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The first coordination complex of (5*R*,6*R*,7*S*)-5-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidin-6-amine with zinc(II) acetate-chloride

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Keywords: (5*R*,6*R*,7*S*)-5-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*α*]pyri]pyrimidin-6-aminozinc(II)acetate-chloride; polymeric coordination complex; molecular structure; crystal structure; Hirshfeld surface analysis.

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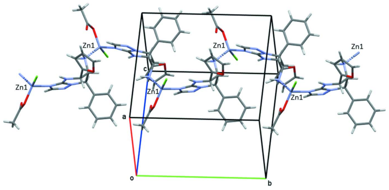
The title complex, systematic name *catena*-poly[[[acetatochloridozinc(II)]-μ-(5*R*,6*R*,7*S*)-5-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-*a*]-pyrimidin-6-amine] monohydrate], $\{[Zn(C_2H_3O_2)Cl(C_{15}H_{15}N_5O)]\cdot H_2O\}_n$, is the first coordination complex in which the neutral tetrahydrotriazolopyrimidine derivative acts as bridging ligand between two zinc molecules. As a result, polymeric chains of the coordination complex are found. The coordination of the zinc metal atom occurs with the lone pairs of the triazolo nitrogen atom and amino group. The positive charge of the zinc atom is compensated by the chlorine anion and deprotonated acetic acid. The coordination complex exists as a monohydrate in the crystalline phase. The water molecules bind neighbouring polymeric chains by the formation of O—H⋯O, O—H⋯Cl and N—H⋯O hydrogen bonds.



1. Chemical context

Multicomponent reactions of 3-amino-1,2,4-triazole and carbonyl compounds have divergent selectivity, allowing the synthesis of alternative products from the same set of starting reagents (Sedash *et al.*, 2012). Such a phenomenon is used in diversity-oriented synthesis to increase the molecular space of biologically active compounds. In previous research, we suggested a plausible reaction mechanism for the annulation of triazole with a tetrahydropyrimidine ring occurring in reactions of 3-amino-1,2,4-triazole, aromatic aldehydes and ketocompounds (Gümüş *et al.*, 2017*a*,*b*). Generally, such reactions proceed *via* the intermediate formation of a Schiff base from the aminoazole and the aldehyde. One of the key stages of the mechanism is a nucleophilic attack of the electron-rich enol carbon atom onto the electron-deficit azomethine carbon, with the formation of a C—C bond in the cyclization. If the suggested hypothesis is true, other reagents with a polar C═C bond similar to the C═C bond in enoles should possess similar reactivity. Using this analogy, we performed a multicomponent reaction between 3-amino-1,2,4-triazole, β-nitrostyrene and furfural. As expected, a derivative of tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidine **1** was obtained in high regio- and stereoselectivity. Further reduction of the nitro group in this compound unexpectedly resulted in formation of the zinc polycomplex **2**. A single crystal of this compound was characterized by X-ray diffraction.

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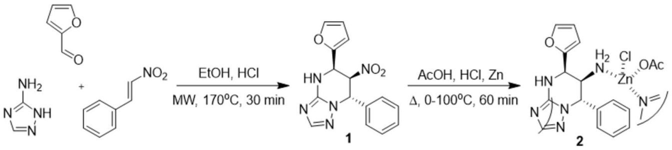

2. Structural commentary

The title compound **2** is a coordination complex (Fig. 1) in which the zinc cation forms a salt with a chlorine anion and deprotonated acetic acid and is coordinated additionally by 5-furan-2-yl-7-phenyl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]-pyrimidin-6-amine through interaction with the electron lone pairs of the N4 atom of the triazole ring and the pyramidal amino group [the sum of bond angles, centered at the N5 atom, is 324°]. Thus, the zinc coordination polyhedron is tetrahedral.

The tetrahydropyrimidine ring of the neutral organic ligand adopts an asymmetric half-chair conformation (Fig. 1) with puckering parameters (Zefirov *et al.*, 1990) of $S = 0.73$, $\Theta = 35.0°$, $\Psi = 20.3°$. The C2 and C1 atoms deviate from the mean-square plane of the remaining atoms of the ring by 0.76 and 0.18 Å, respectively. The three vicinal substituents have different orientations: the furan ring is located in the equatorial position, while the phenyl substituent and amino group are located in axial positions [the C4—N1—C3—C12_1/C12_2, N2—C1—C2—N5 and C4—N2—C1—C6 torsion angles are 161.4 (2), 161.4 (2), −78.2 (2) and 105.5 (3)° respectively].

The amino group and furan ring are *cis*-oriented. The furan ring is disordered over two positions with an occupancy ratio of 0.707 (11):0.293 (11) and twisted in relation to the N1—C3 endocyclic bond [the N1—C3—C12_1—C13_1 and N1—C3—C12_2—O1_2 torsion angles are −27.6 (9) and −36.5 (8)°, respectively]. This may be due to the strong bifurcated intramolecular N—H⋯π hydrogen bonds (N5—H5*A*⋯C12_1/C12_2, N5—H5*B*⋯C13_1 and N5—H5*B*⋯O1_2; Table 1). The phenyl substituent is *trans*-oriented to the amino group and twisted with respect to the N2—C1 endocyclic bond [N2—C1—C6—C11 = −15.4 (4)°].

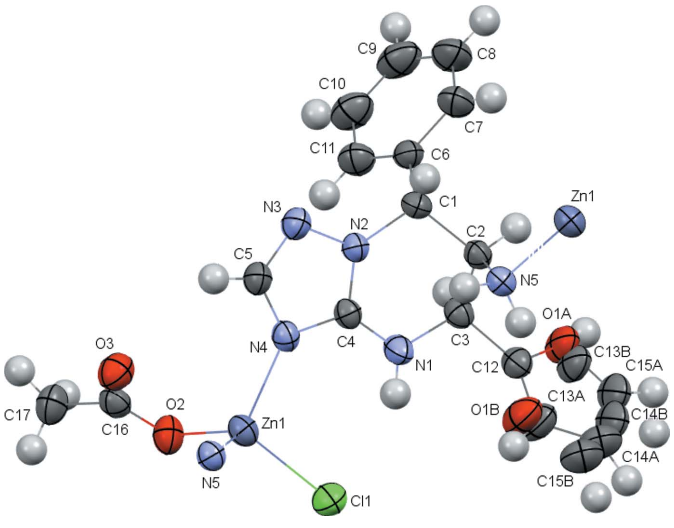

Figure 1
The molecular structure of compound **2** (solvent molecule and hydrogen atoms are omitted for clarity). Displacement ellipsoids are shown at the 50% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*S*—H1*SA*⋯O2	0.98	1.91	2.830 (3)	155
O1*S*—H1*SB*⋯Cl1	0.98	2.47	3.321 (2)	144
N1—H1⋯Cl1	0.86	2.42	3.198 (2)	151
N5—H5*A*⋯O3^{i}	0.89	2.48	2.961 (3)	114
N5—H5*A*⋯C12_1	0.89	2.49	2.966 (3)	114
N5—H5*A*⋯C13_1	0.89	2.67	3.422 (11)	143
N5—H5*A*⋯O1_2	0.89	2.33	3.086 (17)	144
N5—H5*A*⋯C12_2	0.89	2.49	2.966 (3)	114
N5—H5*B*⋯O1*S*^{ii}	0.89	2.03	2.904 (3)	169

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

3. Supramolecular features

In the crystal, the coordination complex forms polymeric chains in the [010] direction, in which the neutral organic molecule is bridged between two zinc cations (Fig. 2). The coordination polymer exists as a monohydrate in the crystal. The organic molecule is linked to the chlorine and acetic anions by N1—H⋯Cl and N5—H5*A*⋯O3^{i} hydrogen bonds (Table 1). Neighbouring polymeric chains are connected through the water molecules by O1*S*—H1*SA*⋯O2, O1*S*—H1*SB*⋯Cl and N5—H5*B*⋯O1*S*^{ii} hydrogen bonds (Table 1).

4. Hirshfeld surface analysis

Hirshfeld surface analysis (Turner *et al.*, 2017) was used to identify and visualize different types of intra- and intermolecular interactions in the crystal structure. The molecular Hirshfeld surface of the coordination complex was constructed using a standard surface resolution with three-dimensional $d_{\rm norm}$ surfaces. The areas coloured red on the $d_{\rm norm}$ surfaces correspond to strong intermolecular O—H⋯O and N—H⋯O hydrogen bonds (Fig. 3). Bright red spots are

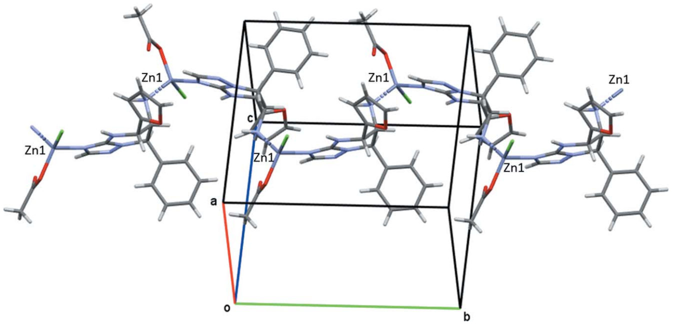

Figure 2
The chain of molecules of **2** linked by N—H⋯Cl and N—H⋯O hydrogen bonds.

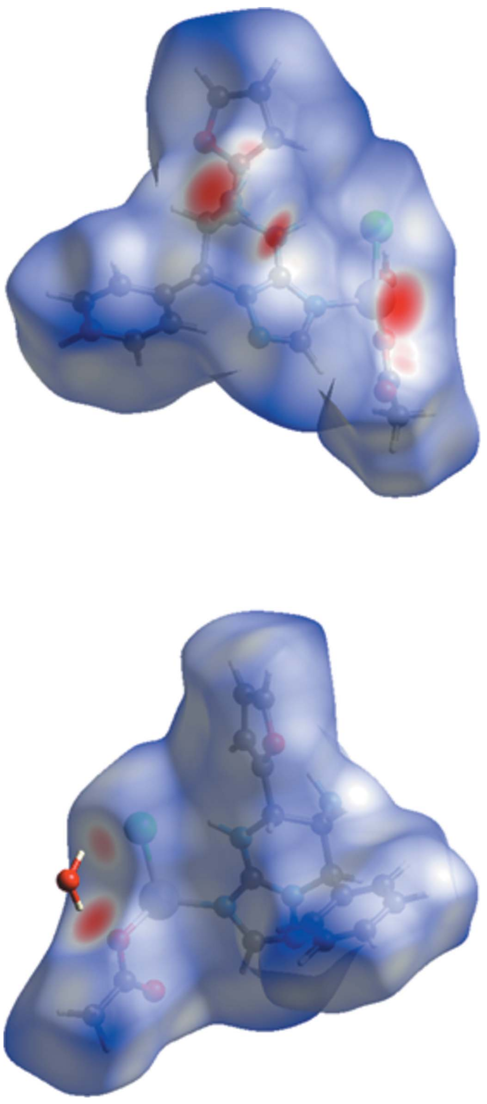

Figure 3
Two views of the Hirshfeld surface of compound **2** mapped over $d_{\rm norm}$ in the range −0.603 to 1.696 a.u.

also observed at the nitrogen atom of the triazole ring, chlorine atom and one of the oxygen atoms of the acetic anion.

The pair of sharp spikes in the two-dimensional fingerprint plot (Fig. 4*a*) indicates the presence of strong hydrogen bonds in the crystal structure. The main contribution to the Hirshfeld surface is provided by H⋯H contacts (44.5%), shown in Fig. 4*b*. The contributions of O⋯H/H⋯O (15.3%) and C⋯H/H⋯C (14.8%) contacts associated with X—H⋯O and X—H⋯π hydrogen bonds are much smaller (Fig. 4*c*, 4*d*). The smallest contributions in the total Hirshfeld surface are provided by Cl⋯H/H⋯Cl (8.5%) and N⋯H/H⋯N (7.3%) (Fig. 4*e*, 4*f*) interactions associated with X—H⋯Cl and X—H⋯N hydrogen bonds.

5. Database survey

A search of the Cambridge Structural Database (CSD Version 5.42, update of November 2020; Groom *et al.*, 2016) for the triazolopyrimidine fragment revealed 28 hits of which only 14 have a molecular structure close to that of the neutral molecules in the studied coordination complex [refcodes: CAGVIQ (Desenko *et al.*, 1999), EYATUU (Rudenko *et al.*, 2011), HEXKEA(Desenko *et al.*, 1994), HUVCAD (Gorobets *et al.*, 2010), OPIMIK (Lipson *et al.*, 2009), PUGDIF (Huang, 2009), QISRIW, QISRUI, QISSAP, QISSET (Zemlyanaya *et al.*, 2018), QOZMEY (Chen *et al.*, 2009), TOMPAN (Sakhno *et al.*, 2008), VEFXEL (Sedash *et al.*, 2012), YEHREK (Yu *et al.*, 2011)]. However, no triazolopyrimidine derivatives coordinated to a metal atom have been deposited in the Cambridge Structural Database.

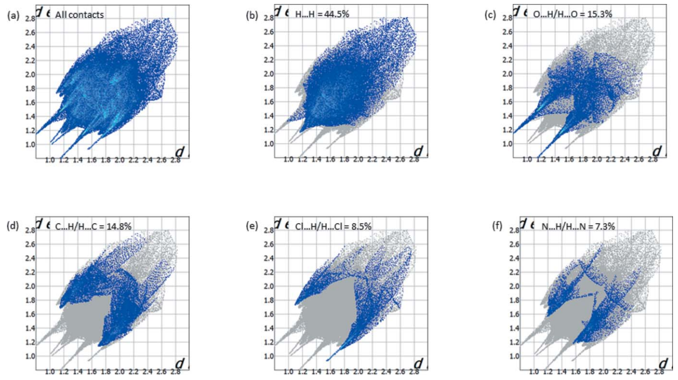

Figure 4
Two-dimensional fingerprint plots for compound **2** showing (*a*) all interactions, and delineated into (*b*) H⋯H, (*c*) O⋯H/H⋯O, (*d*) C⋯H/H⋯C, (*e*) Cl⋯H/H⋯Cl and (*f*) N⋯H/H⋯N contacts.

6. Synthesis and crystallization

Microwave irradiation experiments were carried out using an Emrys™ Creator EXP (Biotage, Uppsala) equipped with an outer IR temperature sensor. The reaction was performed in a sealed microwave process vial using the 'very high' mode, which decreased the initial power to 90 W. Reaction time under microwave conditions refers to the time that the reaction mixture was kept at the set temperature (fixed hold time).

(5*R*,6*R*,7*S*)-5-(Furan-2-yl)-6-nitro-7-phenyl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidine (1): In a microwave process vial, a volume of 0.2 mL of 40% HCl solution in EtOH was added to an equimolar mixture (4.0 mmol) of 3-amino-1,2,4-triazole, furfural, and β-nitrostyrene in 2.0 mL of methanol. The vessel was sealed and irradiated at 443 K for 40 min. After cooling, the precipitate that had formed was filtered off and washed with 2–3 mL of methanol. Drying gave compound **1** in a 41% yield, obtained in a mixture with its diastereomer in a ratio of 12:1. Pure compound **1** was obtained by recrystallization from ethanol.

(5*R*,6*R*,7*S*)-5-(Furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidin-6-amine with zinc(II) acetate-chloride (2): To a solution of 4.0 mmol of **1** in 5.0 mL of acetic acid was added 4.5 mL of concentrated hydrochloric acid. The mixture was cooled down in an ice–water bath and 1.0 g of zinc dust was slowly added to the mixture portionwise. After the addition, the cooling bath was removed and the mixture was stirred for 30 min and then refluxed until the reducing agent was completely dissolved. The reaction mixture was left undisturbed overnight, and the single crystal used for the X-ray diffraction study was taken directly from the reaction mixture. The isolated yield of **2** was 67%.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located in difference-Fourier maps. They were included in calculated positions and treated as riding with C—H = 0.96 Å, $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl groups, O—H = 0.98 Å, $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) for the water molecule, Car—H = 0.93 Å, Csp^3—H = 0.97 Å, N—H = 0.89 Å and $U_{\rm iso}$(H) = 1.2Ueq(parent atom) for all other hydrogen atoms. The furan ring is disordered over two positions with an occupancy ratio of 0.707 (11):0.293 (11).

Funding information

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Table 2
Experimental details.

Crystal data	
Chemical formula	[Zn($C_2H_3O_2$)Cl($C_{15}H_{15}N_5O$)]·H_2O
M_r	459.20
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	10.6267 (4), 12.8015 (5), 15.1646 (7)
β (°)	104.788 (4)
V (Å^3)	1994.63 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.40
Crystal size (mm)	0.2 × 0.2 × 0.1
Data collection	
Diffractometer	Xcalibur, Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
$T_{\rm min}$, $T_{\rm max}$	0.930, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15201, 4572, 3174
$R_{\rm int}$	0.042
(sin $\theta/\lambda)_{\rm max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.102, 1.02
No. of reflections	4572
No. of parameters	291
No. of restraints	90
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.36, −0.32

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2017/1* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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The first coordination complex of (5*R*,6*R*,7*S*)-5-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidin-6-amine with zinc(II) acetate-chloride

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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: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

catena-Poly[[[acetatochloridozinc(II)]-*µ*-(5*R*,6*R*,7*S*)-5-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-*a*]pyrimidin-6-amine] monohydrate]

Crystal data

$[Zn(C_2H_3O_2)Cl(C_{15}H_{15}N_5O)]\cdot H_2O$
$M_r = 459.20$
Monoclinic, $P2_1/c$
$a = 10.6267\ (4)$ Å
$b = 12.8015\ (5)$ Å
$c = 15.1646\ (7)$ Å
$\beta = 104.788\ (4)°$
$V = 1994.63\ (15)$ Å^3
$Z = 4$
$F(000) = 944$
$D_x = 1.529$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3540 reflections
$\theta = 3.1–29.5°$
$\mu = 1.40$ mm^{-1}
$T = 293$ K
Needle, colourless
0.2 × 0.2 × 0.1 mm

Data collection

Xcalibur, Sapphire3 diffractometer
Detector resolution: 16.1827 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
$T_{min} = 0.930$, $T_{max} = 1.000$
15201 measured reflections
4572 independent reflections
3174 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -13\rightarrow13$
$k = -16\rightarrow16$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 1.02$
4572 reflections
291 parameters
90 restraints
Hydrogen site location: mixed
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.1268P]$ where $P = (F_o^2 + 2F_c^2)/3$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$(\Delta/\sigma)_{max} = 0.001$	$\Delta\rho_{min} = -0.32$ 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}	Occ. (<1)
Zn1	0.42716 (3)	0.16102 (3)	0.59755 (2)	0.03857 (12)	
Cl1	0.62402 (7)	0.20953 (6)	0.58000 (6)	0.0524 (2)	
O1S	0.4892 (2)	0.14368 (17)	0.36476 (14)	0.0552 (6)	
H1SA	0.416347	0.120957	0.389178	0.083*	
H1SB	0.562247	0.163167	0.416278	0.083*	
O2	0.32493 (19)	0.10659 (17)	0.48190 (13)	0.0481 (5)	
O3	0.18743 (19)	0.07023 (18)	0.56429 (15)	0.0545 (6)	
N1	0.5043 (2)	0.42425 (18)	0.62954 (16)	0.0437 (6)	
H1	0.560504	0.381973	0.617396	0.052*	
N2	0.3175 (2)	0.44947 (17)	0.68186 (15)	0.0342 (5)	
N3	0.2161 (2)	0.39097 (19)	0.69900 (16)	0.0424 (6)	
N4	0.3523 (2)	0.28948 (17)	0.64306 (15)	0.0358 (5)	
N5	0.5586 (2)	0.55569 (17)	0.79892 (14)	0.0352 (5)	
H5A	0.638491	0.541918	0.793789	0.042*	
H5B	0.526184	0.496510	0.814732	0.042*	
C1	0.3340 (2)	0.5612 (2)	0.70008 (18)	0.0350 (6)	
H1A	0.316410	0.574588	0.759441	0.042*	
C2	0.4782 (2)	0.5873 (2)	0.70857 (17)	0.0340 (6)	
H2	0.485507	0.663307	0.703691	0.041*	
C3	0.5248 (3)	0.5371 (2)	0.62890 (19)	0.0365 (6)	
H3	0.472603	0.565499	0.571084	0.044*	
C4	0.3965 (2)	0.3877 (2)	0.64934 (17)	0.0328 (6)	
C5	0.2433 (3)	0.2978 (2)	0.67508 (19)	0.0403 (6)	
H5	0.191826	0.240239	0.679448	0.048*	
C6	0.2415 (3)	0.6275 (2)	0.6302 (2)	0.0389 (6)	
C7	0.2274 (3)	0.7316 (2)	0.6495 (2)	0.0541 (8)	
H7	0.273434	0.758626	0.705375	0.065*	
C8	0.1466 (3)	0.7960 (3)	0.5875 (3)	0.0693 (11)	
H8	0.139303	0.866309	0.600944	0.083*	
C9	0.0773 (3)	0.7563 (3)	0.5065 (3)	0.0681 (10)	
H9	0.020910	0.799302	0.465039	0.082*	
C10	0.0898 (3)	0.6544 (3)	0.4856 (3)	0.0641 (10)	
H10	0.042548	0.628125	0.429733	0.077*	
C11	0.1729 (3)	0.5892 (3)	0.5472 (2)	0.0510 (8)	
H11	0.182172	0.519689	0.532211	0.061*	
O1_1	0.6872 (5)	0.6493 (4)	0.5947 (4)	0.0578 (14)	0.707 (11)

C12_1	0.6648 (3)	0.5593 (2)	0.63613 (19)	0.0404 (6)	0.707 (11)
C13_1	0.7773 (9)	0.5100 (9)	0.6723 (8)	0.064 (2)	0.707 (11)
H13_1	0.786583	0.444450	0.699558	0.076*	0.707 (11)
C14_1	0.8815 (6)	0.5769 (7)	0.6613 (6)	0.067 (2)	0.707 (11)
H14_1	0.970497	0.565320	0.682355	0.081*	0.707 (11)
C15_1	0.8216 (7)	0.6599 (5)	0.6139 (5)	0.0609 (17)	0.707 (11)
H15_1	0.864388	0.716553	0.596380	0.073*	0.707 (11)
O1_2	0.7572 (13)	0.4952 (13)	0.6906 (12)	0.054 (3)	0.293 (11)
C12_2	0.6648 (3)	0.5593 (2)	0.63613 (19)	0.0404 (6)	0.293 (11)
C13_2	0.7307 (17)	0.6428 (15)	0.6144 (16)	0.055 (3)	0.293 (11)
H13_2	0.693906	0.703607	0.585317	0.066*	0.293 (11)
C14_2	0.8683 (14)	0.6197 (14)	0.6447 (13)	0.055 (3)	0.293 (11)
H14_2	0.935927	0.660277	0.634767	0.065*	0.293 (11)
C15_2	0.8800 (12)	0.5283 (14)	0.6901 (10)	0.055 (3)	0.293 (11)
H15_2	0.957438	0.493801	0.716452	0.066*	0.293 (11)
C16_2	0.2172 (3)	0.0672 (2)	0.4915 (2)	0.0410 (7)	
C17_2	0.1314 (3)	0.0175 (3)	0.4078 (2)	0.0573 (8)	
H17A_2	0.124694	0.062911	0.356446	0.086*	
H17B_2	0.046435	0.005959	0.417039	0.086*	
H17C_2	0.168324	−0.048027	0.396537	0.086*	

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0440 (2)	0.03285 (19)	0.0390 (2)	−0.00017 (14)	0.01079 (14)	0.00118 (14)
Cl1	0.0451 (4)	0.0508 (5)	0.0657 (5)	−0.0013 (3)	0.0220 (4)	−0.0036 (4)
O1S	0.0621 (14)	0.0589 (15)	0.0466 (13)	−0.0016 (11)	0.0171 (11)	−0.0110 (10)
O2	0.0505 (12)	0.0500 (13)	0.0450 (12)	−0.0136 (10)	0.0144 (10)	−0.0036 (10)
O3	0.0477 (12)	0.0654 (15)	0.0517 (13)	−0.0037 (11)	0.0148 (10)	−0.0044 (11)
N1	0.0453 (13)	0.0337 (13)	0.0596 (16)	−0.0047 (11)	0.0275 (12)	−0.0088 (12)
N2	0.0324 (11)	0.0294 (12)	0.0413 (13)	−0.0018 (9)	0.0105 (10)	0.0006 (10)
N3	0.0356 (12)	0.0390 (14)	0.0541 (15)	−0.0041 (11)	0.0143 (11)	0.0018 (12)
N4	0.0386 (12)	0.0295 (12)	0.0387 (13)	−0.0032 (10)	0.0088 (10)	−0.0003 (10)
N5	0.0370 (12)	0.0307 (12)	0.0380 (13)	0.0005 (10)	0.0100 (10)	−0.0021 (10)
C1	0.0357 (14)	0.0313 (14)	0.0393 (15)	0.0032 (11)	0.0119 (12)	−0.0044 (12)
C2	0.0374 (14)	0.0258 (13)	0.0375 (15)	−0.0002 (11)	0.0075 (11)	0.0006 (11)
C3	0.0415 (15)	0.0324 (14)	0.0366 (15)	−0.0018 (12)	0.0121 (12)	0.0001 (12)
C4	0.0368 (14)	0.0303 (14)	0.0311 (14)	−0.0015 (11)	0.0081 (11)	0.0007 (11)
C5	0.0369 (14)	0.0369 (15)	0.0475 (17)	−0.0056 (12)	0.0118 (13)	0.0003 (13)
C6	0.0320 (14)	0.0336 (15)	0.0517 (18)	0.0024 (12)	0.0119 (13)	0.0030 (13)
C7	0.0497 (18)	0.0392 (18)	0.070 (2)	0.0094 (15)	0.0087 (16)	−0.0005 (16)
C8	0.055 (2)	0.043 (2)	0.108 (3)	0.0121 (17)	0.018 (2)	0.009 (2)
C9	0.0477 (19)	0.069 (3)	0.087 (3)	0.0123 (19)	0.015 (2)	0.028 (2)
C10	0.0494 (19)	0.073 (3)	0.064 (2)	0.0101 (18)	0.0042 (17)	0.013 (2)
C11	0.0472 (17)	0.0461 (18)	0.055 (2)	0.0086 (15)	0.0051 (15)	0.0027 (16)
O1_1	0.046 (2)	0.047 (2)	0.082 (3)	−0.011 (2)	0.019 (2)	0.016 (2)
C12_1	0.0424 (14)	0.0383 (15)	0.0449 (16)	−0.0020 (12)	0.0188 (13)	0.0012 (12)
C13_1	0.054 (4)	0.065 (4)	0.078 (5)	0.005 (3)	0.026 (3)	0.019 (3)

C14_1	0.055 (3)	0.065 (5)	0.085 (5)	0.003 (3)	0.023 (3)	0.008 (4)
C15_1	0.045 (3)	0.053 (3)	0.090 (4)	−0.014 (3)	0.028 (3)	0.006 (3)
O1_2	0.038 (5)	0.066 (5)	0.060 (6)	0.002 (4)	0.016 (4)	0.022 (4)
C12_2	0.0424 (14)	0.0383 (15)	0.0449 (16)	−0.0020 (12)	0.0188 (13)	0.0012 (12)
C13_2	0.044 (6)	0.048 (6)	0.064 (6)	0.000 (5)	−0.003 (6)	0.014 (5)
C14_2	0.041 (5)	0.061 (8)	0.061 (7)	0.000 (5)	0.010 (5)	0.019 (6)
C15_2	0.034 (5)	0.069 (7)	0.061 (6)	0.004 (5)	0.009 (5)	0.017 (5)
C16_2	0.0451 (16)	0.0306 (15)	0.0456 (18)	0.0043 (12)	0.0082 (14)	0.0021 (13)
C17_2	0.0482 (17)	0.059 (2)	0.060 (2)	−0.0102 (16)	0.0043 (15)	−0.0079 (17)

Geometric parameters (Å, º)

Zn1—Cl1	2.2621 (8)	C6—C11	1.374 (4)
Zn1—O2	1.9413 (19)	C7—H7	0.9300
Zn1—N4	2.023 (2)	C7—C8	1.374 (5)
Zn1—N5^{i}	2.046 (2)	C8—H8	0.9300
O1S—H1SA	0.9832	C8—C9	1.360 (5)
O1S—H1SB	0.9829	C9—H9	0.9300
O2—C16_2	1.293 (3)	C9—C10	1.357 (5)
O3—C16_2	1.224 (3)	C10—H10	0.9300
N1—H1	0.8600	C10—C11	1.388 (4)
N1—C3	1.461 (3)	C11—H11	0.9300
N1—C4	1.340 (3)	O1_1—C12_1	1.362 (5)
N2—N3	1.390 (3)	O1_1—C15_1	1.389 (6)
N2—C1	1.459 (3)	C12_1—C13_1	1.338 (10)
N2—C4	1.336 (3)	C13_1—H13_1	0.9300
N3—C5	1.301 (4)	C13_1—C14_1	1.442 (10)
N4—C4	1.337 (3)	C14_1—H14_1	0.9300
N4—C5	1.370 (3)	C14_1—C15_1	1.348 (8)
N5—H5A	0.8900	C15_1—H15_1	0.9300
N5—H5B	0.8900	O1_2—C12_2	1.380 (13)
N5—C2	1.474 (3)	O1_2—C15_2	1.374 (14)
C1—H1A	0.9800	C12_2—C13_2	1.364 (18)
C1—C2	1.542 (3)	C13_2—H13_2	0.9300
C1—C6	1.509 (4)	C13_2—C14_2	1.447 (15)
C2—H2	0.9800	C14_2—H14_2	0.9300
C2—C3	1.557 (4)	C14_2—C15_2	1.346 (15)
C3—H3	0.9800	C15_2—H15_2	0.9300
C3—C12_1	1.491 (4)	C16_2—C17_2	1.501 (4)
C3—C12_2	1.491 (4)	C17_2—H17A_2	0.9600
C5—H5	0.9300	C17_2—H17B_2	0.9600
C6—C7	1.381 (4)	C17_2—H17C_2	0.9600
O2—Zn1—Cl1	108.26 (6)	C11—C6—C7	118.5 (3)
O2—Zn1—N4	114.95 (9)	C6—C7—H7	119.4
O2—Zn1—N5^{i}	111.81 (9)	C8—C7—C6	121.1 (3)
N4—Zn1—Cl1	105.83 (6)	C8—C7—H7	119.4
N4—Zn1—N5^{i}	103.45 (9)	C7—C8—H8	120.2

N5$^{\mathrm{i}}$—Zn1—Cl1	112.44 (6)
H1SA—O1S—H1SB	108.3
C16_2—O2—Zn1	110.22 (17)
C3—N1—H1	120.5
C4—N1—H1	120.5
C4—N1—C3	119.0 (2)
N3—N2—C1	123.6 (2)
C4—N2—N3	109.9 (2)
C4—N2—C1	126.5 (2)
C5—N3—N2	101.8 (2)
C4—N4—Zn1	128.83 (17)
C4—N4—C5	102.4 (2)
C5—N4—Zn1	128.72 (19)
Zn1$^{\mathrm{ii}}$—N5—H5A	108.2
Zn1$^{\mathrm{ii}}$—N5—H5B	108.2
H5A—N5—H5B	107.3
C2—N5—Zn1$^{\mathrm{ii}}$	116.37 (16)
C2—N5—H5A	108.2
C2—N5—H5B	108.2
N2—C1—H1A	107.7
N2—C1—C2	107.3 (2)
N2—C1—C6	113.1 (2)
C2—C1—H1A	107.7
C6—C1—H1A	107.7
C6—C1—C2	113.1 (2)
N5—C2—C1	110.2 (2)
N5—C2—H2	107.7
N5—C2—C3	112.6 (2)
C1—C2—H2	107.7
C1—C2—C3	110.6 (2)
C3—C2—H2	107.7
N1—C3—C2	109.0 (2)
N1—C3—H3	108.8
N1—C3—C12_1	109.6 (2)
N1—C3—C12_2	109.6 (2)
C2—C3—H3	108.8
C12_1—C3—C2	111.9 (2)
C12_1—C3—H3	108.8
C12_2—C3—C2	111.9 (2)
N2—C4—N1	121.9 (2)
N2—C4—N4	109.9 (2)
N4—C4—N1	128.1 (2)
N3—C5—N4	116.0 (2)
N3—C5—H5	122.0
N4—C5—H5	122.0
C7—C6—C1	118.7 (3)
C11—C6—C1	122.8 (3)
C9—C8—C7	119.6 (4)
C9—C8—H8	120.2
C8—C9—H9	119.7
C10—C9—C8	120.5 (3)
C10—C9—H9	119.7
C9—C10—H10	119.9
C9—C10—C11	120.3 (4)
C11—C10—H10	119.9
C6—C11—C10	120.0 (3)
C6—C11—H11	120.0
C10—C11—H11	120.0
C12_1—O1_1—C15_1	106.1 (4)
O1_1—C12_1—C3	114.6 (3)
C13_1—C12_1—C3	135.3 (5)
C13_1—C12_1—O1_1	110.1 (4)
C12_1—C13_1—H13_1	126.1
C12_1—C13_1—C14_1	107.7 (7)
C14_1—C13_1—H13_1	126.1
C13_1—C14_1—H14_1	127.5
C15_1—C14_1—C13_1	104.9 (6)
C15_1—C14_1—H14_1	127.5
O1_1—C15_1—H15_1	124.6
C14_1—C15_1—O1_1	110.8 (5)
C14_1—C15_1—H15_1	124.6
C15_2—O1_2—C12_2	110.2 (9)
O1_2—C12_2—C3	118.3 (6)
C13_2—C12_2—C3	134.1 (8)
C13_2—C12_2—O1_2	106.3 (8)
C12_2—C13_2—H13_2	126.2
C12_2—C13_2—C14_2	107.6 (11)
C14_2—C13_2—H13_2	126.2
C13_2—C14_2—H14_2	126.4
C15_2—C14_2—C13_2	107.1 (12)
C15_2—C14_2—H14_2	126.4
O1_2—C15_2—H15_2	126.1
C14_2—C15_2—O1_2	107.9 (11)
C14_2—C15_2—H15_2	126.1
O2—C16_2—C17_2	115.7 (3)
O3—C16_2—O2	122.0 (3)
O3—C16_2—C17_2	122.3 (3)
C16_2—C17_2—H17A_2	109.5
C16_2—C17_2—H17B_2	109.5
C16_2—C17_2—H17C_2	109.5
H17A_2—C17_2—H17B_2	109.5
H17A_2—C17_2—H17C_2	109.5
H17B_2—C17_2—H17C_2	109.5

Zn1—O2—C16_2—O3	2.8 (4)	C2—C3—C12_2—O1_2	84.5 (10)
Zn1—O2—C16_2—C17_2	−177.2 (2)	C2—C3—C12_2—C13_2	−80.4 (15)
Zn1—N4—C4—N1	−2.3 (4)	C3—N1—C4—N2	−10.4 (4)
Zn1—N4—C4—N2	179.18 (17)	C3—N1—C4—N4	171.3 (3)
Zn1—N4—C5—N3	−179.08 (19)	C3—C12_1—C13_1—C14_1	−176.4 (5)
Zn1^{ii}—N5—C2—C1	−85.3 (2)	C3—C12_2—C13_2—C14_2	175.5 (10)
Zn1^{ii}—N5—C2—C3	150.70 (17)	C4—N1—C3—C2	38.6 (3)
N1—C3—C12_1—O1_1	150.2 (4)	C4—N1—C3—C12_1	161.4 (2)
N1—C3—C12_1—C13_1	−27.6 (9)	C4—N1—C3—C12_2	161.4 (2)
N1—C3—C12_2—O1_2	−36.5 (10)	C4—N2—N3—C5	0.1 (3)
N1—C3—C12_2—C13_2	158.6 (15)	C4—N2—C1—C2	−19.9 (3)
N2—N3—C5—N4	−0.6 (3)	C4—N2—C1—C6	105.5 (3)
N2—C1—C2—N5	−78.2 (2)	C4—N4—C5—N3	0.8 (3)
N2—C1—C2—C3	47.0 (3)	C5—N4—C4—N1	177.8 (3)
N2—C1—C6—C7	166.3 (2)	C5—N4—C4—N2	−0.7 (3)
N2—C1—C6—C11	−15.4 (4)	C6—C1—C2—N5	156.3 (2)
N3—N2—C1—C2	158.2 (2)	C6—C1—C2—C3	−78.5 (3)
N3—N2—C1—C6	−76.3 (3)	C6—C7—C8—C9	1.2 (5)
N3—N2—C4—N1	−178.1 (2)	C7—C6—C11—C10	−1.3 (4)
N3—N2—C4—N4	0.4 (3)	C7—C8—C9—C10	−1.6 (5)
N5—C2—C3—N1	66.3 (3)	C8—C9—C10—C11	0.5 (6)
N5—C2—C3—C12_1	−55.1 (3)	C9—C10—C11—C6	0.9 (5)
N5—C2—C3—C12_2	−55.1 (3)	C11—C6—C7—C8	0.2 (5)
C1—N2—N3—C5	−178.3 (2)	O1_1—C12_1—C13_1—C14_1	5.6 (11)
C1—N2—C4—N1	0.2 (4)	C12_1—O1_1—C15_1—C14_1	3.2 (7)
C1—N2—C4—N4	178.8 (2)	C12_1—C13_1—C14_1—C15_1	−3.5 (11)
C1—C2—C3—N1	−57.5 (3)	C13_1—C14_1—C15_1—O1_1	0.1 (9)
C1—C2—C3—C12_1	−178.9 (2)	C15_1—O1_1—C12_1—C3	176.1 (4)
C1—C2—C3—C12_2	−178.9 (2)	C15_1—O1_1—C12_1—C13_1	−5.5 (8)
C1—C6—C7—C8	178.6 (3)	O1_2—C12_2—C13_2—C14_2	9 (2)
C1—C6—C11—C10	−179.6 (3)	C12_2—O1_2—C15_2—C14_2	7 (2)
C2—C1—C6—C7	−71.5 (3)	C12_2—C13_2—C14_2—C15_2	−5 (2)
C2—C1—C6—C11	106.9 (3)	C13_2—C14_2—C15_2—O1_2	−1 (2)
C2—C3—C12_1—O1_1	−88.7 (4)	C15_2—O1_2—C12_2—C3	−179.0 (10)
C2—C3—C12_1—C13_1	93.4 (9)	C15_2—O1_2—C12_2—C13_2	−10 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*S*—H1*SA*···O2	0.98	1.91	2.830 (3)	155
O1*S*—H1*SB*···Cl1	0.98	2.47	3.321 (2)	144
N1—H1···Cl1	0.86	2.42	3.198 (2)	151
N5—H5*A*···O3^{ii}	0.89	2.48	2.961 (3)	114
N5—H5*A*···C12_1	0.89	2.49	2.966 (3)	114
N5—H5*A*···C13_1	0.89	2.67	3.422 (11)	143
N5—H5*A*···O1_2	0.89	2.33	3.086 (17)	144

N5—H5*A*···C12_2	0.89	2.49	2.966 (3)	114
N5—H5*B*···O1*S*$^{\mathrm{iii}}$	0.89	2.03	2.904 (3)	169

Symmetry codes: (ii) −*x*+1, *y*+1/2, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*+1/2.