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Crystal structure of poly[dichlorido(μ-2,5-dicarboxybenzene-1,4-dicarboxylato-$\kappa^2O^1:O^4$)bis[μ-4′-(pyridin-3-yl)-4,2′:6′,4″-terpyridine-$\kappa^2N^1:N^{4'}$]-dizinc]

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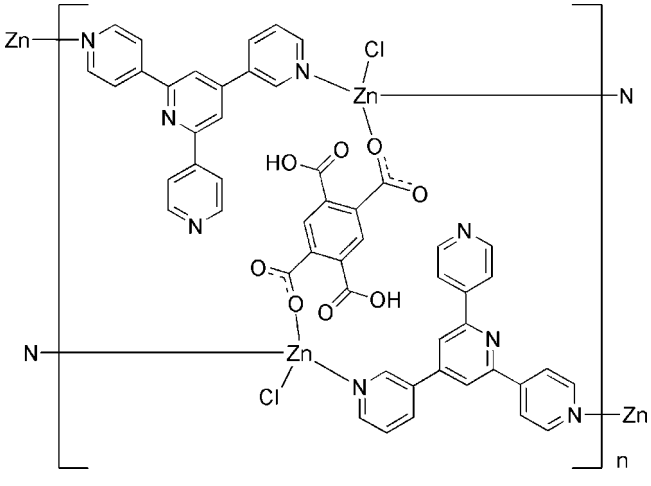
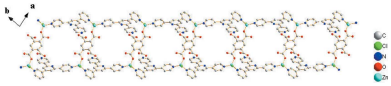
In the title polymeric Zn^{II} complex, $[Zn_2(C_{10}H_4O_8)Cl_2(C_{20}H_{14}N_4)_2]_n$, the Zn^{II} cations are bridged by both 2,5-dicarboxybenzene-1,4-dicarboxylate dianions and 4′-(pyridin-3-yl)-4,2′:6′,4″-terpyridine ligands, forming ladder-like polymeric chains propagating along [1$\bar{1}$0]. The Cl^- anion further coordinates the Zn^{II} cation to complete a distorted tetrahedral environment. In the 4′-(pyridin-3-yl)-4,2′:6′,4″-terpyridine ligand, the three sideward pyridine rings are twisted with respect to the central pyridine ring by 39.27 (12), 14.89 (13) and 3.36 (13)°, respectively. In the crystal, classical O—H···N hydrogen bonds and weak C—H···O and C—H···Cl hydrogen bonds link the chains into a three-dimensional supramolecular architecture. π–π stacking is observed between the pyridine and benzene rings of neighbouring polymeric chains, with a centroid-to-centroid distance of 3.7280 (14) Å.

1. Chemical context

Coordination polymers (CPs) represent a class of crystalline materials which consist of different ligands interconnected by metallic nodes (Yaghi & Li; 1995; Hinterholzinger *et al.*, 2012). Compared to traditional inorganic materials, CPs have fascinating structures with regular pore shape and size obtained by rational design (Kepert, 2006; Brammer, 2004). In addition, studies over several decades have revealed that CPs have multi-functional applications such as gas storage and separation (Rosi *et al.*, 2003; Jiang *et al.*, 2013), chemical purification (Li *et al.*, 2012), catalysis (Seo *et al.*, 2000), and sensors (Kreno *et al.*, 2012), etc.





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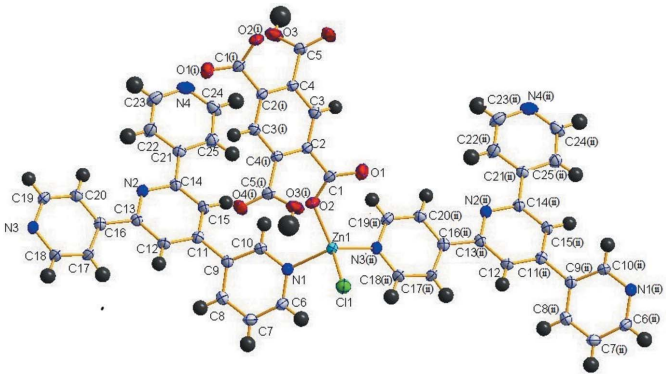

Figure 1
Part of the polymeric structure of the title complex [symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $x+1, y-1, z$]. Displacement ellipsoids are drawn at the 50% probability level.

Pyridine-containing compounds, such as 4,2′:6′,4″-terpyridine derivatives, are of great importance in the design of organic ligands, because conjugated polypyridyl ligands can form a better rigid plane and improve the stability of the network (Hancock, 2013; Li *et al.*, 2011; Bhaumik *et al.*, 2011). As a rigid planar and triangular ligand, 4′-(3-pyridyl)-4,2′:6′,4″-terpyridine (344-pytpy; Housecroft, 2014) is different from commonly employed polypyridyl ligands such as 1,3,5-tri(4-pyridyl)-2,4,6-triazine (Ma & Coppens, 2003; Kumazawa *et al.*, 2003), which have been widely studied in the field of coordination chemistry. Its rigidity and trigonal geometry may lead to the formation of nanosized cages and porous frameworks enclosing cavities and channels (Li *et al.*, 2008; Yoshizawa *et al.*, 2004; Dai *et al.*, 2008). 1,2,4,5-Benzenetetracarbonic acid (H_4bta) is frequently employed due to the rich coordination binding sites of the carboxylate groups (Hou *et al.*, 2011). We selected 344-pytpy and 1,2,4,5-benzenetetracarbonic acid as the organic linkers which, when assembled with Zn cations, resulted in the title coordination polymer $[Zn_2(344\text{-pytpy})_2(H_2bta)Cl_2]_n$.

2. Structural commentary

As shown in Fig. 1, the asymmetric unit of the title compound contains one Zn^{II} cation, one 344-pytpy ligand, a half of an H_2bta^{2-} anion and one coordinating Cl^- anion. The Zn^{II} atom is four-coordinated by two nitrogen atoms (N1, N3) from two different 344-pytpy ligands [Zn1—N1 = 2.070 (2) and Zn1—N3 = 2.0217 (18) Å], one oxygen atom (O2) from an H_2bta^{2-} anion [Zn1—O2 = 1.9171 (16) Å] and one Cl atom [Zn1—Cl1 = 2.2278 (7) Å] in a distorted tetrahedral coordination geometry. The bond lengths around Zn1 are similar to those reported by Wang *et al.* (2009). The X—Zn—X (X = N, O or Cl atom) angles range from 97.21 (8) to 115.73 (8)° and the tetrahedron edge lengths range from 2.992 (3) to 3.591 (2) Å. Each 344-pytpy ligand act as 2-connecting node, linking two Zn atoms by the outer N-terminal atoms (N1, N3), the central and another outer pyridine N atom (N2, N4) are free. The H_2bta^{2-} anion is located on an inversion center, and bridges two Zn^{II} atoms through the two carboxylate groups. In this way, chains propagating along [1$\bar{1}$0] are formed (Fig. 2).

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···N4^{ii}	0.82	1.83	2.633 (3)	167
C15—H15···O1^{iii}	0.93	2.46	3.383 (3)	172
C17—H17···Cl1^{iv}	0.93	2.75	3.678 (3)	173
C22—H22···O4^{v}	0.93	2.59	3.305 (4)	134
C25—H25···O1^{iii}	0.93	2.34	3.267 (3)	175

Symmetry codes: (ii) $-x, -y+1, -z+3$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y+2, -z+1$; (v) $x, y+1, z$.

3. Supramolecular features

In the crystal, classical O—H···N hydrogen bonds, weak C—H···O and C—H···Cl hydrogen bonds (Table 1) link the chains into a three-dimensional supramolecular architecture. π–π stacking is observed between the N3-pyridine ring and benzene ring of the neighboring chain, with a centroid-to-centroid distance of 3.7280 (14) Å.

3.1. Synthesis and crystallization

4′-(3-Pyridyl)-4,2′:6′,4″-terpyridine was synthesized according to a literature method (Yang *et al.*, 2014). 344-pytpy (0.0310 g, 0.1 mmol), $ZnCl_2$ (0.0136 g, 0.1 mmol) and 1,2,4,5-benzenetetracarbonic acid (0.0254 g, 0.1 mmol) were adequately dispersed in 10 mL of distilled water, and then the mixture was sealed and heated to 453 K for three days under hydrothermal conditions. The vial was then allowed to cool to

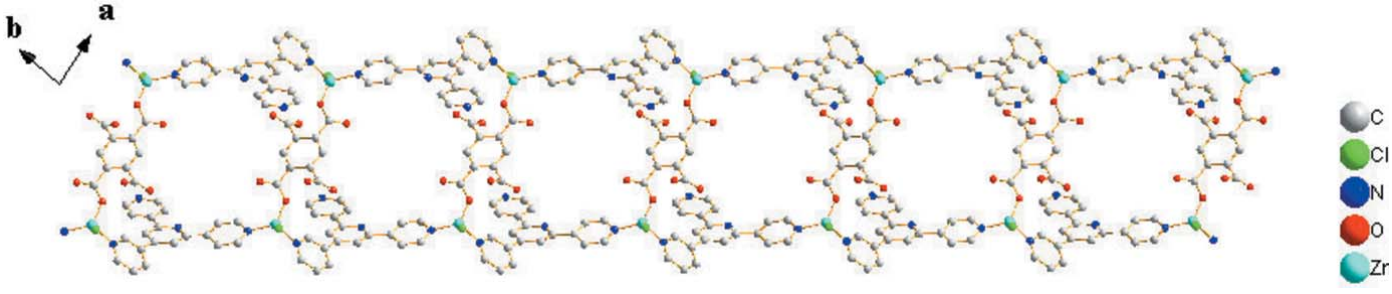

Figure 2
Part of the polymeric chain.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Zn_2(C_{10}H_4O_8)Cl_2(C_{20}H_{14}N_4)_2]$
M_r	537.24
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	8.6557 (6), 12.1432 (8), 12.5842 (9)
α, β, γ (°)	61.396 (1), 74.216 (1), 75.411 (1)
V (Å^3)	1105.83 (13)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.27
Crystal size (mm)	0.23 × 0.22 × 0.17
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2000)
T_{min}, T_{max}	0.758, 0.813
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7896, 3840, 3435
R_{int}	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.080, 1.07
No. of reflections	3840
No. of parameters	317
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.27

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2013* (Sheldrick, 2015).

room temperature. Colorless block-shaped crystals were collected (0.010 g, yield 38.9%, based on Zn).

3.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and treated as riding, with C—H = 0.93 and O—H = 0.82 Å, and with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(O).

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supporting information

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Crystal structure of poly[dichlorido(μ-2,5-dicarboxybenzene-1,4-dicarboxylato-κ^2O^1:O^4)bis[μ-4′-(pyridin-3-yl)-4,2′:6′,4″-terpyridine-κ^2N^1:$N^{4'}$]dizinc]

Yue Tian, Sha-Sha Xu, Jian Su, Yang Zhang, Shao-Shuai Zhao and Yu-Peng Tian

Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Poly[dichlorido(μ-2,5-dicarboxybenzene-1,4-dicarboxylato-κ^2O^1:O^4)bis[μ-4′-(pyridin-3-yl)-4,2′:6′,4″-terpyridine-κ^2N^1:$N^{4'}$]dizinc]

Crystal data

$[Zn_2(C_{10}H_4O_8)Cl_2(C_{20}H_{14}N_4)_2]$
M_r = 537.24
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.6557 (6) Å
b = 12.1432 (8) Å
c = 12.5842 (9) Å
α = 61.396 (1)°
β = 74.216 (1)°
γ = 75.411 (1)°
V = 1105.83 (13) Å^3
Z = 2
$F(000)$ = 546
D_x = 1.613 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4113 reflections
θ = 2.5–26.8°
μ = 1.27 mm^{-1}
T = 296 K
Block, colorless
0.23 × 0.22 × 0.17 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.758, T_{max} = 0.813
7896 measured reflections
3840 independent reflections
3435 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.0°, θ_{min} = 1.9°
h = −10→10
k = −14→12
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.080
S = 1.07
3840 reflections
317 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
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.4805P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3397 (3)	0.4695 (2)	0.8900 (2)	0.0279 (5)
C2	0.1613 (3)	0.4839 (2)	0.9422 (2)	0.0218 (5)
C3	0.1062 (3)	0.3951 (2)	1.0600 (2)	0.0239 (5)
H3	0.1774	0.3240	1.1002	0.029*
C4	−0.0533 (3)	0.4105 (2)	1.11919 (19)	0.0219 (5)
C5	−0.0971 (3)	0.3173 (2)	1.2513 (2)	0.0306 (6)
C6	0.6841 (3)	0.8624 (2)	0.5920 (2)	0.0297 (5)
H6	0.7535	0.8319	0.5380	0.036*
C7	0.6660 (3)	0.9894 (2)	0.5599 (2)	0.0317 (6)
H7	0.7220	1.0438	0.4860	0.038*
C8	0.5628 (3)	1.0346 (2)	0.6398 (2)	0.0280 (5)
H8	0.5457	1.1208	0.6186	0.034*
C9	0.4845 (3)	0.9514 (2)	0.7519 (2)	0.0228 (5)
C10	0.5101 (3)	0.8245 (2)	0.7761 (2)	0.0269 (5)
H10	0.4580	0.7676	0.8505	0.032*
C11	0.3721 (3)	0.9962 (2)	0.8406 (2)	0.0234 (5)
C12	0.2691 (3)	1.1105 (2)	0.7983 (2)	0.0259 (5)
H12	0.2725	1.1608	0.7143	0.031*
C13	0.1608 (3)	1.1490 (2)	0.8828 (2)	0.0236 (5)
C14	0.2517 (3)	0.9694 (2)	1.0459 (2)	0.0230 (5)
C15	0.3640 (3)	0.9256 (2)	0.9672 (2)	0.0254 (5)
H15	0.4331	0.8497	0.9987	0.030*
C16	0.0390 (3)	1.2655 (2)	0.8443 (2)	0.0237 (5)
C17	0.0453 (3)	1.3573 (2)	0.7232 (2)	0.0303 (6)
H17	0.1331	1.3513	0.6632	0.036*
C18	−0.0777 (3)	1.4565 (2)	0.6922 (2)	0.0299 (6)
H18	−0.0715	1.5165	0.6104	0.036*
C19	−0.2098 (3)	1.3857 (2)	0.8926 (2)	0.0251 (5)
H19	−0.2965	1.3958	0.9514	0.030*
C20	−0.0910 (3)	1.2841 (2)	0.9303 (2)	0.0254 (5)
H20	−0.0971	1.2276	1.0133	0.030*
C21	0.2301 (3)	0.8971 (2)	1.1827 (2)	0.0239 (5)

C22	0.1156 (3)	0.9462 (3)	1.2565 (2)	0.0334 (6)
H22	0.0533	1.0248	1.2213	0.040*
C23	0.0956 (3)	0.8769 (3)	1.3826 (2)	0.0374 (6)
H23	0.0199	0.9115	1.4309	0.045*
C24	0.2886 (3)	0.7152 (2)	1.3680 (2)	0.0331 (6)
H24	0.3473	0.6355	1.4060	0.040*
C25	0.3188 (3)	0.7786 (2)	1.2413 (2)	0.0283 (5)
H25	0.3975	0.7426	1.1955	0.034*
Cl1	0.60963 (8)	0.63418 (6)	0.52615 (5)	0.03639 (17)
N1	0.6063 (2)	0.78037 (18)	0.69741 (18)	0.0272 (4)
N2	0.1514 (2)	1.07932 (18)	1.00421 (17)	0.0252 (4)
N3	−0.2072 (2)	1.47156 (17)	0.77436 (17)	0.0234 (4)
N4	0.1792 (3)	0.7629 (2)	1.43877 (18)	0.0352 (5)
O1	0.4167 (2)	0.36497 (18)	0.9094 (2)	0.0572 (6)
O2	0.3980 (2)	0.57395 (16)	0.83257 (16)	0.0351 (4)
O3	−0.1565 (3)	0.37407 (17)	1.32170 (15)	0.0459 (5)
H3A	−0.1605	0.3216	1.3939	0.069*
O4	−0.0721 (4)	0.20509 (19)	1.2873 (2)	0.0792 (9)
Zn1	0.59827 (3)	0.60234 (2)	0.71763 (2)	0.02356 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0224 (12)	0.0315 (14)	0.0246 (12)	−0.0014 (11)	0.0023 (10)	−0.0128 (11)
C2	0.0208 (11)	0.0233 (12)	0.0210 (11)	−0.0041 (9)	0.0016 (9)	−0.0117 (10)
C3	0.0225 (12)	0.0239 (12)	0.0212 (11)	−0.0017 (9)	−0.0032 (9)	−0.0078 (10)
C4	0.0236 (12)	0.0216 (12)	0.0177 (11)	−0.0052 (9)	0.0018 (9)	−0.0085 (9)
C5	0.0269 (13)	0.0289 (14)	0.0248 (12)	−0.0014 (10)	0.0015 (10)	−0.0074 (11)
C6	0.0296 (13)	0.0293 (13)	0.0285 (12)	−0.0070 (10)	0.0075 (10)	−0.0167 (11)
C7	0.0355 (14)	0.0297 (14)	0.0254 (12)	−0.0126 (11)	0.0064 (10)	−0.0110 (11)
C8	0.0319 (13)	0.0198 (12)	0.0285 (12)	−0.0032 (10)	−0.0028 (10)	−0.0094 (10)
C9	0.0232 (12)	0.0207 (12)	0.0222 (11)	0.0001 (9)	−0.0041 (9)	−0.0092 (10)
C10	0.0277 (13)	0.0223 (12)	0.0221 (11)	−0.0024 (10)	0.0034 (10)	−0.0077 (10)
C11	0.0247 (12)	0.0220 (12)	0.0228 (11)	−0.0017 (9)	−0.0027 (9)	−0.0109 (10)
C12	0.0284 (13)	0.0235 (12)	0.0185 (11)	0.0001 (10)	−0.0017 (9)	−0.0065 (10)
C13	0.0244 (12)	0.0206 (12)	0.0217 (11)	0.0007 (9)	−0.0044 (9)	−0.0078 (9)
C14	0.0242 (12)	0.0199 (12)	0.0228 (11)	0.0002 (9)	−0.0046 (9)	−0.0093 (10)
C15	0.0259 (12)	0.0197 (12)	0.0243 (12)	0.0030 (9)	−0.0051 (10)	−0.0075 (10)
C16	0.0240 (12)	0.0212 (12)	0.0244 (11)	−0.0009 (9)	−0.0039 (9)	−0.0102 (10)
C17	0.0240 (12)	0.0294 (13)	0.0234 (12)	0.0045 (10)	0.0034 (10)	−0.0085 (10)
C18	0.0290 (13)	0.0254 (13)	0.0229 (12)	0.0027 (10)	−0.0004 (10)	−0.0063 (10)
C19	0.0228 (12)	0.0279 (13)	0.0235 (11)	−0.0026 (10)	0.0026 (9)	−0.0145 (10)
C20	0.0301 (13)	0.0227 (12)	0.0207 (11)	−0.0015 (10)	−0.0042 (10)	−0.0088 (10)
C21	0.0255 (12)	0.0231 (12)	0.0216 (11)	−0.0030 (9)	−0.0043 (9)	−0.0089 (10)
C22	0.0314 (14)	0.0353 (15)	0.0274 (13)	0.0053 (11)	−0.0047 (11)	−0.0142 (11)
C23	0.0309 (14)	0.0513 (17)	0.0277 (13)	−0.0027 (12)	0.0020 (11)	−0.0207 (13)
C24	0.0459 (16)	0.0254 (13)	0.0254 (12)	−0.0056 (11)	−0.0115 (11)	−0.0062 (11)
C25	0.0338 (13)	0.0264 (13)	0.0236 (12)	0.0003 (10)	−0.0055 (10)	−0.0122 (10)

Cl1	0.0431 (4)	0.0347 (4)	0.0254 (3)	0.0005 (3)	−0.0060 (3)	−0.0116 (3)
N1	0.0283 (11)	0.0197 (10)	0.0263 (10)	−0.0008 (8)	0.0023 (8)	−0.0094 (8)
N2	0.0246 (10)	0.0228 (10)	0.0229 (10)	0.0026 (8)	−0.0027 (8)	−0.0096 (8)
N3	0.0216 (10)	0.0211 (10)	0.0236 (10)	0.0011 (8)	−0.0020 (8)	−0.0098 (8)
N4	0.0430 (13)	0.0395 (13)	0.0204 (10)	−0.0138 (11)	−0.0020 (9)	−0.0092 (10)
O1	0.0329 (11)	0.0332 (11)	0.0777 (15)	0.0026 (9)	0.0135 (10)	−0.0184 (11)
O2	0.0243 (9)	0.0326 (10)	0.0384 (10)	−0.0087 (8)	0.0103 (8)	−0.0140 (8)
O3	0.0776 (15)	0.0351 (11)	0.0173 (8)	−0.0151 (10)	0.0021 (9)	−0.0076 (8)
O4	0.125 (2)	0.0231 (12)	0.0391 (12)	0.0033 (12)	0.0276 (13)	−0.0023 (9)
Zn1	0.02041 (16)	0.01912 (16)	0.02327 (15)	0.00026 (10)	0.00197 (11)	−0.00766 (11)

Geometric parameters (Å, º)

C1—O1	1.217 (3)	C14—C15	1.389 (3)
C1—O2	1.277 (3)	C14—C21	1.493 (3)
C1—C2	1.507 (3)	C15—H15	0.9300
C2—C3	1.389 (3)	C16—C20	1.390 (3)
C2—C4^{i}	1.399 (3)	C16—C17	1.389 (3)
C3—C4	1.393 (3)	C17—C18	1.366 (3)
C3—H3	0.9300	C17—H17	0.9300
C4—C2^{i}	1.399 (3)	C18—N3	1.344 (3)
C4—C5	1.503 (3)	C18—H18	0.9300
C5—O4	1.192 (3)	C19—N3	1.345 (3)
C5—O3	1.298 (3)	C19—C20	1.368 (3)
C6—N1	1.339 (3)	C19—H19	0.9300
C6—C7	1.372 (3)	C20—H20	0.9300
C6—H6	0.9300	C21—C22	1.390 (3)
C7—C8	1.379 (3)	C21—C25	1.392 (3)
C7—H7	0.9300	C22—C23	1.379 (3)
C8—C9	1.390 (3)	C22—H22	0.9300
C8—H8	0.9300	C23—N4	1.333 (3)
C9—C10	1.389 (3)	C23—H23	0.9300
C9—C11	1.488 (3)	C24—N4	1.336 (3)
C10—N1	1.341 (3)	C24—C25	1.379 (3)
C10—H10	0.9300	C24—H24	0.9300
C11—C12	1.390 (3)	C25—H25	0.9300
C11—C15	1.392 (3)	Zn1—Cl1	2.2278 (7)
C12—C13	1.393 (3)	Zn1—N1	2.070 (2)
C12—H12	0.9300	Zn1—O2	1.9171 (16)
C13—N2	1.336 (3)	Zn1—N3^{ii}	2.0217 (18)
C13—C16	1.490 (3)	O3—H3A	0.8200
C14—N2	1.343 (3)		

O1—C1—O2	125.8 (2)	C20—C16—C13	120.1 (2)
O1—C1—C2	120.4 (2)	C17—C16—C13	122.8 (2)
O2—C1—C2	113.6 (2)	C18—C17—C16	119.9 (2)
C3—C2—C4^{i}	119.3 (2)	C18—C17—H17	120.1
C3—C2—C1	118.5 (2)	C16—C17—H17	120.1

C4^{i}—C2—C1	122.0 (2)	N3—C18—C17	123.1 (2)
C2—C3—C4	121.4 (2)	N3—C18—H18	118.4
C2—C3—H3	119.3	C17—C18—H18	118.4
C4—C3—H3	119.3	N3—C19—C20	123.1 (2)
C3—C4—C2^{i}	119.3 (2)	N3—C19—H19	118.5
C3—C4—C5	117.6 (2)	C20—C19—H19	118.5
C2^{i}—C4—C5	122.9 (2)	C19—C20—C16	119.8 (2)
O4—C5—O3	124.4 (2)	C19—C20—H20	120.1
O4—C5—C4	124.0 (2)	C16—C20—H20	120.1
O3—C5—C4	111.4 (2)	C22—C21—C25	117.5 (2)
N1—C6—C7	122.9 (2)	C22—C21—C14	120.1 (2)
N1—C6—H6	118.5	C25—C21—C14	122.4 (2)
C7—C6—H6	118.5	C23—C22—C21	119.2 (2)
C6—C7—C8	118.5 (2)	C23—C22—H22	120.4
C6—C7—H7	120.7	C21—C22—H22	120.4
C8—C7—H7	120.7	N4—C23—C22	123.4 (2)
C7—C8—C9	120.0 (2)	N4—C23—H23	118.3
C7—C8—H8	120.0	C22—C23—H23	118.3
C9—C8—H8	120.0	N4—C24—C25	123.1 (2)
C8—C9—C10	117.3 (2)	N4—C24—H24	118.4
C8—C9—C11	121.7 (2)	C25—C24—H24	118.4
C10—C9—C11	121.0 (2)	C24—C25—C21	119.3 (2)
N1—C10—C9	123.1 (2)	C24—C25—H25	120.4
N1—C10—H10	118.5	C21—C25—H25	120.4
C9—C10—H10	118.5	C6—N1—C10	118.1 (2)
C12—C11—C15	118.0 (2)	C6—N1—Zn1	119.29 (16)
C12—C11—C9	120.2 (2)	C10—N1—Zn1	121.30 (16)
C15—C11—C9	121.8 (2)	C13—N2—C14	118.72 (19)
C11—C12—C13	119.4 (2)	C18—N3—C19	116.97 (19)
C11—C12—H12	120.3	C18—N3—Zn1^{iii}	120.55 (15)
C13—C12—H12	120.3	C19—N3—Zn1^{iii}	121.90 (15)
N2—C13—C12	122.3 (2)	C23—N4—C24	117.5 (2)
N2—C13—C16	115.34 (19)	C1—O2—Zn1	125.37 (16)
C12—C13—C16	122.25 (19)	C5—O3—H3A	109.5
N2—C14—C15	122.2 (2)	O2—Zn1—N3^{ii}	115.73 (8)
N2—C14—C21	114.85 (19)	O2—Zn1—N1	97.21 (8)
C15—C14—C21	122.9 (2)	N3^{ii}—Zn1—N1	115.16 (8)
C11—C15—C14	119.4 (2)	O2—Zn1—Cl1	119.86 (6)
C11—C15—H15	120.3	N3^{ii}—Zn1—Cl1	104.98 (6)
C14—C15—H15	120.3	N1—Zn1—Cl1	103.51 (6)
C20—C16—C17	117.0 (2)		

O1—C1—C2—C3	38.5 (3)	C17—C16—C20—C19	3.6 (3)
O2—C1—C2—C3	−137.7 (2)	C13—C16—C20—C19	−174.3 (2)
O1—C1—C2—C4^{i}	−147.7 (3)	N2—C14—C21—C22	−1.5 (3)
O2—C1—C2—C4^{i}	36.1 (3)	C15—C14—C21—C22	180.0 (2)
C4^{i}—C2—C3—C4	−1.3 (4)	N2—C14—C21—C25	177.0 (2)
C1—C2—C3—C4	172.7 (2)	C15—C14—C21—C25	−1.6 (4)

C2—C3—C4—C2^{i}	1.3 (4)	C25—C21—C22—C23	0.3 (4)
C2—C3—C4—C5	−173.6 (2)	C14—C21—C22—C23	178.9 (2)
C3—C4—C5—O4	−53.0 (4)	C21—C22—C23—N4	−1.1 (4)
C2^{i}—C4—C5—O4	132.3 (3)	N4—C24—C25—C21	−1.2 (4)
C3—C4—C5—O3	123.2 (2)	C22—C21—C25—C24	0.7 (4)
C2^{i}—C4—C5—O3	−51.5 (3)	C14—C21—C25—C24	−177.8 (2)
N1—C6—C7—C8	−0.1 (4)	C7—C6—N1—C10	−1.8 (4)
C6—C7—C8—C9	2.3 (4)	C7—C6—N1—Zn1	165.3 (2)
C7—C8—C9—C10	−2.5 (3)	C9—C10—N1—C6	1.6 (4)
C7—C8—C9—C11	−179.9 (2)	C9—C10—N1—Zn1	−165.17 (18)
C8—C9—C10—N1	0.5 (4)	C12—C13—N2—C14	1.0 (4)
C11—C9—C10—N1	177.9 (2)	C16—C13—N2—C14	176.5 (2)
C8—C9—C11—C12	38.0 (3)	C15—C14—N2—C13	−0.4 (3)
C10—C9—C11—C12	−139.3 (2)	C21—C14—N2—C13	−178.9 (2)
C8—C9—C11—C15	−143.1 (2)	C17—C18—N3—C19	2.2 (4)
C10—C9—C11—C15	39.5 (3)	C17—C18—N3—Zn1^{iii}	−169.2 (2)
C15—C11—C12—C13	−1.1 (3)	C20—C19—N3—C18	−2.1 (3)
C9—C11—C12—C13	177.8 (2)	C20—C19—N3—Zn1^{iii}	169.18 (18)
C11—C12—C13—N2	−0.3 (4)	C22—C23—N4—C24	0.7 (4)
C11—C12—C13—C16	−175.5 (2)	C25—C24—N4—C23	0.4 (4)
C12—C11—C15—C14	1.7 (3)	O1—C1—O2—Zn1	22.1 (4)
C9—C11—C15—C14	−177.2 (2)	C2—C1—O2—Zn1	−161.85 (15)
N2—C14—C15—C11	−1.0 (4)	C1—O2—Zn1—N3^{ii}	−49.0 (2)
C21—C14—C15—C11	177.4 (2)	C1—O2—Zn1—N1	−171.5 (2)
N2—C13—C16—C20	−11.3 (3)	C1—O2—Zn1—Cl1	78.4 (2)
C12—C13—C16—C20	164.2 (2)	C6—N1—Zn1—O2	−152.28 (19)
N2—C13—C16—C17	170.8 (2)	C10—N1—Zn1—O2	14.38 (19)
C12—C13—C16—C17	−13.7 (4)	C6—N1—Zn1—N3^{ii}	84.84 (19)
C20—C16—C17—C18	−3.6 (4)	C10—N1—Zn1—N3^{ii}	−108.50 (18)
C13—C16—C17—C18	174.4 (2)	C6—N1—Zn1—Cl1	−29.16 (19)
C16—C17—C18—N3	0.7 (4)	C10—N1—Zn1—Cl1	137.50 (17)
N3—C19—C20—C16	−0.8 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···N4^{iv}	0.82	1.83	2.633 (3)	167
C15—H15···O1^{v}	0.93	2.46	3.383 (3)	172
C17—H17···Cl1^{vi}	0.93	2.75	3.678 (3)	173
C22—H22···O4^{vii}	0.93	2.59	3.305 (4)	134
C25—H25···O1^{v}	0.93	2.34	3.267 (3)	175

Symmetry codes: (iv) −*x*, −*y*+1, −*z*+3; (v) −*x*+1, −*y*+1, −*z*+2; (vi) −*x*+1, −*y*+2, −*z*+1; (vii) *x*, *y*+1, *z*.