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First crystal structure of a Pigment Red 52 compound: DMSO solvate hydrate of the monosodium salt

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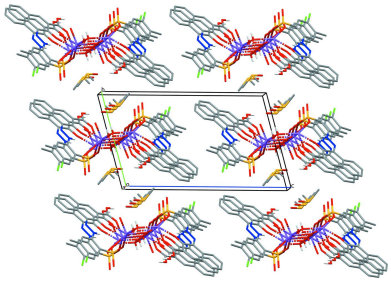
Pigment Red 52, $Na_2[C_{18}H_{11}ClN_2O_6S]$, is an industrially produced hydrazone-laked pigment. It serves as an intermediate in the synthesis of the corresponding Ca^{2+} and Mn^{2+} salts, which are used commercially for printing inks and lacquers. Hitherto, no crystal structure of any salt of Pigment Red 52 is known. Now, single crystals have been obtained of a dimethyl sulfoxide solvate hydrate of the monosodium salt of Pigment Red 52, namely, monosodium 2-[2-(3-carboxy-2-oxo-1,2-dihydronaphthalen-1-ylidene)hydrazin-1-yl]-5-chloro-4-methylbenzenesulfonate dimethyl sulfoxide monosolvate monohydrate, $Na^+\cdot C_{18}H_{12}ClN_2O_6S^-\cdot H_2O\cdot C_2H_6OS$, obtained from in-house synthesized Pigment Red 52. The crystal structure was determined by single-crystal X-ray diffraction at 173 K. In this monosodium salt, the SO_3^- group is deprotonated, whereas the COOH group is protonated. The residues form chains *via* ionic interactions and hydrogen bonds. The chains are arranged in polar/non-polar double layers.

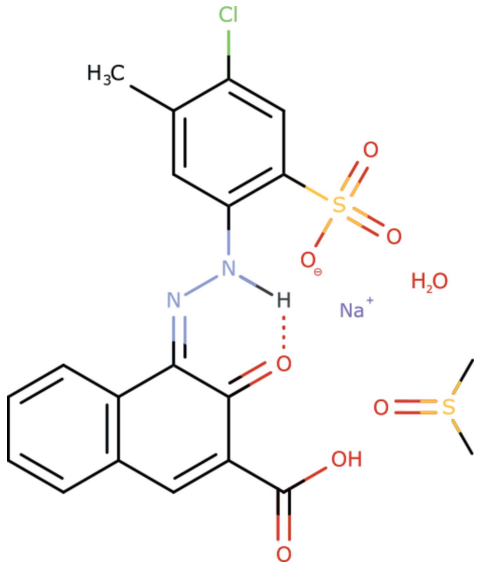
1. Chemical context

Pigment Red 52 (P.R.52, $Na_2[C_{18}H_{11}N_2ClO_6S]$), is produced industrially as an intermediate in the synthesis of Pigment Red 52:1 ($Ca[C_{18}H_{11}N_2ClO_6S]$) and Pigment Red 52:2 ($Mn[C_{18}H_{11}N_2ClO_6S]$) (Czajkowski *et al.*, 1980; Hunger & Schmidt, 2018). P.R.52:1 and P.R.52:2 are used for the colouration of printing inks and lacquers (Hunger & Schmidt, 2018). No crystal structures of P.R.52, or of its various metal salts, have previously been determined. Pigment Red 48 is an isomer of P.R.52, differing by mutual exchange of CH_3 and Cl substituents. Recently, the crystal structures of two hydrates of the monosodium salt of P.R.48 have been published (Tapmeyer *et al.*, 2020). Correspondingly, similar monosodium hydrate phases could also be expected for P.R.52. Hitherto, nothing has been known about the existence of a monosodium salt of P.R.52 or its hydrates or solvates. In attempts to crystallize P.R.52 from dimethylsulfoxide, single crystals were obtained, which turned out to be a mono-DMSO solvate monohydrate of the monosodium salt of P.R.52:1. The crystal structure was determined by X-ray analysis.



2. Structural commentary

Pigment Red 52 monosodium salt DMSO monosolvate monohydrate crystallizes in the triclinic space group $P\overline{1}$ with one pigment anion, one sodium cation, one molecule of DMSO and one water molecule in the asymmetric unit (Fig. 1).



The pigment exhibits the hydrazone tautomeric form, like all industrial hydrazone pigments (formerly known as 'azo pigments') (Gilli *et al.*, 2005; Schmidt *et al.*, 2008; Hunger & Schmidt, 2018). The N—H group forms two intramolecular [$S_1^1(6)$] N—H···O hydrogen bonds (Table 1). The sulfonate group is deprotonated, whereas the carboxylic group is protonated. The protonation site is unambiguously determined by the difference electron density, from the S—O and C—O bond lengths in the SO_3^- and COOH groups, and from the hydrogen-bond pattern. Intramolecular and intermolecular bond lengths and angles are in the usual ranges. The organic anion is nearly planar, with an RMSD of 0.553 Å for all non-hydrogen atoms, except for the oxygen atoms of the sulfonate group. The dihedral angle between the naphthyl moiety and the phenyl ring is 9.84 (16)°.

The carboxylic acid group is coplanar with the naphthyl moiety [dihedral angle of 1.2 (5)°, see Fig. 1]. This coplanarity is a peculiarity, as in most other related structures, the COOH group is rotated out of the naphthyl plane (Table 2).

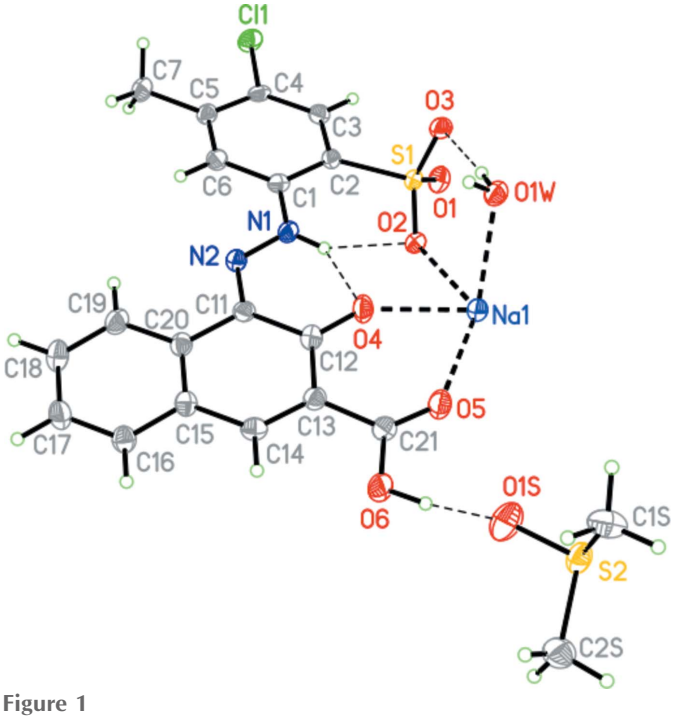


Figure 1
A perspective view of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.82 (4)	2.14 (4)	2.747 (3)	131 (3)
N1—H1···O4	0.82 (4)	1.84 (4)	2.532 (4)	141 (4)
O6—H6···O1*S*	0.92 (5)	1.67 (5)	2.575 (4)	168 (4)
O1*W*—H1*WA*···O5^{i}	0.80 (5)	2.33 (5)	2.944 (3)	134 (4)
O1*W*—H1*WA*···O1*S*^{i}	0.80 (5)	2.48 (5)	3.138 (5)	140 (4)
O1*W*—H1*WB*···O3	0.84 (6)	2.11 (6)	2.942 (3)	176 (5)

Symmetry code: (i) $x+1, y, z$.

3. Supramolecular features

The protonated carboxyl oxygen atom of the COOH group donates a hydrogen bond to the DMSO molecule (Table 1). The other carboxyl oxygen atom accepts a hydrogen bond from the water molecule and additionally coordinates to the sodium ion. The sodium ion is sixfold coordinated to one oxygen atom of the COOH group, the carbonyl group, an oxygen atom of the sulfonate group, and two water molecules (one belonging to the same asymmetric unit, the other one transformed by $-x, 1-y, -z$). The sixth coordination site is occupied by an O atom of a sulfonate group of a neighbouring anion, generated by the symmetry operation $-1+x, y, z$. The coordination polyhedron is a distorted octahedron. The crystal packing is characterized by chains built *via* Na—O coordinations, running along the *a*-axis direction (Fig. 2). Within this chain, the phenyl ring is π-stacked above the O=C—C=N—N—H moiety of a symmetry-equivalent anion $(1+x, y, z)$ with

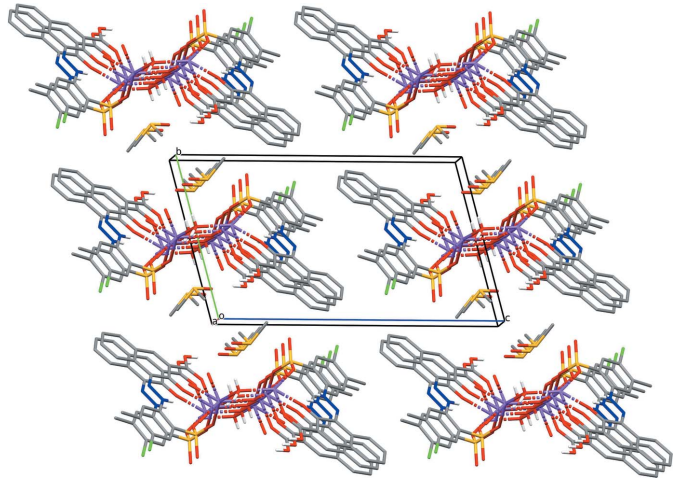


Figure 2
Packing diagram viewed approximately along [100].

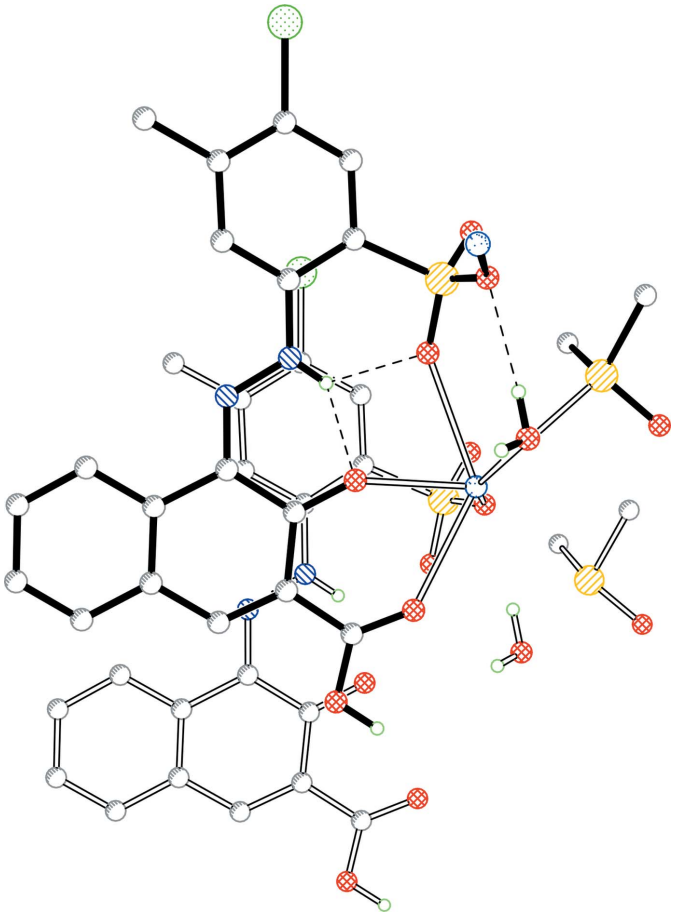


Figure 3
π-stacking of two anions, one drawn with full bonds and the other one with open bonds.

the shortest distance C6···C12 of 3.303 (5) Å. The N–NH unit is stacked above the naphthyl-COOH group with the shortest distance N1···C21 (1 + x, y, z) of 3.304 (4) Å (Fig. 3).

4. Database survey

For Pigment Red 52 and its derivatives, this is the first crystal structure published. Some closely related structures are compared in Table 2, *viz*. bis[6-chloro-3-(3-carboxy-2-oxoanthracenylidenehydrazono)benzenesulfonato]bis(dimethylformamide)calcium (BIHNUC; Kennedy *et al*., 2004), [4-(4,6-dichloro-2-sulfophenyl)azo-3-hydroxy-2-naphthoato]diaquacalcium (KAQSAW; Kennedy *et al*., 2000), {3-carboxy-1-[2-(5-chloro-4-methyl-2-sulfophenyl)diazen-2-ium-1-yl]naphthalen-2-olato}diaquasodium, {3-carboxy-1-[2-(5-chloro-4-methyl-2-sulfophenyl)diazen-2-ium-1-yl]naphthalen-2-olato}-aquasodium (GUNZAT and GUNZEX, respectively; Tapmeyer *et al*., 2020), {3-carboxy-1-[2-(4-methyl-2-sulfophenyl)diazen-2-ium-1-yl]naphthalen-2-olato}calcium, {2-[2-(3-carboxy-2-oxy-1-naphthyl)diazeniumyl]-5-methylbenzenesulfonato}triaquacalcium, {2-[2-(3-carboxy-2-hydroxy-1-naphthyl)diazeniumyl]-5-methylbenzenesulfonato}aquacalcium (FAWQUR, FAWQIF and FAWQOL, respectively; Bekö *et al*., 2012*a*,*b*),

Table 2
Angles (°) of the C–COO(H) plane to the mean plane of the carbon skeleton of the β-oxynaphthoic acid moiety.

Refcode	Salt	Solvate / Hydrate	|Angle|
BIHNUC[a]	$Ca[C_{17}H_{10}N_2O_6ClS]_2$	2 DMF	0.09
GUNZAT	$Na[C_{18}H_{12}ClN_2O_6S]$	2 H_2O	2.43
FAWQUR	$Ca[C_{18}H_{12}N_2O_6S]$		22.5
KAQSAW	$Ca[C_{17}H_8C_{l2}N_2O_6S]$	2 H_2O	23.3
FAWQIF	$Ca[C_{18}H_{14}N_2O_7S]$	2 H_2O	26.3
GUNZEX	$Na[C_{18}H_{12}ClN_2O_6S]$	1 H_2O	28.6
BOGDUZ[a]	$Dy[C_{13}H_7N_5O_3][BONA]^b$	2 DMF, 2 H_2O	36.6
FAWQOL	$Ca[C_{18}H_{12}N_2O_6S]$	1 H_2O	37.7
BOGFIP[a]	$Eu[C_{13}H_7N_5O_3][BONA]^b$	DMF, 4 H_2O	39.0
BOGFAH[a]	$Tb[C_{13}H_7N_5O_3][BONA]^b$	DMF, 4 H_2O	39.0
BOGFEL[a]	$Sm[C_{13}H_7N_5O_3][BONA]^b$	DMF, 4 H_2O	39.1

Notes: (*a*) This is not a pigment with a Colour Index number; (*b*) BONA = β-oxynaphthoic acid.

bis(3-oxido-4-[(1*H*-1,2,4-triazol-3-yl)diazenyl]naphthalene-2-carboxylato)bis(3-hydroxynaphthalene-2-carboxylato)tetrakis(aqua)didysprosium(III) *N*,*N*-dimethylformamide solvate, bis{3-oxido-4-[(1*H*-1,2,4-triazol-3-yl)diazenyl]naphthalene-2-carboxylato}bis(3-hydroxynaphthalene-2-carboxylato)tetrakis(aqua)dieuropium(III) *N*,*N*-dimethylformamide solvate, bis{3-oxido-4-[(1*H*-1,2,4-triazol-3-yl)diazenyl]naphthalene-2-carboxylato}bis(3-hydroxynaphthalene-2-carboxylato)tetrakis(aqua)diterbium(III) *N*,*N*-dimethylformamide solvate, bis(3-oxido-4-[(1*H*-1,2,4-triazol-3-yl)diazenyl]naphthalene-2-carboxylato)bis(3-hydroxynaphthalene-2-carboxylato)tetrakis(aqua)disamarium(III) *N*,*N*-dimethylformamide solvate (BOGDUZ, BOGFIP, BOGFAH and BOGFEL, respectively; Xie *et al*., 2019).

5. Synthesis and crystallization

The title compound was obtained by recrystallization experiments of in-house synthesized P.R.52.

5.1. Synthesis of Pigment Red 52

2-Amino-5-chloro-*p*-toluenesulfonic acid (22.15 g, 0.1 mol) was dissolved with sodium hydroxide (6.4 g) in water (500 ml). The temperature was set at 278 K and concentrated hydrochloric acid (40 ml) as well as sodium nitrite (7.2 g) in water (100 ml) were added. The suspension was stirred for 30 min. The suspension was treated with amidosulfonic acid until all excess nitrous acid was destroyed. The suspension was then added dropwise to a solution of β-oxynaphthoic acid (18.8 g, 0.1 mol) with NaOH (20.1 g) in water (550 ml). The pH was kept at alkaline conditions, around 11 to 9, maintained by the addition of 2 *M* NaOH solution as required, and the temperature was maintained at 278 K. When the dropwise addition of the suspension was finished, the solution was allowed to accommodate to room temperature and subsequently heated to 353 K for half an hour. The red suspension was then neutralized with 2 *M* HCl, filtered off and the obtained red powder was washed with water and dried at 323 K. The yield of the crude product was about 98%, but

Table 3
Experimental details.

Crystal data	
Chemical formula	$Na^+ \cdot C_{18}H_{12}ClN_2O_6S^- \cdot C_2H_6OS \cdot H_2O$
M_r	538.94
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	5.7347 (4), 10.9336 (8), 18.4692 (12)
α, β, γ (°)	104.844 (5), 97.478 (5), 95.404 (6)
V (Å^3)	1100.00 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.44
Crystal size (mm)	0.23 × 0.09 × 0.02
Data collection	
Diffractometer	STOE IPDS II two-circle
Absorption correction	Multi-scan (*X-AREA*; Stoe & Cie, 2001)
T_{min}, T_{max}	0.445, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14981, 3864, 2992
R_{int}	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.098, 1.08
No. of reflections	3864
No. of parameters	324
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.33

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* and *XP* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

X-ray powder diffraction revealed the presence of some sodium chloride as impurity.

5.2. Crystallization of the title compound

The crude in-house synthesized P.R.52 (0.59 g) was dissolved in DMSO (60 ml). The solution was transferred to a glass vessel, which in turn was placed into a further, larger vessel with water (100 ml). The outer vessel was closed with a plastic lid and stored for 20 days at room temperature, allowing the water to diffuse into the DMSO *via* the gas phase. Single crystals of the title compound were picked from the solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms bonded to C were refined using a riding model with C—H = 0.95 Å and with U_{iso}(H) = 1.2U_{eq}(C) or with C_{methyl}—H = 0.98 Å and with U_{iso}(H) = 1.5U_{eq}(C). The methyl group attached to the phenyl ring was allowed to rotate but not to tip. The H atoms bonded to N and O were found in the difference-Fourier synthesis and freely refined.

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supporting information

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First crystal structure of a Pigment Red 52 compound: DMSO solvate hydrate of the monosodium salt

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA* (Stoe & Cie, 2001); data reduction: *X-AREA* (Stoe & Cie, 2001); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *XP* (Sheldrick, 2015b) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Monosodium 2-[2-(3-carboxy-2-oxo-1,2-dihydronaphthalen-1-ylidene)hydrazin-1-yl]-5-chloro-4-methylbenzenesulfonate dimethyl sulfoxide monosolvate monohydrate

Crystal data

$Na^{+}\cdot C_{18}H_{12}ClN_2O_6S^{-}\cdot C_2H_6OS\cdot H_2O$
$M_r = 538.94$
Triclinic, $P\overline{1}$
$a = 5.7347$ (4) Å
$b = 10.9336$ (8) Å
$c = 18.4692$ (12) Å
$\alpha = 104.844$ (5)°
$\beta = 97.478$ (5)°
$\gamma = 95.404$ (6)°
$V = 1100.00$ (14) Å^3
$Z = 2$
$F(000) = 556$
$D_x = 1.627$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 12767 reflections
$\theta = 3.4$–27.4°
$\mu = 0.44$ mm^{-1}
$T = 173$ K
Needle, red
0.23 × 0.09 × 0.02 mm

Data collection

STOE IPDS II two-circle diffractometer
Radiation source: Genix 3D IμS microfocus X-ray source
ω scans
Absorption correction: multi-scan (X-Area; Stoe & Cie, 2001)
$T_{min} = 0.445$, $T_{max} = 1.000$
14981 measured reflections
3864 independent reflections
2992 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.4°$
$h = -6\rightarrow6$
$k = -12\rightarrow12$
$l = -21\rightarrow21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.098$
$S = 1.08$
3864 reflections
324 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.0815P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ 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}
Cl1	1.33825 (14)	0.84822 (8)	0.39943 (5)	0.0267 (2)
S1	0.52780 (13)	0.72725 (7)	0.20025 (4)	0.01767 (18)
N1	0.4274 (5)	0.5113 (2)	0.28158 (16)	0.0202 (6)
H1	0.327 (7)	0.519 (3)	0.248 (2)	0.030 (10)*
N2	0.3632 (4)	0.4232 (2)	0.31510 (14)	0.0190 (6)
O1	0.5585 (4)	0.8648 (2)	0.21703 (13)	0.0255 (5)
O2	0.2857 (4)	0.6713 (2)	0.19634 (12)	0.0233 (5)
O3	0.6302 (4)	0.6669 (2)	0.13374 (12)	0.0233 (5)
O4	0.0393 (4)	0.4384 (2)	0.19077 (13)	0.0304 (6)
O5	−0.3920 (4)	0.3586 (2)	0.10391 (13)	0.0289 (5)
O6	−0.6211 (4)	0.2111 (2)	0.13512 (14)	0.0318 (6)
H6	−0.722 (8)	0.211 (4)	0.092 (3)	0.053 (13)*
C1	0.6441 (5)	0.5895 (3)	0.30879 (17)	0.0182 (6)
C2	0.7033 (5)	0.6915 (3)	0.27795 (17)	0.0176 (6)
C3	0.9189 (5)	0.7691 (3)	0.30758 (17)	0.0195 (7)
H3	0.961076	0.838914	0.287912	0.023*
C4	1.0722 (5)	0.7460 (3)	0.36520 (18)	0.0192 (7)
C5	1.0206 (5)	0.6441 (3)	0.39538 (17)	0.0197 (7)
C6	0.8039 (5)	0.5675 (3)	0.36633 (17)	0.0198 (7)
H6A	0.763355	0.497883	0.386333	0.024*
C7	1.1910 (6)	0.6171 (3)	0.45670 (19)	0.0250 (7)
H7A	1.190008	0.680328	0.505018	0.038*
H7B	1.351237	0.621942	0.443631	0.038*
H7C	1.142866	0.531421	0.461406	0.038*
C11	0.1537 (5)	0.3519 (3)	0.29167 (17)	0.0189 (6)
C12	−0.0153 (6)	0.3617 (3)	0.22721 (18)	0.0220 (7)
C13	−0.2443 (5)	0.2803 (3)	0.20857 (18)	0.0200 (7)
C14	−0.2928 (6)	0.1985 (3)	0.25062 (18)	0.0206 (7)
H14	−0.441828	0.145890	0.237181	0.025*
C15	−0.1318 (6)	0.1870 (3)	0.31425 (17)	0.0198 (7)
C16	−0.1975 (6)	0.1025 (3)	0.35634 (18)	0.0232 (7)
H16	−0.349077	0.052284	0.342594	0.028*
C17	−0.0435 (6)	0.0924 (3)	0.41705 (19)	0.0277 (8)
H17	−0.088209	0.034856	0.445145	0.033*
C18	0.1790 (6)	0.1664 (3)	0.4379 (2)	0.0289 (8)
H18	0.284455	0.158951	0.480198	0.035*
C19	0.2474 (6)	0.2504 (3)	0.39741 (19)	0.0259 (7)
H19	0.399428	0.300111	0.411918	0.031*
C20	0.0923 (5)	0.2620 (3)	0.33504 (18)	0.0201 (7)

C21	−0.4220 (5)	0.2885 (3)	0.14433 (18)	0.0204 (7)
Na1	−0.0772 (2)	0.53586 (12)	0.09912 (7)	0.0231 (3)
S2	−1.06094 (15)	0.18210 (8)	−0.06033 (5)	0.0275 (2)
O1S	−0.8734 (5)	0.1866 (3)	0.00506 (17)	0.0598 (9)
C1S	−1.0132 (7)	0.0551 (4)	−0.1364 (2)	0.0370 (9)
H1S1	−1.131988	0.047817	−0.181088	0.055*
H1S2	−0.854081	0.072376	−0.148510	0.055*
H1S3	−1.027239	−0.024884	−0.121697	0.055*
C2S	−1.3286 (7)	0.1091 (4)	−0.0416 (2)	0.0360 (9)
H2S1	−1.457635	0.103949	−0.083129	0.054*
H2S2	−1.308418	0.022976	−0.037569	0.054*
H2S3	−1.367318	0.160165	0.006106	0.054*
O1W	0.2484 (4)	0.4817 (3)	0.02986 (13)	0.0235 (5)
H1WA	0.288 (8)	0.415 (5)	0.034 (3)	0.056 (15)*
H1WB	0.359 (9)	0.536 (5)	0.058 (3)	0.065 (16)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0170 (4)	0.0301 (4)	0.0295 (5)	−0.0030 (3)	−0.0035 (3)	0.0075 (3)
S1	0.0161 (4)	0.0210 (4)	0.0164 (4)	0.0031 (3)	0.0008 (3)	0.0066 (3)
N1	0.0148 (13)	0.0246 (14)	0.0211 (15)	−0.0007 (11)	−0.0017 (12)	0.0093 (11)
N2	0.0185 (14)	0.0214 (13)	0.0176 (14)	0.0037 (11)	0.0022 (11)	0.0062 (11)
O1	0.0285 (13)	0.0213 (11)	0.0253 (13)	0.0036 (9)	−0.0013 (10)	0.0067 (9)
O2	0.0157 (11)	0.0332 (12)	0.0229 (12)	0.0025 (9)	0.0006 (9)	0.0123 (10)
O3	0.0200 (11)	0.0314 (12)	0.0184 (12)	0.0077 (9)	0.0034 (9)	0.0052 (9)
O4	0.0238 (12)	0.0412 (14)	0.0280 (13)	−0.0070 (10)	−0.0064 (10)	0.0218 (11)
O5	0.0265 (13)	0.0308 (12)	0.0299 (14)	−0.0025 (10)	−0.0044 (10)	0.0159 (11)
O6	0.0218 (13)	0.0412 (14)	0.0291 (14)	−0.0110 (11)	−0.0098 (11)	0.0162 (11)
C1	0.0155 (15)	0.0198 (15)	0.0182 (16)	0.0020 (12)	0.0033 (12)	0.0029 (12)
C2	0.0182 (15)	0.0204 (15)	0.0151 (16)	0.0044 (12)	0.0030 (12)	0.0058 (12)
C3	0.0182 (16)	0.0214 (16)	0.0183 (16)	0.0019 (13)	0.0039 (13)	0.0042 (12)
C4	0.0111 (15)	0.0246 (16)	0.0196 (17)	0.0013 (12)	0.0021 (12)	0.0024 (13)
C5	0.0189 (16)	0.0232 (16)	0.0170 (17)	0.0061 (13)	0.0027 (13)	0.0043 (13)
C6	0.0177 (16)	0.0221 (15)	0.0186 (17)	0.0001 (12)	0.0006 (13)	0.0055 (13)
C7	0.0213 (17)	0.0307 (17)	0.0221 (18)	0.0036 (14)	−0.0033 (14)	0.0087 (14)
C11	0.0159 (16)	0.0232 (15)	0.0161 (16)	0.0010 (12)	0.0016 (12)	0.0038 (12)
C12	0.0231 (17)	0.0230 (16)	0.0204 (17)	0.0039 (13)	0.0017 (13)	0.0072 (13)
C13	0.0192 (16)	0.0214 (15)	0.0190 (17)	0.0030 (12)	0.0020 (13)	0.0053 (13)
C14	0.0187 (16)	0.0185 (15)	0.0213 (17)	−0.0008 (12)	0.0024 (13)	0.0012 (13)
C15	0.0239 (16)	0.0181 (15)	0.0161 (16)	0.0031 (12)	0.0019 (13)	0.0031 (12)
C16	0.0259 (17)	0.0212 (16)	0.0219 (18)	0.0018 (13)	0.0021 (14)	0.0062 (13)
C17	0.0328 (19)	0.0266 (17)	0.0269 (19)	0.0037 (15)	0.0038 (15)	0.0140 (14)
C18	0.034 (2)	0.0289 (18)	0.0237 (19)	0.0048 (15)	−0.0024 (15)	0.0103 (14)
C19	0.0214 (17)	0.0296 (17)	0.0257 (18)	0.0018 (14)	−0.0024 (14)	0.0095 (14)
C20	0.0222 (16)	0.0198 (15)	0.0188 (17)	0.0057 (13)	0.0036 (13)	0.0051 (12)
C21	0.0196 (16)	0.0198 (15)	0.0180 (17)	−0.0020 (13)	−0.0003 (13)	0.0016 (13)
Na1	0.0209 (6)	0.0316 (7)	0.0194 (7)	0.0071 (5)	0.0034 (5)	0.0104 (5)

S2	0.0263 (5)	0.0274 (4)	0.0254 (5)	−0.0001 (3)	−0.0056 (4)	0.0073 (4)
O1S	0.0366 (16)	0.098 (3)	0.0368 (17)	−0.0043 (16)	−0.0163 (13)	0.0204 (17)
C1S	0.030 (2)	0.038 (2)	0.039 (2)	−0.0021 (16)	0.0134 (17)	0.0039 (17)
C2S	0.033 (2)	0.046 (2)	0.029 (2)	0.0064 (17)	0.0096 (17)	0.0072 (17)
O1W	0.0214 (12)	0.0267 (13)	0.0211 (13)	0.0055 (11)	0.0001 (10)	0.0051 (10)

Geometric parameters (Å, º)

Cl1—C4	1.744 (3)	C12—C13	1.463 (5)
S1—O1	1.445 (2)	C13—C14	1.358 (4)
S1—O2	1.449 (2)	C13—C21	1.487 (4)
S1—O3	1.461 (2)	C14—C15	1.437 (4)
S1—C2	1.792 (3)	C14—H14	0.9500
N1—N2	1.321 (4)	C15—C16	1.407 (4)
N1—C1	1.395 (4)	C15—C20	1.408 (5)
N1—H1	0.82 (4)	C16—C17	1.369 (5)
N2—C11	1.324 (4)	C16—H16	0.9500
O2—Na1	2.614 (3)	C17—C18	1.396 (5)
O3—Na1^{i}	2.353 (2)	C17—H17	0.9500
O4—C12	1.244 (4)	C18—C19	1.384 (5)
O4—Na1	2.283 (2)	C18—H18	0.9500
O5—C21	1.215 (4)	C19—C20	1.402 (4)
O5—Na1	2.548 (3)	C19—H19	0.9500
O6—C21	1.320 (4)	Na1—O1W^{ii}	2.408 (3)
O6—H6	0.92 (5)	Na1—O1W	2.432 (3)
C1—C6	1.395 (4)	Na1—S2^{iii}	3.3866 (15)
C1—C2	1.410 (4)	Na1—Na1^{ii}	3.782 (2)
C2—C3	1.392 (4)	S2—O1S	1.496 (3)
C3—C4	1.380 (4)	S2—C1S	1.774 (4)
C3—H3	0.9500	S2—C2S	1.778 (4)
C4—C5	1.393 (4)	C1S—H1S1	0.9800
C5—C6	1.390 (4)	C1S—H1S2	0.9800
C5—C7	1.504 (4)	C1S—H1S3	0.9800
C6—H6A	0.9500	C2S—H2S1	0.9800
C7—H7A	0.9800	C2S—H2S2	0.9800
C7—H7B	0.9800	C2S—H2S3	0.9800
C7—H7C	0.9800	O1W—H1WA	0.80 (5)
C11—C20	1.464 (4)	O1W—H1WB	0.84 (6)
C11—C12	1.467 (4)		

O1—S1—O2	113.86 (13)	C17—C18—H18	119.7
O1—S1—O3	112.63 (13)	C18—C19—C20	119.9 (3)
O2—S1—O3	112.10 (13)	C18—C19—H19	120.0
O1—S1—C2	105.64 (13)	C20—C19—H19	120.0
O2—S1—C2	107.23 (13)	C19—C20—C15	119.1 (3)
O3—S1—C2	104.56 (13)	C19—C20—C11	122.1 (3)
N2—N1—C1	119.8 (3)	C15—C20—C11	118.8 (3)
N2—N1—H1	115 (3)	O5—C21—O6	122.3 (3)

C1—N1—H1	125 (3)	O5—C21—C13	124.8 (3)
N1—N2—C11	120.3 (3)	O6—C21—C13	112.9 (3)
S1—O2—Na1	141.39 (13)	O4—Na1—O3^{iv}	111.35 (10)
S1—O3—Na1^{i}	140.63 (13)	O4—Na1—O1W^{ii}	149.04 (11)
C12—O4—Na1	147.7 (2)	O3^{iv}—Na1—O1W^{ii}	85.77 (8)
C21—O5—Na1	137.0 (2)	O4—Na1—O1W	94.69 (9)
C21—O6—H6	112 (3)	O3^{iv}—Na1—O1W	151.14 (10)
N1—C1—C6	120.5 (3)	O1W^{ii}—Na1—O1W	77.20 (9)
N1—C1—C2	120.0 (3)	O4—Na1—O5	67.73 (8)
C6—C1—C2	119.5 (3)	O3^{iv}—Na1—O5	83.28 (8)
C3—C2—C1	118.4 (3)	O1W^{ii}—Na1—O5	90.04 (9)
C3—C2—S1	116.2 (2)	O1W—Na1—O5	119.38 (10)
C1—C2—S1	125.3 (2)	O4—Na1—O2	68.36 (8)
C4—C3—C2	120.8 (3)	O3^{iv}—Na1—O2	98.90 (8)
C4—C3—H3	119.6	O1W^{ii}—Na1—O2	136.49 (9)
C2—C3—H3	119.6	O1W—Na1—O2	78.79 (9)
C3—C4—C5	121.9 (3)	O5—Na1—O2	133.44 (8)
C3—C4—Cl1	118.0 (2)	O4—Na1—S2^{iii}	137.82 (8)
C5—C4—Cl1	120.1 (2)	O3^{iv}—Na1—S2^{iii}	71.38 (6)
C6—C5—C4	117.2 (3)	O1W^{ii}—Na1—S2^{iii}	71.14 (7)
C6—C5—C7	121.1 (3)	O1W—Na1—S2^{iii}	81.06 (7)
C4—C5—C7	121.8 (3)	O5—Na1—S2^{iii}	149.09 (7)
C5—C6—C1	122.2 (3)	O2—Na1—S2^{iii}	69.67 (6)
C5—C6—H6A	118.9	O4—Na1—Na1^{ii}	126.76 (9)
C1—C6—H6A	118.9	O3^{iv}—Na1—Na1^{ii}	121.08 (8)
C5—C7—H7A	109.5	O1W^{ii}—Na1—Na1^{ii}	38.83 (6)
C5—C7—H7B	109.5	O1W—Na1—Na1^{ii}	38.37 (6)
H7A—C7—H7B	109.5	O5—Na1—Na1^{ii}	108.42 (8)
C5—C7—H7C	109.5	O2—Na1—Na1^{ii}	109.67 (7)
H7A—C7—H7C	109.5	S2^{iii}—Na1—Na1^{ii}	72.20 (4)
H7B—C7—H7C	109.5	O1S—S2—C1S	105.97 (19)
N2—C11—C20	116.4 (3)	O1S—S2—C2S	106.36 (19)
N2—C11—C12	123.4 (3)	C1S—S2—C2S	97.93 (17)
C20—C11—C12	120.2 (3)	O1S—S2—Na1^{iii}	103.09 (14)
O4—C12—C13	122.4 (3)	C1S—S2—Na1^{iii}	109.51 (13)
O4—C12—C11	119.5 (3)	C2S—S2—Na1^{iii}	131.85 (13)
C13—C12—C11	118.1 (3)	S2—C1S—H1S1	109.5
C14—C13—C12	119.5 (3)	S2—C1S—H1S2	109.5
C14—C13—C21	120.7 (3)	H1S1—C1S—H1S2	109.5
C12—C13—C21	119.8 (3)	S2—C1S—H1S3	109.5
C13—C14—C15	123.9 (3)	H1S1—C1S—H1S3	109.5
C13—C14—H14	118.1	H1S2—C1S—H1S3	109.5
C15—C14—H14	118.1	S2—C2S—H2S1	109.5
C16—C15—C20	119.9 (3)	S2—C2S—H2S2	109.5
C16—C15—C14	120.5 (3)	H2S1—C2S—H2S2	109.5
C20—C15—C14	119.6 (3)	S2—C2S—H2S3	109.5
C17—C16—C15	120.1 (3)	H2S1—C2S—H2S3	109.5
C17—C16—H16	119.9	H2S2—C2S—H2S3	109.5

C15—C16—H16	119.9	Na1^{ii}—O1W—Na1	102.80 (9)
C16—C17—C18	120.3 (3)	Na1^{ii}—O1W—H1WA	111 (3)
C16—C17—H17	119.9	Na1—O1W—H1WA	111 (3)
C18—C17—H17	119.9	Na1^{ii}—O1W—H1WB	128 (4)
C19—C18—C17	120.7 (3)	Na1—O1W—H1WB	100 (3)
C19—C18—H18	119.7	H1WA—O1W—H1WB	103 (5)
C1—N1—N2—C11	177.3 (3)	Na1—O4—C12—C11	−172.1 (3)
O1—S1—O2—Na1	109.0 (2)	N2—C11—C12—O4	1.6 (5)
O3—S1—O2—Na1	−20.3 (2)	C20—C11—C12—O4	−179.9 (3)
C2—S1—O2—Na1	−134.49 (19)	N2—C11—C12—C13	−178.0 (3)
O1—S1—O3—Na1^{i}	118.6 (2)	C20—C11—C12—C13	0.4 (4)
O2—S1—O3—Na1^{i}	−111.4 (2)	O4—C12—C13—C14	179.9 (3)
C2—S1—O3—Na1^{i}	4.4 (2)	C11—C12—C13—C14	−0.4 (4)
N2—N1—C1—C6	6.2 (4)	O4—C12—C13—C21	−0.5 (5)
N2—N1—C1—C2	−173.9 (3)	C11—C12—C13—C21	179.2 (3)
N1—C1—C2—C3	178.7 (3)	C12—C13—C14—C15	0.7 (5)
C6—C1—C2—C3	−1.5 (4)	C21—C13—C14—C15	−178.9 (3)
N1—C1—C2—S1	−3.8 (4)	C13—C14—C15—C16	178.2 (3)
C6—C1—C2—S1	176.0 (2)	C13—C14—C15—C20	−1.0 (5)
O1—S1—C2—C3	−37.7 (3)	C20—C15—C16—C17	−0.5 (5)
O2—S1—C2—C3	−159.4 (2)	C14—C15—C16—C17	−179.7 (3)
O3—S1—C2—C3	81.4 (2)	C15—C16—C17—C18	0.4 (5)
O1—S1—C2—C1	144.8 (3)	C16—C17—C18—C19	−0.2 (5)
O2—S1—C2—C1	23.0 (3)	C17—C18—C19—C20	0.2 (5)
O3—S1—C2—C1	−96.2 (3)	C18—C19—C20—C15	−0.3 (5)
C1—C2—C3—C4	0.7 (4)	C18—C19—C20—C11	178.3 (3)
S1—C2—C3—C4	−177.0 (2)	C16—C15—C20—C19	0.5 (4)
C2—C3—C4—C5	0.9 (5)	C14—C15—C20—C19	179.7 (3)
C2—C3—C4—Cl1	−179.8 (2)	C16—C15—C20—C11	−178.2 (3)
C3—C4—C5—C6	−1.6 (4)	C14—C15—C20—C11	1.0 (4)
Cl1—C4—C5—C6	179.1 (2)	N2—C11—C20—C19	−0.8 (4)
C3—C4—C5—C7	178.3 (3)	C12—C11—C20—C19	−179.4 (3)
Cl1—C4—C5—C7	−1.0 (4)	N2—C11—C20—C15	177.8 (3)
C4—C5—C6—C1	0.8 (4)	C12—C11—C20—C15	−0.7 (4)
C7—C5—C6—C1	−179.1 (3)	Na1—O5—C21—O6	173.8 (2)
N1—C1—C6—C5	−179.4 (3)	Na1—O5—C21—C13	−5.9 (5)
C2—C1—C6—C5	0.8 (4)	C14—C13—C21—O5	−179.7 (3)
N1—N2—C11—C20	−176.5 (3)	C12—C13—C21—O5	0.8 (5)
N1—N2—C11—C12	2.0 (4)	C14—C13—C21—O6	0.6 (4)
Na1—O4—C12—C13	7.6 (6)	C12—C13—C21—O6	−178.9 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.82 (4)	2.14 (4)	2.747 (3)	131 (3)

N1—H1···O4	0.82 (4)	1.84 (4)	2.532 (4)	141 (4)
O6—H6···O1*S*	0.92 (5)	1.67 (5)	2.575 (4)	168 (4)
O1*W*—H1*WA*···O5^{i}	0.80 (5)	2.33 (5)	2.944 (3)	134 (4)
O1*W*—H1*WA*···O1*S*^{i}	0.80 (5)	2.48 (5)	3.138 (5)	140 (4)
O1*W*—H1*WB*···O3	0.84 (6)	2.11 (6)	2.942 (3)	176 (5)

Symmetry code: (i) *x*+1, *y*, *z*.