Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(2-amino-1,3-benzothiazol-3-ium) tetrachloridozincate(II)

Riadh Kefi,[a] Erwann Jeanneau,[b] Frédéric Lefebvre[c] and Cherif Ben Nasr[a]*

[a]Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia, [b]Universtié Lyon 1, Centre de Diffractométrie Henri Longchambon, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France, and [c]Laboratoire de Chimie Organometallique de Surface (LCOMS), École Supérieure de Chimie Physique Électronique, 69622 Villeurbanne Cedex, France
Correspondence e-mail: cherif_bennasr@yahoo.fr

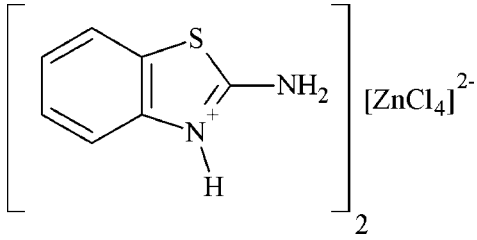
Received 8 March 2011; accepted 26 April 2011

Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.008 Å; R factor = 0.054; wR factor = 0.111; data-to-parameter ratio = 20.6.

The asymmetric unit of the title compound, $(C_7H_7N_2S)_2[ZnCl_4]$, contains a network of 2-aminobenzothiazolium cations and tetrahedral $[ZnCl_4]^{2-}$ anions. The crystal packing is influenced by cation-to-anion N—H···Cl and C—H···Cl hydrogen bonds. The $[ZnCl_4]^{2-}$ anions have a distorded tetrahedral geometry. Intermolecular π–π stacking interactions are present between neighboring benzene rings, thiazole and benzene rings and neighboring thiazole rings [centroid–centroid distances = 3.711 (2), 3.554 (1), 3.536 (2) and 3.572 (1) Å].

Related literature

For common applications of organic–inorganic hybrid materials, see: Bringley & Rajeswaran (2006); Pierpont & Jung (1994); Dai *et al.* (2002). For the geometry around the zinc atom, see: Harrison (2005). For the weighting scheme used, see: Prince (1982); Watkin (1994) and for the extinction correction, see: Larson (1970).



Experimental

Crystal data

$(C_7H_7N_2S)_2[ZnCl_4]$
M_r = 509.61
Triclinic, $P\overline{1}$
a = 7.543 (1) Å
b = 7.828 (1) Å
c = 17.109 (2) Å
α = 94.250 (1)°
β = 100.930 (1)°
γ = 92.465 (1)°
V = 987.5 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.00 mm^{-1}
T = 110 K
0.49 × 0.23 × 0.14 mm

Data collection

Agilent Xcalibur Atlas Gemini ultra diffractometer
Absorption correction: analytical [using a multifaceted crystal model based on expressions derived by Clark & Reid (1995), implemented in *CrysAlis PRO* (Agilent, 2010)]
T_{min} = 0.498, T_{max} = 0.771
10196 measured reflections
4685 independent reflections
3630 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.111
S = 0.94
4685 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.03 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N8—H81···Cl3^{i}	0.88	2.43	3.190 (5)	145
N15—H151···Cl3	0.86	2.42	3.235 (5)	157
N15—H152···Cl2^{i}	0.86	2.42	3.274 (5)	176
N25—H251···Cl5^{ii}	0.86	2.41	3.215 (5)	155
N16—H161···Cl4^{ii}	0.86	2.34	3.196 (5)	177
N16—H162···Cl2^{iii}	0.86	2.37	3.215 (5)	166
C20—H201···Cl2	0.93	2.69	3.473 (6)	142
C22—H221···Cl5^{iv}	0.94	2.78	3.701 (5)	167
C11—H111···Cl4^{v}	0.93	2.73	3.592 (6)	154

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

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *CRYSTALS*.

We would like to acknowledge the support provided by the Secretary of State for Scientific Research and Technology of Tunisia.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VN2006).

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supporting information

Acta Cryst. (2011). E**67**, m654–m655 [doi:10.1107/S1600536811015753]

Bis(2-amino-1,3-benzothiazol-3-ium) tetrachloridozincate(II)

Riadh Kefi, Erwann Jeanneau, Frédéric Lefebvre and Cherif Ben Nasr

S1. Comment

Inorganic-organic hybrid compounds provide a class of materials displaying interesting technological importance (Bringley & Rajeswaran, 2006; Pierpont & Jung, 1994; Dai *et al.*, 2002). We report the crystal structure of one such compound, $(C_7H_7N_2S)_2[ZnCl_4]$ (I), formed from the reaction of 2-aminobenzothiazole with zinc chloride. As shown in Fig.1, only the nitrogen atom of the thiazole ring of the title compound is protonated, but not that of the amine group. Thus, to ensure charge equilibrium, the structure associates each tetrachlorizincate anion with two (2-aminobenzothiazolium) cations. Fig.2 shows that the atomic arrangement of the title hybrid material can be described as inorganic $ZnCl_4^{2-}$ units isolated from each other by the organic cations. The different entities are held together by coulombic attraction and multiple hydrogen bonds to form a three dimensional network. The tetraclorozincate anion geometrical features show that the Zn—Cl bond lengths vary between 2.245 (1) and 2.282 (1) Å and the Cl—Zn—Cl angles range from 103.35 (5) to 112.21 (5) °. These values, which are in good agreement with those reported previously, clearly indicate that the $[ZnCl_4]^{2-}$ anion has a slightly distorted tetrahedral stereochemistry (Harrison, 2005). Intermolecular π-π stacking interactions are present between neighboring phenyl rings (centroid-centroid distance = 3.711 (2) Å), thiazole-phenyl rings (centroid-centroid distance = 3.554 (1) Å) and thiazole-thiazole rings (centroid-centroid distances = 3.536 (2) and 3.572 (1) Å) (Fig. 3).

S2. Experimental

A mixture of an aqueous solution of 2-aminobenzothiazole (3 mmol, 0.450 g), zinc chloride (1.5 mmol, 0.297 g) and HCl (10 ml, 0.3 *M*) in a Petri dish was slowly evaporated at room temperature. Colorless single crystals of the title compound were isolated after several days (yield 58%).

S3. Refinement

All non hydrogen atoms were refined anisotropically. The H atoms were all located in a difference map. They were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

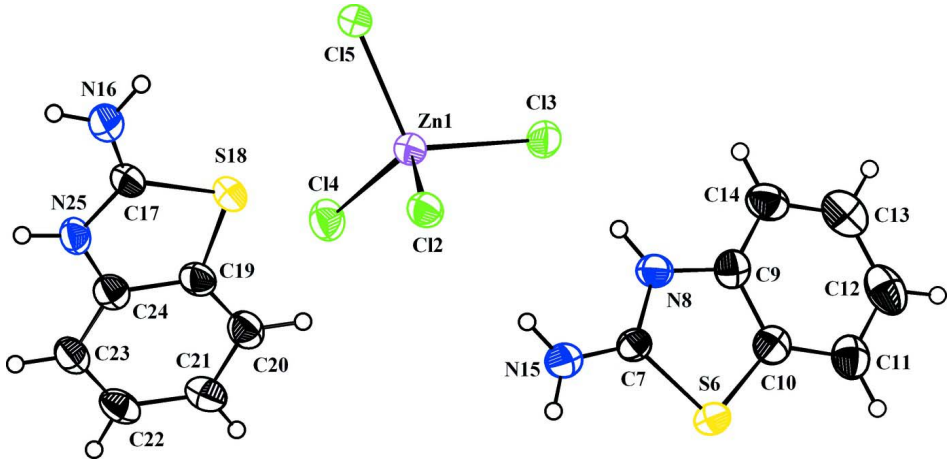

Figure 1

View of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms.

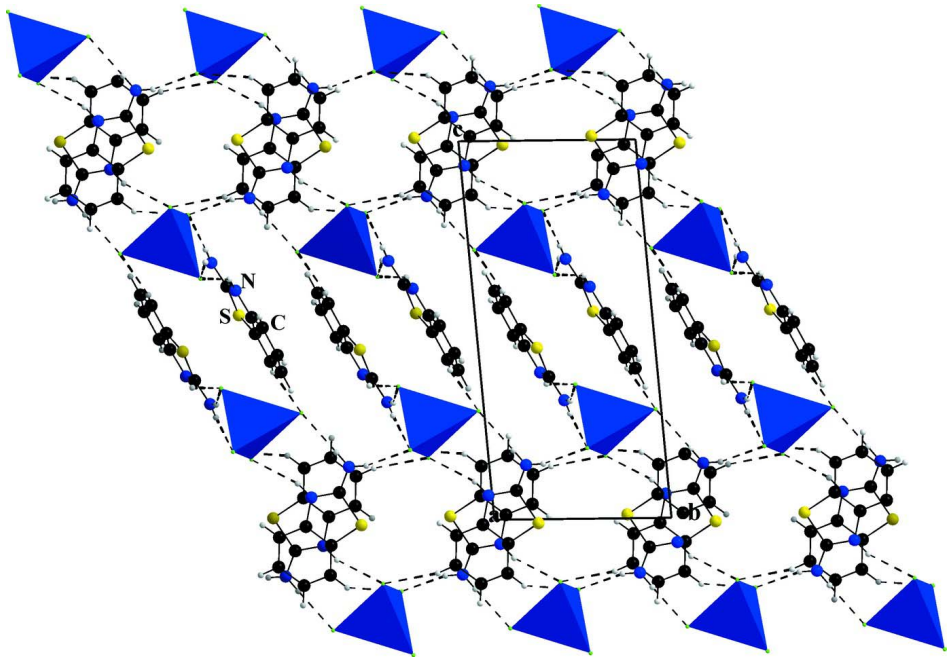

Figure 2

The crystal packing of the title compound viewed along the *a* axis. Hydrogen bonds are denoted by dotted lines. $ZnCl_4$ is given in tetrahedral representation.

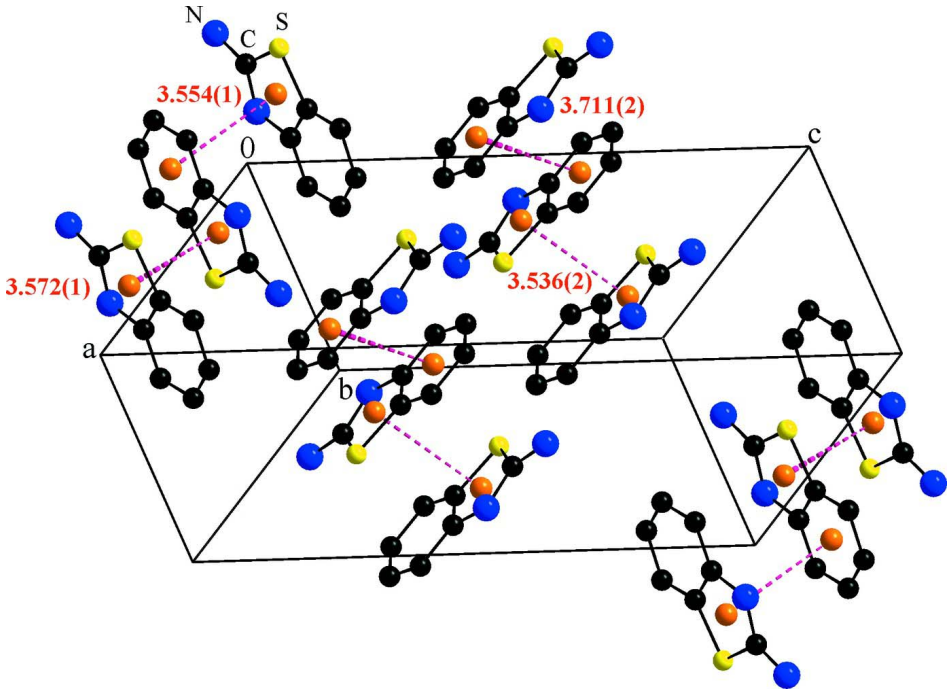

Figure 3

π–π stacking interactions in $(C_7H_7N_2S)_2[ZnCl_4]$. The centroids of the rings are indicated by orange spheres.

Bis(2-amino-1,3-benzothiazol-3-ium) tetrachloridozincate(II)

Crystal data

$(C_7H_7N_2S)_2[ZnCl_4]$
$M_r = 509.61$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.543$ (1) Å
$b = 7.828$ (1) Å
$c = 17.109$ (2) Å
$\alpha = 94.250$ (1)°
$\beta = 100.930$ (1)°
$\gamma = 92.465$ (1)°
$V = 987.5$ (2) Å^3
$Z = 2$
$F(000) = 512$
$D_x = 1.714$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
Cell parameters from 3221 reflections
$\theta = 3.4$–$29.4°$
$\mu = 2.00$ mm^{-1}
$T = 110$ K
Plate, colorless
0.49 × 0.23 × 0.14 mm

Data collection

Agilent Xcalibur Atlas Gemini ultra diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.4685 pixels mm^{-1}
ω scans
Absorption correction: analytical [using a multifaceted crystal model based on expressions derived by Clark & Reid (1995), implemented in *CrysAlis PRO* (Agilent, 2010)]
$T_{min} = 0.498$, $T_{max} = 0.771$
10196 measured reflections
4685 independent reflections
3630 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 29.5°$, $\theta_{min} = 3.4°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -22 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.111$
$S = 0.94$
4685 reflections
227 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 0.230E + 04 0.321E + 04 0.179E + 04 528.
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -1.23$ e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 20 (3)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.49814 (8)	0.31162 (7)	0.75071 (4)	0.0243
Cl2	0.29039 (16)	0.43801 (16)	0.81360 (8)	0.0274
Cl3	0.50293 (17)	0.47084 (17)	0.64494 (8)	0.0312
Cl4	0.43482 (19)	0.03141 (16)	0.71252 (8)	0.0327
Cl5	0.76785 (17)	0.33826 (17)	0.83422 (9)	0.0348
S6	0.80197 (17)	0.66813 (17)	0.54732 (8)	0.0271
C7	0.9702 (6)	0.6161 (6)	0.6239 (3)	0.0238
N8	1.1348 (6)	0.6629 (5)	0.6125 (3)	0.0270
C9	1.1369 (7)	0.7391 (6)	0.5413 (3)	0.0259
C10	0.9660 (7)	0.7508 (6)	0.4981 (3)	0.0274
C11	0.9378 (8)	0.8213 (7)	0.4244 (3)	0.0334
C12	1.0891 (9)	0.8761 (7)	0.3964 (4)	0.0399
C13	1.2610 (8)	0.8636 (7)	0.4407 (4)	0.0371
C14	1.2880 (7)	0.7940 (7)	0.5137 (4)	0.0332
N15	0.9376 (6)	0.5413 (6)	0.6864 (3)	0.0301
N16	0.4666 (6)	0.2078 (6)	1.1438 (3)	0.0318
C17	0.3739 (7)	0.1401 (6)	1.0765 (3)	0.0267
S18	0.33424 (17)	0.24680 (16)	0.98962 (8)	0.0267
C19	0.2084 (7)	0.0651 (7)	0.9370 (3)	0.0272
C20	0.1203 (7)	0.0453 (7)	0.8583 (3)	0.0289
C21	0.0273 (7)	−0.1091 (7)	0.8316 (3)	0.0305
C22	0.0266 (7)	−0.2424 (6)	0.8813 (3)	0.0298
C23	0.1155 (7)	−0.2224 (6)	0.9596 (3)	0.0279
C24	0.2056 (7)	−0.0673 (6)	0.9873 (3)	0.0258
N25	0.2989 (6)	−0.0203 (5)	1.0642 (3)	0.0256
H111	0.8216	0.8312	0.3963	0.0401*
H121	1.0765	0.9226	0.3472	0.0479*
H131	1.3614	0.9009	0.4205	0.0452*
H141	1.4023	0.7848	0.5425	0.0398*
H201	0.1216	0.1333	0.8250	0.0348*
H211	−0.0354	−0.1254	0.7796	0.0368*

H221	−0.0350	−0.3478	0.8606	0.0360*
H231	0.1136	−0.3105	0.9923	0.0341*
H152	1.0268	0.5160	0.7218	0.0362*
H162	0.5251	0.3062	1.1464	0.0382*
H161	0.4973	0.1448	1.1825	0.0382*
H151	0.8275	0.5082	0.6881	0.0364*
H81	1.2342	0.6334	0.6426	0.0335*
H251	0.3111	−0.0904	1.1014	0.0316*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0209 (3)	0.0234 (3)	0.0286 (3)	0.0006 (2)	0.0037 (2)	0.0055 (2)
Cl2	0.0251 (6)	0.0269 (6)	0.0310 (6)	0.0003 (5)	0.0074 (5)	0.0040 (5)
Cl3	0.0238 (6)	0.0367 (7)	0.0359 (7)	0.0048 (5)	0.0079 (5)	0.0140 (5)
Cl4	0.0414 (7)	0.0246 (6)	0.0303 (6)	−0.0007 (5)	0.0031 (5)	0.0032 (5)
Cl5	0.0256 (6)	0.0321 (7)	0.0434 (8)	−0.0064 (5)	−0.0049 (5)	0.0156 (6)
S6	0.0210 (6)	0.0287 (6)	0.0299 (6)	0.0014 (5)	0.0004 (5)	0.0036 (5)
C7	0.018 (2)	0.024 (2)	0.031 (3)	0.0051 (18)	0.0061 (19)	0.004 (2)
N8	0.022 (2)	0.025 (2)	0.034 (2)	0.0004 (16)	0.0037 (17)	0.0024 (18)
C9	0.028 (3)	0.024 (2)	0.028 (2)	0.0062 (19)	0.009 (2)	0.002 (2)
C10	0.032 (3)	0.021 (2)	0.028 (3)	0.003 (2)	0.004 (2)	−0.003 (2)
C11	0.045 (3)	0.025 (3)	0.029 (3)	−0.001 (2)	0.004 (2)	−0.001 (2)
C12	0.061 (4)	0.026 (3)	0.032 (3)	−0.009 (3)	0.013 (3)	−0.003 (2)
C13	0.043 (3)	0.029 (3)	0.044 (3)	0.002 (2)	0.023 (3)	−0.004 (2)
C14	0.026 (3)	0.030 (3)	0.045 (3)	0.001 (2)	0.010 (2)	0.001 (2)
N15	0.026 (2)	0.035 (2)	0.029 (2)	−0.0015 (18)	0.0020 (18)	0.0060 (19)
N16	0.034 (2)	0.028 (2)	0.032 (2)	−0.0031 (19)	0.0012 (19)	0.0066 (19)
C17	0.023 (2)	0.026 (2)	0.032 (3)	−0.0024 (19)	0.007 (2)	0.006 (2)
S18	0.0268 (6)	0.0231 (6)	0.0308 (6)	−0.0029 (5)	0.0068 (5)	0.0054 (5)
C19	0.021 (2)	0.029 (3)	0.034 (3)	0.0000 (19)	0.010 (2)	0.006 (2)
C20	0.028 (3)	0.027 (3)	0.035 (3)	0.002 (2)	0.011 (2)	0.005 (2)
C21	0.029 (3)	0.031 (3)	0.030 (3)	−0.007 (2)	0.008 (2)	−0.002 (2)
C22	0.029 (3)	0.019 (2)	0.041 (3)	−0.0046 (19)	0.010 (2)	−0.004 (2)
C23	0.028 (3)	0.022 (2)	0.036 (3)	−0.0003 (19)	0.011 (2)	0.004 (2)
C24	0.022 (2)	0.025 (2)	0.032 (3)	0.0034 (19)	0.011 (2)	0.003 (2)
N25	0.028 (2)	0.0190 (19)	0.031 (2)	0.0027 (16)	0.0072 (18)	0.0060 (17)

Geometric parameters (Å, º)

Zn1—Cl2	2.2820 (14)	N15—H152	0.856
Zn1—Cl3	2.2770 (14)	N15—H151	0.865
Zn1—Cl4	2.2462 (14)	N16—C17	1.292 (7)
Zn1—Cl5	2.2452 (14)	N16—H162	0.865
S6—C7	1.728 (5)	N16—H161	0.858
S6—C10	1.750 (5)	C17—S18	1.741 (5)
C7—N8	1.333 (6)	C17—N25	1.340 (6)
C7—N15	1.315 (6)	S18—C19	1.762 (5)

N8—C9	1.397 (6)	C19—C20	1.379 (7)
N8—H81	0.876	C19—C24	1.398 (7)
C9—C10	1.369 (7)	C20—C21	1.372 (7)
C9—C14	1.378 (7)	C20—H201	0.926
C10—C11	1.398 (7)	C21—C22	1.394 (7)
C11—C12	1.383 (8)	C21—H211	0.922
C11—H111	0.926	C22—C23	1.375 (8)
C12—C13	1.384 (9)	C22—H221	0.940
C12—H121	0.932	C23—C24	1.372 (7)
C13—C14	1.384 (8)	C23—H231	0.920
C13—H131	0.934	C24—N25	1.385 (7)
C14—H141	0.917	N25—H251	0.865

Cl2—Zn1—Cl3	103.35 (5)	C7—N15—H152	119.0
Cl2—Zn1—Cl4	114.50 (5)	C7—N15—H151	119.2
Cl3—Zn1—Cl4	112.21 (6)	H152—N15—H151	121.4
Cl2—Zn1—Cl5	108.54 (6)	C17—N16—H162	120.4
Cl3—Zn1—Cl5	110.34 (5)	C17—N16—H161	119.8
Cl4—Zn1—Cl5	107.81 (6)	H162—N16—H161	117.3
C7—S6—C10	90.0 (2)	N16—C17—S18	123.7 (4)
S6—C7—N8	112.2 (4)	N16—C17—N25	124.7 (5)
S6—C7—N15	123.3 (4)	S18—C17—N25	111.6 (4)
N8—C7—N15	124.5 (5)	C17—S18—C19	90.6 (2)
C7—N8—C9	114.5 (4)	S18—C19—C20	128.4 (4)
C7—N8—H81	123.0	S18—C19—C24	110.2 (4)
C9—N8—H81	121.8	C20—C19—C24	121.4 (5)
N8—C9—C10	111.9 (5)	C19—C20—C21	117.2 (5)
N8—C9—C14	126.5 (5)	C19—C20—H201	121.4
C10—C9—C14	121.6 (5)	C21—C20—H201	121.4
S6—C10—C9	111.4 (4)	C20—C21—C22	121.5 (5)
S6—C10—C11	127.5 (4)	C20—C21—H211	119.3
C9—C10—C11	121.1 (5)	C22—C21—H211	119.2
C10—C11—C12	117.4 (6)	C21—C22—C23	121.1 (5)
C10—C11—H111	120.4	C21—C22—H221	119.2
C12—C11—H111	122.1	C23—C22—H221	119.7
C11—C12—C13	120.8 (6)	C22—C23—C24	117.9 (5)
C11—C12—H121	120.2	C22—C23—H231	120.7
C13—C12—H121	118.9	C24—C23—H231	121.4
C12—C13—C14	121.5 (5)	C19—C24—C23	120.9 (5)
C12—C13—H131	119.5	C19—C24—N25	112.3 (4)
C14—C13—H131	119.0	C23—C24—N25	126.8 (5)
C13—C14—C9	117.5 (5)	C24—N25—C17	115.3 (4)
C13—C14—H141	121.0	C24—N25—H251	122.4
C9—C14—H141	121.5	C17—N25—H251	122.2

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H81···Cl3^{i}	0.88	2.43	3.190 (5)	145
N15—H151···Cl3	0.86	2.42	3.235 (5)	157
N15—H152···Cl2^{i}	0.86	2.42	3.274 (5)	176
N25—H251···Cl5^{ii}	0.86	2.41	3.215 (5)	155
N16—H161···Cl4^{ii}	0.86	2.34	3.196 (5)	177
N16—H162···Cl2^{iii}	0.86	2.37	3.215 (5)	166
C20—H201···Cl2	0.93	2.69	3.473 (6)	142
C22—H221···Cl5^{iv}	0.94	2.78	3.701 (5)	167
C11—H111···Cl4^{v}	0.93	2.73	3.592 (6)	154

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