research communications

Synthesis and crystal structure of catena-poly[[[aqua{2-[(E)-(1-cyano-2-imino-2-methoxyethylidene)hydrazinyl]benzenesulfonato}sodium]-di-μ-aqua] dihydrate]

Vusala A. Aliyeva,[a] Fargana S. Aliyeva,[b] Mehmet Akkurt,[c] Sema Öztürk Yıldırım[d,c] and Ajaya Bhattarai[e]*

[a]Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal, [b]Excellence Center, Baku State University, Z. Xalilov Str. 23, Az 1148 Baku, Azerbaijan, [c]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Türkiye, [d]Department of Physics, Faculty of Science, Eskisehir Technical University, Yunus Emre Campus, 26470 Eskisehir, Türkiye, and [e]Department of Chemistry, M.M.A.M.C. (Tribhuvan University), Biratnagar, Nepal. *Correspondence e-mail: bkajaya@yahoo.com

In the polymeric title compound, $\{[Na(C_{10}H_9N_4O_4S)(H_2O)_3]\cdot 2H_2O\}_n$, sixfold coordinated Na^+ cations are linked into a chain parallel to [010] by sharing common water molecules. Next to the four bridging water molecules, each Na^+ cation of the chain is bonded to the O atom of a terminal water molecule and an O atom of the SO_3^- group of the sulfonate anion. Classical O—H···O, O—H···N and N—H···O hydrogen bonds and additional π–π interactions connect these chains into a three-dimensional network.

1. Chemical context

Hydrazones are interesting compounds in the fields of coordination chemistry, crystal engineering, catalysis, molecular recoginition and synthetic organic chemistry (Ma et al., 2021; Mahmoudi et al., 2017a,b, 2019). Depending on the attached functional groups of the hydrazone ligands, the solubility and catalytic activities of their corresponding metal complexes can be improved (Gurbanov et al., 2022). Hydrazones have been applied as analytical reagents (Mahmudov et al., 2010), as well as building blocks in the construction of supramolecular networks, owing to their capabilities as donor and acceptor groups in hydrogen bonding (Maharramov et al., 2010; Mahmudov et al., 2011, 2012, 2013). Both resonance-assisted hydrogen or chalcogen bonds also play a crucial role in the synthesis and structural chemistry of hydrazone ligands (Gurbanov et al., 2020a,b; Mahmudov et al., 2022). Similar to other classes of N-containing ligands, hydrazones also participate in various types of intermolecular interactions (Polyanskii et al., 2019; Zubkov et al., 2018).
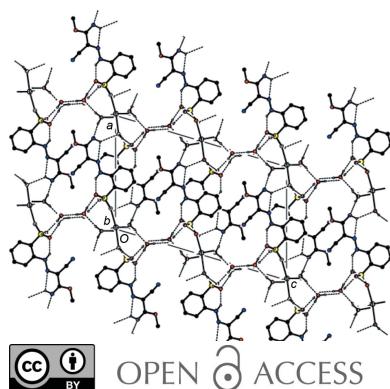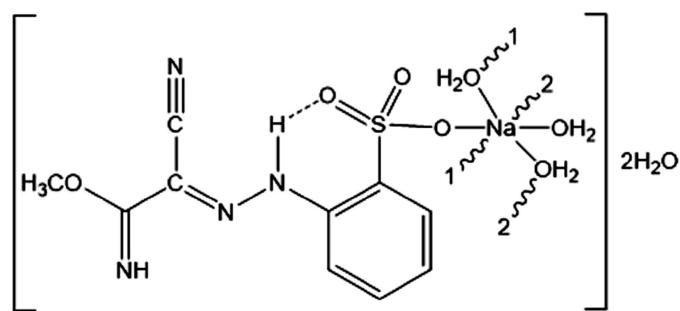
Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$A\cdots$O4[i]	0.85	1.98	2.8243 (13)	173
O5—H5$B\cdots$O6[ii]	0.85	1.92	2.7660 (13)	176
O6—H6$A\cdots$O5	0.85	1.88	2.7295 (15)	174
O6—H6$B\cdots$O3	0.85	1.98	2.8169 (13)	168
O7—H7$A\cdots$O5[iii]	0.85	2.06	2.8978 (13)	171
O7—H7$B\cdots$N4[iv]	0.85	1.98	2.8141 (14)	167
O8—H8$A\cdots$O3[v]	0.85	2.05	2.8874 (14)	168
O8—H8$B\cdots$O2[vi]	0.85	2.18	2.9689 (15)	153
O9—H9$A\cdots$O6	0.85	1.97	2.8241 (14)	178
N4—H4N$\cdots$O8[vii]	0.93	2.38	3.0905 (16)	133

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

Herein, we report the structural features of the hydrazone derivative poly[[di-μ-aqua-{2-[(E)-(1-cyano-2-imino-2-methoxy-ethylidene)hydrazinyl]benzenesulfonato}sodium] dihydrate].

2. Structural commentary

The Na$^+$ cation exhibits a six-coordination by O atoms in the form of a distorted octahedron. Four water molecules (O7, O9 and their symmetry-related counterparts) bridge adjacent cations into a chain extending parallel to [010] (Fig. 1). The coordination sphere is completed by the O atoms of another water molecule (O8), now bonded terminally, and an O atom from the SO$_3^-$ group (O2). The sulfonate anion shows no atypical features.

3. Supramolecular features

Classical O—H$\cdots$O, O—H$\cdots$N and N—H$\cdots$O hydrogen bonds of medium strength (Table 1) form a three-dimensional network (Figs. 2 and 3). Furthermore, the molecules are linked by π–π stacking interactions between the benzene rings [$Cg1\cdots Cg1(-x + 1, -y + 1, -z + 1) = 3.7588$ (8) Å and slip-
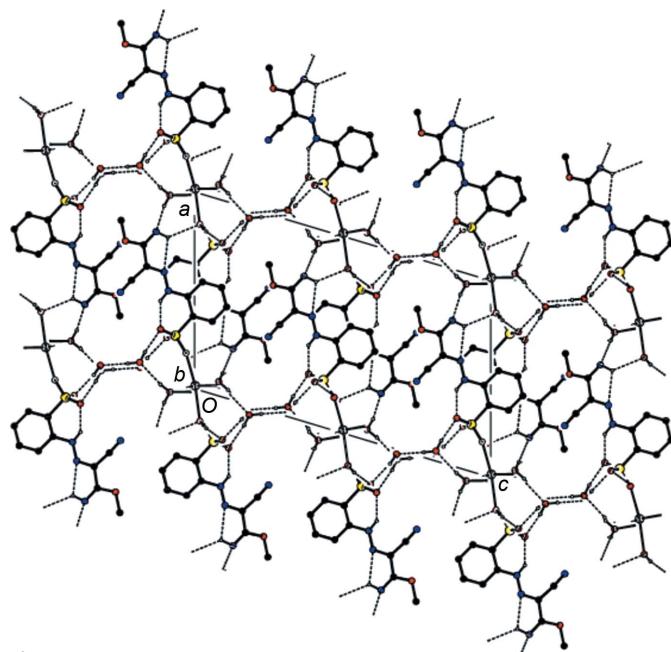
Figure 2
View of the crystal structure along [010], with O—H$\cdots$O, O—H$\cdots$N and N—H$\cdots$O hydrogen bonds shown as dashed lines.

page = 1.684 Å, where $Cg1$ is the centroid of the C1–C6 ring] parallel to [010] (Fig. 4).

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.42, September 2021 update; Groom et al., 2016) for related benzenesulfonates with a monovalent cation gave two matches. In catena-[bis(μ_4-3-carboxy-4-hydroxybenzenesul-fonato)triaquadisilver(I) monohydrate] (CSD refcode FETHES; Gao et al., 2005), both substituted benzenesulfonate anions use two of their sulfonyl O atoms to link to three Ag$^+$
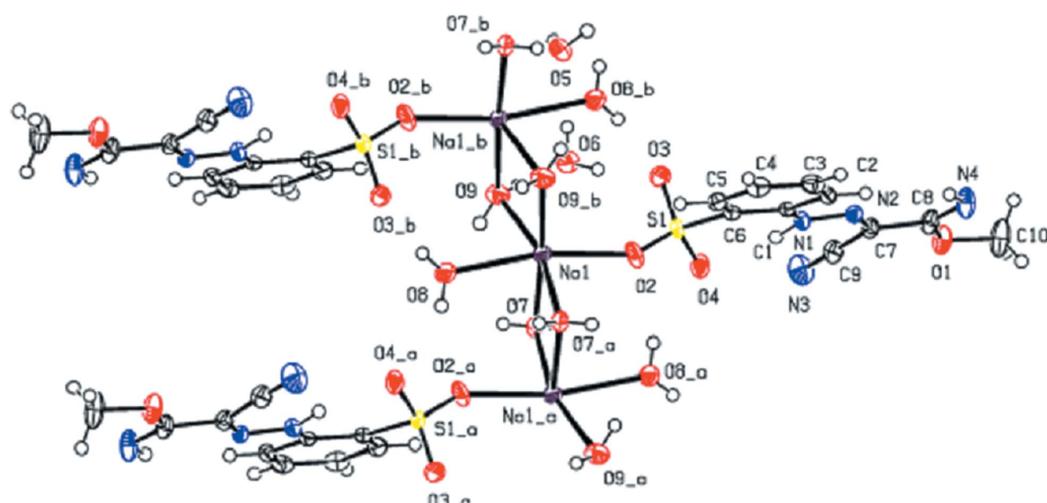
Figure 1
The coordination environment of the Na$^+$ cations in the title compound, leading to the formation of a chain extending parallel to [010]. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (a) $-x, -y, -z + 1$; (b) $-x, -y + 1, -z + 1$.]
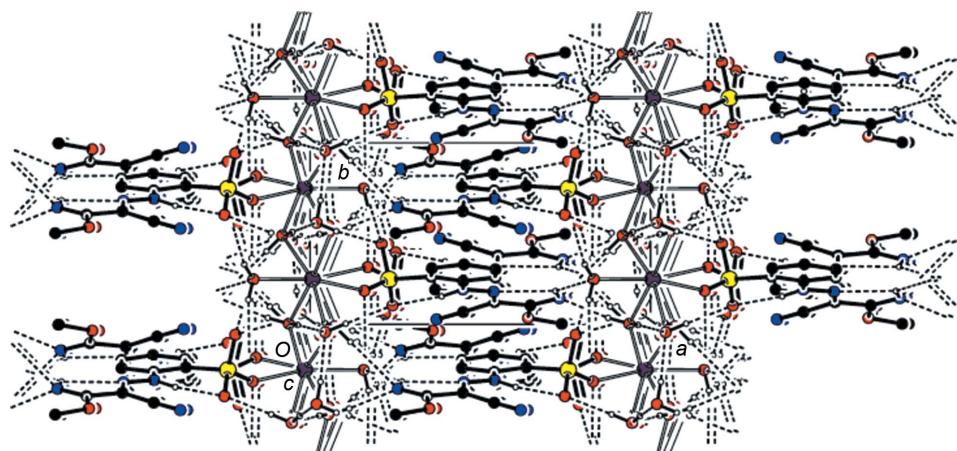
Figure 3
View of the crystal structure along [001]; the hydrogen bonds are as in Fig. 2.

cations and their carbonyl O atom to another Ag$^+$ cation in a μ_4-binding mode. The two symmetry-independent Ag$^+$ cations are additionally coordinated by water molecules, one by one water molecule and the other by two water molecules, so that one Ag$^+$ cation is five- and the other six-coordinate. In *catena*-[μ_5-(3-carboxy-4-hydroxybenzenesulfonate)(μ_2-aqua)rubidium] (FAXGAN; Hu *et al.*, 2005), the 3-carboxy-4-hydroxyben-zenesulfonate anion retains the usual intermolecular hydrogen bond between the phenol and carboxyl O atoms. The Rb$^+$ cation is surrounded by eight O atoms, and the crystal packing is stabilized by intermolecular O—H⋯O hydrogen bonds.

5. Synthesis and crystallization

344 mg (1 mmol) of sodium 2-[2-(dicyanomethylene)hydra-zinyl]benzenesulfonate tetrahydrate (Kopylovich *et al.*, 2013) were dissolved in 60 ml of methanol and refluxed for 6 h. The reaction mixture was kept in air at room temperature for slow evaporation. After *ca* 2–3 d, yellow crystals of the title compound, suitable for X-ray analysis, had formed (yield

84%). The crystals were soluble in DMSO, ethanol and di-methylformamide and insoluble in nonpolar solvents. Elemental analysis (%) for C$_{10}$H$_{19}$N$_4$NaO$_9$S: C 30.41 (calc. 30.46), H 4.83 (4.86), N 14.16 (14.21); IR (KBr): 3390 ν(OH), 2995 and 2867 ν(NH), 1653 ν(C=N) cm^{-1}. ^{1}H NMR in DMSO, internal TMS: δ (ppm) 3.44 (3H, OCH$_3$), 7.16–8.11 (4H, Ar—H), 10.19 (1H, NH), 14.11 (s, 1H, N—H). ^{13}C NMR in DMSO, internal TMS: δ (ppm) 58.2 (OCH$_3$), 111.5 (C=N), 112.3 (C=N), 123.6 (ArC—H), 121.7 (ArC—SO$_3$Na), 122.2 (ArC—H), 126.8 (ArC—H), 129.1 (ArC—H), 142.5 (ArC—NH) and 160.0 (C=NH).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically (C—H = 0.95 and 0.98 Å) and refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). O- and N-bound H atoms were located from difference Fourier maps and refined with U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(O), with their
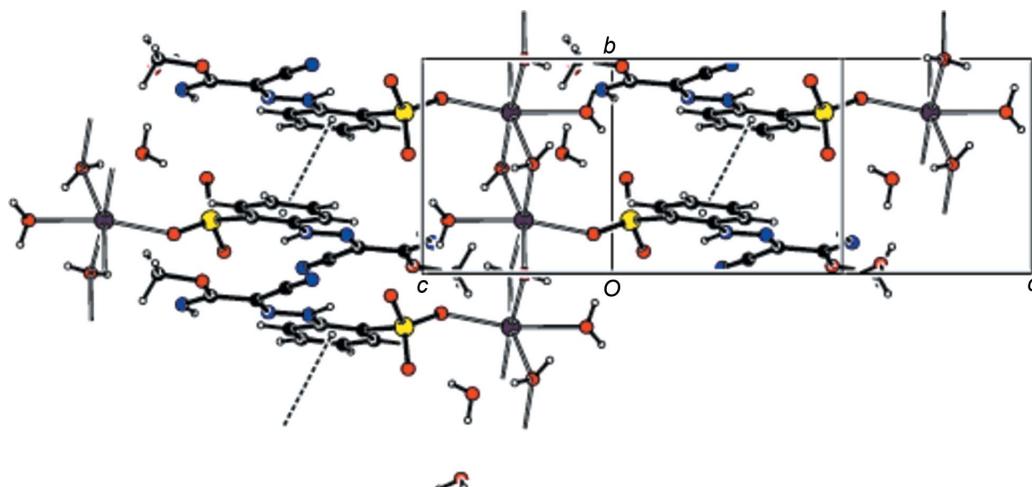

Figure 4
The π–π stacking interactions in the title compound shown with dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Na(C_{10}H_9N_4O_4S)(H_2O)_3]\cdot 2H_2O$
M_r	394.34
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	13.3305 (5), 6.8212 (3), 20.9547 (8)
β (°)	106.681 (1)
V (Å^3)	1825.23 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	$0.27 \times 0.21 \times 0.10$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.926, 0.967
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27710, 3748, 3389
R_{int}	0.021
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.081, 1.07
No. of reflections	3748
No. of parameters	227
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS* (Sheldrick, 2008), *SHELXL2019* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

positions fixed at distances of N—H = 0.93 Å and O—H = 0.85 Å.

References

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gao, S., Zhu, Z.-B., Huo, L.-H. & Ng, S. W. (2005). *Acta Cryst.* E**61**, m279–m281.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Gurbanov, A. V., Kuznetsov, M. L., Demukhamedova, S. D., Alieva, I. N., Godjaev, N. M., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2020*a*). *CrystEngComm*, **22**, 628–633.

Gurbanov, A. V., Kuznetsov, M. L., Karmakar, A., Aliyeva, V. A., Mahmudov, K. T. & Pombeiro, A. J. L. (2022). *Dalton Trans.* **51**, 1019–1031.

Gurbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pombeiro, A. J. L. & Resnati, G. (2020*b*). *Chem. Eur. J.* **26**, 14833–14837.

Hu, M., Du, Y., Li, S., Jiang, Y., Liu, Z. & Geng, C. (2005). *Acta Cryst.* E**61**, m15–m17.

Kopylovich, M. N., Mizar, A., Guedes da Silva, M. F. C., Mac Leod, T. C. O., Mahmudov, K. T. & Pombeiro, A. J. L. (2013). *Chem. Eur. J.* **19**, 588–600.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Ma, Z., Mahmudov, K. T., Aliyeva, V. A., Gurbanov, A. V., Guedes da Silva, M. F. C. & Pombeiro, A. J. L. (2021). *Coord. Chem. Rev.* **437**, 213859.

Maharramov, A. M., Aliyeva, R. A., Aliyev, I. A., Pashaev, F. G., Gasanov, A. G., Azimova, S. I., Askerov, R. K., Kurbanov, A. V. & Mahmudov, K. T. (2010). *Dyes Pigments*, **85**, 1–6.

Mahmoudi, G., Dey, L., Chowdhury, H., Bauzá, A., Ghosh, B. K., Kirillov, A. M., Seth, S. K., Gurbanov, A. V. & Frontera, A. (2017*a*). *Inorg. Chim. Acta*, **461**, 192–205.

Mahmoudi, G., Khandar, A. A., Afkhami, F. A., Miroslaw, B., Gurbanov, A. V., Zubkov, F. I., Kennedy, A., Franconetti, A. & Frontera, A. (2019). *CrystEngComm*, **21**, 108–117.

Mahmoudi, G., Zaręba, J. K., Gurbanov, A. V., Bauzá, A., Zubkov, F. I., Kubicki, M., Stilinović, V., Kinzhybalo, V. & Frontera, A. (2017*b*). *Eur. J. Inorg. Chem.* **2017**, 4763–4772.

Mahmudov, K. T., Guedes da Silva, M. F. C., Glucini, M., Renzi, M., Gabriel, K. C. P., Kopylovich, M. N., Sutradhar, M., Marchetti, F., Pettinari, C., Zamponi, S. & Pombeiro, A. J. L. (2012). *Inorg. Chem. Commun.* **22**, 187–189.

Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Guedes da Silva, M. F. C., Resnati, G. & Pombeiro, A. J. L. (2022). *Coord. Chem. Rev.* **464**, 214556.

Mahmudov, K. T., Kopylovich, M. N. & Pombeiro, A. J. L. (2013). *Coord. Chem. Rev.* **257**, 1244–1281.

Mahmudov, K. T., Maharramov, A. M., Aliyeva, R. A., Aliyev, I. A., Askerov, R. K., Batmaz, R., Kopylovich, M. N. & Pombeiro, A. J. L. (2011). *J. Photochem. Photobiol. Chem.* **219**, 159–165.

Mahmudov, K. T., Maharramov, A. M., Aliyeva, R. A., Aliyev, I. A., Kopylovich, M. N. & Pombeiro, A. J. L. (2010). *Anal. Lett.* **43**, 2923–2938.

Polyanskii, K. B., Alekseeva, K. A., Raspertov, P. V., Kumandin, P. A., Nikitina, E. V., Gurbanov, A. V. & Zubkov, F. I. (2019). *Beilstein J. Org. Chem.* **15**, 769–779.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Zubkov, F. I., Mertsalov, D. F., Zaytsev, V. P., Varlamov, A. V., Gurbanov, A. V., Dorovatovskii, P. V., Timofeeva, T. V., Khrustalev, V. N. & Mahmudov, K. T. (2018). *J. Mol. Liq.* **249**, 949–952.

Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

supporting information

Synthesis and crystal structure of *catena*-poly[[[aqua{2-[(*E*)-(1-cyano-2-imino-2-methoxyethylidene)hydrazinyl]benzenesulfonato}sodium]-di-*μ*-aqua] dihydrate]

Vusala A. Aliyeva, Fargana S. Aliyeva, Mehmet Akkurt, Sema Öztürk Yıldırım and Ajaya Bhattarai

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2019* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

catena-**Poly**[[[aqua{2-[(*E*)-(1-cyano-2-imino-2-methoxyethylidene)hydrazinyl]benzenesulfonato}sodium]-di-*μ*-aqua] dihydrate]

Crystal data

[Na(C$_{10}$H$_9$N$_4$O$_4$S)(H$_2$O)$_3$]·2H$_2$O	$F(000) = 824$
$M_r = 394.34$	$D_x = 1.435$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.3305\,(5)$ Å	Cell parameters from 9914 reflections
$b = 6.8212\,(3)$ Å	$\theta = 3.2$–26.5°
$c = 20.9547\,(8)$ Å	$\mu = 0.25$ mm^{-1}
$\beta = 106.681\,(1)°$	$T = 150$ K
$V = 1825.23\,(13)$ Å^3	Needle, yellow
$Z = 4$	$0.27 \times 0.21 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer	3748 independent reflections
	3389 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)	$\theta_{max} = 26.5°$, $\theta_{min} = 2.2°$
	$h = -16 \rightarrow 16$
$T_{min} = 0.926$, $T_{max} = 0.967$	$k = -8 \rightarrow 7$
27710 measured reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.081$	
$S = 1.07$	Hydrogen site location: mixed
3748 reflections	H-atom parameters constrained
227 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.8377P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$ $\Delta\rho_{min} = -0.36$ e Å^{-3}

$\Delta\rho_{max} = 0.35$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Na1	0.01633 (4)	0.24885 (7)	0.50226 (3)	0.02094 (13)
S1	0.24044 (2)	0.24765 (4)	0.43523 (2)	0.01763 (9)
O1	0.64543 (8)	0.03548 (17)	0.26660 (5)	0.0316 (2)
O2	0.16843 (7)	0.18478 (17)	0.47128 (5)	0.0312 (2)
O3	0.21772 (7)	0.44290 (14)	0.40648 (5)	0.0250 (2)
O4	0.24943 (7)	0.10353 (15)	0.38547 (5)	0.0292 (2)
O5	0.05048 (7)	0.95638 (15)	0.31489 (4)	0.0259 (2)
H5A	0.111073	1.003570	0.332701	0.039*
H5B	0.026423	0.994300	0.274741	0.039*
O6	0.02512 (8)	0.55977 (15)	0.31795 (5)	0.0278 (2)
H6A	0.036537	0.682516	0.319429	0.042*
H6B	0.083707	0.512606	0.340269	0.042*
O7	−0.05415 (7)	0.00275 (14)	0.41756 (4)	0.0214 (2)
H7A	−0.029422	−0.003553	0.384492	0.032*
H7B	−0.116822	0.035287	0.397482	0.032*
O8	−0.15677 (8)	0.24814 (14)	0.51810 (5)	0.0267 (2)
H8A	−0.183026	0.329914	0.539397	0.040*
H8B	−0.170926	0.135404	0.530527	0.040*
O9	−0.07335 (8)	0.48983 (15)	0.41848 (5)	0.0292 (2)
H9A	−0.044937	0.508569	0.387489	0.044*
H9B	−0.120247	0.402548	0.405278	0.044*
N1	0.45695 (8)	0.19223 (16)	0.41179 (5)	0.0173 (2)
H1N	0.394133	0.153936	0.384683	0.021*
N2	0.54648 (8)	0.17969 (16)	0.39713 (5)	0.0184 (2)
N3	0.37653 (11)	0.0270 (2)	0.24994 (7)	0.0407 (3)
N4	0.73936 (9)	0.1439 (2)	0.37031 (6)	0.0331 (3)
H4N	0.728594	0.183478	0.410070	0.040*
C1	0.45890 (9)	0.23787 (17)	0.47751 (6)	0.0160 (2)
C2	0.55436 (10)	0.25797 (18)	0.52682 (7)	0.0203 (3)
H2	0.618229	0.240330	0.515954	0.024*
C3	0.55603 (11)	0.3035 (2)	0.59141 (6)	0.0243 (3)
H3	0.621321	0.316534	0.624649	0.029*
C4	0.46382 (11)	0.3304 (2)	0.60838 (6)	0.0254 (3)
H4	0.465840	0.363154	0.652795	0.030*
C5	0.36862 (10)	0.30915 (19)	0.55994 (6)	0.0220 (3)
H5	0.305188	0.326402	0.571371	0.026*

C6	0.36531 (9)	0.26271 (17)	0.49470 (6)	0.0167 (2)
C7	0.54846 (10)	0.12221 (19)	0.33855 (6)	0.0206 (3)
C8	0.65335 (10)	0.1044 (2)	0.32786 (6)	0.0254 (3)
C9	0.45515 (11)	0.0676 (2)	0.28728 (6)	0.0253 (3)
C10	0.74403 (13)	0.0023 (3)	0.25222 (8)	0.0457 (5)
H10C	0.730573	−0.048535	0.206797	0.069*
H10D	0.785594	−0.093168	0.283906	0.069*
H10E	0.782662	0.126071	0.256239	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0226 (3)	0.0185 (3)	0.0246 (3)	0.00087 (19)	0.0112 (2)	0.00084 (19)
S1	0.01257 (15)	0.01943 (17)	0.02187 (16)	−0.00042 (10)	0.00653 (12)	0.00011 (11)
O1	0.0268 (5)	0.0499 (7)	0.0209 (5)	0.0097 (5)	0.0111 (4)	−0.0017 (4)
O2	0.0193 (5)	0.0428 (6)	0.0354 (5)	−0.0046 (4)	0.0140 (4)	0.0061 (5)
O3	0.0219 (4)	0.0237 (5)	0.0267 (5)	0.0024 (4)	0.0027 (4)	0.0043 (4)
O4	0.0163 (4)	0.0326 (5)	0.0361 (5)	−0.0006 (4)	0.0034 (4)	−0.0151 (4)
O5	0.0229 (4)	0.0335 (5)	0.0192 (4)	−0.0052 (4)	0.0025 (4)	0.0012 (4)
O6	0.0286 (5)	0.0276 (5)	0.0229 (5)	0.0014 (4)	0.0007 (4)	0.0009 (4)
O7	0.0172 (4)	0.0256 (5)	0.0218 (4)	0.0030 (3)	0.0063 (3)	0.0015 (4)
O8	0.0287 (5)	0.0237 (5)	0.0316 (5)	0.0012 (4)	0.0147 (4)	−0.0001 (4)
O9	0.0352 (5)	0.0240 (5)	0.0305 (5)	−0.0043 (4)	0.0126 (4)	0.0006 (4)
N1	0.0139 (5)	0.0202 (5)	0.0183 (5)	−0.0010 (4)	0.0052 (4)	−0.0009 (4)
N2	0.0170 (5)	0.0173 (5)	0.0226 (5)	0.0020 (4)	0.0085 (4)	0.0034 (4)
N3	0.0338 (7)	0.0553 (9)	0.0308 (7)	−0.0053 (6)	0.0059 (6)	−0.0077 (6)
N4	0.0215 (6)	0.0581 (9)	0.0214 (5)	0.0079 (6)	0.0088 (5)	0.0006 (6)
C1	0.0175 (6)	0.0125 (5)	0.0180 (6)	−0.0012 (4)	0.0053 (5)	0.0013 (4)
C2	0.0172 (6)	0.0191 (6)	0.0233 (6)	−0.0015 (4)	0.0038 (5)	0.0011 (5)
C3	0.0259 (6)	0.0215 (6)	0.0211 (6)	−0.0039 (5)	−0.0005 (5)	0.0009 (5)
C4	0.0372 (7)	0.0224 (7)	0.0165 (6)	−0.0018 (6)	0.0076 (5)	−0.0009 (5)
C5	0.0270 (6)	0.0195 (6)	0.0230 (6)	0.0003 (5)	0.0125 (5)	0.0008 (5)
C6	0.0169 (6)	0.0141 (6)	0.0194 (6)	−0.0003 (4)	0.0059 (5)	0.0014 (4)
C7	0.0208 (6)	0.0220 (6)	0.0202 (6)	0.0030 (5)	0.0079 (5)	0.0028 (5)
C8	0.0237 (6)	0.0334 (7)	0.0220 (6)	0.0083 (5)	0.0111 (5)	0.0053 (5)
C9	0.0275 (7)	0.0299 (7)	0.0214 (6)	0.0019 (6)	0.0118 (5)	−0.0008 (5)
C10	0.0317 (8)	0.0826 (14)	0.0273 (7)	0.0189 (8)	0.0155 (6)	−0.0014 (8)

Geometric parameters (Å, º)

Na1—O2	2.3407 (11)	O9—H9B	0.8500
Na1—O7[i]	2.3530 (10)	N1—N2	1.3178 (14)
Na1—O9[ii]	2.4061 (11)	N1—C1	1.4049 (15)
Na1—O8	2.4237 (11)	N1—H1N	0.9050
Na1—O7	2.4276 (10)	N2—C7	1.2961 (16)
Na1—O9	2.4511 (11)	N3—C9	1.1474 (19)
Na1—Na1[i]	3.4206 (10)	N4—C8	1.2621 (18)
Na1—Na1[ii]	3.4517 (10)	N4—H4N	0.9254

Na1—H9B	2.5336	C1—C2	1.3967 (17)
S1—O2	1.4466 (9)	C1—C6	1.4045 (17)
S1—O3	1.4572 (10)	C2—C3	1.3826 (19)
S1—O4	1.4627 (10)	C2—H2	0.9500
S1—C6	1.7730 (13)	C3—C4	1.386 (2)
O1—C8	1.3424 (16)	C3—H3	0.9500
O1—C10	1.4482 (17)	C4—C5	1.3864 (19)
O5—H5A	0.8498	C4—H4	0.9500
O5—H5B	0.8501	C5—C6	1.3916 (18)
O6—H6A	0.8500	C5—H5	0.9500
O6—H6B	0.8500	C7—C9	1.4398 (18)
O7—H7A	0.8496	C7—C8	1.4832 (17)
O7—H7B	0.8500	C10—H10C	0.9800
O8—H8A	0.8500	C10—H10D	0.9800
O8—H8B	0.8503	C10—H10E	0.9800
O9—H9A	0.8501		

O2—Na1—O7ⁱ	92.10 (4)	Na1ⁱ—O7—H7B	121.5
O2—Na1—O9ⁱⁱ	101.69 (4)	Na1—O7—H7B	107.5
O7ⁱ—Na1—O9ⁱⁱ	94.98 (4)	H7A—O7—H7B	99.5
O2—Na1—O8	166.44 (4)	Na1—O8—H8A	128.5
O7ⁱ—Na1—O8	85.30 (3)	Na1—O8—H8B	110.3
O9ⁱⁱ—Na1—O8	91.80 (4)	H8A—O8—H8B	105.8
O2—Na1—O7	81.51 (4)	Na1ⁱⁱ—O9—Na1	90.57 (4)
O7ⁱ—Na1—O7	88.64 (3)	Na1ⁱⁱ—O9—H9A	107.1
O9ⁱⁱ—Na1—O7	175.04 (4)	Na1—O9—H9A	114.5
O8—Na1—O7	85.12 (3)	Na1ⁱⁱ—O9—H9B	143.2
O2—Na1—O9	102.11 (4)	Na1—O9—H9B	85.7
O7ⁱ—Na1—O9	163.96 (4)	H9A—O9—H9B	107.7
O9ⁱⁱ—Na1—O9	89.43 (4)	N2—N1—C1	118.67 (10)
O8—Na1—O9	79.14 (4)	N2—N1—H1N	124.9
O7—Na1—O9	86.18 (4)	C1—N1—H1N	115.6
O2—Na1—Na1ⁱ	85.44 (3)	C7—N2—N1	120.42 (11)
O7ⁱ—Na1—Na1ⁱ	45.20 (3)	C8—N4—H4N	110.6
O9ⁱⁱ—Na1—Na1ⁱ	140.07 (4)	C2—C1—C6	119.09 (11)
O8—Na1—Na1ⁱ	83.29 (3)	C2—C1—N1	120.22 (11)
O7—Na1—Na1ⁱ	43.45 (2)	C6—C1—N1	120.68 (11)
O9—Na1—Na1ⁱ	127.86 (4)	C3—C2—C1	120.10 (12)
O2—Na1—Na1ⁱⁱ	106.87 (4)	C3—C2—H2	120.0
O7ⁱ—Na1—Na1ⁱⁱ	137.99 (4)	C1—C2—H2	120.0
O9ⁱⁱ—Na1—Na1ⁱⁱ	45.24 (3)	C2—C3—C4	120.96 (12)
O8—Na1—Na1ⁱⁱ	83.58 (3)	C2—C3—H3	119.5
O7—Na1—Na1ⁱⁱ	130.32 (3)	C4—C3—H3	119.5
O9—Na1—Na1ⁱⁱ	44.19 (3)	C3—C4—C5	119.41 (12)
Na1ⁱ—Na1—Na1ⁱⁱ	166.02 (3)	C3—C4—H4	120.3
O2—Na1—H9B	109.6	C5—C4—H4	120.3
O7ⁱ—Na1—H9B	146.3	C4—C5—C6	120.48 (12)
O9ⁱⁱ—Na1—H9B	105.0	C4—C5—H5	119.8

O8—Na1—H9B	67.5	C6—C5—H5	119.8
O7—Na1—H9B	70.2	C5—C6—C1	119.95 (11)
O9—Na1—H9B	19.5	C5—C6—S1	117.54 (10)
Na1ⁱ—Na1—H9B	109.4	C1—C6—S1	122.45 (9)
Na1ⁱⁱ—Na1—H9B	60.7	N2—C7—C9	122.47 (11)
O2—S1—O3	113.36 (6)	N2—C7—C8	116.37 (11)
O2—S1—O4	112.05 (6)	C9—C7—C8	121.07 (11)
O3—S1—O4	111.68 (6)	N4—C8—O1	123.70 (12)
O2—S1—C6	106.26 (6)	N4—C8—C7	125.53 (12)
O3—S1—C6	106.22 (5)	O1—C8—C7	110.75 (11)
O4—S1—C6	106.71 (5)	N3—C9—C7	174.65 (14)
C8—O1—C10	115.26 (11)	O1—C10—H10C	109.5
S1—O2—Na1	147.89 (7)	O1—C10—H10D	109.5
H5A—O5—H5B	111.1	H10C—C10—H10D	109.5
H6A—O6—H6B	103.1	O1—C10—H10E	109.5
Na1ⁱ—O7—Na1	91.36 (3)	H10C—C10—H10E	109.5
Na1ⁱ—O7—H7A	119.5	H10D—C10—H10E	109.5
Na1—O7—H7A	118.2		
O3—S1—O2—Na1	5.69 (15)	N1—C1—C6—S1	−2.39 (16)
O4—S1—O2—Na1	−121.84 (12)	O2—S1—C6—C5	−30.12 (12)
C6—S1—O2—Na1	121.98 (12)	O3—S1—C6—C5	90.88 (10)
C1—N1—N2—C7	174.30 (11)	O4—S1—C6—C5	−149.84 (10)
N2—N1—C1—C2	−3.68 (17)	O2—S1—C6—C1	152.62 (10)
N2—N1—C1—C6	176.71 (11)	O3—S1—C6—C1	−86.38 (11)
C6—C1—C2—C3	−0.59 (18)	O4—S1—C6—C1	32.90 (12)
N1—C1—C2—C3	179.80 (11)	N1—N2—C7—C9	−0.71 (19)
C1—C2—C3—C4	−0.2 (2)	N1—N2—C7—C8	−177.34 (11)
C2—C3—C4—C5	0.7 (2)	C10—O1—C8—N4	1.9 (2)
C3—C4—C5—C6	−0.5 (2)	C10—O1—C8—C7	−176.78 (13)
C4—C5—C6—C1	−0.26 (19)	N2—C7—C8—N4	−1.5 (2)
C4—C5—C6—S1	−177.60 (10)	C9—C7—C8—N4	−178.15 (15)
C2—C1—C6—C5	0.81 (17)	N2—C7—C8—O1	177.19 (12)
N1—C1—C6—C5	−179.58 (11)	C9—C7—C8—O1	0.51 (18)
C2—C1—C6—S1	178.00 (9)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O4ⁱⁱⁱ	0.85	1.98	2.8243 (13)	173
O5—H5*B*···O6ⁱᵛ	0.85	1.92	2.7660 (13)	176
O6—H6*A*···O5	0.85	1.88	2.7295 (15)	174
O6—H6*B*···O3	0.85	1.98	2.8169 (13)	168
O7—H7*A*···O5ᵛ	0.85	2.06	2.8978 (13)	171
O7—H7*B*···N4ᵛⁱ	0.85	1.98	2.8141 (14)	167
O8—H8*A*···O3ⁱⁱ	0.85	2.05	2.8874 (14)	168

O8—H8*B*···O2^i	0.85	2.18	2.9689 (15)	153
O9—H9*A*···O6	0.85	1.97	2.8241 (14)	178
N4—H4*N*···O8^{vii}	0.93	2.38	3.0905 (16)	133

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