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Key indicators

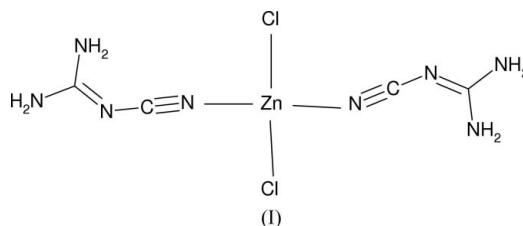
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{N}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.035
 wR factor = 0.077
Data-to-parameter ratio = 18.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

A monoclinic polymorph of dichlorobis-(cyanoguanidine)zinc(II)

The molecular title compound, β -[ZnCl₂(C₂H₄N₄)₂], crystallizes as a monoclinic polymorph of the known triclinic structure of this material. A complex network of N—H···N and N—H···Cl hydrogen bonds help to establish the crystal packing.

Comment

The title compound, (I) (Fig. 1), crystallizes as a monoclinic polymorph (space group $P2_1/c$) of the known triclinic structure (hereafter known as the α polymorph) of this material (Pickardt & Kuhn, 1995). Polymorph (I) contains isolated [ZnCl₂(C₂H₄N₄)₂] molecules, with the Zn²⁺ cations coordinated by two chloride ions and two cyanide N atoms of the cyanoguanidine ligands. The geometries of the zinc ions in (I) (Table 1) and in the α polymorph [Zn—N = 1.975 (6) and 1.977 (5) Å; Zn—Cl = 2.236 (2) and 2.2565 (17) Å] are very similar. There are no significant differences in the geometries of the organic groups in the two structures. Slight differences arise in terms of the orientation of the guanidine 'arms' of the ligands. In (I), the dihedral angle between the mean planes of the C2/N2/N3/N3 and C4/N6/N7/N8 groupings is 27.7 (2)°. The equivalent value of 42.7 (5)° for the α polymorph shows that these two groupings are significantly more twisted in the triclinic polymorph (data calculated with *PLATON*; Spek, 2003).



As well as van der Waals forces, the molecules of (I) interact by way of N—H···N and N—H···Cl hydrogen bonds (Table 2) of varied lengths and strengths. The N—H···N bonds link the molecules into [100] stacks of dimers and the N—H···Cl bonds crosslink the [100] columns into a three-dimensional network (Fig. 2). Unfortunately, some of the H-atom positions in the α polymorph appear to be incorrect, so a detailed comparison of the hydrogen bonding in the two structures is not possible.

Other compounds with the stoichiometry [M(C₂H₄N₄)₂X₂] (M = divalent metal cation and X = halide) include [Cd(C₂H₄N₄)₂I₂] (Chiesi Villa *et al.*, 1974) and [Cd(C₂H₄N₄)₂Br₂] (Pickardt & Kuhn, 1996). Neither of these shares a structure with the zinc compounds discussed here.

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The iodide is molecular (space group *Pbcn*), whereas the bromide is polymeric, via Cd—(Br,Br)—Cd bridges.

Experimental

The following solutions were mixed at 293 K in a Petri dish, resulting in a colourless mixture: 10 ml of 0.1 M cyanoguanidine, 1 ml of 1 M ZnCl₂ and 1 ml of dilute HCl. Colourless rods and bars of (I) grew over the course of a few days as the water evaporated at 293 K.

Crystal data

[CnCl ₂ (C ₄ H ₈ N ₈)]	$D_x = 1.814 \text{ Mg m}^{-3}$
$M_r = 304.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2094 reflections
$a = 4.9315 (3) \text{ \AA}$	$\theta = 2.6\text{--}26.8^\circ$
$b = 14.6161 (10) \text{ \AA}$	$\mu = 2.66 \text{ mm}^{-1}$
$c = 15.5026 (11) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 93.928 (2)^\circ$	Bar, colourless
$V = 1114.79 (13) \text{ \AA}^3$	$0.31 \times 0.08 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART1000 CCD diffractometer	2444 independent reflections
ω scans	1610 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.051$
$T_{\text{min}} = 0.495$, $T_{\text{max}} = 0.950$	$\theta_{\text{max}} = 27.0^\circ$
7331 measured reflections	$h = -6 \rightarrow 6$
	$k = -18 \rightarrow 13$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2]$
$wR(F^2) = 0.077$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2444 reflections	$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$
136 parameters	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Zn1—N1	1.974 (3)	Zn1—Cl2	2.2302 (10)
Zn1—N5	1.984 (3)	Zn1—Cl1	2.2664 (10)
Cl1—N1—Zn1	166.5 (3)	C3—N5—Zn1	174.2 (3)

Table 2

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N4—H3 \cdots N6 ⁱ	0.86	2.46	3.082 (4)	130
N4—H4 \cdots N2 ⁱⁱ	0.86	2.31	3.156 (4)	168
N3—H1 \cdots Cl1 ⁱⁱⁱ	0.86	2.57	3.365 (3)	155
N4—H3 \cdots Cl1 ⁱⁱⁱ	0.86	2.77	3.520 (3)	147
N7—H5 \cdots Cl2 ^{iv}	0.86	2.47	3.282 (3)	158
N7—H6 \cdots Cl1 ^v	0.86	2.56	3.368 (3)	156
N8—H7 \cdots Cl2 ^{iv}	0.86	2.63	3.402 (3)	151
N8—H8 \cdots Cl1 ^{vi}	0.86	2.50	3.322 (3)	160

Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x + 3, -y, -z + 1$; (iii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x - 1, y, z$; (vi) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

The H atoms were placed in idealized positions (N—H = 0.86 \AA) and refined as riding with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ applied.

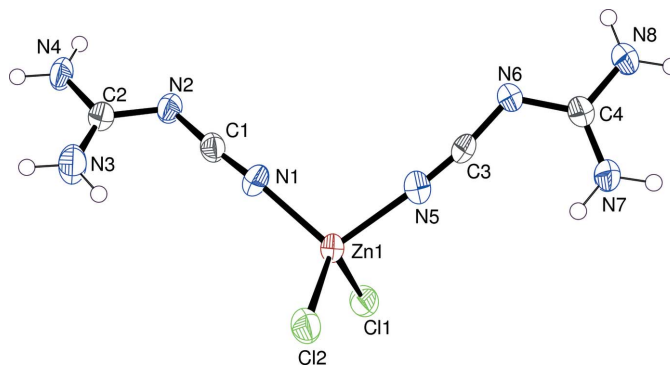


Figure 1

The molecular structure of (I), showing 50% displacement ellipsoids (H atoms are drawn as spheres of arbitrary radius).

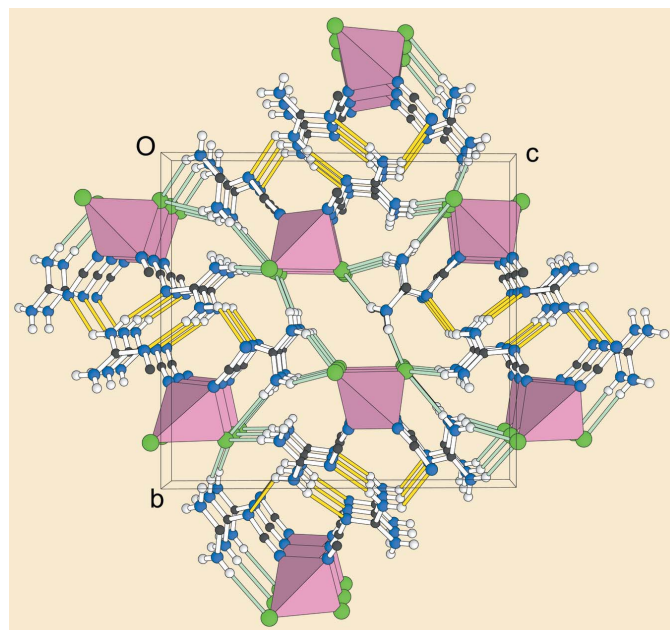


Figure 2

[100] projection of the packing in (I), with the ZnN₂Cl₂ groupings represented by polyhedra. Colour key: C black, H white, N blue, and Cl green. The H \cdots N and H \cdots Cl portions of the hydrogen bonds are highlighted in yellow and green, respectively.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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supporting information

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S1. Comment

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As well as van der Waals forces, the molecules of (I) interact by way of $\text{N—H}\cdots\text{N}$ and $\text{N—H}\cdots\text{Cl}$ hydrogen bonds (Table 2) of varied lengths and strengths. The $\text{N—H}\cdots\text{N}$ bonds link the molecules into [100] stacks of dimers and the $\text{N—H}\cdots\text{Cl}$ bonds crosslink the [100] columns into a three-dimensional network (Fig. 2). Unfortunately, some of the H-atom positions in the α polymorph appear to be incorrect, so a detailed comparison of the hydrogen bonding in the two structures is not possible.

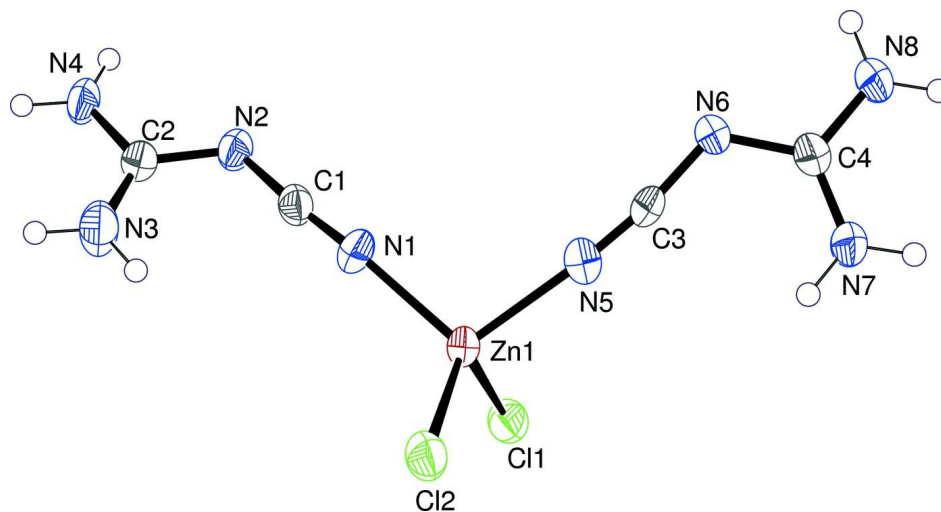
Other compounds with the stoichiometry $M(\text{C}_2\text{H}_4\text{N}_4)_2\text{X}_2$ (M = divalent metal cation and X = halide) include $\text{Cd}(\text{C}_2\text{H}_4\text{N}_4)_2\text{I}_2$ (Chiesi Villa *et al.*, 1974) and $\text{Cd}(\text{C}_2\text{H}_4\text{N}_4)_2\text{Br}_2$ (Pickardt & Kuhn, 1996). Neither of these shares a structure with the zinc compounds discussed here. The iodide is molecular (space group *Pbcn*), whereas the bromide is polymeric, *via* Cd—(Br,Br)—Cd bridges.

S2. Experimental

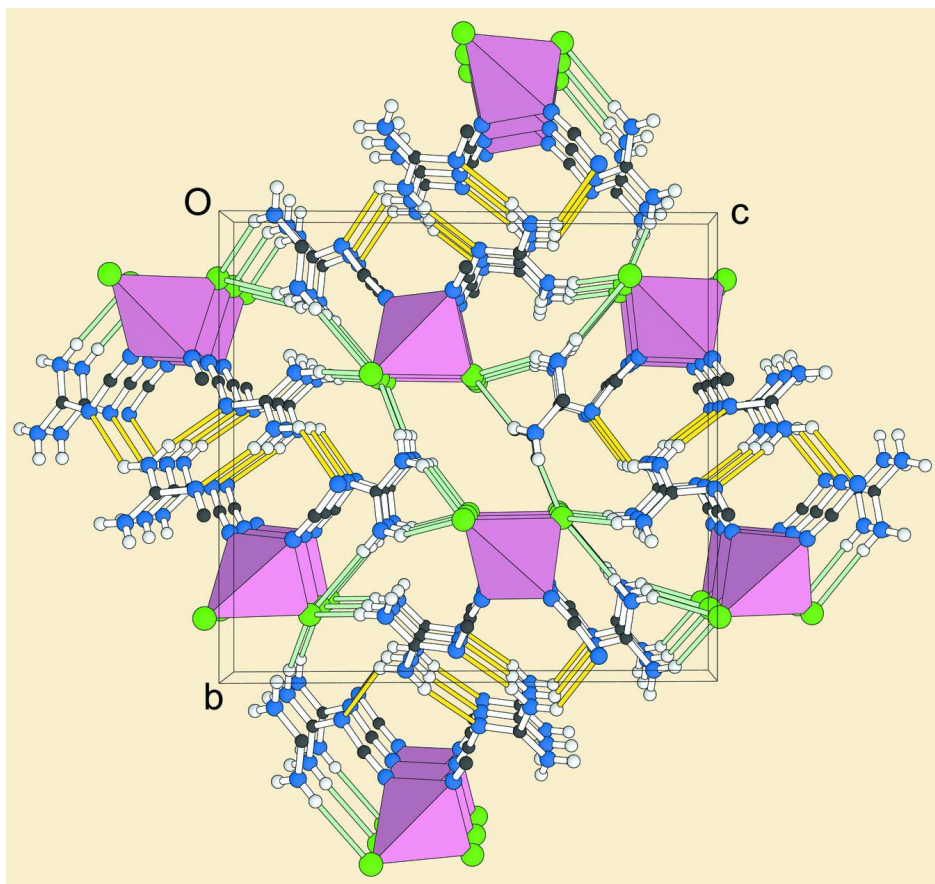
The following solutions were mixed at 293 K in a Petri dish, resulting in a colourless mixture: 10 ml of 0.1 *M* cyanoguanidine, 1 ml of 1 *M* ZnCl_2 and 1 ml of dilute HCl. Colourless rods and bars of (I) grew over the course of a few days as the water evaporated at 293 K.

S3. Refinement

The H atoms were placed in idealized positions ($\text{N—H} = 0.86$ Å) and refined as riding with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ applied.

**Figure 1**

The molecular structure of (I), showing 50% displacement ellipsoids (H atoms are drawn as spheres of arbitrary radius).

**Figure 2**

[100] projection of the packing in (I), with the ZnN_2Cl_2 groupings represented by polyhedra. Colour key: C black, H white, N blue, and Cl green. The $\text{H}\cdots\text{N}$ and $\text{H}\cdots\text{Cl}$ portions of the hydrogen bonds are highlighted in yellow and green, respectively.

dichlorobis(cyanoguanidine)zinc(II)

Crystal data

[ZnCl₂(C₄H₈N₆)]
M_r = 304.45
 Monoclinic, *P*2₁/*c*
 Hall symbol: -*P* 2ybc
a = 4.9315 (3) Å
b = 14.6161 (10) Å
c = 15.5026 (11) Å
 β = 93.928 (2)°
V = 1114.79 (13) Å³
Z = 4

F(000) = 608
D_x = 1.814 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 2094 reflections
 θ = 2.6–26.8°
 μ = 2.66 mm⁻¹
T = 293 K
 Bar, colourless
 0.31 × 0.08 × 0.02 mm

Data collection

Bruker SMART1000 CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 1999)
T_{min} = 0.495, *T_{max}* = 0.950

7331 measured reflections
 2444 independent reflections
 1610 reflections with *I* > 2σ(*I*)
R_{int} = 0.051
 θ_{\max} = 27.0°, θ_{\min} = 1.9°
h = -6→6
k = -18→13
l = -19→19

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.035
wR(*F*²) = 0.077
S = 0.91
 2444 reflections
 136 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0345P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

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 > σ(*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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
Zn1	0.57190 (7)	0.26684 (3)	0.41448 (2)	0.03114 (12)
Cl1	0.77571 (18)	0.35115 (6)	0.31465 (5)	0.0421 (2)
Cl2	0.35476 (17)	0.35081 (7)	0.50813 (6)	0.0427 (2)
N1	0.8270 (5)	0.1795 (2)	0.47356 (17)	0.0377 (7)

C1	1.0125 (7)	0.1372 (2)	0.4988 (2)	0.0305 (7)
N2	1.2201 (5)	0.0859 (2)	0.52099 (17)	0.0358 (7)
C2	1.3399 (7)	0.0944 (2)	0.6013 (2)	0.0324 (8)
N3	1.2696 (6)	0.1547 (2)	0.65774 (19)	0.0515 (9)
H1	1.3542	0.1569	0.7081	0.062*
H2	1.1387	0.1921	0.6446	0.062*
N4	1.5405 (6)	0.0377 (2)	0.62248 (18)	0.0463 (8)
H3	1.6237	0.0405	0.6730	0.056*
H4	1.5885	-0.0023	0.5858	0.056*
N5	0.3319 (6)	0.1889 (2)	0.33726 (18)	0.0390 (7)
C3	0.2135 (7)	0.1398 (2)	0.2928 (2)	0.0328 (8)
N6	0.1010 (6)	0.0754 (2)	0.2464 (2)	0.0501 (9)
C4	-0.0951 (7)	0.0945 (3)	0.1849 (2)	0.0374 (8)
N7	-0.2052 (6)	0.1752 (2)	0.17497 (18)	0.0440 (8)
H5	-0.3277	0.1847	0.1338	0.053*
H6	-0.1555	0.2189	0.2097	0.053*
N8	-0.1731 (7)	0.0286 (2)	0.1315 (2)	0.0587 (10)
H7	-0.2957	0.0388	0.0905	0.070*
H8	-0.1016	-0.0249	0.1375	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0351 (2)	0.0310 (2)	0.02591 (19)	0.00114 (19)	-0.00776 (14)	0.00054 (18)
C11	0.0544 (5)	0.0371 (6)	0.0336 (5)	-0.0095 (4)	-0.0057 (4)	0.0064 (4)
C12	0.0458 (5)	0.0462 (6)	0.0349 (5)	0.0078 (4)	-0.0073 (4)	-0.0088 (4)
N1	0.0362 (15)	0.0371 (19)	0.0380 (16)	0.0058 (14)	-0.0092 (13)	0.0066 (14)
C1	0.0336 (17)	0.033 (2)	0.0238 (16)	-0.0042 (15)	-0.0018 (14)	0.0007 (14)
N2	0.0376 (15)	0.0360 (18)	0.0323 (15)	0.0105 (13)	-0.0083 (12)	-0.0020 (13)
C2	0.0345 (16)	0.033 (2)	0.0289 (17)	0.0001 (15)	-0.0026 (14)	0.0023 (15)
N3	0.0550 (18)	0.063 (3)	0.0347 (17)	0.0247 (17)	-0.0107 (15)	-0.0110 (16)
N4	0.0561 (18)	0.044 (2)	0.0356 (17)	0.0196 (16)	-0.0203 (14)	-0.0042 (14)
N5	0.0400 (15)	0.040 (2)	0.0350 (16)	-0.0022 (14)	-0.0094 (13)	-0.0020 (14)
C3	0.0372 (17)	0.031 (2)	0.0291 (17)	0.0031 (15)	-0.0086 (15)	0.0076 (15)
N6	0.065 (2)	0.0292 (19)	0.0513 (19)	0.0025 (15)	-0.0324 (17)	-0.0066 (15)
C4	0.0428 (19)	0.034 (2)	0.0335 (18)	-0.0035 (16)	-0.0102 (16)	-0.0018 (16)
N7	0.0536 (17)	0.038 (2)	0.0375 (17)	0.0079 (15)	-0.0196 (14)	-0.0067 (14)
N8	0.072 (2)	0.037 (2)	0.061 (2)	0.0068 (17)	-0.0378 (19)	-0.0153 (17)

Geometric parameters (Å, °)

Zn1—N1	1.974 (3)	N4—H3	0.860
Zn1—N5	1.984 (3)	N4—H4	0.860
Zn1—C12	2.2302 (10)	N5—C3	1.130 (4)
Zn1—C11	2.2664 (10)	C3—N6	1.287 (4)
N1—C1	1.150 (4)	N6—C4	1.340 (4)
C1—N2	1.296 (4)	C4—N7	1.303 (5)
N2—C2	1.347 (4)	C4—N8	1.310 (4)

C2—N3	1.305 (4)	N7—H5	0.860
C2—N4	1.315 (4)	N7—H6	0.860
N3—H1	0.860	N8—H7	0.860
N3—H2	0.860	N8—H8	0.860
N1—Zn1—N5	104.10 (13)	C2—N4—H3	120.0
N1—Zn1—Cl2	111.92 (9)	C2—N4—H4	120.0
N5—Zn1—Cl2	114.55 (9)	H3—N4—H4	120.0
N1—Zn1—Cl1	111.74 (9)	C3—N5—Zn1	174.2 (3)
N5—Zn1—Cl1	100.03 (9)	N5—C3—N6	172.2 (4)
Cl2—Zn1—Cl1	113.61 (4)	C3—N6—C4	120.5 (3)
C1—N1—Zn1	166.5 (3)	N7—C4—N8	119.3 (3)
N1—C1—N2	175.1 (4)	N7—C4—N6	123.1 (3)
C1—N2—C2	118.7 (3)	N8—C4—N6	117.5 (3)
N3—C2—N4	119.2 (3)	C4—N7—H5	120.0
N3—C2—N2	124.2 (3)	C4—N7—H6	120.0
N4—C2—N2	116.5 (3)	H5—N7—H6	120.0
C2—N3—H1	120.0	C4—N8—H7	120.0
C2—N3—H2	120.0	C4—N8—H8	120.0
H1—N3—H2	120.0	H7—N8—H8	120.0
N5—Zn1—N1—C1	112.9 (12)	C1—N2—C2—N3	-3.6 (5)
Cl2—Zn1—N1—C1	-122.8 (12)	C1—N2—C2—N4	176.5 (3)
Cl1—Zn1—N1—C1	5.9 (13)	C3—N6—C4—N8	170.1 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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