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Crystal structure of poly[(acetonitrile-κN)(μ_3-7-{[bis(pyridin-2-ylmethyl)amino]methyl}-8-hydroxyquinoline-5-sulfonato-$\kappa^4 N,O:O':O''$)sodium]

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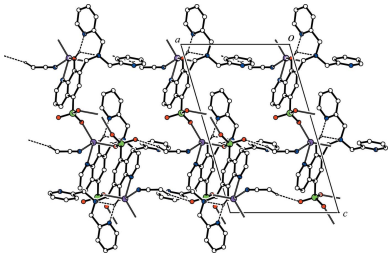
In the title compound, $[Na(C_{22}H_{19}N_4O_4S)(CH_3CN)]_n$, the Na^I atom adopts a distorted square-pyramidal coordination geometry, formed by one N and one O atom of the qunolinol moiety in the ligand, two O atoms of sulfonate moieties of two adjacent ligands and the N atom of the coordinated acetonitrile solvent. The Na^I atom is located well above the mean basal plane of the square-based pyramid. The apical position is occupied by a sulfonate O atom of a neighboring ligand. Three N atoms of the bis(pyridin-2-ylmethyl)amine moiety in the ligand are not coordinated by the sodium atom. The molecule forms an intramolecular bifurcated O—H···[N(tertiary amine),N(pyridine)] hydrogen bond, generating $S(6)$ and $S(5)$ rings. In the crystal, four molecules are linked by four Na—O(sulfonato) bridged coordination bonds, forming a supramolecular centrosymmetric tetramer unit comprising an eight-membered ring, and generating a two-dimensional network sheet. The molecules of different sheets form intermolecular C—H···O hydrogen bonds, and thereby a three-dimensional network structure.

1. Chemical context

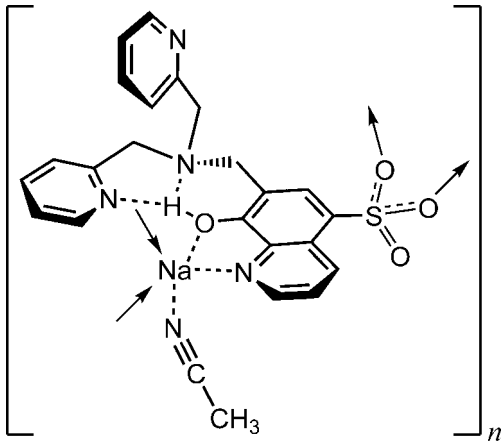
8-Quinolinol (Hq) is a well-known chelating ligand and analytical reagent (Wiberley *et al.*, 1949). Metal complexes with Hq derivatives have been investigated as pharmaceutical treatments (Mo *et al.*, 2021), magnetic materials (Ma *et al.*, 2021) and organic light-emitting diodes (Huo *et al.* 2015; Back *et al.*, 2016). As part of our research into the development of fluorescent chelate reagents for the determination of metal ions and anions, we synthesized the pentadentate ligand, 7-{[bis-(pyridin-2-ylmethyl)amino]methyl}-5-chloroquinolin-8-ol (HClqdpa) containing Hq and bis(pyridin-2-ylmethyl)amine [di-(2-picolyl)amine] (dpa) moieties (RUTSIK; Kubono *et al.*, 2015). This ligand has only rather poor water solubility. To improve the solubility, we synthesized a new and now water-soluble fluorescent chelate reagent, based on Hq containing sulfonato-sodium and dpa moieties. Herein we report the respective synthesis and the crystal structure of its acetonitrile solvate complex.



2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The Na^I atom (Na2) of the asymmetric unit adopts a distorted square-pyramidal geometry and coordinates N and

O atoms of the quinolinol moiety in the ligand, two O atoms of the sulfonate moieties of two neighboring ligands and the N atom of acetonitrile solvent. The phenolic hydrogen atom H3 of the quinolinol moiety is bound to the O3 atom. The proton, therefore, does not dissociate. Three N atoms of the dpa moiety in the ligand are not coordinated by the Na^{I} atom.



The five-coordinate geometry index, $\tau = (\beta - \alpha)/60$, derived from the two largest angles (α, β) in a structure has ideal values of 0 for square-pyramidal and of 1 for trigonal–bipyramidal geometry (Addison *et al.*, 1984). In the title compound it is equal to 0.310. The Na^{I} atom is located 0.7311 (8) Å above the mean basal plane [O3/N7/N11/O5^{iii}; symmetry code: (iii) x, $\frac{1}{2} - y$, $z - \frac{1}{2}$] of the square-based pyramid. The apical position is occupied by the O4^{i} atom of the sulfonate moiety in a neighboring ligand with the Na2—O4^{i} bond being 2.2602 (16) Å long [symmetry code: (i) $2 - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$]. The Na2—O3(quinolinol) bond distance is 2.4248 (15) Å, longer than the equatorial Na—O(sulfonato) bond [Na2—O5^{iii}; 2.2500 (16) Å]. The Na2—N7(quinolinol) distance is 2.467 (2) Å, shorter than the Na2—N11(acetonitrile) bond [2.487 (2) Å]. The chelate angle O3—Na2—N7 is 65.83 (5)°, the smallest of all the coordination angels. It agrees well with that of a related compound, (8-hydroxyquinoline-5-sulfonato-N^{1},O^{8})sodium(I) [UGUNOZ; Baskar Raj *et al.*, 2002; O—Na—N; 64.86 (4)°]. The τ-parameter of this related compound is 0.505, and indicative of a significantly distorted trigonal–bipyramidal geometry with bond distances of Na—O(quinolinol) and Na—N(quinolinol) of 2.4892 (14) and 2.4418 (15) Å, respectively.

The title molecule forms in its crystal structure an intramolecular bifurcated O3—H3···(N8, N9) hydrogen bond (Table 1), resulting in S(6) and S(5) rings, which stabilize the conformation of the molecule. The N10 atom in the pyridine ring is not engaged in a coordination bond, hydrogen bond or any other inter- or intramolecular interaction. The dihedral angle between two pyridine rings in the title compound is 88.37 (11)°. In a related compound, 7-{[bis(pyridin-2-ylmethyl)amino]methyl}-5-chloroquinolin-8-ol, HClqdpa (RUTSIK; Kubono *et al.*, 2015), the dihedral angle between two pyridine rings is 80.97 (12)°.

Even though in HClqdpa the dpa moiety is metal-free, and only one pyridine N atom forms an intramolecular hydrogen bond with the OH group, these angles are relatively similar. The quinoline ring of the title compound is slightly bent, with r.m.s. deviations of 0.020 (2) Å. The S—O bond distances are in the range 1.4469 (14)–1.4585 (15) Å, with O—S—O angles ranging from 112.87 (9) to 113.25 (9)°. The bond lengths and angles largely agree with those values in the related compound [UGUNOZ; Baskar Raj *et al.*, 2002; S—O; 1.4482 (12)–1.4731 (12) Å, O—S—O; 110.92 (7)–114.35 (7)°]. The O6 atom is not coordinated by the Na^{I} atom, and the bond distance S1—O6 is shorter than the other two.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···N8	0.88 (2)	2.46 (3)	3.057 (2)	125 (2)
O3—H3···N9	0.88 (2)	1.87 (2)	2.7120 (19)	158 (3)
C31—H31···O6^{i}	0.95	2.53	3.397 (3)	152
C35—H35A···O6^{ii}	0.98	2.55	3.502 (4)	166

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

3. Supramolecular features

In the crystal, four molecules of the title compound are linked by four bridging Na—O coordination bonds, forming a supramolecular centrosymmetric structure based on a central eight-membered ring (Na2/O4^{i}/S1^{i}/O5^{i}/Na2^{vi}/O4^{iii}/S1^{iii}/O5^{iii}) [symmetry code: (vi) $2 - x, -y, 1 - z$]. The tetrameric building block is shown in Fig. 2. A two-dimensional coordination polymer is formed by bridging coordination bonds between

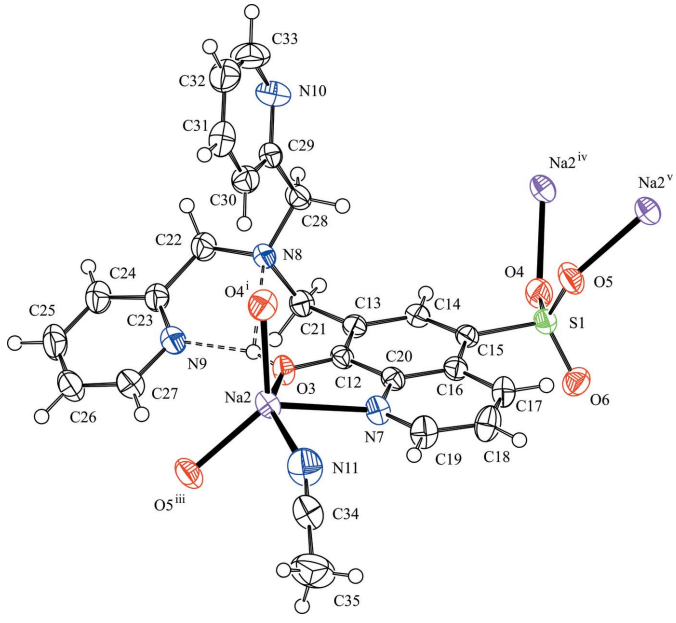


Figure 1
The molecular structure of the title compound with atom labeling. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radius. The intramolecular O—H···N hydrogen bonds are shown as double-dashed lines. [Symmetry codes: (i) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $2 - x, y + \frac{1}{2}, \frac{3}{2} - z$; (v) $x, \frac{1}{2} - y, z + \frac{1}{2}$.]

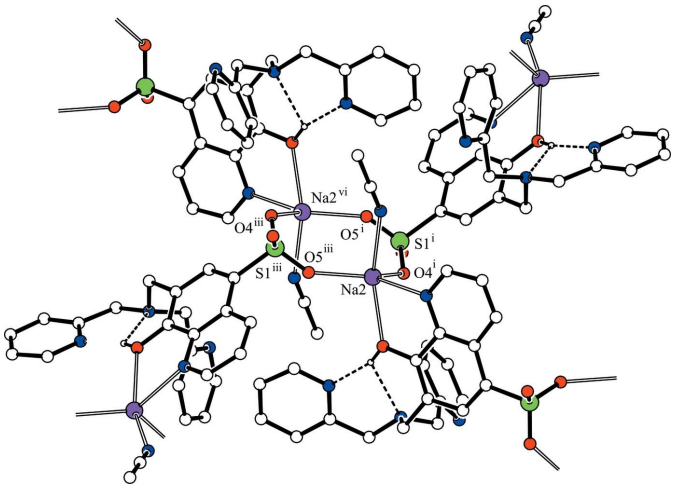


Figure 2
Supramolecular centrosymmetric tetrameric component of the crystal packing motif in the title compound formed by bridging coordination bonds. The intramolecular hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions are omitted for clarity. [Symmetry code: (i) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $2-x, -y, 1-z$.]

the Na^{I} atom and two sulfonato O atoms of two adjacent ligands (Na2—O4^{i} and Na2—O5^{iii}) in the *bc* plane (Fig. 3). An intermolecular C—H···O hydrogen bond (C31—H31···O6^{i}, Table 1) is observed, forming a *C*(12) chain motif along the *b*-axis direction. In the crystal structure, molecules are further linked by an intermolecular C—H···O hydrogen bond [C35—H35*A*···O6^{ii}; symmetry code: (ii) $3-x, y-\frac{1}{2}, \frac{3}{2}-z$] (Table 1), forming a *C*(8) chain motif running along the *a*-axis direction (Fig. 4). The molecules are linked through the bridging Na2—O4^{i} and Na2—O5^{iii} coordination bonds and the intermolecular C35—H35*A*···O6^{ii} hydrogen bonds, forming a three-dimensional network structure.

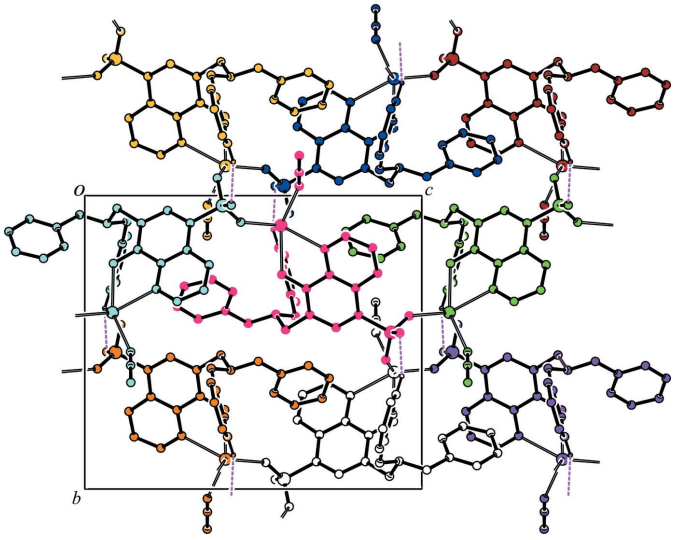


Figure 3
A projection along the *a* axis of the crystal packing of the title compound. The C—H···O hydrogen bonds are shown as dashed magenta lines. H atoms not involved in the interactions are omitted for clarity.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.44; April 2023; Groom *et al.*, 2016) using *ConQuest* (Bruno *et al.*, 2002) for the quinolin-8-ol-5-sulfonato fragment gave 78 hits. Of these, only two structures are Na^{I} complexes with the quinolin-8-ol-5-sulfonato ligand, *viz*. (8-hydroxyquinoline-5-sulfonato-N^{1},O^{8})sodium(I) (UGUNOZ; Baskar Raj *et al.*, 2002) and its trihydrate (BOXKOO; Viossat *et al.*, 1982). Both the anhydrate and trihydrate of (quinolin-8-ol-5-sulfonato)sodium form centrosymmetric dimeric structures in their crystals. Centrosymmetric dimer structures are observed in the crystals of various metal complexes with quinolin-8-ol-5-sulfonate and its derivatives. In the crystal of the anhydrous sodium complex, four Na—O(sulfonato) bridged coordination bonds construct a supramolecular centrosymmetric eight-membered ring, similar to the title complex. A search for the fragment of 7-methyl-quinolin-8-ol-5-sulfonato gave two hits, which are 8-hydroxy-7-[(morpholin-4-ium-4-yl)methyl]quinoline-5-sulfonate acetonitrile solvate (UPAYIW; Kumar *et al.*, 2021) and 8-hydroxy-7-[(piperidin-1-ium-1-yl)methyl]quinoline-5-sulfonate monohydrate (UPAYOC; Kumar *et al.*, 2021). These compounds are metal-free ligands, and the crystal structures of their sodium salts or complexes are not reported. A search for a compound fragment in which the substituent is moved to the pyridyl ring, 2-methyl-quinolin-8-ol-5-sulfonato, gave two hits, namely aqua-{2,2′-[(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diyl)-bis(methylene)]bis[8-(hydroxy)quinoline-5-sulfonato]}-barium octahydrate (BINXEE; Thiele *et al.*, 2018), and 2-methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate (MHQUSO; Merritt Jr, *et al.*, 1970).

5. Synthesis and crystallization

A suspension of paraformaldehyde (0.41 g, 14 mmol) and bis(2-pyridylmethyl)amine (1.99 g, 10 mmol) in 100 mL of MeOH was stirred for 18 h at room temperature. The solvent

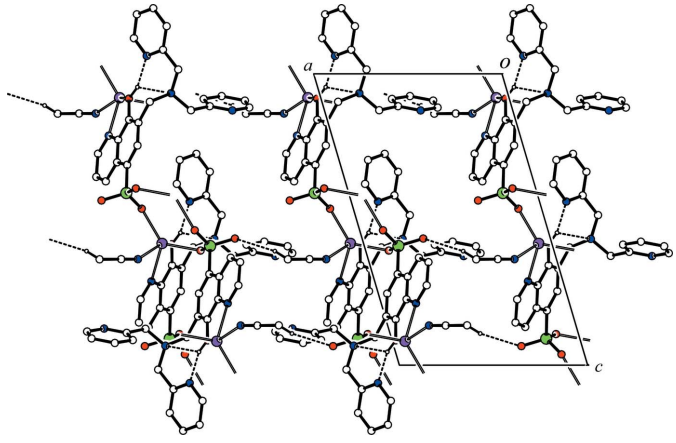


Figure 4
A projection along the *b* axis of the crystal packing of the title compound. The O—H···N and C—H···O hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions are omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Na(C_{22}H_{19}N_4O_4S)(C_2H_3N)]$
M_r	499.52
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	10.4951 (4), 14.1401 (5), 16.9249 (6)
β (°)	106.378 (8)
V (Å^3)	2409.77 (18)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.19
Crystal size (mm)	0.25 × 0.20 × 0.15
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.867, 0.971
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	23162, 5490, 4023
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.648
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.103, 1.01
No. of reflections	5490
No. of parameters	321
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.30

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SIR92* (Altomare, *et al.*, 1993), *SHELXL2014/7* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *CrystalStructure* (Rigaku, 2016).

was removed *in vacuo*. To the product was added 90 mL of methanol, 8-hydroxyquinoline-5-sulfonic acid monohydrate (1.80 g, 10 mmol) and sodium hydroxide (0.40 g, 10 mmol) in 10 mL of water, the mixture was heated for 24 h at 353 K. The solvent was removed *in vacuo* to give an oily product, which was precipitated by addition of acetone (0.72 g, 31.4%). A small amount of crude solid was recrystallized from acetonitrile to obtain colorless crystals of the title compound. ^{1}H NMR (CD_3OD, 400 MHz): δ = 2.03 (*s*, 3H, acetonitrile), 3.90 (*s*, 4H), 3.97 (*s*, 2H), 7.23–7.26 (*m*, 2H), 7.56–7.59 (*dd*, J = 8.8 Hz, J = 4.4 Hz, 1H), 7.63 (*d*, J = 8.0 Hz, 2H), 7.75–7.78 (*td*, J = 8.0 Hz, J = 1.6 Hz, 2H), 8.22 (*s*, 1H), 8.45–8.47 (*m*, 2H), 8.81–8.83 (*dd*, J = 4.4 Hz, J = 1.6 Hz, 1H), 9.10–9.15 (*dd*, J = 8.8 Hz, J = 1.6 Hz, 1H). TG: expected weight loss for acetonitrile: 8.21%; found: 8.23% (around 447 to 465 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy H atom was located in a difference-Fourier map and freely refined. All H atoms bound to carbon were positioned geometrically and refined using a riding model, with C—H = 0.95–0.99 Å and U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

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Crystal structure of poly[(acetonitrile-κN)(μ_3-7-{[bis(pyridin-2-ylmethyl)amino]-methyl}-8-hydroxyquinoline-5-sulfonato-$\kappa^4N,O:O':O''$)sodium]

Koji Kubono, Ryoichi Tanaka, Yukiyasu Kashiwagi, Keita Tani and Kunihiko Yokoi

Computing details

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO* (Rigaku, 2006); data reduction: *RAPID-AUTO* (Rigaku, 2006); program(s) used to solve structure: *SIR92* (Altomare, *et al.*, 1993); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2016).

Poly[(acetonitrile-κN)(μ_3-7-{[bis(pyridin-2-ylmethyl)amino]methyl}-8-hydroxyquinoline-5-sulfonato-$\kappa^4N,O:O':O''$)sodium]

Crystal data

$[Na(C_{22}H_{19}N_4O_4S)(C_2H_3N)]$
$M_r = 499.52$
Monoclinic, $P2_1/c$
$a = 10.4951$ (4) Å
$b = 14.1401$ (5) Å
$c = 16.9249$ (6) Å
$\beta = 106.378$ (8)°
$V = 2409.77$ (18) Å^3
$Z = 4$
$F(000) = 1040.00$
$D_x = 1.377$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 16856 reflections
$\theta = 2.1$–$27.4°$
$\mu = 0.19$ mm^{-1}
$T = 173$ K
Block, colorless
0.25 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
$T_{min} = 0.867$, $T_{max} = 0.971$
23162 measured reflections
5490 independent reflections
4023 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int} = 0.042$
$\theta_{max} = 27.4°$, $\theta_{min} = 2.5°$
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.103$
$S = 1.01$
5490 reflections
321 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 1.2511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max}$ = 0.32 e Å^{-3} $\Delta\rho_{min}$ = −0.30 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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.18114 (5)	0.46635 (3)	0.90911 (3)	0.03024 (12)
Na2	1.07043 (8)	0.10172 (5)	0.58208 (5)	0.03309 (19)
O3	1.02142 (14)	0.26904 (9)	0.58507 (8)	0.0319 (3)
O4	1.12279 (14)	0.55994 (10)	0.89339 (9)	0.0394 (3)
O5	1.12432 (16)	0.40982 (11)	0.96284 (9)	0.0444 (4)
O6	1.32483 (13)	0.46752 (10)	0.93467 (9)	0.0395 (3)
N7	1.18687 (17)	0.18141 (11)	0.71220 (10)	0.0315 (4)
N8	0.78852 (16)	0.40512 (11)	0.56663 (9)	0.0291 (3)
N9	0.85965 (17)	0.32740 (12)	0.43831 (10)	0.0363 (4)
N10	0.49005 (19)	0.36242 (14)	0.62557 (13)	0.0472 (5)
N11	1.2229 (2)	−0.03275 (15)	0.63619 (14)	0.0582 (6)
C12	1.05317 (18)	0.31647 (13)	0.65748 (11)	0.0261 (4)
C13	1.00738 (18)	0.40634 (12)	0.66745 (11)	0.0269 (4)
C14	1.04797 (18)	0.44926 (13)	0.74581 (11)	0.0272 (4)
H14	1.014363	0.510196	0.752534	0.033*
C15	1.13363 (18)	0.40683 (13)	0.81249 (11)	0.0267 (4)
C16	1.18340 (18)	0.31472 (13)	0.80365 (11)	0.0275 (4)
C17	1.2732 (2)	0.26440 (14)	0.86880 (12)	0.0349 (5)
H17	1.301928	0.291025	0.922443	0.042*
C18	1.3174 (2)	0.17810 (15)	0.85359 (13)	0.0421 (5)
H18	1.378379	0.144070	0.896296	0.051*
C19	1.2722 (2)	0.13945 (14)	0.77409 (13)	0.0388 (5)
H19	1.305452	0.079314	0.764561	0.047*
C20	1.14255 (18)	0.26954 (12)	0.72610 (11)	0.0260 (4)
C21	0.91430 (19)	0.45661 (13)	0.59585 (12)	0.0303 (4)
H21A	0.896845	0.521199	0.612841	0.036*
H21B	0.956231	0.462263	0.550483	0.036*
C22	0.7130 (2)	0.43493 (15)	0.48490 (12)	0.0364 (5)
H22A	0.716550	0.504736	0.481568	0.044*
H22B	0.618938	0.416526	0.475797	0.044*
C23	0.7636 (2)	0.39248 (14)	0.41728 (12)	0.0324 (4)
C24	0.7072 (2)	0.42029 (16)	0.33616 (13)	0.0409 (5)
H24	0.640408	0.467689	0.323134	0.049*
C25	0.7503 (2)	0.37761 (18)	0.27478 (13)	0.0487 (6)
H25	0.713422	0.395451	0.218858	0.058*

C26	0.8473 (2)	0.30886 (17)	0.29556 (14)	0.0475 (6)
H26	0.877040	0.277717	0.254261	0.057*
C27	0.9004 (2)	0.28629 (17)	0.37764 (14)	0.0437 (5)
H27	0.968416	0.239856	0.392049	0.052*
C28	0.7092 (2)	0.41116 (14)	0.62489 (12)	0.0329 (4)
H28A	0.666499	0.474147	0.619956	0.040*
H28B	0.768646	0.405127	0.681603	0.040*
C29	0.60371 (19)	0.33608 (14)	0.61095 (12)	0.0313 (4)
C30	0.6250 (2)	0.24534 (14)	0.58610 (13)	0.0375 (5)
H30	0.706913	0.229419	0.575984	0.045*
C31	0.5256 (2)	0.17819 (16)	0.57619 (13)	0.0448 (5)
H31	0.537800	0.115726	0.558990	0.054*
C32	0.4090 (2)	0.20405 (19)	0.59181 (15)	0.0523 (6)
H32	0.338984	0.159710	0.586228	0.063*
C33	0.3958 (2)	0.2952 (2)	0.61563 (18)	0.0590 (7)
H33	0.314422	0.312303	0.625879	0.071*
C34	1.3112 (3)	−0.07824 (16)	0.63605 (14)	0.0474 (6)
C35	1.4259 (3)	−0.1369 (2)	0.6367 (2)	0.0806 (10)
H35A	1.481852	−0.103827	0.608024	0.121*
H35B	1.395569	−0.196938	0.608878	0.121*
H35C	1.477330	−0.149253	0.693795	0.121*
H3	0.958 (2)	0.2949 (17)	0.5457 (16)	0.051 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0311 (2)	0.0346 (3)	0.0258 (2)	−0.0037 (2)	0.00925 (19)	−0.00541 (19)
Na2	0.0414 (4)	0.0325 (4)	0.0282 (4)	−0.0002 (3)	0.0143 (3)	−0.0019 (3)
O3	0.0414 (8)	0.0307 (7)	0.0218 (7)	0.0043 (6)	0.0058 (6)	0.0001 (5)
O4	0.0424 (8)	0.0370 (8)	0.0375 (8)	0.0038 (6)	0.0093 (7)	−0.0093 (6)
O5	0.0543 (10)	0.0549 (9)	0.0285 (8)	−0.0145 (8)	0.0190 (7)	−0.0051 (6)
O6	0.0324 (7)	0.0416 (8)	0.0412 (8)	−0.0034 (6)	0.0048 (6)	−0.0066 (7)
N7	0.0405 (9)	0.0257 (8)	0.0282 (9)	0.0011 (7)	0.0095 (7)	0.0010 (6)
N8	0.0304 (8)	0.0344 (8)	0.0232 (8)	0.0014 (7)	0.0088 (7)	0.0002 (6)
N9	0.0389 (10)	0.0418 (10)	0.0293 (9)	0.0014 (8)	0.0112 (8)	−0.0003 (7)
N10	0.0402 (10)	0.0538 (12)	0.0549 (12)	0.0031 (9)	0.0255 (9)	0.0010 (9)
N11	0.0693 (15)	0.0459 (12)	0.0577 (14)	0.0152 (11)	0.0152 (11)	−0.0014 (10)
C12	0.0290 (9)	0.0279 (9)	0.0238 (9)	−0.0044 (7)	0.0112 (8)	−0.0003 (7)
C13	0.0265 (9)	0.0287 (9)	0.0266 (9)	−0.0023 (7)	0.0093 (8)	0.0021 (7)
C14	0.0285 (9)	0.0265 (9)	0.0285 (9)	−0.0006 (7)	0.0112 (8)	−0.0006 (7)
C15	0.0264 (9)	0.0303 (9)	0.0255 (9)	−0.0039 (7)	0.0106 (8)	−0.0035 (7)
C16	0.0281 (9)	0.0298 (9)	0.0258 (9)	−0.0046 (8)	0.0096 (8)	0.0020 (7)
C17	0.0411 (12)	0.0346 (11)	0.0258 (10)	−0.0037 (9)	0.0044 (9)	0.0001 (8)
C18	0.0497 (13)	0.0323 (11)	0.0354 (12)	0.0048 (10)	−0.0026 (10)	0.0054 (9)
C19	0.0490 (13)	0.0281 (10)	0.0361 (11)	0.0064 (9)	0.0066 (10)	0.0025 (8)
C20	0.0294 (9)	0.0261 (9)	0.0249 (9)	−0.0023 (7)	0.0115 (8)	0.0019 (7)
C21	0.0337 (10)	0.0292 (10)	0.0281 (10)	−0.0002 (8)	0.0090 (8)	0.0027 (8)
C22	0.0367 (11)	0.0412 (11)	0.0295 (11)	0.0061 (9)	0.0061 (9)	0.0025 (9)

C23	0.0343 (11)	0.0340 (10)	0.0275 (10)	−0.0041 (9)	0.0065 (8)	0.0010 (8)
C24	0.0452 (12)	0.0435 (12)	0.0306 (11)	−0.0026 (10)	0.0053 (9)	0.0036 (9)
C25	0.0575 (15)	0.0606 (15)	0.0256 (11)	−0.0131 (12)	0.0079 (10)	0.0011 (10)
C26	0.0533 (14)	0.0608 (15)	0.0327 (12)	−0.0085 (12)	0.0191 (11)	−0.0100 (10)
C27	0.0448 (13)	0.0514 (13)	0.0371 (12)	−0.0003 (11)	0.0153 (10)	−0.0065 (10)
C28	0.0358 (11)	0.0349 (11)	0.0305 (10)	0.0031 (8)	0.0133 (9)	−0.0036 (8)
C29	0.0312 (10)	0.0397 (11)	0.0233 (9)	0.0025 (8)	0.0081 (8)	0.0029 (8)
C30	0.0357 (11)	0.0387 (11)	0.0372 (12)	0.0026 (9)	0.0087 (9)	−0.0010 (9)
C31	0.0507 (14)	0.0426 (12)	0.0350 (12)	−0.0069 (10)	0.0021 (10)	0.0012 (9)
C32	0.0462 (14)	0.0641 (16)	0.0454 (14)	−0.0189 (12)	0.0112 (11)	0.0054 (12)
C33	0.0385 (13)	0.0741 (19)	0.0722 (19)	−0.0056 (13)	0.0286 (13)	0.0041 (15)
C34	0.0618 (16)	0.0419 (13)	0.0405 (13)	0.0019 (12)	0.0179 (12)	0.0003 (10)
C35	0.074 (2)	0.087 (2)	0.092 (2)	0.0236 (18)	0.0406 (19)	−0.0027 (19)

Geometric parameters (Å, º)

S1—O6	1.4469 (14)	C17—H17	0.9500
S1—O4	1.4510 (15)	C18—C19	1.405 (3)
S1—O5	1.4585 (15)	C18—H18	0.9500
S1—C15	1.7808 (18)	C19—H19	0.9500
S1—Na2^{i}	3.2984 (9)	C21—H21A	0.9900
Na2—O5^{ii}	2.2500 (16)	C21—H21B	0.9900
Na2—O4^{iii}	2.2602 (16)	C22—C23	1.515 (3)
Na2—O3	2.4248 (15)	C22—H22A	0.9900
Na2—N7	2.4690 (18)	C22—H22B	0.9900
Na2—N11	2.487 (2)	C23—C24	1.390 (3)
Na2—Na2^{iv}	3.9829 (15)	C24—C25	1.383 (3)
O3—C12	1.354 (2)	C24—H24	0.9500
O3—H3	0.88 (3)	C25—C26	1.380 (3)
N7—C19	1.312 (3)	C25—H25	0.9500
N7—C20	1.373 (2)	C26—C27	1.380 (3)
N8—C22	1.449 (2)	C26—H26	0.9500
N8—C28	1.461 (2)	C27—H27	0.9500
N8—C21	1.466 (2)	C28—C29	1.504 (3)
N9—C23	1.337 (3)	C28—H28A	0.9900
N9—C27	1.350 (3)	C28—H28B	0.9900
N10—C29	1.338 (3)	C29—C30	1.388 (3)
N10—C33	1.347 (3)	C30—C31	1.386 (3)
N11—C34	1.129 (3)	C30—H30	0.9500
C12—C13	1.386 (3)	C31—C32	1.372 (3)
C12—C20	1.433 (3)	C31—H31	0.9500
C13—C14	1.411 (3)	C32—C33	1.369 (4)
C13—C21	1.504 (3)	C32—H32	0.9500
C14—C15	1.367 (3)	C33—H33	0.9500
C14—H14	0.9500	C34—C35	1.459 (4)
C15—C16	1.427 (3)	C35—H35A	0.9800
C16—C20	1.413 (3)	C35—H35B	0.9800
C16—C17	1.423 (3)	C35—H35C	0.9800

C17—C18	1.356 (3)		
O6—S1—O4	113.25 (9)	C17—C18—H18	120.3
O6—S1—O5	113.25 (9)	C19—C18—H18	120.3
O4—S1—O5	112.87 (9)	N7—C19—C18	123.96 (19)
O6—S1—C15	106.16 (9)	N7—C19—H19	118.0
O4—S1—C15	105.55 (9)	C18—C19—H19	118.0
O5—S1—C15	104.82 (9)	N7—C20—C16	122.71 (17)
O6—S1—Na2^{i}	139.46 (6)	N7—C20—C12	117.21 (16)
O4—S1—Na2^{i}	34.63 (6)	C16—C20—C12	120.07 (16)
O5—S1—Na2^{i}	79.43 (7)	N8—C21—C13	110.84 (15)
C15—S1—Na2^{i}	107.18 (6)	N8—C21—H21A	109.5
O5^{ii}—Na2—O4^{iii}	127.68 (7)	C13—C21—H21A	109.5
O5^{ii}—Na2—O3	101.42 (6)	N8—C21—H21B	109.5
O4^{iii}—Na2—O3	92.56 (6)	C13—C21—H21B	109.5
O5^{ii}—Na2—N7	130.30 (7)	H21A—C21—H21B	108.1
O4^{iii}—Na2—N7	101.50 (6)	N8—C22—C23	113.07 (16)
O3—Na2—N7	65.83 (5)	N8—C22—H22A	109.0
O5^{ii}—Na2—N11	88.66 (7)	C23—C22—H22A	109.0
O4^{iii}—Na2—N11	104.46 (7)	N8—C22—H22B	109.0
O3—Na2—N11	148.91 (7)	C23—C22—H22B	109.0
N7—Na2—N11	85.14 (7)	H22A—C22—H22B	107.8
O5^{ii}—Na2—S1^{iii}	113.91 (5)	N9—C23—C24	122.47 (19)
O4^{iii}—Na2—S1^{iii}	21.39 (4)	N9—C23—C22	118.05 (17)
O3—Na2—S1^{iii}	112.83 (4)	C24—C23—C22	119.46 (19)
N7—Na2—S1^{iii}	115.19 (5)	C25—C24—C23	118.7 (2)
N11—Na2—S1^{iii}	88.83 (6)	C25—C24—H24	120.6
O5^{ii}—Na2—Na2^{iv}	57.30 (5)	C23—C24—H24	120.6
O4^{iii}—Na2—Na2^{iv}	76.32 (5)	C26—C25—C24	119.3 (2)
O3—Na2—Na2^{iv}	132.85 (5)	C26—C25—H25	120.3
N7—Na2—Na2^{iv}	160.89 (5)	C24—C25—H25	120.3
N11—Na2—Na2^{iv}	77.20 (6)	C25—C26—C27	118.6 (2)
S1^{iii}—Na2—Na2^{iv}	57.86 (2)	C25—C26—H26	120.7
C12—O3—Na2	120.18 (11)	C27—C26—H26	120.7
C12—O3—H3	114.9 (16)	N9—C27—C26	122.8 (2)
Na2—O3—H3	120.7 (16)	N9—C27—H27	118.6
S1—O4—Na2^{i}	123.98 (9)	C26—C27—H27	118.6
S1—O5—Na2^{v}	148.14 (10)	N8—C28—C29	112.78 (16)
C19—N7—C20	117.48 (17)	N8—C28—H28A	109.0
C19—N7—Na2	124.08 (13)	C29—C28—H28A	109.0
C20—N7—Na2	117.42 (12)	N8—C28—H28B	109.0
C22—N8—C28	111.39 (16)	C29—C28—H28B	109.0
C22—N8—C21	112.06 (15)	H28A—C28—H28B	107.8
C28—N8—C21	111.93 (15)	N10—C29—C30	122.79 (19)
C23—N9—C27	118.06 (18)	N10—C29—C28	115.47 (18)
C29—N10—C33	116.2 (2)	C30—C29—C28	121.73 (18)
C34—N11—Na2	151.4 (2)	C31—C30—C29	119.4 (2)
O3—C12—C13	124.01 (17)	C31—C30—H30	120.3

O3—C12—C20	116.23 (16)	C29—C30—H30	120.3
C13—C12—C20	119.75 (17)	C32—C31—C30	118.4 (2)
C12—C13—C14	119.07 (17)	C32—C31—H31	120.8
C12—C13—C21	120.28 (17)	C30—C31—H31	120.8
C14—C13—C21	120.64 (16)	C33—C32—C31	118.5 (2)
C15—C14—C13	122.77 (17)	C33—C32—H32	120.8
C15—C14—H14	118.6	C31—C32—H32	120.8
C13—C14—H14	118.6	N10—C33—C32	124.7 (2)
C14—C15—C16	119.26 (17)	N10—C33—H33	117.6
C14—C15—S1	119.96 (14)	C32—C33—H33	117.6
C16—C15—S1	120.78 (14)	N11—C34—C35	179.4 (3)
C20—C16—C17	117.06 (17)	C34—C35—H35A	109.5
C20—C16—C15	119.07 (17)	C34—C35—H35B	109.5
C17—C16—C15	123.87 (17)	H35A—C35—H35B	109.5
C18—C17—C16	119.36 (19)	C34—C35—H35C	109.5
C18—C17—H17	120.3	H35A—C35—H35C	109.5
C16—C17—H17	120.3	H35B—C35—H35C	109.5
C17—C18—C19	119.39 (19)		

O6—S1—O4—Na2^{i}	−146.44 (9)	Na2—N7—C20—C12	−13.3 (2)
O5—S1—O4—Na2^{i}	−16.08 (13)	C17—C16—C20—N7	−0.6 (3)
C15—S1—O4—Na2^{i}	97.84 (10)	C15—C16—C20—N7	179.29 (17)
O6—S1—O5—Na2^{v}	78.3 (2)	C17—C16—C20—C12	−179.41 (17)
O4—S1—O5—Na2^{v}	−52.0 (2)	C15—C16—C20—C12	0.5 (3)
C15—S1—O5—Na2^{v}	−166.41 (18)	O3—C12—C20—N7	−0.3 (2)
Na2^{i}—S1—O5—Na2^{v}	−61.26 (19)	C13—C12—C20—N7	−178.66 (16)
Na2—O3—C12—C13	−167.32 (14)	O3—C12—C20—C16	178.61 (16)
Na2—O3—C12—C20	14.4 (2)	C13—C12—C20—C16	0.2 (3)
O3—C12—C13—C14	−179.49 (17)	C22—N8—C21—C13	−163.21 (16)
C20—C12—C13—C14	−1.2 (3)	C28—N8—C21—C13	70.82 (19)
O3—C12—C13—C21	1.3 (3)	C12—C13—C21—N8	63.1 (2)
C20—C12—C13—C21	179.60 (16)	C14—C13—C21—N8	−116.12 (18)
C12—C13—C14—C15	1.6 (3)	C28—N8—C22—C23	−155.23 (16)
C21—C13—C14—C15	−179.20 (17)	C21—N8—C22—C23	78.5 (2)
C13—C14—C15—C16	−0.9 (3)	C27—N9—C23—C24	−1.4 (3)
C13—C14—C15—S1	179.41 (14)	C27—N9—C23—C22	176.90 (19)
O6—S1—C15—C14	−126.08 (15)	N8—C22—C23—N9	6.4 (3)
O4—S1—C15—C14	−5.59 (17)	N8—C22—C23—C24	−175.17 (18)
O5—S1—C15—C14	113.80 (16)	N9—C23—C24—C25	1.3 (3)
Na2^{i}—S1—C15—C14	30.51 (16)	C22—C23—C24—C25	−177.0 (2)
O6—S1—C15—C16	54.26 (17)	C23—C24—C25—C26	0.1 (3)
O4—S1—C15—C16	174.74 (15)	C24—C25—C26—C27	−1.3 (3)
O5—S1—C15—C16	−65.86 (17)	C23—N9—C27—C26	0.2 (3)
Na2^{i}—S1—C15—C16	−149.16 (13)	C25—C26—C27—N9	1.2 (4)
C14—C15—C16—C20	−0.1 (3)	C22—N8—C28—C29	72.0 (2)
S1—C15—C16—C20	179.53 (13)	C21—N8—C28—C29	−161.71 (16)
C14—C15—C16—C17	179.75 (18)	C33—N10—C29—C30	0.6 (3)
S1—C15—C16—C17	−0.6 (3)	C33—N10—C29—C28	−178.2 (2)

C20—C16—C17—C18	1.6 (3)	N8—C28—C29—N10	−145.01 (18)
C15—C16—C17—C18	−178.31 (19)	N8—C28—C29—C30	36.2 (3)
C16—C17—C18—C19	−0.9 (3)	N10—C29—C30—C31	−0.4 (3)
C20—N7—C19—C18	1.9 (3)	C28—C29—C30—C31	178.36 (19)
Na2—N7—C19—C18	−166.24 (17)	C29—C30—C31—C32	−0.3 (3)
C17—C18—C19—N7	−0.9 (4)	C30—C31—C32—C33	0.7 (3)
C19—N7—C20—C16	−1.1 (3)	C29—N10—C33—C32	−0.2 (4)
Na2—N7—C20—C16	167.84 (13)	C31—C32—C33—N10	−0.4 (4)
C19—N7—C20—C12	177.74 (18)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···N8	0.88 (2)	2.46 (3)	3.057 (2)	125 (2)
O3—H3···N9	0.88 (2)	1.87 (2)	2.7120 (19)	158 (3)
C31—H31···O6^{iii}	0.95	2.53	3.397 (3)	152
C35—H35*A*···O6^{vi}	0.98	2.55	3.502 (4)	166

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