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The synthesis and structural properties of a chloridobis{*N*-[(4-methoxyphenyl)imino]pyrrolidine-1-carboxamide}zinc(II) (acetonitrile)trichloridozincate coordination complex

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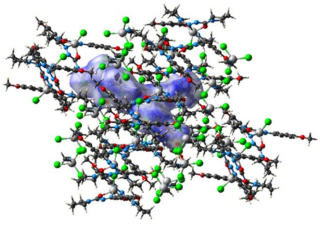
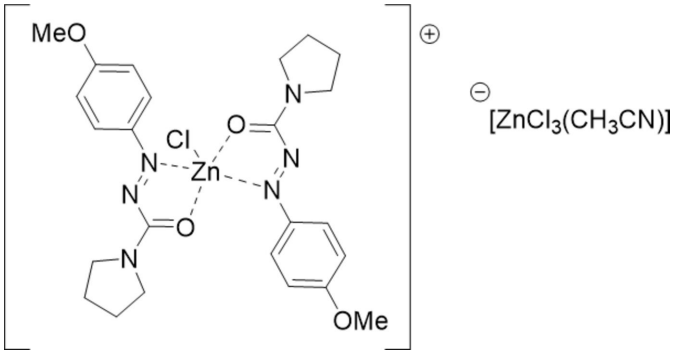
The title complex, $[ZnCl(C_{12}H_{15}N_3O_2)_2][ZnCl_3(CH_3CN)]$, was synthesized and its structure was fully characterized through single-crystal X-ray diffraction analysis. The complex crystallizes in the orthorhombic system, space group *Pbca* (61), with a central zinc atom coordinating one chlorine atom and two pyrrolidinyl-4-methoxyphenyl azoformamide ligands in a bidentate manner, utilizing both the nitrogen and oxygen atoms in a 1,3-heterodiene (N═N—C═O) motif for coordinative bonding, yielding an overall positively (+1) charged complex. The complex is accompanied by a $[(CH_3CN)ZnCl_3]^-$ counter-ion. The crystal data show that the harder oxygen atoms in the heterodiene zinc chelate form bonding interactions with distances of 2.002 (3) and 2.012 (3) Å, while nitrogen atoms are coordinated by the central zinc cation with bond lengths of 2.207 (3) and 2.211 (3) Å. To gain further insight into the intermolecular interactions within the crystal, Hirshfeld surface analysis was performed, along with the calculation of two-dimensional fingerprint plots. This analysis revealed that H···H (39.9%), Cl···H/H···Cl (28.2%) and C···H/H···C (7.2%) interactions are dominant. This unique crystal structure sheds light on arrangement and bonding interactions with azoformamide ligands, and their unique qualities over similar semicarbazone and azothioformamide structures.

1. Chemical context

Herein is presented pyrrolidinyl-4-methoxyphenylazoformamide, an arylazoformamide (AAF), acting as a ligand through its 1,3-heterodiene N═N—C═O motif to form a coordination complex with a zinc(II) metal atom. AAFs belong to the semicarbazone ligand family and there have been numerous reports and reviews of their use as ligands (Casas *et al.*, 2000; Mir *et al.*, 2024; Padhyé & Kauffman, 1985). Semicarbazones and thiosemicarbazones have the capability to coordinate with late transition metals (*e.g.* Cu, Pd, Zn, and Ni) and these complexes have found applications due to their thermal stability, noteworthy biological properties, and high synthetic flexibility (Casas *et al.*, 2000; Garg & Jain, 1988; Kasuga *et al.*, 2003; Siji *et al.*, 2010). Extending from the semicarbazones, numerous zinc(II) complexes have been reported to form with Schiff base ligands, exhibiting applications in catalysis and demonstrating antibacterial and anticancer properties (Kasuga *et al.*, 2003; Pieczonka *et al.*, 2014). AAFs, however, have been underexplored as ligands yet have been indicated as reagents for the Mitsunobu reaction (Hirose, *et al.*, 2018). As ligands, AAFs differ from semicarbazones in the manner of the 1,3-heterodiene motif; where the semicarbazones form a five-membered coordination ring through a Schiff base of type *R*—C═**N**—NH(*R*)—C═**O**, the



azoformamide uses the R—**N**═N—C═**O** to generate the five-membered metal-chelate. For the coordination process described herein, two AAF ligands are coordinated by zinc(II) chloride, displacing a chloride that is then taken on by a separate acetonitrile-coordinated zinc(II) chloride, creating an acetonitrile zinc(II) trichloride anion and resulting in a 2:1 ratio of ligands to the metal atom in the formed cationic complex. The ligands remain neutral while the resultant zinc interaction is similar to the complexes formed with azothioformamide ligands when bound to copper(I) and silver(I) coordination complexes (Groner *et al.*, 2019; Johnson *et al.*, 2017; Pradhan *et al.*, 2023).



2. Structural commentary

The X-ray crystal structure of the asymmetric unit of the title complex **1** and its packing structure are shown in Fig. 1. This complex crystallizes in the orthorhombic space group *Pbca* (61). In this structure, the Zn^{II} ion coordinates two nitrogen atoms and two oxygen atoms of two pyrrolidine *p*-methoxy phenylazoformamide molecules along with one chlorine atom, providing a distorted trigonal–bipyramidal shape and rendering the complex positively charged. This positive charge is counterbalanced by the presence of $[(CH_3CN)ZnCl_3]$ as counter-ion. Notably, the bond length of Zn1 and the attached chlorine atom (Cl2) is 2.2202 (10) Å; Zn1 and the O1 atom of the azoformamide are measured at 2.002 (3) and 2.012 (3) in the two ligands whereas the Zn1—N1 bonds are 2.207 (3) and 2.211 (3) Å.

3. Supramolecular features, Hirshfeld surface analysis and 2D fingerprint plots

In the crystal, the positive complexes alternate with inverted $[(CH_3CN)ZnCl_3]$ counter-ions, as seen in Fig. 1*b*.

In order to visualize the intermolecular interactions, a Hirshfeld surface (HS) analysis was carried out using *Crystal Explorer 17.5* (Spackman *et al.*, 2021), which was also used to generate the associated two-dimensional fingerprint plots. Red and blue dots on the Hirshfeld surfaces (Fig. 2) indicate intermolecular contacts with distances shorter and longer than the van der Waals radii, respectively.

The two-dimensional fingerprint plots of the most abundant contacts are presented in Fig. 3 and indicate that H···H (39.9%) and H···Cl/Cl···H (28.2%) contacts are responsible for the largest contributions to the Hirshfeld surface. Besides these contacts, C···H/H···C (7.2%), H···N/N···H (6.8%) and H···O/O···H (6.2%) interactions also contribute to the total Hirshfeld surface. The contributions of further contacts are only minor and amount to C···N/N···C (3.8%), C···C (3.6%), C···O/O···C (1.6%), H···Zn/Zn···H (1.2%), O···O (0.3%), N···O/O···N (0.3%), N···Cl/Cl···N (0.3%), O···Cl/Cl···O (0.3%), and C···Cl/Cl···C (0.3%).

4. Synthesis and crystallization

The pyrrolidinyl-4-methoxyphenylazoformamide ligand was prepared in a two-step synthesis from commercially available

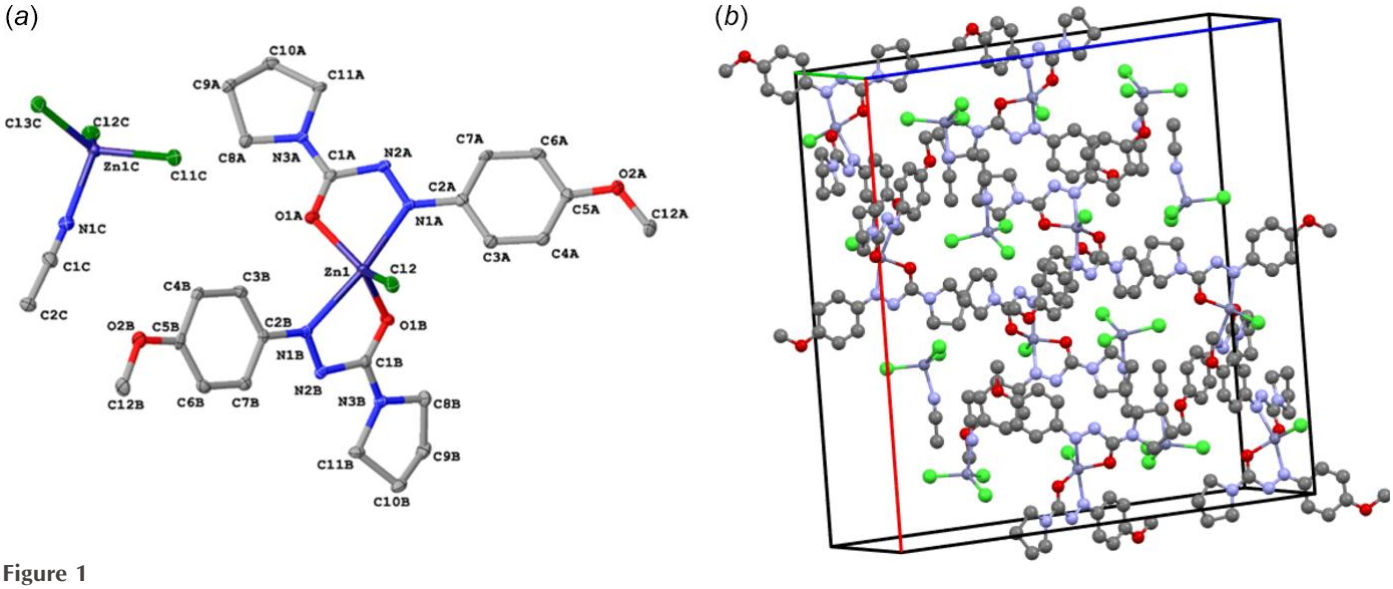


Figure 1
(*a*) A view of the molecular structure of the title complex in its found asymmetric unit, with atom labeling. All displacement ellipsoids are drawn at the 50% probability level. (*b*) Crystal packing diagram of the title complex in ball-and-stick format.

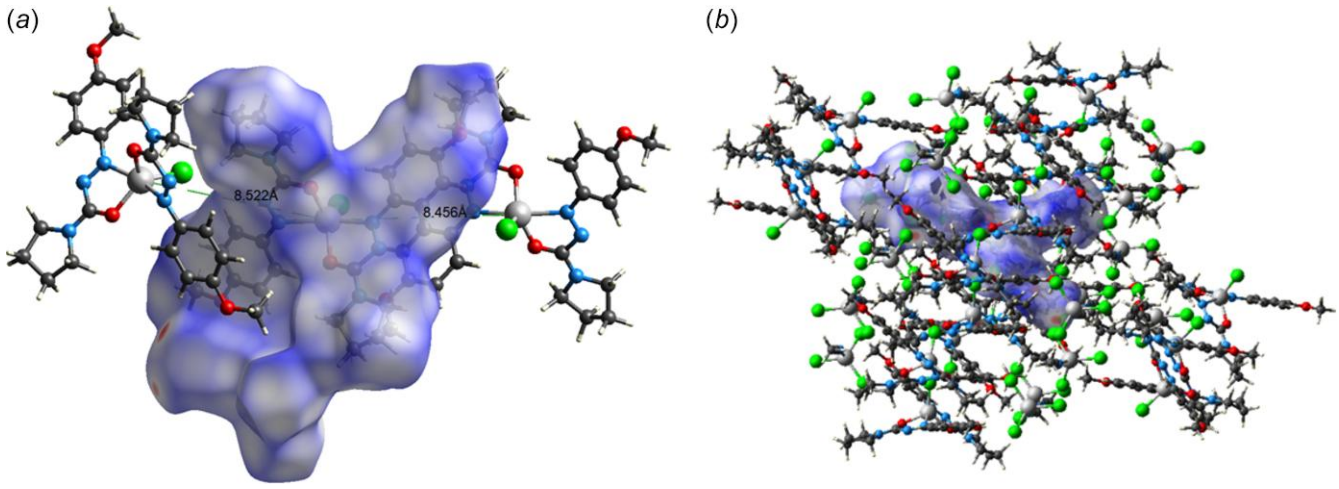


Figure 2
(*a*) Hirshfeld surface of the title compound mapped over d_{norm} with Zn—Zn bond lengths in Å. (*b*) Arrangement of the compound in the crystal with interactions indicated.

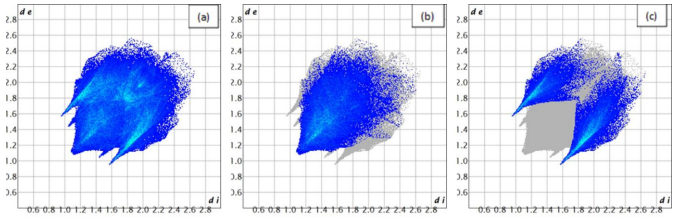


Figure 3
Two-dimensional fingerprint plots for the title compound showing (*a*) all interactions and delineated into (*b*) H···H (39.9%) and (*c*) H···Cl/Cl···H (28.2%) contacts. The values d_i (*x*-axis) and d_e (*y*-axis) are the closest internal and external distances from given places on the Hirshfeld surface (in Å).

4-methoxyphenylhydrazine·HCl and methyl chloroformate as shown in Fig. 4. The intermediate ester was isolated prior to forming the formamide similar to a recently reported synthesis of biologically active arylazothioformamides (Pradhan *et al.*, 2023).

Pyrrolidinyl-4-methoxyphenylazoformamide (4): 4-methoxyphenylhydrazine·HCl (5.00 mmol, 0.873 g) was dissolved in 20 mL of dichloromethane in a round-bottom flask fitted with a magnetic stirrer followed by degassing under nitrogen flow. Then, pre-dried pyridine (10.0 mmol, 0.805 mL) was added to the solution followed by a dropwise addition of methyl chloroformate (5.5 mmol, 0.425 mL). The reaction was stirred for 30 minutes at 273 K and 1 h at room temperature. The mixture was diluted with 20 mL of water and was extracted with ether (3 × 40 mL), before the organic layer was separated and concentrated *in vacuo*. Pure product was obtained from column chromatography (3:2 hexane: ethyl acetate) yielding the ester as a light brown solid (0.892 g, 77% yield) identified as methyl 2-(4-methoxyphenyl)hydrazine-1-carboxylate and matching previously reported NMR data (Käsnänen *et al.*, 2013). This ester, **3** (4 mmol, 0.785 g), was dissolved in 10 mL of toluene and to the solution was added pyrrolidine (4.8 mmol, 0.473 mL) followed by triethylamine (6.0 mmol, 0.855 mL). The solution was refluxed at 363 K under nitrogen for 48 h. The solution was then cooled to room temperature, opened to air, and stirred for 4 h. The solution was then washed with brine (2 × 25 mL), extracted with ethyl acetate, and dried with $MgSO_4$. After concentration, the crude product was subjected to column chromatography (7:3 hexane: ethyl acetate) to give 0.612 g of a bright-orange solid (65% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (*d*, *J* = 9.1 Hz, 2H), 6.98 (*d*, *J* = 9.1 Hz, 2H), 3.89 (*s*, 3H), 3.71–3.68 (*m*, 2H), 3.64 (*t*, *J* = 6.8 Hz, 2H), 1.98–1.95 (*m*, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.114, 146.612, 126.022, 114.429, 114.421, 55.801, 46.781, 26.183, 24.470 FTIR (cm^{-1}): 2974, 2884, 1690, 1500, 1256, 1025, 848. HRMS $[M + H]^+$, Measured: 234.1243; found: 234.1236, m.p.339 K.

Chloridobis{*N*-[(4-methoxyphenyl)imino]pyrrolidine-1-carboxamide}zinc(II) (acetonitrile)trichloridozincate (1): Zinc(II) chloride (0.136 g, 1.00 mmol) was added to a solution of pyrrolidine-4-methoxyphenylazoformamide, **4** (0.233 g, 1 mmol) in 5 ml of toluene and the mixture was refluxed for 2 h at 363 K to obtain a yellow solution of the zinc complex. The solution was concentrated by rotary evaporation, and the

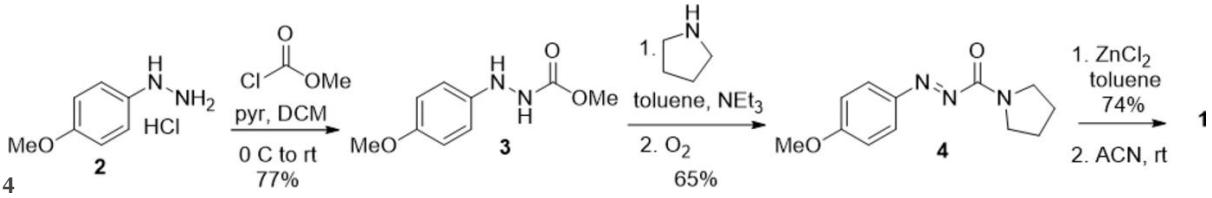


Figure 4
Synthesis of the pyrrolidinyl-4-methoxyphenylazoformamide ligand from phenylhydrazine hydrochloride.

resulting solid was purified using several cold hexane washes to remove any residual ligand, yielding 0.569 g (74% yield) of a yellow solid. 15–25 mg of the material were dissolved in 2 mL of acetonitrile for crystallization. After 2 days of slow evaporation, yellow plate-like crystals were obtained. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (*d*, *J* = 8.5 Hz, 4H), 7.04 (*d*, *J* = 7.2 Hz, 4H), 3.92 (*s*, 6H), 3.76 (*dt*, *J* = 12.7, 6.0 Hz, 8H), 2.07–1.98 (*m*, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.150, 161.404, 146.278, 127.316, 114.971, 56.062, 47.320, 26.143, 24.515. FTIR (cm^{-1}): 2979, 1647, 1370, 1267, 1047, 846; m.p. 467 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The hydrogen atoms were placed in calculated positions with C—H distances of 0.95 Å and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(C). Methyl H atoms were positioned geometrically and were allowed to ride on C atoms and rotate around the C—C bond, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C).

Table 1
Experimental details.

Crystal data	
Chemical formula	$[ZnCl(C_{12}H_{15}N_3O_2)_2]$-$[ZnCl_3(C_2H_3N)]$
M_r	780.13
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, *b*, *c* (Å)	28.4313 (7), 7.6516 (2), 29.5461 (9)
V (Å^3)	6427.6 (3)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	1.87
Crystal size (mm)	0.19 × 0.17 × 0.02
Data collection	
Diffractometer	Bruker D8 VENTURE Duo
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.665, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	167426, 7354, 5790
R_{int}	0.088
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.104, 1.15
No. of reflections	7354
No. of parameters	391
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.05, −0.54

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), and Macrae *et al.*, 2020).

Acknowledgements

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The synthesis and structural properties of a chloridobis{*N*-[(4-methoxyphenyl)-imino]pyrrolidine-1-carboxamide}zinc(II) (acetonitrile)trichloridozincate coordination complex

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Computing details

Chloridobis{*N*-[(4-methoxyphenyl)imino]pyrrolidine-1-carboxamide}zinc(II) (acetonitrile)trichloridozincate

Crystal data

$[ZnCl(C_{12}H_{15}N_3O_2)_2][ZnCl_3(C_2H_3N)]$
M_r = 780.13
Orthorhombic, *Pbca*
a = 28.4313 (7) Å
b = 7.6516 (2) Å
c = 29.5461 (9) Å
V = 6427.6 (3) Å^3
Z = 8
F(000) = 3184
D_x = 1.612 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 9702 reflections
θ = 2.8–27.4°
μ = 1.87 mm^{-1}
T = 100 K
Plate, yellow
0.19 × 0.17 × 0.02 mm

Data collection

Bruker D8 VENTURE Duo diffractometer
Radiation source: sealed tube, fine-focus
TRIUMPH graphite monochromator
Detector resolution: 7.39 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.665, T_{max} = 0.746
167426 measured reflections
7354 independent reflections
5790 reflections with $I > 2\sigma(I)$
R_{int} = 0.088
θ_{max} = 27.5°, θ_{min} = 2.6°
h = −36→31
k = −9→9
l = −38→38

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.104
S = 1.15
7354 reflections
391 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 31.9684P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.38392 (2)	0.32189 (6)	0.53246 (2)	0.01362 (10)
Cl2	0.35537 (3)	0.06498 (13)	0.51090 (3)	0.01896 (19)
O1A	0.41294 (9)	0.3767 (4)	0.59256 (9)	0.0187 (6)
O2A	0.55202 (9)	0.1012 (4)	0.36437 (9)	0.0229 (6)
N1A	0.46035 (10)	0.2952 (4)	0.52134 (10)	0.0133 (6)
N2A	0.48565 (10)	0.3201 (4)	0.55606 (10)	0.0154 (6)
N3A	0.48118 (10)	0.3960 (4)	0.63111 (10)	0.0142 (6)
C1A	0.45700 (13)	0.3661 (5)	0.59420 (12)	0.0148 (7)
C2A	0.48421 (13)	0.2478 (5)	0.48157 (12)	0.0155 (7)
C3A	0.45684 (13)	0.2099 (5)	0.44347 (12)	0.0172 (8)
H3A	0.423563	0.219067	0.445091	0.021*
C4A	0.47807 (13)	0.1593 (5)	0.40346 (12)	0.0167 (8)
H4A	0.459493	0.131954	0.377685	0.020*
C5A	0.52690 (13)	0.1487 (5)	0.40129 (13)	0.0169 (8)
C6A	0.55441 (13)	0.1885 (6)	0.43970 (14)	0.0223 (9)
H6A	0.587724	0.181919	0.437899	0.027*
C7A	0.53351 (13)	0.2365 (6)	0.47949 (13)	0.0188 (8)
H7A	0.552075	0.261920	0.505402	0.023*
C8A	0.45700 (13)	0.4426 (6)	0.67395 (12)	0.0177 (8)
H8AA	0.430842	0.360891	0.680413	0.021*
H8AB	0.444552	0.563336	0.672826	0.021*
C9A	0.49607 (13)	0.4258 (5)	0.70924 (13)	0.0186 (8)
H9AA	0.497786	0.305092	0.721214	0.022*
H9AB	0.490918	0.507573	0.734723	0.022*
C10A	0.54098 (13)	0.4729 (5)	0.68302 (13)	0.0193 (8)
H10A	0.544762	0.601197	0.680722	0.023*
H10B	0.569137	0.422980	0.697896	0.023*
C11A	0.53340 (12)	0.3916 (5)	0.63639 (12)	0.0168 (8)
H11A	0.549077	0.461079	0.612492	0.020*
H11B	0.545399	0.270177	0.635372	0.020*
C12A	0.52662 (14)	0.0592 (6)	0.32387 (13)	0.0218 (9)
H12A	0.548822	0.024803	0.300113	0.033*
H12B	0.508739	0.161675	0.313882	0.033*
H12C	0.504936	−0.037576	0.329936	0.033*
O1B	0.37393 (9)	0.5185 (4)	0.48827 (9)	0.0157 (5)
O2B	0.20169 (9)	0.1946 (4)	0.68988 (9)	0.0215 (6)
N1B	0.31512 (10)	0.4348 (4)	0.55143 (10)	0.0130 (6)
N2B	0.29743 (11)	0.5328 (4)	0.52118 (10)	0.0139 (6)
N3B	0.31713 (10)	0.6878 (4)	0.45738 (10)	0.0145 (6)

C1B	0.33246 (12)	0.5774 (5)	0.48798 (12)	0.0132 (7)
C2B	0.28426 (13)	0.3787 (5)	0.58569 (12)	0.0134 (7)
C3B	0.30428 (13)	0.3026 (5)	0.62401 (13)	0.0168 (8)
H3B	0.337426	0.289260	0.626118	0.020*
C4B	0.27560 (13)	0.2466 (5)	0.65894 (13)	0.0167 (8)
H4B	0.289068	0.199929	0.685771	0.020*
C5B	0.22695 (14)	0.2588 (5)	0.65466 (13)	0.0170 (8)
C6B	0.20650 (13)	0.3330 (5)	0.61614 (13)	0.0179 (8)
H6B	0.173273	0.340930	0.613448	0.021*
C7B	0.23534 (13)	0.3947 (5)	0.58204 (13)	0.0167 (8)
H7B	0.221930	0.448156	0.556045	0.020*
C8B	0.34803 (13)	0.7567 (5)	0.42103 (13)	0.0176 (8)
H8BA	0.357293	0.663033	0.399685	0.021*
H8BB	0.376717	0.811038	0.433778	0.021*
C9B	0.31677 (14)	0.8932 (5)	0.39776 (13)	0.0211 (8)
H9BA	0.321348	1.010256	0.411355	0.025*
H9BB	0.323686	0.899791	0.364963	0.025*
C10B	0.26686 (14)	0.8269 (5)	0.40602 (13)	0.0193 (8)
H10C	0.243535	0.922170	0.402726	0.023*
H10D	0.258748	0.730994	0.384933	0.023*
C11B	0.26919 (13)	0.7620 (5)	0.45464 (13)	0.0174 (8)
H11C	0.265053	0.859231	0.476389	0.021*
H11D	0.245005	0.671737	0.460494	0.021*
C12B	0.15132 (13)	0.1884 (6)	0.68501 (14)	0.0245 (9)
H12D	0.143225	0.125226	0.657227	0.037*
H12E	0.138870	0.307660	0.683382	0.037*
H12F	0.137575	0.128065	0.711113	0.037*
Zn1C	0.36227 (2)	0.31087 (6)	0.79662 (2)	0.01579 (11)
Cl1C	0.37575 (3)	0.15712 (13)	0.73339 (3)	0.0198 (2)
Cl2C	0.40356 (3)	0.55957 (13)	0.79884 (3)	0.0216 (2)
Cl3C	0.36050 (3)	0.17133 (13)	0.86338 (3)	0.0205 (2)
N1C	0.29085 (12)	0.3713 (5)	0.78907 (12)	0.0232 (8)
C1C	0.25046 (15)	0.3671 (5)	0.78836 (13)	0.0209 (8)
C2C	0.19989 (13)	0.3640 (6)	0.78872 (14)	0.0213 (9)
H2CA	0.187897	0.435302	0.763698	0.032*
H2CB	0.188409	0.411243	0.817500	0.032*
H2CC	0.188907	0.243370	0.785197	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.00912 (19)	0.0189 (2)	0.0128 (2)	−0.00014 (17)	−0.00164 (15)	−0.00036 (18)
Cl2	0.0149 (4)	0.0205 (5)	0.0215 (5)	−0.0035 (4)	0.0028 (4)	−0.0032 (4)
O1A	0.0113 (12)	0.0294 (15)	0.0154 (13)	−0.0016 (11)	−0.0021 (10)	−0.0013 (12)
O2A	0.0149 (13)	0.0378 (17)	0.0160 (14)	0.0033 (12)	0.0018 (11)	−0.0041 (13)
N1A	0.0108 (14)	0.0183 (16)	0.0110 (15)	−0.0008 (12)	−0.0008 (11)	0.0010 (12)
N2A	0.0129 (14)	0.0217 (17)	0.0116 (15)	−0.0002 (13)	−0.0022 (12)	0.0015 (13)
N3A	0.0092 (14)	0.0216 (17)	0.0116 (15)	−0.0005 (12)	0.0012 (12)	0.0010 (13)

C1A	0.0144 (17)	0.0174 (18)	0.0124 (17)	−0.0014 (14)	−0.0002 (14)	0.0019 (14)
C2A	0.0157 (17)	0.0172 (18)	0.0137 (18)	0.0016 (15)	−0.0001 (14)	0.0021 (15)
C3A	0.0128 (17)	0.023 (2)	0.0158 (19)	−0.0017 (15)	0.0006 (14)	0.0000 (16)
C4A	0.0145 (17)	0.023 (2)	0.0124 (17)	−0.0017 (15)	−0.0012 (14)	0.0004 (16)
C5A	0.0176 (18)	0.020 (2)	0.0128 (17)	0.0037 (15)	0.0025 (15)	0.0027 (15)
C6A	0.0086 (16)	0.036 (2)	0.022 (2)	0.0011 (17)	0.0003 (15)	0.0020 (19)
C7A	0.0151 (18)	0.030 (2)	0.0117 (18)	0.0007 (16)	−0.0051 (14)	−0.0007 (16)
C8A	0.0142 (18)	0.026 (2)	0.0130 (18)	−0.0022 (16)	0.0002 (14)	−0.0001 (16)
C9A	0.0190 (19)	0.025 (2)	0.0119 (18)	0.0012 (16)	−0.0030 (15)	−0.0002 (16)
C10A	0.0148 (18)	0.023 (2)	0.020 (2)	−0.0004 (16)	−0.0046 (15)	−0.0007 (16)
C11A	0.0115 (17)	0.026 (2)	0.0126 (18)	0.0001 (15)	−0.0032 (14)	0.0025 (16)
C12A	0.024 (2)	0.027 (2)	0.0146 (19)	0.0010 (18)	0.0008 (16)	−0.0061 (17)
O1B	0.0103 (12)	0.0208 (14)	0.0162 (13)	0.0003 (10)	0.0012 (10)	0.0032 (11)
O2B	0.0159 (13)	0.0321 (16)	0.0164 (13)	−0.0041 (12)	0.0037 (11)	0.0020 (12)
N1B	0.0126 (14)	0.0149 (15)	0.0115 (15)	−0.0017 (12)	−0.0023 (12)	−0.0016 (12)
N2B	0.0130 (14)	0.0172 (16)	0.0115 (15)	−0.0032 (12)	0.0012 (12)	0.0012 (12)
N3B	0.0133 (14)	0.0170 (15)	0.0131 (15)	−0.0007 (13)	0.0008 (12)	0.0016 (13)
C1B	0.0118 (17)	0.0161 (18)	0.0118 (17)	−0.0026 (14)	0.0000 (13)	−0.0027 (14)
C2B	0.0155 (17)	0.0143 (17)	0.0105 (17)	−0.0002 (14)	0.0023 (14)	−0.0022 (14)
C3B	0.0108 (16)	0.021 (2)	0.0184 (19)	0.0008 (15)	−0.0009 (14)	0.0005 (16)
C4B	0.0182 (18)	0.0217 (19)	0.0101 (17)	−0.0004 (16)	−0.0002 (14)	−0.0003 (15)
C5B	0.0219 (19)	0.0193 (19)	0.0098 (17)	−0.0024 (16)	0.0015 (15)	−0.0038 (15)
C6B	0.0107 (16)	0.023 (2)	0.0198 (19)	−0.0008 (15)	0.0005 (14)	−0.0040 (17)
C7B	0.0153 (17)	0.021 (2)	0.0140 (18)	0.0001 (15)	−0.0018 (14)	−0.0011 (15)
C8B	0.0168 (18)	0.0205 (19)	0.0153 (18)	−0.0012 (15)	0.0034 (15)	0.0025 (15)
C9B	0.030 (2)	0.020 (2)	0.0137 (19)	−0.0012 (17)	0.0000 (16)	0.0037 (16)
C10B	0.0230 (19)	0.0192 (19)	0.0157 (18)	0.0027 (16)	−0.0045 (15)	0.0023 (16)
C11B	0.0153 (18)	0.0179 (19)	0.0189 (19)	0.0034 (15)	−0.0041 (15)	0.0018 (15)
C12B	0.0146 (18)	0.039 (3)	0.020 (2)	−0.0044 (18)	0.0067 (15)	0.0000 (19)
Zn1C	0.0128 (2)	0.0178 (2)	0.0167 (2)	0.00073 (17)	0.00144 (16)	0.00044 (18)
Cl1C	0.0193 (4)	0.0226 (5)	0.0174 (4)	0.0003 (4)	0.0029 (4)	−0.0003 (4)
Cl2C	0.0193 (4)	0.0212 (5)	0.0244 (5)	−0.0042 (4)	−0.0017 (4)	0.0005 (4)
Cl3C	0.0222 (4)	0.0211 (5)	0.0180 (4)	0.0010 (4)	0.0017 (4)	0.0022 (4)
N1C	0.0196 (18)	0.031 (2)	0.0189 (18)	0.0049 (15)	−0.0022 (14)	−0.0016 (15)
C1C	0.021 (2)	0.020 (2)	0.021 (2)	0.0044 (16)	0.0020 (17)	−0.0002 (16)
C2C	0.0155 (19)	0.027 (2)	0.022 (2)	0.0029 (16)	−0.0005 (16)	0.0000 (17)

Geometric parameters (Å, º)

Zn1—Cl2	2.2202 (10)	O2B—C12B	1.440 (5)
Zn1—O1A	2.002 (3)	N1B—N2B	1.270 (4)
Zn1—N1A	2.207 (3)	N1B—C2B	1.407 (5)
Zn1—O1B	2.012 (3)	N2B—C1B	1.439 (5)
Zn1—N1B	2.211 (3)	N3B—C1B	1.311 (5)
O1A—C1A	1.256 (4)	N3B—C8B	1.484 (5)
O2A—C5A	1.354 (4)	N3B—C11B	1.479 (5)
O2A—C12A	1.434 (5)	C2B—C3B	1.395 (5)
N1A—N2A	1.267 (4)	C2B—C7B	1.400 (5)

N1A—C2A	1.405 (5)	C3B—H3B	0.9500
N2A—C1A	1.435 (5)	C3B—C4B	1.383 (5)
N3A—C1A	1.309 (5)	C4B—H4B	0.9500
N3A—C8A	1.484 (5)	C4B—C5B	1.392 (5)
N3A—C11A	1.493 (4)	C5B—C6B	1.399 (5)
C2A—C3A	1.399 (5)	C6B—H6B	0.9500
C2A—C7A	1.406 (5)	C6B—C7B	1.382 (5)
C3A—H3A	0.9500	C7B—H7B	0.9500
C3A—C4A	1.383 (5)	C8B—H8BA	0.9900
C4A—H4A	0.9500	C8B—H8BB	0.9900
C4A—C5A	1.392 (5)	C8B—C9B	1.535 (5)
C5A—C6A	1.412 (5)	C9B—H9BA	0.9900
C6A—H6A	0.9500	C9B—H9BB	0.9900
C6A—C7A	1.367 (6)	C9B—C10B	1.527 (6)
C7A—H7A	0.9500	C10B—H10C	0.9900
C8A—H8AA	0.9900	C10B—H10D	0.9900
C8A—H8AB	0.9900	C10B—C11B	1.521 (5)
C8A—C9A	1.529 (5)	C11B—H11C	0.9900
C9A—H9AA	0.9900	C11B—H11D	0.9900
C9A—H9AB	0.9900	C12B—H12D	0.9800
C9A—C10A	1.536 (5)	C12B—H12E	0.9800
C10A—H10A	0.9900	C12B—H12F	0.9800
C10A—H10B	0.9900	Zn1C—Cl1C	2.2408 (10)
C10A—C11A	1.527 (5)	Zn1C—Cl2C	2.2368 (11)
C11A—H11A	0.9900	Zn1C—Cl3C	2.2435 (10)
C11A—H11B	0.9900	Zn1C—N1C	2.095 (3)
C12A—H12A	0.9800	N1C—C1C	1.149 (5)
C12A—H12B	0.9800	C1C—C2C	1.438 (5)
C12A—H12C	0.9800	C2C—H2CA	0.9800
O1B—C1B	1.262 (4)	C2C—H2CB	0.9800
O2B—C5B	1.356 (5)	C2C—H2CC	0.9800

O1A—Zn1—Cl2	126.20 (9)	N2B—N1B—Zn1	113.7 (2)
O1A—Zn1—N1A	75.27 (11)	N2B—N1B—C2B	116.1 (3)
O1A—Zn1—O1B	118.48 (11)	C2B—N1B—Zn1	128.0 (2)
O1A—Zn1—N1B	93.31 (11)	N1B—N2B—C1B	110.2 (3)
N1A—Zn1—Cl2	103.62 (9)	C1B—N3B—C8B	122.1 (3)
N1A—Zn1—N1B	160.92 (12)	C1B—N3B—C11B	126.3 (3)
O1B—Zn1—Cl2	115.10 (8)	C11B—N3B—C8B	111.7 (3)
O1B—Zn1—N1A	96.41 (11)	O1B—C1B—N2B	123.9 (3)
O1B—Zn1—N1B	75.36 (11)	O1B—C1B—N3B	123.0 (3)
N1B—Zn1—Cl2	95.47 (8)	N3B—C1B—N2B	113.1 (3)
C1A—O1A—Zn1	115.6 (2)	C3B—C2B—N1B	117.2 (3)
C5A—O2A—C12A	117.8 (3)	C3B—C2B—C7B	120.3 (3)
N2A—N1A—Zn1	115.1 (2)	C7B—C2B—N1B	122.5 (3)
N2A—N1A—C2A	116.2 (3)	C2B—C3B—H3B	120.2
C2A—N1A—Zn1	128.6 (2)	C4B—C3B—C2B	119.6 (3)
N1A—N2A—C1A	110.5 (3)	C4B—C3B—H3B	120.2

C1A—N3A—C8A	120.6 (3)	C3B—C4B—H4B	120.1
C1A—N3A—C11A	127.2 (3)	C3B—C4B—C5B	119.8 (4)
C8A—N3A—C11A	112.1 (3)	C5B—C4B—H4B	120.1
O1A—C1A—N2A	123.5 (3)	O2B—C5B—C4B	115.6 (4)
O1A—C1A—N3A	123.0 (3)	O2B—C5B—C6B	123.5 (3)
N3A—C1A—N2A	113.5 (3)	C4B—C5B—C6B	120.9 (4)
N1A—C2A—C7A	122.3 (3)	C5B—C6B—H6B	120.5
C3A—C2A—N1A	117.3 (3)	C7B—C6B—C5B	119.0 (3)
C3A—C2A—C7A	120.5 (4)	C7B—C6B—H6B	120.5
C2A—C3A—H3A	119.9	C2B—C7B—H7B	119.9
C4A—C3A—C2A	120.2 (3)	C6B—C7B—C2B	120.2 (4)
C4A—C3A—H3A	119.9	C6B—C7B—H7B	119.9
C3A—C4A—H4A	120.3	N3B—C8B—H8BA	111.2
C3A—C4A—C5A	119.4 (4)	N3B—C8B—H8BB	111.2
C5A—C4A—H4A	120.3	N3B—C8B—C9B	102.9 (3)
O2A—C5A—C4A	125.4 (4)	H8BA—C8B—H8BB	109.1
O2A—C5A—C6A	114.4 (3)	C9B—C8B—H8BA	111.2
C4A—C5A—C6A	120.2 (4)	C9B—C8B—H8BB	111.2
C5A—C6A—H6A	119.7	C8B—C9B—H9BA	111.0
C7A—C6A—C5A	120.6 (3)	C8B—C9B—H9BB	111.0
C7A—C6A—H6A	119.7	H9BA—C9B—H9BB	109.0
C2A—C7A—H7A	120.4	C10B—C9B—C8B	103.9 (3)
C6A—C7A—C2A	119.2 (4)	C10B—C9B—H9BA	111.0
C6A—C7A—H7A	120.4	C10B—C9B—H9BB	111.0
N3A—C8A—H8AA	111.2	C9B—C10B—H10C	111.2
N3A—C8A—H8AB	111.2	C9B—C10B—H10D	111.2
N3A—C8A—C9A	103.0 (3)	H10C—C10B—H10D	109.2
H8AA—C8A—H8AB	109.1	C11B—C10B—C9B	102.6 (3)
C9A—C8A—H8AA	111.2	C11B—C10B—H10C	111.2
C9A—C8A—H8AB	111.2	C11B—C10B—H10D	111.2
C8A—C9A—H9AA	111.0	N3B—C11B—C10B	102.6 (3)
C8A—C9A—H9AB	111.0	N3B—C11B—H11C	111.3
C8A—C9A—C10A	103.9 (3)	N3B—C11B—H11D	111.3
H9AA—C9A—H9AB	109.0	C10B—C11B—H11C	111.3
C10A—C9A—H9AA	111.0	C10B—C11B—H11D	111.3
C10A—C9A—H9AB	111.0	H11C—C11B—H11D	109.2
C9A—C10A—H10A	111.0	O2B—C12B—H12D	109.5
C9A—C10A—H10B	111.0	O2B—C12B—H12E	109.5
H10A—C10A—H10B	109.0	O2B—C12B—H12F	109.5
C11A—C10A—C9A	104.0 (3)	H12D—C12B—H12E	109.5
C11A—C10A—H10A	111.0	H12D—C12B—H12F	109.5
C11A—C10A—H10B	111.0	H12E—C12B—H12F	109.5
N3A—C11A—C10A	103.0 (3)	Cl1C—Zn1C—Cl3C	119.15 (4)
N3A—C11A—H11A	111.2	Cl2C—Zn1C—Cl1C	112.42 (4)
N3A—C11A—H11B	111.2	Cl2C—Zn1C—Cl3C	113.01 (4)
C10A—C11A—H11A	111.2	N1C—Zn1C—Cl1C	101.12 (10)
C10A—C11A—H11B	111.2	N1C—Zn1C—Cl2C	108.91 (11)
H11A—C11A—H11B	109.1	N1C—Zn1C—Cl3C	100.19 (10)

O2A—C12A—H12A	109.5	C1C—N1C—Zn1C	164.7 (4)
O2A—C12A—H12B	109.5	N1C—C1C—C2C	178.4 (5)
O2A—C12A—H12C	109.5	C1C—C2C—H2CA	109.5
H12A—C12A—H12B	109.5	C1C—C2C—H2CB	109.5
H12A—C12A—H12C	109.5	C1C—C2C—H2CC	109.5
H12B—C12A—H12C	109.5	H2CA—C2C—H2CB	109.5
C1B—O1B—Zn1	113.8 (2)	H2CA—C2C—H2CC	109.5
C5B—O2B—C12B	117.5 (3)	H2CB—C2C—H2CC	109.5

Zn1—O1A—C1A—N2A	0.7 (5)	C11A—N3A—C1A—O1A	−178.3 (4)
Zn1—O1A—C1A—N3A	−179.2 (3)	C11A—N3A—C1A—N2A	1.8 (6)
Zn1—N1A—N2A—C1A	−2.0 (4)	C11A—N3A—C8A—C9A	−12.7 (4)
Zn1—N1A—C2A—C3A	−0.7 (5)	C12A—O2A—C5A—C4A	0.5 (6)
Zn1—N1A—C2A—C7A	179.8 (3)	C12A—O2A—C5A—C6A	−179.8 (4)
Zn1—O1B—C1B—N2B	10.7 (4)	O2B—C5B—C6B—C7B	−180.0 (4)
Zn1—O1B—C1B—N3B	−170.1 (3)	N1B—N2B—C1B—O1B	3.5 (5)
Zn1—N1B—N2B—C1B	−14.5 (4)	N1B—N2B—C1B—N3B	−175.8 (3)
Zn1—N1B—C2B—C3B	31.2 (5)	N1B—C2B—C3B—C4B	179.4 (3)
Zn1—N1B—C2B—C7B	−147.8 (3)	N1B—C2B—C7B—C6B	178.2 (3)
O2A—C5A—C6A—C7A	−179.3 (4)	N2B—N1B—C2B—C3B	−166.9 (3)
N1A—N2A—C1A—O1A	1.0 (5)	N2B—N1B—C2B—C7B	14.0 (5)
N1A—N2A—C1A—N3A	−179.1 (3)	N3B—C8B—C9B—C10B	−27.7 (4)
N1A—C2A—C3A—C4A	−178.8 (4)	C1B—N3B—C8B—C9B	−173.7 (3)
N1A—C2A—C7A—C6A	179.6 (4)	C1B—N3B—C11B—C10B	−161.6 (4)
N2A—N1A—C2A—C3A	176.5 (3)	C2B—N1B—N2B—C1B	−178.9 (3)
N2A—N1A—C2A—C7A	−3.0 (6)	C2B—C3B—C4B—C5B	3.1 (6)
N3A—C8A—C9A—C10A	30.7 (4)	C3B—C2B—C7B—C6B	−0.9 (6)
C1A—N3A—C8A—C9A	168.0 (3)	C3B—C4B—C5B—O2B	177.6 (4)
C1A—N3A—C11A—C10A	168.6 (4)	C3B—C4B—C5B—C6B	−2.4 (6)
C2A—N1A—N2A—C1A	−179.5 (3)	C4B—C5B—C6B—C7B	0.0 (6)
C2A—C3A—C4A—C5A	−0.9 (6)	C5B—C6B—C7B—C2B	1.6 (6)
C3A—C2A—C7A—C6A	0.2 (6)	C7B—C2B—C3B—C4B	−1.5 (6)
C3A—C4A—C5A—O2A	−179.9 (4)	C8B—N3B—C1B—O1B	−1.8 (6)
C3A—C4A—C5A—C6A	0.3 (6)	C8B—N3B—C1B—N2B	177.6 (3)
C4A—C5A—C6A—C7A	0.5 (6)	C8B—N3B—C11B—C10B	19.8 (4)
C5A—C6A—C7A—C2A	−0.8 (7)	C8B—C9B—C10B—C11B	40.2 (4)
C7A—C2A—C3A—C4A	0.7 (6)	C9B—C10B—C11B—N3B	−36.3 (4)
C8A—N3A—C1A—O1A	0.9 (6)	C11B—N3B—C1B—O1B	179.7 (3)
C8A—N3A—C1A—N2A	−179.0 (3)	C11B—N3B—C1B—N2B	−0.9 (5)
C8A—N3A—C11A—C10A	−10.6 (4)	C11B—N3B—C8B—C9B	4.9 (4)
C8A—C9A—C10A—C11A	−38.0 (4)	C12B—O2B—C5B—C4B	−173.9 (4)
C9A—C10A—C11A—N3A	29.5 (4)	C12B—O2B—C5B—C6B	6.1 (6)