

Sodium 5-amino-1,3,4-thiadiazole-2-thiolate dihydrate

Jiayi Wu, Yifeng Wang, Guo Yi and Shuping Luo*

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou, 310014, People's Republic of China
Correspondence e-mail: jiaiyiwu1984@163.com

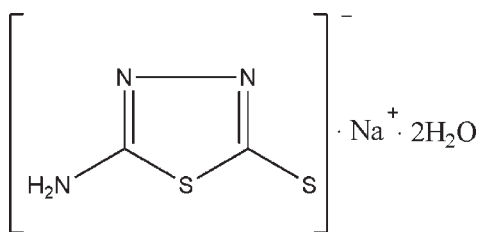
Received 5 November 2009; accepted 2 December 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{N}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.059; data-to-parameter ratio = 18.5.

There are two 5-amino-1,3,4-thiadiazole-2(3*H*)-thiolate anions in the asymmetric unit of the title compound, $\text{Na}^+ \cdot \text{C}_2\text{H}_2\text{N}_3\text{S}_2^- \cdot 2\text{H}_2\text{O}$, which are almost perpendicular to each other [dihedral angle = $84.64(6)^\circ$]. The two Na^+ cations are in distorted fourfold coordinations by O atoms of the water molecules. The crystal structure is stabilized by $\text{N}-\text{H} \cdots \text{S}$, $\text{O}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{S}$ hydrogen bonds.

Related literature

For use of 5-amino-1,3,4-thiadiazole-2(3*i*H/*i*))-thione derivatives as intermediates for pharmaceuticals, see: John & Gilmer (1960); John (1962); For related structures, see: Downie *et al.* (1972); Deng *et al.* (2005); Ma *et al.* (2007).



Experimental

Crystal data

$\text{Na}^+ \cdot \text{C}_2\text{H}_2\text{N}_3\text{S}_2^- \cdot 2\text{H}_2\text{O}$	$c = 8.4351(3)$ Å
$M_r = 191.21$	$\beta = 91.026(1)^\circ$
Monoclinic, $P2_1/c$	$V = 1485.53(8)$ Å ³
$a = 8.7810(3)$ Å	$Z = 8$
$b = 20.0593(5)$ Å	Mo $K\alpha$ radiation

$\mu = 0.72$ mm⁻¹
 $T = 296$ K

$0.38 \times 0.28 \times 0.17$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.758$, $T_{\max} = 0.885$

14264 measured reflections
3376 independent reflections
2974 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.059$
 $S = 1.00$
3376 reflections

182 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O}2\text{A}-\text{H}104 \cdots \text{N}3\text{B}$	0.85	1.99	2.8113 (18)	161
$\text{O}1\text{A}-\text{H}102 \cdots \text{S}1\text{B}$	0.87	2.39	3.2563 (14)	172
$\text{O}2\text{B}-\text{H}201 \cdots \text{S}1\text{B}^{\text{i}}$	0.86	2.45	3.2962 (12)	169
$\text{O}2\text{B}-\text{H}202 \cdots \text{N}2\text{B}^{\text{ii}}$	0.86	1.95	2.8024 (18)	170
$\text{N}1\text{A}-\text{H}1\text{A}2 \cdots \text{S}1\text{B}^{\text{iii}}$	0.86	2.57	3.4081 (16)	165
$\text{N}1\text{B}-\text{H}1\text{B}2 \cdots \text{S}1\text{A}^{\text{iv}}$	0.86	2.43	3.2589 (17)	161

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

Data collection: *PROCESS-AUTO* (Rigaku/MS, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2208).

References

- Deng, Q.-J., Yao, M.-X. & Zeng, M.-H. (2005). *Acta Cryst.* **E61**, o2239–o2240.
Downie, T. C., Harrison, W., Raper, E. S. & Hepworth, M. A. (1972). *Acta Cryst.* **B28**, 1584–1590.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
John, S. (1962). US Patent 3033901.
John, S. & Gilmer, T. W. (1960). US Patent 2966495.
Ma, C., Sun, J., Zheng, R. & Wang, D. (2007). *Organomet. Chem.* **692**, 4029–4042.
Rigaku/MS (2006). *PROCESS-AUTO*. Rigaku/MS, The Woodlands, Texas, USA.
Rigaku/MS (2007). *CrystalStructure*. Rigaku/MS, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2010). E66, m20 [doi:10.1107/S1600536809051897]

Sodium 5-amino-1,3,4-thiadiazole-2-thiolate dihydrate

J. Wu, Y. Wang, G. Yi and S. Luo

Comment

Interest in the study of 5-amino-1,3,4-thiadiazole-2(3*H*)-thione derivatives stems from their use as intermediates of pharmaceuticals (John *et al.*, 1960; John, 1962). Nonetheless, there are few articles that describe this kind of crystal structure (Downie *et al.*, 1972; Deng *et al.*, 2005; Ma *et al.*, 2007). As part of our studies of agrochemicals, the title compound 5-amino-2-thione-1,3,4-thiadiazole sodium dihydrate has been synthesized, and its crystal structure is reported in this article. The complex is located across an inversion centre, and is bridged by two symmetry equivalent water molecules Na—O (bridge) distances of 2.3776 (14) Å and 2.5141 (15) Å and an Na—O—Na bond angle of 98.99 (3)°. It has two 5-amino-1,3,4-thiadiazole-2(3*H*)-thione molecules in the asymmetric unit that are almost perpendicular to each other [dihedral angle = 84.64 (6)°]. The structure is stabilized by N—H···S, O—H···N and O—H···S hydrogen bonds.

Experimental

5-amino-1,3,4-thiadiazole-2(3*H*)-thione(0.1 mmol) and sodium hydroxide (0.1 mmol) were dissolved in water (10 ml) and stirred for 3 h. The water was then removed under reduced pressure. Single crystals were obtained by slow evaporation of a methanol solution at room temperature.

Refinement

All H atoms were initially located in a difference Fourier map. N-bound H atoms were located in a difference map and refined with an N—H distance restraint of 0.86 (1) Å. The water H atoms were refined using a riding model, with $U_{\text{iso}}(\text{H})=1.5_{\text{eq}}(\text{O})$.

Figures

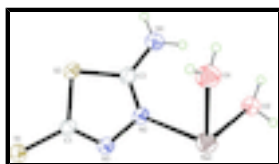


Fig. 1. The asymmetric unit of the title compound with the atomic labeling scheme. Displacement ellipsoids are drawn at the 40% probability level.

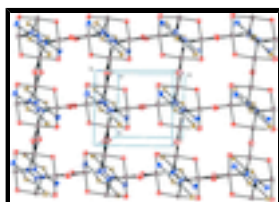


Fig. 2. A partial packing diagram of title compound.

Sodium 5-amino-1,3,4-thiadiazole-2-thiolate dihydrate

Crystal data

$\text{Na}^+ \cdot \text{C}_2\text{H}_2\text{N}_3\text{S}_2^- \cdot 2\text{H}_2\text{O}$	$F(000) = 784$
$M_r = 191.21$	$D_x = 1.710 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P 2_1bc$	Cell parameters from 11555 reflections
$a = 8.7810 (3) \text{ \AA}$	$\theta = 3.0\text{--}27.4^\circ$
$b = 20.0593 (5) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$c = 8.4351 (3) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 91.026 (1)^\circ$	Block, colorless
$V = 1485.53 (8) \text{ \AA}^3$	$0.38 \times 0.28 \times 0.17 \text{ mm}$
$Z = 8$	

Data collection

Rigaku R-Axis RAPID diffractometer	3376 independent reflections
Radiation source: rolling anode graphite	2974 reflections with $I > 2\sigma(I)$
Detector resolution: $10.00 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.026$
ω scans	$\theta_{\text{max}} = 27.4^\circ$, $\theta_{\text{min}} = 3.1^\circ$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.758$, $T_{\text{max}} = 0.885$	$k = -25 \rightarrow 25$
14264 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.026$	H-atom parameters constrained
$wR(F^2) = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 1.P]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
3376 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
182 parameters	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL, $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: $0.0516 (12)$

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S2B	0.46866 (5)	0.720405 (18)	0.04494 (5)	0.03114 (11)
S2A	0.97675 (5)	0.708164 (18)	0.53837 (5)	0.03013 (10)
S1B	0.71560 (5)	0.66512 (2)	-0.16488 (6)	0.03952 (12)
S1A	1.23359 (5)	0.65778 (2)	0.75020 (5)	0.03794 (12)
Na1B	0.71086 (8)	0.49937 (4)	0.47238 (8)	0.04359 (19)
Na1A	0.98033 (7)	0.50450 (3)	0.20940 (8)	0.03560 (16)
O2A	0.70915 (13)	0.49947 (6)	0.18979 (14)	0.0359 (3)
H104	0.6554	0.5221	0.1237	0.054*
H103	0.6897	0.4585	0.1699	0.054*
O1A	0.99706 (15)	0.58368 (6)	0.00068 (15)	0.0446 (3)
H101	1.0720	0.6080	-0.0267	0.067*
H102	0.9227	0.6081	-0.0358	0.067*
O2B	0.75550 (13)	0.50610 (6)	0.74664 (14)	0.0347 (3)
H204	0.5182	0.6062	0.4294	0.052*
H203	0.5156	0.6066	0.5812	0.052*
N2B	0.41175 (17)	0.60144 (7)	0.13535 (18)	0.0379 (3)
N2A	0.93910 (16)	0.58939 (6)	0.43221 (16)	0.0320 (3)
N3B	0.53241 (16)	0.59605 (7)	0.03004 (17)	0.0356 (3)
O1B	0.50110 (17)	0.57964 (7)	0.50136 (16)	0.0540 (4)
H201	0.7328	0.5460	0.7754	0.081*
H202	0.6964	0.4767	0.7880	0.081*
N3A	1.05908 (15)	0.58553 (6)	0.54520 (15)	0.0307 (3)
C2A	0.88628 (18)	0.65001 (7)	0.41696 (18)	0.0278 (3)
N1A	0.76956 (18)	0.66682 (7)	0.31696 (18)	0.0426 (4)
H1A1	0.7261	0.6368	0.2592	0.051*
H1A2	0.7391	0.7075	0.3114	0.051*
C1B	0.57417 (17)	0.65311 (7)	-0.02914 (18)	0.0277 (3)
C2B	0.36620 (18)	0.66293 (8)	0.15350 (18)	0.0304 (3)
N1B	0.24845 (18)	0.67989 (8)	0.2467 (2)	0.0479 (4)
H1B1	0.2000	0.6496	0.2972	0.057*
H1B2	0.2221	0.7210	0.2554	0.057*
C1A	1.09218 (17)	0.64295 (7)	0.61080 (17)	0.0262 (3)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2B	0.0345 (2)	0.02059 (18)	0.0384 (2)	-0.00051 (15)	0.00191 (16)	0.00096 (15)
S2A	0.0354 (2)	0.02064 (18)	0.0342 (2)	0.00192 (15)	-0.00284 (16)	-0.00291 (15)
S1B	0.0396 (2)	0.0309 (2)	0.0485 (3)	0.00355 (17)	0.01226 (19)	0.00579 (18)
S1A	0.0416 (2)	0.0306 (2)	0.0411 (2)	-0.00624 (17)	-0.01399 (18)	0.00242 (17)
Na1B	0.0385 (4)	0.0584 (5)	0.0339 (4)	0.0037 (3)	0.0013 (3)	0.0044 (3)
Na1A	0.0322 (3)	0.0395 (4)	0.0351 (3)	0.0030 (3)	0.0002 (3)	-0.0019 (3)
O2A	0.0390 (6)	0.0304 (6)	0.0380 (6)	0.0020 (5)	-0.0086 (5)	-0.0004 (5)
O1A	0.0437 (7)	0.0404 (7)	0.0497 (7)	-0.0024 (6)	0.0003 (6)	0.0079 (6)
O2B	0.0352 (6)	0.0321 (6)	0.0370 (6)	-0.0011 (5)	0.0036 (5)	0.0002 (5)
N2B	0.0408 (8)	0.0264 (7)	0.0467 (8)	0.0025 (6)	0.0098 (6)	0.0080 (6)
N2A	0.0395 (7)	0.0238 (6)	0.0323 (7)	0.0009 (6)	-0.0083 (6)	-0.0022 (5)
N3B	0.0383 (8)	0.0251 (7)	0.0437 (8)	0.0045 (6)	0.0069 (6)	0.0060 (6)
O1B	0.0642 (9)	0.0502 (8)	0.0478 (8)	0.0032 (7)	0.0073 (7)	0.0103 (6)
N3A	0.0358 (7)	0.0230 (6)	0.0330 (7)	0.0014 (5)	-0.0071 (6)	-0.0008 (5)
C2A	0.0318 (8)	0.0251 (7)	0.0266 (7)	-0.0002 (6)	-0.0001 (6)	-0.0010 (6)
N1A	0.0486 (9)	0.0313 (7)	0.0473 (9)	0.0050 (6)	-0.0182 (7)	-0.0007 (6)
C1B	0.0284 (7)	0.0240 (7)	0.0304 (7)	0.0020 (6)	-0.0050 (6)	0.0014 (6)
C2B	0.0325 (8)	0.0278 (8)	0.0308 (8)	-0.0020 (6)	-0.0017 (6)	0.0029 (6)
N1B	0.0521 (10)	0.0336 (8)	0.0588 (10)	0.0017 (7)	0.0236 (8)	0.0014 (7)
C1A	0.0296 (7)	0.0233 (7)	0.0257 (7)	-0.0010 (6)	0.0020 (6)	0.0029 (6)

Geometric parameters (\AA , $^\circ$)

S2B—C2B	1.7340 (16)	O2B—Na1A ⁱⁱ	2.3521 (13)
S2B—C1B	1.7583 (15)	O2B—H201	0.8609
S2A—C2A	1.7354 (15)	O2B—H202	0.8632
S2A—C1A	1.7578 (15)	N2B—C2B	1.306 (2)
S1B—C1B	1.7211 (16)	N2B—N3B	1.3989 (19)
S1A—C1A	1.7207 (16)	N2A—C2A	1.3071 (19)
Na1B—O2B	2.3433 (13)	N2A—N3A	1.4100 (18)
Na1B—O2A	2.3835 (13)	N3B—C1B	1.304 (2)
Na1B—O1B ⁱ	2.4576 (17)	O1B—Na1B ⁱ	2.4576 (17)
Na1B—O1B	2.4619 (16)	O1B—H204	0.8227
Na1B—Na1A	3.2739 (10)	O1B—H203	0.8710
Na1A—O2B ⁱⁱ	2.3521 (13)	N3A—C1A	1.3082 (19)
Na1A—O1A	2.3776 (14)	N3A—Na1B ⁱⁱ	2.6485 (15)
Na1A—O2A	2.3862 (14)	N3A—Na1A ⁱⁱ	2.7735 (15)
Na1A—O1A ⁱⁱⁱ	2.5141 (15)	C2A—N1A	1.358 (2)
O2A—H104	0.8538	N1A—H1A1	0.8600
O2A—H103	0.8559	N1A—H1A2	0.8600
O1A—Na1A ⁱⁱⁱ	2.5141 (15)	C2B—N1B	1.354 (2)
O1A—H101	0.8545	N1B—H1B1	0.8600
O1A—H102	0.8684	N1B—H1B2	0.8600

C2B—S2B—C1B	87.65 (8)	Na1B—Na1A—Na1A ⁱⁱⁱ	139.01 (3)
C2A—S2A—C1A	87.70 (7)	O2B ⁱⁱ —Na1A—Na1B ⁱⁱ	36.27 (3)
O2B—Na1B—O2A	170.14 (5)	O1A—Na1A—Na1B ⁱⁱ	119.10 (4)
O2B—Na1B—O1B ⁱ	93.54 (5)	O2A—Na1A—Na1B ⁱⁱ	138.61 (4)
O2A—Na1B—O1B ⁱ	95.71 (5)	O1A ⁱⁱⁱ —Na1A—Na1B ⁱⁱ	114.91 (4)
O2B—Na1B—O1B	88.66 (5)	N2A—Na1A—Na1B ⁱⁱ	66.59 (3)
O2A—Na1B—O1B	96.17 (5)	N3A ⁱⁱ —Na1A—Na1B ⁱⁱ	63.54 (3)
O1B ⁱ —Na1B—O1B	81.01 (6)	Na1B—Na1A—Na1B ⁱⁱ	92.07 (2)
O2B—Na1B—N3A ⁱⁱ	88.74 (5)	Na1A ⁱⁱⁱ —Na1A—Na1B ⁱⁱ	128.47 (3)
O2A—Na1B—N3A ⁱⁱ	86.31 (5)	Na1B—O2A—Na1A	86.69 (4)
O1B ⁱ —Na1B—N3A ⁱⁱ	99.79 (5)	Na1B—O2A—H104	130.3
O1B—Na1B—N3A ⁱⁱ	177.32 (5)	Na1A—O2A—H104	124.2
O2B—Na1B—N2A	88.52 (5)	Na1B—O2A—H103	101.1
O2A—Na1B—N2A	82.33 (4)	Na1A—O2A—H103	104.4
O1B ⁱ —Na1B—N2A	177.48 (5)	H104—O2A—H103	106.1
O1B—Na1B—N2A	97.60 (5)	Na1A—O1A—Na1A ⁱⁱⁱ	93.36 (5)
N3A ⁱⁱ —Na1B—N2A	81.70 (5)	Na1A—O1A—H101	129.8
O2B—Na1B—Na1A	123.85 (4)	Na1A ⁱⁱⁱ —O1A—H101	98.1
O2A—Na1B—Na1A	46.69 (3)	Na1A—O1A—H102	125.7
O1B ⁱ —Na1B—Na1A	129.72 (5)	Na1A ⁱⁱⁱ —O1A—H102	102.5
O1B—Na1B—Na1A	126.71 (4)	H101—O1A—H102	99.2
N3A ⁱⁱ —Na1B—Na1A	54.62 (3)	Na1B—O2B—Na1A ⁱⁱ	107.31 (5)
N2A—Na1B—Na1A	49.64 (3)	Na1B—O2B—H201	107.3
O2B—Na1B—Na1B ⁱ	91.44 (4)	Na1A ⁱⁱ —O2B—H201	105.8
O2A—Na1B—Na1B ⁱ	97.82 (4)	Na1B—O2B—H202	105.6
O1B ⁱ —Na1B—Na1B ⁱ	40.55 (4)	Na1A ⁱⁱ —O2B—H202	118.2
O1B—Na1B—Na1B ⁱ	40.46 (4)	H201—O2B—H202	112.2
N3A ⁱⁱ —Na1B—Na1B ⁱ	140.27 (5)	C2B—N2B—N3B	112.60 (13)
N2A—Na1B—Na1B ⁱ	138.02 (5)	C2A—N2A—N3A	112.15 (12)
Na1A—Na1B—Na1B ⁱ	144.42 (3)	C2A—N2A—Na1A	126.84 (10)
O2B—Na1B—Na1A ⁱⁱ	36.43 (3)	N3A—N2A—Na1A	110.19 (9)
O2A—Na1B—Na1A ⁱⁱ	134.54 (4)	C2A—N2A—Na1B	111.62 (10)
O1B ⁱ —Na1B—Na1A ⁱⁱ	117.21 (4)	N3A—N2A—Na1B	114.97 (9)
O1B—Na1B—Na1A ⁱⁱ	118.11 (4)	Na1A—N2A—Na1B	76.41 (4)
N3A ⁱⁱ —Na1B—Na1A ⁱⁱ	59.24 (3)	C1B—N3B—N2B	113.37 (13)
N2A—Na1B—Na1A ⁱⁱ	65.29 (3)	Na1B ⁱ —O1B—Na1B	98.99 (6)
Na1A—Na1B—Na1A ⁱⁱ	87.93 (2)	Na1B ⁱ —O1B—H204	129.2
Na1B ⁱ —Na1B—Na1A ⁱⁱ	127.63 (3)	Na1B—O1B—H204	101.7
O2B ⁱⁱ —Na1A—O1A	95.93 (5)	Na1B ⁱ —O1B—H203	115.5
O2B ⁱⁱ —Na1A—O2A	170.82 (5)	Na1B—O1B—H203	112.5
O1A—Na1A—O2A	92.97 (5)	H204—O1B—H203	98.3
O2B ⁱⁱ —Na1A—O1A ⁱⁱⁱ	87.56 (5)	C1A—N3A—N2A	113.29 (12)

supplementary materials

O1A—Na1A—O1A ⁱⁱⁱ	86.64 (5)	C1A—N3A—Na1B ⁱⁱ	115.21 (10)
O2A—Na1A—O1A ⁱⁱⁱ	90.73 (5)	N2A—N3A—Na1B ⁱⁱ	123.97 (9)
O2B ⁱⁱ —Na1A—N2A	95.52 (5)	C1A—N3A—Na1A ⁱⁱ	106.70 (10)
O1A—Na1A—N2A	96.34 (5)	N2A—N3A—Na1A ⁱⁱ	116.01 (9)
O2A—Na1A—N2A	85.71 (5)	Na1B ⁱⁱ —N3A—Na1A ⁱⁱ	74.25 (4)
O1A ⁱⁱⁱ —Na1A—N2A	175.46 (5)	N2A—C2A—N1A	123.68 (14)
O2B ⁱⁱ —Na1A—N3A ⁱⁱ	87.67 (4)	N2A—C2A—S2A	114.17 (11)
O1A—Na1A—N3A ⁱⁱ	176.24 (5)	N1A—C2A—S2A	122.15 (12)
O2A—Na1A—N3A ⁱⁱ	83.48 (4)	C2A—N1A—H1A1	120.0
O1A ⁱⁱⁱ —Na1A—N3A ⁱⁱ	94.61 (4)	C2A—N1A—H1A2	120.0
N2A—Na1A—N3A ⁱⁱ	82.20 (4)	H1A1—N1A—H1A2	120.0
O2B ⁱⁱ —Na1A—Na1B	127.81 (4)	N3B—C1B—S1B	126.07 (12)
O1A—Na1A—Na1B	125.29 (4)	N3B—C1B—S2B	112.60 (12)
O2A—Na1A—Na1B	46.62 (3)	S1B—C1B—S2B	121.34 (9)
O1A ⁱⁱⁱ —Na1A—Na1B	121.51 (4)	N2B—C2B—N1B	122.96 (15)
N2A—Na1A—Na1B	53.95 (4)	N2B—C2B—S2B	113.76 (12)
N3A ⁱⁱ —Na1A—Na1B	51.13 (3)	N1B—C2B—S2B	123.27 (13)
O2B ⁱⁱ —Na1A—Na1A ⁱⁱⁱ	92.23 (4)	C2B—N1B—H1B1	120.0
O1A—Na1A—Na1A ⁱⁱⁱ	44.83 (4)	C2B—N1B—H1B2	120.0
O2A—Na1A—Na1A ⁱⁱⁱ	92.49 (4)	H1B1—N1B—H1B2	120.0
O1A ⁱⁱⁱ —Na1A—Na1A ⁱⁱⁱ	41.81 (3)	N3A—C1A—S1A	126.40 (12)
N2A—Na1A—Na1A ⁱⁱⁱ	141.05 (5)	N3A—C1A—S2A	112.69 (11)
N3A ⁱⁱ —Na1A—Na1A ⁱⁱⁱ	136.32 (4)	S1A—C1A—S2A	120.89 (9)
O2B—Na1B—Na1A—O2B ⁱⁱ	13.17 (9)	Na1A—Na1B—O2B—Na1A ⁱⁱ	-10.87 (7)
O2A—Na1B—Na1A—O2B ⁱⁱ	-170.38 (7)	Na1B ⁱ —Na1B—O2B—Na1A ⁱⁱ	173.99 (4)
O1B ⁱ —Na1B—Na1A—O2B ⁱⁱ	-117.66 (7)	O2B ⁱⁱ —Na1A—N2A—C2A	119.25 (13)
O1B—Na1B—Na1A—O2B ⁱⁱ	130.87 (7)	O1A—Na1A—N2A—C2A	22.63 (14)
N3A ⁱⁱ —Na1B—Na1A—O2B ⁱⁱ	-46.25 (6)	O2A—Na1A—N2A—C2A	-69.88 (14)
N2A—Na1B—Na1A—O2B ⁱⁱ	65.53 (6)	N3A ⁱⁱ —Na1A—N2A—C2A	-153.88 (14)
Na1B ⁱ —Na1B—Na1A—O2B ⁱⁱ	-175.20 (6)	Na1B—Na1A—N2A—C2A	-107.01 (14)
Na1A ⁱⁱ —Na1B—Na1A—O2B ⁱⁱ	6.74 (5)	Na1A ⁱⁱⁱ —Na1A—N2A—C2A	18.77 (17)
O2B—Na1B—Na1A—O1A	-122.01 (6)	Na1B ⁱⁱ —Na1A—N2A—C2A	141.65 (14)
O2A—Na1B—Na1A—O1A	54.43 (6)	O2B ⁱⁱ —Na1A—N2A—N3A	-21.79 (10)
O1B ⁱ —Na1B—Na1A—O1A	107.16 (7)	O1A—Na1A—N2A—N3A	-118.40 (10)
O1B—Na1B—Na1A—O1A	-4.31 (8)	O2A—Na1A—N2A—N3A	149.09 (10)
N3A ⁱⁱ —Na1B—Na1A—O1A	178.56 (6)	N3A ⁱⁱ —Na1A—N2A—N3A	65.09 (10)
N2A—Na1B—Na1A—O1A	-69.65 (6)	Na1B—Na1A—N2A—N3A	111.96 (10)
Na1B ⁱ —Na1B—Na1A—O1A	49.61 (9)	Na1A ⁱⁱⁱ —Na1A—N2A—N3A	-122.26 (9)
Na1A ⁱⁱ —Na1B—Na1A—O1A	-128.44 (5)	Na1B ⁱⁱ —Na1A—N2A—N3A	0.61 (8)
O2B—Na1B—Na1A—O2A	-176.45 (7)	O2B ⁱⁱ —Na1A—N2A—Na1B	-133.74 (4)
O1B ⁱ —Na1B—Na1A—O2A	52.73 (7)	O1A—Na1A—N2A—Na1B	129.64 (4)

O1B—Na1B—Na1A—O2A	-58.74 (7)	O2A—Na1A—N2A—Na1B	37.13 (4)
N3A ⁱⁱ —Na1B—Na1A—O2A	124.13 (6)	N3A ⁱⁱ —Na1A—N2A—Na1B	-46.86 (4)
N2A—Na1B—Na1A—O2A	-124.09 (6)	Na1A ⁱⁱⁱ —Na1A—N2A—Na1B	125.78 (6)
Na1B ⁱ —Na1B—Na1A—O2A	-4.82 (7)	Na1B ⁱⁱ —Na1A—N2A—Na1B	-111.34 (3)
Na1A ⁱⁱ —Na1B—Na1A—O2A	177.12 (5)	O2B—Na1B—N2A—C2A	-96.54 (11)
O2B—Na1B—Na1A—O1A ⁱⁱⁱ	127.53 (6)	O2A—Na1B—N2A—C2A	87.15 (11)
O2A—Na1B—Na1A—O1A ⁱⁱⁱ	-56.03 (6)	O1B—Na1B—N2A—C2A	-8.10 (11)
O1B ⁱ —Na1B—Na1A—O1A ⁱⁱⁱ	-3.30 (8)	N3A ⁱⁱ —Na1B—N2A—C2A	174.51 (11)
O1B—Na1B—Na1A—O1A ⁱⁱⁱ	-114.77 (7)	Na1A—Na1B—N2A—C2A	124.59 (11)
N3A ⁱⁱ —Na1B—Na1A—O1A ⁱⁱⁱ	68.10 (6)	Na1B ⁱ —Na1B—N2A—C2A	-6.04 (14)
N2A—Na1B—Na1A—O1A ⁱⁱⁱ	179.89 (6)	Na1A ⁱⁱ —Na1B—N2A—C2A	-125.60 (11)
Na1B ⁱ —Na1B—Na1A—O1A ⁱⁱⁱ	-60.85 (8)	O2B—Na1B—N2A—N3A	32.66 (10)
Na1A ⁱⁱ —Na1B—Na1A—O1A ⁱⁱⁱ	121.10 (5)	O2A—Na1B—N2A—N3A	-143.65 (10)
O2B—Na1B—Na1A—N2A	-52.36 (6)	O1B—Na1B—N2A—N3A	121.10 (10)
O2A—Na1B—Na1A—N2A	124.09 (6)	N3A ⁱⁱ —Na1B—N2A—N3A	-56.29 (11)
O1B ⁱ —Na1B—Na1A—N2A	176.81 (7)	Na1A—Na1B—N2A—N3A	-106.21 (10)
O1B—Na1B—Na1A—N2A	65.34 (7)	Na1B ⁱ —Na1B—N2A—N3A	123.16 (10)
N3A ⁱⁱ —Na1B—Na1A—N2A	-111.79 (5)	Na1A ⁱⁱ —Na1B—N2A—N3A	3.60 (9)
Na1B ⁱ —Na1B—Na1A—N2A	119.27 (8)	O2B—Na1B—N2A—Na1A	138.86 (4)
Na1A ⁱⁱ —Na1B—Na1A—N2A	-58.79 (4)	O2A—Na1B—N2A—Na1A	-37.45 (4)
O2B—Na1B—Na1A—N3A ⁱⁱ	59.43 (6)	O1B—Na1B—N2A—Na1A	-132.69 (5)
O2A—Na1B—Na1A—N3A ⁱⁱ	-124.13 (6)	N3A ⁱⁱ —Na1B—N2A—Na1A	49.92 (4)
O1B ⁱ —Na1B—Na1A—N3A ⁱⁱ	-71.40 (6)	Na1B ⁱ —Na1B—N2A—Na1A	-130.63 (6)
O1B—Na1B—Na1A—N3A ⁱⁱ	177.13 (7)	Na1A ⁱⁱ —Na1B—N2A—Na1A	109.80 (3)
N2A—Na1B—Na1A—N3A ⁱⁱ	111.79 (5)	C2B—N2B—N3B—C1B	-0.4 (2)
Na1B ⁱ —Na1B—Na1A—N3A ⁱⁱ	-128.95 (8)	O2B—Na1B—O1B—Na1B ⁱ	-93.80 (5)
Na1A ⁱⁱ —Na1B—Na1A—N3A ⁱⁱ	52.99 (4)	O2A—Na1B—O1B—Na1B ⁱ	94.83 (5)
O2B—Na1B—Na1A—Na1A ⁱⁱⁱ	178.67 (5)	O1B ⁱ —Na1B—O1B—Na1B ⁱ	0.0
O2A—Na1B—Na1A—Na1A ⁱⁱⁱ	-4.89 (6)	N2A—Na1B—O1B—Na1B ⁱ	177.88 (5)
O1B ⁱ —Na1B—Na1A—Na1A ⁱⁱⁱ	47.84 (8)	Na1A—Na1B—O1B—Na1B ⁱ	133.56 (5)
O1B—Na1B—Na1A—Na1A ⁱⁱⁱ	-63.63 (8)	Na1A ⁱⁱ —Na1B—O1B—Na1B ⁱ	-116.13 (5)
N3A ⁱⁱ —Na1B—Na1A—Na1A ⁱⁱⁱ	119.24 (6)	C2A—N2A—N3A—C1A	0.06 (19)
N2A—Na1B—Na1A—Na1A ⁱⁱⁱ	-128.97 (7)	Na1A—N2A—N3A—C1A	147.14 (11)
Na1B ⁱ —Na1B—Na1A—Na1A ⁱⁱⁱ	-9.71 (10)	Na1B—N2A—N3A—C1A	-128.88 (11)
Na1A ⁱⁱ —Na1B—Na1A—Na1A ⁱⁱⁱ	172.24 (6)	C2A—N2A—N3A—Na1B ⁱⁱ	-148.06 (11)
O2B—Na1B—Na1A—Na1B ⁱⁱ	6.43 (4)	Na1A—N2A—N3A—Na1B ⁱⁱ	-0.97 (13)
O2A—Na1B—Na1A—Na1B ⁱⁱ	-177.12 (5)	Na1B—N2A—N3A—Na1B ⁱⁱ	83.01 (11)
O1B ⁱ —Na1B—Na1A—Na1B ⁱⁱ	-124.39 (6)	C2A—N2A—N3A—Na1A ⁱⁱ	123.98 (12)
O1B—Na1B—Na1A—Na1B ⁱⁱ	124.14 (6)	Na1A—N2A—N3A—Na1A ⁱⁱ	-88.94 (9)
N3A ⁱⁱ —Na1B—Na1A—Na1B ⁱⁱ	-52.99 (4)	Na1B—N2A—N3A—Na1A ⁱⁱ	-4.96 (12)
N2A—Na1B—Na1A—Na1B ⁱⁱ	58.79 (4)	N3A—N2A—C2A—N1A	-179.29 (15)

supplementary materials

Na1B ⁱ —Na1B—Na1A—Na1B ⁱⁱ	178.06 (7)	Na1A—N2A—C2A—N1A	40.3 (2)
Na1A ⁱⁱ —Na1B—Na1A—Na1B ⁱⁱ	0.0	Na1B—N2A—C2A—N1A	-48.62 (19)
O1B ⁱ —Na1B—O2A—Na1A	-142.04 (5)	N3A—N2A—C2A—S2A	-0.11 (17)
O1B—Na1B—O2A—Na1A	136.43 (5)	Na1A—N2A—C2A—S2A	-140.52 (9)
N3A ⁱⁱ —Na1B—O2A—Na1A	-42.56 (4)	Na1B—N2A—C2A—S2A	130.56 (8)
N2A—Na1B—O2A—Na1A	39.55 (4)	C1A—S2A—C2A—N2A	0.09 (13)
Na1B ⁱ —Na1B—O2A—Na1A	177.17 (4)	C1A—S2A—C2A—N1A	179.29 (15)
Na1A ⁱⁱ —Na1B—O2A—Na1A	-4.04 (7)	N2B—N3B—C1B—S1B	-178.64 (12)
O1A—Na1A—O2A—Na1B	-138.33 (5)	N2B—N3B—C1B—S2B	1.37 (18)
O1A ⁱⁱⁱ —Na1A—O2A—Na1B	135.00 (4)	C2B—S2B—C1B—N3B	-1.48 (13)
N2A—Na1A—O2A—Na1B	-42.18 (4)	C2B—S2B—C1B—S1B	178.53 (10)
N3A ⁱⁱ —Na1A—O2A—Na1B	40.44 (4)	N3B—N2B—C2B—N1B	178.31 (16)
Na1A ⁱⁱⁱ —Na1A—O2A—Na1B	176.79 (4)	N3B—N2B—C2B—S2B	-0.78 (19)
Na1B ⁱⁱ —Na1A—O2A—Na1B	4.35 (7)	C1B—S2B—C2B—N2B	1.26 (13)
O2B ⁱⁱ —Na1A—O1A—Na1A ⁱⁱⁱ	87.19 (5)	C1B—S2B—C2B—N1B	-177.82 (16)
O2A—Na1A—O1A—Na1A ⁱⁱⁱ	-90.55 (5)	N2A—N3A—C1A—S1A	-178.68 (11)
O1A ⁱⁱⁱ —Na1A—O1A—Na1A ⁱⁱⁱ	0.0	Na1B ⁱⁱ —N3A—C1A—S1A	-27.64 (17)
N2A—Na1A—O1A—Na1A ⁱⁱⁱ	-176.56 (5)	Na1A ⁱⁱ —N3A—C1A—S1A	52.46 (15)
Na1B—Na1A—O1A—Na1A ⁱⁱⁱ	-126.85 (5)	N2A—N3A—C1A—S2A	0.01 (17)
Na1B ⁱⁱ —Na1A—O1A—Na1A ⁱⁱⁱ	116.75 (4)	Na1B ⁱⁱ —N3A—C1A—S2A	151.06 (7)
O1B ⁱ —Na1B—O2B—Na1A ⁱⁱ	133.46 (6)	Na1A ⁱⁱ —N3A—C1A—S2A	-128.85 (8)
O1B—Na1B—O2B—Na1A ⁱⁱ	-145.64 (5)	C2A—S2A—C1A—N3A	-0.06 (12)
N3A ⁱⁱ —Na1B—O2B—Na1A ⁱⁱ	33.73 (5)	C2A—S2A—C1A—S1A	178.72 (10)
N2A—Na1B—O2B—Na1A ⁱⁱ	-48.00 (5)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2A—H104 \cdots N3B	0.85	1.99	2.8113 (18)	161.
O1A—H102 \cdots S1B	0.87	2.39	3.2563 (14)	172.
O2B—H201 \cdots S1B ^{iv}	0.86	2.45	3.2962 (12)	169.
O2B—H202 \cdots N2B ⁱ	0.86	1.95	2.8024 (18)	170.
N1A—H1A2 \cdots S1B ^v	0.86	2.57	3.4081 (16)	165.
N1B—H1B2 \cdots S1A ^{vi}	0.86	2.43	3.2589 (17)	161.

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

Fig. 1

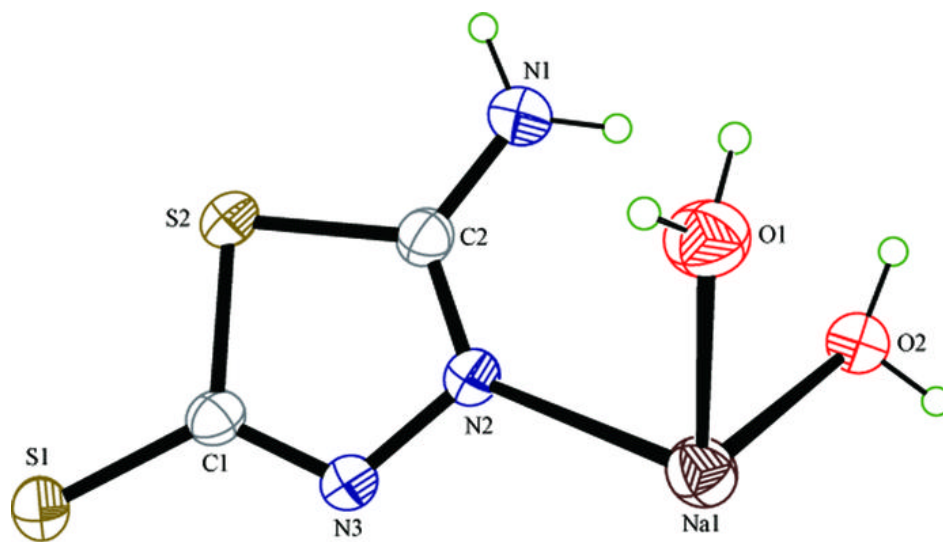


Fig. 2

