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2,2′-Diamino-5,5′-dimethyl-4,4′-bi-1,3-thiazolium tetrachloridozincate(II)

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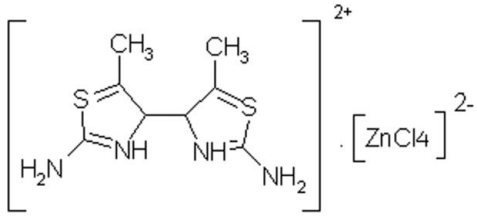
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.029; wR factor = 0.077; data-to-parameter ratio = 19.5.

In the dianion of the title compound, $(C_8H_{12}N_4S_2)[ZnCl_4]$, the Zn^{II} ion is in a slightly distorted tetrahedral environment. In the cation, the mean planes of the thiazole rings form a dihedral angle of 67.81 (6) Å. In the crystal structure, anions and cations are linked into a three-dimensional network *via* intermolecular N—H···Cl hydrogen bonds.

Related literature

For the potential applications of metal-organic coordination compounds as antitumor drugs, polymers and luminescent materials, see: Hosseinian & Mahjoub (2006). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$(C_8H_{12}N_4S_2)[ZnCl_4]$
M_r = 435.51
Triclinic, $P\overline{1}$
a = 8.9149 (6) Å
b = 9.6487 (7) Å
c = 11.7361 (8) Å
α = 65.754 (5)°
β = 89.126 (5)°
γ = 62.496 (5)°
V = 797.22 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.46 mm^{-1}
T = 120 K
0.30 × 0.30 × 0.25 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.484, T_{max} = 0.535
6168 measured reflections
3368 independent reflections
3152 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
S = 1.05
3368 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.2531 (6)	Zn1—Cl2	2.2707 (6)
Zn1—Cl3	2.2642 (6)	Zn1—Cl4	2.2788 (6)
Cl1—Zn1—Cl3	110.69 (3)	Cl1—Zn1—Cl4	111.25 (3)
Cl1—Zn1—Cl2	110.34 (2)	Cl3—Zn1—Cl4	108.19 (3)
Cl3—Zn1—Cl2	106.06 (2)	Cl2—Zn1—Cl4	110.16 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2^{i}	0.87	2.78	3.440 (3)	133
N2—H2A···Cl4^{ii}	0.89	2.79	3.487 (2)	137
N3—H3A···Cl4^{iii}	0.87	2.50	3.322 (3)	156
N3—H3B···Cl2^{iv}	0.83	2.36	3.196 (3)	179
N4—H4A···Cl1^{v}	0.87	2.44	3.280 (3)	162
N4—H4B···Cl3^{ii}	0.89	2.38	3.189 (2)	151

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2898).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
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Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
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supporting information

Acta Cryst. (2009). E**65**, m1456 [https://doi.org/10.1107/S1600536809042007]

2,2′-Diamino-5,5′-dimethyl-4,4′-bi-1,3-thiazolium tetrachloridozincate(II)

Akram Hosseinian and Ali Reza Mahjoub

S1. Comment

In coordination chemistry there are many studies on the interaction of Zn^{II} ions with biomolecules (Hosseinian & Mahjoub, 2006: and references cited therein). Coordination between an organic ligand and Zn^{II} ions improves or modifies the properties of biological molecules. In the human body the second abundant trace metal is zinc and it can be considered as a non toxic metal. The presence of zinc is vital to 300 enzyme structures, regulations and catalytic actions. As part of our research in the field of Zn^{II} complexes of organic molecules the crystal structure of the title complexes is presented herein.

The asymmetric unit of the title compound is shown in Fig. 1. The bond lengths have normal values (Allen *et al.*, 1987). In the crystal structure, anions and cations are linked into a three-dimensional network via intermolecular N-H···Cl hydrogen bonds. In addition, there are fairly close intermolecular S···Cl contacts ca. 3.24Å.

S2. Experimental

To a methanol solution of $ZnCl_2$ (1 mmol, 0. 136 g) was added, 2,2′-Diamino-5,5′-Dimethyl-4,4′-bithiazole (dadmbtz) (1 mmol, 0. 226 g). The mixture was refluxed for 2 h. The solution was cooled and filtrate was slow evaporated at room temperature. After 12 days, yellow block shaped crystals of the title compound were obtained.

S3. Refinement

The hydrogen atoms boned to N atoms were located in difference Fourier maps and refined in 'as found′ positions in a riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(N)$. H atoms boned to C atoms were placed in calculated positions and refined in a riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms.

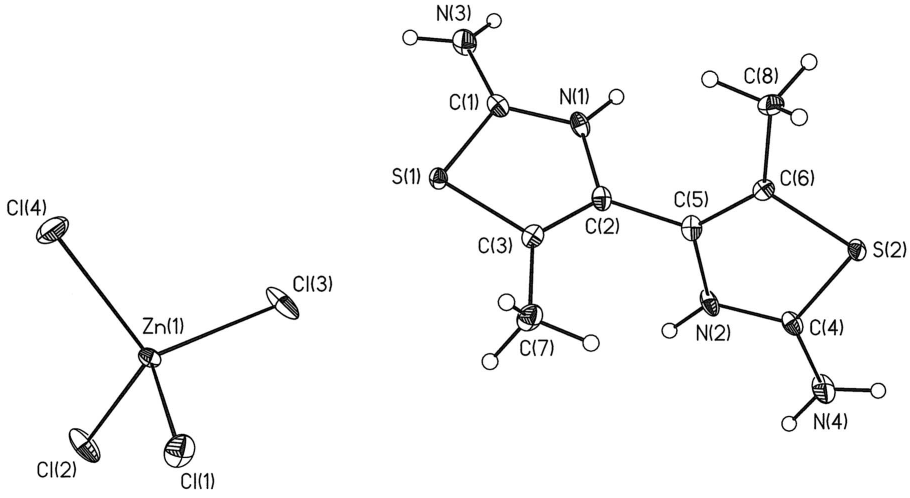

Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

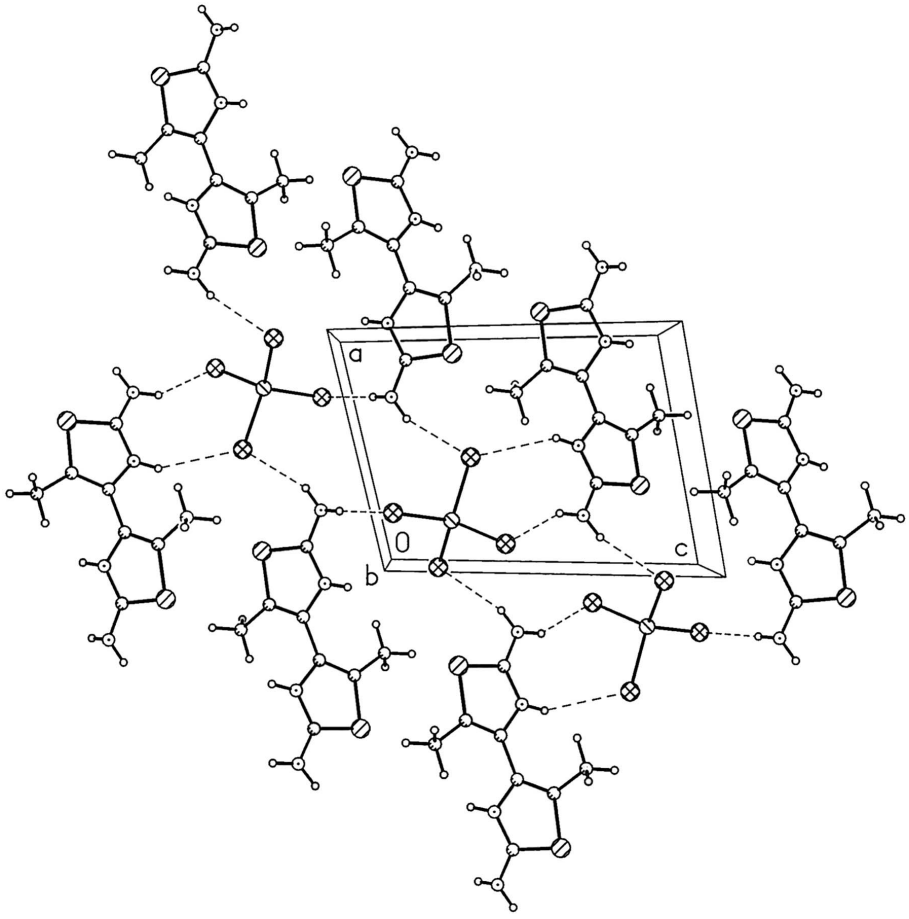

Figure 2

Part of the crystal structure with dashed lines indicating hydrogen bonds. Only H atoms involved in hydrogen bonds are shown.

2,2′-Diamino-5,5′-dimethyl-4,4′-bi-1,3-thiazolium tetrachloridozincate(II)

Crystal data

$(C_8H_{12}N_4S_2)[ZnCl_4]$
$M_r = 435.51$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.9149$ (6) Å
$b = 9.6487$ (7) Å
$c = 11.7361$ (8) Å
$\alpha = 65.754$ (5)°
$\beta = 89.126$ (5)°
$\gamma = 62.496$ (5)°
$V = 797.22$ (12) Å^3
$Z = 2$
$F(000) = 436$
$D_x = 1.814$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5086 reflections
$\theta = 2.5$–$28.0°$
$\mu = 2.46$ mm^{-1}
$T = 120$ K
Prism, yellow
0.30 × 0.30 × 0.25 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.484$, $T_{max} = 0.535$
6168 measured reflections
3368 independent reflections
3152 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.0°$, $\theta_{min} = 2.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.05$
3368 reflections
173 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 1.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0179 (16)

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}
Zn1	0.77593 (3)	0.86751 (3)	0.75845 (2)	0.00894 (10)
Cl1	0.97516 (7)	0.91131 (8)	0.83034 (6)	0.01767 (14)

Cl2	0.74022 (9)	0.66200 (8)	0.92201 (5)	0.01983 (15)
Cl3	0.86565 (9)	0.76054 (8)	0.61574 (5)	0.02216 (15)
Cl4	0.51769 (7)	1.12209 (8)	0.66076 (6)	0.02434 (16)
S1	−0.09151 (6)	0.72895 (7)	0.35203 (5)	0.00929 (13)
S2	0.63717 (7)	0.43870 (7)	0.16847 (5)	0.01112 (13)
N1	0.0383 (2)	0.6517 (3)	0.17917 (18)	0.0122 (4)
H1A	0.0506	0.6334	0.1118	0.015*
N2	0.4708 (3)	0.3426 (3)	0.33075 (19)	0.0131 (4)
H2A	0.4395	0.2785	0.3941	0.016*
N3	−0.2658 (3)	0.7787 (3)	0.1413 (2)	0.0169 (4)
H3A	−0.3569	0.8179	0.1731	0.020*
H3B	−0.2635	0.7475	0.0846	0.020*
N4	0.7579 (3)	0.1184 (3)	0.3653 (2)	0.0194 (4)
H4A	0.8469	0.0961	0.3298	0.023*
H4B	0.7476	0.0411	0.4354	0.023*
C1	−0.1143 (3)	0.7216 (3)	0.2097 (2)	0.0111 (4)
C2	0.1792 (3)	0.6012 (3)	0.2685 (2)	0.0106 (4)
C3	0.1324 (3)	0.6365 (3)	0.3667 (2)	0.0101 (4)
C4	0.6262 (3)	0.2791 (3)	0.3020 (2)	0.0118 (4)
C5	0.3552 (3)	0.5195 (3)	0.2475 (2)	0.0111 (4)
C6	0.4236 (3)	0.5932 (3)	0.1553 (2)	0.0099 (4)
C7	0.2430 (3)	0.6131 (3)	0.4750 (2)	0.0159 (5)
H7A	0.3644	0.5591	0.4682	0.024*
H7B	0.2304	0.5370	0.5564	0.024*
H7C	0.2066	0.7276	0.4715	0.024*
C8	0.3418 (3)	0.7794 (3)	0.0535 (2)	0.0145 (5)
H8A	0.2226	0.8453	0.0610	0.022*
H8B	0.3411	0.7821	−0.0309	0.022*
H8C	0.4081	0.8325	0.0638	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01114 (14)	0.00947 (15)	0.00651 (15)	−0.00633 (11)	0.00174 (10)	−0.00251 (11)
Cl1	0.0133 (3)	0.0225 (3)	0.0240 (3)	−0.0108 (2)	0.0033 (2)	−0.0142 (3)
Cl2	0.0385 (3)	0.0201 (3)	0.0117 (3)	−0.0224 (3)	0.0131 (2)	−0.0079 (2)
Cl3	0.0459 (4)	0.0147 (3)	0.0096 (3)	−0.0169 (3)	0.0118 (3)	−0.0070 (2)
Cl4	0.0107 (3)	0.0210 (3)	0.0218 (3)	−0.0008 (2)	0.0008 (2)	−0.0011 (2)
S1	0.0094 (2)	0.0116 (3)	0.0101 (3)	−0.0057 (2)	0.00321 (19)	−0.0072 (2)
S2	0.0108 (2)	0.0074 (3)	0.0111 (3)	−0.0043 (2)	0.00468 (19)	−0.0010 (2)
N1	0.0165 (9)	0.0154 (10)	0.0116 (9)	−0.0103 (8)	0.0072 (7)	−0.0096 (8)
N2	0.0187 (9)	0.0095 (9)	0.0126 (9)	−0.0087 (8)	0.0098 (8)	−0.0047 (8)
N3	0.0162 (9)	0.0258 (11)	0.0145 (10)	−0.0111 (8)	0.0032 (8)	−0.0134 (9)
N4	0.0217 (10)	0.0070 (9)	0.0184 (10)	−0.0043 (8)	0.0096 (8)	−0.0001 (8)
C1	0.0161 (10)	0.0096 (10)	0.0106 (10)	−0.0081 (9)	0.0045 (8)	−0.0052 (8)
C2	0.0124 (10)	0.0098 (10)	0.0135 (11)	−0.0081 (8)	0.0058 (8)	−0.0059 (9)
C3	0.0107 (9)	0.0075 (10)	0.0143 (11)	−0.0058 (8)	0.0029 (8)	−0.0054 (8)
C4	0.0168 (10)	0.0091 (10)	0.0110 (10)	−0.0076 (9)	0.0059 (8)	−0.0047 (9)

C5	0.0128 (10)	0.0099 (10)	0.0150 (11)	−0.0072 (8)	0.0056 (8)	−0.0077 (9)
C6	0.0101 (9)	0.0085 (10)	0.0116 (10)	−0.0044 (8)	0.0018 (8)	−0.0053 (9)
C7	0.0121 (10)	0.0199 (12)	0.0187 (12)	−0.0077 (9)	0.0019 (9)	−0.0116 (10)
C8	0.0125 (10)	0.0106 (11)	0.0130 (11)	−0.0035 (9)	0.0001 (9)	−0.0016 (9)

Geometric parameters (Å, º)

Zn1—Cl1	2.2531 (6)	N3—H3B	0.8322
Zn1—Cl3	2.2642 (6)	N4—C4	1.317 (3)
Zn1—Cl2	2.2707 (6)	N4—H4A	0.8693
Zn1—Cl4	2.2788 (6)	N4—H4B	0.8932
S1—C1	1.720 (2)	C2—C3	1.340 (3)
S1—C3	1.746 (2)	C2—C5	1.466 (3)
S2—C4	1.729 (2)	C3—C7	1.495 (3)
S2—C6	1.752 (2)	C5—C6	1.340 (3)
N1—C1	1.330 (3)	C6—C8	1.497 (3)
N1—C2	1.403 (3)	C7—H7A	0.9800
N1—H1A	0.8730	C7—H7B	0.9800
N2—C4	1.334 (3)	C7—H7C	0.9800
N2—C5	1.402 (3)	C8—H8A	0.9800
N2—H2A	0.8877	C8—H8B	0.9800
N3—C1	1.324 (3)	C8—H8C	0.9800
N3—H3A	0.8747		

Cl1—Zn1—Cl3	110.69 (3)	N1—C2—C5	119.60 (19)
Cl1—Zn1—Cl2	110.34 (2)	C2—C3—C7	128.8 (2)
Cl3—Zn1—Cl2	106.06 (2)	C2—C3—S1	110.42 (16)
Cl1—Zn1—Cl4	111.25 (3)	C7—C3—S1	120.71 (16)
Cl3—Zn1—Cl4	108.19 (3)	N4—C4—N2	126.2 (2)
Cl2—Zn1—Cl4	110.16 (3)	N4—C4—S2	122.76 (17)
C1—S1—C3	91.07 (10)	N2—C4—S2	110.99 (17)
C4—S2—C6	91.00 (11)	C6—C5—N2	113.51 (19)
C1—N1—C2	114.04 (18)	C6—C5—C2	127.9 (2)
C1—N1—H1A	123.1	N2—C5—C2	118.63 (19)
C2—N1—H1A	122.8	C5—C6—C8	128.4 (2)
C4—N2—C5	114.14 (18)	C5—C6—S2	110.35 (17)
C4—N2—H2A	123.8	C8—C6—S2	121.27 (16)
C5—N2—H2A	121.9	C3—C7—H7A	109.5
C1—N3—H3A	117.0	C3—C7—H7B	109.5
C1—N3—H3B	116.7	H7A—C7—H7B	109.5
H3A—N3—H3B	123.6	C3—C7—H7C	109.5
C4—N4—H4A	114.3	H7A—C7—H7C	109.5
C4—N4—H4B	119.7	H7B—C7—H7C	109.5
H4A—N4—H4B	125.8	C6—C8—H8A	109.5
N3—C1—N1	125.5 (2)	C6—C8—H8B	109.5
N3—C1—S1	123.29 (17)	H8A—C8—H8B	109.5
N1—C1—S1	111.22 (16)	C6—C8—H8C	109.5
C3—C2—N1	113.22 (18)	H8A—C8—H8C	109.5

C3—C2—C5	127.2 (2)	H8B—C8—H8C	109.5
C2—N1—C1—N3	−179.8 (2)	C6—S2—C4—N4	−178.7 (2)
C2—N1—C1—S1	0.0 (2)	C6—S2—C4—N2	0.43 (18)
C3—S1—C1—N3	−179.3 (2)	C4—N2—C5—C6	−1.1 (3)
C3—S1—C1—N1	0.85 (17)	C4—N2—C5—C2	178.5 (2)
C1—N1—C2—C3	−1.2 (3)	C3—C2—C5—C6	−112.4 (3)
C1—N1—C2—C5	179.0 (2)	N1—C2—C5—C6	67.4 (3)
N1—C2—C3—C7	−175.7 (2)	C3—C2—C5—N2	68.0 (3)
C5—C2—C3—C7	4.1 (4)	N1—C2—C5—N2	−112.2 (2)
N1—C2—C3—S1	1.8 (2)	N2—C5—C6—C8	−177.4 (2)
C5—C2—C3—S1	−178.40 (18)	C2—C5—C6—C8	3.0 (4)
C1—S1—C3—C2	−1.52 (18)	N2—C5—C6—S2	1.3 (2)
C1—S1—C3—C7	176.21 (19)	C2—C5—C6—S2	−178.20 (18)
C5—N2—C4—N4	179.3 (2)	C4—S2—C6—C5	−1.01 (17)
C5—N2—C4—S2	0.2 (2)	C4—S2—C6—C8	177.88 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl2^{i}	0.87	2.78	3.440 (3)	133
N2—H2*A*···Cl4^{ii}	0.89	2.79	3.487 (2)	137
N3—H3*A*···Cl4^{iii}	0.87	2.50	3.322 (3)	156
N3—H3*B*···Cl2^{iv}	0.83	2.36	3.196 (3)	179
N4—H4*A*···Cl1^{v}	0.87	2.44	3.280 (3)	162
N4—H4*B*···Cl3^{ii}	0.89	2.38	3.189 (2)	151

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