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(4,6-Dimethyl-2-sulfanylidenepyrimidin-1-ium) trichlorido(thiourea-κS)zinc(II)

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The title compound, $(C_6H_9N_2S)[ZnCl_3{SC(NH_2)_2}]$, exists as a zincate where the zinc(II) centre is coordinated by three chloride ligands and a thiourea ligand to form the anion. The organic cation adopts the protonated 4,6-dimethyl-2-sulfanyl-idenepyrimidin-1-ium (*L*) form of 4,6-dimethylpyrimidine-2(1*H*)-thione. Two short N-H···Cl hydrogen bonds involving the pyrimidine H atoms and the $[ZnCl_3L]^-$ anion form a crystallographically centrosymmetric dimeric unit consisting of two anions and two cations. The packing structure is completed by longer-range hydrogen bonds donated by the thiourea NH₂ groups to chloride ligand hydrogen-bond acceptors.

Comment

In recent decades, coordination compounds, and in particular supramolecular coordination compounds, have received much attention. This is not only because of the diversity of their structures, but also because of their potentially useful properties, such as luminescent or magnetic behaviour. A further source of interest is their chemical activity in fields such as biomedicine and catalysis (Cui et al., 2012; Kurmoo, 2009; Horcajada et al., 2012; Lee et al., 2009). Substituted pyrimidine-2-thiols, which possess both nitrogen and sulfur potential coordination sites, have been widely used in the preparation of traditional metal complexes and their coordination modes have been thoroughly investigated. In most cases, they are found as the anion and coordinate to metal centres through both S and N atoms (see, for example, Rodríguez et al., 2011). Other coordination modes are found more rarely. These are anionic species where only sulfur is coordinated to the metal (Vergara et al., 2011) and neutral thione tautomers where again only sulfur is coordinated to the metal centre (Das et al., 2011). Note that 4,6-dimethylpyrimidine-2(1H)-thione is the isomer of 4,6-dimethylpyrimidine-2-thiol with an H atom bound to an N rather than to the S atom and thus has an S=C



double bond. Also structurally characterized are species where protonated 4.6-dimethylpyrimidine-2(1H)-thione plays the role of cation with halide or polyhalide (MX_n) anions (Gave et al., 2009). Meanwhile, thiourea is most commonly encountered as a raw material in organic syntheses, but can also play a role in coordination chemistry. Structural reports of thiourea-coordinated Zn complexes, with carboxylic acid derivatives (Burrows et al., 2004) or chloride anions as additional ligands, are known, though the latter are rare and only two examples exist to date (Bombicz et al., 2007; Wu et al., 2004). In all of these complexes, multiple thiourea ligands are coordinated to Zn. To the best of our knowledge, a monothiourea-coordinated Zn complex has not yet been structurally described. Combining these topics, the crystal structure of the title compound, (I), is reported herein and compared with other related structures, including that of bis(4,6-dimethyl-2-sulfanylidenepyrimidinium) tetrachloridozinc(II) monohydrate (Godino-Salido et al., 1995), where an additional chloride ligand replaces the thiourea molecule of (I).



In (I) (Fig. 1), the Zn^{II} centre is coordinated by three Cl⁻ anions and one thiourea molecule (the thiourea is believed to originate as an impurity carried over from the prior synthesis of the sulfanylidenepyridinium starting material). The distances between the Zn and Cl atoms are given in Table 1, along with other selected geometric parameters. These bond distances are similiar to those in related compounds, such as bis(4,6-dimethyl-2-sulfanylidenepyrimidinium) tetrachloridozincate(II) (2.241, 2.277, 2.270 and 2.267 Å; Godino-Salido et al., 1995), dichloridobis(thiourea)zinc(II) bis(4,5-diazafluoren-9-one) [2.2475 (19) and 2.2685 (9) Å; Wu et al., 2004] and dichloridobis(thiourea-*kS*)zinc(II) (2.310 and 2.273 Å; Bombicz et al., 2007), though they are slightly longer than most of these literature cases. The distance between Zn and the S atom in (I) is 2.3252 (4) Å, which is also similiar to, if slightly shorter than, those in dichloridobis(thiourea- κS)zinc(II) (2.341 Å;



Figure 1

A view of the contents of the asymmetric unit of (I), showing the atomnumbering scheme. Displacement ellipsoids are drawn at the 30% probability level.





Packing diagrams for (I), viewed (a) along the *a* direction and (b) along the *b* direction. Hydrogen bonds are indicated by dashed lines (blue for the shortest two and green for the others in the electronic version of the paper).

Bombicz et al., 2007) and dichloridobis(thiourea)zinc(II) bis(4,5-diazafluoren-9-one) [2.3619 (10) and 2.3403 (9) Å; Wu et al., 2004]. The angles around the Zn atom range from 104.946 (13) to 115.248 $(13)^\circ$, showing a distorted tetrahedral coordination geometry. Whilst the S2-C7 bond length of 1.7257 (14) Å shows only a slight difference from those in other thiourea complexes [1.712 (Bombicz et al., 2007), and 1.715 (3) and 1.718 (3) Å (Wu et al., 2004)], it can be suggested that it displays a lengthening of the double C-S bond compared with uncoordinated thiourea complexes [typical range = 1.700 (Thaimattam et al., 1998) to 1.719 Å (Palmer et al., 2012)]. Of course, saturated mercapto compounds have much longer S-C distances [for example, 1.822 (Ratajczak-Sitarz et al., 1988), 1.793 (Selvakumar et al., 2011) and 1.814 Å (Kim et al., 2002)]. The Zn1-S2-C7 angle is again only slightly different from similar angles in the more sterically crowded dichloridobis(thiourea- κS)zinc(II) (108.4°; Bombicz et al., 2007) and dichloridobis(thiourea)zinc(II) bis(4,5-diazafluoren-9-one) [107.56 (9) and 109.26 (9)°; Wu et al., 2004] species. The remaining bond lengths and angles of the thiourea unit in (I) are also in good agreement with those of other coordinated thiourea ligands.

In the pyrimidine cation of (I), the distances between the N and C atoms forming the six-membered ring are typical of the

bond lengths of an aromatic ring and show no real evidence of alternating long and short bonds. The distance between atom S1 and adjacent atom C2 is 1.6469 (13) Å, which is shorter than that in other thiophenol (1.735 Å; Mock et al., 2011) or thiopyrimidine complexes [1.713 (Maslen et al. 1958) and 1.698 Å (Srinivasan & Chandrasekharan, 1968)]. Taken together, these bond lengths support the identification of the tautomer adopted as that resulting from a proton transfer from S to N and thus transformation from the thiol form to the thione form. It is interesting to note that, despite potential contributions from the thiol tautomer, the C=S bond in the cation is much shorter than that in the neutral thiourea molecule. Other protonated cationic pyrimidines are known and the thione form is the one commonly found, as is shown by HL·HCl·H₂O [1.644 (2) Å for the C=S bond; Seth *et al.*, 1996], (HL₃)[BiCl₆]₂·H₂O (1.636 Å; Battaglia & Corradi, 1986), $(HL)[Re_{3}Cl_{9}(H_{2}O)_{3}]_{2}$ ·HCl·2H₂O (1.645 Å; Battaglia *et* al., 1987), (HL)[CdCl₃] (1.649 Å; López-Garzón et al., 1995) and (HL)₂[ZnCl₄]·H₂O (1.650 Å; Godino-Salido et al., 1995), where L is 4,6-dimethylpyrimidine-2(1H)-thione.

In the crystal structure of (I), there are six kinds of hydrogen bonds, one for each N-H group. All hydrogen bonds are between N-H donors and Cl acceptors. The donor-acceptor distances of N1-H1···Cl3ⁱ and N2-H2...Cl1ⁱⁱ are considerably shorter than those involving the thiourea ligand (see Table 2), but are similiar to their counterparts in similar species, such as $(H_2L)_2[ZnCl_4]\cdot H_2O$ (3.264 and 3.190 Å; Godino-Salido et al., 1995). Linked by these two stronger and shorter hydrogen bonds, a crystallographically centrosymmetric dimer consisting of two cations and two anions is formed (Fig. 2). Across the inner space of the dimers, there are some short face-to-face interactions [e.g. $S1 \cdots N2(-x + 2, -y + 2, -z) = 3.4891 (11) Å$, but the centroid-centroid distance (Fig. 3) between the centroids of the pyrimidine rings is 5.3369(7) Å, which indicates offset and hence little scope for π - π and C···C interactions. The angle between the pyrimidine ring plane and the plane of the



Figure 3

An alternative packing diagram for (I). The disposition of the ring centroids is highlighted by the line with long dashes. The lines with short dashes represent hydrogen bonds.

neighbouring thiourea molecule is 9.1° , indicating near coplanarity. The supramolecular structure expands further through the three remaining longer intermolecular N-H···Cl thiourea-to-chlorine contacts, whilst the final N-H group completes the hydrogen bonding by forming an intramolecular interaction. The interaction distances of these hydrogen bonds also have literature equivalents in related complexes [3.344 (2) and 3.324 (2) (Wu *et al.*, 2004), and 3.2043 Å (Bombicz *et al.*, 2007)]. These interactions combine to give the complete polymeric network shown in Figs. 2 and 3.

Experimental

All reagents and solvents were commercially available and were used without further purification. 4,6-Dimethylpyrimidine-2-thiol was prepared according to the literature method of Carter *et al.* (1992). 4,6-Dimethylpyrimidine-2-thiol (0.140 g, 1 mmol) was dissolved in methanol (10 ml) and distilled water (1:1 ν/ν). Zinc chloride (0.136 g) was also dissolved in a mixture of methanol and distilled water (10 ml, 1:1 ν/ν). The latter solution was added dropwise to the former and the mixed solution gradually turned a pale-green–yellow colour. After stirring for 2 h at room temperature, the solution was filtered. After being allowed to stand for several days, colourless block-shaped crystals of (I) were obtained.

It is believed that the thiourea ligand in the title compound was introduced with 4,6-dimethylpyrimidine-2-thiol as an impurity. In the synthesis of 4,6-dimethylpyrimidine-2-thiol, a mixture of acetylacetone, thiourea, hydrochloric acid and methanol was stirred at room temperature for 24 h and the resulting yellow crystals were isolated by filtration but were not recrystallized or otherwise purified.

Crystal data

$(C_6H_9N_2S)[ZnCl_3(CH_4N_2S)]$	$V = 3004.31 (13) \text{ Å}^3$
$M_r = 389.05$	Z = 8
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 15.3648 (4) Å	$\mu = 2.43 \text{ mm}^{-1}$
b = 7.3374 (2) Å	T = 123 K
c = 26.7111 (6) Å	$0.17 \times 0.15 \times 0.14 \text{ mm}$
$\beta = 93.919 \ (1)^{\circ}$	

40204 measured reflections

 $R_{\rm int} = 0.023$

3285 independent reflections

3166 reflections with $I > 2\sigma(I)$

Data collection

Bruker APEXII CCD area-detector diffractometer Absorption correction: multi-scan (SADABS; Bruker, 2008) T_{min} = 0.683, T_{max} = 0.727

Refinement

$$\begin{split} R[F^2 > 2\sigma(F^2)] &= 0.015 & \text{H atoms treated by a mixture of} \\ wR(F^2) &= 0.040 & \text{independent and constrained} \\ S &= 1.06 & \text{refinement} \\ 3285 \text{ reflections} & \Delta\rho_{\text{max}} &= 0.31 \text{ e } \text{ Å}^{-3} \\ 174 \text{ parameters} & \Delta\rho_{\text{min}} &= -0.19 \text{ e } \text{ Å}^{-3} \end{split}$$

H atoms bonded to C atoms were positioned geometrically and refined using a riding-model approximation, with C-H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic H atom, and C-H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. H atoms bonded to N atoms were found by difference synthesis. Those on the thiurea ligand were refined freely and isotropically, whilst the pyrimidine H atoms were refined with restraints such that the N-H distances approximated 0.88 (1) Å.

Table 1

Selected geometric parameters (Å, °).

Zn1-Cl3	2.2710 (3)	C2-N2	1.3753 (16)
Zn1-Cl1	2.2775 (3)	C2-N1	1.3767 (16)
Zn1-Cl2	2.2863 (3)	C2-S1	1.6469 (13)
Zn1-S2	2.3252 (4)	C3-N2	1.3422 (17)
C1-N1	1.3507 (17)	C3-C4	1.3826 (18)
C1-C4	1.3782 (18)	C3-C6	1.4876 (18)
C1-C5	1.4912 (18)		
Cl3-Zn1-Cl1	110.883 (13)	Cl1-Zn1-S2	108.749 (13)
Cl3-Zn1-Cl2	105.508 (12)	Cl2-Zn1-S2	115.248 (13)
Cl1-Zn1-Cl2	104.946 (13)	C7-S2-Zn1	106.28 (5)
Cl3-Zn1-S2	111.316 (13)		

Table 2

Hydrogen-bond geometry (Å, °).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$N1 - H1 \cdots Cl3^i$	0.87(1)	2.40(1)	3.2420 (11)	164 (1)
$N2-H2\cdots Cl1^{ii}$	0.86 (1)	2.34 (1)	3.1952 (11)	178 (2)
$N3-H3A\cdots Cl2^{iii}$	0.828 (19)	2.787 (19)	3.5216 (16)	148.7 (16)
$N3-H3B\cdots Cl1^{iv}$	0.869 (19)	2.680 (18)	3.4050 (14)	141.6 (15)
$N4-H4B\cdots Cl2^{iii}$	0.81(2)	2.57 (2)	3.3410 (14)	158.6 (18)
$N4 - H4A \cdots Cl2$	0.82 (2)	2.53 (2)	3.3399 (14)	168.8 (18)

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KY3022). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Crystal data (C₆H₉N₂S)[ZnCl₃(CH₄N₂S)] $M_r = 389.05$ Monoclinic, C2/c Hall symbol: -C 2yc a = 15.3648 (4) Å b = 7.3374 (2) Å c = 26.7111 (6) Å $\beta = 93.919$ (1)° V = 3004.31 (13) Å³ Z = 8

Data collection

Bruker APEXII CCD area-detector diffractometer Radiation source: fine-focus sealed tube Graphite monochromator φ and ω scans Absorption correction: multi-scan (*SADABS*; Bruker, 2008) $T_{\min} = 0.683, T_{\max} = 0.727$

Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.015$ $wR(F^2) = 0.040$ S = 1.063285 reflections 174 parameters 2 restraints Primary atom site location: structure-invariant direct methods F(000) = 1568 $D_x = 1.720 \text{ Mg m}^{-3}$ Mo K\alpha radiation, $\lambda = 0.71073 \text{ Å}$ Cell parameters from 9718 reflections $\theta = 3.1-36.3^{\circ}$ $\mu = 2.43 \text{ mm}^{-1}$ T = 123 KBlock, colourless $0.17 \times 0.15 \times 0.14 \text{ mm}$

40204 measured reflections 3285 independent reflections 3166 reflections with $I > 2\sigma(I)$ $R_{int} = 0.023$ $\theta_{max} = 27.0^{\circ}, \theta_{min} = 2.7^{\circ}$ $h = -19 \rightarrow 19$ $k = -9 \rightarrow 9$ $l = -34 \rightarrow 34$

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 $w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 3.2453P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} = 0.001$ $\Delta\rho_{max} = 0.31$ e Å⁻³ $\Delta\rho_{min} = -0.19$ e Å⁻³

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.

	x	У	Ζ	$U_{\rm iso}^*/U_{\rm eq}$
Znl	0.158445 (9)	0.36606 (2)	0.143070 (5)	0.01699 (5)
C1	1.01043 (8)	0.83474 (17)	0.13185 (5)	0.0191 (2)
C2	1.06449 (8)	0.83285 (17)	0.04895 (5)	0.0178 (2)
C3	0.92225 (8)	0.71085 (18)	0.06348 (5)	0.0203 (2)
C4	0.93385 (8)	0.75250 (18)	0.11398 (5)	0.0213 (3)
H4	0.8897	0.7249	0.1360	0.026*
C5	1.02883 (9)	0.8889 (2)	0.18534 (5)	0.0255 (3)
H5A	1.0834	0.8320	0.1986	0.038*
H5B	0.9809	0.8485	0.2050	0.038*
H5C	1.0344	1.0217	0.1876	0.038*
C6	0.84299 (9)	0.6208 (2)	0.03986 (6)	0.0292 (3)
H6A	0.8289	0.6733	0.0066	0.044*
H6B	0.7939	0.6398	0.0609	0.044*
H6C	0.8539	0.4899	0.0366	0.044*
C7	0.31245 (9)	0.66412 (17)	0.16888 (5)	0.0213 (3)
Cl1	0.04641 (2)	0.33090 (5)	0.083500 (11)	0.02363 (7)
C12	0.09307 (2)	0.43667 (4)	0.214950 (11)	0.02243 (7)
C13	0.228033 (19)	0.09711 (4)	0.159042 (11)	0.01977 (7)
N1	1.07231 (7)	0.86972 (15)	0.09959 (4)	0.0181 (2)
H1	1.1205 (7)	0.921 (2)	0.1108 (6)	0.022*
N2	0.98620 (7)	0.75282 (15)	0.03367 (4)	0.0187 (2)
H2	0.9787 (10)	0.732 (2)	0.0020 (3)	0.022*
N3	0.38639 (8)	0.75308 (17)	0.16300 (6)	0.0283 (3)
H3A	0.4115 (12)	0.806 (3)	0.1873 (7)	0.034*
H3B	0.4036 (11)	0.764 (3)	0.1328 (7)	0.034*
N4	0.28743 (9)	0.64036 (18)	0.21465 (5)	0.0281 (3)
H4B	0.3136 (12)	0.692 (3)	0.2380 (7)	0.034*
H4A	0.2399 (13)	0.593 (3)	0.2192 (7)	0.034*
S 1	1.14037 (2)	0.87802 (5)	0.010083 (12)	0.02336 (7)
S2	0.25353 (2)	0.58583 (4)	0.115888 (12)	0.02081 (7)

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

Atomic displacement parameters $(Å^2)$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01646 (8)	0.01852 (8)	0.01574 (8)	0.00082 (5)	-0.00078 (5)	-0.00103 (5)
C1	0.0209 (6)	0.0174 (6)	0.0191 (6)	0.0040 (5)	0.0015 (5)	0.0007 (5)
C2	0.0180 (6)	0.0160 (6)	0.0191 (6)	0.0018 (5)	-0.0008(5)	0.0015 (5)
C3	0.0155 (6)	0.0194 (6)	0.0258 (6)	0.0018 (5)	-0.0002 (5)	0.0007 (5)
C4	0.0170 (6)	0.0232 (6)	0.0240 (6)	0.0009 (5)	0.0039 (5)	0.0001 (5)
C5	0.0272 (7)	0.0292 (7)	0.0202 (6)	-0.0001 (6)	0.0012 (5)	-0.0029 (5)
C6	0.0195 (7)	0.0380 (8)	0.0298 (7)	-0.0063 (6)	-0.0013 (5)	-0.0035 (6)
C7	0.0197 (6)	0.0154 (6)	0.0284 (7)	0.0033 (5)	-0.0012 (5)	0.0008 (5)

supplementary materials

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CII	0.02204 (15)	0.02911 (16)	0.01874 (14)	0.00231 (12)	-0.00582 (11)	-0.00248 (12)
Cl2	0.02158 (15)	0.02705 (16)	0.01908 (14)	0.00397 (12)	0.00450 (11)	0.00046 (12)
C13	0.01821 (14)	0.01841 (14)	0.02238 (14)	0.00181 (11)	-0.00090 (11)	-0.00059 (11)
N1	0.0154 (5)	0.0196 (5)	0.0187 (5)	-0.0012 (4)	-0.0015 (4)	-0.0009 (4)
N2	0.0181 (5)	0.0213 (5)	0.0163 (5)	-0.0001 (4)	-0.0019 (4)	-0.0001 (4)
N3	0.0209 (6)	0.0257 (6)	0.0380 (7)	-0.0023 (5)	-0.0002 (5)	-0.0002 (5)
N4	0.0293 (7)	0.0323 (7)	0.0221 (6)	-0.0085 (5)	-0.0030 (5)	-0.0044 (5)
S1	0.02034 (16)	0.02867 (17)	0.02140 (15)	-0.00419 (13)	0.00389 (12)	0.00046 (13)
S2	0.02219 (15)	0.02254 (15)	0.01770 (14)	-0.00115 (12)	0.00141 (12)	0.00199 (12)

Geometric parameters (Å, °)

Zn1—Cl3	2.2710 (3)	C5—H5B	0.9800
Zn1—Cl1	2.2775 (3)	С5—Н5С	0.9800
Zn1—Cl2	2.2863 (3)	С6—Н6А	0.9800
Zn1—S2	2.3252 (4)	С6—Н6В	0.9800
C1—N1	1.3507 (17)	С6—Н6С	0.9800
C1—C4	1.3782 (18)	C7—N4	1.3179 (19)
C1—C5	1.4912 (18)	C7—N3	1.3289 (18)
C2—N2	1.3753 (16)	C7—S2	1.7257 (14)
C2—N1	1.3767 (16)	N1—H1	0.866 (9)
C2—S1	1.6469 (13)	N2—H2	0.860 (9)
C3—N2	1.3422 (17)	N3—H3A	0.828 (19)
C3—C4	1.3826 (18)	N3—H3B	0.869 (19)
C3—C6	1.4876 (18)	N4—H4B	0.81 (2)
C4—H4	0.9500	N4—H4A	0.82 (2)
С5—Н5А	0.9800		
Cl3—Zn1—Cl1	110.883 (13)	H5B—C5—H5C	109.5
Cl3—Zn1—Cl2	105.508 (12)	С3—С6—Н6А	109.5
Cl1—Zn1—Cl2	104.946 (13)	С3—С6—Н6В	109.5
Cl3—Zn1—S2	111.316 (13)	H6A—C6—H6B	109.5
Cl1—Zn1—S2	108.749 (13)	С3—С6—Н6С	109.5
Cl2—Zn1—S2	115.248 (13)	Н6А—С6—Н6С	109.5
N1—C1—C4	118.92 (12)	H6B—C6—H6C	109.5
N1—C1—C5	117.71 (12)	N4—C7—N3	118.73 (13)
C4—C1—C5	123.36 (12)	N4—C7—S2	123.16 (11)
N2—C2—N1	113.03 (11)	N3—C7—S2	118.12 (11)
N2-C2-S1	122.78 (10)	C1—N1—C2	124.86 (11)
N1—C2—S1	124.19 (10)	C1—N1—H1	119.0 (10)
N2—C3—C4	118.51 (12)	C2—N1—H1	116.1 (10)
N2—C3—C6	117.49 (12)	C3—N2—C2	125.65 (11)
C4—C3—C6	124.00 (12)	C3—N2—H2	119.3 (10)
C1—C4—C3	119.00 (12)	C2—N2—H2	115.0 (10)
C1—C4—H4	120.5	C7—N3—H3A	119.6 (13)
C3—C4—H4	120.5	C7—N3—H3B	118.1 (12)
C1—C5—H5A	109.5	H3A—N3—H3B	122.0 (17)
C1—C5—H5B	109.5	C7—N4—H4B	119.3 (13)
H5A—C5—H5B	109.5	C7—N4—H4A	120.6 (13)
C1—C5—H5C	109.5	H4B—N4—H4A	118.6 (18)

supplementary materials

Н5А—С5—Н5С	109.5	C7—S2—Zn1	106.28 (5)
N1—C1—C4—C3	-0.94 (19)	C6—C3—N2—C2	-178.69 (12)
C5—C1—C4—C3	178.69 (12)	N1—C2—N2—C3	-0.51 (18)
N2-C3-C4-C1	-0.20 (19)	S1—C2—N2—C3	179.26 (10)
C6—C3—C4—C1	179.44 (13)	N4—C7—S2—Zn1	-18.07 (13)
C4—C1—N1—C2	1.48 (19)	N3—C7—S2—Zn1	162.16 (10)
C5—C1—N1—C2	-178.17 (12)	Cl3—Zn1—S2—C7	-78.35 (5)
N2-C2-N1-C1	-0.76 (17)	Cl1—Zn1—S2—C7	159.20 (5)
S1—C2—N1—C1	179.48 (10)	Cl2—Zn1—S2—C7	41.74 (5)
C4—C3—N2—C2	0.97 (19)		

Hydrogen-bond geometry (Å, °)

D—H···A	<i>D</i> —Н	H···A	D····A	<i>D</i> —H··· <i>A</i>
N1—H1…Cl3 ⁱ	0.87(1)	2.40(1)	3.2420 (11)	164 (1)
N2—H2····Cl1 ⁱⁱ	0.86(1)	2.34 (1)	3.1952 (11)	178 (2)
N3—H3A····Cl2 ⁱⁱⁱ	0.828 (19)	2.787 (19)	3.5216 (16)	148.7 (16)
N3—H3 <i>B</i> ···Cl1 ^{iv}	0.869 (19)	2.680 (18)	3.4050 (14)	141.6 (15)
N4—H4 <i>B</i> ···Cl2 ⁱⁱⁱ	0.81 (2)	2.57 (2)	3.3410 (14)	158.6 (18)
N4—H4A····Cl2	0.82 (2)	2.53 (2)	3.3399 (14)	168.8 (18)

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

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