

# Poly[hexaaquacopper(II) [di- $\mu_3$ -sulfato-disodiate(I)]]

 Wen Wu,<sup>a,b</sup> J.-M. Xie,<sup>b\*</sup> D.-P. Xie<sup>a</sup> and Y.-W. Xuan<sup>a</sup>
<sup>a</sup>Department of Chemistry, Zhou Kou Normal University, 466001, People's Republic of China, and <sup>b</sup>Department of Chemistry, Jiangsu University, Zhenjiang 212003, People's Republic of China

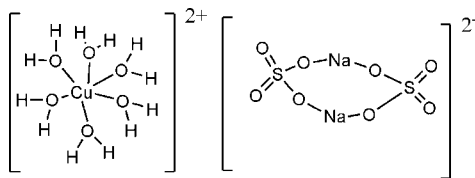
Correspondence e-mail: chinawuwen@126.com

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 Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{Cu}-\text{O}) = 0.003$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.092; data-to-parameter ratio = 11.7.

The title compound,  $\{[\text{Cu}(\text{H}_2\text{O})_6][\text{Na}_2(\text{SO}_4)_2]\}_n$ , has been prepared under mild hydrothermal conditions and has been structurally characterized. It exhibits a structure in which the inorganic frameworks are three-dimensional, participating in extensive hydrogen bonding. Copper occupies a special position ( $\bar{1}$ ). The Na atom is coordinated by five O atoms of four sulfates [Na—O distances are between 2.825 (3) and 2.983 (3) Å]. The four O atoms of the sulfate ligand are coordinated to four Na atoms, the sulfate ligands coordinating in a chelating/bridging tetradentate mode.

## Related literature

 For the structure of  $[\text{C}_6\text{H}_{18}\text{N}_2]_{0.5}[\text{Fe}(\text{SO}_4)_2(\text{H}_2\text{O})_2]$ , see: Fu *et al.* (2006)


## Experimental

### Crystal data

$[\text{Cu}(\text{H}_2\text{O})_6][\text{Na}_2(\text{SO}_4)_2]$	$V = 680.1$ (3) Å <sup>3</sup>
$M_r = 409.74$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.2345$ (12) Å	$\mu = 2.04$ mm <sup>-1</sup>
$b = 12.333$ (3) Å	$T = 291$ (2) K
$c = 9.1822$ (18) Å	$0.20 \times 0.17 \times 0.17$ mm
$\beta = 105.56$ (3)°	

### Data collection

Rigaku R-Axis IV diffractometer	2371 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	1322 independent reflections
$T_{\min} = 0.607$ , $T_{\max} = 0.709$	1257 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.092$	$\Delta\rho_{\text{max}} = 0.51$ e Å <sup>-3</sup>
$S = 1.09$	$\Delta\rho_{\text{min}} = -0.42$ e Å <sup>-3</sup>
1322 reflections	
113 parameters	
4 restraints	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2F}\cdots\text{O4}^{\text{i}}$	0.90 (3)	1.915 (15)	2.790 (3)	166 (4)
$\text{O3}-\text{H3F}\cdots\text{O6}^{\text{ii}}$	0.80 (5)	1.89 (5)	2.674 (4)	167 (5)
$\text{O1}-\text{H1F}\cdots\text{O5}^{\text{iii}}$	0.90 (3)	1.82 (3)	2.719 (4)	175 (5)
$\text{O1}-\text{H1E}\cdots\text{O7}^{\text{iv}}$	0.80 (5)	1.96 (5)	2.759 (4)	173 (4)
$\text{O2}-\text{H2E}\cdots\text{O7}$	0.90 (4)	1.93 (4)	2.800 (4)	164 (5)
$\text{O3}-\text{H3E}\cdots\text{O4}$	0.89 (3)	1.83 (3)	2.712 (3)	174 (4)

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

Data collection: *PROCESS* (Rigaku, 1996); cell refinement: *PROCESS*; data reduction: *PROCESS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1997); software used to prepare material for publication: *TEXSAN*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2054).

## References

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 Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.

## supporting information

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**Poly[hexaaquacopper(II) [di- $\mu_3$ -sulfato-disodiate(I)]]**

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**S1. Comment**

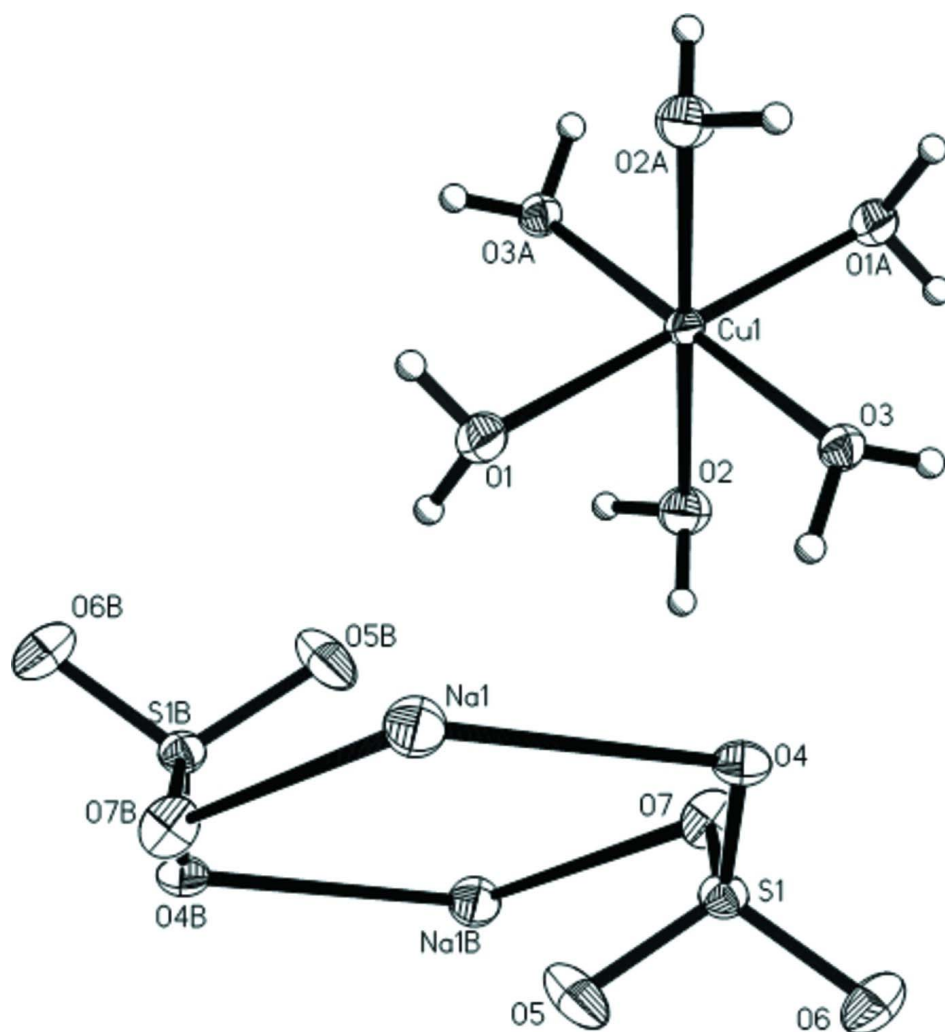
The structure of the title compound consists of an infinite three-dimensional  $[\text{Na}_2(\text{SO}_4)_2]_n^{2n-}$  network, the  $[\text{Cu}(\text{H}_2\text{O})_6]_n^{2n+}$  cations reside between inorganic layers, balancing charge and donating hydrogen bonds to the layers. The asymmetric unit contains one Cu(II) cation, three water molecules, one sulfate dianion and one sodium cation. (Fig. 1). To the best of our knowledge, the title compound is the first layer structure of inorganically templated sodium sulfate. As shown in Fig. 2, sodium atoms are bridged by sulfate groups into an infinite layer structure parallel to the *ab*-plane. The Cu(II) cation is approximately octahedrally coordinated by the oxygen atoms of six  $\text{H}_2\text{O}$ . In each sulfate group, four oxygen atoms are coordinated to sodium, for bridged oxygen atoms, the angles of S—O—Na range from 99.08 (10) to 122.97 (13)°.

**S2. Experimental**

All the reagents were of AR grade and used without further purification, a mixture of potassium hydrogen phthalate (0.2040 g, 1 mmol), and NaOH (0.0040 g, 1 mmol) were dissolved in 50 ml EtOH/ $\text{H}_2\text{O}$  (V:V = 1:1) solution, and then the resultant solution was added in 10 ml double-distilled water containing  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.2426 g, 1 mmol) and  $\text{Fe}_2(\text{SO}_4)_3$  (0.39974 g, 1 mmol). The resulting solution was heated at 373 K for 96 h. After cooling to room temperature, blue crystals were obtained in a yield up to 56.32% based on Cu..

**S3. Refinement**

H1F, H2F, H2E and H3E atoms bonded to O atoms were located in a difference map and refined with distance restraints of O—H=0.90 Å, and with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}$ , other H atoms were positioned geometrically and refined freely. The maximum peak and deepest hole are located 0.51 Å and -0.42 Å, respectively, from Cu.

**Figure 1**

ORTEP plot of 1 with 30% probability ellipsoid.

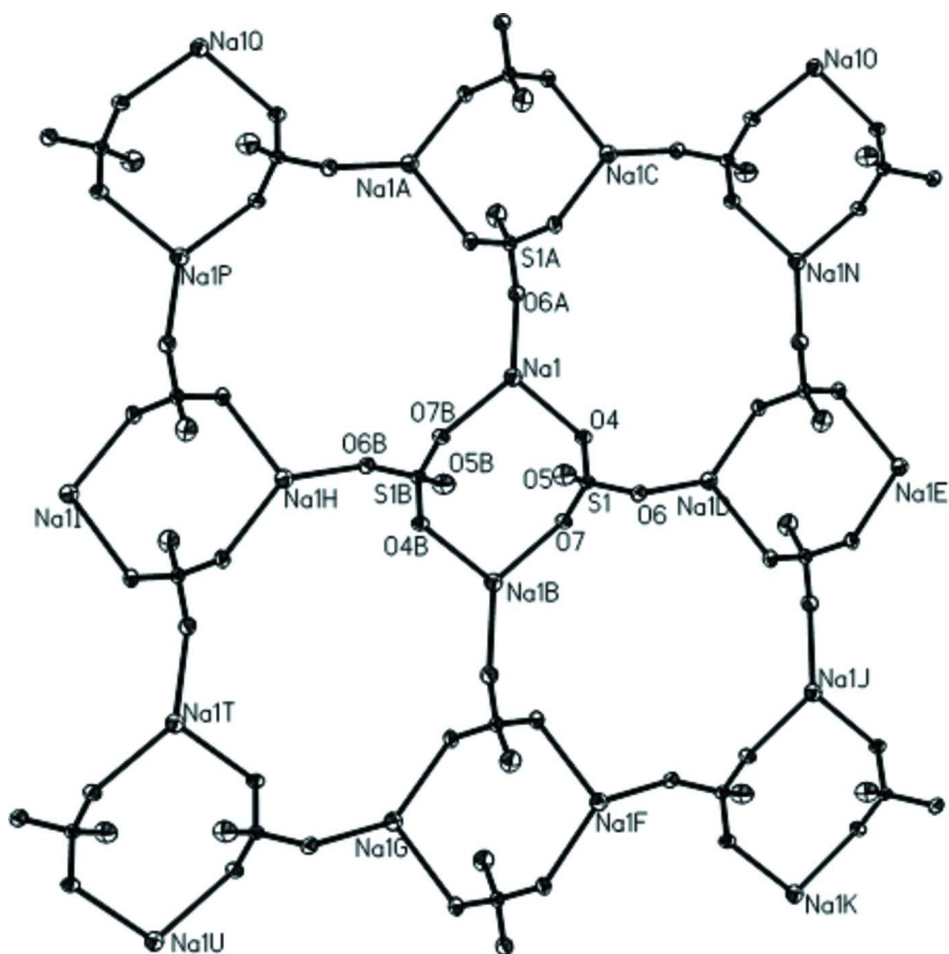


Figure 2

$[\text{Na}_2(\text{SO}_4)_2]_n^{2n-}$  network in title compound 1.

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#### Crystal data

$[\text{Cu}(\text{H}_2\text{O})_6][\text{Na}_2(\text{SO}_4)_2]$

$M_r = 409.74$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.2345$  (12) Å

$b = 12.333$  (3) Å

$c = 9.1822$  (18) Å

$\beta = 105.56$  (3)°

$V = 680.1$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 414$

$D_x = 2.001$  Mg m<sup>-3</sup>

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

Cell parameters from 289 reflections

$\theta = 2\text{--}25.1^\circ$

$\mu = 2.04$  mm<sup>-1</sup>

$T = 291$  K

Prismatic, blue

$0.20 \times 0.17 \times 0.17$  mm

#### Data collection

Rigaku R-AXIS IV

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 0 pixels mm<sup>-1</sup>

Oscillation frames scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2004)

$T_{\min} = 0.607$ ,  $T_{\max} = 0.709$

2371 measured reflections

1322 independent reflections  
 1257 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$   
 $\theta_{\text{max}} = 26.0^\circ$ ,  $\theta_{\text{min}} = 2.8^\circ$

$h = 0 \rightarrow 7$   
 $k = -15 \rightarrow 15$   
 $l = -11 \rightarrow 10$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.092$   
 $S = 1.09$   
 1322 reflections  
 113 parameters  
 4 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map

Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 1.2605P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.51 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick,  
 1997),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.053 (4)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	1.0000	0.0195 (2)
S1	0.76455 (13)	0.63853 (6)	0.59661 (9)	0.0249 (2)
Na1	0.8483 (3)	0.35098 (12)	0.62649 (17)	0.0382 (4)
O1	0.5346 (4)	0.3875 (2)	0.8249 (3)	0.0340 (6)
O2	0.3313 (4)	0.6137 (2)	0.8339 (3)	0.0360 (6)
H2F	0.192 (3)	0.594 (4)	0.786 (4)	0.045 (12)*
H2E	0.409 (8)	0.620 (4)	0.765 (4)	0.062 (15)*
O3	0.7863 (4)	0.5650 (2)	0.9976 (3)	0.0253 (5)
H3F	0.801 (8)	0.627 (4)	1.025 (6)	0.054 (15)*
O4	0.8777 (4)	0.56884 (18)	0.7250 (2)	0.0289 (5)
O5	0.7360 (5)	0.5768 (3)	0.4569 (3)	0.0486 (8)
O6	0.9065 (4)	0.7338 (2)	0.5942 (3)	0.0412 (7)
O7	0.5467 (4)	0.6744 (2)	0.6153 (3)	0.0357 (6)
H3E	0.825 (7)	0.563 (3)	0.911 (3)	0.036 (11)*
H1F	0.439 (7)	0.401 (4)	0.734 (3)	0.068 (16)*
H1E	0.503 (7)	0.327 (4)	0.846 (5)	0.038 (12)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0200 (3)	0.0198 (3)	0.0185 (3)	-0.00122 (18)	0.0047 (2)	0.00199 (18)
S1	0.0269 (4)	0.0244 (4)	0.0222 (4)	0.0025 (3)	0.0046 (3)	0.0043 (3)
Na1	0.0385 (8)	0.0395 (8)	0.0391 (8)	-0.0010 (6)	0.0149 (7)	-0.0020 (6)
O1	0.0213 (14)	0.0204 (14)	0.0257 (13)	-0.0061 (11)	0.0075 (11)	0.0023 (11)
O2	0.0210 (13)	0.0221 (15)	0.0255 (13)	-0.0063 (11)	0.0076 (11)	0.0023 (11)
O3	0.0262 (11)	0.0255 (12)	0.0260 (12)	-0.0027 (9)	0.0099 (9)	-0.0009 (9)
O4	0.0315 (12)	0.0313 (13)	0.0239 (11)	0.0042 (10)	0.0075 (9)	0.0080 (9)
O5	0.0633 (19)	0.0553 (18)	0.0234 (13)	0.0095 (15)	0.0051 (12)	-0.0072 (12)
O6	0.0347 (14)	0.0320 (13)	0.0557 (17)	-0.0018 (11)	0.0100 (12)	0.0155 (12)
O7	0.0258 (12)	0.0333 (13)	0.0477 (15)	0.0045 (10)	0.0094 (11)	0.0033 (11)

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

Cu1—O3 <sup>i</sup>	1.962 (2)	Na1—O7 <sup>ii</sup>	2.856 (3)
Cu1—O3	1.962 (2)	Na1—O6 <sup>iii</sup>	2.983 (3)
Cu1—O2 <sup>i</sup>	2.130 (3)	O1—H1F	0.90 (3)
Cu1—O2	2.130 (3)	O1—H1E	0.81 (5)
Cu1—O1	2.178 (3)	O2—H2F	0.90 (3)
Cu1—O1 <sup>i</sup>	2.178 (3)	O2—H2E	0.90 (4)
S1—O5	1.461 (3)	O3—H3F	0.80 (5)
S1—O6	1.475 (3)	O3—H3E	0.89 (3)
S1—O4	1.476 (2)	O6—Na1 <sup>iv</sup>	2.983 (3)
S1—O7	1.482 (3)	O7—Na1 <sup>ii</sup>	2.856 (3)
Na1—O4	2.825 (3)		
O3 <sup>i</sup> —Cu1—O3	180.0	O5—S1—O7	110.99 (17)
O3 <sup>i</sup> —Cu1—O2 <sup>i</sup>	89.95 (10)	O6—S1—O7	109.63 (15)
O3—Cu1—O2 <sup>i</sup>	90.05 (10)	O4—S1—O7	109.74 (14)
O3 <sup>i</sup> —Cu1—O2	90.05 (10)	O4—Na1—O7 <sup>ii</sup>	108.76 (8)
O3—Cu1—O2	89.95 (10)	O4—Na1—O6 <sup>iii</sup>	102.19 (8)
O2 <sup>i</sup> —Cu1—O2	180.000 (1)	O7 <sup>ii</sup> —Na1—O6 <sup>iii</sup>	138.69 (9)
O3 <sup>i</sup> —Cu1—O1	91.07 (10)	Cu1—O1—H1F	113 (4)
O3—Cu1—O1	88.93 (10)	Cu1—O1—H1E	109 (3)
O2 <sup>i</sup> —Cu1—O1	88.93 (10)	H1F—O1—H1E	104 (5)
O2—Cu1—O1	91.07 (10)	Cu1—O2—H2F	113 (3)
O3 <sup>i</sup> —Cu1—O1 <sup>i</sup>	88.93 (10)	Cu1—O2—H2E	108 (3)
O3—Cu1—O1 <sup>i</sup>	91.07 (10)	H2F—O2—H2E	109 (4)
O2 <sup>i</sup> —Cu1—O1 <sup>i</sup>	91.07 (10)	Cu1—O3—H3F	114 (4)
O2—Cu1—O1 <sup>i</sup>	88.93 (10)	Cu1—O3—H3E	118 (3)
O1—Cu1—O1 <sup>i</sup>	180.000 (1)	H3F—O3—H3E	105 (4)
O5—S1—O6	109.52 (18)	S1—O4—Na1	108.78 (12)
O5—S1—O4	108.50 (16)	S1—O6—Na1 <sup>iv</sup>	122.98 (15)
O6—S1—O4	108.40 (15)	S1—O7—Na1 <sup>ii</sup>	120.20 (14)
O5—S1—O4—Na1	-16.47 (19)	O4—S1—O6—Na1 <sup>iv</sup>	-41.0 (2)

O6—S1—O4—Na1	-135.34 (14)	O7—S1—O6—Na1 <sup>iv</sup>	78.82 (19)
O7—S1—O4—Na1	104.95 (14)	O5—S1—O7—Na1 <sup>ii</sup>	-9.3 (2)
O7 <sup>ii</sup> —Na1—O4—S1	-28.50 (15)	O6—S1—O7—Na1 <sup>ii</sup>	111.83 (17)
O6 <sup>iii</sup> —Na1—O4—S1	179.25 (12)	O4—S1—O7—Na1 <sup>ii</sup>	-129.22 (15)
O5—S1—O6—Na1 <sup>iv</sup>	-159.17 (16)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2F...O4 <sup>v</sup>	0.90 (3)	1.92 (2)	2.790 (3)	166 (4)
O3—H3F...O6 <sup>vi</sup>	0.80 (5)	1.89 (5)	2.674 (4)	167 (5)
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O2—H2E...O7	0.90 (4)	1.93 (4)	2.800 (4)	164 (5)
O3—H3E...O4	0.89 (3)	1.83 (3)	2.712 (3)	174 (4)

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