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Construction of a supramolecule comprising [2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninato]zinc(II) and (5,10,15,20-tetraphenylporphyrinato)zinc(II)

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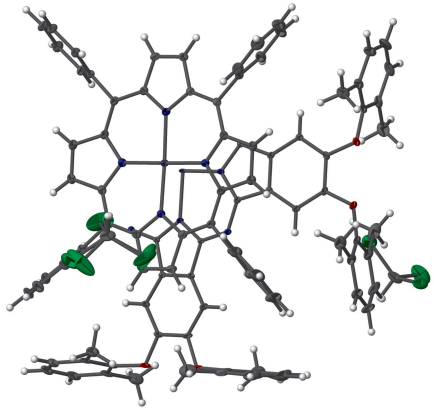
The supramolecular features in the title compound, [2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninato]zinc(II) bis[(5,10,15,20-tetraphenylporphyrinato)zinc(II)] chloroform tetrasolvate, $[Zn(C_{96}H_{80}N_8O_8)][Zn(C_{44}H_{28}N_4)]_2\cdot 4CHCl_3$ or $[Zn(Pc)][Zn(TPP)]_2\cdot 4CHCl_3$, result from a self-assembly of one molecule of [2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninato]zinc(II) (ZnPc) and two molecules of (5,10,15,20-tetraphenylporphyrinato)zinc(II) (ZnTPP). One half ZnPc, one ZnTPP and two chloroform molecules define the asymmetric unit, with the zinc(II) cation of ZnPc situated on an inversion centre. In the supramolecule, the central ZnPc moiety is sandwiched between two ZnTPPs moieties in a co-facial conformation with a π-conjugated system, leading to a nearly H-type aggregate with a distance of 3.4967 (5) Å between adjacent zinc sites. The ZnTPP units are slightly glided away to form a partial ecliptic arrangement. Each phenyl group of the TPP ligand is anchored above the N atom of the isoindole linker of the Pc ligand through weak C—H···N hydrogen bonds and is held into the crevice between the two dimethylphenoxy groups of phthalocyanine via van der Waals interactions. In the crystal, chloroform solvent molecules are situated between the supramolecules. There is another solvent-accessible void of 341 (2) Å^3. The contribution of disordered solvent molecules situated in this void was removed from the diffraction data using SQUEEZE in *PLATON* [Spek (2015). *Acta Cryst.* C**71**, 9–18]. The given chemical formula and other crystal data do not consider this unknown solvent molecule(*s*).

3D view



Chemical scheme

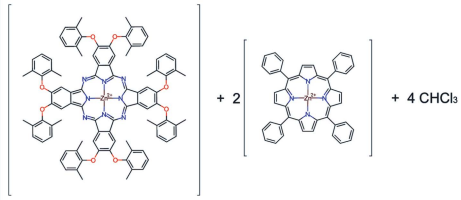


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Table 1
Selected bond lengths (Å).

Zn1—N1	1.9700 (14)	Zn2—N6	2.0332 (15)
Zn1—N3	1.9920 (14)	Zn2—N7	2.0524 (15)
Zn2—N5	2.0234 (15)	Zn2—N8	2.0269 (14)

Structure description

Phthalocyanine, porphyrin and their metal complexes have attracted great attention because their characteristic physicochemical properties are derived from their extended π-conjugation systems. Phthalocyanine and porphyrin comprise an intensive *Q* band of approximately 600–900 nm and a Soret band of approximately 400–500 nm. Thus, the combination of these two π-conjugated systems could cover the entire range of the visible region, which is a promising strategy for the development of photo-functional materials, such as dye-sensitized solar cells (DSCs), or for efficient light-energy conversion (O'Regan & Grätzel, 1991; Walter *et al.*, 2010). As part of our efforts to design more efficient dyes for DSCs (Noda *et al.*, 2009; Iwata *et al.*, 2018), we discovered that 2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyanine (Pc) with zinc(II) as the central metal cation (ZnPc) and 5,10,15,20-tetraphenylporphyrin (TPP) with another central zinc(II) cation (ZnTPP) formed a supramolecular self-assembly as analysed both by photometric and NMR titration studies. Here, we report the structural analysis of the resulting solvated ZnPc–ZnTPP complex, $[Zn(PC)][Zn(TPP)_2]\cdot 4CHCl_3$ (I).

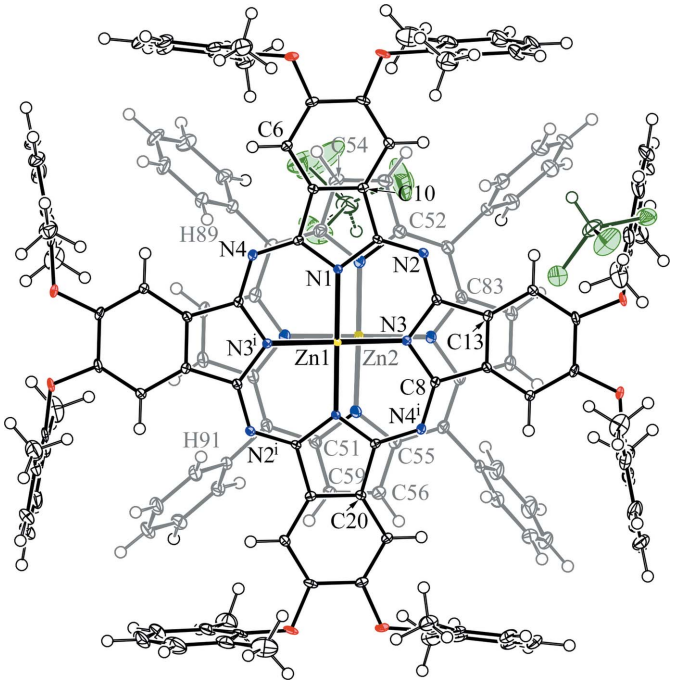

Figure 1
The expanded asymmetric unit of the title supramolecule in a view from the ZnPc macrocycle, with displacement ellipsoids drawn at the 50% probability level. Atom labels of ZnPc and ZnTPP are black and grey, respectively. ZnTPP and chloroform molecules generated by inversion operation through the origin at Zn1 have been omitted for clarity [symmetry code: (i) $-x+1, -y+1, -z+1$].

Table 2
Hydrogen-bond geometry and centroid–centroid distances for π–π interactions (Å, °).

*Cg*1–*Cg*12 are the centroids of the five- or six-membered rings, where *Cg*1: N1–C8–C20–C10–C9, *Cg*2: N3–C7–C18–C13–C11, *Cg*3: Zn1–N1–C9–N2–C11–N3, *Cg*4: Zn1–N1–C8–N4–C7i–N3^{i}, *Cg*5: N5–C52–C63–C54–C61, *Cg*6: N6–C51–C59–C56–C55, *Cg*7: N8–C65–C50–C66–C83, *Cg*8: N7–C67–C49–C73–C69, *Cg*9: Zn2–N5–C52–C60–C83–N8, *Cg*10: Zn2–N6–C51–C62–C67–N7, *Cg*11: Zn2–N5–C61–C57–C69–N7, *Cg*12: Zn2–N6–C55–C70–C65–N8.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C89—H89···N4	0.95	2.35	3.245 (3)	157
C91—H91···N2^{i}	0.95	2.38	3.263 (3)	154
*Cg*1···*Cg*5			3.6115 (13)	
*Cg*2···*Cg*7			3.5271 (13)	
*Cg*3···*Cg*9			3.4996 (11)	
*Cg*4···*Cg*11			3.6264 (11)	
*Cg*1^{i}···*Cg*6			3.5162 (13)	
*Cg*2^{i}···*Cg*8			3.6819 (13)	
*Cg*3^{i}···*Cg*10			3.6105 (13)	
*Cg*4^{i}···*Cg*12			3.4785 (1)	

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

The asymmetric unit of (I) comprises of one half of ZnPc, one ZnTPP and two chloroform molecules. The Zn(II) cation bound to Pc occupies an inversion centre, and therefore complete complexes are generated using an inversion symmetry operation [symmetry code: (i) $-x+1, -y+1, -z+1$] (Figs. 1 and 2). Neither ZnPc nor ZnTPP have axial ligands; Zn—N bond lengths (Table 1) are in the usual range. The Pc and TPP ligands are held together not only through π–π interactions between phthalocyanine and porphyrin aromatic cores but also via weak C—H···N hydrogen bonds between nitrogen atoms linked to the isoindole unit of Pc and hydrogen atoms of the phenyl group of ZnTPP (Table 2). The ZnTPP core plane is nearly parallel to the Pc core with a dihedral angle between the two central N_4 core planes of 4.76 (6)° but slightly glided along the N2—N2^{i} line of the isoindole unit, forming an eclipsed arrangement with an

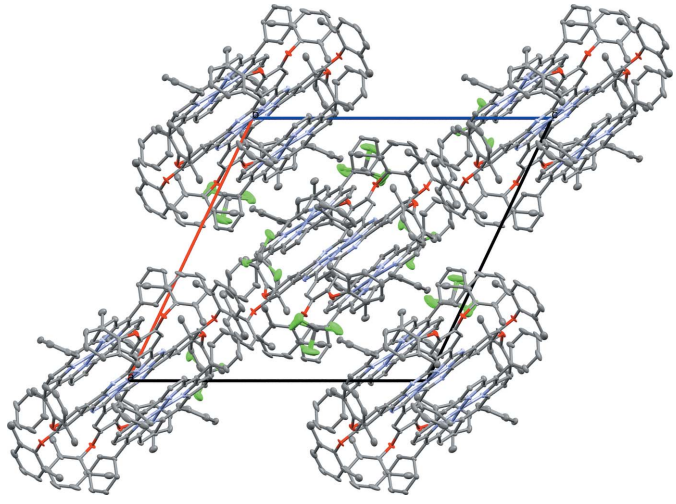

Figure 2
A view along the *b* axis of the crystal, showing the packing of the title compound.

$N3_{Pc}—Zn_{Pc}—Zn_{TPP}$ angle of 61.15 (4)°, and with a distance of 3.4967 (5) Å between adjacent metal sites. Each dimethylphenoxy group lies outside the macrocycle, which may prohibit the formation of columnar stacks of Pc by steric hindrance. The phenyl groups of TPP also lie outside the macrocycle and above the nitrogen atoms linked to the isoindole units of Pc. However, they fit into the crevice between two dimethylphenoxy groups of Pc. This particular side chain conformation could be responsible for the self-assembled supramolecular arrangement. The Zn(II) cation bound to TPP is displaced from the central N_4 core by 0.0475 (9) Å whereas that bound to Pc lies in the phthalocyanine macrocycle plane due to inversion symmetry. The two chloroform molecules are situated in the voids of the packed supramolecules (Fig. 2).

A structure survey using CSD web interface (Groom *et al.*, 2016) returned one entry of a phthalocyanine–TPP complex (CCDC entry 621715), and six compounds similar to the *Pc* moiety of the title compound that were further divided into two groups (CCDC entries 946716, 946717, 946718 and 279644, 761420, 76142, respectively). The phthalocyanine–TPP complex of CCDC 621715 is a (Mn–Cr) μ-hydroxido-bridged complex (Donzello *et al.*, 2006). Conversely, compounds in the first group, which are similar to Pc, differ from Pc only in the types of metal ions (Pr^{III}, Nd^{III} and Sm^{III}; Li *et al.*, 2014). Here, one metal ion is situated between two Pc planes, leading to shallow cone-shaped Pc and double-decker complexes. Compounds in the second group crystallized with cubic symmetry (space group $Pn\bar{3}n$) and comprise of isopropyl groups instead of methyl groups on each phenoxy group, forming a shallow cone shape. Moreover, the compound of CCDC 279644 of the second group has a water molecule as the fifth ligand of Zn^{II} in an axial position (McKeown *et al.*, 2005), and the remaining structures comprise of two macrocycles that are bound together by rigid bridging ligands (Bezzu *et al.*, 2010).

Synthesis and crystallization

n-Hexane (96%), chloroform ($CHCl_3$, 99.8%), zinc(II) chloride and ZnTPP were obtained from Sigma–Aldrich Japan (Tokyo, Japan). Other reagents were purchased from Tokyo Kasei Kogyo Co., Ltd (Tokyo, Japan). A dimethylformamide solution (10 ml) of 4,5-dichlorophthalonitrile (5 mmol), 2,6-dimethylphenol (15 mmol) and potassium carbonate (18 mmol) was prepared and stirred at 373 K for 16 h in a nitrogen atmosphere. After cooling down to room temperature, the solution was poured into 300 ml of water, and the precipitate was filtered off. The crude product was purified by normal-phase chromatography and recrystallized from ethyl acetate by vaporization to obtain 4,5-di(2,6-dimethylphenoxy)phthalonitrile (approximately 70% yield). Subsequently, a dimethylaminoethanol solution (22 ml) of 4,5-di(2,6-dimethylphenoxy)phthalonitrile (2.7 mmol) and zinc(II) chloride (1.4 mmol) was stirred at 413 K for 4 h. After cooling down to room temperature, the solution was evaporated under reduced pressure. The crude product was further purified by the same procedure used for synthesis of 4,5-di(2,6-dimethylphenoxy)phthalonitrile. The yield of ZnPc was approximately 25%. Both ZnPc and ZnTPP were dissolved in chloroform with a final concentration of 1 mg ml^{-1} and were mixed at equal volumes. Single crystals were grown by slow diffusion of *n*-hexane into a chloroform solution.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Zn(C_{96}H_{80}N_8O_8)]$-$[Zn(C_{44}H_{28}N_4)]_2{\cdot}4CHCl_3$
M_r	3372.66
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	20.216 (4), 21.275 (2), 20.8210 (17)
β (°)	115.414 (13)
V (Å^3)	8088 (2)
Z	2
Radiation type	Synchrotron, λ = 0.700 Å
μ (mm^{-1})	0.70
Crystal size (mm)	0.31 × 0.27 × 0.25
Data collection	
Diffractometer	SPring-8 BL26B1 CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	61759, 16900, 15721
R_{int}	0.022
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.634
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.095, 1.06
No. of reflections	16900
No. of parameters	1061
No. of restraints	42
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.70

Computer programs: *BSS* (Ueno *et al.*, 2005), *XDS* (Kabsch, 2010), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Two chloroform molecules are present in the asymmetric unit, with one of them being disordered. Disorder was modelled over two sets of sites with occupancies of 0.723 (16):0.277 (6) and restrained with the RIGU option in *SHELXL*. Additional electron density assignable to disordered (chloroform) molecules near an inversion centre was observed. For the final refinement, the contributions of the disordered solvent molecules were removed from the diffraction data using SQUEEZE in *PLATON* (Spek, 2015). SQUEEZE estimated the electron counts in each of the four voids (volume 316 Å^3) to be 118 electrons.

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full crystallographic data

IUCrData (2018). **3**, x181741 [https://doi.org/10.1107/S2414314618017418]

Construction of a supramolecule comprising [2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninato]zinc(II) and (5,10,15,20-tetraphenylporphyrinato)zinc(II)

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[2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninato]zinc(II) bis[(5,10,15,20-tetraphenylporphyrinato)zinc(II)] chloroform tetrasolvate

Crystal data

$[Zn(C_{96}H_{80}N_8O_8)][Zn(C_{44}H_{28}N_4)]_2\cdot 4CHCl_3$
M_r = 3372.66
Monoclinic, $P2_1/n$
a = 20.216 (4) Å
b = 21.275 (2) Å
c = 20.8210 (17) Å
β = 115.414 (13)°
V = 8088 (2) Å^3
Z = 2
$F(000)$ = 3476
D_x = 1.385 Mg m^{-3}
Synchrotron radiation, λ = 0.700 Å
Cell parameters from 54508 reflections
θ = 2.1–26.4°
μ = 0.70 mm^{-1}
T = 100 K
Block, dark red
0.31 × 0.27 × 0.25 mm

Data collection

SPring-8 BL26B1 CCD diffractometer
Radiation source: synchrotron
ω scan
61759 measured reflections
16900 independent reflections
15721 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 26.4°, θ_{min} = 2.1°
h = −25→25
k = −26→26
l = −26→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.095
S = 1.06
16900 reflections
1061 parameters
42 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 10.9858P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}
Extinction correction: SHELXL2018 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00138 (19)

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. Hydrogen atoms were placed at calculated positions and included in a riding-motion approximation with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zn1	0.500000	0.500000	0.500000	0.00998 (7)	
O1	0.68081 (7)	0.16815 (6)	0.54821 (7)	0.0157 (3)	
O2	0.74682 (7)	0.22143 (6)	0.48340 (8)	0.0164 (3)	
O3	0.73646 (8)	0.62773 (6)	0.30964 (8)	0.0203 (2)	
O4	0.67847 (8)	0.72992 (6)	0.32347 (8)	0.0188 (3)	
N1	0.55163 (8)	0.54354 (6)	0.45134 (8)	0.0085 (3)	
N2	0.61527 (8)	0.45604 (6)	0.42897 (8)	0.0089 (3)	
N3	0.53736 (8)	0.41834 (6)	0.48214 (8)	0.0093 (3)	
N4	0.51002 (8)	0.64975 (6)	0.45427 (8)	0.0095 (3)	
C1	0.60331 (11)	0.09610 (8)	0.57114 (11)	0.0172 (4)	
C2	0.56284 (12)	0.08463 (10)	0.49289 (11)	0.0244 (4)	
H2A	0.540602	0.123980	0.468848	0.037*	
H2B	0.524417	0.053258	0.484108	0.037*	
H2C	0.597008	0.069135	0.474458	0.037*	
C3	0.76046 (13)	0.20000 (11)	0.69371 (13)	0.0309 (5)	
H3A	0.741822	0.239805	0.668793	0.046*	
H3B	0.800853	0.185040	0.683575	0.046*	
H3C	0.778096	0.206456	0.745019	0.046*	
C4	0.86945 (13)	0.59944 (12)	0.42521 (13)	0.0323 (5)	
H4A	0.920790	0.588036	0.453843	0.048*	
H4B	0.841745	0.593857	0.453570	0.048*	
H4C	0.866528	0.643463	0.410361	0.048*	
C5	0.67099 (14)	0.56114 (13)	0.18184 (14)	0.0390 (6)	
H5A	0.631653	0.559114	0.197396	0.058*	
H5B	0.658949	0.533727	0.140494	0.058*	
H5C	0.676334	0.604492	0.168874	0.058*	
C6	0.60826 (10)	0.67840 (8)	0.37815 (10)	0.0124 (3)	
H6	0.585721	0.716366	0.382407	0.015*	
C7	0.53128 (9)	0.36277 (8)	0.51247 (9)	0.0089 (3)	
C8	0.54841 (9)	0.60672 (8)	0.43861 (9)	0.0090 (3)	
C9	0.59685 (9)	0.51641 (8)	0.42595 (9)	0.0088 (3)	
C10	0.62535 (9)	0.56540 (8)	0.39548 (9)	0.0101 (3)	
C11	0.59012 (9)	0.41191 (8)	0.45775 (9)	0.0091 (3)	
C12	0.63395 (11)	0.78305 (8)	0.30971 (11)	0.0180 (4)	
C13	0.61861 (9)	0.34791 (8)	0.47169 (9)	0.0093 (3)	
C14	0.59961 (9)	0.25684 (8)	0.53264 (9)	0.0105 (3)	
H14	0.574043	0.236517	0.555875	0.013*	

C15	0.83975 (14)	0.26771 (12)	0.37508 (15)	0.0356 (6)
H15	0.835282	0.262574	0.328061	0.043*
C16	0.67474 (9)	0.31761 (8)	0.46164 (9)	0.0112 (3)
H16	0.699665	0.337681	0.437624	0.013*
C17	0.69253 (9)	0.25743 (8)	0.48797 (10)	0.0120 (3)
C18	0.58185 (9)	0.31771 (8)	0.50616 (9)	0.0092 (3)
C19	0.68995 (10)	0.62091 (9)	0.34140 (10)	0.0147 (4)
C20	0.59341 (9)	0.62155 (8)	0.40222 (9)	0.0097 (3)
C21	0.56708 (12)	0.78316 (9)	0.24985 (11)	0.0203 (4)
C22	0.67449 (10)	0.56435 (8)	0.36482 (10)	0.0129 (3)
H22	0.696564	0.526253	0.360166	0.016*
C23	0.78749 (12)	0.24107 (10)	0.39372 (12)	0.0245 (4)
C24	0.79648 (10)	0.25088 (8)	0.46278 (11)	0.0173 (3)
C25	0.65682 (10)	0.67750 (8)	0.34796 (10)	0.0139 (3)
C26	0.90587 (13)	0.30882 (10)	0.49253 (17)	0.0372 (6)
H26	0.946792	0.331361	0.525804	0.045*
C27	0.68390 (13)	0.11697 (10)	0.71670 (11)	0.0247 (4)
H27	0.710898	0.123795	0.766323	0.030*
C28	0.65937 (10)	0.13984 (8)	0.59692 (10)	0.0141 (3)
C29	0.65563 (9)	0.22739 (8)	0.52379 (9)	0.0112 (3)
C30	0.77244 (11)	0.57341 (9)	0.30418 (12)	0.0203 (2)
C31	0.77862 (14)	0.48609 (11)	0.23673 (14)	0.0335 (5)
H31	0.759717	0.461847	0.194308	0.040*
C32	0.72481 (13)	0.20312 (11)	0.34278 (13)	0.0309 (5)
H32A	0.678728	0.224789	0.333155	0.046*
H32B	0.724829	0.161745	0.363474	0.046*
H32C	0.729739	0.197915	0.298265	0.046*
C33	0.89774 (14)	0.30136 (12)	0.42371 (18)	0.0421 (7)
H33	0.932464	0.319614	0.409785	0.051*
C34	0.55033 (13)	0.88975 (10)	0.27993 (13)	0.0284 (5)
H34	0.521064	0.926604	0.270046	0.034*
C35	0.53963 (13)	0.72610 (10)	0.20334 (12)	0.0256 (4)
H35A	0.580943	0.704365	0.200324	0.038*
H35B	0.504537	0.739002	0.155640	0.038*
H35C	0.515510	0.697723	0.223741	0.038*
C36	0.84235 (14)	0.46768 (11)	0.29304 (15)	0.0348 (6)
H36	0.866128	0.430156	0.289651	0.042*
C37	0.74147 (12)	0.53981 (10)	0.24115 (13)	0.0261 (5)
C38	0.87213 (12)	0.50315 (11)	0.35443 (14)	0.0296 (5)
H38	0.916418	0.490024	0.392724	0.035*
C39	0.58867 (12)	0.06231 (9)	0.62096 (12)	0.0232 (4)
H39	0.550478	0.031989	0.605277	0.028*
C40	0.73327 (14)	0.83225 (11)	0.41917 (13)	0.0300 (5)
H40A	0.743383	0.789081	0.437199	0.045*
H40B	0.731499	0.859864	0.456075	0.045*
H40C	0.772106	0.846429	0.406280	0.045*
C41	0.86128 (13)	0.29108 (12)	0.58786 (14)	0.0355 (6)
H41A	0.820210	0.316250	0.586777	0.053*

H41B	0.907476	0.312309	0.617272	0.053*
H41C	0.860521	0.249597	0.607994	0.053*
C42	0.83776 (11)	0.55809 (10)	0.36072 (12)	0.0217 (4)
C43	0.61742 (13)	0.88815 (9)	0.33805 (12)	0.0260 (5)
H43	0.634243	0.924406	0.367232	0.031*
C44	0.70021 (11)	0.15212 (9)	0.66883 (11)	0.0193 (4)
C45	0.52537 (12)	0.83797 (10)	0.23591 (13)	0.0256 (4)
H45	0.479232	0.839742	0.195670	0.031*
C46	0.62920 (14)	0.07252 (10)	0.69297 (12)	0.0269 (5)
H46	0.619181	0.048635	0.726332	0.032*
C47	0.66128 (12)	0.83436 (9)	0.35504 (11)	0.0215 (4)
C48	0.85460 (12)	0.28359 (9)	0.51394 (13)	0.0261 (5)
Zn2	0.39384 (2)	0.41679 (2)	0.34482 (2)	0.01065 (6)
N5	0.44485 (8)	0.46055 (7)	0.29229 (8)	0.0120 (3)
N6	0.33761 (8)	0.37279 (7)	0.39268 (8)	0.0115 (3)
N7	0.34715 (8)	0.50037 (7)	0.35269 (8)	0.0135 (3)
N8	0.43642 (8)	0.33343 (7)	0.33379 (8)	0.0111 (3)
C49	0.26457 (10)	0.57107 (9)	0.35957 (11)	0.0172 (4)
H49	0.227223	0.588622	0.370225	0.021*
C50	0.47186 (10)	0.22969 (8)	0.34670 (10)	0.0149 (4)
H50	0.475168	0.186451	0.359078	0.018*
C51	0.28889 (9)	0.39896 (8)	0.41481 (9)	0.0117 (3)
C52	0.49125 (10)	0.43348 (8)	0.26774 (10)	0.0137 (3)
C53	0.15067 (11)	0.54246 (9)	0.48395 (11)	0.0194 (4)
H53	0.156327	0.573853	0.518377	0.023*
C54	0.48444 (10)	0.53517 (9)	0.23714 (10)	0.0165 (4)
H54	0.491102	0.574653	0.219422	0.020*
C55	0.34195 (10)	0.31005 (8)	0.40990 (9)	0.0122 (3)
C56	0.29622 (10)	0.29738 (8)	0.44533 (10)	0.0147 (3)
H56	0.289853	0.257874	0.463193	0.018*
C57	0.39476 (10)	0.56733 (8)	0.28496 (10)	0.0135 (3)
C58	0.68766 (14)	0.35076 (12)	0.25550 (16)	0.0384 (6)
H58	0.736394	0.366345	0.277122	0.046*
C59	0.26398 (10)	0.35196 (8)	0.44858 (10)	0.0143 (3)
H59	0.230862	0.358131	0.469401	0.017*
C60	0.51101 (10)	0.37011 (8)	0.27394 (10)	0.0137 (3)
C61	0.43923 (10)	0.52288 (8)	0.27309 (10)	0.0132 (3)
C62	0.26551 (9)	0.46168 (8)	0.40480 (10)	0.0126 (3)
C63	0.51580 (10)	0.48024 (9)	0.23310 (10)	0.0165 (4)
H63	0.548093	0.473710	0.211409	0.020*
C64	0.38693 (10)	0.63029 (8)	0.25032 (10)	0.0147 (3)
C65	0.42708 (10)	0.27640 (8)	0.35929 (9)	0.0122 (3)
C66	0.50811 (10)	0.25898 (8)	0.31407 (10)	0.0160 (4)
H66	0.542175	0.240351	0.299504	0.019*
C67	0.29288 (10)	0.50837 (8)	0.37522 (10)	0.0136 (3)
C68	0.40533 (13)	0.17957 (10)	0.48381 (12)	0.0257 (5)
H68	0.431188	0.208723	0.520666	0.031*
C69	0.35181 (10)	0.55631 (8)	0.32160 (10)	0.0145 (3)

C70	0.38248 (10)	0.26475 (8)	0.39374 (9)	0.0122 (3)	
C71	0.20302 (10)	0.47882 (8)	0.42156 (10)	0.0129 (3)	
C72	0.54560 (13)	0.30721 (10)	0.19119 (12)	0.0260 (5)	
H72	0.496553	0.292531	0.168233	0.031*	
C73	0.30072 (10)	0.60051 (8)	0.32697 (11)	0.0171 (4)	
H73	0.293716	0.642736	0.310548	0.021*	
C74	0.13501 (10)	0.45010 (9)	0.38492 (10)	0.0159 (4)	
H74	0.129502	0.418036	0.351240	0.019*	
C75	0.56506 (11)	0.34988 (9)	0.24672 (11)	0.0187 (4)	
C76	0.37610 (10)	0.19836 (8)	0.41340 (11)	0.0159 (4)	
C77	0.33078 (14)	0.09330 (10)	0.37734 (17)	0.0365 (6)	
H77	0.305462	0.063780	0.340734	0.044*	
C78	0.35706 (11)	0.63429 (9)	0.17654 (11)	0.0194 (4)	
H78	0.344949	0.597001	0.148755	0.023*	
C79	0.63663 (12)	0.37220 (10)	0.27855 (13)	0.0259 (5)	
H79	0.650568	0.402068	0.315998	0.031*	
C80	0.36249 (12)	0.74687 (9)	0.18325 (12)	0.0244 (4)	
H80	0.353164	0.786629	0.160262	0.029*	
C81	0.07529 (10)	0.46782 (9)	0.39709 (11)	0.0187 (4)	
H81	0.029243	0.447887	0.371896	0.022*	
C82	0.33932 (12)	0.15473 (9)	0.36025 (13)	0.0248 (4)	
H82	0.319877	0.167179	0.311778	0.030*	
C83	0.48548 (10)	0.32396 (8)	0.30539 (10)	0.0128 (3)	
C84	0.34491 (12)	0.69239 (10)	0.14341 (11)	0.0248 (4)	
H84	0.324365	0.694744	0.093001	0.030*	
C85	0.08297 (11)	0.51469 (10)	0.44613 (11)	0.0209 (4)	
H85	0.041930	0.527678	0.453727	0.025*	
C86	0.59716 (17)	0.28581 (11)	0.16889 (15)	0.0382 (6)	
H86	0.583436	0.256409	0.131007	0.046*	
C87	0.35910 (16)	0.07514 (10)	0.44756 (18)	0.0419 (7)	
H87	0.352702	0.033195	0.459511	0.050*	
C88	0.66842 (16)	0.30727 (13)	0.20178 (17)	0.0443 (7)	
H88	0.704052	0.291984	0.187285	0.053*	
C89	0.40584 (10)	0.68551 (9)	0.29003 (10)	0.0165 (4)	
H89	0.427293	0.683405	0.340483	0.020*	
C90	0.39654 (16)	0.11762 (12)	0.50021 (15)	0.0388 (6)	
H90	0.416757	0.104602	0.548514	0.047*	
C91	0.21007 (10)	0.52464 (9)	0.47175 (10)	0.0164 (4)	
H91	0.256307	0.543946	0.497996	0.020*	
C92	0.39367 (11)	0.74352 (9)	0.25663 (11)	0.0206 (4)	
H92	0.406744	0.780952	0.284154	0.025*	
Cl4	0.94297 (4)	0.42044 (3)	0.74187 (4)	0.04808 (18)	
Cl5	1.05152 (3)	0.36172 (2)	0.70601 (3)	0.02959 (12)	
Cl6	1.09747 (5)	0.43513 (3)	0.83329 (4)	0.05050 (19)	
C94	1.03091 (15)	0.42686 (10)	0.74552 (13)	0.0305 (5)	
H94	1.032248	0.465264	0.718406	0.037*	
Cl1A	0.30848 (13)	0.45766 (13)	0.12147 (9)	0.0351 (6)	0.723 (16)
Cl2A	0.26359 (17)	0.47673 (18)	−0.02796 (16)	0.0601 (7)	0.723 (16)

Cl3A	0.3838 (2)	0.39087 (17)	0.0532 (3)	0.0748 (11)	0.723 (16)
Cl1B	0.3008 (6)	0.4644 (5)	0.1130 (7)	0.078 (3)	0.277 (16)
Cl2B	0.2766 (9)	0.4592 (8)	−0.0305 (5)	0.106 (4)	0.277 (16)
Cl3B	0.3892 (5)	0.3947 (5)	0.0654 (8)	0.082 (3)	0.277 (16)
C93	0.30061 (13)	0.42107 (10)	0.04345 (13)	0.0283 (5)	
H93	0.265180	0.385460	0.032888	0.034*	0.723 (16)
H93A	0.267542	0.383999	0.035255	0.034*	0.277 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01549 (14)	0.00335 (12)	0.01945 (15)	0.00120 (10)	0.01545 (12)	0.00138 (10)
O1	0.0217 (7)	0.0078 (6)	0.0249 (7)	0.0085 (5)	0.0169 (6)	0.0070 (5)
O2	0.0166 (6)	0.0091 (5)	0.0318 (7)	0.0071 (4)	0.0182 (5)	0.0042 (5)
O3	0.0258 (6)	0.0145 (5)	0.0367 (6)	0.0008 (4)	0.0286 (5)	0.0039 (4)
O4	0.0239 (7)	0.0097 (6)	0.0348 (8)	0.0000 (5)	0.0239 (6)	0.0064 (5)
N1	0.0097 (6)	0.0049 (6)	0.0148 (7)	0.0005 (5)	0.0090 (6)	0.0012 (5)
N2	0.0100 (6)	0.0066 (6)	0.0133 (7)	0.0007 (5)	0.0082 (6)	0.0007 (5)
N3	0.0118 (7)	0.0053 (6)	0.0148 (7)	0.0011 (5)	0.0096 (6)	0.0017 (5)
N4	0.0103 (6)	0.0057 (6)	0.0147 (7)	0.0013 (5)	0.0076 (6)	0.0017 (5)
C1	0.0247 (10)	0.0087 (8)	0.0223 (10)	0.0043 (7)	0.0141 (8)	0.0011 (7)
C2	0.0321 (11)	0.0184 (10)	0.0238 (11)	−0.0023 (8)	0.0130 (9)	−0.0026 (8)
C3	0.0290 (11)	0.0256 (11)	0.0291 (12)	−0.0014 (9)	0.0040 (9)	0.0000 (9)
C4	0.0314 (12)	0.0334 (12)	0.0349 (13)	−0.0038 (10)	0.0170 (10)	−0.0014 (10)
C5	0.0360 (13)	0.0460 (15)	0.0369 (14)	−0.0124 (11)	0.0174 (11)	−0.0031 (11)
C6	0.0158 (8)	0.0067 (7)	0.0195 (9)	0.0001 (6)	0.0121 (7)	0.0018 (6)
C7	0.0097 (7)	0.0064 (7)	0.0119 (8)	0.0009 (6)	0.0058 (6)	0.0010 (6)
C8	0.0095 (7)	0.0065 (7)	0.0126 (8)	−0.0001 (6)	0.0064 (6)	0.0018 (6)
C9	0.0091 (7)	0.0080 (7)	0.0128 (8)	0.0007 (6)	0.0081 (6)	0.0015 (6)
C10	0.0112 (8)	0.0079 (7)	0.0138 (8)	−0.0001 (6)	0.0078 (7)	0.0016 (6)
C11	0.0095 (7)	0.0079 (8)	0.0120 (8)	0.0009 (6)	0.0065 (6)	−0.0002 (6)
C12	0.0267 (10)	0.0103 (8)	0.0288 (10)	0.0010 (7)	0.0232 (9)	0.0073 (7)
C13	0.0108 (8)	0.0065 (7)	0.0118 (8)	0.0010 (6)	0.0061 (6)	0.0005 (6)
C14	0.0132 (8)	0.0066 (7)	0.0152 (8)	0.0013 (6)	0.0094 (7)	0.0015 (6)
C15	0.0375 (13)	0.0341 (13)	0.0553 (16)	0.0186 (10)	0.0391 (13)	0.0178 (11)
C16	0.0125 (8)	0.0085 (8)	0.0170 (8)	0.0010 (6)	0.0104 (7)	0.0007 (6)
C17	0.0110 (8)	0.0090 (8)	0.0183 (9)	0.0038 (6)	0.0086 (7)	−0.0004 (6)
C18	0.0094 (7)	0.0074 (7)	0.0132 (8)	0.0003 (6)	0.0072 (6)	−0.0009 (6)
C19	0.0165 (9)	0.0146 (9)	0.0212 (9)	−0.0005 (7)	0.0159 (8)	0.0021 (7)
C20	0.0102 (7)	0.0083 (8)	0.0138 (8)	0.0004 (6)	0.0082 (7)	0.0012 (6)
C21	0.0288 (10)	0.0137 (9)	0.0287 (11)	−0.0027 (8)	0.0222 (9)	0.0059 (8)
C22	0.0140 (8)	0.0093 (8)	0.0213 (9)	0.0014 (6)	0.0131 (7)	0.0010 (7)
C23	0.0257 (10)	0.0211 (10)	0.0373 (12)	0.0134 (8)	0.0235 (10)	0.0084 (9)
C24	0.0161 (7)	0.0095 (7)	0.0344 (8)	0.0077 (6)	0.0184 (6)	0.0051 (6)
C25	0.0165 (8)	0.0089 (8)	0.0210 (9)	−0.0010 (6)	0.0126 (7)	0.0037 (7)
C26	0.0212 (11)	0.0167 (10)	0.082 (2)	0.0026 (8)	0.0299 (12)	−0.0019 (11)
C27	0.0370 (12)	0.0200 (10)	0.0163 (10)	0.0110 (9)	0.0106 (9)	0.0045 (8)
C28	0.0203 (9)	0.0072 (8)	0.0192 (9)	0.0082 (6)	0.0127 (7)	0.0053 (6)

C29	0.0138 (8)	0.0048 (7)	0.0153 (8)	0.0017 (6)	0.0066 (7)	0.0012 (6)
C30	0.0257 (6)	0.0145 (5)	0.0366 (7)	0.0008 (4)	0.0286 (5)	0.0039 (5)
C31	0.0445 (14)	0.0272 (11)	0.0459 (14)	−0.0101 (10)	0.0357 (12)	−0.0128 (10)
C32	0.0334 (12)	0.0341 (12)	0.0307 (12)	0.0112 (10)	0.0188 (10)	0.0034 (9)
C33	0.0358 (13)	0.0283 (12)	0.088 (2)	0.0104 (10)	0.0504 (15)	0.0155 (13)
C34	0.0428 (13)	0.0123 (9)	0.0447 (14)	0.0059 (9)	0.0325 (11)	0.0113 (9)
C35	0.0309 (11)	0.0198 (10)	0.0306 (11)	−0.0035 (8)	0.0175 (10)	0.0030 (8)
C36	0.0459 (14)	0.0204 (10)	0.0625 (17)	0.0034 (10)	0.0466 (14)	−0.0032 (10)
C37	0.0299 (11)	0.0247 (10)	0.0360 (12)	−0.0083 (9)	0.0259 (10)	−0.0031 (9)
C38	0.0234 (11)	0.0288 (11)	0.0488 (14)	0.0056 (9)	0.0272 (11)	0.0070 (10)
C39	0.0336 (11)	0.0115 (9)	0.0320 (11)	−0.0013 (8)	0.0211 (10)	0.0016 (8)
C40	0.0396 (13)	0.0257 (11)	0.0302 (12)	−0.0049 (9)	0.0201 (10)	−0.0001 (9)
C41	0.0244 (11)	0.0313 (12)	0.0460 (15)	0.0024 (9)	0.0105 (10)	−0.0116 (11)
C42	0.0230 (10)	0.0198 (10)	0.0337 (11)	−0.0026 (8)	0.0229 (9)	0.0006 (8)
C43	0.0449 (13)	0.0118 (9)	0.0348 (12)	−0.0024 (8)	0.0299 (11)	0.0023 (8)
C44	0.0219 (10)	0.0135 (9)	0.0207 (10)	0.0072 (7)	0.0075 (8)	0.0020 (7)
C45	0.0279 (11)	0.0186 (10)	0.0362 (12)	0.0015 (8)	0.0193 (10)	0.0127 (9)
C46	0.0462 (13)	0.0167 (9)	0.0275 (11)	0.0074 (9)	0.0250 (10)	0.0090 (8)
C47	0.0341 (11)	0.0141 (9)	0.0276 (11)	−0.0033 (8)	0.0239 (9)	0.0040 (8)
C48	0.0210 (10)	0.0138 (9)	0.0480 (14)	0.0062 (8)	0.0193 (10)	0.0003 (9)
Zn2	0.01339 (10)	0.00573 (10)	0.01621 (11)	0.00043 (7)	0.00956 (8)	−0.00065 (7)
N5	0.0139 (7)	0.0077 (7)	0.0171 (7)	0.0003 (5)	0.0092 (6)	0.0001 (5)
N6	0.0127 (7)	0.0087 (7)	0.0159 (7)	0.0002 (5)	0.0087 (6)	−0.0010 (5)
N7	0.0161 (7)	0.0081 (7)	0.0195 (8)	0.0017 (5)	0.0106 (6)	0.0005 (6)
N8	0.0131 (7)	0.0069 (7)	0.0158 (7)	0.0000 (5)	0.0086 (6)	−0.0011 (5)
C49	0.0180 (9)	0.0118 (8)	0.0252 (10)	0.0044 (7)	0.0125 (8)	0.0000 (7)
C50	0.0179 (9)	0.0088 (8)	0.0201 (9)	0.0023 (7)	0.0101 (7)	−0.0010 (7)
C51	0.0116 (8)	0.0108 (8)	0.0134 (8)	−0.0007 (6)	0.0059 (7)	−0.0023 (6)
C52	0.0139 (8)	0.0120 (8)	0.0171 (9)	−0.0010 (6)	0.0084 (7)	−0.0016 (7)
C53	0.0210 (9)	0.0155 (9)	0.0256 (10)	0.0025 (7)	0.0136 (8)	−0.0045 (7)
C54	0.0195 (9)	0.0105 (8)	0.0223 (10)	−0.0030 (7)	0.0116 (8)	0.0013 (7)
C55	0.0126 (8)	0.0097 (8)	0.0146 (8)	−0.0011 (6)	0.0061 (7)	−0.0010 (6)
C56	0.0163 (8)	0.0112 (8)	0.0189 (9)	−0.0011 (7)	0.0097 (7)	0.0004 (7)
C57	0.0161 (8)	0.0080 (8)	0.0156 (9)	−0.0011 (6)	0.0062 (7)	0.0001 (6)
C58	0.0269 (12)	0.0345 (13)	0.0681 (18)	0.0104 (10)	0.0338 (13)	0.0236 (12)
C59	0.0140 (8)	0.0137 (8)	0.0185 (9)	−0.0008 (7)	0.0101 (7)	−0.0010 (7)
C60	0.0130 (8)	0.0129 (8)	0.0177 (9)	−0.0001 (6)	0.0090 (7)	−0.0024 (7)
C61	0.0153 (8)	0.0095 (8)	0.0151 (9)	−0.0018 (6)	0.0068 (7)	−0.0005 (6)
C62	0.0115 (8)	0.0104 (8)	0.0168 (9)	0.0004 (6)	0.0069 (7)	−0.0026 (6)
C63	0.0180 (9)	0.0154 (9)	0.0213 (9)	−0.0020 (7)	0.0133 (8)	0.0003 (7)
C64	0.0133 (8)	0.0111 (8)	0.0208 (9)	0.0019 (6)	0.0084 (7)	0.0038 (7)
C65	0.0134 (8)	0.0080 (8)	0.0152 (8)	−0.0003 (6)	0.0061 (7)	−0.0016 (6)
C66	0.0185 (9)	0.0112 (8)	0.0220 (9)	0.0021 (7)	0.0122 (8)	−0.0014 (7)
C67	0.0134 (8)	0.0114 (8)	0.0178 (9)	0.0020 (6)	0.0083 (7)	−0.0013 (7)
C68	0.0344 (12)	0.0222 (10)	0.0310 (11)	0.0125 (9)	0.0241 (10)	0.0088 (9)
C69	0.0171 (9)	0.0092 (8)	0.0177 (9)	0.0012 (7)	0.0081 (7)	−0.0001 (7)
C70	0.0139 (8)	0.0078 (8)	0.0152 (8)	−0.0005 (6)	0.0065 (7)	−0.0003 (6)
C71	0.0127 (8)	0.0100 (8)	0.0184 (9)	0.0016 (6)	0.0090 (7)	0.0015 (7)

C72	0.0362 (12)	0.0181 (10)	0.0353 (12)	0.0033 (8)	0.0265 (10)	0.0003 (8)
C73	0.0197 (9)	0.0088 (8)	0.0245 (10)	0.0038 (7)	0.0110 (8)	0.0022 (7)
C74	0.0167 (9)	0.0133 (8)	0.0190 (9)	0.0004 (7)	0.0089 (7)	−0.0011 (7)
C75	0.0223 (9)	0.0128 (8)	0.0298 (11)	0.0042 (7)	0.0197 (9)	0.0048 (7)
C76	0.0185 (9)	0.0091 (8)	0.0277 (10)	0.0045 (7)	0.0172 (8)	0.0036 (7)
C77	0.0346 (13)	0.0110 (10)	0.0717 (19)	−0.0015 (9)	0.0304 (13)	−0.0027 (10)
C78	0.0205 (9)	0.0157 (9)	0.0219 (10)	−0.0017 (7)	0.0089 (8)	0.0016 (7)
C79	0.0218 (10)	0.0203 (10)	0.0404 (13)	0.0041 (8)	0.0179 (9)	0.0105 (9)
C80	0.0244 (10)	0.0138 (9)	0.0324 (12)	0.0003 (8)	0.0099 (9)	0.0119 (8)
C81	0.0132 (9)	0.0202 (9)	0.0241 (10)	−0.0005 (7)	0.0094 (8)	0.0005 (8)
C82	0.0250 (10)	0.0131 (9)	0.0382 (12)	0.0004 (8)	0.0153 (9)	−0.0019 (8)
C83	0.0127 (8)	0.0110 (8)	0.0168 (9)	0.0001 (6)	0.0083 (7)	−0.0034 (6)
C84	0.0258 (11)	0.0248 (11)	0.0194 (10)	−0.0016 (8)	0.0056 (8)	0.0075 (8)
C85	0.0161 (9)	0.0217 (10)	0.0305 (11)	0.0036 (7)	0.0153 (8)	−0.0003 (8)
C86	0.0651 (18)	0.0256 (12)	0.0484 (15)	0.0146 (11)	0.0476 (15)	0.0081 (10)
C87	0.0523 (16)	0.0116 (10)	0.086 (2)	0.0099 (10)	0.0528 (16)	0.0161 (12)
C88	0.0531 (16)	0.0394 (14)	0.0713 (19)	0.0250 (12)	0.0560 (16)	0.0260 (14)
C89	0.0174 (9)	0.0123 (8)	0.0204 (9)	0.0025 (7)	0.0086 (7)	0.0023 (7)
C90	0.0547 (16)	0.0332 (13)	0.0514 (16)	0.0240 (12)	0.0444 (14)	0.0260 (12)
C91	0.0139 (8)	0.0136 (8)	0.0229 (10)	0.0003 (7)	0.0089 (7)	−0.0021 (7)
C92	0.0197 (9)	0.0106 (8)	0.0306 (11)	0.0013 (7)	0.0097 (8)	0.0023 (8)
Cl4	0.0584 (4)	0.0354 (3)	0.0707 (5)	0.0144 (3)	0.0470 (4)	0.0157 (3)
Cl5	0.0397 (3)	0.0218 (2)	0.0354 (3)	−0.0050 (2)	0.0238 (2)	−0.0027 (2)
Cl6	0.0830 (5)	0.0337 (3)	0.0291 (3)	−0.0021 (3)	0.0187 (3)	−0.0034 (2)
C94	0.0502 (14)	0.0162 (10)	0.0321 (12)	−0.0002 (9)	0.0243 (11)	0.0047 (8)
Cl1A	0.0421 (9)	0.0356 (9)	0.0267 (11)	−0.0191 (6)	0.0139 (8)	−0.0112 (6)
Cl2A	0.0692 (10)	0.0636 (14)	0.0447 (9)	−0.0085 (10)	0.0218 (9)	0.0216 (8)
Cl3A	0.0617 (17)	0.0321 (10)	0.170 (3)	−0.0161 (9)	0.087 (2)	−0.0255 (12)
Cl1B	0.094 (5)	0.038 (3)	0.143 (7)	−0.017 (3)	0.091 (5)	−0.043 (4)
Cl2B	0.133 (7)	0.076 (6)	0.043 (3)	−0.055 (5)	−0.027 (3)	0.025 (3)
Cl3B	0.029 (3)	0.060 (4)	0.149 (6)	0.000 (2)	0.029 (3)	−0.044 (3)
C93	0.0300 (11)	0.0226 (10)	0.0375 (13)	−0.0135 (9)	0.0196 (10)	−0.0088 (9)

Geometric parameters (Å, º)

Zn1—N1^{i}	1.9700 (14)	C43—H43	0.9500
Zn1—N1	1.9700 (14)	C43—C47	1.397 (3)
Zn1—N3	1.9920 (14)	C45—H45	0.9500
Zn1—N3^{i}	1.9919 (14)	C46—H46	0.9500
O1—C28	1.399 (2)	Zn2—N5	2.0234 (15)
O1—C29	1.372 (2)	Zn2—N6	2.0332 (15)
O2—C17	1.375 (2)	Zn2—N7	2.0524 (15)
O2—C24	1.398 (2)	Zn2—N8	2.0269 (14)
O3—C19	1.370 (2)	N5—C52	1.373 (2)
O3—C30	1.396 (2)	N5—C61	1.376 (2)
O4—C12	1.396 (2)	N6—C51	1.372 (2)
O4—C25	1.374 (2)	N6—C55	1.375 (2)
N1—C8	1.366 (2)	N7—C67	1.376 (2)

N1—C9	1.365 (2)	N7—C69	1.377 (2)
N2—C9	1.331 (2)	N8—C65	1.370 (2)
N2—C11	1.327 (2)	N8—C83	1.370 (2)
N3—C7	1.370 (2)	C49—H49	0.9500
N3—C11	1.371 (2)	C49—C67	1.433 (2)
N4—C7^{i}	1.321 (2)	C49—C73	1.346 (3)
N4—C8	1.328 (2)	C50—H50	0.9500
C1—C2	1.496 (3)	C50—C65	1.442 (2)
C1—C28	1.384 (3)	C50—C66	1.347 (3)
C1—C39	1.394 (3)	C51—C59	1.432 (2)
C2—H2A	0.9800	C51—C62	1.401 (2)
C2—H2B	0.9800	C52—C60	1.396 (2)
C2—H2C	0.9800	C52—C63	1.436 (2)
C3—H3A	0.9800	C53—H53	0.9500
C3—H3B	0.9800	C53—C85	1.385 (3)
C3—H3C	0.9800	C53—C91	1.383 (3)
C3—C44	1.499 (3)	C54—H54	0.9500
C4—H4A	0.9800	C54—C61	1.432 (3)
C4—H4B	0.9800	C54—C63	1.349 (3)
C4—H4C	0.9800	C55—C56	1.434 (2)
C4—C42	1.500 (3)	C55—C70	1.396 (2)
C5—H5A	0.9800	C56—H56	0.9500
C5—H5B	0.9800	C56—C59	1.347 (3)
C5—H5C	0.9800	C57—C61	1.398 (3)
C5—C37	1.500 (4)	C57—C64	1.497 (2)
C6—H6	0.9500	C57—C69	1.400 (3)
C6—C20	1.390 (2)	C58—H58	0.9500
C6—C25	1.374 (2)	C58—C79	1.388 (3)
C7—C18	1.448 (2)	C58—C88	1.373 (4)
C8—C20	1.447 (2)	C59—H59	0.9500
C9—C10	1.461 (2)	C60—C75	1.494 (2)
C10—C20	1.393 (2)	C60—C83	1.396 (3)
C10—C22	1.393 (2)	C62—C67	1.402 (3)
C11—C13	1.458 (2)	C62—C71	1.493 (2)
C12—C21	1.391 (3)	C63—H63	0.9500
C12—C47	1.393 (3)	C64—C78	1.391 (3)
C13—C16	1.397 (2)	C64—C89	1.392 (3)
C13—C18	1.392 (2)	C65—C70	1.394 (2)
C14—H14	0.9500	C66—H66	0.9500
C14—C18	1.393 (2)	C66—C83	1.443 (2)
C14—C29	1.374 (2)	C68—H68	0.9500
C15—H15	0.9500	C68—C76	1.384 (3)
C15—C23	1.393 (3)	C68—C90	1.392 (3)
C15—C33	1.376 (4)	C69—C73	1.436 (2)
C16—H16	0.9500	C70—C76	1.492 (2)
C16—C17	1.378 (2)	C71—C74	1.395 (3)
C17—C29	1.414 (2)	C71—C91	1.391 (3)
C19—C22	1.383 (2)	C72—H72	0.9500

C19—C25	1.413 (2)	C72—C75	1.388 (3)
C21—C35	1.503 (3)	C72—C86	1.387 (3)
C21—C45	1.395 (3)	C73—H73	0.9500
C22—H22	0.9500	C74—H74	0.9500
C23—C24	1.385 (3)	C74—C81	1.388 (3)
C23—C32	1.493 (3)	C75—C79	1.391 (3)
C24—C48	1.387 (3)	C76—C82	1.390 (3)
C26—H26	0.9500	C77—H77	0.9500
C26—C33	1.380 (4)	C77—C82	1.385 (3)
C26—C48	1.399 (3)	C77—C87	1.377 (4)
C27—H27	0.9500	C78—H78	0.9500
C27—C44	1.394 (3)	C78—C84	1.385 (3)
C27—C46	1.376 (3)	C79—H79	0.9500
C28—C44	1.389 (3)	C80—H80	0.9500
C30—C37	1.386 (3)	C80—C84	1.380 (3)
C30—C42	1.379 (3)	C80—C92	1.382 (3)
C31—H31	0.9500	C81—H81	0.9500
C31—C36	1.375 (4)	C81—C85	1.387 (3)
C31—C37	1.392 (3)	C82—H82	0.9500
C32—H32A	0.9800	C84—H84	0.9500
C32—H32B	0.9800	C85—H85	0.9500
C32—H32C	0.9800	C86—H86	0.9500
C33—H33	0.9500	C86—C88	1.381 (4)
C34—H34	0.9500	C87—H87	0.9500
C34—C43	1.377 (4)	C87—C90	1.371 (4)
C34—C45	1.383 (3)	C88—H88	0.9500
C35—H35A	0.9800	C89—H89	0.9500
C35—H35B	0.9800	C89—C92	1.386 (3)
C35—H35C	0.9800	C90—H90	0.9500
C36—H36	0.9500	C91—H91	0.9500
C36—C38	1.380 (4)	C92—H92	0.9500
C38—H38	0.9500	Cl4—C94	1.752 (3)
C38—C42	1.394 (3)	Cl5—C94	1.751 (2)
C39—H39	0.9500	Cl6—C94	1.752 (3)
C39—C46	1.383 (3)	C94—H94	1.0000
C40—H40A	0.9800	Cl1A—C93	1.746 (3)
C40—H40B	0.9800	Cl2A—C93	1.794 (4)
C40—H40C	0.9800	Cl3A—C93	1.729 (4)
C40—C47	1.495 (3)	Cl1B—C93	1.715 (8)
C41—H41A	0.9800	Cl2B—C93	1.621 (9)
C41—H41B	0.9800	Cl3B—C93	1.741 (9)
C41—H41C	0.9800	C93—H93	1.0000
C41—C48	1.495 (4)	C93—H93A	1.0000

N1^{i}—Zn1—N1	180.0	C27—C46—C39	120.55 (19)
N1—Zn1—N3	89.26 (6)	C27—C46—H46	119.7
N1^{i}—Zn1—N3	90.74 (6)	C39—C46—H46	119.7
N1^{i}—Zn1—N3^{i}	89.26 (6)	C12—C47—C40	122.19 (19)

N1—Zn1—N3^{i}	90.74 (6)	C12—C47—C43	116.5 (2)
N3^{i}—Zn1—N3	180.0	C43—C47—C40	121.3 (2)
C29—O1—C28	118.87 (13)	C24—C48—C26	116.5 (2)
C17—O2—C24	118.13 (13)	C24—C48—C41	121.1 (2)
C19—O3—C30	116.18 (14)	C26—C48—C41	122.4 (2)
C25—O4—C12	116.97 (14)	N5—Zn2—N6	176.94 (6)
C8—N1—Zn1	124.80 (11)	N5—Zn2—N7	90.18 (6)
C9—N1—Zn1	126.24 (11)	N5—Zn2—N8	90.09 (6)
C9—N1—C8	108.95 (13)	N6—Zn2—N7	89.24 (6)
C11—N2—C9	123.40 (14)	N8—Zn2—N6	90.38 (6)
C7—N3—Zn1	123.38 (11)	N8—Zn2—N7	177.84 (6)
C7—N3—C11	108.81 (13)	C52—N5—Zn2	126.62 (12)
C11—N3—Zn1	125.02 (11)	C52—N5—C61	106.29 (15)
C7^{i}—N4—C8	123.87 (15)	C61—N5—Zn2	127.09 (12)
C28—C1—C2	120.39 (17)	C51—N6—Zn2	127.64 (12)
C28—C1—C39	117.26 (19)	C51—N6—C55	106.32 (14)
C39—C1—C2	122.31 (19)	C55—N6—Zn2	126.03 (12)
C1—C2—H2A	109.5	C67—N7—Zn2	126.55 (12)
C1—C2—H2B	109.5	C67—N7—C69	106.18 (14)
C1—C2—H2C	109.5	C69—N7—Zn2	125.77 (12)
H2A—C2—H2B	109.5	C65—N8—Zn2	126.53 (12)
H2A—C2—H2C	109.5	C65—N8—C83	106.42 (14)
H2B—C2—H2C	109.5	C83—N8—Zn2	126.79 (12)
H3A—C3—H3B	109.5	C67—C49—H49	126.3
H3A—C3—H3C	109.5	C73—C49—H49	126.3
H3B—C3—H3C	109.5	C73—C49—C67	107.31 (16)
C44—C3—H3A	109.5	C65—C50—H50	126.5
C44—C3—H3B	109.5	C66—C50—H50	126.5
C44—C3—H3C	109.5	C66—C50—C65	107.03 (16)
H4A—C4—H4B	109.5	N6—C51—C59	109.63 (15)
H4A—C4—H4C	109.5	N6—C51—C62	125.55 (16)
H4B—C4—H4C	109.5	C62—C51—C59	124.80 (16)
C42—C4—H4A	109.5	N5—C52—C60	125.79 (16)
C42—C4—H4B	109.5	N5—C52—C63	109.57 (15)
C42—C4—H4C	109.5	C60—C52—C63	124.63 (17)
H5A—C5—H5B	109.5	C85—C53—H53	119.9
H5A—C5—H5C	109.5	C91—C53—H53	119.9
H5B—C5—H5C	109.5	C91—C53—C85	120.19 (18)
C37—C5—H5A	109.5	C61—C54—H54	126.4
C37—C5—H5B	109.5	C63—C54—H54	126.4
C37—C5—H5C	109.5	C63—C54—C61	107.26 (16)
C20—C6—H6	121.3	N6—C55—C56	109.48 (15)
C25—C6—H6	121.3	N6—C55—C70	125.84 (16)
C25—C6—C20	117.37 (16)	C70—C55—C56	124.66 (16)
N3—C7—C18	108.84 (14)	C55—C56—H56	126.4
N4^{i}—C7—N3	128.13 (15)	C59—C56—C55	107.24 (16)
N4^{i}—C7—C18	122.95 (15)	C59—C56—H56	126.4
N1—C8—C20	109.14 (14)	C61—C57—C64	117.59 (16)

N4—C8—N1	127.93 (15)	C61—C57—C69	125.41 (16)
N4—C8—C20	122.91 (15)	C69—C57—C64	116.77 (16)
N1—C9—C10	108.73 (14)	C79—C58—H58	119.7
N2—C9—N1	127.57 (15)	C88—C58—H58	119.7
N2—C9—C10	123.67 (15)	C88—C58—C79	120.7 (2)
C20—C10—C9	106.37 (14)	C51—C59—H59	126.3
C22—C10—C9	132.80 (16)	C56—C59—C51	107.30 (16)
C22—C10—C20	120.83 (15)	C56—C59—H59	126.3
N2—C11—N3	127.34 (15)	C52—C60—C75	118.03 (16)
N2—C11—C13	123.74 (15)	C83—C60—C52	125.01 (16)
N3—C11—C13	108.85 (14)	C83—C60—C75	116.94 (16)
C21—C12—O4	118.59 (18)	N5—C61—C54	109.66 (15)
C21—C12—C47	123.79 (18)	N5—C61—C57	125.44 (16)
C47—C12—O4	117.53 (19)	C57—C61—C54	124.88 (16)
C16—C13—C11	132.69 (15)	C51—C62—C67	124.67 (16)
C18—C13—C11	106.32 (14)	C51—C62—C71	117.58 (16)
C18—C13—C16	120.79 (15)	C67—C62—C71	117.57 (15)
C18—C14—H14	121.4	C52—C63—H63	126.4
C29—C14—H14	121.4	C54—C63—C52	107.20 (16)
C29—C14—C18	117.25 (15)	C54—C63—H63	126.4
C23—C15—H15	119.5	C78—C64—C57	119.53 (17)
C33—C15—H15	119.5	C78—C64—C89	118.85 (17)
C33—C15—C23	121.0 (2)	C89—C64—C57	121.56 (17)
C13—C16—H16	121.3	N8—C65—C50	109.77 (15)
C17—C16—C13	117.34 (15)	N8—C65—C70	125.74 (16)
C17—C16—H16	121.3	C70—C65—C50	124.48 (16)
O2—C17—C16	124.74 (16)	C50—C66—H66	126.4
O2—C17—C29	113.73 (15)	C50—C66—C83	107.13 (16)
C16—C17—C29	121.53 (15)	C83—C66—H66	126.4
C13—C18—C7	107.16 (14)	N7—C67—C49	109.67 (16)
C13—C18—C14	121.97 (15)	N7—C67—C62	125.79 (16)
C14—C18—C7	130.67 (15)	C62—C67—C49	124.42 (16)
O3—C19—C22	124.61 (16)	C76—C68—H68	120.3
O3—C19—C25	114.11 (15)	C76—C68—C90	119.5 (2)
C22—C19—C25	121.27 (16)	C90—C68—H68	120.3
C6—C20—C8	131.30 (16)	N7—C69—C57	125.77 (16)
C6—C20—C10	121.91 (15)	N7—C69—C73	109.43 (16)
C10—C20—C8	106.77 (14)	C57—C69—C73	124.60 (17)
C12—C21—C35	121.60 (18)	C55—C70—C76	117.30 (16)
C12—C21—C45	117.15 (19)	C65—C70—C55	125.25 (16)
C45—C21—C35	121.2 (2)	C65—C70—C76	117.43 (15)
C10—C22—H22	121.3	C74—C71—C62	119.97 (16)
C19—C22—C10	117.46 (16)	C91—C71—C62	121.50 (16)
C19—C22—H22	121.3	C91—C71—C74	118.50 (16)
C15—C23—C32	122.4 (2)	C75—C72—H72	119.7
C24—C23—C15	116.8 (2)	C86—C72—H72	119.7
C24—C23—C32	120.81 (19)	C86—C72—C75	120.6 (2)
C23—C24—O2	117.35 (18)	C49—C73—C69	107.38 (16)

C23—C24—C48	124.27 (19)	C49—C73—H73	126.3
C48—C24—O2	118.17 (18)	C69—C73—H73	126.3
O4—C25—C6	124.22 (16)	C71—C74—H74	119.6
O4—C25—C19	114.60 (15)	C81—C74—C71	120.77 (18)
C6—C25—C19	121.17 (16)	C81—C74—H74	119.6
C33—C26—H26	119.6	C72—C75—C60	120.85 (18)
C33—C26—C48	120.8 (2)	C72—C75—C79	119.02 (19)
C48—C26—H26	119.6	C79—C75—C60	120.10 (19)
C44—C27—H27	119.6	C68—C76—C70	121.09 (18)
C46—C27—H27	119.6	C68—C76—C82	119.34 (19)
C46—C27—C44	120.8 (2)	C82—C76—C70	119.57 (18)
C1—C28—O1	117.72 (17)	C82—C77—H77	120.1
C1—C28—C44	123.59 (17)	C87—C77—H77	120.1
C44—C28—O1	118.34 (17)	C87—C77—C82	119.8 (2)
O1—C29—C14	124.40 (16)	C64—C78—H78	119.8
O1—C29—C17	114.49 (15)	C84—C78—C64	120.31 (19)
C14—C29—C17	121.10 (15)	C84—C78—H78	119.8
C37—C30—O3	117.7 (2)	C58—C79—C75	119.9 (2)
C42—C30—O3	117.88 (19)	C58—C79—H79	120.1
C42—C30—C37	124.37 (19)	C75—C79—H79	120.1
C36—C31—H31	119.6	C84—C80—H80	120.0
C36—C31—C37	120.8 (2)	C84—C80—C92	119.91 (18)
C37—C31—H31	119.6	C92—C80—H80	120.0
C23—C32—H32A	109.5	C74—C81—H81	120.1
C23—C32—H32B	109.5	C85—C81—C74	119.88 (18)
C23—C32—H32C	109.5	C85—C81—H81	120.1
H32A—C32—H32B	109.5	C76—C82—H82	119.7
H32A—C32—H32C	109.5	C77—C82—C76	120.6 (2)
H32B—C32—H32C	109.5	C77—C82—H82	119.7
C15—C33—C26	120.6 (2)	N8—C83—C60	125.50 (16)
C15—C33—H33	119.7	N8—C83—C66	109.64 (15)
C26—C33—H33	119.7	C60—C83—C66	124.85 (16)
C43—C34—H34	119.9	C78—C84—H84	119.8
C43—C34—C45	120.3 (2)	C80—C84—C78	120.3 (2)
C45—C34—H34	119.9	C80—C84—H84	119.8
C21—C35—H35A	109.5	C53—C85—C81	119.76 (17)
C21—C35—H35B	109.5	C53—C85—H85	120.1
C21—C35—H35C	109.5	C81—C85—H85	120.1
H35A—C35—H35B	109.5	C72—C86—H86	120.0
H35A—C35—H35C	109.5	C88—C86—C72	120.0 (3)
H35B—C35—H35C	109.5	C88—C86—H86	120.0
C31—C36—H36	119.7	C77—C87—H87	120.0
C31—C36—C38	120.7 (2)	C90—C87—C77	120.0 (2)
C38—C36—H36	119.7	C90—C87—H87	120.0
C30—C37—C5	120.5 (2)	C58—C88—C86	119.8 (2)
C30—C37—C31	116.7 (2)	C58—C88—H88	120.1
C31—C37—C5	122.9 (2)	C86—C88—H88	120.1
C36—C38—H38	119.7	C64—C89—H89	119.7

C36—C38—C42	120.6 (2)	C92—C89—C64	120.60 (18)
C42—C38—H38	119.7	C92—C89—H89	119.7
C1—C39—H39	119.7	C68—C90—H90	119.6
C46—C39—C1	120.6 (2)	C87—C90—C68	120.9 (2)
C46—C39—H39	119.7	C87—C90—H90	119.6
H40A—C40—H40B	109.5	C53—C91—C71	120.87 (18)
H40A—C40—H40C	109.5	C53—C91—H91	119.6
H40B—C40—H40C	109.5	C71—C91—H91	119.6
C47—C40—H40A	109.5	C80—C92—C89	119.96 (19)
C47—C40—H40B	109.5	C80—C92—H92	120.0
C47—C40—H40C	109.5	C89—C92—H92	120.0
H41A—C41—H41B	109.5	Cl4—C94—Cl6	111.33 (13)
H41A—C41—H41C	109.5	Cl4—C94—H94	108.2
H41B—C41—H41C	109.5	Cl5—C94—Cl4	111.07 (13)
C48—C41—H41A	109.5	Cl5—C94—Cl6	109.78 (14)
C48—C41—H41B	109.5	Cl5—C94—H94	108.2
C48—C41—H41C	109.5	Cl6—C94—H94	108.2
C30—C42—C4	120.69 (19)	Cl1A—C93—Cl2A	108.41 (18)
C30—C42—C38	116.8 (2)	Cl1A—C93—H93	108.3
C38—C42—C4	122.5 (2)	Cl2A—C93—H93	108.2
C34—C43—H43	119.3	Cl3A—C93—Cl1A	111.1 (2)
C34—C43—C47	121.4 (2)	Cl3A—C93—Cl2A	112.4 (2)
C47—C43—H43	119.3	Cl3A—C93—H93	108.2
C27—C44—C3	121.6 (2)	Cl1B—C93—Cl3B	108.8 (6)
C28—C44—C3	121.26 (19)	Cl1B—C93—H93A	109.1
C28—C44—C27	117.13 (19)	Cl2B—C93—Cl1B	115.1 (6)
C21—C45—H45	119.6	Cl2B—C93—Cl3B	105.4 (8)
C34—C45—C21	120.8 (2)	Cl2B—C93—H93A	109.1
C34—C45—H45	119.6	Cl3B—C93—H93A	109.1

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

Hydrogen-bond geometry (Å, º)

*Cg*1–*Cg*12 are the centroids of the five- or six-membered rings, where *Cg*1: N1–C8–C20–C10–C9, *Cg*2: N3–C7–C18–C13–C11, *Cg*3: Zn1–N1–C9–N2–C11–N3, *Cg*4: Zn1–N1–C8–N4–C7i–N3^{i}, *Cg*5: N5–C52–C63–C54–C61, *Cg*6: N6–C51–C59–C56–C55, *Cg*7: N8–C65–C50–C66–C83, Cg8: N7–C67–C49–C73–C69, *Cg*9: Zn2–N5–C52–C60–C83–N8, *Cg*10: Zn2–N6–C51–C62–C67–N7, *Cg*11: Zn2–N5–C61–C57–C69–N7, *Cg*12: Zn2–N6–C55–C70–C65–N8.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C89—H89···N4	0.95	2.35	3.245 (3)	157
C91—H91···N2^{i}	0.95	2.38	3.263 (3)	154
*Cg*1···*Cg*5			3.6115 (13)	
*Cg*2···*Cg*7			3.5271 (13)	
*Cg*3···*Cg*9			3.4996 (11)	
*Cg*4···*Cg*11			3.6264 (11)	
*Cg*1^{i}···*Cg*6			3.5162 (13)	
*Cg*2^{i}···*Cg*8			3.6819 (13)	

$Cg3^{i}\cdots Cg10$	3.6105 (13)
$Cg4^{i}\cdots Cg12$	3.4785 (1)

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