Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Methylpiperazine-1,4-diium tetrachloridozincate hemihydrate

Sondra Walha, Houcine Naïli,* Samia Yahyaoui and Tahar Mhiri

Laboratoire de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, BP 1171, 3000 Sfax, Tunisia
Correspondence e-mail: houcine_naili@yahoo.com

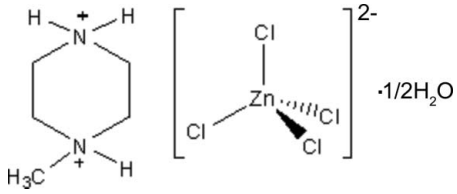
Received 9 September 2011; accepted 18 October 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.050; wR factor = 0.080; data-to-parameter ratio = 36.8.

The crystal structure of the title compound, $(C_5H_{14}N_2)[ZnCl_4]\cdot 0.5H_2O$, is built up from discrete 1-methylpiperazine-diium cations with chair conformation, tetrahedral tetrachloridozincate anions and uncoordinated solvent water molecules linked together by three types of intermolecular hydrogen bonds, *viz.* N—H···Cl, N—H···O and O—H···Cl.

Related literature

For background on organic–inorganic hybrid materials, see: Lacroix *et al.* (1994); Mitzi (2001); Pecaut *et al.* (1993). For related structures, see: Deeth *et al.* (1984); Fowkes & Harrison (2004); Walha *et al.* (2010, 2011).



Experimental

Crystal data

$(C_5H_{14}N_2)[ZnCl_4]\cdot 0.5H_2O$
M_r = 318.36
Monoclinic, $C2/c$
a = 14.3210 (5) Å
b = 12.7590 (5) Å
c = 13.7970 (3) Å
β = 102.821 (3)°
V = 2458.16 (14) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.83 mm^{-1}
T = 293 K
0.47 × 0.11 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.393, T_{max} = 0.661
27355 measured reflections
4237 independent reflections
2996 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.080
S = 1.24
4237 reflections
115 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn—Cl1	2.2449 (8)	Zn—Cl4	2.2615 (8)
Zn—Cl2	2.2614 (7)	Zn—Cl3	2.3004 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl4^{i}	0.91	2.31	3.189 (2)	164
N2—H3···Cl3^{ii}	0.96	2.57	3.353 (2)	139
N2—H3···Cl2^{ii}	0.96	2.69	3.259 (2)	119
O—H*W*1···Cl3	0.96	2.33	3.2692 (12)	167
N2—H2···O	0.96	1.95	2.908 (3)	174

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Grateful thanks are expressed to Dr J. Jaud (Service Rayons X, CEMES/CNRS Toulouse) for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2122).

References

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Deeth, R. J., Hitchman, M. A., Lehmann, G. & Sachs, H. (1984). *Inorg. Chem.* **23**, 1310–1320.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fowkes, A. & Harrison, W. T. A. (2004). *Acta Cryst.* E**60**, m59–m61.
Lacroix, P. G., Clément, R., Nakatani, K., Zyss, J. & Ledoux, I. (1994). *Science*, **263**, 658–660.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Mitzi, D. B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1–12.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Pecaut, J., Levy, J. P. & Masse, R. (1993). *J. Mater. Chem.* **3**, 999–1003.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Walha, S., Naili, H., Yahyaoui, S., Ali, B. F., Turnbull, M. M., Mhiri, T. & Bataille, T. (2011). *Solid State Sci.* **13**, 204-208.
Walha, S., Yahyaoui, S., Naili, H., Mhiri, T. & Bataille, T. (2010). *J. Coord. Chem.* pp. 1358–1368.

supporting information

Acta Cryst. (2011). E**67**, m1605 [doi:10.1107/S1600536811043236]

1-Methylpiperazine-1,4-diium tetrachloridozincate hemihydrate

Sondra Walha, Houcine Naïli, Samia Yahyaoui and Tahar Mhiri

S1. Comment

Preparation of organic-inorganic hybrid materials attracts great attention in chemistry and materials sciences because of their abilities to combine the properties of organic and inorganic compounds within one single molecular scale, such as second-order nonlinear optical (NLO) response, luminescence, magnetism and even multifonctional properties (Mitzi, 2001; Pecaut *et al.*, 1993; Lacroix *et al.*, 1994). In connection with ongoing studies (Walha *et al.*, 2010; Walha *et al.*, 2011), we report here the crystal structure of a new organic-inorganic hybrid with cations and tetrachloridozincate anions.

The asymmetric unit of the title compound (Fig. 1) contains one inorganic $ZnCl_4^{2-}$ anion, one organic *N*-methylpiperazinediium cation and one half-molecule of water, which lies on a two-fold rotation axis. The isolated molecules form organic-inorganic layers parallels to the (b,c) plane and alternate along the *a* axis (Fig. 2). These layers are stabilized and interconnected by three types of hydrogen bonds: N—H···Cl, N—H···O and O—H···Cl. The anion exhibits a tetrahedral geometry with the Zn^{II} ion surrounded by four Cl atoms with a mean Zn—Cl bond length of 2.267 (2) Å and Cl—Zn—Cl bond angles ranging from 106.24 (3) to 112.42 (3)° (Deeth *et al.*, 1984). The $ZnCl_4$ tetrahedra are linked to water molecules into zig-zag chains by O—H···Cl hydrogen bonds along the *c* axis, as illustrated in Fig. 3. The organic species adopts a typical chair conformation with average C—C and C—N of 1.501 (4) and 1.491 (3) Å, respectively (Fowkes & Harrison, 2004). The water molecules are located above and below the layers and they connect them *via* hydrogen bonds. Indeed, they participate in two types of hydrogen bonds O—H···Cl and N—H···O as donor or acceptor, respectively (Table 2), playing a subordinative role in the stabilization of the crystal structure.

S2. Experimental

$ZnCl_2$ (1 mmol) and methylpiperazine dihydrochloride (1 mmol) were dissolved in water. The solution was mixed with hydrochloric acid (1 mmol) and allowed to stand. Colourless plate-shaped crystals of the title compound were formed by slow evaporation of the solvent and separated from the solution after three days.

S3. Refinement

H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atom, with C—H = 0.96 Å, N—H = 0.89 Å and $U_{iso} = 1.2U_{eq}$(C, N).

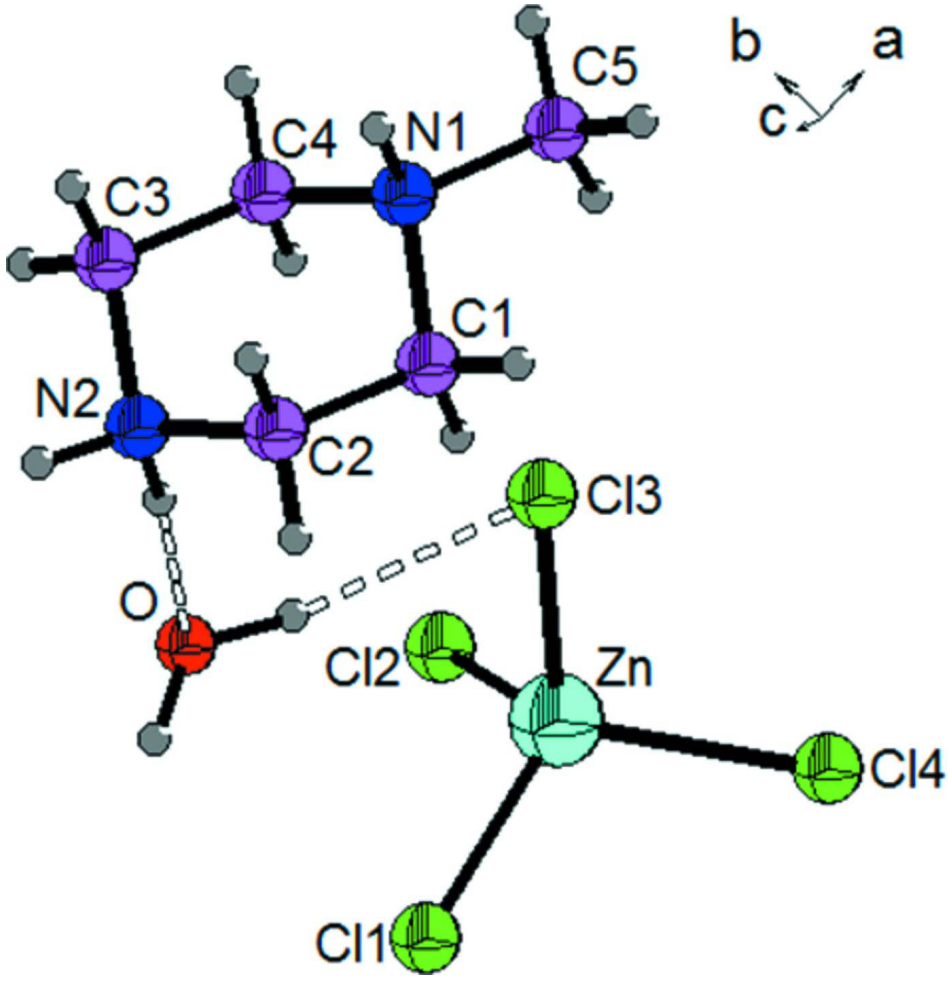


Figure 1

The asymmetric unit of the title compound, with the non-H atoms represented by 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radius.

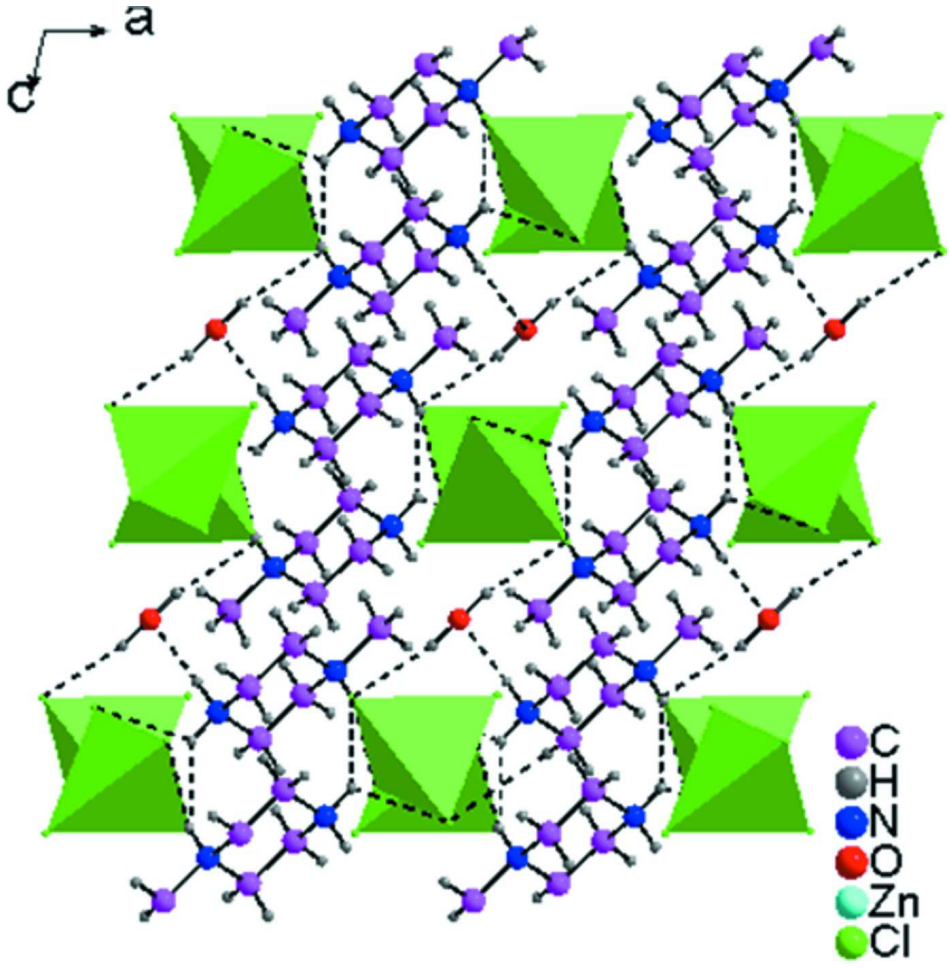


Figure 2

Projection of the crystal structure of the title compound along the *b* axis, with hydrogen bonds indicated as dashed lines.

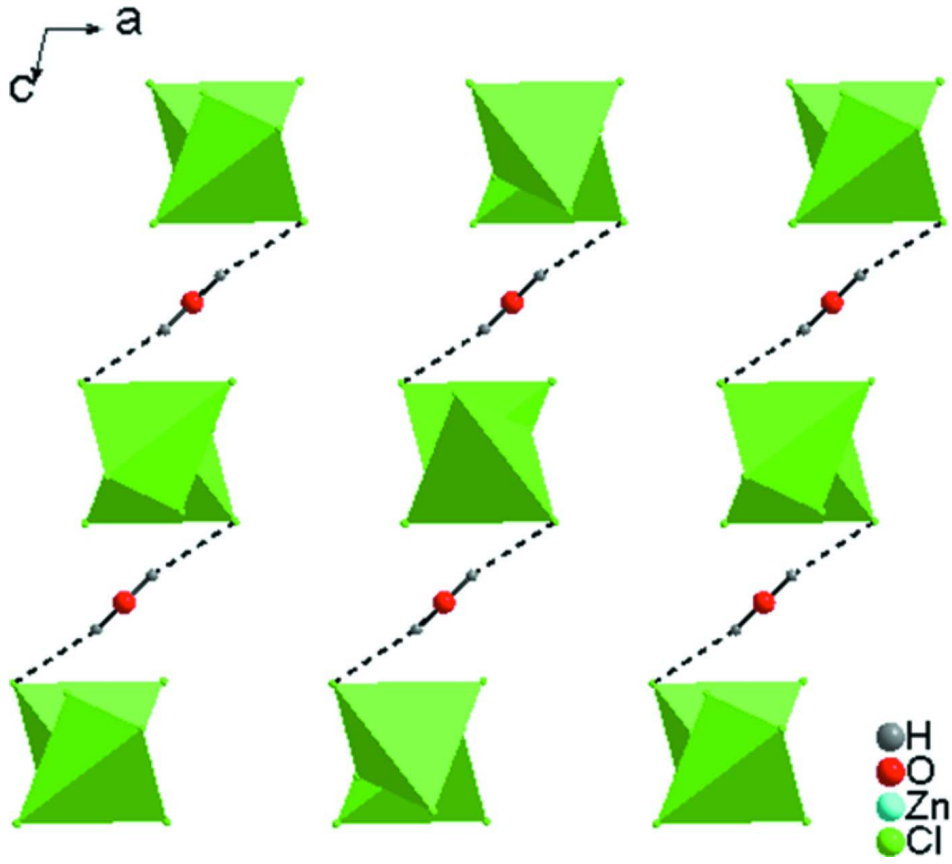


Figure 3

Zig-zag chains formed by the interactions of $ZnCl_4$ and H_2O molecules with O—H···Cl hydrogen bonds along the *c* axis.

1-Methylpiperazine-1,4-diium tetrachloridozincate hemihydrate

Crystal data

$(C_5H_{14}N_2)[ZnCl_4]\cdot 0.5H_2O$
$M_r = 318.36$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 14.3210\ (5)$ Å
$b = 12.7590\ (5)$ Å
$c = 13.7970\ (3)$ Å
$\beta = 102.821\ (3)°$
$V = 2458.16\ (14)$ Å^3
$Z = 8$
$F(000) = 1288$
$D_x = 1.720$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\theta = 3.5–32.0°$
$\mu = 2.83$ mm^{-1}
$T = 293$ K
Plate-shaped, colourless
0.47 × 0.11 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images, thick slices scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.393$, $T_{max} = 0.661$
4237 measured reflections
4237 independent reflections
2996 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 32.0°$, $\theta_{min} = 3.5°$
$h = -21\rightarrow 20$
$k = 0\rightarrow 19$
$l = 0\rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.080$
$S = 1.24$
4237 reflections
115 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
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 3.8346P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.0000

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn	0.01435 (2)	0.25139 (2)	0.52565 (2)	0.02734 (8)
Cl1	−0.08951 (5)	0.20675 (6)	0.61886 (5)	0.04259 (18)
Cl3	0.14474 (5)	0.34080 (6)	0.61526 (5)	0.03835 (16)
Cl2	−0.05717 (5)	0.35910 (7)	0.40099 (6)	0.0468 (2)
Cl4	0.07327 (5)	0.11031 (6)	0.45991 (5)	0.04292 (19)
N2	0.14425 (16)	0.5183 (2)	0.90999 (19)	0.0396 (6)
H3	0.1119	0.5425	0.9598	0.048*
H2	0.0992	0.4842	0.8576	0.048*
N1	0.31874 (14)	0.49919 (18)	0.83935 (15)	0.0288 (5)
H1	0.3598	0.5316	0.8904	0.035*
C1	0.27548 (19)	0.4078 (2)	0.8808 (2)	0.0326 (6)
H1A	0.3258	0.3607	0.9112	0.039*
H1B	0.2325	0.3726	0.8274	0.039*
C2	0.2207 (2)	0.4431 (2)	0.9561 (2)	0.0360 (6)
H2A	0.1925	0.3832	0.9804	0.043*
H2B	0.2644	0.4764	1.0101	0.043*
C3	0.1851 (2)	0.6107 (2)	0.8677 (2)	0.0424 (7)
H3B	0.2258	0.6492	0.9203	0.051*
H3A	0.1339	0.6550	0.8341	0.051*
C4	0.2429 (2)	0.5757 (2)	0.7943 (2)	0.0344 (6)
H4A	0.2004	0.5427	0.7391	0.041*
H4B	0.2719	0.6359	0.7714	0.041*
C5	0.3743 (2)	0.4655 (3)	0.7650 (2)	0.0464 (8)

H5A	0.3369	0.4268	0.7103	0.056*
H5B	0.4265	0.4215	0.7970	0.056*
H5C	0.3991	0.5263	0.7382	0.056*
O	0.0000	0.4275 (2)	0.7500	0.0420 (7)
HW1	0.0338	0.3954	0.7050	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.02624 (14)	0.02913 (16)	0.02555 (15)	0.00289 (13)	0.00340 (10)	0.00195 (13)
Cl1	0.0478 (4)	0.0476 (4)	0.0363 (4)	−0.0085 (3)	0.0176 (3)	0.0033 (3)
Cl3	0.0348 (3)	0.0437 (4)	0.0338 (4)	−0.0077 (3)	0.0017 (3)	−0.0049 (3)
Cl2	0.0306 (3)	0.0632 (5)	0.0451 (4)	0.0098 (3)	0.0053 (3)	0.0291 (4)
Cl4	0.0473 (4)	0.0451 (4)	0.0321 (4)	0.0176 (3)	−0.0002 (3)	−0.0089 (3)
N2	0.0286 (12)	0.0513 (16)	0.0420 (14)	−0.0053 (11)	0.0141 (10)	−0.0153 (12)
N1	0.0209 (10)	0.0452 (14)	0.0197 (10)	−0.0038 (9)	0.0030 (8)	0.0009 (9)
C1	0.0307 (13)	0.0359 (15)	0.0315 (14)	0.0033 (11)	0.0074 (11)	0.0070 (11)
C2	0.0350 (14)	0.0465 (18)	0.0285 (14)	−0.0083 (13)	0.0117 (11)	0.0023 (12)
C3	0.0401 (16)	0.0379 (17)	0.0486 (18)	0.0067 (13)	0.0088 (13)	−0.0043 (14)
C4	0.0363 (14)	0.0353 (16)	0.0305 (14)	0.0031 (12)	0.0054 (11)	0.0054 (12)
C5	0.0294 (14)	0.081 (2)	0.0313 (15)	0.0083 (15)	0.0129 (12)	0.0041 (15)
O	0.0452 (17)	0.0406 (17)	0.0374 (16)	0.000	0.0033 (13)	0.000

Geometric parameters (Å, º)

Zn—Cl1	2.2449 (8)	C1—H1A	0.9600
Zn—Cl2	2.2614 (7)	C1—H1B	0.9599
Zn—Cl4	2.2615 (8)	C2—H2A	0.9599
Zn—Cl3	2.3004 (7)	C2—H2B	0.9601
N2—C2	1.488 (4)	C3—C4	1.511 (4)
N2—C3	1.490 (4)	C3—H3B	0.9599
N2—H3	0.9600	C3—H3A	0.9599
N2—H2	0.9599	C4—H4A	0.9601
N1—C4	1.489 (3)	C4—H4B	0.9600
N1—C1	1.492 (3)	C5—H5A	0.9601
N1—C5	1.494 (3)	C5—H5B	0.9599
N1—H1	0.9100	C5—H5C	0.9601
C1—C2	1.503 (4)	O—HW1	0.9600
Cl1—Zn—Cl2	110.12 (3)	N2—C2—C1	110.2 (2)
Cl1—Zn—Cl4	112.42 (3)	N2—C2—H2A	109.6
Cl2—Zn—Cl4	108.97 (3)	C1—C2—H2A	109.2
Cl1—Zn—Cl3	112.33 (3)	N2—C2—H2B	109.7
Cl2—Zn—Cl3	106.50 (3)	C1—C2—H2B	108.6
Cl4—Zn—Cl3	106.24 (3)	H2A—C2—H2B	109.5
C2—N2—C3	111.2 (2)	N2—C3—C4	110.5 (2)
C2—N2—H3	109.1	N2—C3—H3B	109.6
C3—N2—H3	108.6	C4—C3—H3B	109.1

C2—N2—H2	109.7	N2—C3—H3A	109.4
C3—N2—H2	108.7	C4—C3—H3A	108.9
H3—N2—H2	109.5	H3B—C3—H3A	109.5
C4—N1—C1	110.2 (2)	N1—C4—C3	111.8 (2)
C4—N1—C5	110.6 (2)	N1—C4—H4A	108.6
C1—N1—C5	111.6 (2)	C3—C4—H4A	108.4
C4—N1—H1	108.1	N1—C4—H4B	109.5
C1—N1—H1	108.1	C3—C4—H4B	109.1
C5—N1—H1	108.1	H4A—C4—H4B	109.5
N1—C1—C2	110.8 (2)	N1—C5—H5A	113.4
N1—C1—H1A	108.8	N1—C5—H5B	109.4
C2—C1—H1A	110.0	H5A—C5—H5B	107.6
N1—C1—H1B	108.7	N1—C5—H5C	109.3
C2—C1—H1B	109.0	H5A—C5—H5C	107.6
H1A—C1—H1B	109.5	H5B—C5—H5C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl4^{i}	0.91	2.31	3.189 (2)	164
N2—H3···Cl3^{ii}	0.96	2.57	3.353 (2)	139
N2—H3···Cl2^{ii}	0.96	2.69	3.259 (2)	119
O—H*W*1···Cl3	0.96	2.33	3.2692 (12)	167
N2—H2···O	0.96	1.95	2.908 (3)	174

Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $x, -y+1, z+1/2$.