3—Na—O1 <sup>v</sup>   | -33.58 (5)   | O3—S1—Na—Na <sup>iii</sup>               | -147.30 (7)   |
| Na <sup>i</sup> —O3—Na—O1 <sup>v</sup>    | 56.42 (8)    | C1—S1—Na—Na <sup>iii</sup>               | 120.59 (8)    |
| S1—O3—Na—S1 <sup>v</sup>                  | 168.89 (5)   | Na <sup>i</sup> —S1—Na—Na <sup>iii</sup> | -110.811 (19) |
| Na <sup>iv</sup> —O3—Na—S1 <sup>v</sup>   | -28.48 (6)   | O2—S1—Na—Na <sup>vi</sup>                | -8.67 (11)    |
| Na <sup>i</sup> —O3—Na—S1 <sup>v</sup>    | 61.52 (8)    | O1—S1—Na—Na <sup>vi</sup>                | -101.19 (12)  |
| Na <sup>iv</sup> —O3—Na—S1                | 162.63 (10)  | O3—S1—Na—Na <sup>vi</sup>                | 176.24 (12)   |
| Na <sup>i</sup> —O3—Na—S1                 | -107.37 (11) | C1—S1—Na—Na <sup>vi</sup>                | 84.13 (12)    |
| S1—O3—Na—Na <sup>iv</sup>                 | -162.63 (10) | Na <sup>i</sup> —S1—Na—Na <sup>vi</sup>  | -147.27 (9)   |

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

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

| $D-H\cdots A$                      | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| C6—H6A $\cdots$ O1 <sup>vii</sup>  | 0.93  | 2.37        | 3.282 (3)   | 165           |
| C7—H7A $\cdots$ O4 <sup>viii</sup> | 0.96  | 2.56        | 3.407 (4)   | 148           |

Symmetry codes: (vii)  $-x+3/2, y+1/2, z$ ; (viii)  $-x+1, y+1/2, -z+3/2$ .