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Diaquabis{μ-1,5-bis[(pyridin-2-yl)methylidene]-carbonohydrazide(1−)}di-μ-chlorido-tetrachlorido-tetrazinc(II)

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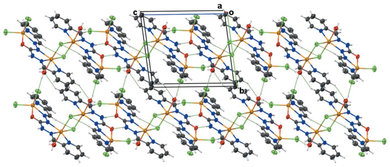
A tetranuclear Zn^{II} complex, $[Zn_4(C_{13}H_{11}N_6O)_2Cl_6(H_2O)_2]$ or $\{[Zn_2(HL)(H_2O)(Cl_2)](\mu Cl)_2[Zn_2(HL)(H_2O)(Cl)]\}_2$, was synthesized by mixing an equimolar amount of a methanol solution containing $ZnCl_2$ and a methanol solution containing the ligand H_2L [1,5-bis(pyridin-2-ylmethylene)carbonohydrazide]. In the tetranuclear complex, each of the two ligand molecules forms a dinuclear unit that is connected to another dinuclear unit by two bridging chloride anions. In each dinuclear unit, one Zn^{II} cation is pentacoordinated in a N_2OCl_2 in a distorted square-pyramidal geometry, while the other Zn^{II} cation is hexacoordinated in a N_3OCl_2 environment with a distorted octahedral geometry. The basal plane around the pentacoordinated Zn^{II} cation is formed by one chloride anion, one oxygen atom, one imino nitrogen atom and one pyridine nitrogen atom with the apical position occupied by a chloride anion. The basal plane of the hexacoordinated Zn^{II} cation is formed by one chloride anion, one hydrazinyl nitrogen atom, one imino nitrogen atom and one pyridine nitrogen atom with the apical positions occupied by a water oxygen atom and a bridged chloro anion from another dinuclear unit, leading to a tetranuclear complex. A series of intramolecular C—H⋯Cl hydrogen bonds is observed in each tetranuclear unit. In the crystal, the tetranuclear units are connected by intermolecular C—H⋯Cl, C—H⋯O and N—H⋯O hydrogen bonds, forming a planar two-dimensional structure in the *ac* plane.



1. Chemical context

Symmetrical dicarbonohydrazide Schiff bases possess two cavitiess, which make them versatile. During complexation, either one or both of the cages can be occupied by a metal ion depending on the reaction conditions. The presence of an amidic bond in these molecules leads to the keto-enol tautomer, which can act in neutral or deprotonated forms. These compounds can adopt two different configurations, *e.g.* *S-cis* or *S-trans*, yielding different structures with the same metal cation. These ligands can coordinate to transition metals in a pentadentate or hexadentate manner (El-Gammal *et al.*, 2012; Sow *et al.*, 2013), as well as in the ketonic or enolic form (Zhang *et al.*, 2014). When the configuration of this kind of ligand is *S-trans*, it acts in a hexadentate fashion. In this case, the formation of a dinuclear complex with a μ-*N*,*N* bridge is generally observed, for example in a dinuclear copper(II) complex (Dragancea *et al.*, 2014). The *S-cis–enol* configuration leads to the formation of square-grid complexes by directed

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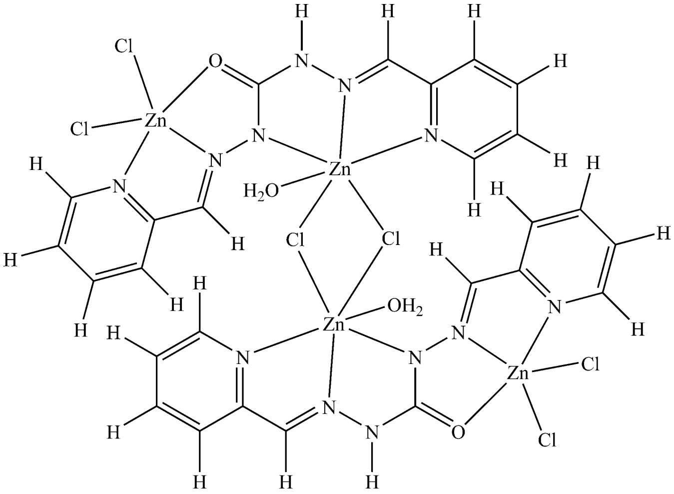
self-assembly (Bikas *et al.*, 2015; Sow *et al.*, 2013; Li *et al.*, 2014). In these complexes, μ-*O* and μ-*N*,*N* atoms bridge the metal ions, which display N_4O_2 or N_5O octahedral environments (Shuvaev *et al.*, 2010).



The behavior of these molecules has attracted the interest of chemists working in coordination chemistry. The free dicarbonohydrazide exhibits biological activities (Bacchi *et al.*, 1999; Kothari & Sharma, 2010), which are increased upon complexation with certain transition metals (Wu *et al.*, 2009; Bikas *et al.*, 2015). The synthesis of high nuclearity complexes of transition metals derived from these types of ligands are highly targeted because of their magnetic (Sow *et al.*, 2013; Zhang *et al.*, 2014*a*; Dragancea *et al.*, 2014), catalytic (Bikas *et al.*, 2015), biological (Zhang *et al.*, 2014) and optical (Easwaran potti *et al.*, 2007) properties. Recently, our research group synthesized a new tetranuclear grid complex $[Zn_4(HL^1)_4](NO_3)_4\cdot 2H_2O$ where H_2L^1 is 1,5-bis[1-(pyridin-2-yl)ethylidene)carbonohydrazide]. The study of the fluorescence properties of the ligand H_2L^1 and its complex revealed that complexation increased the fluorescent properties of the ligand (Seck *et al.*, 2018). In a continuation of our work on symmetrical dicarbonohydrazide ligands, we have synthesized and characterized a new tetranuclear zinc(II) complex formulated as $\{[Zn_2(HL)(H_2O)(Cl_2)](\mu Cl)_2[Zn_2(HL)(H_2O)(Cl)]\}_2$ where H_2L is 1,5-bis(pyridin-2-ylmethylene)carbonohydrazide.

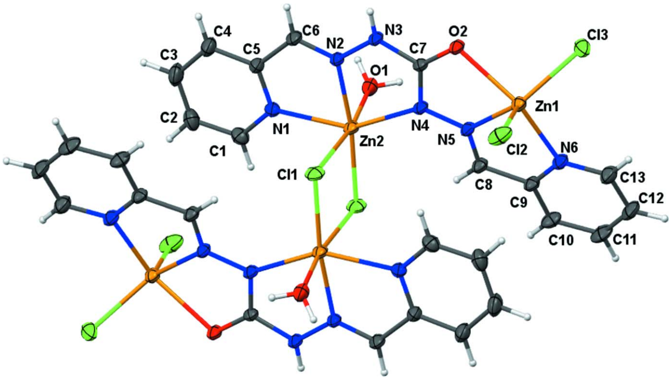


Figure 1
A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level. Unlabelled atoms are generated by the symmetry operation $1 - x$, $1 - y$, $-z$.

Table 1
Selected geometric parameters (Å, °).

Zn1—N5	2.069 (2)	Zn2—O1	2.132 (3)
Zn1—N6	2.191 (3)	Zn2—N4	2.139 (3)
Zn1—O2	2.237 (2)	Zn2—N1	2.184 (3)
Zn1—Cl3	2.2477 (9)	Zn2—Cl1	2.2873 (8)
Zn1—Cl2	2.2573 (10)	Zn2—Cl1^{i}	2.7489 (10)
Zn2—N2	2.117 (2)		
N5—Zn1—N6	75.82 (10)	N2—Zn2—N1	74.29 (9)
N5—Zn1—O2	72.76 (9)	O1—Zn2—N1	87.40 (10)
N6—Zn1—O2	144.87 (10)	N4—Zn2—N1	148.24 (10)
N5—Zn1—Cl3	138.36 (8)	N2—Zn2—Cl1	171.67 (8)
N6—Zn1—Cl3	97.10 (8)	O1—Zn2—Cl1	95.98 (8)
O2—Zn1—Cl3	96.00 (6)	N4—Zn2—Cl1	111.20 (7)
N5—Zn1—Cl2	110.85 (8)	N1—Zn2—Cl1	100.33 (7)
N6—Zn1—Cl2	108.19 (9)	N2—Zn2—Cl1^{i}	85.59 (8)
O2—Zn1—Cl2	97.45 (7)	O1—Zn2—Cl1^{i}	172.20 (7)
Cl3—Zn1—Cl2	110.31 (4)	N4—Zn2—Cl1^{i}	92.27 (8)
N2—Zn2—O1	90.19 (11)	N1—Zn2—Cl1^{i}	85.15 (8)
N2—Zn2—N4	73.95 (9)	Cl1—Zn2—Cl1^{i}	87.63 (3)
O1—Zn2—N4	92.86 (10)	Zn2—Cl1—Zn2^{i}	92.37 (3)

Symmetry code: (i) $-x+1, -y+1, -z$.

2. Structural commentary

The title compound is a centrosymmetric tetranuclear Zn^{II} complex composed by two dinuclear entities. Each dinuclear entity contains one ligand molecule acting in mono-deprotonated form, three bonded chloride anions, one bonded water molecule, and two Zn^{II} cations. The two units are linked by two choride anions acting as bridges (Fig. 1). Each mono-deprotonated organic molecule acts through two azomethine nitrogen atoms, two pyridine nitrogen atoms, one hydrazinyl nitrogen atom and one carbonyl oxygen atom, resulting in a hexadentate ligand. The Zn1 and Zn2 cations are situated, respectively in N_2OCl_2 and N_3OCl_2 coordination sites (Fig. 1). In the structure of the complex, the two ligand molecules are arranged in the *Z*–*E* form.

The Zn1 atom is pentacoordinated by one pyridine nitrogen atom, one azomethine nitrogen atom, one oxygen atom, and two terminal chloride anions. According to the Addison (1984) index, the coordination geometry around a pentacoordinated metal center can be discussed in terms of the τ parameter [defined as $\tau = (\beta - \alpha)/60$ where β and α are the largest values of the bond angles around the central atom]; $\tau = 0$ for a perfect square pyramidal geometry while $\tau = 1$ for a perfect trigonal–bipyramidal geometry. In the case of the title complex, the τ value of 0.1085 is indicative of a distorted square-pyramidal geometry around the Zn1 center. The equatorial plane is occupied by atoms N5, N6, Cl3, O2 while the apical position is occupied by Cl2. The angles N5—Zn1—O2 [72.76 (9)°], O2—Zn1—Cl3 [96.00 (6)°], Cl3—Zn1—N6 [97.10 (8)°] and N6—Zn1—N5 [75.82 (10)°] deviate from those for a regular square pyramid. The *transoid* angles in the

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl3^{ii}	0.82 (2)	2.27 (2)	3.052 (3)	161 (5)
O1—H1*B*···Cl2^{iii}	0.82 (2)	2.32 (2)	3.129 (3)	169 (5)
C8—H8···Cl1	0.93	2.82	3.649 (3)	149
C2—H2···O1^{iv}	0.93	2.50	3.342 (4)	151
C6—H6···Cl3^{v}	0.93	2.55	3.425 (3)	158
N3—H3*N*···O2^{v}	0.85 (4)	2.00 (4)	2.837 (3)	170 (4)

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

basal plane O2—Zn1—N6 and N5—Zn1—Cl3 deviate severely from linearity with values of 144.87 (10) and 138.36 (8)°, respectively (Table 1). The angles involving the atoms in the axial position deviate severely from the ideal value of 90°, being in the range 97.45 (7)–110.85 (8)°.

The geometry around the hexacoordinated Zn2 atom is best described as distorted octahedral. The basal plane is occupied by atoms N2, N4, N1 and Cl1 with *cissoid* bond angles in the range 73.95 (9)–111.20 (7)° and *transoid* angles of 171.67 (8)° [N2—Zn2—Cl1] and 148.24 (10)° [N4—Zn2—N1]. The sum of the angles subtended by the atoms in the plane is 359.77°. The apical positions are occupied by O1 and Cl1^{i} with O 1—Zn2—Cl1^{i} = 172.20 (7)° (Table 1). The deviation of the angles around the Zn2 cation with respect to the valence angles for a regular octahedron (180 and 90°) indicates that the geometry around the Zn2 ion is a distorted octahedron (Fig. 1). The five-membered rings (NCNNZn and NCCNZn) formed by the ligand with Zn2 impose large distortions on the ideal angles of a regular octahedron with bite angles in the range 73.95 (9)–74.29 (9)°.

The Zn2—Cl1—Zn2^{i} angle of 92.37 (3)° is in accordance with the value reported for the complex di-μ-chlorido-bis{[2-({[2-(2-pyridyl)ethyl](2-pyridylmethyl)amino}methyl)-phenol]zinc(II)} bis(perchlorate) dihydrate (Coelho *et al.*, 2010). The zinc–halogen distances Zn2—Cl1 and Zn2^{i}—Cl1 of 2.2873 (8) and 2.7489 (10) Å, respectively, agree with those for a chloride anion in a bridging position (Coelho *et al.*, 2010; Yu *et al.*, 2009). The distances Zn1—Cl2 and Zn1—Cl3 of 2.2573 (10) and 2.2477 (9) Å, respectively, are indicative of a unidentate terminal chloride anion (Sanyal *et al.*, 2014).

Only one weak intramolecular C—H···O hydrogen bond (Table 2) occurs.

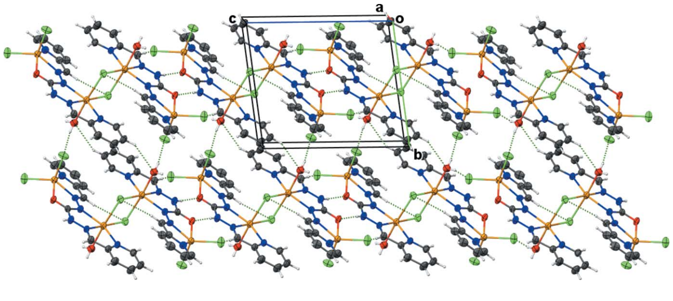


Figure 2
View of the chains formed by hydrogen bonds in the *ac* plane.

3. Supramolecular features

In the crystal, numerous intermolecular O—H···Cl, C—H···O, C—H···Cl and N—H···O hydrogen bonds are observed (Fig. 2, Table 2). An N—H···O type occurs between the oxygen atom O2 of the ligand, which acts as a proton acceptor, and the nitrogen atom of the hydrazinyl group, which acts as the proton donor. An O—H···Cl link is established between a water molecule in the apical position of the Zn2 ion, acting as proton donor, and a terminal chloride ions linked to Zn1 as proton acceptor. These intermolecular hydrogen bonds ensure the cohesion of the crystal, developing a planar two-dimensional structure in the *ac* plane.

4. Database survey

A survey of the Cambridge Structural Database (CSD, Version 5.40, October 2019; Groom *et al.*, 2016) reveals five examples of crystal structures containing H_2L derivatives where the molecule is monoprotonated (H_3L^+) or diprotonated (H_4L^{2+}) and additionally one Dy complex molecule in which HL^- and L^{2-} are present as ligands. Among the diprotonated molecules, three different counter-ions are present: I^- in AVOSOV (Hoque *et al.*, 2016), ClO_4^- in LOFDUH (Hoque *et al.*, 2014), and SO_4^{2-} in LOFFAP (Hoque *et al.*, 2014) and LOFFAP01 (Hoque *et al.*, 2016). In the structure incorporating monoprotonated H_3L^+, $H_2PO_4^-$ is the counter-ion (LOFFIX; Hoque *et al.*, 2014). The tetranuclear Dy^{3+} complex has a [2 x 2] grid structure (DIGQER; Randell *et al.*, 2013).

5. Synthesis and crystallization

Synthesis of the H_2L ligand

Carbonohydrazide (2 g, 22.2 mmol) was introduced into a 100 mL flask containing 20 mL of methanol. To the resulting suspension was added a methanolic solution containing 2-pyridinecarbaldehyde (4.757 g 44.4 mmol) and two drops of glacial acetic acid. The mixture was stirred under reflux for 2 h. After being kept for two days at 277 K, the resulting orange solution yielded a precipitate, which was recovered by filtration. The solid was washed successively with cold methanol (2 × 10 mL) and diethyl ether (2 × 10 mL) before being dried under P_2O_5; m.p. 489 K, yield 82%. Analysis calculated for [$C_{13}H_{12}N_6O$] C, 58.20; H, 4.51; N, 31.33. Found: C, 58.17; H, 4.49; N, 31.30. IR (cm^{-1}): 3439, 3204, 3198, 3055, 2936, 1684, 1582, 1610, 1582, 1532, 1467, 1360, 1274, 1131. ^{1}H NMR (DMSO-d_6, δ in ppm): 7.6–8.72 (*m*, 8H, H_{Py}); 10.82 (*s*, 2H, H—N); 8.03 (*s*, 2H, H—C=N). ^{13}C NMR (DMSO-d_6, δ in ppm): 157.9 (C=O); 154.70 (C_{Py}); 148.07 (C_{Py}); 146.67 (C=N) imine; 137.60 (CPy); 123.00 (C_{Py}); 119.09 (C_{Py}).

Synthesis of the title complex

The title complex was prepared by mixing a solution of H_2L (134.15 mg, 0.5 mmol) in 10 mL of methanol and a methanolic solution of $ZnCl_2$ (68.15 mg, 0.5 mmol). A yellow solution was obtained after stirring for 1 h at room temperature. The solution was filtered, and the filtrate left for slow evaporation.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Zn_4(C_{13}H_{11}N_6O)_2Cl_6(H_2O)_2]$
M_r	1044.77
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	9.2002 (4), 9.4306 (4), 11.7651 (4)
α, β, γ (°)	94.639 (3), 110.091 (4), 97.599 (3)
V (Å^3)	941.47 (7)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.99
Crystal size (mm)	0.21 × 0.10 × 0.05
Data collection	
Diffractometer	XtaLAB AFC12 (RINC): Kappa single
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.375, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15934, 4132, 3343
R_{int}	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.103, 1.05
No. of reflections	4127
No. of parameters	244
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.80, −0.94

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *ORTEP-3 for Windows* (Farrugia, 2012).

After two weeks, yellow crystals suitable for X-ray diffraction were collected, yield 87.9%. Analysis calculated for $[C_{26}H_{26}Cl_6Zn_4N_{12}O_4]$ C, 29.89; H, 2.51; N, 16.09. Found: C, 29.88; H, 2.49; N, 16.05. Λ_M (S cm^2 mol$^-$): 11. IR (cm^{-1}): 3428, 3116, 3043, 1585, 1553, 1497, 1461, 1377, 1313, 1226, 1143, 820.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. N- and C-bound H atoms were refined with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$. C atoms were placed in calculated positions and refined as riding with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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Diaquabis{μ-1,5-bis[(pyridin-2-yl)methylidene]carbonohydrazide(1–)}di-μ-chlorido-tetrachloridotetrazinc(II)

Thierno Moussa Seck, Papa Aly Gaye, Cheikh Ndoye, Ibrahima Elhadji Thiam, Ousmane Diouf, Pascal Retailleau and Mohamed Gaye

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012).

Diaquabis{μ-1,5-bis[(pyridin-2-yl)methylidene]carbonohydrazide(1-)}di-μ-chlorido-tetrachloridotetrazinc(II)

Crystal data

$[Zn_4(C_{13}H_{11}N_6O)_2Cl_6(H_2O)_2]$
$M_r = 1044.77$
Triclinic, $P\overline{1}$
$a = 9.2002$ (4) Å
$b = 9.4306$ (4) Å
$c = 11.7651$ (4) Å
$\alpha = 94.639$ (3)°
$\beta = 110.091$ (4)°
$\gamma = 97.599$ (3)°
$V = 941.47$ (7) Å^3

$Z = 1$
$F(000) = 520$
$D_x = 1.843$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6440 reflections
$\theta = 4.3$–30.7°
$\mu = 2.99$ mm^{-1}
$T = 293$ K
Tab, pale yellow
0.21 × 0.10 × 0.05 mm

Data collection

XtaLAB AFC12 (RINC): Kappa single diffractometer
Radiation source: micro-focus sealed X-ray tube, Rigaku (Mo) X-ray Source
Mirror monochromator
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
$T_{min} = 0.375$, $T_{max} = 1.000$

15934 measured reflections
4132 independent reflections
3343 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.1°$, $\theta_{min} = 4.4°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.103$
$S = 1.05$
4127 reflections
244 parameters
2 restraints

Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.5038P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.80$ e Å^{-3}

$\Delta\rho_{min} = -0.94$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.80255 (4)	0.26414 (4)	0.42860 (3)	0.03096 (12)
Zn2	0.57362 (4)	0.62337 (4)	0.14274 (3)	0.03302 (12)
Cl1	0.66995 (10)	0.59565 (10)	−0.01140 (7)	0.0390 (2)
Cl2	0.61634 (11)	0.06523 (11)	0.34885 (11)	0.0537 (3)
Cl3	0.93484 (10)	0.25785 (12)	0.62765 (8)	0.0500 (3)
O1	0.7387 (3)	0.8113 (3)	0.2417 (2)	0.0427 (6)
H1A	0.823 (3)	0.802 (5)	0.291 (4)	0.064*
H1B	0.718 (6)	0.878 (4)	0.278 (4)	0.064*
N1	0.4062 (3)	0.7669 (3)	0.0700 (2)	0.0312 (6)
N4	0.6695 (3)	0.4927 (3)	0.2813 (2)	0.0316 (6)
N5	0.7847 (3)	0.4085 (3)	0.3030 (2)	0.0290 (5)
O2	0.6460 (3)	0.4146 (3)	0.4577 (2)	0.0366 (5)
N2	0.4518 (3)	0.6419 (3)	0.2652 (2)	0.0297 (5)
C5	0.3207 (4)	0.7960 (4)	0.1389 (3)	0.0345 (7)
C7	0.6080 (4)	0.4865 (3)	0.3697 (3)	0.0291 (6)
N3	0.4932 (3)	0.5689 (3)	0.3617 (3)	0.0362 (7)
H3N	0.442 (5)	0.567 (4)	0.409 (4)	0.043*
C1	0.3864 (4)	0.8307 (4)	−0.0303 (3)	0.0397 (8)
H1	0.444294	0.809996	−0.078687	0.048*
C10	1.1160 (4)	0.3293 (4)	0.2278 (4)	0.0423 (8)
H10	1.115666	0.386847	0.167216	0.051*
N6	0.9966 (3)	0.2407 (3)	0.3647 (3)	0.0359 (6)
C9	1.0000 (4)	0.3243 (4)	0.2777 (3)	0.0325 (7)
C4	0.2147 (5)	0.8905 (4)	0.1096 (4)	0.0481 (9)
H4	0.156102	0.908579	0.158053	0.058*
C8	0.8767 (4)	0.4134 (4)	0.2430 (3)	0.0327 (7)
H8	0.866238	0.470241	0.180546	0.039*
C2	0.2826 (5)	0.9266 (4)	−0.0646 (3)	0.0480 (9)
H2	0.270608	0.969450	−0.135049	0.058*
C11	1.2334 (5)	0.2466 (5)	0.2698 (4)	0.0510 (10)
H11	1.312414	0.247754	0.237298	0.061*
C6	0.3499 (4)	0.7248 (4)	0.2481 (3)	0.0385 (8)
H6	0.297366	0.738940	0.301839	0.046*
C3	0.1979 (5)	0.9572 (5)	0.0069 (4)	0.0544 (10)
H3	0.129191	1.022847	−0.013639	0.065*
C13	1.1100 (4)	0.1625 (4)	0.4044 (4)	0.0459 (9)

H13	1.107789	0.104825	0.464524	0.055*
C12	1.2309 (5)	0.1637 (5)	0.3596 (4)	0.0522 (10)
H12	1.309318	0.108995	0.390059	0.063*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0313 (2)	0.0364 (2)	0.0331 (2)	0.01189 (15)	0.01808 (15)	0.00942 (15)
Zn2	0.0394 (2)	0.0418 (2)	0.0306 (2)	0.01887 (17)	0.02281 (16)	0.01138 (16)
Cl1	0.0456 (5)	0.0475 (5)	0.0364 (4)	0.0111 (4)	0.0291 (4)	0.0070 (3)
Cl2	0.0430 (5)	0.0450 (5)	0.0757 (7)	0.0007 (4)	0.0311 (5)	−0.0103 (5)
Cl3	0.0343 (4)	0.0852 (7)	0.0373 (4)	0.0232 (5)	0.0152 (4)	0.0142 (4)
O1	0.0397 (14)	0.0429 (15)	0.0450 (15)	0.0176 (12)	0.0110 (11)	0.0047 (11)
N1	0.0327 (13)	0.0373 (15)	0.0285 (13)	0.0097 (11)	0.0152 (11)	0.0078 (11)
N4	0.0349 (14)	0.0408 (15)	0.0309 (13)	0.0187 (12)	0.0209 (11)	0.0106 (11)
N5	0.0287 (13)	0.0330 (14)	0.0329 (13)	0.0123 (11)	0.0173 (11)	0.0077 (11)
O2	0.0470 (13)	0.0480 (14)	0.0323 (12)	0.0270 (11)	0.0263 (10)	0.0183 (10)
N2	0.0337 (13)	0.0371 (14)	0.0275 (12)	0.0163 (11)	0.0175 (11)	0.0101 (11)
C5	0.0331 (16)	0.0419 (18)	0.0329 (16)	0.0152 (14)	0.0136 (13)	0.0077 (14)
C7	0.0296 (15)	0.0359 (17)	0.0279 (15)	0.0123 (13)	0.0155 (12)	0.0047 (12)
N3	0.0420 (16)	0.0511 (18)	0.0326 (14)	0.0273 (14)	0.0251 (12)	0.0166 (13)
C1	0.0441 (19)	0.043 (2)	0.0340 (17)	0.0059 (16)	0.0165 (15)	0.0098 (15)
C10	0.0406 (19)	0.047 (2)	0.052 (2)	0.0100 (16)	0.0311 (17)	0.0059 (16)
N6	0.0330 (14)	0.0446 (16)	0.0402 (15)	0.0168 (12)	0.0212 (12)	0.0092 (12)
C9	0.0285 (15)	0.0394 (17)	0.0359 (16)	0.0083 (13)	0.0188 (13)	0.0046 (13)
C4	0.046 (2)	0.056 (2)	0.052 (2)	0.0282 (19)	0.0211 (18)	0.0166 (18)
C8	0.0348 (16)	0.0367 (17)	0.0377 (17)	0.0136 (14)	0.0230 (14)	0.0102 (13)
C2	0.049 (2)	0.052 (2)	0.043 (2)	0.0120 (18)	0.0111 (17)	0.0210 (17)
C11	0.0386 (19)	0.057 (2)	0.070 (3)	0.0108 (18)	0.0369 (19)	0.001 (2)
C6	0.0401 (18)	0.053 (2)	0.0368 (17)	0.0227 (16)	0.0247 (15)	0.0124 (15)
C3	0.049 (2)	0.057 (3)	0.062 (3)	0.029 (2)	0.0153 (19)	0.023 (2)
C13	0.046 (2)	0.054 (2)	0.051 (2)	0.0236 (18)	0.0266 (17)	0.0155 (18)
C12	0.040 (2)	0.065 (3)	0.065 (3)	0.0294 (19)	0.0281 (19)	0.011 (2)

Geometric parameters (Å, º)

Zn1—N5	2.069 (2)	C7—N3	1.374 (4)
Zn1—N6	2.191 (3)	N3—H3N	0.85 (4)
Zn1—O2	2.237 (2)	C1—C2	1.384 (5)
Zn1—Cl3	2.2477 (9)	C1—H1	0.9300
Zn1—Cl2	2.2573 (10)	C10—C9	1.381 (4)
Zn2—N2	2.117 (2)	C10—C11	1.391 (5)
Zn2—O1	2.132 (3)	C10—H10	0.9300
Zn2—N4	2.139 (3)	N6—C13	1.333 (4)
Zn2—N1	2.184 (3)	N6—C9	1.348 (4)
Zn2—Cl1	2.2873 (8)	C9—C8	1.465 (4)
Zn2—Cl1^{i}	2.7489 (10)	C4—C3	1.378 (5)
O1—H1A	0.816 (19)	C4—H4	0.9300

O1—H1B	0.819 (19)	C8—H8	0.9300
N1—C1	1.335 (4)	C2—C3	1.367 (6)
N1—C5	1.346 (4)	C2—H2	0.9300
N4—C7	1.345 (4)	C11—C12	1.369 (6)
N4—N5	1.374 (3)	C11—H11	0.9300
N5—C8	1.274 (4)	C6—H6	0.9300
O2—C7	1.258 (4)	C3—H3	0.9300
N2—C6	1.273 (4)	C13—C12	1.385 (5)
N2—N3	1.344 (3)	C13—H13	0.9300
C5—C4	1.382 (5)	C12—H12	0.9300
C5—C6	1.457 (4)		

N5—Zn1—N6	75.82 (10)	C4—C5—C6	122.1 (3)
N5—Zn1—O2	72.76 (9)	O2—C7—N4	126.6 (3)
N6—Zn1—O2	144.87 (10)	O2—C7—N3	117.8 (3)
N5—Zn1—Cl3	138.36 (8)	N4—C7—N3	115.6 (3)
N6—Zn1—Cl3	97.10 (8)	N2—N3—C7	116.7 (3)
O2—Zn1—Cl3	96.00 (6)	N2—N3—H3N	120 (3)
N5—Zn1—Cl2	110.85 (8)	C7—N3—H3N	123 (3)
N6—Zn1—Cl2	108.19 (9)	N1—C1—C2	122.3 (3)
O2—Zn1—Cl2	97.45 (7)	N1—C1—H1	118.9
Cl3—Zn1—Cl2	110.31 (4)	C2—C1—H1	118.9
N2—Zn2—O1	90.19 (11)	C9—C10—C11	118.9 (3)
N2—Zn2—N4	73.95 (9)	C9—C10—H10	120.6
O1—Zn2—N4	92.86 (10)	C11—C10—H10	120.6
N2—Zn2—N1	74.29 (9)	C13—N6—C9	118.7 (3)
O1—Zn2—N1	87.40 (10)	C13—N6—Zn1	128.7 (2)
N4—Zn2—N1	148.24 (10)	C9—N6—Zn1	112.5 (2)
N2—Zn2—Cl1	171.67 (8)	N6—C9—C10	121.8 (3)
O1—Zn2—Cl1	95.98 (8)	N6—C9—C8	115.8 (3)
N4—Zn2—Cl1	111.20 (7)	C10—C9—C8	122.3 (3)
N1—Zn2—Cl1	100.33 (7)	C3—C4—C5	118.5 (4)
N2—Zn2—Cl1^{i}	85.59 (8)	C3—C4—H4	120.8
O1—Zn2—Cl1^{i}	172.20 (7)	C5—C4—H4	120.8
N4—Zn2—Cl1^{i}	92.27 (8)	N5—C8—C9	116.3 (3)
N1—Zn2—Cl1^{i}	85.15 (8)	N5—C8—H8	121.9
Cl1—Zn2—Cl1^{i}	87.63 (3)	C9—C8—H8	121.9
Zn2—Cl1—Zn2^{i}	92.37 (3)	C3—C2—C1	118.7 (3)
Zn2—O1—H1A	119 (3)	C3—C2—H2	120.6
Zn2—O1—H1B	124 (4)	C1—C2—H2	120.6
H1A—O1—H1B	101 (5)	C12—C11—C10	119.1 (3)
C1—N1—C5	118.6 (3)	C12—C11—H11	120.4
C1—N1—Zn2	127.0 (2)	C10—C11—H11	120.4
C5—N1—Zn2	114.4 (2)	N2—C6—C5	115.8 (3)
C7—N4—N5	108.9 (2)	N2—C6—H6	122.1
C7—N4—Zn2	116.75 (19)	C5—C6—H6	122.1
N5—N4—Zn2	134.33 (19)	C2—C3—C4	119.9 (3)
C8—N5—N4	120.9 (3)	C2—C3—H3	120.1

C8—N5—Zn1	119.3 (2)	C4—C3—H3	120.1
N4—N5—Zn1	119.75 (19)	N6—C13—C12	122.5 (4)
C7—O2—Zn1	109.38 (18)	N6—C13—H13	118.7
C6—N2—N3	123.3 (3)	C12—C13—H13	118.7
C6—N2—Zn2	119.7 (2)	C11—C12—C13	119.0 (3)
N3—N2—Zn2	116.96 (18)	C11—C12—H12	120.5
N1—C5—C4	122.1 (3)	C13—C12—H12	120.5
N1—C5—C6	115.8 (3)		

C7—N4—N5—C8	−169.4 (3)	C13—N6—C9—C8	−176.8 (3)
Zn2—N4—N5—C8	10.8 (5)	Zn1—N6—C9—C8	0.1 (4)
C7—N4—N5—Zn1	13.8 (3)	C11—C10—C9—N6	−0.7 (6)
Zn2—N4—N5—Zn1	−166.03 (17)	C11—C10—C9—C8	176.9 (4)
C1—N1—C5—C4	−0.6 (5)	N1—C5—C4—C3	−0.5 (6)
Zn2—N1—C5—C4	176.8 (3)	C6—C5—C4—C3	177.8 (4)
C1—N1—C5—C6	−179.0 (3)	N4—N5—C8—C9	177.2 (3)
Zn2—N1—C5—C6	−1.6 (4)	Zn1—N5—C8—C9	−6.0 (4)
Zn1—O2—C7—N4	−10.3 (4)	N6—C9—C8—N5	3.7 (5)
Zn1—O2—C7—N3	170.3 (2)	C10—C9—C8—N5	−174.0 (3)
N5—N4—C7—O2	−1.0 (5)	N1—C1—C2—C3	0.2 (6)
Zn2—N4—C7—O2	178.8 (3)	C9—C10—C11—C12	−0.4 (6)
N5—N4—C7—N3	178.4 (3)	N3—N2—C6—C5	179.5 (3)
Zn2—N4—C7—N3	−1.7 (4)	Zn2—N2—C6—C5	2.9 (4)
C6—N2—N3—C7	−178.3 (3)	N1—C5—C6—N2	−0.7 (5)
Zn2—N2—N3—C7	−1.6 (4)	C4—C5—C6—N2	−179.1 (4)
O2—C7—N3—N2	−178.4 (3)	C1—C2—C3—C4	−1.3 (7)
N4—C7—N3—N2	2.2 (5)	C5—C4—C3—C2	1.5 (7)
C5—N1—C1—C2	0.8 (5)	C9—N6—C13—C12	−0.1 (6)
Zn2—N1—C1—C2	−176.2 (3)	Zn1—N6—C13—C12	−176.5 (3)
C13—N6—C9—C10	0.9 (5)	C10—C11—C12—C13	1.2 (7)
Zn1—N6—C9—C10	177.9 (3)	N6—C13—C12—C11	−1.0 (7)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl3$^{\text{ii}}$	0.82 (2)	2.27 (2)	3.052 (3)	161 (5)
O1—H1*B*···Cl2$^{\text{iii}}$	0.82 (2)	2.32 (2)	3.129 (3)	169 (5)
C8—H8···Cl1	0.93	2.82	3.649 (3)	149
C2—H2···O1$^{\text{iv}}$	0.93	2.50	3.342 (4)	151
C6—H6···Cl3$^{\text{v}}$	0.93	2.55	3.425 (3)	158
N3—H3*N*···O2$^{\text{v}}$	0.85 (4)	2.00 (4)	2.837 (3)	170 (4)

Symmetry codes: (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*, *y*+1, *z*; (iv) −*x*+1, −*y*+2, −*z*; (v) −*x*+1, −*y*+1, −*z*+1.