

Crystal structure and Hirshfeld surface analysis of bis(6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-5-ium) tetrachloridozincate

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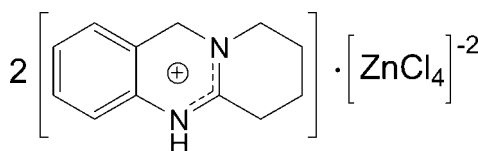
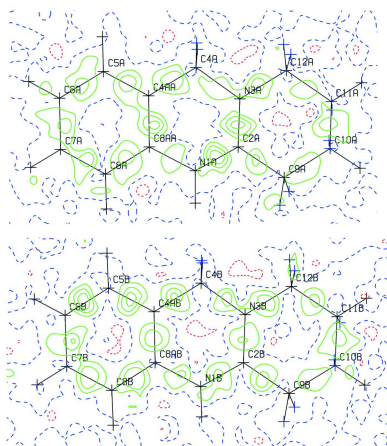
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The title compound, (C₁₂H₁₅N₂)₂[ZnCl₄], is a salt with two symmetrically independent, essentially planar heterocyclic cations and a slightly distorted tetrahedral chlorozincate dianion. N—H···Cl hydrogen bonds link these ionic constituents into a discrete aggregate, which comprises one formula unit. The effect of hydrogen bonding is reflected in the minor distortions of the [ZnCl₄]²⁻ moiety: distances between the cation and chlorido ligands engaged in classical hydrogen bonds are significantly longer than the others. Secondary interactions comprise C—H···π hydrogen bonding and weak π–π stacking. A Hirshfeld surface analysis indicates that the most abundant contacts in packing stem from H···H (47.8%) and Cl···H/H···Cl (29.3%) interactions.

1. Chemical context

Tricyclic quinazolines are counted among the most exciting quinazoline alkaloids. Specifically, the alkaloid mackinazoline was isolated from *Mackinlaya sp.* (Johns & Lamberton, 1965). Tricyclic quinazolines have several different reactive sites and can react with electrophilic and nucleophilic reagents to form various derivatives with potential biological activity (Michael, 2004). As quinazoline alkaloids are scarcely available from natural sources, multiple methods for their synthesis have been developed (Shakhidoyatov & Elmuradov, 2014). In the context of these synthetic efforts, reaction intermediates similar to the title compound have been studied (Sharma *et al.*, 1993; Sargazakov *et al.*, 1991; Tozhiboev *et al.*, 2005). We investigated the crystal structure of bis(6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-5-ium) tetrachloridozincate, an intermediate in the synthesis of mackinazolinone, using high-resolution diffraction data and Hirshfeld surface analysis.



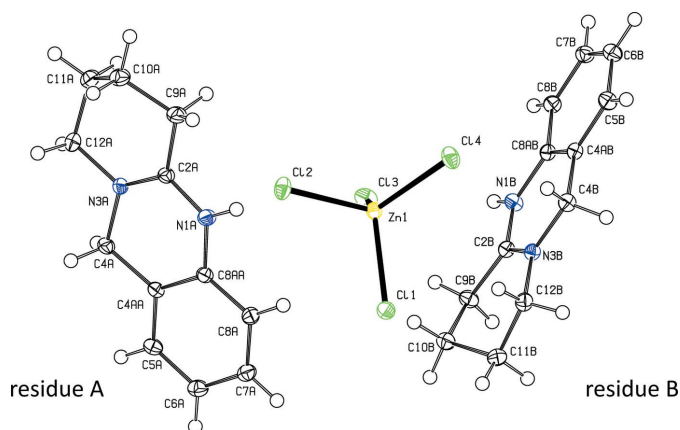


Figure 1
Asymmetric unit of the title compound with the atom-numbering scheme (Spek, 2020). Displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level.

2. Structural commentary

The title compound crystallizes in the $P2_1/n$ space group, with two $[C_{12}H_{15}N_2]^+$ cations and a $[ZnCl_4]^{2-}$ counter-anion in the asymmetric unit (Fig. 1). The benzene and pyrimidine rings in either cation and the attached carbon atoms of the aliphatic ring (C9A and C12A for residue A and C9B and C12B for residue B) are essentially coplanar, with r.m.s. deviations of 0.0437 and 0.0168 Å for molecules A and B, respectively. The remaining atoms of the third ring are significantly displaced above the opposite faces of these planes with deviations of 0.3877 (12) Å for C10A and 0.3831 (11) Å for C11A in residue A and 0.4705 (11) Å for C10B and 0.2495 (11) Å for C11B in residue B. Fig. 2 shows that the independent cations are almost superimposable including the conformationally soft aliphatic ring.

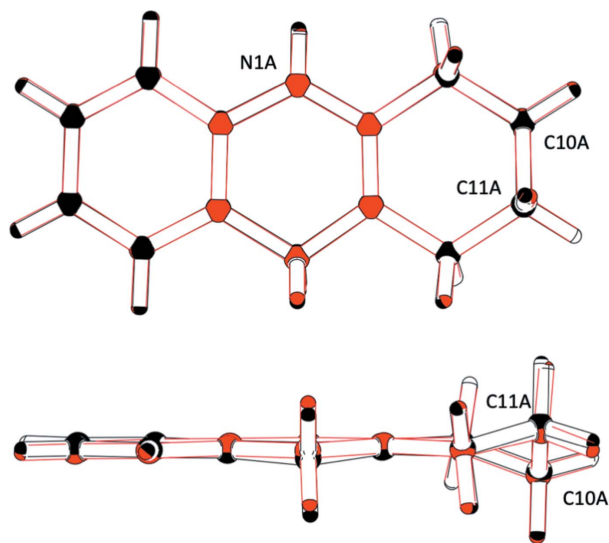


Figure 2
Overlay (Spek, 2020) of the independent cations in the title compound in the least-squares (top) and most-squares plane (bottom); residue A was depicted in black, residue B in red.

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl4	2.2484 (3)	N1A—C2A	1.3373 (11)
Zn1—Cl3	2.2664 (4)	N1B—C2B	1.3317 (10)
Zn1—Cl2	2.2868 (4)	C2A—N3A	1.3102 (10)
Zn1—Cl1	2.3019 (3)	C2B—N3B	1.3114 (9)
Cl4—Zn1—Cl3	111.219 (10)	Cl4—Zn1—Cl1	109.994 (13)
Cl4—Zn1—Cl2	115.057 (11)	Cl3—Zn1—Cl1	110.340 (12)
Cl3—Zn1—Cl2	106.573 (10)	Cl2—Zn1—Cl1	103.331 (11)

The protonation of the ring occurs at the basic heteroatoms of the pyrimidine rings, N1A and N1B, respectively, and the acquired positive charge is delocalized within the $-N-C-N-$ moiety in the ring, where the N1A—C2A and N1B—C2B bonds are only slightly longer than C2A—N3A and C2B—N3B (Table 1). Similar differences were observed in related reported complexes (Sharma *et al.*, 1993; Turgunov *et al.*, 2003; Tozhiboev *et al.*, 2005).

However, these C—N bond lengths are shorter than those in the related tricyclic protonated (PYQAZP: Reck *et al.*, 1974) and non-protonated (GUCZUZ: Le Gall *et al.*, 1999; LIZMOX: Zhang *et al.*, 2008) quinazoline derivatives. In these three compounds, the sp^3 character of the carbon atom between the two nitrogen atoms and the lack of the C=N double bond within the $-N-C-N-$ moiety hampers the delocalization of the positive charge within this unit. It is

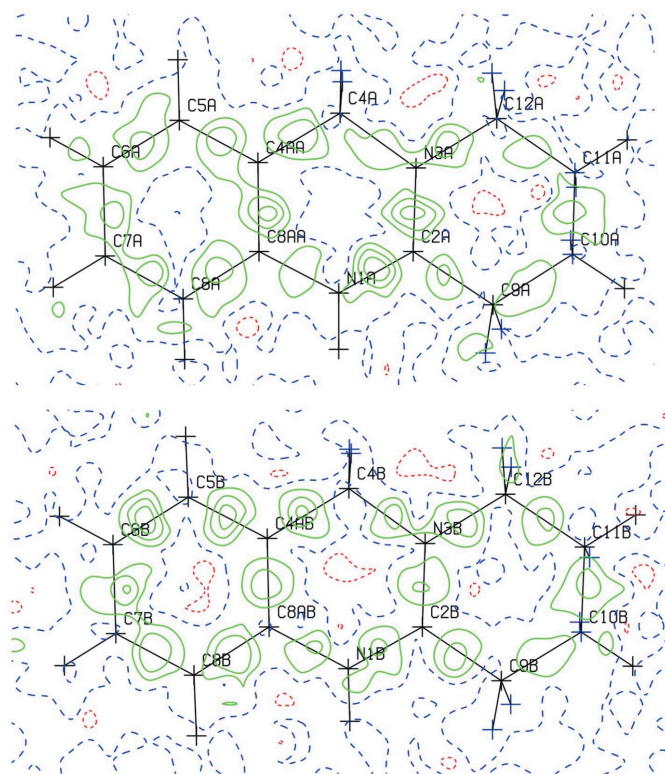


Figure 3
Residual electron density in the planes through C2A, C4A and C8AA (top) and C2B, C4B and C4AB (bottom); contour lines are drawn at 0.2 e Å⁻³. Covalent bonds in the heterocyclic cations clearly show up as local density maxima.

Table 2

Hydrogen-bond geometry (Å, °).

 $Cg3$ and $Cg9$ are the centroids of the $C5A-C8A/C4AA/C8AA$ and $C5B-C8B/C4AB/C8AB$ rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1A-H1A\cdots Cl2$	0.89 (2)	2.44 (2)	3.2659 (8)	155.9 (19)
$N1B-H1B\cdots Cl1^i$	0.83 (2)	2.352 (19)	3.1661 (7)	166.6 (18)
$C11A-H11A\cdots Cg9^{ii}$	0.99	2.67	3.5718 (10)	151
$C12B-H12D\cdots Cg3^{iii}$	0.99	2.57	3.4002 (10)	142

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

instead delocalized over the $-N=CH-C(\text{phenylene})$ fragment (see Table S1 in the supporting information).

Analysis of the residual electron density (Spek, 2020) reveals that the covalent bonds in the heterocyclic cations clearly show up as local density maxima (Fig. 3).

The Zn^{II} centre in the dianion adopts a slightly distorted geometry, with $\tau^4 = 0.95$ (Yang *et al.*, 2007). The high resolution ($\theta_{\max} = 109.6^\circ$, $\sin \theta/\lambda = 1.150 \text{ \AA}^{-1}$, $d = 0.43 \text{ \AA}$) and the very favourable ratio between observations and variables (100:1) in our diffraction data result in small standard uncertainties for atomic coordinates and derived geometric parameters and allow to discuss more subtle details. The most acute angle of $103.33 (11)^\circ$ within the tetrachloridozincate dianion (Table 1) is subtended by Cl1 and Cl2. These atoms are associated with the longest Zn–Cl distances, which, in turn, are correlated with the most relevant intermolecular interactions in the structure: Cl1 is involved in the shortest and most linear $N-H\cdots Cl$ hydrogen bond (see Table 2) and represents the most distant ligand in the anion. Cl2 is signifi-

cantly closer to Zn1 and is engaged in a longer and presumably weaker hydrogen bond. The remaining chlorido ligands are not associated with any classical short contacts. Similar features have been reported for structurally related compounds (Sharma *et al.*, 1993; Sargazakov *et al.*, 1991; Tozhiboev *et al.*, 2005; Wang *et al.*, 2017).

3. Supramolecular features

In the crystal structure, the protonated N1A and N1B nitrogen atoms in the cations interact with the chlorido ligands Cl2 and Cl1, respectively, *via* relatively short $N-H\cdots Cl$ bonds and generate a $D_2^2(5)$ graph-set motif (Bernstein *et al.*, 1995) (Table 2 and Fig. 4).

The crystal packing is further stabilized by intermolecular $C-H\cdots \pi$ interactions (Table 2) and additional short contacts between Cl3 and the N–C–N segment of the pyrimidine rings. The shortest contact distance occurs between Cl3 and C2B [$3.5273 (9) \text{ \AA}$] and involves an interaction between the electron-rich equatorial region of the halogen atom and the ring atom attached to two N-atom neighbours, most probably the most electron-deficient atom in the heterocycle. These contacts link anions and cations into a three-dimensional network. Weak $\pi-\pi$ stacking interactions occur between pyrimidine ($Cg1, Cg7$) and benzene ($Cg3, Cg9$) rings of anti-parallel pairs of cations and involve contact distances of $Cg1\cdots Cg3 (-x, -y, -z) = 3.6225 (5) \text{ \AA}$ (slippage 0.857 \AA) and of $Cg7\cdots Cg9 (1-x, -y, 1-z) = 3.6246 (7) \text{ \AA}$ (slippage 0.994 \AA).

4. Hirshfeld surface analysis

A Hirshfeld surface (HS) analysis (Spackman & Jayatilaka, 2009) was carried out using *CrystalExplorer17.5* (Turner *et al.*, 2017) to visualize interactions between the constituents of the title compound. The HS mapped with d_{norm} is represented in Fig. 5. The white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue

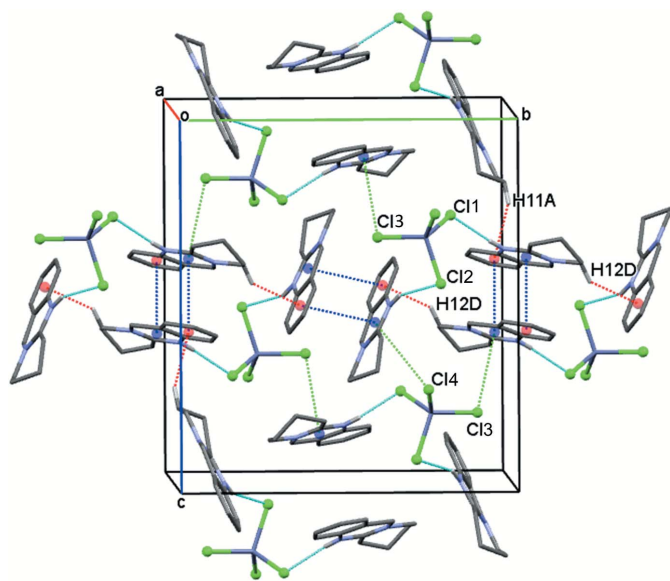


Figure 4

Crystal packing and short contacts in the title compound. Colour code: $N-H\cdots Cl$ interactions light-blue dashed lines, intermolecular $C-H\cdots \pi$ contacts red dashed lines, $Zn-Cl\cdots \pi$ contacts green dashed lines, $\pi-\pi$ stacking interactions dark-blue dashed lines. Centroid for the pyrimidine ($Cg1, Cg7$) and benzene rings ($Cg3, Cg9$) are shown as blue and red spheres, respectively.

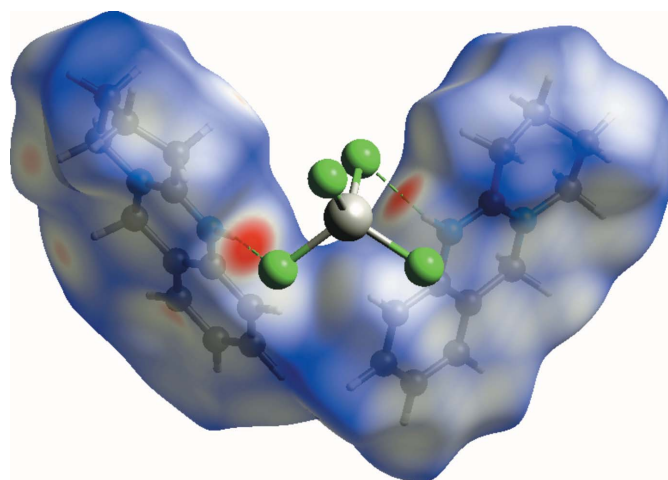


Figure 5

Three-dimensional Hirshfeld surface of the title compound mapped with d_{norm} .

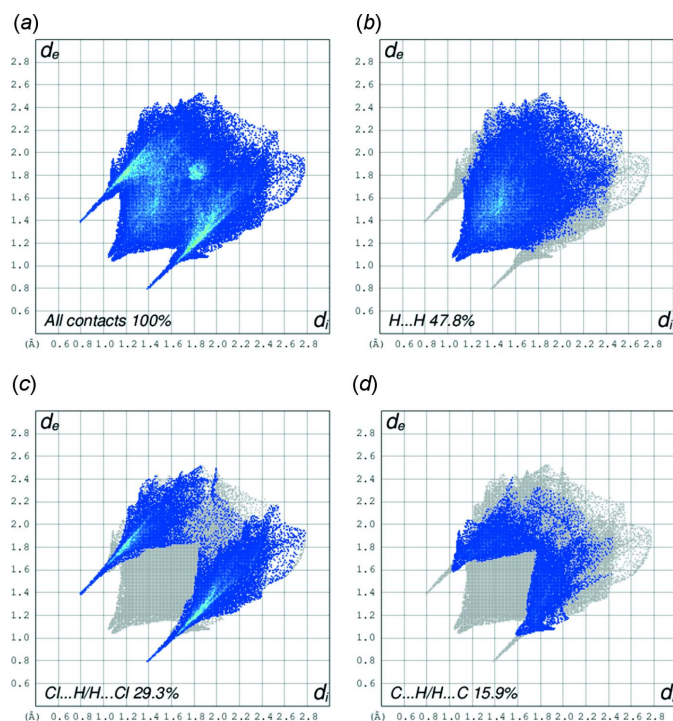


Figure 6 Two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and decomposed into (b) H...H, (c) Cl...H/H...Cl, (d) C...H/H...C interactions. Values for d_i and d_e represent the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

colours indicate distances shorter or longer than the van der Waals radii, respectively. The bright-red spot near Cl1 indicates its role as a hydrogen-bond donor towards N1.

The classical N—H...Cl hydrogen bonds correspond to Cl...H/H...Cl contacts (29.3% contribution) in Fig. 6c and show up as a pair of spikes. The most abundant contributions to the Hirshfeld surface arise from H...H contacts at 47.8%. Cl...H/H...Cl and C...H/H...C interactions follow with contributions of 29.3% and 15.9%, respectively (Fig. 6). Minor contributors are due to C...N/N...C (2.2%), N...H/H...N (2.0%), C...C (1.9%), C...Cl/Cl...C (0.4%), N...Cl/Cl...N (0.3%) and Zn...H/H...Zn (0.3%) contacts.

5. Database survey

A search in the Cambridge Structural Database (CSD, version 5.41, including the update of January 2020; Groom *et al.*, 2016) confirmed that four related compounds had been structurally characterized in which similar cations interact with $[\text{ZnCl}_4]^{2-}$

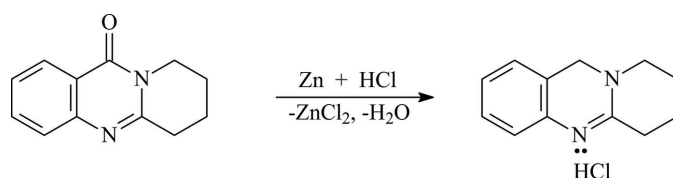


Figure 7 Synthesis scheme for 2,3-tetramethylene-3,4-dihydroquinazoline hydrochloride.

Table 3 Experimental details.

Crystal data	
Chemical formula	$(\text{C}_{12}\text{H}_{15}\text{N}_2)_2[\text{ZnCl}_4]$
M_r	581.69
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.2910 (13), 15.682 (2), 17.275 (2)
β (°)	95.642 (2)
V (Å ³)	2504.7 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.43
Crystal size (mm)	0.30 × 0.25 × 0.23
Data collection	
Diffractometer	Bruker D8 goniometer with APEX CCD detector
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.634, 0.751
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	170944, 31478, 21664
R_{int}	0.071
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	1.150
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.124, 1.04
No. of reflections	31478
No. of parameters	306
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.29, -0.54

Computer programs: APEX2 (Bruker, 2008), and SAINT (Bruker, 2008), SHELXS97 (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2015), PLATON (Spek, 2020), publCIF (Westrip, 2010).

anions. They are associated with refcodes PODLUP (Sharma *et al.*, 1993), PODLUP01 (Sargazakov *et al.*, 1991) and SECFAI and SECFAI01 (Tozhiboev *et al.*, 2005). An additional match for a similar cation interacting with a Cl^- anion was identified: EYUHEL (Turgunov *et al.*, 2003) and PYQAZP (Reck *et al.*, 1974).

6. Synthesis and crystallization

3 g (0.015 mol) of 2,3-tetramethylenquinazoline-4-one (Fig. 7) were placed in a 300 mL flat-bottom flask equipped with a magnetic stirrer and a reflux condenser. 72 mL of hydrochloric acid (15%) were added under stirring. 12 g of Zn powder were added in small portions over a period of 1 h, and the mixture was heated in a water bath for 4 h. The hot reaction mixture was filtered and the filtrate was left to precipitate overnight. The precipitate corresponding to 2,3-tetramethylenquinazoline hydrochloride was removed by filtration (Fig. 7). Colourless single crystals of the title compound were obtained by slow evaporation of the resulting filtrate at room temperature.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to C were

positioned geometrically, with C—H = 0.95 Å (for aromatic) or C—H = 0.99 Å (for methylene H atoms), and were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bonded to nitrogen were located in a difference-Fourier map, and their positional and isotropic displacement parameters were freely refined.

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supporting information

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Crystal structure and Hirshfeld surface analysis of bis(6,7,8,9-tetrahydro-11H-pyrido[2,1-*b*]quinazolin-5-ium) tetrachloridozincate

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Bis(6,7,8,9-tetrahydro-11H-pyrido[2,1-*b*]quinazolin-5-ium) tetrachloridozincate

Crystal data

(C₁₂H₁₅N₂)₂[ZnCl₄]

M_r = 581.69

Monoclinic, *P*2₁/*n*

a = 9.2910 (13) Å

b = 15.682 (2) Å

c = 17.275 (2) Å

β = 95.642 (2)°

V = 2504.7 (6) Å³

Z = 4

F(000) = 1200

D_x = 1.543 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 9853 reflections

θ = 2.4–53.5°

μ = 1.43 mm⁻¹

T = 100 K

Block, colourless

0.30 × 0.25 × 0.23 mm

Data collection

Bruker D8 goniometer with APEX CCD detector diffractometer

Radiation source: Incoatec microsource

Multilayer optics monochromator

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2008)

T_{min} = 0.634, *T_{max}* = 0.751

170944 measured reflections

31478 independent reflections

21664 reflections with *I* > 2 σ (*I*)

R_{int} = 0.071

θ_{\max} = 54.8°, θ_{\min} = 1.8°

h = -21→20

k = -35→35

l = -39→37

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.047

wR(*F*²) = 0.124

S = 1.04

31478 reflections

306 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[$\sigma^2(F_o^2) + (0.0465P)^2 + 0.1208P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

$\Delta\rho_{\max}$ = 1.29 e Å⁻³

$\Delta\rho_{\min}$ = -0.54 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.40341 (2)	0.23046 (2)	0.17943 (2)	0.01331 (2)
Cl1	0.22695 (2)	0.31275 (2)	0.22716 (2)	0.01745 (3)
N1A	0.16789 (8)	0.13353 (5)	-0.01919 (5)	0.01731 (11)
H1A	0.233 (2)	0.1607 (14)	0.0126 (12)	0.033 (5)*
N1B	0.38700 (8)	-0.02546 (4)	0.36997 (4)	0.01498 (9)
H1B	0.344 (2)	-0.0665 (13)	0.3479 (11)	0.027 (5)*
Cl2	0.40142 (3)	0.27504 (2)	0.05329 (2)	0.01999 (4)
C2A	0.20841 (8)	0.09703 (5)	-0.08356 (5)	0.01372 (9)
C2B	0.31376 (8)	0.04719 (5)	0.37362 (4)	0.01304 (9)
Cl3	0.33617 (3)	0.09149 (2)	0.17498 (2)	0.01962 (4)
N3A	0.11462 (7)	0.05870 (4)	-0.13348 (4)	0.01329 (8)
N3B	0.37680 (8)	0.11694 (4)	0.40176 (4)	0.01312 (8)
Cl4	0.61489 (3)	0.24837 (2)	0.25278 (2)	0.02103 (4)
C4A	-0.04199 (9)	0.06077 (6)	-0.12794 (5)	0.01591 (11)
H4AA	-0.081466	0.002500	-0.136382	0.019*
H4AB	-0.088035	0.097703	-0.169781	0.019*
C4B	0.53321 (9)	0.12358 (5)	0.42526 (5)	0.01502 (10)
H4BA	0.548031	0.145493	0.479203	0.018*
H4BB	0.576081	0.165215	0.391071	0.018*
C4AA	-0.08071 (8)	0.09313 (5)	-0.05096 (4)	0.01320 (9)
C4AB	0.61022 (8)	0.04003 (5)	0.42109 (4)	0.01289 (9)
C5A	-0.22295 (9)	0.09044 (5)	-0.03207 (5)	0.01629 (11)
H5AA	-0.295685	0.064510	-0.066819	0.020*
C5B	0.75850 (9)	0.03353 (5)	0.44269 (5)	0.01662 (11)
H5BA	0.811468	0.082125	0.462049	0.020*
C6A	-0.25917 (10)	0.12560 (6)	0.03755 (6)	0.01813 (12)
H6AA	-0.356791	0.124795	0.049536	0.022*
C6B	0.82907 (10)	-0.04420 (6)	0.43590 (5)	0.01798 (12)
H6BA	0.929998	-0.048320	0.450822	0.022*
C7A	-0.15242 (10)	0.16192 (6)	0.08958 (5)	0.01727 (11)
H7AA	-0.177180	0.185134	0.137308	0.021*
C7B	0.75264 (10)	-0.11583 (5)	0.40740 (5)	0.01668 (11)
H7BA	0.801428	-0.168535	0.402655	0.020*
C8A	-0.00940 (10)	0.16428 (5)	0.07178 (5)	0.01643 (11)
H8AA	0.063845	0.188750	0.107176	0.020*
C8B	0.60526 (9)	-0.11006 (5)	0.38597 (5)	0.01506 (10)
H8BA	0.552357	-0.158681	0.366592	0.018*
C8AA	0.02476 (8)	0.13018 (5)	0.00118 (5)	0.01397 (10)
C8AB	0.53532 (8)	-0.03207 (5)	0.39314 (4)	0.01263 (9)

C9A	0.36640 (9)	0.09994 (6)	-0.09460 (6)	0.01879 (13)
H9AA	0.417435	0.055347	-0.061905	0.023*
H9AB	0.406030	0.155936	-0.076687	0.023*
C9B	0.15598 (9)	0.04381 (6)	0.34654 (5)	0.01737 (11)
H9BA	0.104080	0.016581	0.387400	0.021*
H9BB	0.141921	0.007614	0.299452	0.021*
C10A	0.39598 (10)	0.08639 (6)	-0.17905 (6)	0.01922 (13)
H10A	0.364050	0.136876	-0.210599	0.023*
H10B	0.500890	0.078255	-0.182272	0.023*
C10B	0.08950 (10)	0.13131 (6)	0.32782 (5)	0.01831 (12)
H10C	0.120478	0.152492	0.278085	0.022*
H10D	-0.017322	0.126944	0.322279	0.022*
C11A	0.31331 (10)	0.00783 (6)	-0.20972 (5)	0.01870 (12)
H11A	0.334131	-0.003545	-0.263874	0.022*
H11B	0.344925	-0.042305	-0.177597	0.022*
C11B	0.13845 (11)	0.19299 (6)	0.39317 (6)	0.01927 (13)
H11C	0.096932	0.250072	0.380703	0.023*
H11D	0.101903	0.173279	0.442051	0.023*
C12A	0.15251 (10)	0.02154 (6)	-0.20731 (5)	0.01692 (11)
H12A	0.116845	0.059773	-0.250607	0.020*
H12B	0.102340	-0.033882	-0.215627	0.020*
C12B	0.30183 (10)	0.19950 (5)	0.40475 (5)	0.01622 (11)
H12C	0.334665	0.237291	0.364075	0.019*
H12D	0.330136	0.226467	0.455799	0.019*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01365 (3)	0.01277 (3)	0.01329 (3)	-0.00112 (2)	0.00014 (2)	-0.00022 (2)
Cl1	0.02079 (8)	0.01451 (6)	0.01701 (7)	0.00525 (6)	0.00166 (5)	0.00210 (5)
N1A	0.0117 (2)	0.0220 (3)	0.0181 (3)	-0.00204 (19)	0.00103 (18)	-0.0070 (2)
N1B	0.0141 (2)	0.01106 (19)	0.0192 (3)	-0.00093 (16)	-0.00121 (18)	-0.00287 (17)
Cl2	0.02268 (9)	0.02343 (9)	0.01374 (7)	-0.00702 (7)	0.00123 (6)	0.00172 (6)
C2A	0.0117 (2)	0.0145 (2)	0.0149 (2)	-0.00067 (18)	0.00108 (17)	-0.00124 (18)
C2B	0.0142 (2)	0.0115 (2)	0.0135 (2)	-0.00064 (17)	0.00143 (17)	-0.00060 (16)
Cl3	0.01743 (8)	0.01217 (6)	0.02897 (10)	-0.00094 (5)	0.00082 (6)	-0.00157 (6)
N3A	0.0132 (2)	0.0139 (2)	0.0127 (2)	-0.00007 (16)	0.00030 (15)	-0.00098 (15)
N3B	0.0150 (2)	0.01093 (18)	0.0134 (2)	-0.00029 (16)	0.00118 (16)	-0.00126 (15)
Cl4	0.01708 (8)	0.02447 (9)	0.02043 (8)	-0.00490 (7)	-0.00384 (6)	0.00143 (6)
C4A	0.0116 (2)	0.0189 (3)	0.0168 (3)	-0.0002 (2)	-0.00079 (19)	-0.0033 (2)
C4B	0.0157 (3)	0.0120 (2)	0.0171 (3)	-0.00189 (19)	0.0005 (2)	-0.00154 (18)
C4AA	0.0116 (2)	0.0128 (2)	0.0150 (2)	0.00039 (17)	0.00005 (17)	-0.00033 (17)
C4AB	0.0142 (2)	0.0118 (2)	0.0128 (2)	-0.00191 (18)	0.00138 (17)	-0.00057 (16)
C5A	0.0123 (2)	0.0165 (3)	0.0201 (3)	-0.0004 (2)	0.0017 (2)	0.0008 (2)
C5B	0.0146 (3)	0.0158 (3)	0.0192 (3)	-0.0023 (2)	0.0005 (2)	-0.0004 (2)
C6A	0.0158 (3)	0.0180 (3)	0.0212 (3)	0.0010 (2)	0.0052 (2)	0.0023 (2)
C6B	0.0142 (3)	0.0190 (3)	0.0206 (3)	0.0000 (2)	0.0011 (2)	0.0011 (2)
C7A	0.0192 (3)	0.0164 (3)	0.0169 (3)	0.0027 (2)	0.0048 (2)	0.0008 (2)

C7B	0.0165 (3)	0.0154 (3)	0.0182 (3)	0.0022 (2)	0.0023 (2)	0.0003 (2)
C8A	0.0177 (3)	0.0159 (3)	0.0156 (3)	0.0021 (2)	0.0011 (2)	-0.0019 (2)
C8B	0.0161 (3)	0.0125 (2)	0.0165 (3)	0.00052 (19)	0.0011 (2)	-0.00113 (18)
C8AA	0.0123 (2)	0.0140 (2)	0.0154 (2)	0.00074 (18)	0.00041 (18)	-0.00140 (18)
C8AB	0.0134 (2)	0.0115 (2)	0.0130 (2)	-0.00062 (17)	0.00100 (17)	-0.00091 (16)
C9A	0.0123 (3)	0.0234 (3)	0.0208 (3)	-0.0012 (2)	0.0024 (2)	-0.0026 (3)
C9B	0.0138 (3)	0.0171 (3)	0.0209 (3)	-0.0010 (2)	0.0007 (2)	-0.0004 (2)
C10A	0.0168 (3)	0.0210 (3)	0.0207 (3)	-0.0002 (2)	0.0060 (2)	0.0014 (2)
C10B	0.0165 (3)	0.0192 (3)	0.0190 (3)	0.0028 (2)	0.0008 (2)	-0.0008 (2)
C11A	0.0203 (3)	0.0198 (3)	0.0167 (3)	0.0020 (2)	0.0057 (2)	0.0001 (2)
C11B	0.0195 (3)	0.0196 (3)	0.0190 (3)	0.0047 (2)	0.0032 (2)	-0.0025 (2)
C12A	0.0190 (3)	0.0186 (3)	0.0130 (2)	-0.0003 (2)	0.0012 (2)	-0.0017 (2)
C12B	0.0206 (3)	0.0122 (2)	0.0158 (3)	0.0021 (2)	0.0009 (2)	-0.00163 (19)

Geometric parameters (Å, °)

Zn1—C14	2.2484 (3)	C6A—H6AA	0.9500
Zn1—C13	2.2664 (4)	C6B—C7B	1.3928 (13)
Zn1—C12	2.2868 (4)	C6B—H6BA	0.9500
Zn1—C11	2.3019 (3)	C7A—C8A	1.3936 (13)
N1A—C2A	1.3373 (11)	C7A—H7AA	0.9500
N1A—C8AA	1.4096 (11)	C7B—C8B	1.3858 (12)
N1A—H1A	0.89 (2)	C7B—H7BA	0.9500
N1B—C2B	1.3317 (10)	C8A—C8AA	1.3965 (11)
N1B—C8AB	1.4005 (10)	C8A—H8AA	0.9500
N1B—H1B	0.83 (2)	C8B—C8AB	1.3962 (11)
C2A—N3A	1.3102 (10)	C8B—H8BA	0.9500
C2A—C9A	1.4994 (12)	C9A—C10A	1.5257 (14)
C2B—N3B	1.3114 (9)	C9A—H9AA	0.9900
C2B—C9B	1.4952 (12)	C9A—H9AB	0.9900
N3A—C4A	1.4680 (11)	C9B—C10B	1.5262 (13)
N3A—C12A	1.4759 (11)	C9B—H9BA	0.9900
N3B—C12B	1.4735 (10)	C9B—H9BB	0.9900
N3B—C4B	1.4735 (11)	C10A—C11A	1.5193 (14)
C4A—C4AA	1.4998 (11)	C10A—H10A	0.9900
C4A—H4AA	0.9900	C10A—H10B	0.9900
C4A—H4AB	0.9900	C10B—C11B	1.5218 (13)
C4B—C4AB	1.4981 (11)	C10B—H10C	0.9900
C4B—H4BA	0.9900	C10B—H10D	0.9900
C4B—H4BB	0.9900	C11A—C12A	1.5140 (13)
C4AA—C8AA	1.3912 (11)	C11A—H11A	0.9900
C4AA—C5A	1.3927 (11)	C11A—H11B	0.9900
C4AB—C8AB	1.3891 (10)	C11B—C12B	1.5149 (14)
C4AB—C5B	1.3951 (12)	C11B—H11C	0.9900
C5A—C6A	1.3941 (13)	C11B—H11D	0.9900
C5A—H5AA	0.9500	C12A—H12A	0.9900
C5B—C6B	1.3944 (13)	C12A—H12B	0.9900
C5B—H5BA	0.9500	C12B—H12C	0.9900

C6A—C7A	1.3930 (14)	C12B—H12D	0.9900
C14—Zn1—C13	111.219 (10)	C7A—C8A—C8AA	119.08 (8)
C14—Zn1—C12	115.057 (11)	C7A—C8A—H8AA	120.5
C13—Zn1—C12	106.573 (10)	C8AA—C8A—H8AA	120.5
C14—Zn1—C11	109.994 (13)	C7B—C8B—C8AB	119.32 (7)
C13—Zn1—C11	110.340 (12)	C7B—C8B—H8BA	120.3
C12—Zn1—C11	103.331 (11)	C8AB—C8B—H8BA	120.3
C2A—N1A—C8AA	122.76 (7)	C4AA—C8AA—C8A	121.28 (7)
C2A—N1A—H1A	119.3 (14)	C4AA—C8AA—N1A	118.41 (7)
C8AA—N1A—H1A	117.9 (14)	C8A—C8AA—N1A	120.31 (7)
C2B—N1B—C8AB	122.87 (6)	C4AB—C8AB—C8B	121.48 (7)
C2B—N1B—H1B	117.3 (14)	C4AB—C8AB—N1B	118.97 (7)
C8AB—N1B—H1B	119.4 (14)	C8B—C8AB—N1B	119.53 (7)
N3A—C2A—N1A	121.36 (7)	C2A—C9A—C10A	112.83 (7)
N3A—C2A—C9A	121.75 (7)	C2A—C9A—H9AA	109.0
N1A—C2A—C9A	116.87 (7)	C10A—C9A—H9AA	109.0
N3B—C2B—N1B	121.29 (7)	C2A—C9A—H9AB	109.0
N3B—C2B—C9B	122.27 (7)	C10A—C9A—H9AB	109.0
N1B—C2B—C9B	116.41 (7)	H9AA—C9A—H9AB	107.8
C2A—N3A—C4A	123.12 (7)	C2B—C9B—C10B	113.48 (7)
C2A—N3A—C12A	123.38 (7)	C2B—C9B—H9BA	108.9
C4A—N3A—C12A	112.78 (6)	C10B—C9B—H9BA	108.9
C2B—N3B—C12B	123.39 (7)	C2B—C9B—H9BB	108.9
C2B—N3B—C4B	123.61 (7)	C10B—C9B—H9BB	108.9
C12B—N3B—C4B	112.65 (6)	H9BA—C9B—H9BB	107.7
N3A—C4A—C4AA	113.01 (6)	C11A—C10A—C9A	108.29 (7)
N3A—C4A—H4AA	109.0	C11A—C10A—H10A	110.0
C4AA—C4A—H4AA	109.0	C9A—C10A—H10A	110.0
N3A—C4A—H4AB	109.0	C11A—C10A—H10B	110.0
C4AA—C4A—H4AB	109.0	C9A—C10A—H10B	110.0
H4AA—C4A—H4AB	107.8	H10A—C10A—H10B	108.4
N3B—C4B—C4AB	112.81 (6)	C11B—C10B—C9B	109.21 (7)
N3B—C4B—H4BA	109.0	C11B—C10B—H10C	109.8
C4AB—C4B—H4BA	109.0	C9B—C10B—H10C	109.8
N3B—C4B—H4BB	109.0	C11B—C10B—H10D	109.8
C4AB—C4B—H4BB	109.0	C9B—C10B—H10D	109.8
H4BA—C4B—H4BB	107.8	H10C—C10B—H10D	108.3
C8AA—C4AA—C5A	119.02 (7)	C12A—C11A—C10A	109.98 (7)
C8AA—C4AA—C4A	120.02 (7)	C12A—C11A—H11A	109.7
C5A—C4AA—C4A	120.88 (7)	C10A—C11A—H11A	109.7
C8AB—C4AB—C5B	118.77 (7)	C12A—C11A—H11B	109.7
C8AB—C4AB—C4B	120.22 (7)	C10A—C11A—H11B	109.7
C5B—C4AB—C4B	120.99 (7)	H11A—C11A—H11B	108.2
C4AA—C5A—C6A	120.35 (8)	C12B—C11B—C10B	111.30 (7)
C4AA—C5A—H5AA	119.8	C12B—C11B—H11C	109.4
C6A—C5A—H5AA	119.8	C10B—C11B—H11C	109.4
C6B—C5B—C4AB	120.10 (8)	C12B—C11B—H11D	109.4

C6B—C5B—H5BA	120.0	C10B—C11B—H11D	109.4
C4AB—C5B—H5BA	120.0	H11C—C11B—H11D	108.0
C7A—C6A—C5A	120.09 (8)	N3A—C12A—C11A	113.56 (7)
C7A—C6A—H6AA	120.0	N3A—C12A—H12A	108.9
C5A—C6A—H6AA	120.0	C11A—C12A—H12A	108.9
C7B—C6B—C5B	120.48 (8)	N3A—C12A—H12B	108.9
C7B—C6B—H6BA	119.8	C11A—C12A—H12B	108.9
C5B—C6B—H6BA	119.8	H12A—C12A—H12B	107.7
C6A—C7A—C8A	120.15 (8)	N3B—C12B—C11B	114.03 (7)
C6A—C7A—H7AA	119.9	N3B—C12B—H12C	108.7
C8A—C7A—H7AA	119.9	C11B—C12B—H12C	108.7
C8B—C7B—C6B	119.85 (8)	N3B—C12B—H12D	108.7
C8B—C7B—H7BA	120.1	C11B—C12B—H12D	108.7
C6B—C7B—H7BA	120.1	H12C—C12B—H12D	107.6
C8AA—N1A—C2A—N3A	2.92 (13)	C5A—C4AA—C8AA—C8A	0.18 (12)
C8AA—N1A—C2A—C9A	-175.40 (8)	C4A—C4AA—C8AA—C8A	177.12 (8)
C8AB—N1B—C2B—N3B	-2.13 (12)	C5A—C4AA—C8AA—N1A	-179.12 (8)
C8AB—N1B—C2B—C9B	179.87 (7)	C4A—C4AA—C8AA—N1A	-2.18 (11)
N1A—C2A—N3A—C4A	7.04 (12)	C7A—C8A—C8AA—C4AA	-0.81 (12)
C9A—C2A—N3A—C4A	-174.72 (8)	C7A—C8A—C8AA—N1A	178.47 (8)
N1A—C2A—N3A—C12A	176.62 (8)	C2A—N1A—C8AA—C4AA	-5.18 (13)
C9A—C2A—N3A—C12A	-5.15 (12)	C2A—N1A—C8AA—C8A	175.52 (8)
N1B—C2B—N3B—C12B	177.97 (7)	C5B—C4AB—C8AB—C8B	-0.34 (12)
C9B—C2B—N3B—C12B	-4.15 (12)	C4B—C4AB—C8AB—C8B	177.67 (7)
N1B—C2B—N3B—C4B	5.30 (12)	C5B—C4AB—C8AB—N1B	-178.78 (7)
C9B—C2B—N3B—C4B	-176.82 (7)	C4B—C4AB—C8AB—N1B	-0.77 (11)
C2A—N3A—C4A—C4AA	-13.21 (11)	C7B—C8B—C8AB—C4AB	0.19 (12)
C12A—N3A—C4A—C4AA	176.22 (7)	C7B—C8B—C8AB—N1B	178.62 (8)
C2B—N3B—C4B—C4AB	-5.72 (11)	C2B—N1B—C8AB—C4AB	-0.11 (12)
C12B—N3B—C4B—C4AB	-179.08 (7)	C2B—N1B—C8AB—C8B	-178.59 (8)
N3A—C4A—C4AA—C8AA	10.43 (11)	N3A—C2A—C9A—C10A	21.96 (12)
N3A—C4A—C4AA—C5A	-172.68 (7)	N1A—C2A—C9A—C10A	-159.73 (8)
N3B—C4B—C4AB—C8AB	3.35 (10)	N3B—C2B—C9B—C10B	20.32 (12)
N3B—C4B—C4AB—C5B	-178.68 (7)	N1B—C2B—C9B—C10B	-161.70 (8)
C8AA—C4AA—C5A—C6A	0.99 (12)	C2A—C9A—C10A—C11A	-49.37 (10)
C4A—C4AA—C5A—C6A	-175.93 (8)	C2B—C9B—C10B—C11B	-46.34 (10)
C8AB—C4AB—C5B—C6B	0.16 (12)	C9A—C10A—C11A—C12A	61.61 (10)
C4B—C4AB—C5B—C6B	-177.84 (8)	C9B—C10B—C11B—C12B	57.99 (10)
C4AA—C5A—C6A—C7A	-1.52 (13)	C2A—N3A—C12A—C11A	17.27 (11)
C4AB—C5B—C6B—C7B	0.17 (14)	C4A—N3A—C12A—C11A	-172.19 (7)
C5A—C6A—C7A—C8A	0.87 (13)	C10A—C11A—C12A—N3A	-45.61 (10)
C5B—C6B—C7B—C8B	-0.33 (14)	C2B—N3B—C12B—C11B	15.61 (11)
C6A—C7A—C8A—C8AA	0.29 (13)	C4B—N3B—C12B—C11B	-171.01 (7)
C6B—C7B—C8B—C8AB	0.15 (13)	C10B—C11B—C12B—N3B	-42.79 (10)

Hydrogen-bond geometry (\AA , $^\circ$)

$Cg3$ and $Cg9$ are the centroids of the $C5A-C8A/C4AA/C8AA$ and $C5B-C8B/C4AB/C8AB$ rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1A-H1A\cdots C12$	0.89 (2)	2.44 (2)	3.2659 (8)	155.9 (19)
$N1B-H1B\cdots C11^i$	0.83 (2)	2.352 (19)	3.1661 (7)	166.6 (18)
$C11A-H11A\cdots Cg9^{ii}$	0.99	2.67	3.5718 (10)	151
$C12B-H12D\cdots Cg3^{iii}$	0.99	2.57	3.4002 (10)	142

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