The first coordination complex of (5R,6R,7S)-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

Mariia O. Shyshkina,* Svitlana V Shishkina, Konstantin S. Ostras, Nikolay Yu. Gorobets, Valentyn A. Chebanov and Sergey M. Desenko

SSI Institute for Single Crystals, NAS of Ukraine, 60 Nauky ave., Kharkiv 61001, Ukraine. *Correspondence e-mail: masha.o.shishkina@gmail.com

The title complex, systematic name catena-poly[[acetatochloridozinc(II)]-μ-(5R,6R,7S)-5-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-a]pyrimidin-6-amine] monohydrate, ([Zn(C2H3O2)Cl(C15H15N5O)]/C1H2O)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 annihilation of triazole with a tetrahydropyrimidine ring occurring in reactions of 3-amino-1,2,4-triazole, aromatic aldehydes and ketocompounds (Gümüş et al., 2017a,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.
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 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]. This may be due to the strong bifurcated intramolecular N—H⋯−π hydrogen bonds (N5—H5A⋯C12_1/C12_2, N5—H5B⋯C13_1 and N5—H5B⋯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)°].

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—H5A⋯O3 hydrogen bonds (Table 1). Neighbouring polymeric chains are connected through the water molecules by O1S—H1SA⋯O2, O1S—H1SB⋯Cl and N5—H5B⋯O1S 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 $d_{norm}$ surfaces. The areas coloured red on the $d_{norm}$ surfaces correspond to strong intermolecular O⋯H⋯O and N⋯H⋯O hydrogen bonds (Fig. 3). Bright red spots are

![Figure 1](https://example.com/figure1.png)

**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.

![Figure 2](https://example.com/figure2.png)

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

| Table 1 | Hydrogen-bond geometry (Å, °). |
|---------|--------------------------------|
| $D—H—A$ | $D—H$ | $H⋯A$ | $D⋯A$ | $D—H⋯A$ |
| O1S—H1SA⋯O2 | 0.98 | 1.91 | 2.830 (3) | 155 |
| O1S—H1SB⋯C1 | 0.98 | 2.47 | 3.321 (2) | 144 |
| N1—H1⋯C1 | 0.86 | 2.42 | 3.198 (2) | 151 |
| N5—H5A⋯O3 | 0.89 | 2.48 | 2.961 (3) | 114 |
| N5—H5A⋯C12_1 | 0.89 | 2.49 | 2.966 (3) | 114 |
| N5—H5A⋯C13_1 | 0.89 | 2.67 | 3.422 (11) | 143 |
| N5—H5A⋯O1_2 | 0.89 | 2.33 | 3.086 (17) | 144 |
| N5—H5B⋯O1S | 0.89 | 2.03 | 2.904 (3) | 169 |

Symmetry codes: (i) $x+\frac{1}{2}, y+\frac{1}{2}, z \pm \frac{1}{2}$; (ii) $x, y+\frac{1}{2}, z+\frac{1}{2}$
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) indicates the presence of strong hydrogen bonds in the crystal structure. The main contribution to the Hirshfeld surface is provided by H···C1/H contact (44.5%), shown in Fig. 4b. 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. 4c, 4d). 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. 4e, 4f) 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), OOZMEY (Chen et al., 2009), TOMPAN (Sakno 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.

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).

(5R,6R,7S)-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 2-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.

(5R,6R,7S)-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, Uiso(H) = 1.5Ueq(C) for methyl groups, O—H = 0.98 Å, Uiso(H) = 1.5Ueq(O) for the water molecule, Car—H = 0.93 Å, Csp3—H = 0.97 Å, N—H = 0.89 Å and Uiso(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).

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Table 2

| Crystal data | Chemical formula | [Zn(C2H3O2)Cl(C15H15N5O)]·H2O |
|-------------|-----------------|--------------------------------|
| Crystal system, space group | Monoclinic, P21/c |
| Temperature (K) | 293 |
| a, b, c (Å) | 10.6267 (4), 12.8015 (5), 15.1646 (7) |
| β (°) | 94.788 (4) |
| V (Å3) | 1994.63 (15) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm−1) | 1.40 |
| Data collection | Xcalibur, Sapphire3 |
| Diffractometer | Multi-scan (CrysAlis PRO; Rigaku OD, 2018) |
| Absorption correction | Δρmax, Δρmin (e Å−3) |
| | 0.36, −0.32 |

Computer programs: CrysAlis PRO (Rigaku OD, 2018), SHELXT2016/5 (Sheldrick, 2015a), SHELXL2015/1 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and OLEX2 (Dolomanov et al., 2009).

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The first coordination complex of \((5R,6R,7S)-5-(furan-2-yl)-7-phenyl-4,5,6,7\)-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)]-\(\mu-(5R,6R,7S)-5-(furan-2-yl)-7-phenyl-4,5,6,7\)-tetrahydro[1,2,4]triazolo[1,5-a]pyrimidin-6-amine] monohydrate

Crystal data

\([\text{Zn(C}_2\text{H}_3\text{O}_2\text{Cl(C}_1\text{H}_3\text{N}_5\text{O})}]\cdot\text{H}_2\text{O}\)  
\(F(000) = 944\)  
\(D_x = 1.529\) Mg m\(^{-3}\)  
Mo Kα radiation, \(\lambda = 0.71073\) Å  
Cell parameters from 3540 reflections  
\(\theta = 3.1-29.5^\circ\)  
\(\mu = 1.40\) 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\(^{-1}\)  
\(\omega\) scans  
Absorption correction: multi-scans  
(CrysAlisPro; Rigaku OD, 2018)  
\(T_{\text{min}} = 0.930, T_{\text{max}} = 1.000\)  
15201 measured reflections  
4572 independent reflections  
3174 reflections with \(I > 2\sigma(I)\)  
\(R_{\text{int}} = 0.042\)  
\(\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 3.0^\circ\)  
\(h = -13\rightarrow13\)  
\(k = -16\rightarrow16\)  
\(l = -19\rightarrow19\)

Refinement

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

Supporting information

Acta Cryst. (2021). E77, 1323-1326 [https://doi.org/10.1107/S2056989021012226]
w = 1/[σ²(Fo²) + (0.0493P)² + 0.1268P]
where P = (Fo² + 2Fc²)/3
(A/σ)max = 0.001

Δρmax = 0.36 e Å⁻³
Δρmin = −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 (Å²)

| Atom  | x      | y      | z      | Uiso/Un equivalence | Occ. (<1) |
|-------|--------|--------|--------|---------------------|-----------|
| Zn1   | 0.42716 (3) | 0.16102 (3) | 0.59755 (2) | 0.03857 (12) | 0.0552 (6) |
| Cl1   | 0.62402 (7)  | 0.20953 (6)  | 0.58000 (6)  | 0.0524 (2)   | 0.0545 (6) |
| O1S   | 0.4892 (2)   | 0.14368 (17) | 0.36476 (14) | 0.0552 (6)   | 0.0545 (6) |
| H1SA  | 0.416347     | 0.120957     | 0.389178     | 0.083*       | 0.0352 (5) |
| H1SB  | 0.562247     | 0.163167     | 0.416278     | 0.083*       | 0.0352 (5) |
| O2    | 0.32493 (19) | 0.10659 (17) | 0.48190 (13) | 0.0481 (5)   | 0.0445 (6) |
| O3    | 0.18743 (19) | 0.07023 (18) | 0.56429 (15) | 0.0545 (6)   | 0.0545 (6) |
| N1    | 0.5043 (2)   | 0.42425 (18) | 0.62954 (16) | 0.0437 (6)   | 0.0545 (6) |
| H1    | 0.560504     | 0.381973     | 0.617396     | 0.052*       | 0.052*     |
| N2    | 0.3175 (2)   | 0.44947 (17) | 0.68186 (15) | 0.0342 (5)   | 0.0342 (5) |
| N3    | 0.2161 (2)   | 0.39097 (19) | 0.69900 (16) | 0.0424 (6)   | 0.0424 (6) |
| N4    | 0.3523 (2)   | 0.28948 (17) | 0.64306 (15) | 0.0358 (5)   | 0.0358 (5) |
| N5    | 0.5586 (2)   | 0.55569 (17) | 0.79892 (14) | 0.0352 (5)   | 0.0352 (5) |
| H5A   | 0.638491     | 0.541918     | 0.793789     | 0.042*       | 0.042*     |
| H5B   | 0.526184     | 0.496510     | 0.814732     | 0.042*       | 0.042*     |
| C1    | 0.3340 (2)   | 0.5612 (2)   | 0.70008 (18) | 0.0350 (6)   | 0.0350 (6) |
| H1A   | 0.316410     | 0.574588     | 0.759441     | 0.042*       | 0.042*     |
| C2    | 0.4782 (2)   | 0.5873 (2)   | 0.70857 (17) | 0.0340 (6)   | 0.0340 (6) |
| H2    | 0.485507     | 0.663307     | 0.703691     | 0.041*       | 0.041*     |
| C3    | 0.5248 (3)   | 0.5371 (2)   | 0.62890 (19) | 0.0365 (6)   | 0.0365 (6) |
| H3    | 0.472603     | 0.565499     | 0.571084     | 0.044*       | 0.044*     |
| C4    | 0.3965 (2)   | 0.3877 (2)   | 0.64934 (17) | 0.0328 (6)   | 0.0328 (6) |
| C5    | 0.2433 (3)   | 0.2978 (2)   | 0.67508 (19) | 0.0403 (6)   | 0.0403 (6) |
| H5    | 0.191826     | 0.240239     | 0.679448     | 0.048*       | 0.048*     |
| C6    | 0.2415 (3)   | 0.6275 (2)   | 0.6302 (2)   | 0.0389 (6)   | 0.0389 (6) |
| C7    | 0.2274 (3)   | 0.7316 (2)   | 0.6495 (2)   | 0.0541 (8)   | 0.0541 (8) |
| H7    | 0.273434     | 0.758626     | 0.705375     | 0.065*       | 0.065*     |
| C8    | 0.1466 (3)   | 0.7960 (3)   | 0.5875 (3)   | 0.0693 (11)  | 0.0693 (11) |
| H8    | 0.139303     | 0.866309     | 0.600944     | 0.083*       | 0.083*     |
| C9    | 0.0773 (3)   | 0.7563 (3)   | 0.5065 (3)   | 0.0681 (10)  | 0.0681 (10) |
| H9    | 0.020910     | 0.799302     | 0.465039     | 0.082*       | 0.082*     |
| C10   | 0.0898 (3)   | 0.6544 (3)   | 0.4856 (3)   | 0.0641 (10)  | 0.0641 (10) |
| H10   | 0.042548     | 0.628125     | 0.429733     | 0.077*       | 0.077*     |
| C11   | 0.1729 (3)   | 0.5892 (3)   | 0.5472 (2)   | 0.0510 (8)   | 0.0510 (8) |
| H11   | 0.182172     | 0.519689     | 0.532211     | 0.061*       | 0.061*     |
| O1_1  | 0.6872 (5)   | 0.6493 (4)   | 0.5947 (4)   | 0.0578 (14)  | 0.707 (11)  |

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Atomic displacement parameters (Å²)

|     | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|-----|------|------|------|------|------|------|
| Zn1 | 0.0440 (2) | 0.03285 (19) | 0.0390 (2) | -0.00017 (14) | 0.01079 (14) | 0.00118 (14) |
| C11 | 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) | -0.0013 (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  | 0.046 (2) | 0.047 (2) | 0.082 (3) | -0.011 (2) | 0.019 (2) | 0.016 (2) |
| C12 | 0.0424 (14) | 0.0383 (15) | 0.0449 (16) | -0.0020 (12) | 0.0188 (13) | 0.0012 (12) |
| C13 | 0.054 (4) | 0.065 (4) | 0.078 (5) | 0.005 (3) | 0.026 (3) | 0.019 (3) |

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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) 0.064 (6) 0.005 (5) 0.010 (5) 0.019 (6)  
C13_2 0.041 (5) 0.056 (6) 0.061 (7) 0.000 (5) 0.009 (5) 0.017 (5)  
C14_2 0.041 (5) 0.053 (3) 0.061 (7) 0.000 (5) 0.009 (5) 0.017 (5)  
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, °)

| Bond or Angle | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 |
|---------------|---------|---------|---------|---------|---------|
| 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—N5i       | 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) |
| C2—C1         | 1.542 (3) | C12_2—C13_2 | 1.364 (18) |
| C1—C6         | 1.509 (4) | C13_2—H13_2 | 0.9300 |
| 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—N5i    | 111.81 (9) | C8—C7—C6  | 121.1 (3) |
| N4—Zn1—Cl1    | 105.83 (6) | C8—C7—H7  | 119.4 |
| N4—Zn1—N5i    | 103.45 (9) | C7—C8—H8  | 120.2 |
N5—Zn1—Cl1 112.44 (6)  C9—C8—C7  119.6 (4)
H1SA—O1S—H1SB 108.3  C9—C8—H8  120.2
C16_2—O2—Zn1 110.22 (17)  C8—C9—H9  119.7
C3—N1—H1 120.5  C10—C9—C8  120.5 (3)
C4—N1—H1 120.5  C10—C9—H9  119.7
C4—N1—C3 119.0 (2)  C9—C10—H10  119.9
N3—N2—C1 123.6 (2)  C9—C10—C11  120.3 (4)
C4—N2—N3 109.9 (2)  C11—C10—H10  119.9
C4—N2—C1 126.5 (2)  C6—C11—C10  120.0 (3)
C5—N3—N2 101.8 (2)  C6—C11—H11  120.0
C4—N4—Zn1 128.83 (17)  C10—C11—H11  120.0
C4—N4—C5 102.4 (2)  C12_1—O1_1—C15_1  106.1 (4)
C5—N4—Zn1 128.72 (19)  O1_1—C12_1—C3  114.6 (3)
Zn1ii—N5—H5A 108.2  C13_1—C12_1—C3  135.3 (5)
Zn1ii—N5—H5B 108.2  C13_1—C12_1—O1_1  110.1 (4)
H5A—N5—H5B 107.3  C12_1—C13_1—H13_1  126.1
C2—N5—Zn1 ii 116.37 (16)  C12_1—C13_1—C14_1  107.7 (7)
C2—N5—H5A 108.2  C14_1—C13_1—H13_1  126.1
C2—N5—H5B 108.2  C13_1—C14_1—H14_1  127.5
N2—C1—H1A 107.7  C15_1—C14_1—C13_1  104.9 (6)
N2—C1—C2 107.3 (2)  C15_1—C14_1—H14_1  127.5
N2—C1—C6 113.1 (2)  O1_1—C15_1—H15_1  124.6
C2—C1—H1A 107.7  C14_1—C15_1—O1_1  110.8 (5)
C6—C1—H1A 107.7  C14_1—C15_1—H15_1  124.6
C6—C1—C2 113.1 (2)  C15_2—O1_2—C12_2  110.2 (9)
N5—C2—C1 110.2 (2)  O1_2—C12_2—C3  118.3 (6)
N5—C2—H2 107.7  C13_2—C12_2—C3  134.1 (8)
N5—C2—C3 112.6 (2)  C13_2—C12_2—O1_2  106.3 (8)
C1—C2—H2 107.7  C12_2—C13_2—H13_2  126.2
C1—C2—C3 110.6 (2)  C12_2—C13_2—C14_2  107.6 (11)
C3—C2—H2 107.7  C14_2—C13_2—H13_2  126.2
N1—C3—C2 109.0 (2)  C13_2—C14_2—H14_2  126.4
N1—C3—H3 108.8  C15_2—C14_2—C13_2  107.1 (12)
N1—C3—C12_1 109.6 (2)  C15_2—C14_2—H14_2  126.4
N1—C3—C12_2 109.6 (2)  O1_2—C15_2—H15_2  126.1
C2—C3—H3 108.8  C14_2—C15_2—O1_2  107.9 (11)
C12_1—C3—C2 111.9 (2)  C14_2—C15_2—H15_2  126.1
C12_1—C3—H3 108.8  O2—C16_2—C17_2  115.7 (3)
C12_2—C3—C2 111.9 (2)  O3—C16_2—O2  122.0 (3)
N2—C4—N1 121.9 (2)  O3—C16_2—C17_2  122.3 (3)
N2—C4—N4 109.9 (2)  C16_2—C17_2—H17A_2  109.5
N4—C4—N1 128.1 (2)  C16_2—C17_2—H17B_2  109.5
N3—C5—N4 116.0 (2)  C16_2—C17_2—H17C_2  109.5
N3—C5—H5 122.0  H17A_2—C17_2—H17B_2  109.5
N4—C5—H5 122.0  H17A_2—C17_2—H17C_2  109.5
C7—C6—C1 118.7 (3)  H17B_2—C17_2—H17C_2  109.5
C11—C6—C1 122.8 (3)
### Supporting Information

Zn1—O2—C16_2—O3 2.8 (4)  
Zn1—O2—C16_2—C17_2 −177.2 (2)  
Zn1—N4—C4—N1 2.3 (4)  
Zn1—N4—C4—N2 179.18 (17)  
Zn1—N4—C5—N3 −179.08 (19)  
Zn1ii—N5—C2—C1 −85.3 (2)  
Zn1ii—N5—C2—C3 150.70 (17)  
N1—C3—C12_1—O1_1 150.2 (4)  
N1—C3—C12_1—C13_1 −27.6 (9)  
N1—C3—C12_2—O1_2 −78.2 (2)  
N1—C3—C12_2—C13_2 −178.1 (2)  
N1—C3—C12_1—O1_1 150.2 (4)  
N1—C3—C12_1—C13_1 −27.6 (9)  
N1—C3—C12_2—O1_2 −78.2 (2)  
N1—C3—C12_2—C13_2 −178.1 (2)  
N2—N3—C5—N4 −0.6 (3)  
N2—C1—C2—N5 −78.2 (2)  
N2—C1—C2—C3 47.0 (3)  
N2—C1—C6—C7 166.3 (2)  
N2—C1—C6—C11 −15.4 (4)  
N3—N2—C1—C2 158.2 (2)  
N3—N2—C1—C6 −27.6 (9)  
N3—N2—C4—N1 −178.1 (2)  
N3—N2—C4—N4 47.0 (3)  
N5—C2—C3—N1 66.3 (3)  
N5—C2—C3—C12_1 −55.1 (3)  
N5—C2—C3—C12_2 −55.1 (3)  
C1—N2—N3—C5 −178.3 (2)  
C1—N2—C4—N1 −0.2 (4)  
C1—N2—C4—N4 178.8 (2)  
C1—C2—C3—N1 −57.5 (3)  
C1—C2—C3—C12_1 178.9 (2)  
C1—C2—C3—C12_2 −178.9 (2)  
C1—C6—C7—C8 178.6 (3)  
C1—C6—C11—C10 −179.6 (3)  
C2—C1—C6—C7 −71.5 (3)  
C2—C1—C6—C11 106.9 (3)  
C2—C3—C12_1—O1_1 −88.7 (4)  
C2—C3—C12_1—C13_1 93.4 (9)  

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

### Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A  | D···A  | D—H···A |
|-----------|------|-------|-------|--------|
| O1S—H1S4···O2 | 0.98 | 1.91 | 2.830 (3) | 155 |
| O1S—H1S6···Cl1 | 0.98 | 2.47 | 3.321 (2) | 144 |
| N1—H1···C11 | 0.86 | 2.42 | 3.198 (2) | 151 |
| N5—H5d···O3 ii | 0.89 | 2.48 | 2.961 (3) | 114 |
| N5—H5d···C12_1 | 0.89 | 2.49 | 2.966 (3) | 114 |
| N5—H5d···C13_1 | 0.89 | 2.67 | 3.422 (11) | 143 |
| N5—H5d···O1_2 | 0.89 | 2.33 | 3.086 (17) | 144 |

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|       |        |        |        |        |
|-------|--------|--------|--------|--------|
| N5—H5A···C12_2 | 0.89   | 2.49   | 2.966 (3) | 114    |
| N5—H5B···O1S \( ^{ii} \) | 0.89   | 2.03   | 2.904 (3) | 169    |

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