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Sodium 2-mercaptoethanesulfonate monohydrate (coenzyme M sodium salt monohydrate)

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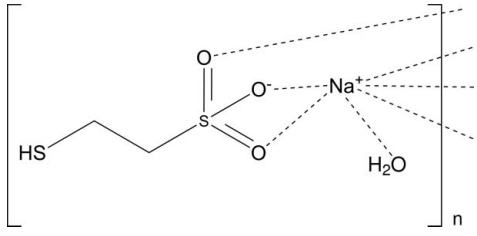
Key indicators: single-crystal X-ray study; T = 223 K; mean σ(C–C) = 0.007 Å; R factor = 0.038; wR factor = 0.131; data-to-parameter ratio = 17.4.

The 2-thioethanesulfonate anion is the smallest known coenzyme in nature (HS–CoM) and plays a key role in methanogenesis by anaerobic archaea, as well as in the oxidation of alkenes by Gram-negative and Gram-positive eubacteria. The title compound, $Na^+\cdot C_2H_5O_3S_2^-\cdot H_2O$, is the Na^+ salt of HS–CoM crystallized as the monohydrate. Six O atoms form a distorted octahedral coordination geometry around the Na atom, at distances in the range 2.312 (4)–2.517 (3) Å. Two O atoms of the sulfonate group, one O atom of each of three other symmetry-related sulfonate groups plus the water O atom form the coordination environment of the Na^+ ion. This arrangement forms Na–O–Na layers in the crystal structure, parallel to (100).

Related literature

For related literature about HS–CoM, see: Allen *et al.* (1999); Bruchhausen *et al.* (1993); Günther & Hattendorf (2005); Graham *et al.* (2002); Latkoczy & Günther (2002); Mackay *et al.* (1999); Schramm *et al.* (1955); Thauer (1998). For the structure of the unhydrated Na HS–CoM salt, see: Bambagiotti-Alberti *et al.* (2007).



Experimental

Crystal data

$Na^+\cdot C_2H_5O_3S_2^-\cdot H_2O$
M_r = 182.19
Orthorhombic, $Pna2_1$
a = 23.4301 (8) Å
b = 5.0324 (2) Å
c = 6.1254 (2) Å
V = 722.24 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.74 mm^{-1}
T = 223 K
0.26 × 0.20 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
1647 measured reflections
1534 independent reflections
1263 reflections with $I > 2\sigma(I)$
R_{int} = 0.065

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.131
S = 0.95
1534 reflections
88 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Absolute structure: Flack (1983), **627 Friedel pairs**
Flack parameter: 0.13 (18)

Table 1
Selected bond lengths (Å).

Na9—O5^{i}	2.312 (4)	Na9—O6^{iii}	2.416 (2)
Na9—O8^{ii}	2.322 (4)	Na9—O5	2.456 (3)
Na9—O7	2.404 (3)	Na9—O8	2.517 (3)

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

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek 2003); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2190).

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supporting information

Acta Cryst. (2008). E**64**, m1476–m1477 [doi:10.1107/S1600536808031814]

Sodium 2-mercaptoethanesulfonate monohydrate (coenzyme M sodium salt monohydrate)

Stefan Mayr, Detlef Günther, Bernhard Jaun and W. Bernd Schweizer

S1. Comment

The title compound includes 2-thioethanesulfonate ion, the smallest known coenzyme in nature, coenzyme M, which plays a key role in methanogenesis by anaerobic archaea (Thauer, 1998) and in the oxidation of alkenes by gram-negative and gram-positive eubacteria (Allen *et al.*, 1999). Furthermore its sodium salt (mesna) is medically used as mucolytics and to prevent urotoxic side effects of certain anticancer drugs (Bruchhausen *et al.*, 1993). Whereas the biosynthesis of coenzyme M starts by sulfitation of phosphoenolpyruvate (Graham *et al.*, 2002), the chemical synthesis begins from sodium 2-bromoethanesulfonate and thiourea in ammoniacal solution (Bruchhausen *et al.*, 1993). Since 2-thioethanesulfonic acid represents a highly viscous oil decomposing under release of hydrogen sulfide at room temperature, it is usually stored and sold as stable sodium or ammonium salt (Schramm *et al.*, 1955). The title compound is the monohydrate of the sodium salt.

Six O atoms show a distorted octahedral coordination geometry around the Na atom at distances in the range of 2.312 (4)–2.517 (3) Å (Fig. 1). Two O atoms of a SO_3 group and one O of three other SO_3 groups plus the water O atom form the coordination sphere of the Na^+ ion. This forms Na–O–Na layers parallel to (100) in the crystal (Fig. 2).

The crystal structure of the unhydrated form (Bambagiotti-Alberti *et al.*, 2007; CSD refcode *UDUVUL*) shows a similar six-fold coordination of the Na atom where the water O atom is replaced by an O-atom of a SO_3 group. The conformation of the S atoms is *antiperiplanar* in our compound and *gauche* in the unhydrated form.

S2. Experimental

When adding pure ethanol to a concentrated solution of 2-thioethanesulfonic acid in water, we noticed a precipitating white crystalline mass never described before in the literature. Micro elementary analysis based on the empirical formula ($C_2H_8O_4S_2$) of the hydrated acid ($HS–CoM^-H_3O^+$) showed significantly low values for C and H. At the same time ^1H and ^{13}C NMR analysis of the precipitate in D_2O ruled out any organic impurities. Investigations into the crystals by laser ablation inductively coupled plasma sector field mass spectrometry (LA-ICP-SF MS), however, clearly revealed the presence of sodium in hyperstoichiometric amounts: molar ratio (Na-23)/(S-32) = 1.34 (RSD: 8,5%, n = 9) (Günther & Hattendorf, 2005; Latkoczy & Günther, 2002). The white precipitate consisted of two different types of crystals, needles and thin plates. The needles were used for structure analysis by X-ray diffraction.

S3. Refinement

H-positions for the methylene CH_2 groups have been calculated with fixed distance of 1.08 Å. H atoms for the water molecule and the thiol group have been taken from a difference map and were included in the refinement in their as-found positions.

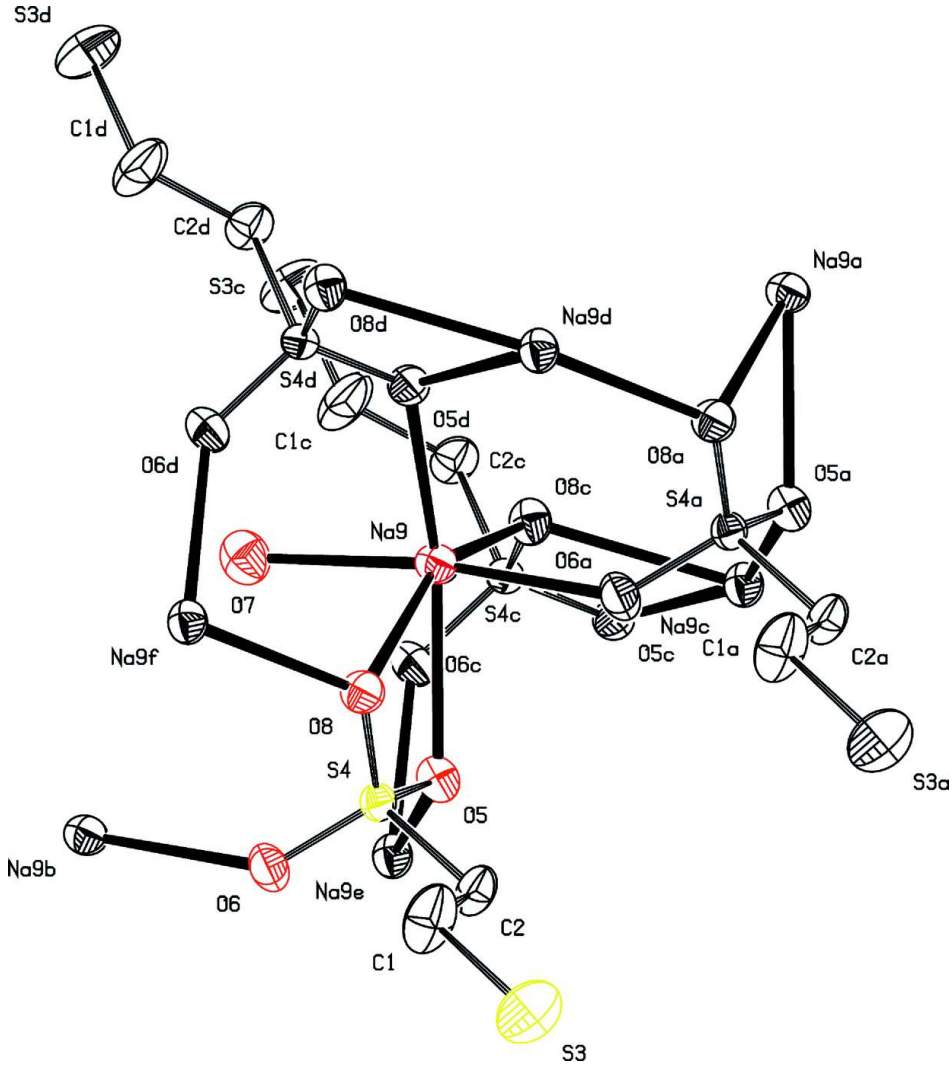

Figure 1

The molecular structure of sodium 2-thioethanesulfonate hydrate with 50% probability displacement ellipsoids. H atoms are omitted for clarity. The complete coordination of the Na atom is shown. Symmetry codes: (a) *x*, -1+*y*, *z*; (b) *x*, 1+*y*, *z*; (c) 1/2-*x*, -1/2+*y*, -1/2+*z*; (d) 1/2-*x*, -1/2+*y*, 1/2+*z*; (e) 1/2-*x*, 1/2+*y*, -1/2+*z*; (f) 1/2-*x*, 1/2+*y*, 1/2+*z*.

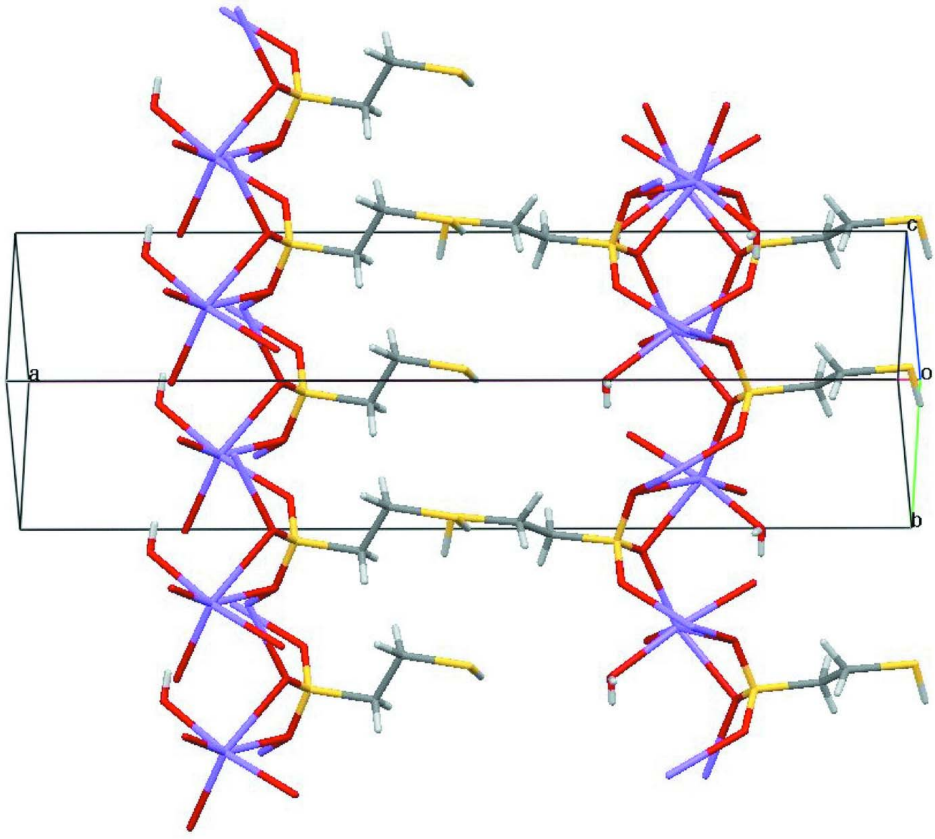

Figure 2

Crystal structure viewed down the diagonal of the *a*–*b* axis, showing the layer structure of Na—O clusters.

sodium 2-mercaptoethanesulfonate monohydrate

Crystal data

$Na^{+}\cdot C_2H_5O_3S_2^{-}\cdot H_2O$
M_r = 182.19
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
a = 23.4301 (8) Å
b = 5.0324 (2) Å
c = 6.1254 (2) Å
V = 722.24 (4) Å^3
Z = 4
F(000) = 376.0
D_x = 1.676 Mg m^{-3}
Melting point: 473 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5975 reflections
θ = 2.3–27.5°
μ = 0.74 mm^{-1}
T = 223 K
Plate, colourless
0.26 × 0.20 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
CCD scans
1647 measured reflections
1534 independent reflections
1263 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 27.5°, θ_{min} = 3.4°
h = −29→30
k = −6→6
l = −7→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.131$
$S = 0.95$
1534 reflections
88 parameters
1 restraint
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Absolute structure: Flack (1983), 627 Friedel pairs
Absolute structure parameter: 0.13 (18)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S3	−0.00830 (4)	0.7465 (2)	0.8298 (4)	0.0483 (4)
H3	−0.0154	0.8542	0.6813	0.058*
S4	0.17410 (3)	0.75424 (11)	0.66676 (19)	0.0185 (2)
Na9	0.26442 (4)	0.3309 (2)	0.6658 (4)	0.0238 (3)
O5	0.19813 (10)	0.6264 (6)	0.4720 (5)	0.0239 (7)
O6	0.18238 (8)	1.0402 (4)	0.6710 (8)	0.0286 (5)
O7	0.33586 (10)	0.6737 (5)	0.6717 (8)	0.0338 (5)
H1	0.3259	0.8098	0.7595	0.023 (11)*
H2	0.3374	0.7465	0.5332	0.047 (16)*
O8	0.19475 (10)	0.6245 (6)	0.8649 (5)	0.0257 (7)
C1	0.06798 (17)	0.8051 (9)	0.8424 (9)	0.0464 (11)
H1A	0.0756	1.0166	0.8509	0.056*
H1B	0.0846	0.7169	0.9900	0.056*
C2	0.09943 (14)	0.6946 (6)	0.6517 (10)	0.0279 (8)
H2A	0.0829	0.7827	0.5039	0.033*
H2B	0.0920	0.4830	0.6431	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S3	0.0235 (5)	0.0688 (8)	0.0526 (8)	−0.0031 (4)	0.0074 (6)	0.0024 (6)
S4	0.0182 (4)	0.0178 (4)	0.0194 (4)	−0.00146 (19)	0.0008 (4)	0.0002 (7)
Na9	0.0267 (6)	0.0228 (6)	0.0219 (6)	0.0034 (4)	−0.0009 (9)	−0.0004 (10)
O5	0.0302 (16)	0.0223 (15)	0.0191 (18)	−0.0013 (11)	0.0050 (14)	−0.0031 (12)
O6	0.0325 (10)	0.0188 (10)	0.0344 (12)	−0.0029 (8)	0.0011 (17)	−0.003 (2)
O7	0.0398 (13)	0.0345 (11)	0.0271 (13)	0.0012 (10)	0.004 (2)	−0.005 (2)
O8	0.0301 (16)	0.0271 (17)	0.0197 (18)	0.0020 (12)	−0.0011 (13)	−0.0027 (14)
C1	0.0228 (17)	0.063 (3)	0.053 (3)	−0.0050 (17)	0.010 (2)	−0.013 (3)
C2	0.0182 (14)	0.0364 (16)	0.029 (2)	−0.0033 (12)	−0.001 (2)	−0.008 (2)

Geometric parameters (Å, º)

S3—C1	1.813 (4)	Na9—Na9^{i}	4.0207 (5)
S3—H3	1.0714	Na9—Na9^{ii}	4.0207 (5)
S4—O6	1.4522 (19)	Na9—Na9^{v}	4.0207 (5)
S4—O8	1.460 (4)	O5—Na9^{v}	2.312 (4)
S4—O5	1.468 (3)	O6—Na9^{vi}	2.416 (2)
S4—C2	1.778 (3)	O7—H1	0.9012
S4—Na9	3.0028 (13)	O7—H2	0.9247
Na9—O5^{i}	2.312 (4)	O8—Na9^{iv}	2.322 (4)
Na9—O8^{ii}	2.322 (4)	C1—C2	1.489 (6)
Na9—O7	2.404 (3)	C1—H1A	1.0800
Na9—O6^{iii}	2.416 (2)	C1—H1B	1.0800
Na9—O5	2.456 (3)	C2—H2A	1.0800
Na9—O8	2.517 (3)	C2—H2B	1.0800
Na9—Na9^{iv}	4.0207 (5)		

C1—S3—H3	96.1	O8—Na9—Na9^{i}	83.64 (8)
O6—S4—O8	112.6 (2)	S4—Na9—Na9^{i}	108.91 (6)
O6—S4—O5	113.4 (2)	Na9^{iv}—Na9—Na9^{i}	77.477 (11)
O8—S4—O5	110.64 (11)	O5^{i}—Na9—Na9^{ii}	113.78 (8)
O6—S4—C2	107.43 (13)	O8^{ii}—Na9—Na9^{ii}	35.38 (7)
O8—S4—C2	107.1 (2)	O7—Na9—Na9^{ii}	125.28 (13)
O5—S4—C2	105.2 (2)	O6^{iii}—Na9—Na9^{ii}	59.83 (11)
O6—S4—Na9	127.52 (9)	O5—Na9—Na9^{ii}	84.52 (8)
O8—S4—Na9	56.70 (12)	O8—Na9—Na9^{ii}	128.86 (8)
O5—S4—Na9	54.35 (12)	S4—Na9—Na9^{ii}	109.09 (5)
C2—S4—Na9	125.01 (11)	Na9^{iv}—Na9—Na9^{ii}	160.65 (6)
O5^{i}—Na9—O8^{ii}	106.77 (8)	Na9^{i}—Na9—Na9^{ii}	99.226 (14)
O5^{i}—Na9—O7	92.45 (14)	O5^{i}—Na9—Na9^{v}	163.76 (8)
O8^{ii}—Na9—O7	92.65 (14)	O8^{ii}—Na9—Na9^{v}	75.20 (9)
O5^{i}—Na9—O6^{iii}	91.25 (13)	O7—Na9—Na9^{v}	71.31 (12)
O8^{ii}—Na9—O6^{iii}	93.87 (12)	O6^{iii}—Na9—Na9^{v}	104.78 (10)
O7—Na9—O6^{iii}	171.25 (9)	O5—Na9—Na9^{v}	31.43 (7)
O5^{i}—Na9—O5	154.34 (14)	O8—Na9—Na9^{v}	83.84 (8)
O8^{ii}—Na9—O5	98.49 (14)	S4—Na9—Na9^{v}	55.88 (5)
O7—Na9—O5	90.75 (11)	Na9^{iv}—Na9—Na9^{v}	99.226 (14)
O6^{iii}—Na9—O5	82.52 (10)	Na9^{i}—Na9—Na9^{v}	160.65 (6)
O5^{i}—Na9—O8	96.56 (14)	Na9^{ii}—Na9—Na9^{v}	77.476 (11)
O8^{ii}—Na9—O8	156.12 (14)	S4—O5—Na9^{v}	127.60 (18)
O7—Na9—O8	91.32 (12)	S4—O5—Na9	96.60 (16)
O6^{iii}—Na9—O8	80.38 (10)	Na9^{v}—O5—Na9	114.93 (10)
O5—Na9—O8	57.90 (7)	S4—O6—Na9^{vi}	134.91 (12)
O5^{i}—Na9—S4	125.55 (10)	Na9—O7—H1	112.0
O8^{ii}—Na9—S4	127.54 (10)	Na9—O7—H2	107.3
O7—Na9—S4	88.94 (7)	H1—O7—H2	104.9
O6^{iii}—Na9—S4	82.46 (6)	S4—O8—Na9^{iv}	126.59 (19)
O5—Na9—S4	29.05 (8)	S4—O8—Na9	94.29 (16)

O8—Na9—S4	29.01 (8)	Na9^{iv}—O8—Na9	112.33 (10)
O5^{i}—Na9—Na9^{iv}	74.00 (8)	C2—C1—S3	113.2 (3)
O8^{ii}—Na9—Na9^{iv}	162.52 (8)	C2—C1—H1A	108.9
O7—Na9—Na9^{iv}	69.91 (11)	S3—C1—H1A	108.9
O6^{iii}—Na9—Na9^{iv}	103.59 (10)	C2—C1—H1B	108.9
O5—Na9—Na9^{iv}	83.28 (8)	S3—C1—H1B	108.9
O8—Na9—Na9^{iv}	32.29 (7)	H1A—C1—H1B	107.8
S4—Na9—Na9^{iv}	55.67 (5)	C1—C2—S4	112.5 (3)
O5^{i}—Na9—Na9^{i}	33.64 (7)	C1—C2—H2A	109.1
O8^{ii}—Na9—Na9^{i}	113.20 (9)	S4—C2—H2A	109.1
O7—Na9—Na9^{i}	123.68 (13)	C1—C2—H2B	109.1
O6^{iii}—Na9—Na9^{i}	58.49 (11)	S4—C2—H2B	109.1
O5—Na9—Na9^{i}	129.85 (9)	H2A—C2—H2B	107.8

O6—S4—Na9—O5^{i}	91.9 (3)	O8—Na9—O5—S4	4.61 (8)
O8—S4—Na9—O5^{i}	−2.37 (19)	Na9^{iv}—Na9—O5—S4	−16.81 (12)
O5—S4—Na9—O5^{i}	−174.30 (19)	Na9^{i}—Na9—O5—S4	50.69 (17)
C2—S4—Na9—O5^{i}	−90.6 (3)	Na9^{ii}—Na9—O5—S4	148.14 (13)
O6—S4—Na9—O8^{ii}	−92.9 (3)	Na9^{v}—Na9—O5—S4	−137.0 (2)
O8—S4—Na9—O8^{ii}	172.8 (2)	O5^{i}—Na9—O5—Na9^{v}	147.7 (2)
O5—S4—Na9—O8^{ii}	0.92 (18)	O8^{ii}—Na9—O5—Na9^{v}	−42.28 (14)
C2—S4—Na9—O8^{ii}	84.6 (3)	O7—Na9—O5—Na9^{v}	50.50 (18)
O6—S4—Na9—O7	−0.3 (3)	O6^{iii}—Na9—O5—Na9^{v}	−135.11 (15)
O8—S4—Na9—O7	−94.6 (2)	O8—Na9—O5—Na9^{v}	141.6 (2)
O5—S4—Na9—O7	93.4 (2)	S4—Na9—O5—Na9^{v}	137.0 (2)
C2—S4—Na9—O7	177.2 (2)	Na9^{iv}—Na9—O5—Na9^{v}	120.17 (13)
O6—S4—Na9—O6^{iii}	178.0 (4)	Na9^{i}—Na9—O5—Na9^{v}	−172.34 (6)
O8—S4—Na9—O6^{iii}	83.75 (18)	Na9^{ii}—Na9—O5—Na9^{v}	−74.88 (13)
O5—S4—Na9—O6^{iii}	−88.17 (17)	O8—S4—O6—Na9^{vi}	67.2 (4)
C2—S4—Na9—O6^{iii}	−4.5 (3)	O5—S4—O6—Na9^{vi}	−59.3 (4)
O6—S4—Na9—O5	−93.8 (3)	C2—S4—O6—Na9^{vi}	−175.1 (4)
O8—S4—Na9—O5	171.92 (14)	Na9—S4—O6—Na9^{vi}	2.7 (5)
C2—S4—Na9—O5	83.7 (3)	O6—S4—O8—Na9^{iv}	1.0 (3)
O6—S4—Na9—O8	94.3 (3)	O5—S4—O8—Na9^{iv}	129.03 (19)
O5—S4—Na9—O8	−171.92 (14)	C2—S4—O8—Na9^{iv}	−116.9 (2)
C2—S4—Na9—O8	−88.2 (3)	Na9—S4—O8—Na9^{iv}	122.0 (2)
O6—S4—Na9—Na9^{iv}	65.9 (3)	O6—S4—O8—Na9	−121.06 (16)
O8—S4—Na9—Na9^{iv}	−28.43 (14)	O5—S4—O8—Na9	7.01 (12)
O5—S4—Na9—Na9^{iv}	159.65 (14)	C2—S4—O8—Na9	121.08 (15)
C2—S4—Na9—Na9^{iv}	−116.6 (2)	O5^{i}—Na9—O8—S4	178.06 (16)
O6—S4—Na9—Na9^{i}	125.1 (3)	O8^{ii}—Na9—O8—S4	−14.1 (4)
O8—S4—Na9—Na9^{i}	30.82 (14)	O7—Na9—O8—S4	85.44 (17)
O5—S4—Na9—Na9^{i}	−141.11 (14)	O6^{iii}—Na9—O8—S4	−91.78 (16)
C2—S4—Na9—Na9^{i}	−57.4 (2)	O5—Na9—O8—S4	−4.62 (8)
O6—S4—Na9—Na9^{ii}	−127.6 (3)	Na9^{iv}—Na9—O8—S4	132.6 (2)
O8—S4—Na9—Na9^{ii}	138.14 (14)	Na9^{i}—Na9—O8—S4	−150.81 (13)
O5—S4—Na9—Na9^{ii}	−33.78 (14)	Na9^{ii}—Na9—O8—S4	−54.07 (17)
C2—S4—Na9—Na9^{ii}	49.9 (2)	Na9^{v}—Na9—O8—S4	14.40 (12)

O6—S4—Na9—Na9^{v}	−68.3 (3)	O5^{i}—Na9—O8—Na9^{iv}	45.45 (13)
O8—S4—Na9—Na9^{v}	−162.63 (14)	O8^{ii}—Na9—O8—Na9^{iv}	−146.7 (2)
O5—S4—Na9—Na9^{v}	25.45 (14)	O7—Na9—O8—Na9^{iv}	−47.17 (17)
C2—S4—Na9—Na9^{v}	109.2 (2)	O6^{iii}—Na9—O8—Na9^{iv}	135.61 (15)
O6—S4—O5—Na9^{v}	−8.3 (3)	O5—Na9—O8—Na9^{iv}	−137.2 (2)
O8—S4—O5—Na9^{v}	−135.9 (2)	S4—Na9—O8—Na9^{iv}	−132.6 (2)
C2—S4—O5—Na9^{v}	108.8 (2)	Na9^{i}—Na9—O8—Na9^{iv}	76.58 (13)
Na9—S4—O5—Na9^{v}	−128.7 (2)	Na9^{ii}—Na9—O8—Na9^{iv}	173.32 (6)
O6—S4—O5—Na9	120.40 (17)	Na9^{v}—Na9—O8—Na9^{iv}	−118.21 (13)
O8—S4—O5—Na9	−7.21 (12)	S3—C1—C2—S4	179.9 (2)
C2—S4—O5—Na9	−122.50 (16)	O6—S4—C2—C1	−60.6 (4)
O5^{i}—Na9—O5—S4	10.8 (4)	O8—S4—C2—C1	60.6 (4)
O8^{ii}—Na9—O5—S4	−179.26 (15)	O5—S4—C2—C1	178.3 (3)
O7—Na9—O5—S4	−86.47 (18)	Na9—S4—C2—C1	121.5 (3)
O6^{iii}—Na9—O5—S4	87.92 (15)		

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