Poly[aqua[μ-4-(4-chlorophenyl)-2-thioxo-2,3-dihydrothiazol-3-olato]-sodium(I)]

Jens Hartung,[a] Janina Bachmann,[a] Ingrid Svoboda[b] and Hartmut Fuess[b]*

[a]Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany, and [b]Strukturforschung, FB 11, Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstrasse 23, D-64287 Darmstadt, Germany
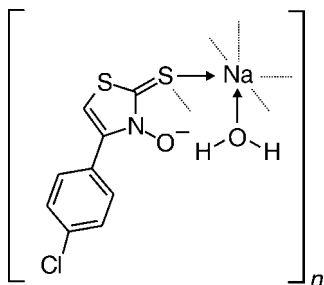
Correspondence e-mail: hartung@chemie.uni-kl.de

The packing of the title compound, $[Na(C_9H_5ClNOS_2)(H_2O)]_n$, in the crystal structure occurs by pairwise attachment of $+sc$- and $-sc$-arranged 4-(4-chlorophenyl)-2-thioxo-2,3-dihydrothiazol-3-olate subunits via S to sodium. Water molecules that are bound in the axial position of the distorted octahedral coordination octahedron give rise to a stereogenic center at sodium.

Related literature

For related literature, see: Allen *et al.* (1987); Hartung *et al.* (1996, 1999, 2007); Nardelli (1999).

Experimental

Crystal data

$[Na(C_9H_5ClNOS_2)(H_2O)]$
$M_r = 283.72$
Orthorhombic, $Pca2_1$
$a = 39.264$ (5) Å
$b = 4.168$ (1) Å
$c = 7.097$ (1) Å

$V = 1161.4$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.71$ mm^{-1}
$T = 300$ (2) K
$0.60 \times 0.28 \times 0.02$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford

Diffraction, 2007)
$T_{min} = 0.677$, $T_{max} = 0.986$
5052 measured reflections
2288 independent reflections
1860 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.173$
$S = 1.20$
2288 reflections
151 parameters
10 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}
Absolute structure: Flack (1983), 1009 Friedel pairs
Flack parameter: 0.1 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A⋯O1^i	0.88 (5)	1.80 (5)	2.675 (8)	175 (9)
O2—H2A⋯N3^i	0.88 (5)	2.61 (6)	3.434 (9)	156 (8)
O2—H2B⋯O1^{ii}	0.89 (5)	1.91 (6)	2.770 (8)	164 (9)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2452).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. A. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hartung, J., Gross, A. & Bergsträsser, U. (2007). *Acta Cryst.* E**63**, o2743–o2745.
Hartung, J., Schwarz, M., Svoboda, I., Fuess, H. & Duarte, M. T. (1999). *Eur. J. Org. Chem.* pp. 1275–1290.
Hartung, J., Svoboda, I. & Fuess, H. (1996). *Acta Cryst.* C**52**, 2841–2844.
Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.
Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Poly[aqua[*μ*-4-(4-chlorophenyl)-2-thioxo-2,3-dihydrothiazol-3-olato]sodium(I)]

Jens Hartung, Janina Bachmann, Ingrid Svoboda and Hartmut Fuess

S1. Comment

Neutralization of 4(4-chlorophenyl)-3-hydroxythiazole-2(3*H*)-thione (Hartung *et al.*, 1999) with sodium hydroxide in CH₃OH furnishes sodium 4-(4-chlorophenyl)-2-thiooxo-2,3-dihydrothiazole-3-olate. The compound crystallizes as monohydrate, (I), from a saturated solution of CH₃CN/hexane as yellowish prisms. The compound was investigated by X-ray diffraction in order to explore the structural chemistry of an alkali metal thiohydroxamate. The results of the study are summarized in the following section.

Fundamental differences between heterocyclic subunits of sodium 4-(4-chlorophenyl)-2-thiooxo-2,3-dihydrothiazole-3-olate monohydrate, (I) (Fig. 1), and the parent acid, *i.e.*, 4(4-chlorophenyl)-3-hydroxythiazole-2(3*H*)-thione (Hartung *et al.*, 1999) originate from a shortening of the N3—O3 distance from 1.379 (2) Å to 1.329 (8) Å and a lengthening of C2—S2 from 1.684 (2) Å to 1.699 (8) Å. The N3—O1 distance in (I) is closer to values reported for heterocyclic N– oxides than for thiohydroxamic acids (Hartung *et al.*, 1996, 1999, 2007). The C2—S2 bond length lies in between typical values of C—S single and double bonds (Allen *et al.*, 1987, Hartung *et al.*, 1999). The distance C2—N3 [1.33 (1) Å] in sodium salt (I) agrees with the corresponding bond length of 4(4-chlorophenyl)-3-hydroxythiazole-2(3*H*)-thione (Hartung *et al.*, 1999).

The parameters of the thiohydroxamate functional group in (I) are distinctively different from distances reported for 4(4-chlorophenyl)-3-isopropoxy-thiazole-2(3*H*)-thione [N3—O1 = 1.369 (3) Å, C2—S2 = 1.658 (3) Å, C2—N3 = 1.353 (3) Å] and further *N*-alkoxy derivatives thereof (Hartung *et al.*, 1999). One possible explanation for this finding is associated with a significant contribution of the *N*-oxidothiolato formulae for the description of ground state properties of (I) apart from the well established thione resonance formulae. Support for this argumentation comes from sodium atom positioning in the unit cell of (I). The proximity to the metal is in line with 4-(4-chlorophenyl)-2-thiooxo-2,3-dihydrothiazole-3-olate binding as monodentate S-donor ligand to sodium [Na1—S1 = 3.001 (4) Å, S2—Na1A= 2.998 (4) Å, S2—Na1B = 2.958 (4) Å, S2—Na1A = 2.961 (4) Å]. The N-oxide oxygen atom O1 forms hydrogen bonds toward the hydrate water that is attached at either side of the apex of a octahedrally distorted coordination polyhedron at sodium [N3—O1···H2 = 162.2 (3) °, O1···O2A = 2.770 (4) Å] (Figure 2). O1 therefore does not participate in a chelate type of interaction with the metal atom [Na1···O1 = 3.855 (5) A].

The *p*-chlorophenyl substituent is characterized by two different arrangements with respect to the heterocyclic core, *i.e.* positive (+) and negative (-) synclinal [N3—C4—C6—C7 = ± 42 (1) °]. The sodium atom is offset from the heterocyclic plane by Na1—S2—C2—N3 = 53.9 (8) °. A pairwise +*sc* and –sc arrangement of 4-(4-chlorophenyl)-2-thiooxo-2,3-di-hydrothiazole-3-olate entities in the equatorial plane in association with a non linearity of the O2—Na1—O2A axis [162.1 (3) °] gives rise to a stereogenic center at sodium (Fig. 2). Chirality thus originates from the packing of individual components of (I) in the solid state.

S2. Experimental

Sodium hydroxide (40.0 mg, 1.00 mmol, 1 equiv) was added to a solution of 4-(4-chlorphenyl)-3-hydroxythiazol-2(3*H*)-thione (244 mg, 1.00 mmol) in CH_3OH (5 ml) at 294 K. The reaction mixture was stirred at this temperature for 1.5 h. The volatiles were subsequently removed to afford a yellowish powder. The material was freeze-dried and subsequently dissolved in CH_3CN/hexane [1/1 (*v*/*v*)]. Yellowish prisms suitable for X-ray diffraction were grown by slowly allowing the solvent to evaporate at 293 K. Analysis calculated for $C_9H_7ClNNaO_2S_2$ (283.7 g/mol): C 38.10, H 2.49, N 4.94%; found C 38.15, H 2.39, N 4.92%; ^{1}H NMR (400 MHz, DMSO, p.p.m.): 7.06 (s, 1 H), 7.44 (d, J = 8.52 Hz, 2 H), 8.01 (d, J = 8.52 Hz, 2 H); ^{13}C (150 MHz, DMSO, p.p.m.): 104.5, 127.9, 129.5, 130.3, 132.8, 142.0, 162.2.

S3. Refinement

All H Atoms were positioned geometrically and treated as riding atoms (C—H = 0.93 Å), with U^{iso}(H)=1.2 U_{eq}(C) except H2A and H2B. The latter H atoms were located in a difference Fourier map and were refined with restrained geometry (Nardelli, 1999). The O—H distance was restained to 0.85 (6)Å and H···H distances were restained to 1.365Å thus leading to an angle of 107 Å.
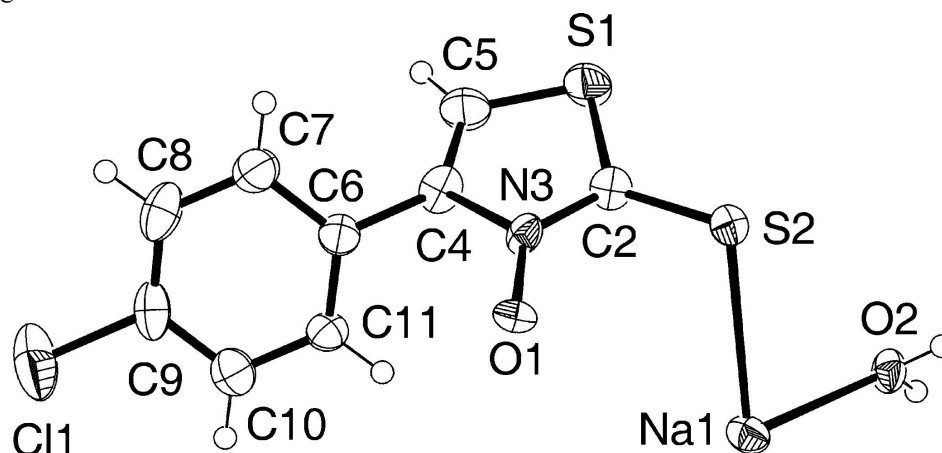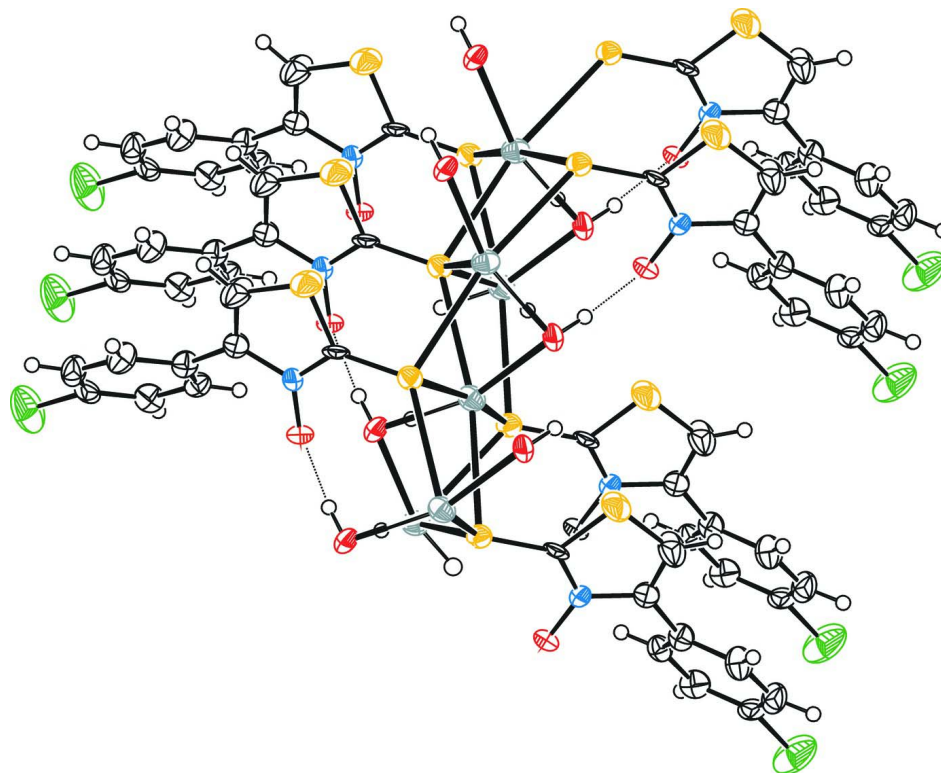

Figure 1
Molecular structure of (I). Displacement ellipsoids are plotted at the 50% probability level.

Figure 2

Packing and hydrogen bonding (dashed lines) of (I) in the solid state. S atoms are depicted in yellow, Cl in green, O in red, N in blue, and Na in gray).

poly[aqua[*µ*-4-(4-chlorophenyl)-2-thioxo-2,3-dihydrothiazol-\3-olato]sodium(I)]

Crystal data

[Na(C$_9$H$_5$ClNOS$_2$)(H$_2$O)]	$F(000) = 576$
$M_r = 283.72$	$D_x = 1.623$ Mg m^{-3}
Orthorhombic, *Pca*2$_1$	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2c -2ac	Cell parameters from 1313 reflections
$a = 39.264$ (5) Å	$\theta = 2.1$–$23.1°$
$b = 4.168$ (1) Å	$\mu = 0.71$ mm^{-1}
$c = 7.097$ (1) Å	$T = 300$ K
$V = 1161.4$ (4) Å^3	Prism, light yellow
$Z = 4$	$0.60 \times 0.28 \times 0.02$ mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD detector diffractometer	$T_{min} = 0.677$, $T_{max} = 0.986$
	5052 measured reflections
Radiation source: Enhance (Mo) X-ray Source	2288 independent reflections
Graphite monochromator	1860 reflections with $I > 2\sigma(I)$
Detector resolution: 8.4012 pixels mm^{-1}	$R_{int} = 0.036$
Rotation method data acquisition using ω and φ scans	$\theta_{max} = 26.4°$, $\theta_{min} = 3.1°$
	$h = -47 \rightarrow 48$
	$k = -2 \rightarrow 5$
Absorption correction: multi-scan	$l = -8 \rightarrow 8$
(*CrysAlis RED*; Oxford Diffraction, 2007)	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.081$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.173$	
$S = 1.20$	$w = 1/[\sigma^2(F_o^2) + 10.6487P]$
2288 reflections	where $P = (F_o^2 + 2F_c^2)/3$
151 parameters	$(\Delta/\sigma)_{max} = 0.069$
10 restraints	$\Delta\rho_{max} = 0.61$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.83$ e Å^{-3}
	Absolute structure: Flack (1983), 1009 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.1 (2)

Special details

Experimental. empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C2	−0.1784 (2)	−0.0666 (19)	0.0522 (12)	0.0262 (19)
C4	−0.1251 (2)	0.049 (2)	0.1720 (12)	0.028 (2)
C5	−0.1183 (3)	0.058 (3)	−0.0110 (13)	0.049 (3)
H5	−0.0969	0.1047	−0.0602	0.059*
C6	−0.1010 (2)	0.136 (2)	0.3269 (12)	0.030 (2)
C7	−0.0672 (2)	0.018 (3)	0.3149 (14)	0.041 (3)
H7	−0.0608	−0.1245	0.2202	0.049*
C8	−0.0438 (2)	0.122 (3)	0.4503 (16)	0.043 (3)
H8	−0.0211	0.0592	0.4419	0.051*
C9	−0.0540 (2)	0.314 (3)	0.5942 (14)	0.038 (3)
C10	−0.0872 (2)	0.429 (2)	0.6068 (15)	0.037 (2)
H10	−0.0936	0.5677	0.7031	0.044*
C11	−0.1107 (2)	0.330 (2)	0.4701 (12)	0.030 (2)
H11	−0.1332	0.3973	0.4781	0.036*
N3	−0.15955 (17)	−0.031 (2)	0.2072 (9)	0.0271 (18)
O1	−0.17113 (14)	−0.0646 (14)	0.3820 (7)	0.0230 (13)
O2	−0.28942 (14)	0.4205 (16)	−0.0027 (9)	0.0314 (15)
H2A	−0.302 (2)	0.266 (16)	−0.047 (12)	0.038*
H2B	−0.299 (2)	0.587 (15)	−0.058 (12)	0.038*
S1	−0.15330 (7)	−0.0274 (8)	−0.1467 (3)	0.0431 (7)
S2	−0.22082 (5)	−0.1443 (5)	0.0407 (3)	0.0271 (4)

Cl1	−0.02523 (8)	0.4352 (8)	0.7662 (5)	0.0758 (11)
Na1	−0.25584 (8)	0.3625 (9)	0.2703 (5)	0.0320 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.034 (4)	0.021 (5)	0.023 (4)	−0.004 (3)	0.002 (4)	0.015 (5)
C4	0.030 (4)	0.022 (5)	0.033 (5)	−0.001 (4)	0.006 (3)	0.024 (4)
C5	0.042 (6)	0.076 (9)	0.031 (5)	−0.010 (6)	0.009 (4)	−0.007 (6)
C6	0.030 (4)	0.023 (5)	0.037 (5)	−0.004 (4)	−0.001 (4)	−0.002 (4)
C7	0.037 (5)	0.041 (6)	0.045 (7)	−0.004 (5)	0.003 (4)	−0.005 (5)
C8	0.027 (5)	0.034 (6)	0.067 (7)	−0.005 (5)	−0.005 (5)	0.010 (6)
C9	0.033 (5)	0.032 (6)	0.050 (7)	−0.008 (5)	−0.016 (4)	0.022 (5)
C10	0.044 (6)	0.028 (6)	0.039 (5)	−0.004 (5)	−0.003 (4)	−0.003 (4)
C11	0.031 (5)	0.024 (5)	0.034 (5)	−0.002 (4)	0.002 (4)	0.000 (4)
N3	0.021 (3)	0.035 (5)	0.026 (4)	0.006 (3)	0.001 (3)	0.007 (4)
O1	0.032 (3)	0.018 (3)	0.018 (3)	−0.002 (3)	0.006 (2)	0.000 (3)
O2	0.025 (3)	0.032 (4)	0.037 (4)	0.005 (3)	−0.008 (3)	0.003 (3)
S1	0.0447 (14)	0.0600 (19)	0.0245 (11)	−0.0061 (14)	0.0058 (11)	0.0009 (15)
S2	0.0295 (10)	0.0234 (10)	0.0283 (10)	−0.0021 (9)	−0.0025 (10)	0.0016 (12)
Cl1	0.070 (2)	0.061 (2)	0.097 (3)	−0.0061 (17)	−0.048 (2)	−0.006 (2)
Na1	0.037 (2)	0.0337 (18)	0.0253 (17)	0.0020 (17)	−0.0014 (16)	0.0000 (19)

Geometric parameters (Å, º)

C2—N3	1.334 (10)	C11—H11	0.9300
C2—S2	1.699 (8)	N3—O1	1.329 (8)
C2—S1	1.729 (9)	O2—Na1	2.356 (7)
C4—C5	1.326 (13)	O2—Na1^i	2.411 (7)
C4—N3	1.415 (10)	O2—H2A	0.88 (5)
C4—C6	1.495 (12)	O2—H2B	0.89 (5)
C5—S1	1.716 (10)	S2—Na1^{ii}	2.958 (4)
C5—H5	0.9300	S2—Na1^{iii}	2.961 (4)
C6—C11	1.352 (12)	S2—Na1^i	2.998 (4)
C6—C7	1.420 (12)	S2—Na1	3.001 (4)
C7—C8	1.398 (13)	Na1—O2^{iv}	2.411 (7)
C7—H7	0.9300	Na1—S2^v	2.958 (4)
C8—C9	1.359 (14)	Na1—S2^{vi}	2.961 (4)
C8—H8	0.9300	Na1—S2^{iv}	2.998 (4)
C9—C10	1.389 (13)	Na1—Na1^i	3.5780 (10)
C9—Cl1	1.738 (9)	Na1—Na1^{iv}	3.5780 (10)
C10—C11	1.402 (12)	Na1—Na1^{vi}	4.1680 (10)
C10—H10	0.9300	Na1—Na1^{iii}	4.1680 (10)
N3—C2—S2	127.2 (6)	Na1^i—S2—Na1	73.23 (9)
N3—C2—S1	110.3 (6)	O2—Na1—O2^{iv}	162.1 (3)
S2—C2—S1	122.5 (5)	O2—Na1—S2^v	106.8 (2)
C5—C4—N3	111.8 (9)	O2^{iv}—Na1—S2^v	74.03 (18)

C5—C4—C6	125.8 (8)	O2—Na1—S2^{vi}	74.71 (19)
N3—C4—C6	122.1 (7)	O2^{iv}—Na1—S2^{vi}	87.46 (18)
C4—C5—S1	112.5 (8)	S2^{v}—Na1—S2^{vi}	91.06 (13)
C4—C5—H5	123.8	O2—Na1—S2^{iv}	115.3 (2)
S1—C5—H5	123.8	O2^{iv}—Na1—S2^{iv}	82.42 (17)
C11—C6—C7	121.1 (8)	S2^{v}—Na1—S2^{iv}	88.82 (11)
C11—C6—C4	121.3 (8)	S2^{vi}—Na1—S2^{iv}	169.51 (13)
C7—C6—C4	117.6 (8)	O2—Na1—S2	83.24 (19)
C8—C7—C6	117.7 (9)	O2^{iv}—Na1—S2	95.48 (18)
C8—C7—H7	121.2	S2^{v}—Na1—S2	169.51 (13)
C6—C7—H7	121.2	S2^{vi}—Na1—S2	88.70 (11)
C9—C8—C7	120.4 (9)	S2^{iv}—Na1—S2	89.52 (12)
C9—C8—H8	119.8	O2—Na1—Na1^{i}	41.94 (16)
C7—C8—H8	119.8	O2^{iv}—Na1—Na1^{i}	124.6 (2)
C8—C9—C10	121.9 (9)	S2^{v}—Na1—Na1^{i}	133.11 (9)
C8—C9—Cl1	120.4 (8)	S2^{vi}—Na1—Na1^{i}	52.77 (9)
C10—C9—Cl1	117.7 (9)	S2^{iv}—Na1—Na1^{i}	132.39 (9)
C9—C10—C11	118.1 (10)	S2—Na1—Na1^{i}	53.34 (9)
C9—C10—H10	120.9	O2—Na1—Na1^{iv}	152.5 (2)
C11—C10—H10	120.9	O2^{iv}—Na1—Na1^{iv}	40.77 (15)
C6—C11—C10	120.7 (9)	S2^{v}—Na1—Na1^{iv}	52.85 (8)
C6—C11—H11	119.6	S2^{vi}—Na1—Na1^{iv}	119.08 (11)
C10—C11—H11	119.7	S2^{iv}—Na1—Na1^{iv}	53.43 (8)
O1—N3—C2	124.6 (7)	S2—Na1—Na1^{iv}	118.65 (11)
O1—N3—C4	121.1 (6)	Na1^{i}—Na1—Na1^{iv}	165.3 (2)
C2—N3—C4	114.2 (7)	O2—Na1—Na1^{vi}	84.11 (18)
Na1—O2—Na1^{i}	97.3 (2)	O2^{iv}—Na1—Na1^{vi}	84.24 (18)
Na1—O2—H2A	123 (6)	S2^{v}—Na1—Na1^{vi}	45.98 (8)
Na1^{i}—O2—H2A	97 (6)	S2^{vi}—Na1—Na1^{vi}	46.04 (8)
Na1—O2—H2B	134 (6)	S2^{iv}—Na1—Na1^{vi}	134.80 (8)
Na1^{i}—O2—H2B	96 (6)	S2—Na1—Na1^{vi}	134.74 (8)
H2A—O2—H2B	100 (6)	Na1^{i}—Na1—Na1^{vi}	90.0
C5—S1—C2	91.0 (4)	Na1^{iv}—Na1—Na1^{vi}	90.0
C2—S2—Na1^{ii}	117.9 (3)	O2—Na1—Na1^{iii}	95.89 (18)
C2—S2—Na1^{iii}	124.2 (3)	O2^{iv}—Na1—Na1^{iii}	95.76 (18)
Na1^{ii}—S2—Na1^{iii}	74.38 (9)	S2^{v}—Na1—Na1^{iii}	134.02 (8)
C2—S2—Na1^{i}	101.3 (3)	S2^{vi}—Na1—Na1^{iii}	133.96 (8)
Na1^{ii}—S2—Na1^{i}	88.82 (11)	S2^{iv}—Na1—Na1^{iii}	45.20 (8)
Na1^{iii}—S2—Na1^{i}	134.38 (7)	S2—Na1—Na1^{iii}	45.26 (8)
C2—S2—Na1	106.8 (3)	Na1^{i}—Na1—Na1^{iii}	90.0
Na1^{ii}—S2—Na1	134.38 (7)	Na1^{iv}—Na1—Na1^{iii}	90.0
Na1^{iii}—S2—Na1	88.70 (11)	Na1^{vi}—Na1—Na1^{iii}	180.000 (1)
N3—C4—C5—S1	0.3 (14)	Na1^{i}—O2—Na1—S2	−39.9 (2)
C6—C4—C5—S1	−174.8 (8)	Na1^{i}—O2—Na1—Na1^{iv}	175.14 (18)
C5—C4—C6—C11	133.0 (12)	Na1^{i}—O2—Na1—Na1^{vi}	96.6 (2)
N3—C4—C6—C11	−41.7 (13)	Na1^{i}—O2—Na1—Na1^{iii}	−83.4 (2)
C5—C4—C6—C7	−45.0 (15)	C2—S2—Na1—O2	129.3 (3)

N3—C4—C6—C7	140.3 (10)	Na1ii—S2—Na1—O2	−38.8 (3)
C11—C6—C7—C8	−3.5 (15)	Na1iii—S2—Na1—O2	−105.24 (18)
C4—C6—C7—C8	174.5 (9)	Na1i—S2—Na1—O2	32.28 (18)
C6—C7—C8—C9	4.0 (16)	C2—S2—Na1—O2iv	−32.8 (3)
C7—C8—C9—C10	−3.7 (16)	Na1ii—S2—Na1—O2iv	159.16 (19)
C7—C8—C9—Cl1	178.3 (8)	Na1iii—S2—Na1—O2iv	92.68 (18)
C8—C9—C10—C11	2.7 (15)	Na1i—S2—Na1—O2iv	−129.80 (19)
Cl1—C9—C10—C11	−179.2 (7)	C2—S2—Na1—S2v	−34.2 (10)
C7—C6—C11—C10	2.7 (14)	Na1ii—S2—Na1—S2v	157.7 (7)
C4—C6—C11—C10	−175.2 (8)	Na1iii—S2—Na1—S2v	91.2 (9)
C9—C10—C11—C6	−2.2 (14)	Na1i—S2—Na1—S2v	−131.3 (9)
S2—C2—N3—O1	3.1 (13)	C2—S2—Na1—S2vi	54.6 (3)
S1—C2—N3—O1	−176.2 (7)	Na1ii—S2—Na1—S2vi	−113.52 (17)
S2—C2—N3—C4	−177.0 (7)	Na1iii—S2—Na1—S2vi	180.0
S1—C2—N3—C4	3.7 (10)	Na1i—S2—Na1—S2vi	−42.48 (9)
C5—C4—N3—O1	177.3 (9)	C2—S2—Na1—S2iv	−115.1 (3)
C6—C4—N3—O1	−7.4 (14)	Na1ii—S2—Na1—S2iv	76.8 (2)
C5—C4—N3—C2	−2.7 (13)	Na1iii—S2—Na1—S2iv	10.34 (13)
C6—C4—N3—C2	172.7 (8)	Na1i—S2—Na1—S2iv	147.86 (14)
C4—C5—S1—C2	1.5 (10)	C2—S2—Na1—Na1i	97.1 (3)
N3—C2—S1—C5	−2.9 (8)	Na1ii—S2—Na1—Na1i	−71.04 (19)
S2—C2—S1—C5	177.7 (6)	Na1iii—S2—Na1—Na1i	−137.52 (9)
N3—C2—S2—Na1ii	−135.5 (7)	C2—S2—Na1—Na1iv	−68.2 (3)
S1—C2—S2—Na1ii	43.7 (6)	Na1ii—S2—Na1—Na1iv	123.7 (2)
N3—C2—S2—Na1iii	−46.0 (9)	Na1iii—S2—Na1—Na1iv	57.21 (18)
S1—C2—S2—Na1iii	133.2 (4)	Na1i—S2—Na1—Na1iv	−165.27 (19)
N3—C2—S2—Na1i	129.8 (8)	C2—S2—Na1—Na1vi	54.6 (3)
S1—C2—S2—Na1i	−51.0 (6)	Na1ii—S2—Na1—Na1vi	−113.52 (17)
N3—C2—S2—Na1	54.1 (8)	Na1iii—S2—Na1—Na1vi	180.0
S1—C2—S2—Na1	−126.7 (5)	Na1i—S2—Na1—Na1vi	−42.48 (9)
Na1i—O2—Na1—O2iv	47.1 (12)	C2—S2—Na1—Na1iii	−125.4 (3)
Na1i—O2—Na1—S2v	137.05 (17)	Na1ii—S2—Na1—Na1iii	66.48 (17)
Na1i—O2—Na1—S2vi	50.6 (2)	Na1i—S2—Na1—Na1iii	137.52 (9)
Na1i—O2—Na1—S2iv	−126.10 (17)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O1i	0.88 (5)	1.80 (5)	2.675 (8)	175 (9)
O2—H2*A*···N3i	0.88 (5)	2.61 (6)	3.434 (9)	156 (8)
O2—H2*B*···O1vii	0.89 (5)	1.91 (6)	2.770 (8)	164 (9)

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