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Sodium rubidium disaccharinate tetrahydrate

Alexander Y. Nazarenko*

Chemistry Department, SUNY Buffalo State, 1300 Elmwood Ave, Buffalo, NY 14222, USA. *Correspondence e-mail: nazareay@buffalostate.edu

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Keywords: crystal structure; 1,2-benzothiazol-3(2*H*)-one 1,1-dioxide; saccharin; rubidium; sodium; hydrate; binary compound.

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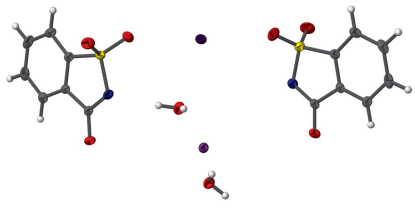
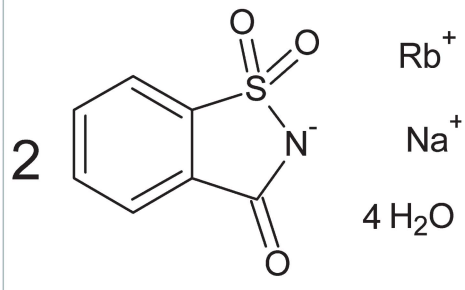
Structural data: full structural data are available from iucrdata.iucr.org

1,2-Benzothiazol-3(2*H*)-one 1,1 dioxide (more commonly known under its commercial name saccharin) forms a double salt with sodium and rubidium, $Na^{+}\cdot Rb^{+}\cdot 2C_7H_4NO_3S^{-}\cdot 4H_2O$. The coordination numbers of the sodium and rubidium ions are 6 and 8, respectively; the coordination polyhedra can be described as distorted triangular and rectangular prisms. Both Rb^{+} and Na^{+} cations and flat saccharinate moieties are positioned at mirror planes parallel to the (010) crystallographic plane. Metal ions and saccharinate anions are assembled into infinite layers parallel to the (001) plane *via* electrostatic interactions and hydrogen-bonded networks. These layers are connected by stacking interactions and C—H···O hydrogen bonds into a three-dimensional structure.

3D view



Chemical scheme



Structure description

Saccharin [1,2-benzothiazol-3(2*H*)-one 1,1-dioxide] is one of the most widely used sweeteners; its water-soluble sodium salt is commonly used as an artificial sweetener in food and beverages, and it is also the major component in the diet of diabetics. Saccharin has a very rich crystal chemistry: the Cambridge Structural Database (CSD version 5.39; Groom *et al.*, 2016) contains several hundred different structures of its compounds. For practical purposes, most interesting are non-toxic saccharin salts with alkali metals. Crystal structures of all simple salts [Na^{+}: refcode MGSACD11 (Naumov *et al.*, 2005), LANBOS (Banerjee *et al.*, 2005); K^{+}: LANBUY (Banerjee *et al.*, 2005); Rb^{+} and Cs^{+}: FAZHAS, FAZHEW, FAZHIA and FAZHOG (Karothu *et al.*, 2017)] and several binary compounds [Na^{+} and K^{+}: COCRIV (Malik *et al.*, 1984); Li^{+} and Na^{+}: MIPSUA (Bhatt & Desiraju, 2007)] have been determined. As a continuation of a structural study of common sweeteners (Nazarenko, 2018), the crystal structure of sodium rubidium di-saccharinate tetrahydrate, **I**, is presented here.

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Table 1
Selected bond lengths (Å).

Rb1—O3^{i}	2.9921 (14)	Rb1—O2^{i}	3.0473 (15)
Rb1—O3	2.9921 (14)	Na1—O1^{iv}	2.5123 (16)
Rb1—O3^{ii}	3.1346 (14)	Na1—O1	2.4696 (16)
Rb1—O3^{iii}	3.1346 (14)	Na1—O1^{i}	2.4696 (16)
Rb1—O6	3.0056 (15)	Na1—O1^{v}	2.5123 (16)
Rb1—O6^{i}	3.0056 (15)	Na1—O2	2.4074 (17)
Rb1—O2	3.0473 (15)	Na1—O2^{i}	2.4074 (16)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O5^{vi}	0.79 (3)	2.02 (3)	2.801 (2)	170 (2)
O1—H1B···O4^{v}	0.84 (3)	1.99 (3)	2.819 (2)	168 (2)
O2—H2A···N2^{vi}	0.81 (3)	2.12 (3)	2.924 (2)	174 (2)
O2—H2B···N1	0.83 (3)	2.09 (3)	2.915 (2)	175 (3)
C5—H5···O4^{vii}	0.95	2.45	3.388 (3)	169
C13—H13···O5^{viii}	0.95	2.47	3.318 (3)	148

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

The numbering scheme for **I** is shown in Fig. 1. Both the sodium and rubidium ions are located on a mirror plane. The Na^{+} ions have a distorted trigonal–prismatic environment (coordination number 6); the coordination sphere of Na1 contains bridging O atoms of water molecules (Table 1, Fig. 2). The coordination sphere of Rb1 (coordination number 8) is a distorted rectangular prism (Table 1, Fig. 2). It contains two pairs of crystallographically identical O atoms of sulfonyl groups (O3 and O6), two crystallographically identical atoms (O3) of bidentate sulfonyl groups and two crystallographically identical water molecules (O2).

Both saccharinate anions are planar with all atoms (except the O atoms of the sulfonyl groups) located on crystallographic mirror planes. The distribution of the Hirshfeld surface electrostatic potential of the anion shows that the negative charge is almost evenly distributed around the carboxyl and sulfonyl oxygen atoms and amide nitrogen atom: the remaining Hirshfeld surface is almost neutral electrostatically.

The coordination polyhedra of the sodium ions are bridged by two edges of a triangle (two crystallographically identical water molecules O1) with an inversion centre located at each edge. This linking forms an infinite chain of hydrated sodium cations along [010].

The coordination polyhedra of the rubidium ions are bridged *via* a common edge containing the sulfonyl oxygen atom O3; again, an inversion centre is located at each of these edges. Two sulfonyl groups of another saccharinate anion (O6) form a bridge to the next rubidium ion (Fig. 3) from each side of the mirror plane. All these interactions result in a zigzag-type chain along [010]. Two parallel chains of Rb^{+} and Na^{+} ions are bound by two identical water molecules (atom O2) related by mirror planes. These bridges form a layer of hydrated cations parallel to the (001) plane (Fig. 3). The hydrogen atoms of both bridging water molecules form electrostatically enhanced hydrogen bonds with the nitrogen atoms and carbonyl oxygen atoms as acceptors (Table 2, Figs. 3 and 4).

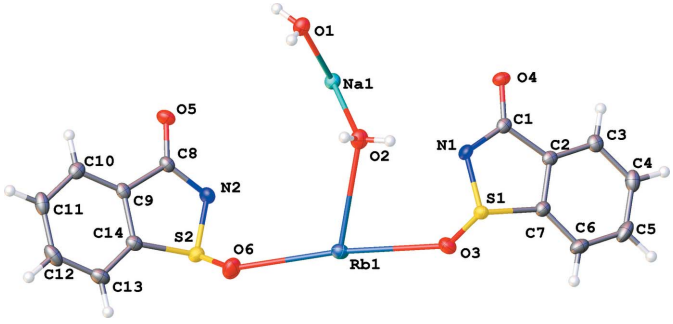

Figure 1
The numbering scheme for the title compound with 50% probability displacement ellipsoids.

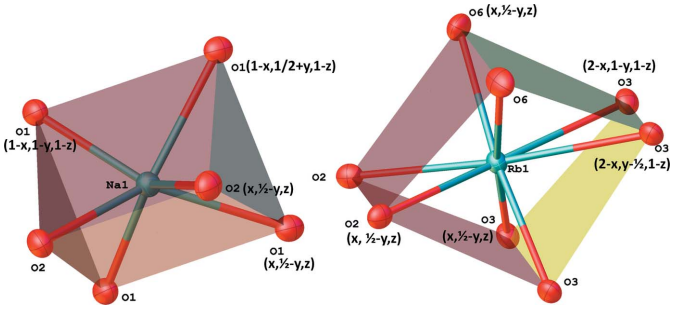

Figure 2
Coordination polyhedra of the metal ions in **I**. For bond lengths and symmetry codes, see Table 1.

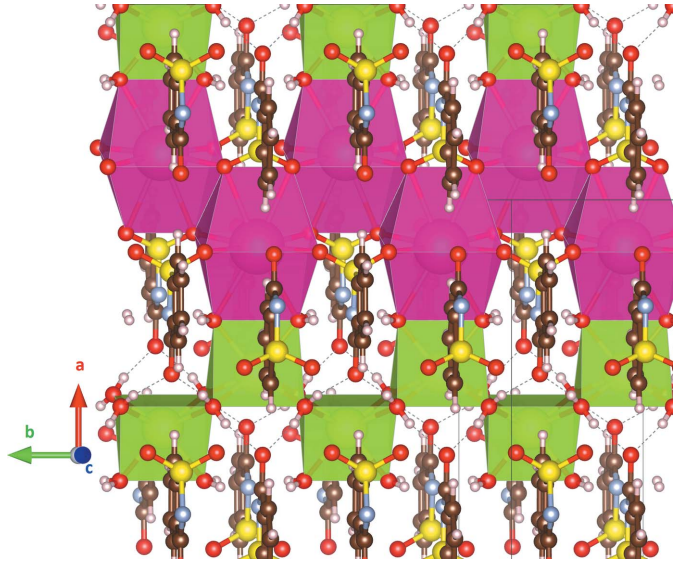

Figure 3
The infinite chains of hydrated sodium (green) and rubidium (purple) ions along the [010] direction. View along [001] vector, with 5° offset.

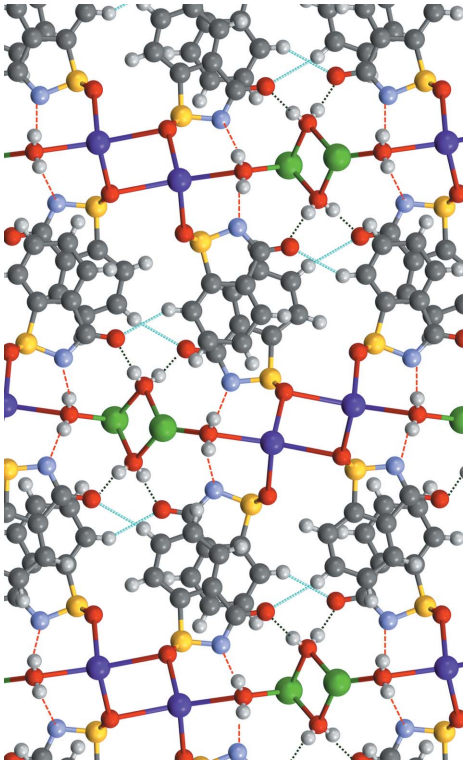

Figure 4
Packing of the title compound viewed along [010]. Sodium ions are green. Hydrogen bonds are shown as dashed lines with the following colour scheme: O—H···N: red, O—H···O: green and C—H···O: blue.

The saccharinate anions are positioned in planes parallel to (010) and are perpendicular to the layer of hydrated cations. Two C—H···O enhanced hydrogen bonds (Table 2, Fig. 4) connect anions from neighbouring layers. Additional interlayer binding comes from the stacking interactions. The distance between the planes of aromatic saccharin moieties is 3.2916 (2) Å (exactly half of cell dimension *b*). This value is short enough to expect an overall attractive interaction of benzene rings (there is no negative electrostatic potential in this area of the saccharine anion).

Synthesis and crystallization

The title compound was crystallized following the published procedure for rubidium saccharinate (Karothu *et al.*, 2017) with a sodium salt being used instead of the acidic form and rubidium chloride instead of rubidium carbonate. Slow crystallization yielded thin needles, some of which were suitable for the single-crystal X-ray experiment. Reaction with caesium chloride under the same conditions yielded the already known caesium saccharinate (refcode FAZHOG; Karothu *et al.*, 2017).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Table 3
Experimental details.

Crystal data	
Chemical formula	$Na^+·Rb^+·2C_7H_4NO_3S^-·4H_2O$
M_r	544.87
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	173
a, *b*, *c* (Å)	14.2754 (9), 6.5831 (4), 21.5365 (13)
V (Å^3)	2023.9 (2)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	2.73
Crystal size (mm)	0.79 × 0.09 × 0.05
Data collection	
Diffractometer	Bruker PHOTON-100 CMOS
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.362, 0.884
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31423, 2724, 2288
R_{int}	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.027, 0.067, 1.05
No. of reflections	2724
No. of parameters	185
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.57, −0.39

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

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Sodium rubidium disaccharinate tetrahydrate

Alexander Y. Nazarenko

Sodium rubidium bis(3-oxo-3*H*-1,2-benzothiazol-2-ide 1,1-dioxide) tetrahydrate

Crystal data

$Na^+·Rb^+·2C_7H_4NO_3S^-·4H_2O$
M_r = 544.87
Orthorhombic, *Pnma*
a = 14.2754 (9) Å
b = 6.5831 (4) Å
c = 21.5365 (13) Å
V = 2023.9 (2) Å^3
Z = 4
F(000) = 1096
D_x = 1.788 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 9989 reflections
θ = 3.0–28.1°
μ = 2.73 mm^{-1}
T = 173 K
Needle, colourless
0.79 × 0.09 × 0.05 mm

Data collection

Bruker PHOTON-100 CMOS diffractometer
Radiation source: sealedtube
ω scans
Absorption correction: numerical (SADABS; Krause *et al.*, 2015)
T_{min} = 0.362, T_{max} = 0.884
31423 measured reflections
2724 independent reflections
2288 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 28.3°, θ_{min} = 2.9°
h = −19→19
k = −8→8
l = −28→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.067
S = 1.05
2724 reflections
185 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 1.4364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Special details

Refinement. Hydrogen atoms of water molecules are refined in isotropic approximation. Aromatic hydrogen atoms are refined with riding coordinates and with U_{iso} (H) = 1.2U_{iso} (carrier C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Rb1	0.88342 (2)	0.250000	0.53575 (2)	0.02062 (8)
S1	0.87768 (4)	0.750000	0.41360 (3)	0.01658 (14)
O3	0.91761 (9)	0.5667 (2)	0.43872 (6)	0.0250 (3)
O4	0.63582 (12)	0.750000	0.35725 (9)	0.0205 (4)
N1	0.76426 (15)	0.750000	0.42033 (10)	0.0190 (5)
C1	0.72184 (18)	0.750000	0.36403 (12)	0.0156 (5)
C2	0.78955 (18)	0.750000	0.31096 (12)	0.0154 (5)
C3	0.76969 (19)	0.750000	0.24776 (12)	0.0193 (5)
H3	0.706937	0.750000	0.233074	0.023*
C4	0.8449 (2)	0.750000	0.20690 (13)	0.0235 (6)
H4	0.833394	0.750000	0.163452	0.028*
C5	0.9367 (2)	0.750000	0.22833 (13)	0.0266 (6)
H5	0.986743	0.750000	0.199277	0.032*
C6	0.95660 (19)	0.750000	0.29150 (13)	0.0224 (6)
H6	1.019247	0.750000	0.306375	0.027*
C7	0.88137 (18)	0.750000	0.33154 (12)	0.0169 (5)
S2	0.82267 (5)	−0.250000	0.65317 (3)	0.02080 (15)
O5	0.56611 (13)	−0.250000	0.66279 (9)	0.0219 (4)
O6	0.87003 (10)	−0.0638 (3)	0.63672 (7)	0.0330 (4)
N2	0.71624 (16)	−0.250000	0.62557 (10)	0.0203 (5)
C8	0.65226 (19)	−0.250000	0.67156 (12)	0.0166 (5)
C9	0.69418 (18)	−0.250000	0.73533 (11)	0.0157 (5)
C10	0.6489 (2)	−0.250000	0.79189 (12)	0.0189 (5)
H10	0.582487	−0.250000	0.794381	0.023*
C11	0.7040 (2)	−0.250000	0.84519 (12)	0.0237 (6)
H11	0.674624	−0.250000	0.884767	0.028*
C12	0.8011 (2)	−0.250000	0.84165 (13)	0.0252 (6)
H12	0.836769	−0.250000	0.878906	0.030*
C13	0.8475 (2)	−0.250000	0.78489 (13)	0.0224 (6)
H13	0.913937	−0.250000	0.782258	0.027*
C14	0.79153 (18)	−0.250000	0.73245 (12)	0.0177 (5)
Na1	0.56939 (7)	0.250000	0.50765 (5)	0.0186 (2)
O1	0.48492 (10)	0.4992 (2)	0.57256 (6)	0.0215 (3)
O2	0.69978 (10)	0.4792 (2)	0.51854 (7)	0.0241 (3)
H1A	0.5133 (17)	0.561 (4)	0.5976 (11)	0.033 (7)*
H1B	0.4428 (17)	0.437 (4)	0.5921 (11)	0.032 (7)*
H2A	0.7002 (18)	0.553 (4)	0.5485 (12)	0.037 (7)*
H2B	0.7148 (19)	0.558 (5)	0.4902 (12)	0.046 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.01761 (14)	0.02122 (14)	0.02303 (14)	0.000	−0.00236 (10)	0.000
S1	0.0138 (3)	0.0200 (3)	0.0159 (3)	0.000	−0.0008 (2)	0.000
O3	0.0222 (7)	0.0272 (7)	0.0256 (7)	0.0031 (6)	−0.0034 (6)	0.0056 (6)

O4	0.0138 (9)	0.0230 (10)	0.0246 (10)	0.000	0.0016 (7)	0.000
N1	0.0162 (11)	0.0258 (12)	0.0151 (10)	0.000	0.0039 (8)	0.000
C1	0.0176 (13)	0.0104 (11)	0.0189 (12)	0.000	0.0024 (10)	0.000
C2	0.0164 (12)	0.0099 (11)	0.0199 (13)	0.000	0.0014 (10)	0.000
C3	0.0233 (14)	0.0139 (12)	0.0206 (13)	0.000	−0.0008 (11)	0.000
C4	0.0372 (16)	0.0161 (13)	0.0170 (13)	0.000	0.0032 (12)	0.000
C5	0.0310 (16)	0.0214 (14)	0.0274 (15)	0.000	0.0152 (12)	0.000
C6	0.0167 (13)	0.0206 (13)	0.0299 (15)	0.000	0.0048 (11)	0.000
C7	0.0170 (13)	0.0148 (12)	0.0189 (12)	0.000	0.0018 (10)	0.000
S2	0.0174 (3)	0.0257 (3)	0.0193 (3)	0.000	0.0009 (2)	0.000
O5	0.0179 (10)	0.0241 (10)	0.0238 (10)	0.000	−0.0061 (8)	0.000
O6	0.0280 (8)	0.0393 (9)	0.0318 (8)	−0.0114 (7)	0.0021 (6)	0.0078 (7)
N2	0.0196 (12)	0.0258 (12)	0.0156 (11)	0.000	−0.0028 (9)	0.000
C8	0.0191 (13)	0.0140 (12)	0.0167 (12)	0.000	−0.0037 (10)	0.000
C9	0.0208 (13)	0.0098 (11)	0.0166 (12)	0.000	−0.0026 (10)	0.000
C10	0.0216 (13)	0.0124 (12)	0.0228 (13)	0.000	0.0027 (11)	0.000
C11	0.0414 (17)	0.0143 (13)	0.0154 (12)	0.000	−0.0005 (12)	0.000
C12	0.0364 (17)	0.0173 (13)	0.0218 (14)	0.000	−0.0126 (12)	0.000
C13	0.0202 (13)	0.0195 (13)	0.0274 (14)	0.000	−0.0073 (11)	0.000
C14	0.0180 (13)	0.0137 (12)	0.0213 (13)	0.000	−0.0029 (10)	0.000
Na1	0.0193 (5)	0.0170 (5)	0.0194 (5)	0.000	0.0012 (4)	0.000
O1	0.0223 (7)	0.0213 (7)	0.0207 (7)	−0.0049 (6)	0.0012 (6)	−0.0017 (6)
O2	0.0278 (8)	0.0195 (7)	0.0249 (7)	−0.0051 (6)	0.0006 (6)	0.0005 (6)

Geometric parameters (Å, º)

Rb1—S1^{i}	3.5807 (7)	S2—O6^{v}	1.4438 (15)
Rb1—O3^{ii}	2.9921 (14)	S2—N2	1.632 (2)
Rb1—O3	2.9921 (14)	S2—C14	1.764 (3)
Rb1—O3^{i}	3.1346 (14)	O5—C8	1.244 (3)
Rb1—O3^{iii}	3.1346 (14)	N2—C8	1.347 (3)
Rb1—O6	3.0056 (15)	C8—C9	1.498 (3)
Rb1—O6^{ii}	3.0056 (15)	C9—C10	1.379 (4)
Rb1—O2	3.0473 (15)	C9—C14	1.391 (4)
Rb1—O2^{ii}	3.0473 (15)	C10—H10	0.9500
S1—O3^{iv}	1.4399 (14)	C10—C11	1.392 (4)
S1—O3	1.4399 (14)	C11—H11	0.9500
S1—N1	1.626 (2)	C11—C12	1.389 (4)
S1—C7	1.768 (3)	C12—H12	0.9500
O4—C1	1.237 (3)	C12—C13	1.390 (4)
N1—C1	1.355 (3)	C13—H13	0.9500
C1—C2	1.497 (3)	C13—C14	1.384 (4)
C2—C3	1.390 (4)	Na1—O1^{vi}	2.5123 (16)
C2—C7	1.384 (4)	Na1—O1	2.4696 (16)
C3—H3	0.9500	Na1—O1^{ii}	2.4696 (16)
C3—C4	1.388 (4)	Na1—O1^{vii}	2.5123 (16)
C4—H4	0.9500	Na1—O2	2.4074 (17)
C4—C5	1.389 (4)	Na1—O2^{ii}	2.4074 (16)

C5—H5	0.9500	O1—H1A	0.79 (3)
C5—C6	1.390 (4)	O1—H1B	0.84 (3)
C6—H6	0.9500	O2—H2A	0.81 (3)
C6—C7	1.377 (4)	O2—H2B	0.83 (3)
S2—O6	1.4438 (15)		

O3^{ii}—Rb1—S1^{i}	93.29 (3)	C6—C5—H5	119.4
O3^{i}—Rb1—S1^{i}	23.58 (3)	C5—C6—H6	121.5
O3—Rb1—S1^{i}	93.29 (3)	C7—C6—C5	117.0 (3)
O3^{iii}—Rb1—S1^{i}	23.58 (3)	C7—C6—H6	121.5
O3—Rb1—O3^{iii}	104.06 (3)	C2—C7—S1	106.98 (18)
O3—Rb1—O3^{i}	72.93 (4)	C6—C7—S1	130.5 (2)
O3^{ii}—Rb1—O3^{iii}	72.93 (4)	C6—C7—C2	122.5 (2)
O3^{i}—Rb1—O3^{iii}	45.28 (5)	O6—S2—O6^{v}	116.16 (13)
O3^{ii}—Rb1—O3^{i}	104.06 (3)	O6—S2—N2	110.28 (7)
O3^{ii}—Rb1—O3	88.35 (5)	O6^{v}—S2—N2	110.28 (7)
O3^{ii}—Rb1—O6	92.10 (4)	O6—S2—C14	110.83 (8)
O3—Rb1—O6	174.09 (4)	O6^{v}—S2—C14	110.83 (8)
O3^{ii}—Rb1—O6^{ii}	174.09 (4)	N2—S2—C14	96.77 (12)
O3—Rb1—O6^{ii}	92.10 (4)	S2—O6—Rb1	142.26 (9)
O3—Rb1—O2^{ii}	113.60 (4)	C8—N2—S2	111.31 (17)
O3^{ii}—Rb1—O2^{ii}	73.16 (4)	O5—C8—N2	124.0 (2)
O3—Rb1—O2	73.16 (4)	O5—C8—C9	122.3 (2)
O3^{ii}—Rb1—O2	113.60 (4)	N2—C8—C9	113.8 (2)
O6^{ii}—Rb1—S1^{i}	80.80 (3)	C10—C9—C8	128.5 (2)
O6—Rb1—S1^{i}	80.80 (3)	C10—C9—C14	120.5 (2)
O6^{ii}—Rb1—O3^{iii}	101.26 (4)	C14—C9—C8	111.0 (2)
O6—Rb1—O3^{i}	101.26 (4)	C9—C10—H10	121.2
O6—Rb1—O3^{iii}	70.50 (4)	C9—C10—C11	117.6 (3)
O6^{ii}—Rb1—O3^{i}	70.50 (4)	C11—C10—H10	121.2
O6^{ii}—Rb1—O6	86.85 (6)	C10—C11—H11	119.4
O6^{ii}—Rb1—O2^{ii}	111.94 (4)	C12—C11—C10	121.3 (3)
O6—Rb1—O2	111.94 (4)	C12—C11—H11	119.4
O6^{ii}—Rb1—O2	72.12 (4)	C11—C12—H12	119.2
O6—Rb1—O2^{ii}	72.12 (4)	C11—C12—C13	121.6 (3)
O2^{ii}—Rb1—S1^{i}	148.92 (3)	C13—C12—H12	119.2
O2—Rb1—S1^{i}	148.92 (3)	C12—C13—H13	121.9
O2^{ii}—Rb1—O3^{iii}	127.61 (4)	C14—C13—C12	116.3 (3)
O2—Rb1—O3^{iii}	172.50 (4)	C14—C13—H13	121.9
O2—Rb1—O3^{i}	127.61 (4)	C9—C14—S2	107.16 (19)
O2^{ii}—Rb1—O3^{i}	172.50 (4)	C13—C14—S2	130.1 (2)
O2^{ii}—Rb1—O2	59.35 (5)	C13—C14—C9	122.7 (3)
O3^{iv}—S1—Rb1^{i}	60.56 (6)	O1^{vii}—Na1—O1^{vi}	82.18 (7)
O3—S1—Rb1^{i}	60.56 (6)	O1^{ii}—Na1—O1^{vi}	132.46 (5)
O3—S1—O3^{iv}	113.84 (12)	O1—Na1—O1^{vi}	78.58 (5)
O3^{iv}—S1—N1	111.15 (7)	O1—Na1—O1^{ii}	83.25 (8)
O3—S1—N1	111.15 (7)	O1^{ii}—Na1—O1^{vii}	78.58 (5)
O3—S1—C7	111.33 (7)	O1—Na1—O1^{vii}	132.46 (5)

O3^{iv}—S1—C7	111.33 (7)	O2^{ii}—Na1—O1	137.62 (7)
N1—S1—Rb1^{i}	157.14 (8)	O2—Na1—O1^{vi}	83.90 (5)
N1—S1—C7	96.83 (11)	O2—Na1—O1^{ii}	137.62 (7)
C7—S1—Rb1^{i}	106.03 (9)	O2^{ii}—Na1—O1^{ii}	84.61 (5)
Rb1—O3—Rb1^{i}	107.07 (4)	O2—Na1—O1	84.61 (5)
S1—O3—Rb1^{i}	95.86 (7)	O2—Na1—O1^{vii}	135.84 (7)
S1—O3—Rb1	141.42 (8)	O2^{ii}—Na1—O1^{vii}	83.90 (5)
C1—N1—S1	111.42 (17)	O2^{ii}—Na1—O1^{vi}	135.84 (7)
O4—C1—N1	123.3 (2)	O2—Na1—O2^{ii}	77.61 (8)
O4—C1—C2	123.4 (2)	Na1—O1—Na1^{vi}	101.42 (5)
N1—C1—C2	113.2 (2)	Na1^{vi}—O1—H1A	106.7 (18)
C3—C2—C1	128.0 (2)	Na1—O1—H1A	118.8 (18)
C7—C2—C1	111.5 (2)	Na1—O1—H1B	107.9 (17)
C7—C2—C3	120.5 (2)	Na1^{vi}—O1—H1B	116.4 (16)
C2—C3—H3	121.2	H1A—O1—H1B	106 (2)
C4—C3—C2	117.6 (3)	Rb1—O2—H2A	101.2 (18)
C4—C3—H3	121.2	Rb1—O2—H2B	100.2 (19)
C3—C4—H4	119.4	Na1—O2—Rb1	111.51 (5)
C3—C4—C5	121.3 (3)	Na1—O2—H2A	117.3 (18)
C5—C4—H4	119.4	Na1—O2—H2B	121.4 (19)
C4—C5—H5	119.4	H2A—O2—H2B	102 (3)
C4—C5—C6	121.2 (3)		

Rb1^{i}—S1—O3—Rb1	127.00 (13)	C7—S1—O3—Rb1^{i}	96.89 (9)
Rb1^{i}—S1—N1—C1	180.000 (1)	C7—S1—N1—C1	0.000 (1)
Rb1^{i}—S1—C7—C2	180.000 (1)	C7—C2—C3—C4	0.000 (1)
Rb1^{i}—S1—C7—C6	0.000 (1)	S2—N2—C8—O5	180.000 (1)
S1—N1—C1—O4	180.000 (1)	S2—N2—C8—C9	0.000 (1)
S1—N1—C1—C2	0.000 (1)	O5—C8—C9—C10	0.000 (1)
O3^{iv}—S1—O3—Rb1	97.06 (14)	O5—C8—C9—C14	180.000 (1)
O3^{iv}—S1—O3—Rb1^{i}	−29.94 (12)	O6^{v}—S2—O6—Rb1	92.86 (16)
O3—S1—N1—C1	−116.05 (7)	O6^{v}—S2—N2—C8	115.19 (8)
O3^{iv}—S1—N1—C1	116.05 (7)	O6—S2—N2—C8	−115.19 (8)
O3^{iv}—S1—C7—C2	−115.91 (7)	O6^{v}—S2—C14—C9	−114.75 (8)
O3—S1—C7—C2	115.91 (7)	O6—S2—C14—C9	114.75 (8)
O3^{iv}—S1—C7—C6	64.09 (7)	O6^{v}—S2—C14—C13	65.25 (8)
O3—S1—C7—C6	−64.09 (7)	O6—S2—C14—C13	−65.25 (8)
O4—C1—C2—C3	0.000 (1)	N2—S2—O6—Rb1	−33.53 (17)
O4—C1—C2—C7	180.000 (1)	N2—S2—C14—C9	0.000 (1)
N1—S1—O3—Rb1	−29.37 (15)	N2—S2—C14—C13	180.000 (1)
N1—S1—O3—Rb1^{i}	−156.38 (8)	N2—C8—C9—C10	180.000 (1)
N1—S1—C7—C2	0.000 (1)	N2—C8—C9—C14	0.000 (1)
N1—S1—C7—C6	180.000 (1)	C8—C9—C10—C11	180.000 (1)
N1—C1—C2—C3	180.000 (1)	C8—C9—C14—S2	0.000 (1)
N1—C1—C2—C7	0.000 (1)	C8—C9—C14—C13	180.000 (1)
C1—C2—C3—C4	180.000 (1)	C9—C10—C11—C12	0.000 (1)
C1—C2—C7—S1	0.000 (1)	C10—C9—C14—S2	180.000 (1)
C1—C2—C7—C6	180.000 (1)	C10—C9—C14—C13	0.000 (1)

C2—C3—C4—C5	0.000 (1)	C10—C11—C12—C13	0.000 (1)
C3—C2—C7—S1	180.000 (1)	C11—C12—C13—C14	0.000 (1)
C3—C2—C7—C6	0.000 (1)	C12—C13—C14—S2	180.000 (1)
C3—C4—C5—C6	0.000 (1)	C12—C13—C14—C9	0.000 (1)
C4—C5—C6—C7	0.000 (1)	C14—S2—O6—Rb1	−139.50 (14)
C5—C6—C7—S1	180.000 (1)	C14—S2—N2—C8	0.000 (1)
C5—C6—C7—C2	0.000 (1)	C14—C9—C10—C11	0.000 (1)
C7—S1—O3—Rb1	−136.11 (13)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O5^{viii}	0.79 (3)	2.02 (3)	2.801 (2)	170 (2)
O1—H1*B*···O4^{vii}	0.84 (3)	1.99 (3)	2.819 (2)	168 (2)
O2—H2*A*···N2^{viii}	0.81 (3)	2.12 (3)	2.924 (2)	174 (2)
O2—H2*B*···N1	0.83 (3)	2.09 (3)	2.915 (2)	175 (3)
C5—H5···O4^{ix}	0.95	2.45	3.388 (3)	169
C13—H13···O5^{x}	0.95	2.47	3.318 (3)	148

Symmetry codes: (vii) −*x*+1, *y*−1/2, −*z*+1; (viii) *x*, *y*+1, *z*; (ix) *x*+1/2, −*y*+3/2, −*z*+1/2; (x) *x*+1/2, −*y*−1/2, −*z*+3/2.