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2,2′-(Disulfanediyl)dianilinium dichloride dihydrate

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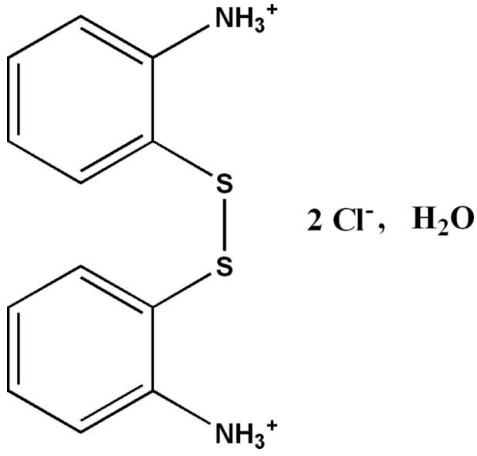
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.008 Å; R factor = 0.063; wR factor = 0.134; data-to-parameter ratio = 18.4.

In the title hydrated molecular salt, $C_{12}H_{14}N_2S_2^{2+}\cdot 2Cl^-\cdot 2H_2O$, the dihedral angle between the benzene rings in the dication is 9.03 (17)° and the C—S—S—C torsion angle is 96.8 (2)°. The crystal packing can be described as alternating organic and anionic water layers lying parallel to (100), which are linked by N—H···Cl and N—H···O hydrogen bonds. O—H···Cl hydrogen bonds and aromatic π–π stacking interactions [centroid–centroid separation = 3.730 (3) Å] are also observed.

Related literature

For related structures and background to disulfides, see: Benmebarek *et al.* (2012, 2013). For related structures, see: Tang *et al.* (2011); Goh *et al.* (2010); Song & Fan (2009).



Experimental

Crystal data

$C_{12}H_{14}N_2S_2^{2+}\cdot 2Cl^-\cdot 2H_2O$
M_r = 357.32
Orthorhombic, $Pna2_1$
a = 17.826 (7) Å
b = 13.358 (5) Å
c = 7.120 (3) Å
V = 1695.4 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.63 mm^{-1}
T = 150 K
0.16 × 0.13 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
10760 measured reflections
3584 independent reflections
2409 reflections with $I > 2\sigma(I)$
R_{int} = 0.097

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.134
S = 1.05
3584 reflections
195 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Absolute structure: Flack (1983), 1369 Friedel pairs
Flack parameter: −0.12 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1W^{i}	0.89	1.83	2.723 (6)	178
N1—H1B···Cl2^{i}	0.89	2.24	3.108 (4)	166
N1—H1C···Cl1^{i}	0.89	2.25	3.103 (4)	160
N2—H2A···O2W^{ii}	0.89	1.84	2.727 (6)	177
N2—H2B···Cl2^{iii}	0.89	2.26	3.111 (4)	160
N2—H2C···Cl2	0.89	2.30	3.157 (4)	163
O2W—H4W···Cl2	0.86 (5)	2.36 (5)	3.157 (5)	155 (5)
O2W—H3W···Cl1^{iv}	0.85 (5)	2.23 (5)	3.078 (4)	171 (6)
O1W—H1W···Cl1^{v}	0.85 (5)	2.27 (5)	3.096 (5)	167 (5)
O1W—H2W···Cl1^{iv}	0.86 (5)	2.27 (5)	3.127 (5)	176 (7)

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

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7089).

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supporting information

Acta Cryst. (2013). E**69**, o1078–o1079 [https://doi.org/10.1107/S1600536813015742]

2,2′-(Disulfanediyl)dianilinium dichloride dihydrate

Hasna Bouchareb, Mhamed Boudraa, Sofiane Bouacida and Hocin Merazig

S1. Comment

As part of our ongoing studies on the synthesis, structures and biological activity of organometallic complexes based in sulfur (Benmebarek *et al.* 2012 and Benmebarek *et al.* 2013), we have synthesized and determined the crystal structure of the title compound (I), (Fig. 1). In the cation the S—S bond length is 2.061 (2)°, indicating the single bond character similar to that found in 4,4′-diaminophenyldisulfide (Tang *et al.*, 2011; Goh *et al.* 2010). In the diprotoned 2,2′-dithio-dianiline moiety, the dihedral angle between the benzene rings is 9.03 (17)°; different to that found in [67.82 (9)°] 1,2-Bis(2-nitrophenyl)disulfane (Song & Fan, 2009) and [39.9 (2)°]4,4′- diaminophenyldisulfide (Tang *et al.*, 2011). The crystal packing can be described as alternating layers parallel to (100) plane, wich are linked toghether by N—H···Cl and N—H···O interactions involving molecule of water and anions chloride. O—H···Cl hydrogen bond and π–π stacking are observed.

S2. Experimental

2-Aminobenzenethiol (0.1 mmol) was added to concentrated HCl (2 ml) and transfered into a 23 ml teflon-lined stainless steel autoclave and heated at 120° C for 3 days. Then the autoclave was cooled to room temperature at 10°/h. Colourless prisms were collected, washed with ethanol and dried in air at room temperature.

S3. Refinement

Approximate positions for all H atoms were first obtained from the difference electron density map. However, the H atoms were situated into idealized positions and the H-atoms have been refined within the riding atom approximation. The applied constraints were as follow: C_{aryl}—H_{aryl} = 0.93 Å and $N_{ammonium}$—$H_{ammonium}$ = 0.89 Å. $U_{iso}(H_{aryl}) = 1.2U_{eq}(C_{aryl})$. $U_{iso}(H_{ammonium}) = 1.5U_{eq}(C_{ammonium})$. Except for H1W, H2W, H3W and H4W (of water molecule) were located in a difference Fourier map and refined isotropically with $U_{iso}(H) = 1.5U_{eq}(O)$.

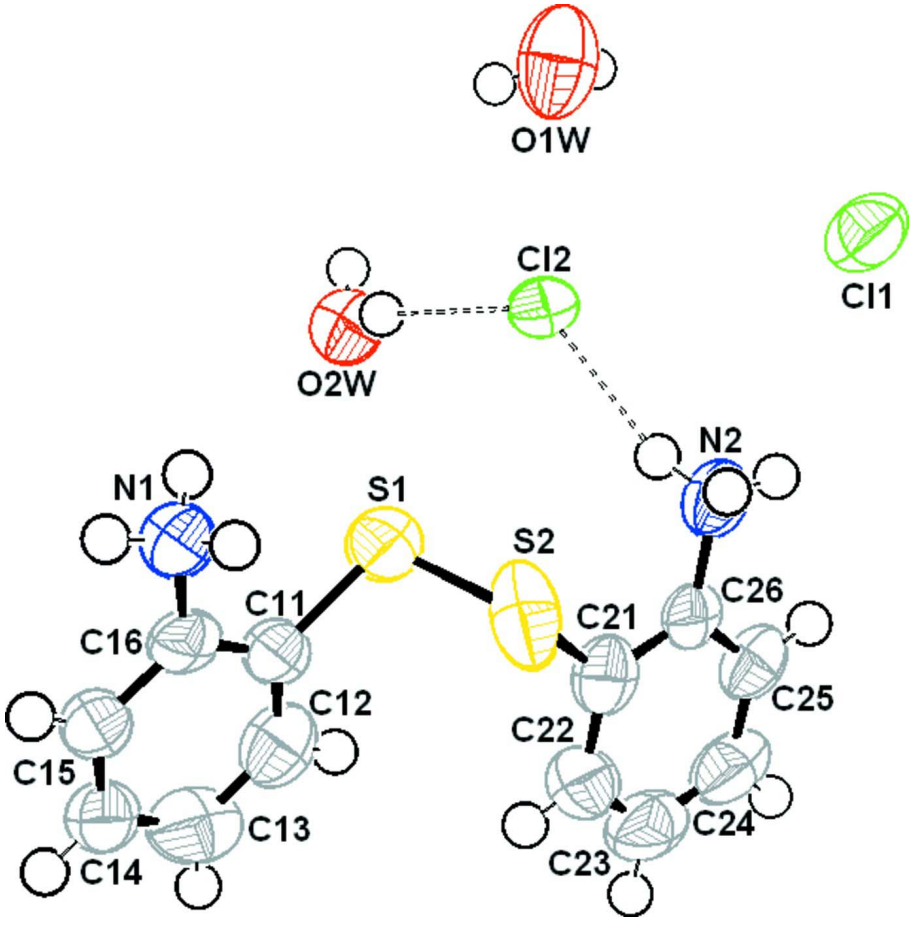

Figure 1

The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level.

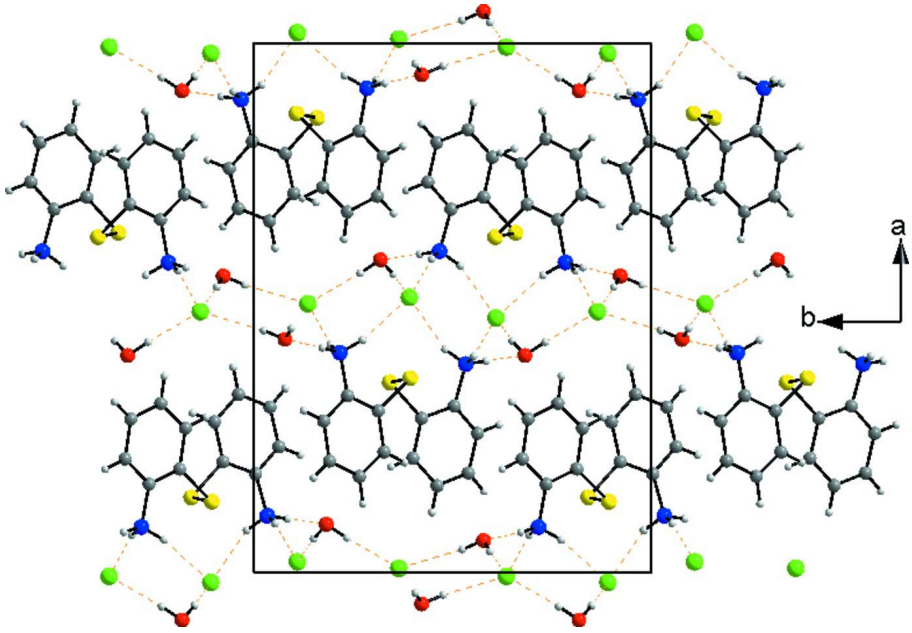

Figure 2

Diagram packing of (I) viwed *via c* axis showing hydrogen bonding in alterning layers.

2,2′-(Disulfanediyl)dianilinium dichloride dihydrate

Crystal data

$C_{12}H_{14}N_2S_2^{2+}\cdot 2Cl^-\cdot 2H_2O$
$M_r = 357.32$
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
$a = 17.826\ (7)$ Å
$b = 13.358\ (5)$ Å
$c = 7.120\ (3)$ Å
$V = 1695.4\ (12)$ Å^3
$Z = 4$
$F(000) = 744$
$D_x = 1.4$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2698 reflections
$\theta = 2.3–28.5°$
$\mu = 0.63$ mm^{-1}
$T = 150$ K
Prism, colourless
0.16 × 0.13 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
10760 measured reflections
3584 independent reflections
2409 reflections with $I > 2\sigma(I)$
$R_{int} = 0.097$
$\theta_{max} = 28.8°$, $\theta_{min} = 2.8°$
$h = -24\rightarrow23$
$k = -18\rightarrow18$
$l = -9\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.134$
$S = 1.05$
3584 reflections
195 parameters
6 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

$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Absolute structure: Flack (1983), 1369 Friedel pairs
Absolute structure parameter: −0.12 (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 $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl2	0.98060 (6)	0.10914 (8)	1.19390 (17)	0.0269 (3)
S1	0.86675 (9)	−0.10667 (11)	1.3286 (2)	0.0412 (4)
Cl1	0.99242 (8)	0.36455 (10)	0.7389 (2)	0.0411 (4)
S2	0.85864 (8)	−0.15845 (11)	1.0567 (2)	0.0395 (4)
O2W	0.9096 (2)	0.1819 (3)	1.5764 (6)	0.0381 (10)
H3W	0.935 (3)	0.233 (3)	1.609 (9)	0.057*
H4W	0.937 (3)	0.150 (4)	1.497 (7)	0.057*
N2	0.8933 (2)	0.0331 (3)	0.8354 (6)	0.0267 (9)
H2A	0.8991	0.0831	0.7542	0.04*
H2B	0.9208	−0.019	0.7989	0.04*
H2C	0.9082	0.0528	0.9489	0.04*
C21	0.7911 (3)	−0.0781 (4)	0.9473 (8)	0.0286 (12)
O1W	1.0599 (3)	0.4223 (3)	1.3483 (6)	0.0534 (12)
H1W	1.043 (4)	0.476 (3)	1.302 (9)	0.08*
H2W	1.039 (4)	0.406 (4)	1.453 (6)	0.08*
N1	0.9146 (2)	−0.2839 (3)	1.5749 (6)	0.0282 (10)
H1A	0.9242	−0.3284	1.6647	0.042*
H1B	0.9388	−0.2271	1.5996	0.042*
H1C	0.9298	−0.3079	1.4647	0.042*
C26	0.8140 (2)	0.0039 (3)	0.8427 (7)	0.0218 (10)
C14	0.7102 (3)	−0.3103 (4)	1.6647 (8)	0.0317 (12)
H14	0.6782	−0.3509	1.7342	0.038*
C12	0.7275 (3)	−0.1730 (4)	1.4523 (8)	0.0332 (13)
H12	0.7073	−0.1212	1.3811	0.04*
C25	0.7627 (3)	0.0625 (3)	0.7478 (8)	0.0272 (11)
H25	0.7787	0.1168	0.6768	0.033*
C15	0.7858 (3)	−0.3249 (3)	1.6726 (7)	0.0268 (11)
H15	0.8055	−0.3753	1.7482	0.032*
C11	0.8050 (3)	−0.1876 (3)	1.4566 (7)	0.0255 (11)
C23	0.6638 (3)	−0.0391 (4)	0.8641 (8)	0.0395 (14)
H23	0.6128	−0.0526	0.8741	0.047*

C24	0.6876 (3)	0.0396 (4)	0.7590 (8)	0.0345 (12)
H24	0.6528	0.0784	0.6943	0.041*
C16	0.8335 (3)	−0.2645 (3)	1.5676 (7)	0.0237 (10)
C13	0.6811 (3)	−0.2350 (4)	1.5534 (8)	0.0381 (13)
H13	0.6294	−0.2262	1.5468	0.046*
C22	0.7156 (3)	−0.1002 (4)	0.9572 (8)	0.0354 (13)
H22	0.6992	−0.1554	1.0255	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0198 (5)	0.0332 (6)	0.0276 (7)	−0.0025 (5)	−0.0034 (6)	0.0026 (5)
S1	0.0445 (9)	0.0428 (7)	0.0364 (8)	−0.0186 (7)	−0.0119 (8)	0.0133 (6)
Cl1	0.0422 (8)	0.0424 (7)	0.0388 (9)	−0.0023 (5)	−0.0125 (7)	0.0027 (6)
S2	0.0429 (8)	0.0445 (7)	0.0310 (8)	0.0133 (6)	0.0111 (8)	0.0111 (6)
O2W	0.040 (2)	0.043 (2)	0.031 (3)	−0.0078 (17)	−0.002 (2)	0.0002 (18)
N2	0.029 (2)	0.030 (2)	0.021 (2)	0.0051 (16)	−0.001 (2)	−0.0027 (17)
C21	0.034 (3)	0.032 (3)	0.019 (3)	0.001 (2)	0.004 (3)	−0.007 (2)
O1W	0.072 (3)	0.051 (3)	0.038 (3)	0.019 (2)	0.003 (3)	−0.003 (2)
N1	0.030 (2)	0.030 (2)	0.025 (3)	−0.0031 (17)	0.000 (2)	−0.0016 (18)
C26	0.022 (2)	0.028 (2)	0.015 (3)	0.0005 (18)	0.003 (2)	−0.0089 (19)
C14	0.028 (3)	0.044 (3)	0.023 (3)	−0.007 (2)	0.002 (3)	−0.004 (2)
C12	0.038 (3)	0.035 (3)	0.027 (3)	0.004 (2)	−0.002 (3)	−0.006 (2)
C25	0.030 (3)	0.030 (2)	0.021 (3)	0.005 (2)	−0.003 (3)	−0.006 (2)
C15	0.033 (3)	0.026 (2)	0.021 (3)	−0.0076 (19)	0.000 (3)	−0.0043 (19)
C11	0.030 (3)	0.028 (2)	0.019 (3)	−0.008 (2)	0.002 (2)	−0.006 (2)
C23	0.026 (3)	0.062 (4)	0.030 (4)	−0.006 (3)	0.002 (3)	−0.015 (3)
C24	0.027 (3)	0.046 (3)	0.030 (3)	0.005 (2)	−0.008 (3)	−0.008 (2)
C16	0.024 (2)	0.027 (2)	0.020 (3)	−0.0046 (18)	0.001 (2)	−0.010 (2)
C13	0.024 (3)	0.052 (3)	0.038 (4)	0.000 (2)	0.009 (3)	−0.017 (3)
C22	0.030 (3)	0.049 (3)	0.028 (3)	−0.008 (3)	0.005 (3)	−0.003 (2)

Geometric parameters (Å, º)

S1—C11	1.792 (5)	C14—C15	1.364 (6)
S1—S2	2.061 (2)	C14—C13	1.380 (8)
S2—C21	1.791 (5)	C14—H14	0.93
O2W—H3W	0.86 (2)	C12—C13	1.375 (8)
O2W—H4W	0.86 (2)	C12—C11	1.396 (7)
N2—C26	1.468 (6)	C12—H12	0.93
N2—H2A	0.89	C25—C24	1.375 (7)
N2—H2B	0.89	C25—H25	0.93
N2—H2C	0.89	C15—C16	1.391 (7)
C21—C22	1.380 (7)	C15—H15	0.93
C21—C26	1.386 (7)	C11—C16	1.391 (7)
O1W—H1W	0.852 (19)	C23—C24	1.358 (8)
O1W—H2W	0.858 (19)	C23—C22	1.399 (8)
N1—C16	1.469 (6)	C23—H23	0.93

N1—H1A	0.89	C24—H24	0.93
N1—H1B	0.89	C13—H13	0.93
N1—H1C	0.89	C22—H22	0.93
C26—C25	1.380 (7)		

C11—S1—S2	103.43 (17)	C13—C12—H12	120
C21—S2—S1	104.74 (18)	C11—C12—H12	120
H3W—O2W—H4W	106 (6)	C24—C25—C26	119.4 (5)
C26—N2—H2A	109.5	C24—C25—H25	120.3
C26—N2—H2B	109.5	C26—C25—H25	120.3
H2A—N2—H2B	109.5	C14—C15—C16	119.9 (5)
C26—N2—H2C	109.5	C14—C15—H15	120
H2A—N2—H2C	109.5	C16—C15—H15	120
H2B—N2—H2C	109.5	C16—C11—C12	118.5 (4)
C22—C21—C26	118.9 (5)	C16—C11—S1	120.7 (4)
C22—C21—S2	120.3 (4)	C12—C11—S1	120.8 (4)
C26—C21—S2	120.6 (4)	C24—C23—C22	120.4 (5)
H1W—O1W—H2W	114 (3)	C24—C23—H23	119.8
C16—N1—H1A	109.5	C22—C23—H23	119.8
C16—N1—H1B	109.5	C23—C24—C25	120.5 (5)
H1A—N1—H1B	109.5	C23—C24—H24	119.7
C16—N1—H1C	109.5	C25—C24—H24	119.7
H1A—N1—H1C	109.5	C15—C16—C11	120.7 (4)
H1B—N1—H1C	109.5	C15—C16—N1	118.7 (4)
C25—C26—C21	121.0 (4)	C11—C16—N1	120.6 (4)
C25—C26—N2	118.1 (4)	C12—C13—C14	120.9 (5)
C21—C26—N2	120.8 (4)	C12—C13—H13	119.5
C15—C14—C13	120.0 (5)	C14—C13—H13	119.5
C15—C14—H14	120	C21—C22—C23	119.6 (5)
C13—C14—H14	120	C21—C22—H22	120.2
C13—C12—C11	120.0 (5)	C23—C22—H22	120.2

C11—S1—S2—C21	96.8 (2)	C22—C23—C24—C25	−2.1 (8)
S1—S2—C21—C22	−87.5 (5)	C26—C25—C24—C23	0.7 (8)
S1—S2—C21—C26	96.2 (4)	C14—C15—C16—C11	1.2 (7)
C22—C21—C26—C25	−0.7 (8)	C14—C15—C16—N1	−178.3 (4)
S2—C21—C26—C25	175.7 (4)	C12—C11—C16—C15	−0.3 (7)
C22—C21—C26—N2	177.1 (4)	S1—C11—C16—C15	177.5 (4)
S2—C21—C26—N2	−6.5 (6)	C12—C11—C16—N1	179.1 (4)
C21—C26—C25—C24	0.7 (7)	S1—C11—C16—N1	−3.0 (6)
N2—C26—C25—C24	−177.1 (5)	C11—C12—C13—C14	2.1 (8)
C13—C14—C15—C16	−0.4 (7)	C15—C14—C13—C12	−1.2 (8)
C13—C12—C11—C16	−1.3 (7)	C26—C21—C22—C23	−0.8 (8)
C13—C12—C11—S1	−179.1 (4)	S2—C21—C22—C23	−177.2 (4)
S2—S1—C11—C16	103.3 (4)	C24—C23—C22—C21	2.2 (9)
S2—S1—C11—C12	−78.8 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1*W*^{i}	0.89	1.83	2.723 (6)	178
N1—H1*B*···Cl2^{i}	0.89	2.24	3.108 (4)	166
N1—H1*C*···Cl1^{i}	0.89	2.25	3.103 (4)	160
N2—H2*A*···O2*W*^{ii}	0.89	1.84	2.727 (6)	177
N2—H2*B*···Cl2^{iii}	0.89	2.26	3.111 (4)	160
N2—H2*C*···Cl2	0.89	2.30	3.157 (4)	163
O2*W*—H4*W*···Cl2	0.86 (5)	2.36 (5)	3.157 (5)	155 (5)
O2*W*—H3*W*···Cl1^{iv}	0.85 (5)	2.23 (5)	3.078 (4)	171 (6)
O1*W*—H1*W*···Cl1^{v}	0.85 (5)	2.27 (5)	3.096 (5)	167 (5)
O1*W*—H2*W*···Cl1^{iv}	0.86 (5)	2.27 (5)	3.127 (5)	176 (7)

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