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1-(4-Chlorophenyl)piperazine-1,4-diium tetrachloridozincate(II) monohydrate

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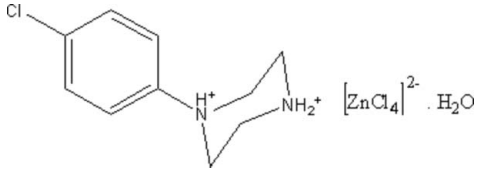
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.053; wR factor = 0.063; data-to-parameter ratio = 18.5.

In the crystal structure of the title compound, $(C_{10}H_{15}ClN_2)[ZnCl_4]\cdot H_2O$, the Zn atom is coordinated by four Cl atoms in a tetrahedral geometry. The water molecules and the 1-(4-chlorophenyl)piperazine-1,4-diium cations interact with the $[ZnCl_4]^{2-}$ anions through O—H···Cl, N—H···Cl, N—H···O and C—H···Cl hydrogen bonds (five simple and one bifurcated). Intermolecular π–π stacking interactions are present between adjacent aromatic rings of 1-(4-chlorophenyl)piperazine-1,4-diium cations (the centroid–centroid distance is 3.453 Å).

Related literature

For related literature, see: Ben Gharbia *et al.* (2005); Guo *et al.* (2007); Valkonen *et al.* (2006); Janiak (2000).



Experimental

Crystal data

$(C_{10}H_{15}ClN_2)[ZnCl_4]\cdot H_2O$
M_r = 423.90
Monoclinic, $P2_1/c$
a = 7.2036 (2) Å
b = 15.1575 (5) Å
c = 15.4870 (5) Å
β = 103.012 (2)°
V = 1647.58 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.29 mm^{-1}
T = 293 K
0.44 × 0.28 × 0.23 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.34, T_{max} = 0.59
20612 measured reflections
3901 independent reflections
3369 reflections with $I > 2\sigma(I)$
R_{int} = 0.085

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.063
S = 0.89
3203 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—Cl1	2.3036 (11)	Zn1—Cl3	2.2495 (13)
Zn1—Cl2	2.2937 (11)	Zn1—Cl4	2.2420 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H15···O1	0.89	1.86	2.742 (6)	169
N2—H16···Cl4^{i}	0.89	2.53	3.249 (4)	137
N2—H16···Cl2^{i}	0.89	2.77	3.352 (3)	123
N2—H17···Cl1	0.89	2.42	3.261 (5)	156
O1—H1···Cl2^{ii}	0.81	2.61	3.342 (3)	149
O1—H2···Cl3^{iii}	0.82	2.52	3.258 (4)	149
C5—H5···Cl4^{iv}	0.93	2.76	3.686 (5)	168

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

Data collection: *COLLECT* (Nonius, 2001).; cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; 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, 1998); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2190).

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supporting information

Acta Cryst. (2008). E**64**, m880 [doi:10.1107/S1600536808016590]

1-(4-Chlorophenyl)piperazine-1,4-diium tetrachloridozincate(II) monohydrate

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S1. Comment

The crystal structure of the title compound, (I), (Fig. 1), contains a $[ZnCl_4]^{2-}$ tetrahedral anion, a 1-(4-chlorophenyl)-piperazine-1,4-dium (2+) cation and a water molecule. Fig. 2 shows the atomic arrangement, which can be described as built up by $[ZnCl_4]$ tetrahedra interconnected through water molecules *via* a O—H···Cl bond to form chains which evolve along the a direction. These $[ZnCl_4].[H_2O]$ chains are interconnected into a three-dimensional network by the organic entities through N—H···Cl, C—H···Cl bonds and π-π interactions. Fig.3 shows the way in which two adjacent aromatic rings of the 1-(4-chlorophenyl)piperazine-1,4-dium cations run parallel in the opposite direction and stack each other by turns in a face-to-face mode. The nearest centroid-centroid distance is 3.453 (1) Å, less than 3.8 Å, the maximum value accepted for π-π interactions (Janiak, 2000). Generally, the Zn—Cl bond lengths and Cl—Zn—Cl bond angles in the $[ZnCl_4]^{2-}$ anion are not equal to one another but vary with the environment around the Cl atoms (Valkonen *et al.*, 2006). In the title compound, the four chlorine atoms of the $[ZnCl_4]^{2-}$ anion are acting as acceptors of the hydrogen bonds. The bond angles Cl—Zn—Cl vary from 103.37 (5) to 115.30 (5)°, and the bond length of the Zn—Cl lie in the range 2.2420 (12) - 2.3036 (11) Å. Owing to these differences in Zn—Cl bond lengths and Cl—Zn—Cl angles, the coordination geometry of the Zn atom can be described as a slightly distorted tetrahedron (as in Guo *et al.*, 2007). The nearst Zn···Zn intra-chain separation is 7.204 (1) Å, while the distance between adjacent chains is 6.370 (2) Å. Examination of the organic cation geometry shows that the piperazine-1,4-dium ring adopts a typical chair conformation and its geometric parameters [d_{av}(C—N) = 1.501 (4) and d_{av}(C—C) = 1.508 (4) Å] are in full agreement with those found in phenyl-piperazinium tetrachlorozincate (Ben Gharbia *et al.*, 2005).

S2. Experimental

$ZnCl_2$, aqueous 1*M* HCl solution and 1-(4-chlorophenyl)piperazine in a 1:2:1 molar ratio were mixed and dissolved in sufficient ethanol. Crystals of (I) grew as the ethanol evaporated at 293 K over the course of a few days.

S3. Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms 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 and O—H = 0.82 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. The refinement was carried out with 3203 reflections with I>3σ(I). The R factors reported are those calculated for I>2σ(I) (3369 reflections)

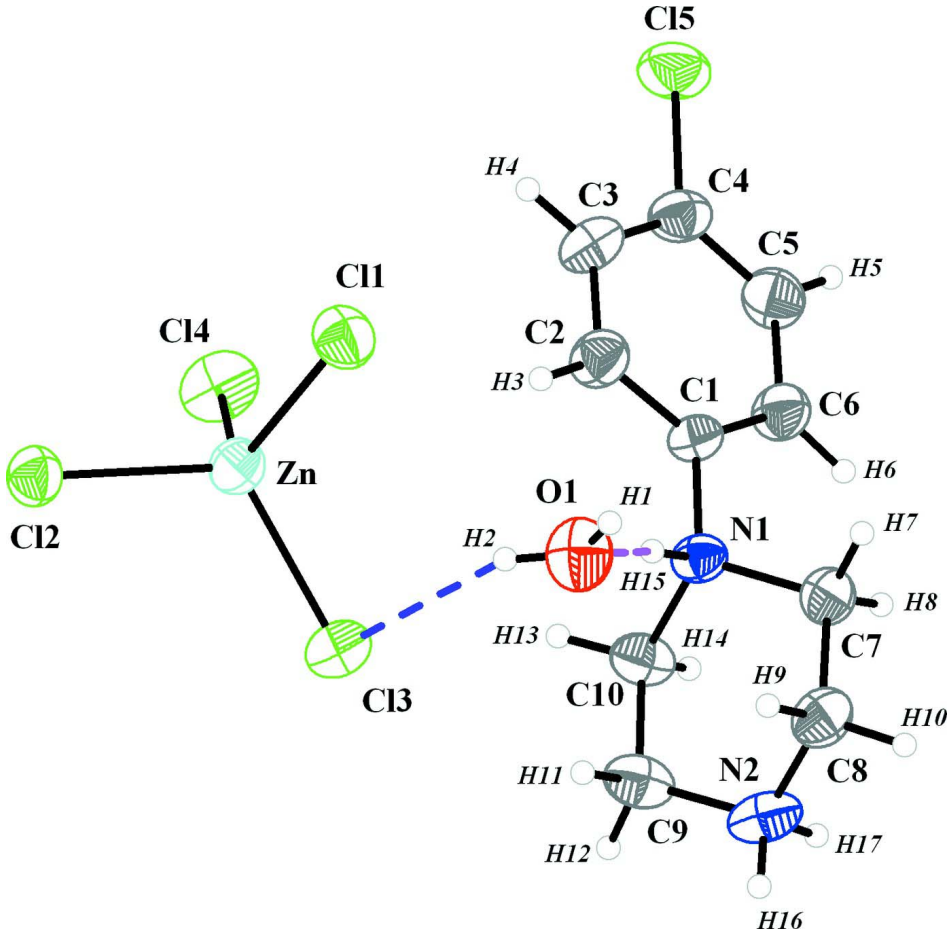

Figure 1

A view of (I), showing 40% probability displacement ellipsoids and arbitrary spheres for the H atoms.

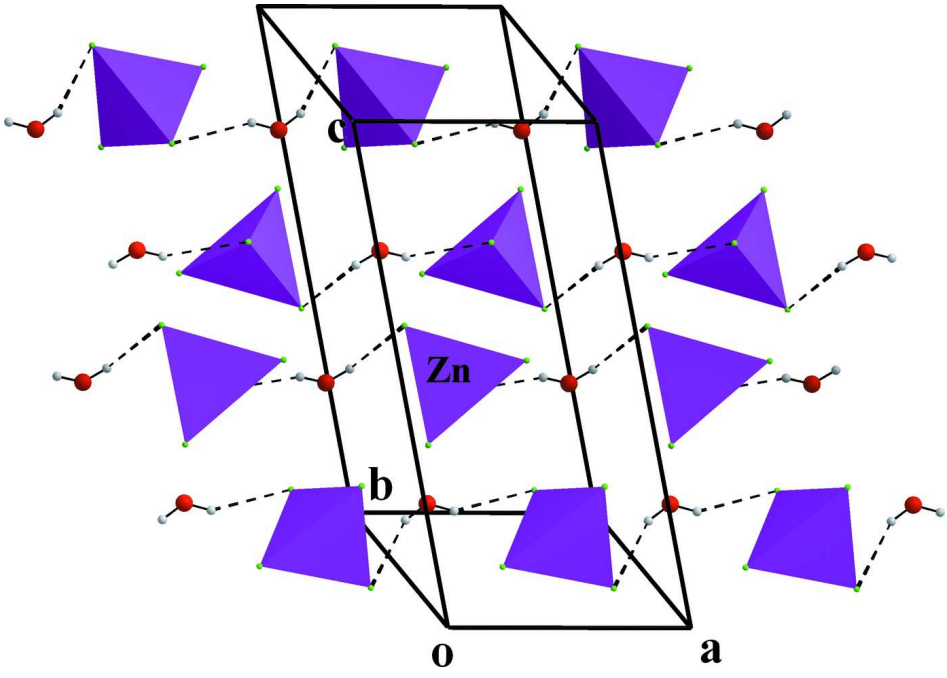

Figure 2

A stereoview of part of the crystal structure showing the formation of (100) chains formed by $[ZnCl_4]^{2-}$ tetrahedral anions interconnected through the water molecules.

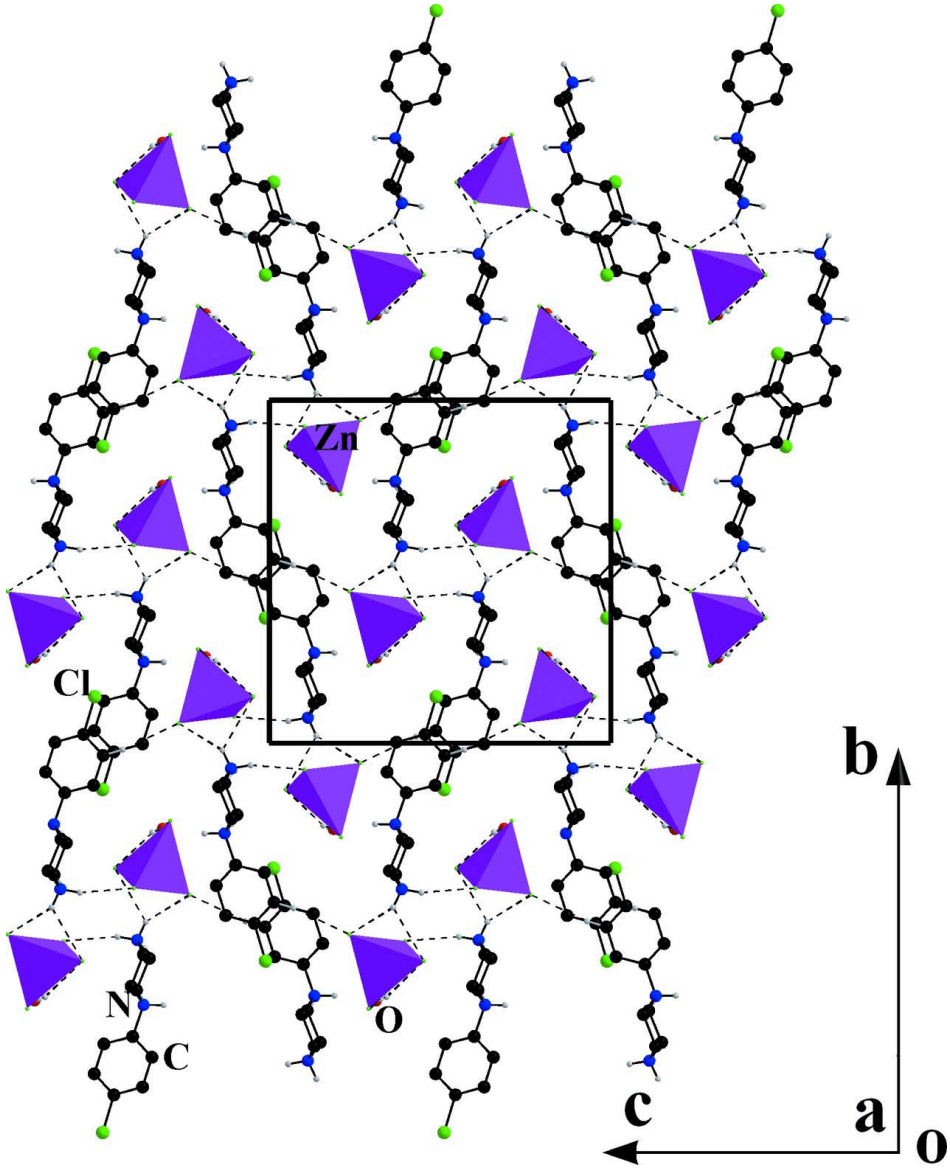

Figure 3

The packing of (I), viewed down the *a* axis, showing the N—H···Cl, C—H···Cl and O—H···Cl hydrogen bonds between the 1-(4-chlorophenyl)piperazine-1,4-dium cations, water molecules and $[ZnCl_4]^{2-}$ anions.

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Crystal data

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.2036$ (2) Å
$b = 15.1575$ (5) Å
$c = 15.4870$ (5) Å
$\beta = 103.012$ (2)°
$V = 1647.58$ (9) Å^3
$Z = 4$
$F(000) = 856$
$D_x = 1.709$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 19642 reflections
$\theta = 0.7$–$27.9°$
$\mu = 2.29$ mm^{-1}

T = 293 K
Plate, colorless

0.44 × 0.28 × 0.23 mm

Data collection

Nonius KappaCCD diffractometer
Graphite monochromator
φ and ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.34, T_{max} = 0.59
20612 measured reflections

3901 independent reflections
3369 reflections with $I > 2\sigma(I)$
R_{int} = 0.085
θ_{max} = 28.0°, θ_{min} = 1.9°
h = −9→9
k = −17→19
l = −20→20

Refinement

Refinement on F
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.063
S = 0.90
3203 reflections
173 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
*w*eight = 1.0/[1.57 + 1.32*x + 0.866*(2x^2-1)] * [1-(delta*F*/6*sigma*F*)^2]^2
where x = *F* /*F*max
$(\Delta/\sigma)_{max}$ = 0.000411
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.58976 (7)	0.36124 (3)	0.65838 (3)	0.0375
Cl1	0.29500 (16)	0.42310 (8)	0.60275 (7)	0.0461
Cl2	0.75399 (15)	0.36476 (7)	0.54758 (6)	0.0415
Cl3	0.5442 (2)	0.22604 (8)	0.70986 (10)	0.0568
Cl4	0.7715 (2)	0.44230 (9)	0.76618 (7)	0.0560
Cl5	0.29277 (18)	−0.13523 (7)	0.48834 (10)	0.0558
C1	0.2020 (5)	0.1446 (2)	0.4005 (2)	0.0312
C2	0.2558 (6)	0.0844 (3)	0.3443 (3)	0.0410
C3	0.2866 (7)	−0.0026 (3)	0.3717 (3)	0.0442
C4	0.2642 (6)	−0.0255 (3)	0.4557 (3)	0.0404
C5	0.2183 (7)	0.0359 (3)	0.5131 (3)	0.0441
C6	0.1869 (7)	0.1230 (3)	0.4851 (3)	0.0399
C7	−0.0002 (6)	0.2802 (3)	0.3894 (3)	0.0404
C8	−0.0229 (6)	0.3724 (3)	0.3515 (3)	0.0433
C9	0.3249 (7)	0.3838 (3)	0.3692 (3)	0.0468
C10	0.3479 (6)	0.2911 (3)	0.4050 (3)	0.0406
N1	0.1724 (5)	0.2369 (2)	0.3687 (2)	0.0313
N2	0.1516 (6)	0.4259 (2)	0.3875 (3)	0.0466
O1	0.0861 (5)	0.2511 (3)	0.1875 (2)	0.0530
H1	−0.0199	0.2401	0.1574	0.0730*
H2	0.1897	0.2453	0.1746	0.0730*
H3	0.2669	0.1008	0.2869	0.0471*
H4	0.3213	−0.0443	0.3350	0.0503*
H5	0.2084	0.0191	0.5702	0.0511*

H6	0.1563	0.1671	0.5231	0.0473*
H7	−0.1133	0.2465	0.3632	0.0448*
H8	0.0133	0.2821	0.4533	0.0447*
H9	−0.0388	0.3688	0.2866	0.0492*
H10	−0.1329	0.4027	0.3654	0.0493*
H11	0.3148	0.3815	0.3047	0.0543*
H12	0.4375	0.4194	0.3985	0.0543*
H13	0.4580	0.2643	0.3887	0.0434*
H14	0.3750	0.2920	0.4706	0.0430*
H15	0.1556	0.2362	0.3097	0.0410*
H16	0.1361	0.4792	0.3623	0.0620*
H17	0.1605	0.4357	0.4450	0.0620*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0394 (2)	0.0380 (2)	0.0350 (2)	−0.00079 (19)	0.00810 (19)	0.00223 (18)
Cl1	0.0445 (5)	0.0526 (6)	0.0407 (5)	0.0090 (5)	0.0082 (4)	0.0053 (4)
Cl2	0.0449 (5)	0.0428 (5)	0.0392 (5)	−0.0021 (4)	0.0146 (4)	−0.0012 (4)
Cl3	0.0650 (7)	0.0405 (6)	0.0698 (7)	0.0029 (5)	0.0255 (6)	0.0136 (5)
Cl4	0.0704 (7)	0.0562 (7)	0.0350 (5)	−0.0084 (6)	−0.0019 (5)	−0.0027 (4)
Cl5	0.0547 (6)	0.0338 (5)	0.0785 (8)	0.0044 (4)	0.0140 (6)	0.0126 (5)
C1	0.0360 (16)	0.0256 (15)	0.0309 (16)	−0.0002 (14)	0.0055 (14)	−0.0033 (13)
C2	0.048 (2)	0.039 (2)	0.0367 (19)	0.0017 (17)	0.0105 (16)	−0.0033 (16)
C3	0.050 (2)	0.034 (2)	0.047 (2)	0.0069 (17)	0.0085 (18)	−0.0077 (17)
C4	0.0367 (18)	0.0305 (18)	0.051 (2)	0.0021 (15)	0.0034 (16)	0.0003 (16)
C5	0.050 (2)	0.042 (2)	0.041 (2)	0.0025 (18)	0.0112 (17)	0.0089 (17)
C6	0.050 (2)	0.037 (2)	0.0339 (19)	0.0010 (16)	0.0124 (16)	−0.0005 (15)
C7	0.0351 (18)	0.037 (2)	0.051 (2)	0.0050 (15)	0.0128 (16)	0.0027 (17)
C8	0.042 (2)	0.039 (2)	0.049 (2)	0.0095 (17)	0.0085 (17)	0.0014 (17)
C9	0.047 (2)	0.035 (2)	0.054 (2)	−0.0055 (17)	0.0040 (18)	0.0071 (18)
C10	0.0354 (18)	0.033 (2)	0.049 (2)	−0.0031 (15)	0.0012 (16)	0.0045 (16)
N1	0.0391 (16)	0.0263 (14)	0.0274 (13)	0.0008 (12)	0.0055 (12)	0.0007 (11)
N2	0.065 (2)	0.0284 (16)	0.0424 (18)	0.0037 (15)	0.0030 (17)	−0.0020 (13)
O1	0.0519 (18)	0.067 (2)	0.0389 (15)	0.0008 (16)	0.0065 (14)	−0.0023 (14)

Geometric parameters (Å, º)

Zn1—Cl1	2.3036 (11)	C7—H7	0.970
Zn1—Cl2	2.2937 (11)	C8—N2	1.494 (6)
Zn1—Cl3	2.2495 (13)	C8—H10	0.980
Zn1—Cl4	2.2420 (12)	C8—H9	0.988
Cl5—C4	1.738 (4)	N2—C9	1.485 (7)
C4—C3	1.389 (7)	N2—H16	0.893
C4—C5	1.378 (6)	N2—H17	0.891
C3—C2	1.388 (6)	C9—C10	1.506 (6)
C3—H4	0.922	C9—H12	0.995
C2—C1	1.376 (5)	C9—H11	0.985

C2—H3	0.943	C10—H14	0.990
C1—N1	1.482 (5)	C10—H13	0.973
C1—C6	1.378 (5)	C6—C5	1.392 (6)
N1—C7	1.504 (5)	C6—H6	0.948
N1—C10	1.507 (5)	C5—H5	0.938
N1—H15	0.893	O1—H2	0.820
C7—C8	1.511 (6)	O1—H1	0.818
C7—H8	0.973		

Cl1—Zn1—Cl2	107.34 (4)	C7—C8—H10	111.7
Cl1—Zn1—Cl3	107.92 (5)	N2—C8—H10	108.6
Cl2—Zn1—Cl3	115.30 (5)	C7—C8—H9	108.8
Cl1—Zn1—Cl4	112.95 (5)	N2—C8—H9	107.7
Cl2—Zn1—Cl4	103.37 (5)	H10—C8—H9	109.7
Cl3—Zn1—Cl4	110.04 (5)	C8—N2—C9	111.6 (3)
Cl5—C4—C3	118.7 (3)	C8—N2—H16	108.4
Cl5—C4—C5	119.2 (3)	C9—N2—H16	109.4
C3—C4—C5	122.1 (4)	C8—N2—H17	109.2
C4—C3—C2	118.6 (4)	C9—N2—H17	112.9
C4—C3—H4	120.8	H16—N2—H17	105.0
C2—C3—H4	120.6	N2—C9—C10	110.9 (4)
C3—C2—C1	119.0 (4)	N2—C9—H12	108.3
C3—C2—H3	119.7	C10—C9—H12	109.1
C1—C2—H3	121.2	N2—C9—H11	109.6
C2—C1—N1	117.1 (3)	C10—C9—H11	108.5
C2—C1—C6	122.5 (4)	H12—C9—H11	110.5
N1—C1—C6	120.3 (3)	N1—C10—C9	111.0 (3)
C1—N1—C7	113.9 (3)	N1—C10—H14	110.2
C1—N1—C10	110.1 (3)	C9—C10—H14	110.2
C7—N1—C10	110.3 (3)	N1—C10—H13	109.9
C1—N1—H15	107.8	C9—C10—H13	108.7
C7—N1—H15	107.2	H14—C10—H13	106.7
C10—N1—H15	107.3	C1—C6—C5	118.7 (4)
N1—C7—C8	110.1 (3)	C1—C6—H6	120.0
N1—C7—H8	109.4	C5—C6—H6	121.2
C8—C7—H8	110.2	C6—C5—C4	119.0 (4)
N1—C7—H7	109.7	C6—C5—H5	120.7
C8—C7—H7	108.5	C4—C5—H5	120.4
H8—C7—H7	108.9	H2—O1—H1	128.4
C7—C8—N2	110.4 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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