ARTICLE IN PRESS – Acta Cryst. E

Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of *cis*-7,8-dihydroxy-5,10,15,20-tetraphenylchlorin and its zinc(II)–ethylenediamine complex

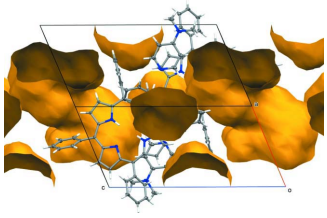
Proof instructions

Proof corrections should be returned by **17 March 2022**. After this period, the Editors reserve the right to publish your article with only the Managing Editor's corrections.

Please
(1) Read these proofs and assess whether any corrections are necessary.
(2) Check that any technical editing queries highlighted in **bold underlined** text have been answered.
(3) Send corrections by e-mail to **checkin@iucr.org**. Please describe corrections using plain text, where possible, giving the line numbers indicated in the proof. Please do not make corrections to the pdf file electronically and please do not return the pdf file. If no corrections are required please let us know.

If you wish to purchase printed offprints, please complete the attached order form and return it by e-mail as soon as possible.

Please check the following details for your article



Thumbnail image for contents page

Abbreviated author list: Chaudhri, N.; Brückner, C.; Zeller, M.

How to cite your article in press

Your article has not yet been assigned page numbers, but may be cited using the doi:

Chaudhri, N., Brückner, C. & Zeller, M. (2022). *Acta Cryst.* E**78**, https://doi.org/10.1107/S2056989022002729.

You will be sent the full citation when your article is published and also given instructions on how to download an electronic reprint of your article.

Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Crystal structure of *cis*-7,8-dihydroxy-5,10,15,20-tetraphenylchlorin and its zinc(II)–ethylenediamine complex

Nivedita Chaudhri,[a] Christian Brückner[a]* and Matthias Zeller[b]

[a]Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060, USA, and [b]Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN, 47907-2084, USA. *Correspondence e-mail: c.bruckner@uconn.edu

Received 21 February 2022
Accepted 10 March 2022

Edited by G. Diaz de Delgado, Universidad de Los Andes, Venezuela

Keywords: crystal structure; porphyrinoids; hydroporphyrins; *meso*-phenylchlorins; *β*-hydroxychlorin.

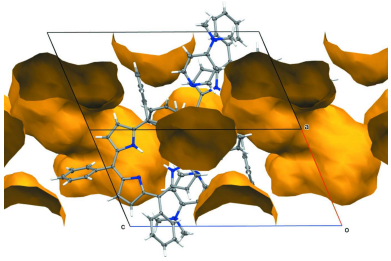
Supporting information: this article has supporting information at journals.iucr.org/e

The title chlorin, $\mathbf{2^{Ph}H_2}$, hydrogen-bonded to dimethylaminopyridine (DMAP), $C_{44}H_{32}N_4O_2{\cdot}C_7H_{10}N_2$, and its corresponding zinc(II) complex, $\mathbf{2^{Ph}Zn}$, axially coordinated to ethylenediamine (EDA), $[Zn(C_{44}H_{30}N_4O_2)]{\cdot}C_2H_8N_2$, were isolated and crystallized by adventitious reduction of the corresponding osmate esters by DMAP and EDA, respectively. Known since 1996 and, *inter alia*, used for the preparation of a wide range of (planar and non-planar) chlorin analogues (so-called pyrrole-modified porphyrins), their conformational analyses in the solid state are important benchmarks. Both macrocycles are only modestly distorted from planarity and both are slightly more non-planar than the corresponding dimethoxy-derivative, but less planar than a free-base *meso*-pentafluorophenyl-based osmate ester. NSD analyses provide quantitative and qualitative analyses of the distortion modes. One origin of the non-planarity is presumably the avoidance of the eclipsed configuration of the two *vic–cis* diols on the pyrroline moiety; the resulting deformation of the pyrroline translates in some cases into the macrocycle. The structure of $\mathbf{2^{Ph}H_2}$ features voids making up *ca* 26% of the unit-cell volume filled with highly disordered solvate molecules (chloroform and hexanes). $\mathbf{2^{Ph}Zn}$ crystallized with a 13.6 (4)% occupied solvate methanol molecule.

1. Chemical context

The study of synthetic chlorins as functional, spectroscopic, or structural models for nature's premiere light-harvesting pigment chlorophyll is one of the central aspects in contemporary porphyrinoid chemistry (Flitsch, 1988; Liu *et al.*, 2018; Taniguchi & Lindsey, 2017; Lindsey, 2015). Because of the facility of the synthesis of a wide range of *meso*-tetraarylporphyrins, their conversion to chlorins has been widely studied (Flitsch, 1988; Taniguchi & Lindsey, 2017).

We contributed to the field the description of the OsO_4-mediated dihydroxylation of *meso*-tetraarylporphyrins $\mathbf{1^{Ar}M}$, generating the corresponding chlorin diols $\mathbf{2^{Ar}M}$ (Fig. 1) (Brückner & Dolphin, 1995*a*; Brückner *et al.*, 1998). Depending on the stoichiometric ratio of OsO_4 used and whether the porphyrin metal complex or free base is used, the reaction may also lead to the regioselective formation of tetrahydroxymetalloisobacteriochlorins or tetrahydroxybacteriochlorins, respectively (Brückner & Dolphin, 1995*b*; Samankumara *et al.*, 2010; Hyland *et al.*, 2012; Bruhn & Brückner, 2015). Chlorin diols $\mathbf{2^{Ar}H_2}$ have shown efficacy as photosensitizers in photodynamic therapy (Macalpine *et al.*, 2002) or are substrates toward their oxidation to the corresponding diones (Starnes *et al.*, 2000, 2001; Daniell *et al.*, 2003).



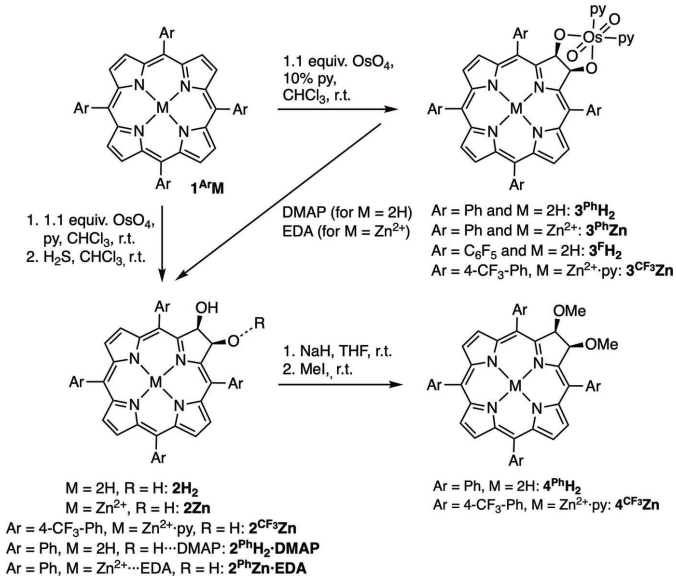


Figure 1
Synthetic pathways towards $\mathbf{2^{Ph}H_2}$**·DMAP** and $\mathbf{2^{Ph}Zn}$**·EDA** and their methoxy ethers.

Importantly, chlorin diols $\mathbf{2^{Ar}M}$ are the starting materials for the generation of a wide range of planar and non-planar chlorin analogues (so-called pyrrole-modified porphyrins) (Brückner, 2016; Sharma *et al.*, 2017; Hewage *et al.*, 2019; Brückner *et al.*, 2020; Luciano *et al.*, 2020; Wu *et al.*, 2020), whereby the parent chlorin diols $\mathbf{2^{Ph}H_2}$ and $\mathbf{2^{Ph}Zn}$ generally serve as spectroscopic benchmarks. Since the conformation of a porphyrinic macrocycle greatly influences its electronic structure, the structural characterization of the benchmark compounds $\mathbf{2^{Ph}H_2}$ and $\mathbf{2^{Ph}Zn}$ is important. Curiously, however, even though these fundamental compounds are known since 1996, crystals suitable for single X-ray crystal structure analyses could not be grown to date. However, related derivatives, such as osmate ester $\mathbf{3^{F}H_2}$ (Hewage *et al.*, 2019), a number of tetrahydroxybacteriochlorins and isobacteriochlorins (Samankumara *et al.*, 2010), and a number of alkylated diol free base and metal complexes $\mathbf{4^{Ar}}\boldsymbol{M}$ (M = 2H, Ni, Cu, Zn, Pd) (Samankumara *et al.*, 2010; Sharma *et al.*, 2017) could be structurally characterized.

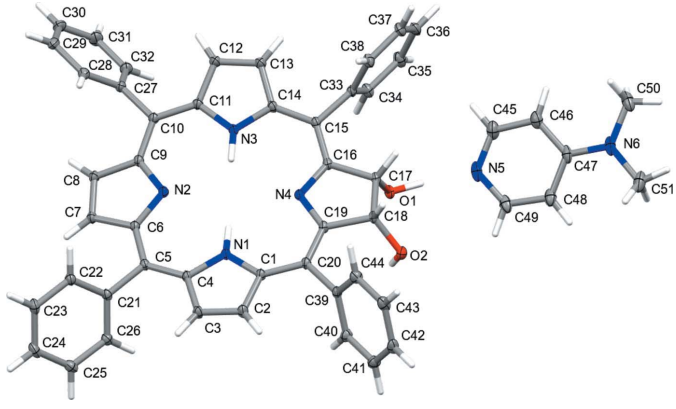
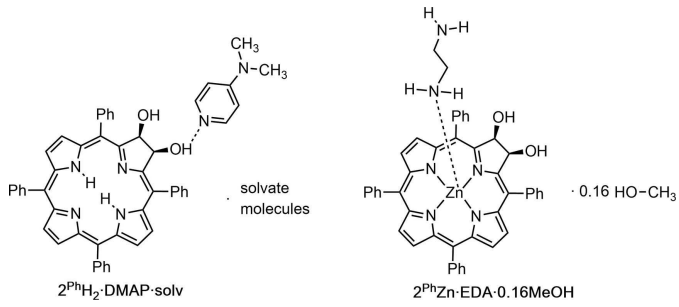


Figure 2
X-ray structure of $\mathbf{2^{Ph}H_2}$**·DMAP** with the atom-labeling scheme for non-H atoms. 50% probability ellipsoids.



In due course of working with the intermediate osmate esters and attempts to form crystals of the amine adducts, we inadvertently reduced the osmate ester and the long-sought parent free base *meso*-phenyl chlorin diol $\mathbf{2^{Ph}H_2}$, as $\mathbf{2^{Ph}H_2}$**·DMAP** hydrogen-bonded to DMAP (4-dimethylaminopyridine) and the zinc(II) complex $\mathbf{2^{Ph}Zn}$, in the form $\mathbf{2^{Ph}Zn}$**·EDA** in which the metal is axially coordinated to ethylenediamine (EDA), crystallized in single-crystal X-ray diffraction quality.

2. Structural commentary

The structures of both $\mathbf{2^{Ph}H_2}$**·DMAP** and $\mathbf{2^{Ph}Zn}$**·EDA** confirm the *cis–vic* stereochemistry of the diol functionality and the near-perpendicular arrangement of the *meso*-phenyl groups – structural features well known for these types of *meso*-aryl-chlorin diols (Hewage *et al.*, 2019; Samankumara *et al.*, 2010; Sharma *et al.*, 2017) or *meso*-arylporphyrinoids, in general (Senge, 2000) (Figs. 2 and 3).

Importantly, the structures allow the determination of the conformation of their chromophores. The dissection of the

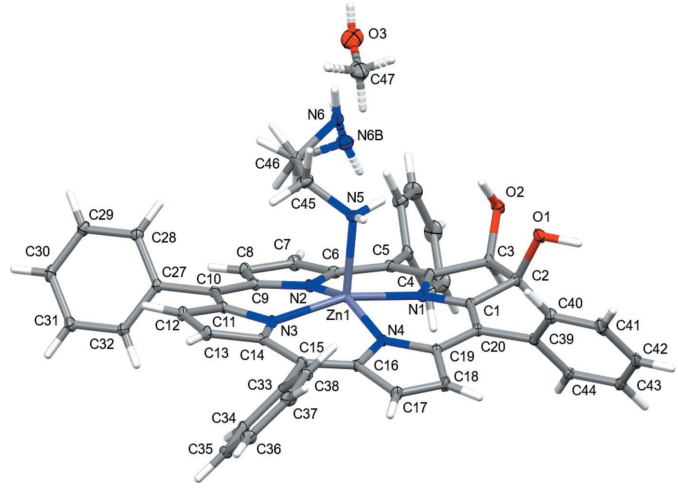


Figure 3
X-ray structure of the zinc(II) complex $\mathbf{2^{Ph}Zn}$**·EDA**, with the atom-labeling scheme for non-H atoms. 50% probability ellipsoids. Dashed bonds indicate the minor disordered amine [11.8 (12)% occupancy], and the partially occupied MeOH solvate [13.6 (4)% occupancy]. Atom labels for the backwards pointing phenyl ring (C21–C26) are omitted for clarity.

conformation of **2^{Ph}H$_2$·DMAP** using a normal mode structural decomposition (NSD) analysis (Kingsbury & Senge, 2021; Shelnutt *et al.*, 1998) shows that its chromophore exhibits a considerable saddling distortion. In comparison, the dimethoxy derivative **4^{Ph}H$_2$** (Samankumara *et al.*, 2010) is more planar, with only very modest distortions evenly spread over a number of distortion modes (Fig. 4*a*). In **4^{Ph}H$_2$**, both methoxy substituents point toward the outside, whereas the corresponding hydroxy groups in **2^{Ph}H$_2$·DMAP** point in opposite directions, with only the hydrogen-bonded (to DMAP) hydroxy group pointing outwards. A slight deformation of the pyrroline moiety in **2^{Ph}H$_2$·DMAP** alleviates the steric interactions between the two hydroxy groups [26.65 (13)° O—C—C—O torsion angle] that would be otherwise forced to be eclipsed. The corresponding torsion angle in **4^{Ph}H$_2$** is slightly smaller [17.23 (17)°; Samankumara *et al.*, 2010]. This *vic*-*cis*-substituents-induced pyrroline deformation was also observed previously (Sharma *et al.*, 2017; Hewage *et al.*, 2019).

The out-of-plane plots (Kingsbury & Senge, 2021) of the two free-base chlorins **2^{Ph}H$_2$·DMAP** and **4^{Ph}H$_2$** also illustrate the qualitative and quantitative differences in the conformations of the two (Fig. 5*a*).

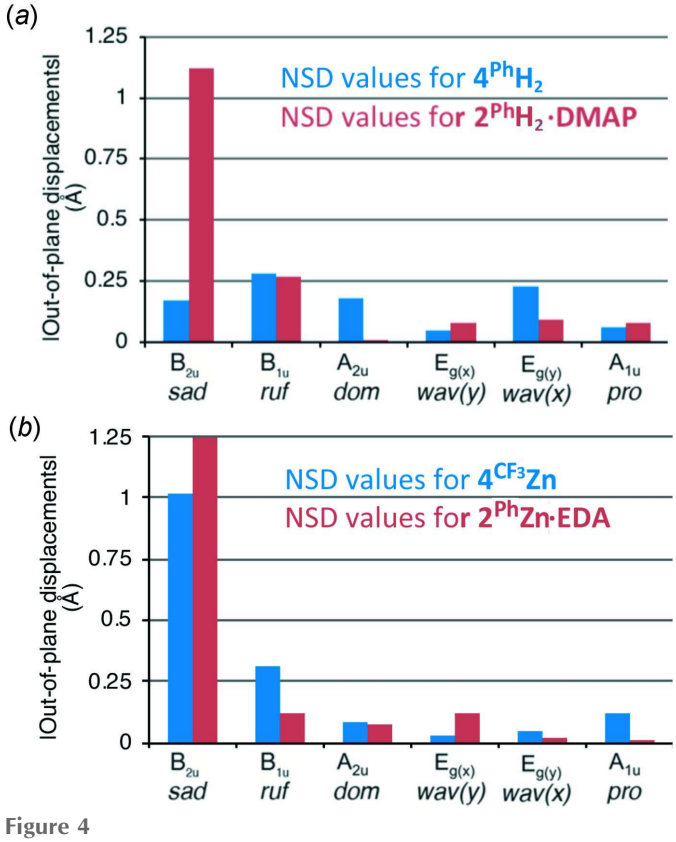


Figure 4
Normal mode Structural Decomposition (NSD) analysis (Kingsbury & Senge, 2021) of (*a*), the chromophore conformations of dihydroxychlorin **2^{Ph}H$_2$·DMAP** (hydrogen-bonded to DMAP) in comparison to the conformation of the chromophore of dimethoxychlorin **4^{Ph}H$_2$** (Samankumara *et al.*, 2010), and (*b*), the equivalent chromophore conformation analysis of **2^{Ph}Zn·EDA** in comparison to the closely related dimethoxy derivative **4^{CF3}Zn** (Sharma *et al.*, 2017).

The saddling deformation is more pronounced in the corresponding zinc(II) complexes but the deformation modes observed in either of the complexes are very similar (Fig. 4*b* and 5*b*). This (small) B_{2u} deformation mode is typical for penta-coordinated, square-pyramidal porphyrinoid zinc(II) complexes (Kingsbury & Senge, 2021). The differences in conformation quality and quantity is only minimal between the parent compound **2^{Ph}Zn·EDA** and its *p*-aryl-substituted and methylated analogue **4^{CF3}Zn·py**. In addition, both molecules carry their axial ligand on the same hemisphere defined by the macrocycle the diol/dimethoxy moieties are located. Nonetheless, there are differences. For instance, a smaller O—C—C—O torsion angle was observed in the diol zinc complex **2^{Ph}Zn·EDA** [O—C_β—C_β—O dihedral angle = 7.86 (17)°], whereas the corresponding angle in the dimethoxy derivative **4^{CF3}Zn** is much larger at 28.1 (4)°(Sharma *et al.*, 2017).

In neither the free base nor the zinc complex of the diol chlorins are any significant in-plane deformations observed. The change in the macrocycle conformation upon methylation and/or hydrogen bonding to an amine acceptor reiterates the conformational malleability of the chlorin chromophore (Kratky *et al.*, 1985), as previously also shown in the varying conformations of a range of transition-metal complexes (Sharma *et al.*, 2017).

3. Supramolecular features

The dominant supramolecular interactions in both **2^{Ph}H$_2$·DMAP** and **2^{Ph}Zn·EDA** are hydrogen-bonding inter-

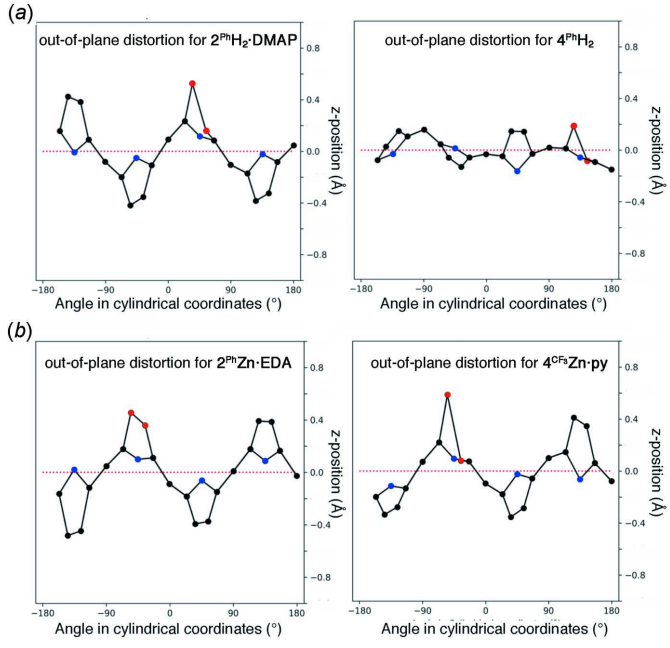


Figure 5
Out-of-plane plots (Kingsbury & Senge, 2021) of the chromophore conformations of (*a*), dihydroxychlorin **2^{Ph}H$_2$·DMAP** and dimethoxychlorin **4^{Ph}H$_2$** (Samankumara *et al.*, 2010), and (*b*), the equivalent plots of **2^{Ph}Zn·EDA** and **4^{CF3}Zn·py** (Sharma *et al.*, 2017). The atoms indicated in red are the pyrroline *β*-carbons carrying the *cis*-hydroxy or methoxy groups.

Table 1
Hydrogen-bond geometry (Å, °) for **2^{Ph}H$_2$**.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N5	0.973 (17)	1.727 (17)	2.6968 (14)	174.1 (14)
O2—H2O···O1^{i}	0.927 (17)	1.882 (17)	2.7798 (12)	162.5 (14)
N1—H1N···N2	0.925 (15)	2.346 (15)	2.9064 (13)	118.7 (11)
N1—H1N···N4	0.925 (15)	2.383 (15)	2.9518 (13)	119.6 (11)
N3—H3N···N2	0.915 (16)	2.292 (16)	2.8868 (13)	122.3 (12)
N3—H3N···N4	0.915 (16)	2.458 (15)	2.9766 (14)	116.1 (12)
C37—H37···O2^{ii}	0.95	2.51	3.3840 (16)	153
C38—H38···C48^{ii}	0.95	2.77	3.6779 (19)	161
C50—H50B···N4^{ii}	0.98	2.57	3.544 (2)	171

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.

actions between the hydroxyl functions of the chlorin molecules, and the DMAP and EDA bases incorporated into the crystal structure.

In **2^{Ph}H$_2$·DMAP** one of the hydroxyl groups acts as a donor towards the DMAP with O1—H1O···N5 = 2.6968 (14) Å. O1 in turn acts as acceptor for an O—H···O bond originating from O2 of a neighboring molecule. A symmetry-equivalent interaction (by inversion) connects the other two oxygen atoms of the same two molecules with each other, creating an inversion-symmetric dimer (Fig. 6). A number of additional interactions that augment the strong hydrogen bonds, among them C—H···O, C—H···N and C–H···π interactions, are listed in the hydrogen-bonding Table 1.

The structure of **2^{Ph}H$_2$·DMAP** also contains 647 Å^3 (*ca* 26% of the unit-cell volume) of solvent-accessible voids occupied by highly disordered solvent molecules that could not be properly modeled or refined (Fig. 7). The content of these voids, presumably chloroform and hexane, the crystallization solvents, were instead included in the model *via* reverse-Fourier-transform methods using the SQUEEZE routine (van der Sluis & Spek, 1990; Spek, 2015) as implemented in the program *PLATON* (Spek, 2020), and added as additional not-model-based structure-factor contributions. The procedure corrected for 162 electrons within the solvent-accessible voids.

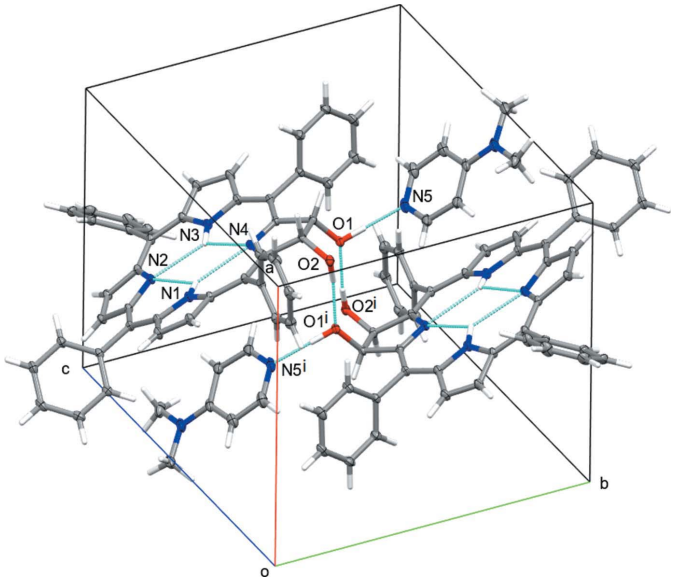


Figure 6
Hydrogen bonding and packing of **2^{Ph}H$_2$·DMAP**. 50% probability ellipsoids. Symmetry code: (i) $1-x, 1-y, 1-z$.

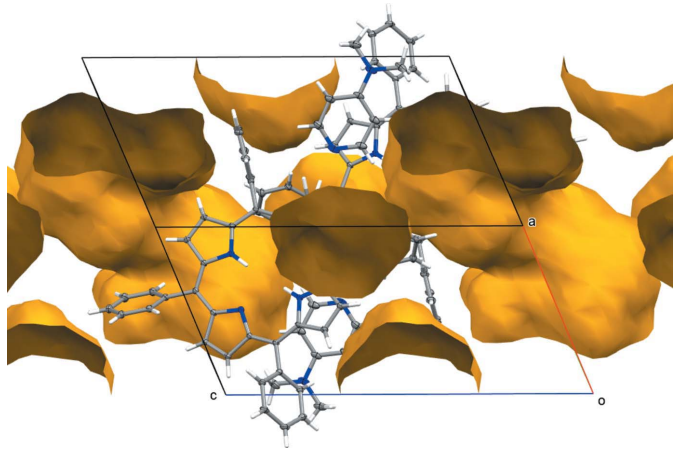


Figure 7
Solvent-accessible voids in **2^{Ph}H$_2$·DMAP**. The void volume is 647 Å^3, or *ca* 26% of the unit-cell volume.

Hydrogen bonding in **2^{Ph}Zn·EDA** is similar to that of **2^{Ph}H$_2$·DMAP**, but more complex. In contrast to the DMAP molecule in **2^{Ph}H$_2$·DMAP**, the amino NH$_2$ groups of the ethylene diamine in **2^{Ph}Zn·EDA** can act as both hydrogen-bond acceptors as well as hydrogen-bond donors. One of the two amine moieties of the EDA base is axially coordinated to the zinc center of the chlorin complex, and is thus not available as a hydrogen-bond acceptor. The partially occupied methanol molecule also takes part in hydrogen-bonding interactions, and the disorder of the not-metal-coordinated amino group further complicates the hydrogen-bonding network of **2^{Ph}Zn·EDA**.

The two hydroxyl groups again both act as hydrogen-bond donors, and similar to in **2^{Ph}H$_2$·DMAP** they form an inversion-symmetric dimer (Fig. 8). O1 again acts as a hydrogen-bond donor towards the base, here the disordered amino group, of the other molecule of the dimer. Different from the DMAP molecule, which lacks acidic H atoms, the amines also act as hydrogen-bond donors. The metal-coordinated amine

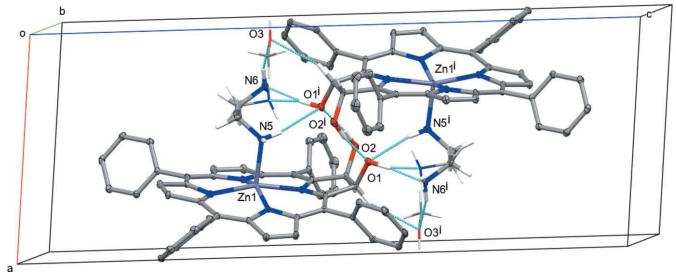


Figure 8
Hydrogen bonding and packing of **2^{Ph}Zn·EDA**. 50% probability ellipsoids. Symmetry code: (i) $1-x, 1-y, 1-z$. 50% ellipsoids for fully occupied and major occupancy non-H atoms. Others in capped stick mode. Phenyl and pyrrole H atoms are omitted for clarity.

Table 2
Hydrogen-bond geometry (Å, °) for **2^{Ph}Zn**.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N6^{i}	0.99	1.73	2.710 (3)	168
O1—H1···N6B^{i}	0.99	1.54	2.510 (17)	165
O2—H2A···O1^{i}	0.99	1.82	2.8056 (18)	171
C2—H2···O3^{i}	1.00	2.53	3.460 (14)	155
N5—H5A···O1^{i}	0.88 (2)	2.38 (2)	3.2442 (18)	166 (2)
C46—H46A···N2	0.99	2.49	3.368 (2)	148
N6—H6A···O3	0.90 (2)	2.08 (2)	2.932 (14)	159 (3)
C46B—H46C···N2	0.99	2.68	3.368 (2)	126
O3—H3O···N4^{ii}	0.84	2.20	2.992 (14)	157

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$.

creates an N—H···O bond that provides an additional connection within the dimer to create a 3D hydrogen-bonding network between the two molecules (Fig. 8).

Several 'terminal' hydrogen bonds or hydrogen-bond-like interactions cap off the not yet used acidic and basic atoms, which are listed in the hydrogen-bonding Table 2 (interactions not shown). The second amine H atom of the metal-coordinated NH_2 group is engaged in an N—H···π interaction towards the π-density of C29 of the phenyl ring of a neighboring molecule. The major moiety of the disordered amino group hydrogen bonds with the partially occupied methanol molecule. However, this interaction is not always present, as the occupancy of the MeOH molecule is only 13.6 (4)%, while that of the amino group is 88.2 (12)%. The second amino H atom is not involved in any directional interactions. One of the H atoms of the minor amino moiety might be engaged in another N—H···π interaction towards the π-density of C43 and C43 of a phenyl ring of the second dimer molecule, but the exact positions of the amino H atoms are not determined accurately given the low occupancy of the amino fragment [11.8 (12)%]. The same is true for the position of the methanol hydroxyl H atom, which appears to be engaged in a weak O—H···π interaction with the porphyrinic π-system of a molecule at $-1+x, y, z$. O3, the methanol oxygen atom, acts as acceptor for a C—H···O interaction originating from a phenyl C atom of a molecule not part of the dimer. The H···O distance is unusually short for a C—H···O interaction, 2.53 Å, which could be an artifact of the low occupancy of the methanol molecule.

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.43, Nov 2021; Groom *et al.*, 2016) for *meso*-tetraarylchlorins or their metal(II) complexes revealed in excess of 75 structures, but few are directly comparable to the title compounds: Most examples contain a variety of bulky substituents or annulated rings at the pyrroline positions [the closest being an imidazolone-annulated dihydroxychlorin, TAKDUI (Luciano *et al.* 2020)] or contain other (sterically encumbering) substituents at the pyrrolic β-positions or on the *meso*-aryl groups. Most metallochlorins contain also a different metal than zinc(II). Only a few compounds are structurally closely related to **2^{Ph}H$_2$·DMAP** or **2^{Ph}Zn·EDA**. Among them is the parent non-hydroxylated chlorin zinc chelate [5,10,15,20-tetraphenylchlorinato]zinc(II)·pyridine complex (HPORZN10; Spaulding *et al.*, 1977), the bis-β-*n*-butylated free base and zinc(II) chlorins (QAKLUJ and QAKMAQ, respectively; Senge *et al.*, 2000), free base 5,10,15,20-tetraphenyl-7-hydroxychlorin (SAZSAP; Samankumara *et al.*, 2010), the β-nitrated analogue of **2^{Ph}H$_2$** (TIPBIF; Worlinsky *et al.*, 2013), dimethoxy derivatives **4^{Ph}H$_2$** (SAZROC; Samankumara *et al.*, 2010) and **4^{CF3}Zn·py** (PEDKER; Sharma *et al.*, 2017), osmate ester **3^{F}H$_2$** (SIZFUF; Hewage *et al.*, 2019), and *trans*-7,8-diol-7,8-dimethyltetraphenylchlorin (ZAZNIZ; Banerjee *et al.*, 2012).

5. Synthesis and crystallization

The OsO_4-mediated dihydroxylation of porphyrin **1H$_2$** is a two-step sequence: the formation of the osmate ester **3^{Ar}H$_2$** in the first step is followed by the reduction of the osmate ester to the target dihydroxychlorin **2^{Ar}H$_2$** (often performed as a two-step, one-pot process) (Brückner & Dolphin, 1995*b*; Samankumara *et al.*, 2010; Hyland *et al.*, 2012). Here, we prepared the intermediate *meso*-tetraphenyl-2,3-*vic*-dihydroxychlorin osmate ester according to the established oxidation of *meso*-tetraphenylporphyrins **1^{Ph}H$_2$** (Brückner *et al.*, 1998). Metalation of the free base **1^{Ph}H$_2$** using $Zn(OAc)_2{\cdot}2H_2O$ under standard conditions (Buchler, 1978) (refluxing $CHCl_3$/MeOH for 35-40 min) formed the corresponding Zn^{II} osmate ester **3^{Ph}Zn**.

While crystallizing the osmate esters in CH_2Cl_2 and layering with the non-solvent hexane in the presence of DMAP (for **3^{Ph}H$_2$**) or by allowing a solution of the ester in CH_2Cl_2/MeOH to slowly evaporate in the presence of EDA (for **3^{Ph}Zn**), both osmate esters adventitiously reduced and diols **2^{Ph}H$_2$·DMAP** and **2^{Ph}Zn·EDA** crystallized, respectively. The spectroscopic data of both known chromophores are as described previously (Brückner *et al.*, 1998).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C—H bond distances were constrained to 0.95 Å for aromatic and alkene C—H groups, and to 1.00, 0.99 and 0.98 Å for aliphatic C—H, CH_2 and CH_3 groups, respectively. Positions of N—H and NH_2 hydrogen atoms were refined. N—H distances within NH_2 groups in **2^{Ph}Zn·EDA** were restrained to 0.88 (2) Å and H—N—H and H–N–C angles were restrained to be similar to each other. Methyl CH_3 and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. The hydroxyl H atom of the partially occupied methanol molecule in **2^{Ph}Zn·EDA** was restrained to hydrogen bond to a porphyrin N atom of a neighboring complex. U_{iso}(H) values were set to a multiple of U_{eq}(C/O/N) with 1.5 for CH_3 and OH, and 1.2 for C–H, CH_2, N—H and NH_2 units, respectively.

In the structure of **2^{Ph}Zn·EDA**, disorder of the not-metal-coordinated amino group of the ethylene diamine molecule is

Table 3
Experimental details.

	$2^{Ph}H_2$	$2^{Ph}Zn$
Crystal data		
Chemical formula	$C_{44}H_{32}N_4O_2{\cdot}C_7H_{10}N_2{\cdot}$[+solvent]	$[Zn(C_{44}H_{30}N_4O_2)]{\cdot}C_2H_8N_2{\cdot}0.136CH_4O$
M_r	770.90	776.57
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
Temperature (K)	150	150
a, b, c (Å)	10.0193 (4), 15.2554 (8), 17.7983 (10)	10.1249 (3), 13.5400 (4), 27.0447 (8)
α, β, γ (°)	69.918 (2), 74.926 (2), 84.140 (2)	90, 95.1464 (11), 90
V (Å^3)	2466.9 (2)	3692.64 (19)
Z	2	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.06	1.32
Crystal size (mm)	0.33 × 0.21 × 0.19	0.27 × 0.25 × 0.18
Data collection		
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)	Bruker AXS D8 Quest diffractometer with PhotonIII-C14 charge-integrating and photon counting pixel array detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.665, 0.746	0.606, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	48645, 14738, 9891	21319, 7551, 7037
R_{int}	0.060	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714	0.638
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.133, 1.04	0.031, 0.088, 1.04
No. of reflections	14738	7551
No. of parameters	549	549
No. of restraints	0	17
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.21	0.31, −0.44

Computer programs: *APEX4* (Bruker, 2021), *APEX3* and *SAINT* (Bruker, 2019), *SHELXT* (Sheldrick, 2015*a*), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015*b*), *ShelXle* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

observed and a methanol solvate molecule is partially occupied. The C—N bonds were restrained to be similar in length. A partially occupied methanol molecule is located nearby the major disordered amino group and hydrogen-bonded to it. The hydroxyl H atom was restrained to hydrogen bond to a porphyrin N atom of a neighboring complex. Subject to these conditions, the occupancy ratio for the amino groups refined to 0.882 (12): 0.118 (12), and the occupancy rate for the methanol molecule refined to 0.136 (4). The occupancy of the methanol molecule is not correlated with the disorder of the amino group (the major 88% occupied amino group is hydrogen-bonded to the 14% occupied methanol molecule).

The structure of **$2^{Ph}H_2$·DMAP** contains 647 Å^3 of solvent-accessible voids occupied by highly disordered solvate molecules (presumably chloroform and hexane, the crystallization solvents). The residual electron-density peaks are not arranged in an interpretable pattern and no unambiguous disorder model could be developed. The structure factors were instead augmented *via* reverse-Fourier-transform methods using the SQUEEZE routine (van Sluis & Spek, 1990; Spek, 2015), as implemented in the program *PLATON* (Spek, 2020). The resultant .fab file containing the structure-factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. The SQUEEZE procedure accounted for 162 electrons within the solvent-accessible voids.

Funding information

Funding for this research was provided by: National Science Foundation (grant No. CHE-1625543 to M. Zeller; grant No. CHE-1800361 to C. Brückner).

References

Banerjee, S., Zeller, M. & Brückner, C. (2012). *J. Porphyrins Phthalocyanines*, **16**, 576–588.
Brückner, C. (2016). *Acc. Chem. Res.* **49**, 1080–1092.
Brückner, C., Atoyebi, A. O., Girouard, D., Lau, K. S. F., Akhigbe, J., Samankumara, L., Damunupola, D., Khalil, G. E., Gouterman, M., Krause, J. A. & Zeller, M. (2020). *Eur. J. Org. Chem.* pp. 475–482.
Brückner, C. & Dolphin, D. (1995*a*). *Tetrahedron Lett.* **36**, 3295–3298.
Brückner, C. & Dolphin, D. (1995*b*). *Tetrahedron Lett.* **36**, 9425–9428.
Brückner, C., Rettig, S. J. & Dolphin, D. (1998). *J. Org. Chem.* **63**, 2094–2098.
Bruhn, T. & Brückner, C. (2015). *J. Org. Chem.* **80**, 4861–4868.
Bruker (2019). *APEX3* and *SAINT*. Bruker Nano Inc., Madison, Wisconsin, USA.
Bruker (2021). *APEX4*. Bruker Nano Inc., Madison, Wisconsin, USA.
Buchler, J. W. (1978). *The Porphyrins*, edited by D. Dolphin, pp. 389–483, New York: Academic Press.

Daniell, H. W., Williams, S. C., Jenkins, H. A. & Brückner, C. (2003). *Tetrahedron Lett.* **44**, 4045–4049.

Flitsch, W. (1988). *Adv. Heterocycl. Chem.* **43**, 73–126.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hewage, N., Daddario, P., Lau, K. S. F., Guberman-Pfeffer, M. J., Gascón, J. A., Zeller, M., Lee, C. O., Khalil, G. E., Gouterman, M. & Brückner, C. (2019). *J. Org. Chem.* **84**, 239–256.

Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.

Hyland, M. A., Morton, M. D. & Brückner, C. (2012). *J. Org. Chem.* **77**, 3038–3048.

Kingsbury, C. J. & Senge, M. O. (2021). *Coord. Chem. Rev.* **431**, 213760.

Kratky, C., Waditschatka, R., Angst, C., Johansen, J. E., Plaquevent, J. C., Schreiber, J. & Eschenmoser, A. (1985). *Helv. Chim. Acta*, **68**, 1312–1337.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Lindsey, J. S. (2015). *Chem. Rev.* **115**, 6534–6620.

Liu, Y., Zhang, S. & Lindsey, J. S. (2018). *Nat. Prod. Rep.* **35**, 879–901.

Luciano, M. P., Atoyebi, A. O., Tardie, W., Zeller, M. & Brückner, C. (2020). *J. Org. Chem.* **85**, 15273–15286.

Macalpine, J. K., Boch, R. & Dolphin, D. (2002). *J. Porphyrins Phthalocyanines*, **06**, 146–155.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.

Samankumara, L. P., Zeller, M., Krause, J. A. & Brückner, C. (2010). *Org. Biomol. Chem.* **8**, 1951–1965.

Senge, M. O. (2000). *The Porphyrin Handbook*, edited by K. M. Kadish, K. M. Smith & R. Guilard, pp. 1–218. San Diego: Academic Press.

Senge, M. O., Kalisch, W. W. & Bischoff, I. (2000). *Chem. Eur. J.* **6**, 2721–2738.

Sharma, M., Ticho, A. L., Samankumara, L., Zeller, M. & Brückner, C. (2017). *Inorg. Chem.* **56**, 11490–11502.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Shelnutt, J. A., Song, X.-Z., Ma, J.-G., Jentzen, W. & Medforth, C. J. (1998). *Chem. Soc. Rev.* **27**, 31–41.

Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* A**46**, 194–201.

Spaulding, L. D., Andrews, L. C. & Williams, G. J. B. (1977). *J. Am. Chem. Soc.* **99**, 6918–6923.

Spek, A. L. (2015). *Acta Cryst.* C**71**, 9–18.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Starnes, S. D., Rudkevich, D. M. & Rebek, J. Jr (2000). *Org. Lett.* **2**, 1995–1998.

Starnes, S. D., Rudkevich, D. M. & Rebek, J. Jr (2001). *J. Am. Chem. Soc.* **123**, 4659–4669.

Taniguchi, M. & Lindsey, J. S. (2017). *Chem. Rev.* **117**, 344–535.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Worlinsky, J. L., Zarate, G., Zeller, M., Ghandehari, M., Khalil, G. & Brückner, C. (2013). *J. Porphyrins Phthalocyanines*, **17**, 836–849.

Wu, Z.-Y., Xue, H., Wang, T., Guo, Y., Meng, Y.-S., Li, X., Zheng, J., Brückner, C., Rao, G., Britt, R. D. & Zhang, J.-L. (2020). *ACS Catal.* **10**, 2177–2188.

supporting information

Crystal structure of *cis*-7,8-*vic*-dihydroxy-5,10,15,20-tetraphenylchlorin and its zinc(II)–ethylenediamine complex

Nivedita Chaudhri, Christian Brückner* and Matthias Zeller

Computing details

Data collection: *APEX4* (Bruker, 2021) for 2PhH2; *APEX3* (Bruker, 2019) for 2PhZn. For both structures, cell refinement: *SAINT* (Bruker, 2019); data reduction: *SAINT* (Bruker, 2019). Program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a) for 2PhH2; *SHELXS97* (Sheldrick, 2008) for 2PhZn. For both structures, program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b), *ShelXle* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

cis-7,8-*vic*-Dihydroxy-5,10,15,20-tetraphenylchlorin dimethylaminopyridine monosolvate (2PhH2)

Crystal data

$C_{44}H_{32}N_4O_2 \cdot C_7H_{10}N_2 \cdot$[+solvent]
M_r = 770.90
Triclinic, $P\overline{1}$
a = 10.0193 (4) Å
b = 15.2554 (8) Å
c = 17.7983 (10) Å
α = 69.918 (2)°
β = 74.926 (2)°
γ = 84.140 (2)°
V = 2466.9 (2) Å^3
Z = 2
$F(000)$ = 812
D_x = 1.038 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9960 reflections
θ = 2.4–31.9°
μ = 0.06 mm^{-1}
T = 150 K
Fragment, black
0.33 × 0.21 × 0.19 mm

Data collection

Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)
Radiation source: fine focus sealed tube X-ray source
Triumph curved graphite crystal monochromator
Detector resolution: 7.4074 pixels mm^{-1}
ω and phi scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.665, T_{max} = 0.746
48645 measured reflections
14738 independent reflections
9891 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 30.5°, θ_{min} = 2.2°
h = −14→14
k = −21→21
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.133
S = 1.04
14738 reflections
549 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.2687P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. The structure contains 647 A ng3 of solvent accessible voids occupied by highly disordered solvate molecules (presumably chloroform and hexane, the crystallization solvents). The residual electron density peaks are not arranged in an interpretable pattern and no unambiguous disorder model could be developed. The structure factors were instead augmented *via* reverse Fourier transform methods using the SQUEEZE routine (P. van der Sluis & A·*L*. Spek (1990). Acta Cryst. A46, 194–201) as implemented in the program *PLATON*. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original *hkl* file in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 162 electrons within the solvent accessible voids.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.62197 (8)	0.52783 (6)	0.53614 (5)	0.03032 (18)
H1O	0.6812 (16)	0.5788 (11)	0.4973 (10)	0.045*
O2	0.65897 (9)	0.42954 (6)	0.42876 (5)	0.03175 (18)
H2O	0.5704 (17)	0.4513 (11)	0.4458 (10)	0.048*
N1	0.43218 (10)	0.14254 (6)	0.68820 (6)	0.02595 (19)
H1N	0.4495 (15)	0.1795 (10)	0.7162 (9)	0.039*
N2	0.37812 (10)	0.12770 (6)	0.86064 (6)	0.02649 (19)
N3	0.55460 (10)	0.28307 (7)	0.82259 (6)	0.0283 (2)
H3N	0.5129 (16)	0.2577 (11)	0.7949 (10)	0.042*
N4	0.59891 (9)	0.30953 (6)	0.64424 (6)	0.02597 (19)
N5	0.79133 (13)	0.66232 (8)	0.42197 (8)	0.0513 (3)
N6	1.09618 (14)	0.82611 (9)	0.22875 (8)	0.0542 (3)
C1	0.48576 (12)	0.15869 (8)	0.60568 (7)	0.0272 (2)
C2	0.43926 (14)	0.08451 (8)	0.58748 (8)	0.0344 (3)
H2	0.461662	0.076127	0.535118	0.041*
C3	0.35751 (13)	0.02790 (8)	0.65773 (7)	0.0329 (3)
H3	0.312720	−0.026520	0.662782	0.039*
C4	0.35068 (11)	0.06429 (7)	0.72235 (7)	0.0261 (2)
C5	0.27900 (11)	0.02833 (7)	0.80485 (7)	0.0258 (2)
C6	0.28682 (11)	0.06218 (8)	0.86799 (7)	0.0258 (2)
C7	0.20051 (12)	0.02932 (8)	0.95097 (7)	0.0292 (2)
H7	0.128291	−0.014687	0.970852	0.035*
C8	0.24279 (12)	0.07350 (8)	0.99458 (7)	0.0300 (2)
H8	0.206040	0.066657	1.051130	0.036*
C9	0.35477 (11)	0.13318 (8)	0.93846 (7)	0.0270 (2)
C10	0.42982 (12)	0.18860 (8)	0.96202 (7)	0.0282 (2)
C11	0.52658 (12)	0.25542 (8)	0.90752 (7)	0.0293 (2)
C12	0.60953 (13)	0.31160 (9)	0.92638 (8)	0.0349 (3)

H12	0.614596	0.307363	0.980081	0.042*
C13	0.68056 (13)	0.37261 (9)	0.85413 (8)	0.0344 (3)
H13	0.742769	0.418500	0.848983	0.041*
C14	0.64544 (12)	0.35568 (8)	0.78779 (7)	0.0290 (2)
C15	0.69121 (11)	0.40654 (7)	0.70330 (7)	0.0266 (2)
C16	0.66552 (11)	0.38612 (7)	0.63837 (7)	0.0256 (2)
C17	0.71366 (11)	0.44961 (8)	0.54998 (7)	0.0269 (2)
H17	0.810994	0.469724	0.538272	0.032*
C18	0.70357 (11)	0.38542 (8)	0.50137 (7)	0.0271 (2)
H18	0.798257	0.359268	0.485428	0.033*
C19	0.61540 (11)	0.30561 (7)	0.56736 (7)	0.0258 (2)
C20	0.56811 (11)	0.23380 (8)	0.54904 (7)	0.0267 (2)
C21	0.18885 (12)	−0.05389 (8)	0.82851 (7)	0.0277 (2)
C22	0.21160 (13)	−0.13703 (8)	0.88883 (8)	0.0340 (3)
H22	0.286768	−0.142088	0.913483	0.041*
C23	0.12514 (15)	−0.21243 (9)	0.91308 (9)	0.0418 (3)
H23	0.141490	−0.268761	0.954185	0.050*
C24	0.01525 (14)	−0.20589 (10)	0.87763 (9)	0.0428 (3)
H24	−0.044311	−0.257364	0.894713	0.051*
C25	−0.00731 (13)	−0.12454 (10)	0.81758 (9)	0.0392 (3)
H25	−0.082307	−0.120161	0.792940	0.047*
C26	0.07881 (12)	−0.04862 (9)	0.79264 (8)	0.0321 (2)
H26	0.062527	0.007135	0.750918	0.039*
C27	0.40379 (12)	0.17673 (9)	1.05123 (7)	0.0306 (2)
C28	0.42357 (13)	0.09033 (9)	1.10829 (8)	0.0350 (3)
H28	0.453285	0.038015	1.090474	0.042*
C29	0.39991 (14)	0.08048 (11)	1.19136 (8)	0.0438 (3)
H29	0.413317	0.021333	1.230008	0.053*
C30	0.35704 (17)	0.15613 (13)	1.21802 (9)	0.0518 (4)
H30	0.341547	0.149010	1.274766	0.062*
C31	0.33677 (18)	0.24209 (12)	1.16204 (9)	0.0532 (4)
H31	0.307152	0.294134	1.180274	0.064*
C32	0.35962 (15)	0.25240 (10)	1.07935 (8)	0.0409 (3)
H32	0.345099	0.311659	1.041196	0.049*
C33	0.77693 (12)	0.48962 (8)	0.68495 (7)	0.0277 (2)
C34	0.71456 (13)	0.57598 (9)	0.68111 (8)	0.0357 (3)
H34	0.617350	0.583199	0.687579	0.043*
C35	0.79380 (15)	0.65217 (10)	0.66780 (9)	0.0435 (3)
H35	0.750570	0.711286	0.664713	0.052*
C36	0.93499 (15)	0.64211 (10)	0.65908 (9)	0.0443 (3)
H36	0.988404	0.693901	0.651294	0.053*
C37	0.99855 (14)	0.55681 (11)	0.66166 (9)	0.0444 (3)
H37	1.095810	0.549926	0.655054	0.053*
C38	0.91967 (13)	0.48109 (9)	0.67397 (9)	0.0379 (3)
H38	0.963808	0.422699	0.674888	0.045*
C39	0.61114 (12)	0.23285 (8)	0.46200 (7)	0.0285 (2)
C40	0.51769 (14)	0.25180 (9)	0.41304 (8)	0.0353 (3)
H40	0.424591	0.267589	0.434044	0.042*

C41	0.55892 (15)	0.24792 (10)	0.33351 (8)	0.0408 (3)
H41	0.494024	0.261266	0.300357	0.049*
C42	0.69418 (15)	0.22468 (9)	0.30227 (8)	0.0405 (3)
H42	0.722094	0.221702	0.247937	0.049*
C43	0.78742 (14)	0.20604 (10)	0.35014 (9)	0.0424 (3)
H43	0.880424	0.190326	0.328850	0.051*
C44	0.74671 (13)	0.20998 (9)	0.42957 (8)	0.0369 (3)
H44	0.812284	0.196878	0.462273	0.044*
C45	0.89678 (18)	0.69732 (11)	0.43549 (10)	0.0546 (4)
H45	0.901928	0.682842	0.491021	0.065*
C46	0.99821 (17)	0.75277 (10)	0.37465 (10)	0.0504 (4)
H46	1.069780	0.775754	0.388603	0.060*
C47	0.99487 (15)	0.77500 (9)	0.29192 (9)	0.0435 (3)
C48	0.88343 (15)	0.73985 (10)	0.27753 (10)	0.0484 (4)
H48	0.873990	0.753889	0.222851	0.058*
C49	0.78732 (15)	0.68461 (10)	0.34342 (11)	0.0504 (4)
H49	0.713560	0.661011	0.331852	0.060*
C50	1.20258 (17)	0.86988 (12)	0.24494 (12)	0.0637 (5)
H50A	1.267695	0.901455	0.192839	0.096*
H50B	1.252073	0.822161	0.281093	0.096*
H50C	1.159873	0.915591	0.271836	0.096*
C51	1.09541 (19)	0.84148 (13)	0.14456 (10)	0.0656 (5)
H51A	1.184094	0.867545	0.108436	0.098*
H51B	1.020473	0.885300	0.129652	0.098*
H51C	1.081150	0.782071	0.138165	0.098*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0308 (4)	0.0229 (4)	0.0316 (4)	−0.0034 (3)	−0.0017 (3)	−0.0053 (3)
O2	0.0346 (4)	0.0310 (4)	0.0244 (4)	−0.0029 (4)	−0.0022 (3)	−0.0055 (3)
N1	0.0303 (5)	0.0227 (4)	0.0226 (4)	−0.0058 (4)	−0.0006 (4)	−0.0074 (4)
N2	0.0297 (5)	0.0251 (4)	0.0228 (5)	−0.0050 (4)	−0.0019 (4)	−0.0075 (4)
N3	0.0328 (5)	0.0262 (5)	0.0241 (5)	−0.0088 (4)	−0.0024 (4)	−0.0070 (4)
N4	0.0278 (4)	0.0240 (4)	0.0237 (5)	−0.0044 (4)	−0.0022 (4)	−0.0068 (4)
N5	0.0458 (7)	0.0300 (6)	0.0536 (8)	−0.0030 (5)	0.0108 (6)	0.0007 (5)
N6	0.0464 (7)	0.0388 (6)	0.0517 (8)	−0.0073 (6)	0.0050 (6)	0.0067 (6)
C1	0.0315 (5)	0.0248 (5)	0.0230 (5)	−0.0046 (4)	−0.0009 (4)	−0.0078 (4)
C2	0.0451 (7)	0.0297 (6)	0.0270 (6)	−0.0103 (5)	0.0010 (5)	−0.0120 (5)
C3	0.0430 (6)	0.0273 (5)	0.0275 (6)	−0.0102 (5)	−0.0015 (5)	−0.0103 (5)
C4	0.0301 (5)	0.0214 (5)	0.0244 (5)	−0.0051 (4)	−0.0025 (4)	−0.0062 (4)
C5	0.0265 (5)	0.0230 (5)	0.0256 (5)	−0.0041 (4)	−0.0028 (4)	−0.0066 (4)
C6	0.0267 (5)	0.0248 (5)	0.0231 (5)	−0.0036 (4)	−0.0025 (4)	−0.0061 (4)
C7	0.0281 (5)	0.0315 (6)	0.0243 (5)	−0.0077 (5)	−0.0002 (4)	−0.0072 (5)
C8	0.0309 (5)	0.0335 (6)	0.0222 (5)	−0.0056 (5)	0.0002 (4)	−0.0082 (5)
C9	0.0287 (5)	0.0258 (5)	0.0240 (5)	−0.0027 (4)	−0.0026 (4)	−0.0071 (4)
C10	0.0323 (5)	0.0263 (5)	0.0240 (5)	−0.0040 (4)	−0.0032 (4)	−0.0073 (4)
C11	0.0339 (6)	0.0281 (5)	0.0250 (5)	−0.0048 (5)	−0.0044 (5)	−0.0083 (4)

C12	0.0417 (7)	0.0355 (6)	0.0280 (6)	−0.0111 (5)	−0.0069 (5)	−0.0091 (5)
C13	0.0386 (6)	0.0351 (6)	0.0308 (6)	−0.0118 (5)	−0.0062 (5)	−0.0107 (5)
C14	0.0324 (5)	0.0251 (5)	0.0285 (6)	−0.0063 (4)	−0.0035 (5)	−0.0087 (4)
C15	0.0277 (5)	0.0227 (5)	0.0270 (5)	−0.0051 (4)	−0.0025 (4)	−0.0069 (4)
C16	0.0252 (5)	0.0229 (5)	0.0250 (5)	−0.0037 (4)	−0.0020 (4)	−0.0053 (4)
C17	0.0256 (5)	0.0242 (5)	0.0256 (5)	−0.0048 (4)	−0.0006 (4)	−0.0044 (4)
C18	0.0264 (5)	0.0264 (5)	0.0238 (5)	−0.0039 (4)	0.0002 (4)	−0.0059 (4)
C19	0.0256 (5)	0.0238 (5)	0.0236 (5)	−0.0023 (4)	−0.0004 (4)	−0.0059 (4)
C20	0.0290 (5)	0.0251 (5)	0.0227 (5)	−0.0032 (4)	−0.0009 (4)	−0.0071 (4)
C21	0.0289 (5)	0.0266 (5)	0.0256 (5)	−0.0062 (4)	0.0013 (4)	−0.0102 (4)
C22	0.0375 (6)	0.0303 (6)	0.0303 (6)	−0.0087 (5)	−0.0032 (5)	−0.0063 (5)
C23	0.0463 (7)	0.0291 (6)	0.0406 (7)	−0.0117 (5)	0.0022 (6)	−0.0059 (5)
C24	0.0380 (7)	0.0378 (7)	0.0496 (8)	−0.0173 (6)	0.0082 (6)	−0.0198 (6)
C25	0.0302 (6)	0.0460 (7)	0.0463 (8)	−0.0084 (5)	−0.0011 (6)	−0.0252 (6)
C26	0.0308 (6)	0.0334 (6)	0.0328 (6)	−0.0036 (5)	−0.0025 (5)	−0.0146 (5)
C27	0.0324 (6)	0.0347 (6)	0.0242 (5)	−0.0088 (5)	−0.0044 (5)	−0.0084 (5)
C28	0.0312 (6)	0.0395 (7)	0.0312 (6)	−0.0064 (5)	−0.0076 (5)	−0.0061 (5)
C29	0.0402 (7)	0.0565 (9)	0.0297 (7)	−0.0134 (6)	−0.0135 (6)	−0.0006 (6)
C30	0.0581 (9)	0.0730 (11)	0.0286 (7)	−0.0243 (8)	−0.0086 (7)	−0.0167 (7)
C31	0.0709 (10)	0.0573 (9)	0.0370 (8)	−0.0205 (8)	−0.0013 (7)	−0.0256 (7)
C32	0.0537 (8)	0.0374 (7)	0.0320 (7)	−0.0110 (6)	−0.0038 (6)	−0.0139 (5)
C33	0.0295 (5)	0.0276 (5)	0.0239 (5)	−0.0075 (4)	−0.0009 (4)	−0.0079 (4)
C34	0.0327 (6)	0.0314 (6)	0.0412 (7)	−0.0070 (5)	0.0012 (5)	−0.0153 (5)
C35	0.0499 (8)	0.0330 (6)	0.0470 (8)	−0.0116 (6)	0.0020 (6)	−0.0193 (6)
C36	0.0509 (8)	0.0459 (8)	0.0363 (7)	−0.0257 (7)	−0.0007 (6)	−0.0140 (6)
C37	0.0332 (6)	0.0545 (8)	0.0392 (7)	−0.0189 (6)	−0.0025 (6)	−0.0072 (6)
C38	0.0301 (6)	0.0364 (6)	0.0413 (7)	−0.0054 (5)	−0.0036 (5)	−0.0076 (6)
C39	0.0349 (6)	0.0239 (5)	0.0237 (5)	−0.0080 (4)	0.0015 (5)	−0.0081 (4)
C40	0.0376 (6)	0.0368 (6)	0.0296 (6)	−0.0028 (5)	−0.0023 (5)	−0.0121 (5)
C41	0.0533 (8)	0.0402 (7)	0.0308 (7)	−0.0056 (6)	−0.0090 (6)	−0.0134 (6)
C42	0.0548 (8)	0.0362 (7)	0.0292 (6)	−0.0141 (6)	0.0052 (6)	−0.0165 (5)
C43	0.0393 (7)	0.0483 (8)	0.0418 (7)	−0.0106 (6)	0.0071 (6)	−0.0272 (7)
C44	0.0352 (6)	0.0403 (7)	0.0374 (7)	−0.0039 (5)	−0.0009 (5)	−0.0204 (6)
C45	0.0650 (10)	0.0410 (8)	0.0440 (8)	−0.0082 (7)	0.0077 (8)	−0.0101 (7)
C46	0.0550 (9)	0.0366 (7)	0.0508 (9)	−0.0091 (6)	0.0013 (7)	−0.0117 (6)
C47	0.0415 (7)	0.0234 (6)	0.0466 (8)	−0.0005 (5)	0.0051 (6)	0.0006 (5)
C48	0.0431 (8)	0.0367 (7)	0.0486 (8)	0.0037 (6)	−0.0048 (6)	0.0013 (6)
C49	0.0368 (7)	0.0340 (7)	0.0629 (10)	0.0013 (6)	−0.0042 (7)	−0.0005 (7)
C50	0.0418 (8)	0.0402 (8)	0.0829 (13)	−0.0060 (7)	−0.0022 (8)	0.0046 (8)
C51	0.0553 (10)	0.0607 (10)	0.0467 (9)	0.0059 (8)	0.0061 (8)	0.0095 (8)

Geometric parameters (Å, º)

O1—C17	1.4214 (14)	C23—C24	1.384 (2)
O1—H1O	0.973 (17)	C23—H23	0.9500
O2—C18	1.4016 (14)	C24—C25	1.375 (2)
O2—H2O	0.927 (17)	C24—H24	0.9500
N1—C1	1.3692 (14)	C25—C26	1.3909 (17)

211	N1—C4	1.3797 (14)	C25—H25	0.9500
212	N1—H1N	0.925 (15)	C26—H26	0.9500
213	N2—C9	1.3737 (14)	C27—C28	1.3929 (18)
214	N2—C6	1.3740 (14)	C27—C32	1.3986 (17)
215	N3—C14	1.3714 (14)	C28—C29	1.3916 (18)
216	N3—C11	1.3811 (15)	C28—H28	0.9500
217	N3—H3N	0.915 (16)	C29—C30	1.382 (2)
218	N4—C19	1.3565 (14)	C29—H29	0.9500
219	N4—C16	1.3639 (14)	C30—C31	1.381 (2)
220	N5—C49	1.331 (2)	C30—H30	0.9500
221	N5—C45	1.340 (2)	C31—C32	1.3843 (19)
222	N6—C47	1.3669 (18)	C31—H31	0.9500
223	N6—C51	1.437 (2)	C32—H32	0.9500
224	N6—C50	1.450 (2)	C33—C34	1.3867 (17)
225	C1—C20	1.4062 (15)	C33—C38	1.3910 (17)
226	C1—C2	1.4284 (16)	C34—C35	1.3924 (17)
227	C2—C3	1.3602 (17)	C34—H34	0.9500
228	C2—H2	0.9500	C35—C36	1.381 (2)
229	C3—C4	1.4232 (16)	C35—H35	0.9500
230	C3—H3	0.9500	C36—C37	1.381 (2)
231	C4—C5	1.3970 (15)	C36—H36	0.9500
232	C5—C6	1.4101 (16)	C37—C38	1.3891 (19)
233	C5—C21	1.4958 (15)	C37—H37	0.9500
234	C6—C7	1.4478 (16)	C38—H38	0.9500
235	C7—C8	1.3508 (16)	C39—C40	1.3840 (18)
236	C7—H7	0.9500	C39—C44	1.3905 (17)
237	C8—C9	1.4445 (16)	C40—C41	1.3879 (17)
238	C8—H8	0.9500	C40—H40	0.9500
239	C9—C10	1.4119 (16)	C41—C42	1.384 (2)
240	C10—C11	1.3977 (16)	C41—H41	0.9500
241	C10—C27	1.4895 (16)	C42—C43	1.368 (2)
242	C11—C12	1.4233 (16)	C42—H42	0.9500
243	C12—C13	1.3651 (18)	C43—C44	1.3864 (18)
244	C12—H12	0.9500	C43—H43	0.9500
245	C13—C14	1.4243 (17)	C44—H44	0.9500
246	C13—H13	0.9500	C45—C46	1.377 (2)
247	C14—C15	1.4094 (16)	C45—H45	0.9500
248	C15—C16	1.3846 (16)	C46—C47	1.402 (2)
249	C15—C33	1.4977 (15)	C46—H46	0.9500
250	C16—C17	1.5166 (16)	C47—C48	1.402 (2)
251	C17—C18	1.5380 (16)	C48—C49	1.383 (2)
252	C17—H17	1.0000	C48—H48	0.9500
253	C18—C19	1.5298 (15)	C49—H49	0.9500
254	C18—H18	1.0000	C50—H50A	0.9800
255	C19—C20	1.4008 (15)	C50—H50B	0.9800
256	C20—C39	1.5008 (15)	C50—H50C	0.9800
257	C21—C26	1.3937 (17)	C51—H51A	0.9800
258	C21—C22	1.3951 (17)	C51—H51B	0.9800

C22—C23	1.3884 (17)	C51—H51C	0.9800	
C22—H22	0.9500			
C17—O1—H1O	103.8 (9)	C25—C24—H24	120.2	
C18—O2—H2O	105.0 (10)	C23—C24—H24	120.2	
C1—N1—C4	110.47 (9)	C24—C25—C26	120.52 (13)	
C1—N1—H1N	123.8 (9)	C24—C25—H25	119.7	
C4—N1—H1N	125.7 (9)	C26—C25—H25	119.7	
C9—N2—C6	104.78 (9)	C25—C26—C21	120.38 (12)	
C14—N3—C11	110.47 (10)	C25—C26—H26	119.8	
C14—N3—H3N	126.2 (10)	C21—C26—H26	119.8	
C11—N3—H3N	123.2 (10)	C28—C27—C32	118.61 (12)	
C19—N4—C16	108.59 (9)	C28—C27—C10	120.80 (11)	
C49—N5—C45	115.86 (13)	C32—C27—C10	120.58 (11)	
C47—N6—C51	120.56 (15)	C29—C28—C27	120.15 (13)	
C47—N6—C50	120.85 (15)	C29—C28—H28	119.9	
C51—N6—C50	118.52 (14)	C27—C28—H28	119.9	
N1—C1—C20	127.44 (10)	C30—C29—C28	120.47 (14)	
N1—C1—C2	106.31 (10)	C30—C29—H29	119.8	
C20—C1—C2	126.24 (10)	C28—C29—H29	119.8	
C3—C2—C1	108.53 (10)	C31—C30—C29	119.90 (13)	
C3—C2—H2	125.7	C31—C30—H30	120.1	
C1—C2—H2	125.7	C29—C30—H30	120.1	
C2—C3—C4	108.18 (10)	C30—C31—C32	119.99 (14)	
C2—C3—H3	125.9	C30—C31—H31	120.0	
C4—C3—H3	125.9	C32—C31—H31	120.0	
N1—C4—C5	125.72 (10)	C31—C32—C27	120.88 (14)	
N1—C4—C3	106.47 (10)	C31—C32—H32	119.6	
C5—C4—C3	127.81 (10)	C27—C32—H32	119.6	
C4—C5—C6	125.26 (10)	C34—C33—C38	118.83 (11)	
C4—C5—C21	117.43 (10)	C34—C33—C15	120.39 (10)	
C6—C5—C21	117.30 (10)	C38—C33—C15	120.75 (11)	
N2—C6—C5	125.47 (10)	C33—C34—C35	120.29 (12)	
N2—C6—C7	110.91 (9)	C33—C34—H34	119.9	
C5—C6—C7	123.59 (10)	C35—C34—H34	119.9	
C8—C7—C6	106.56 (10)	C36—C35—C34	120.24 (13)	
C8—C7—H7	126.7	C36—C35—H35	119.9	
C6—C7—H7	126.7	C34—C35—H35	119.9	
C7—C8—C9	106.62 (10)	C37—C36—C35	120.02 (12)	
C7—C8—H8	126.7	C37—C36—H36	120.0	
C9—C8—H8	126.7	C35—C36—H36	120.0	
N2—C9—C10	125.32 (10)	C36—C37—C38	119.72 (13)	
N2—C9—C8	111.05 (10)	C36—C37—H37	120.1	
C10—C9—C8	123.63 (10)	C38—C37—H37	120.1	
C11—C10—C9	124.84 (11)	C37—C38—C33	120.87 (13)	
C11—C10—C27	116.86 (10)	C37—C38—H38	119.6	
C9—C10—C27	118.30 (10)	C33—C38—H38	119.6	
N3—C11—C10	125.39 (10)	C40—C39—C44	118.43 (11)	

N3—C11—C12	106.27 (10)	C40—C39—C20	121.53 (10)
C10—C11—C12	128.27 (11)	C44—C39—C20	120.02 (11)
C13—C12—C11	108.35 (11)	C39—C40—C41	120.53 (12)
C13—C12—H12	125.8	C39—C40—H40	119.7
C11—C12—H12	125.8	C41—C40—H40	119.7
C12—C13—C14	108.32 (11)	C42—C41—C40	120.31 (13)
C12—C13—H13	125.8	C42—C41—H41	119.8
C14—C13—H13	125.8	C40—C41—H41	119.8
N3—C14—C15	127.08 (10)	C43—C42—C41	119.60 (12)
N3—C14—C13	106.53 (10)	C43—C42—H42	120.2
C15—C14—C13	126.34 (10)	C41—C42—H42	120.2
C16—C15—C14	126.44 (10)	C42—C43—C44	120.28 (12)
C16—C15—C33	118.94 (10)	C42—C43—H43	119.9
C14—C15—C33	114.62 (10)	C44—C43—H43	119.9
N4—C16—C15	126.10 (10)	C43—C44—C39	120.86 (13)
N4—C16—C17	112.44 (9)	C43—C44—H44	119.6
C15—C16—C17	121.45 (10)	C39—C44—H44	119.6
O1—C17—C16	108.57 (9)	N5—C45—C46	124.66 (17)
O1—C17—C18	112.64 (9)	N5—C45—H45	117.7
C16—C17—C18	101.86 (9)	C46—C45—H45	117.7
O1—C17—H17	111.1	C45—C46—C47	119.36 (16)
C16—C17—H17	111.1	C45—C46—H46	120.3
C18—C17—H17	111.1	C47—C46—H46	120.3
O2—C18—C19	117.07 (9)	N6—C47—C46	121.97 (15)
O2—C18—C17	115.00 (9)	N6—C47—C48	121.83 (15)
C19—C18—C17	102.30 (9)	C46—C47—C48	116.18 (13)
O2—C18—H18	107.3	C49—C48—C47	119.59 (16)
C19—C18—H18	107.3	C49—C48—H48	120.2
C17—C18—H18	107.3	C47—C48—H48	120.2
N4—C19—C20	125.15 (10)	N5—C49—C48	124.33 (16)
N4—C19—C18	112.16 (9)	N5—C49—H49	117.8
C20—C19—C18	122.51 (10)	C48—C49—H49	117.8
C19—C20—C1	126.08 (10)	N6—C50—H50A	109.5
C19—C20—C39	118.64 (10)	N6—C50—H50B	109.5
C1—C20—C39	115.24 (10)	H50A—C50—H50B	109.5
C26—C21—C22	118.64 (11)	N6—C50—H50C	109.5
C26—C21—C5	121.07 (11)	H50A—C50—H50C	109.5
C22—C21—C5	120.27 (11)	H50B—C50—H50C	109.5
C23—C22—C21	120.46 (12)	N6—C51—H51A	109.5
C23—C22—H22	119.8	N6—C51—H51B	109.5
C21—C22—H22	119.8	H51A—C51—H51B	109.5
C24—C23—C22	120.31 (13)	N6—C51—H51C	109.5
C24—C23—H23	119.8	H51A—C51—H51C	109.5
C22—C23—H23	119.8	H51B—C51—H51C	109.5
C25—C24—C23	119.69 (12)		

C4—N1—C1—C20	176.83 (11)	C18—C19—C20—C1	−179.31 (11)
C4—N1—C1—C2	−2.11 (13)	N4—C19—C20—C39	−171.75 (10)

N1—C1—C2—C3	1.49 (14)	C18—C19—C20—C39	2.90 (16)
C20—C1—C2—C3	−177.46 (12)	N1—C1—C20—C19	2.4 (2)
C1—C2—C3—C4	−0.35 (15)	C2—C1—C20—C19	−178.88 (12)
C1—N1—C4—C5	−179.30 (11)	N1—C1—C20—C39	−179.76 (11)
C1—N1—C4—C3	1.91 (13)	C2—C1—C20—C39	−1.02 (18)
C2—C3—C4—N1	−0.92 (14)	C4—C5—C21—C26	−60.11 (15)
C2—C3—C4—C5	−179.68 (12)	C6—C5—C21—C26	121.08 (12)
N1—C4—C5—C6	−5.13 (19)	C4—C5—C21—C22	121.51 (12)
C3—C4—C5—C6	173.41 (12)	C6—C5—C21—C22	−57.30 (15)
N1—C4—C5—C21	176.17 (10)	C26—C21—C22—C23	−0.72 (18)
C3—C4—C5—C21	−5.30 (18)	C5—C21—C22—C23	177.70 (11)
C9—N2—C6—C5	−175.53 (11)	C21—C22—C23—C24	0.0 (2)
C9—N2—C6—C7	2.71 (12)	C22—C23—C24—C25	0.6 (2)
C4—C5—C6—N2	−8.48 (18)	C23—C24—C25—C26	−0.5 (2)
C21—C5—C6—N2	170.23 (10)	C24—C25—C26—C21	−0.30 (18)
C4—C5—C6—C7	173.50 (11)	C22—C21—C26—C25	0.88 (17)
C21—C5—C6—C7	−7.80 (16)	C5—C21—C26—C25	−177.52 (10)
N2—C6—C7—C8	−1.69 (13)	C11—C10—C27—C28	−122.22 (13)
C5—C6—C7—C8	176.58 (11)	C9—C10—C27—C28	58.57 (16)
C6—C7—C8—C9	−0.05 (13)	C11—C10—C27—C32	57.43 (16)
C6—N2—C9—C10	176.68 (11)	C9—C10—C27—C32	−121.78 (13)
C6—N2—C9—C8	−2.75 (12)	C32—C27—C28—C29	−0.18 (18)
C7—C8—C9—N2	1.78 (13)	C10—C27—C28—C29	179.47 (11)
C7—C8—C9—C10	−177.66 (11)	C27—C28—C29—C30	−0.2 (2)
N2—C9—C10—C11	9.00 (19)	C28—C29—C30—C31	0.3 (2)
C8—C9—C10—C11	−171.64 (11)	C29—C30—C31—C32	−0.1 (2)
N2—C9—C10—C27	−171.86 (11)	C30—C31—C32—C27	−0.3 (2)
C8—C9—C10—C27	7.50 (17)	C28—C27—C32—C31	0.4 (2)
C14—N3—C11—C10	174.45 (11)	C10—C27—C32—C31	−179.25 (13)
C14—N3—C11—C12	−2.57 (13)	C16—C15—C33—C34	91.51 (14)
C9—C10—C11—N3	5.97 (19)	C14—C15—C33—C34	−89.12 (14)
C27—C10—C11—N3	−173.17 (11)	C16—C15—C33—C38	−90.45 (15)
C9—C10—C11—C12	−177.67 (12)	C14—C15—C33—C38	88.92 (14)
C27—C10—C11—C12	3.18 (19)	C38—C33—C34—C35	−1.03 (19)
N3—C11—C12—C13	1.97 (14)	C15—C33—C34—C35	177.04 (12)
C10—C11—C12—C13	−174.93 (12)	C33—C34—C35—C36	−0.6 (2)
C11—C12—C13—C14	−0.69 (15)	C34—C35—C36—C37	1.5 (2)
C11—N3—C14—C15	−175.45 (11)	C35—C36—C37—C38	−0.7 (2)
C11—N3—C14—C13	2.16 (13)	C36—C37—C38—C33	−0.9 (2)
C12—C13—C14—N3	−0.87 (14)	C34—C33—C38—C37	1.8 (2)
C12—C13—C14—C15	176.76 (12)	C15—C33—C38—C37	−176.26 (12)
N3—C14—C15—C16	−7.9 (2)	C19—C20—C39—C40	−110.08 (13)
C13—C14—C15—C16	174.91 (12)	C1—C20—C39—C40	71.89 (14)
N3—C14—C15—C33	172.75 (11)	C19—C20—C39—C44	71.77 (15)
C13—C14—C15—C33	−4.41 (17)	C1—C20—C39—C44	−106.26 (13)
C19—N4—C16—C15	−169.25 (11)	C44—C39—C40—C41	0.02 (18)
C19—N4—C16—C17	9.77 (12)	C20—C39—C40—C41	−178.16 (11)
C14—C15—C16—N4	−4.65 (19)	C39—C40—C41—C42	0.2 (2)

C33—C15—C16—N4	174.64 (10)	C40—C41—C42—C43	−0.4 (2)
C14—C15—C16—C17	176.41 (11)	C41—C42—C43—C44	0.3 (2)
C33—C15—C16—C17	−4.31 (16)	C42—C43—C44—C39	0.0 (2)
N4—C16—C17—O1	103.05 (10)	C40—C39—C44—C43	−0.12 (19)
C15—C16—C17—O1	−77.88 (13)	C20—C39—C44—C43	178.09 (12)
N4—C16—C17—C18	−16.00 (12)	C49—N5—C45—C46	−0.4 (2)
C15—C16—C17—C18	163.07 (10)	N5—C45—C46—C47	−0.6 (2)
O1—C17—C18—O2	26.65 (13)	C51—N6—C47—C46	175.09 (14)
C16—C17—C18—O2	142.76 (9)	C50—N6—C47—C46	−8.1 (2)
O1—C17—C18—C19	−101.33 (10)	C51—N6—C47—C48	−3.3 (2)
C16—C17—C18—C19	14.78 (10)	C50—N6—C47—C48	173.57 (13)
C16—N4—C19—C20	176.25 (10)	C45—C46—C47—N6	−176.90 (14)
C16—N4—C19—C18	1.12 (12)	C45—C46—C47—C48	1.6 (2)
O2—C18—C19—N4	−137.49 (10)	N6—C47—C48—C49	176.77 (13)
C17—C18—C19—N4	−10.83 (12)	C46—C47—C48—C49	−1.7 (2)
O2—C18—C19—C20	47.23 (15)	C45—N5—C49—C48	0.2 (2)
C17—C18—C19—C20	173.89 (10)	C47—C48—C49—N5	0.9 (2)
N4—C19—C20—C1	6.04 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N5	0.973 (17)	1.727 (17)	2.6968 (14)	174.1 (14)
O2—H2*O*···O1^{i}	0.927 (17)	1.882 (17)	2.7798 (12)	162.5 (14)
N1—H1*N*···N2	0.925 (15)	2.346 (15)	2.9064 (13)	118.7 (11)
N1—H1*N*···N4	0.925 (15)	2.383 (15)	2.9518 (13)	119.6 (11)
N3—H3*N*···N2	0.915 (16)	2.292 (16)	2.8868 (13)	122.3 (12)
N3—H3*N*···N4	0.915 (16)	2.458 (15)	2.9766 (14)	116.1 (12)
C37—H37···O2^{ii}	0.95	2.51	3.3840 (16)	153
C38—H38···C48^{ii}	0.95	2.77	3.6779 (19)	161
C50—H50*B*···N4^{ii}	0.98	2.57	3.544 (2)	171

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

[*cis*-7,8-*vic*-Dihydroxy-5,10,15,20-tetraphenylchlorinato(2-)]zinc(II)–ethylenediamine–methanol (1/1/0.136) (2PhZn)

Crystal data

$[Zn(C_{44}H_{30}N_4O_2)]\cdot C_2H_8N_2\cdot 0.136CH_4O$	$F(000) = 1618$
$M_r = 776.57$	$D_x = 1.397$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 10.1249$ (3) Å	Cell parameters from 9950 reflections
$b = 13.5400$ (4) Å	$\theta = 3.3$–$79.4°$
$c = 27.0447$ (8) Å	$\mu = 1.32$ mm^{-1}
$\beta = 95.1464$ (11)°	$T = 150$ K
$V = 3692.64$ (19) Å^3	Block, black
$Z = 4$	0.27 × 0.25 × 0.18 mm

Data collection

Bruker AXS D8 Quest diffractometer with PhotonIII-C14 charge-integrating and photon counting pixel array detector
Radiation source: I-mu-S microsource X-ray tube
Laterally graded multilayer (Goebel) mirror monochromator
Detector resolution: 7.4074 pixels mm^{-1}
ω and phi scans

Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.606, T_{max} = 0.754
21319 measured reflections
7551 independent reflections
7037 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 79.5°, θ_{min} = 3.3°
h = −12→11
k = −16→15
l = −29→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.088
S = 1.04
7551 reflections
549 parameters
17 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 1.8191P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.44 e $Å^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. The not metal coordinated amino group of an ethylene diamine ligand was refined as disordered. The C—N bonds were restrained to be similar in length. Amine H atom positions were refined and N—H distances were restrained to 0.88 (2) Angstrom. Equivalent H···H and C···H distances were restrained to be similar to each other. Subject to these conditions the occupancy ratio refined to 0.882 (12) to 0.118 (12).
A partially occupied methanol molecule is located nearby the major disordered amino group and H-bonded to it. The hydroxyl H atom was restrained to hydrogen bond to a porphyrin N atom of a neighboring complex. Subject to these conditions the occupancy rate refined to 0.136 (4).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zn1	0.70722 (2)	0.44915 (2)	0.36168 (2)	0.01832 (7)	
O1	0.62030 (12)	0.47166 (9)	0.54271 (4)	0.0308 (2)	
H1	0.6482 (10)	0.4528 (15)	0.5775 (9)	0.046*	
O2	0.56022 (12)	0.65470 (9)	0.51056 (4)	0.0328 (3)	
H2A	0.4922 (17)	0.6092 (15)	0.4949 (8)	0.049*	
N1	0.73694 (12)	0.51455 (9)	0.43385 (4)	0.0204 (2)	
N2	0.68821 (12)	0.58909 (9)	0.33244 (4)	0.0202 (2)	
N3	0.73798 (12)	0.39779 (9)	0.29110 (4)	0.0192 (2)	
N4	0.80823 (12)	0.32619 (9)	0.39012 (4)	0.0201 (2)	
C1	0.76495 (14)	0.46245 (11)	0.47647 (5)	0.0211 (3)	
C2	0.72768 (15)	0.51995 (12)	0.52170 (5)	0.0247 (3)	

H2	0.805841	0.525874	0.546886	0.030*
C3	0.68812 (16)	0.62230 (12)	0.49999 (5)	0.0256 (3)
H3	0.755257	0.671994	0.513274	0.031*
C4	0.70045 (14)	0.60845 (11)	0.44448 (5)	0.0217 (3)
C5	0.67805 (14)	0.68419 (11)	0.41046 (5)	0.0221 (3)
C6	0.67411 (14)	0.67471 (11)	0.35816 (5)	0.0214 (3)
C7	0.65058 (16)	0.75574 (11)	0.32390 (6)	0.0273 (3)
H7	0.638690	0.823086	0.332289	0.033*
C8	0.64860 (16)	0.71772 (11)	0.27743 (6)	0.0274 (3)
H8	0.635401	0.753563	0.247193	0.033*
C9	0.67021 (14)	0.61307 (11)	0.28244 (5)	0.0216 (3)
C10	0.66810 (14)	0.54655 (11)	0.24303 (5)	0.0212 (3)
C11	0.69457 (14)	0.44448 (11)	0.24758 (5)	0.0207 (3)
C12	0.68755 (15)	0.37502 (12)	0.20741 (5)	0.0255 (3)
H12	0.658048	0.388023	0.173700	0.031*
C13	0.73118 (15)	0.28702 (11)	0.22677 (5)	0.0246 (3)
H13	0.737737	0.226813	0.209116	0.030*
C14	0.76550 (14)	0.30210 (11)	0.27891 (5)	0.0200 (3)
C15	0.82584 (14)	0.23173 (11)	0.31236 (5)	0.0205 (3)
C16	0.85130 (14)	0.24664 (11)	0.36358 (5)	0.0221 (3)
C17	0.92352 (17)	0.17956 (12)	0.39728 (6)	0.0295 (3)
H17	0.965688	0.120098	0.388676	0.035*
C18	0.92010 (17)	0.21707 (13)	0.44358 (6)	0.0304 (3)
H18	0.958959	0.188554	0.473521	0.036*
C19	0.84659 (14)	0.30825 (11)	0.43899 (5)	0.0227 (3)
C20	0.81842 (14)	0.36856 (11)	0.47976 (5)	0.0222 (3)
C21	0.66512 (16)	0.78725 (11)	0.42976 (5)	0.0257 (3)
C22	0.54419 (18)	0.83574 (13)	0.42621 (7)	0.0343 (4)
H22	0.466488	0.801861	0.413263	0.041*
C23	0.5353 (2)	0.93293 (15)	0.44131 (8)	0.0464 (5)
H23	0.451780	0.965418	0.438633	0.056*
C24	0.6477 (2)	0.98287 (14)	0.46029 (8)	0.0492 (5)
H24	0.641627	1.049810	0.470365	0.059*
C25	0.7680 (2)	0.93559 (14)	0.46454 (8)	0.0478 (5)
H25	0.845182	0.969597	0.477894	0.057*
C26	0.77712 (19)	0.83764 (13)	0.44927 (7)	0.0370 (4)
H26	0.860658	0.805211	0.452263	0.044*
C27	0.63996 (15)	0.58672 (11)	0.19152 (5)	0.0222 (3)
C28	0.51396 (15)	0.62173 (12)	0.17514 (6)	0.0271 (3)
H28	0.445274	0.620404	0.196869	0.033*
C29	0.48819 (17)	0.65857 (12)	0.12724 (6)	0.0303 (3)
H29	0.401410	0.680622	0.116268	0.036*
C30	0.58747 (18)	0.66344 (12)	0.09542 (6)	0.0317 (3)
H30	0.569838	0.689923	0.062973	0.038*
C31	0.71357 (18)	0.62906 (15)	0.11152 (6)	0.0376 (4)
H31	0.782543	0.632158	0.089955	0.045*
C32	0.73909 (16)	0.59025 (14)	0.15896 (6)	0.0323 (4)
H32	0.825091	0.565819	0.169340	0.039*

C33	0.86940 (14)	0.13604 (11)	0.29145 (5)	0.0213 (3)	
C34	0.95353 (15)	0.13496 (11)	0.25326 (5)	0.0233 (3)	
H34	0.982623	0.195715	0.240408	0.028*	
C35	0.99553 (16)	0.04640 (12)	0.23368 (6)	0.0274 (3)	
H35	1.052341	0.047091	0.207570	0.033*	
C36	0.95451 (17)	−0.04261 (12)	0.25227 (7)	0.0313 (3)	
H36	0.982821	−0.103132	0.238932	0.038*	
C37	0.87209 (17)	−0.04298 (12)	0.29037 (7)	0.0309 (3)	
H37	0.844492	−0.104022	0.303371	0.037*	
C38	0.82924 (16)	0.04546 (11)	0.30982 (6)	0.0263 (3)	
H38	0.772140	0.044189	0.335840	0.032*	
C39	0.85297 (15)	0.32409 (12)	0.53006 (5)	0.0237 (3)	
C40	0.78919 (17)	0.23834 (13)	0.54385 (6)	0.0313 (3)	
H40	0.720053	0.210821	0.522050	0.038*	
C41	0.8254 (2)	0.19268 (15)	0.58903 (7)	0.0394 (4)	
H41	0.782257	0.133703	0.597723	0.047*	
C42	0.92487 (19)	0.23337 (16)	0.62148 (6)	0.0419 (5)	
H42	0.949622	0.202435	0.652456	0.050*	
C43	0.98729 (17)	0.31836 (16)	0.60868 (6)	0.0381 (4)	
H43	1.054483	0.346547	0.631109	0.046*	
C44	0.95294 (15)	0.36380 (13)	0.56300 (6)	0.0291 (3)	
H44	0.997849	0.422012	0.554307	0.035*	
N5	0.50664 (13)	0.40837 (10)	0.36913 (5)	0.0271 (3)	
H5A	0.480 (2)	0.4337 (14)	0.3967 (7)	0.041*	
H5B	0.509 (2)	0.3447 (11)	0.3761 (8)	0.041*	
C45	0.40746 (17)	0.42549 (15)	0.32609 (7)	0.0385 (4)	
H45A	0.329199	0.383047	0.329539	0.046*	
H45B	0.446349	0.405890	0.295254	0.046*	
C46	0.36344 (16)	0.53096 (14)	0.32166 (6)	0.0326 (4)	0.882 (12)
H46A	0.442264	0.574411	0.322569	0.039*	0.882 (12)
H46B	0.311072	0.540812	0.289330	0.039*	0.882 (12)
N6	0.2830 (4)	0.5585 (2)	0.36180 (8)	0.0361 (8)	0.882 (12)
H6A	0.2073 (19)	0.5235 (18)	0.3589 (9)	0.054*	0.882 (12)
H6B	0.257 (3)	0.6185 (13)	0.3606 (9)	0.054*	0.882 (12)
C46B	0.36344 (16)	0.53096 (14)	0.32166 (6)	0.0326 (4)	0.118 (12)
H46C	0.428985	0.567714	0.303754	0.039*	0.118 (12)
H46D	0.277978	0.532993	0.300800	0.039*	0.118 (12)
N6B	0.346 (3)	0.5839 (15)	0.3685 (6)	0.046 (5)	0.118 (12)
H6C	0.305 (16)	0.640 (6)	0.3622 (17)	0.068*	0.118 (12)
H6D	0.425 (5)	0.604 (12)	0.382 (4)	0.068*	0.118 (12)
O3	0.0708 (14)	0.4152 (11)	0.3732 (6)	0.070 (4)	0.136 (4)
H3O	−0.010618	0.402558	0.371916	0.084*	0.136 (4)
C47	0.1402 (18)	0.3301 (15)	0.3759 (7)	0.060 (5)	0.136 (4)
H47A	0.117547	0.291039	0.345850	0.072*	0.136 (4)
H47B	0.118247	0.292480	0.405043	0.072*	0.136 (4)
H47C	0.235366	0.344884	0.378874	0.072*	0.136 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02239 (11)	0.01794 (11)	0.01494 (10)	0.00134 (6)	0.00332 (7)	−0.00039 (6)
O1	0.0343 (6)	0.0355 (6)	0.0240 (6)	0.0011 (5)	0.0097 (4)	0.0021 (5)
O2	0.0390 (6)	0.0310 (6)	0.0299 (6)	0.0063 (5)	0.0107 (5)	−0.0054 (5)
N1	0.0240 (6)	0.0202 (6)	0.0175 (6)	0.0000 (4)	0.0033 (4)	−0.0014 (4)
N2	0.0242 (6)	0.0190 (6)	0.0179 (6)	0.0007 (4)	0.0041 (4)	−0.0005 (4)
N3	0.0241 (6)	0.0187 (6)	0.0153 (5)	0.0017 (4)	0.0038 (4)	0.0000 (4)
N4	0.0235 (6)	0.0220 (6)	0.0148 (5)	0.0035 (4)	0.0027 (4)	−0.0006 (4)
C1	0.0224 (7)	0.0249 (7)	0.0161 (6)	−0.0013 (5)	0.0029 (5)	−0.0024 (5)
C2	0.0277 (7)	0.0281 (8)	0.0182 (7)	0.0010 (6)	0.0019 (5)	−0.0036 (6)
C3	0.0332 (8)	0.0245 (7)	0.0191 (7)	−0.0008 (6)	0.0021 (6)	−0.0044 (6)
C4	0.0229 (6)	0.0229 (7)	0.0196 (7)	−0.0010 (5)	0.0032 (5)	−0.0048 (5)
C5	0.0238 (7)	0.0202 (7)	0.0226 (7)	0.0005 (5)	0.0040 (5)	−0.0036 (5)
C6	0.0230 (7)	0.0184 (7)	0.0233 (7)	−0.0002 (5)	0.0044 (5)	−0.0012 (5)
C7	0.0372 (8)	0.0170 (7)	0.0282 (8)	0.0009 (6)	0.0059 (6)	0.0012 (6)
C8	0.0368 (8)	0.0211 (7)	0.0249 (7)	0.0012 (6)	0.0055 (6)	0.0042 (6)
C9	0.0251 (7)	0.0203 (7)	0.0198 (7)	0.0012 (5)	0.0045 (5)	0.0031 (5)
C10	0.0229 (7)	0.0230 (7)	0.0182 (7)	0.0014 (5)	0.0038 (5)	0.0024 (5)
C11	0.0239 (7)	0.0220 (7)	0.0164 (6)	0.0013 (5)	0.0027 (5)	0.0008 (5)
C12	0.0329 (8)	0.0270 (8)	0.0163 (6)	0.0017 (6)	0.0003 (5)	−0.0013 (6)
C13	0.0322 (8)	0.0224 (7)	0.0190 (7)	0.0008 (6)	0.0008 (6)	−0.0042 (5)
C14	0.0229 (6)	0.0203 (7)	0.0172 (6)	−0.0002 (5)	0.0044 (5)	−0.0020 (5)
C15	0.0223 (6)	0.0203 (7)	0.0193 (7)	0.0012 (5)	0.0040 (5)	−0.0015 (5)
C16	0.0244 (7)	0.0225 (7)	0.0198 (7)	0.0047 (5)	0.0038 (5)	−0.0003 (5)
C17	0.0366 (8)	0.0292 (8)	0.0223 (7)	0.0136 (6)	0.0008 (6)	−0.0007 (6)
C18	0.0377 (8)	0.0332 (9)	0.0197 (7)	0.0148 (7)	−0.0009 (6)	0.0018 (6)
C19	0.0254 (7)	0.0247 (7)	0.0179 (7)	0.0034 (6)	0.0015 (5)	0.0000 (5)
C20	0.0241 (7)	0.0262 (7)	0.0162 (6)	0.0008 (5)	0.0021 (5)	−0.0002 (5)
C21	0.0355 (8)	0.0209 (7)	0.0210 (7)	0.0014 (6)	0.0048 (6)	−0.0030 (5)
C22	0.0375 (9)	0.0282 (9)	0.0377 (9)	0.0053 (7)	0.0059 (7)	−0.0034 (7)
C23	0.0566 (12)	0.0319 (10)	0.0513 (12)	0.0176 (9)	0.0074 (9)	−0.0057 (8)
C24	0.0779 (15)	0.0224 (9)	0.0467 (11)	0.0083 (9)	0.0025 (10)	−0.0114 (8)
C25	0.0609 (13)	0.0278 (9)	0.0529 (12)	−0.0050 (8)	−0.0042 (10)	−0.0136 (8)
C26	0.0414 (9)	0.0290 (9)	0.0397 (10)	0.0009 (7)	−0.0015 (7)	−0.0101 (7)
C27	0.0290 (7)	0.0188 (7)	0.0188 (7)	0.0006 (5)	0.0023 (5)	0.0021 (5)
C28	0.0280 (7)	0.0274 (8)	0.0261 (7)	0.0034 (6)	0.0027 (6)	0.0002 (6)
C29	0.0342 (8)	0.0270 (8)	0.0286 (8)	0.0055 (6)	−0.0041 (6)	0.0016 (6)
C30	0.0430 (9)	0.0290 (8)	0.0219 (7)	−0.0030 (7)	−0.0037 (6)	0.0071 (6)
C31	0.0352 (9)	0.0543 (11)	0.0239 (8)	−0.0044 (8)	0.0059 (6)	0.0111 (7)
C32	0.0269 (8)	0.0463 (10)	0.0240 (8)	0.0030 (7)	0.0039 (6)	0.0084 (7)
C33	0.0238 (7)	0.0219 (7)	0.0179 (6)	0.0036 (5)	−0.0002 (5)	−0.0017 (5)
C34	0.0266 (7)	0.0226 (7)	0.0207 (7)	0.0018 (5)	0.0032 (5)	−0.0014 (5)
C35	0.0271 (7)	0.0319 (8)	0.0236 (7)	0.0058 (6)	0.0044 (6)	−0.0044 (6)
C36	0.0329 (8)	0.0237 (8)	0.0369 (9)	0.0081 (6)	0.0015 (7)	−0.0072 (6)
C37	0.0329 (8)	0.0208 (8)	0.0390 (9)	0.0026 (6)	0.0036 (7)	0.0029 (6)
C38	0.0275 (7)	0.0250 (8)	0.0270 (8)	0.0037 (6)	0.0058 (6)	0.0022 (6)

C39	0.0260 (7)	0.0289 (8)	0.0164 (6)	0.0067 (6)	0.0038 (5)	−0.0004 (6)
C40	0.0390 (9)	0.0319 (9)	0.0230 (7)	0.0024 (7)	0.0037 (6)	0.0014 (6)
C41	0.0496 (10)	0.0411 (10)	0.0290 (8)	0.0103 (8)	0.0120 (7)	0.0109 (7)
C42	0.0438 (10)	0.0636 (13)	0.0191 (8)	0.0266 (9)	0.0067 (7)	0.0104 (8)
C43	0.0298 (8)	0.0623 (12)	0.0212 (8)	0.0162 (8)	−0.0031 (6)	−0.0050 (8)
C44	0.0247 (7)	0.0396 (9)	0.0232 (7)	0.0067 (6)	0.0024 (6)	−0.0034 (6)
N5	0.0246 (6)	0.0233 (7)	0.0341 (7)	0.0007 (5)	0.0062 (5)	0.0004 (5)
C45	0.0281 (8)	0.0444 (10)	0.0419 (10)	−0.0002 (7)	−0.0037 (7)	−0.0157 (8)
C46	0.0270 (8)	0.0478 (10)	0.0229 (8)	0.0033 (7)	0.0011 (6)	0.0014 (7)
N6	0.0404 (17)	0.0460 (14)	0.0224 (9)	0.0156 (12)	0.0061 (10)	0.0046 (8)
C46B	0.0270 (8)	0.0478 (10)	0.0229 (8)	0.0033 (7)	0.0011 (6)	0.0014 (7)
N6B	0.035 (12)	0.049 (10)	0.052 (10)	−0.002 (8)	0.002 (8)	−0.006 (7)
O3	0.064 (8)	0.067 (9)	0.078 (10)	−0.017 (7)	−0.003 (7)	0.016 (7)
C47	0.054 (10)	0.072 (12)	0.056 (10)	−0.017 (9)	0.011 (8)	−0.011 (9)

Geometric parameters (Å, º)

Zn1—N2	2.0556 (12)	C25—H25	0.9500
Zn1—N4	2.0660 (12)	C26—H26	0.9500
Zn1—N3	2.0812 (11)	C27—C32	1.394 (2)
Zn1—N5	2.1315 (13)	C27—C28	1.395 (2)
Zn1—N1	2.1399 (12)	C28—C29	1.391 (2)
O1—C2	1.4294 (19)	C28—H28	0.9500
O1—H1	0.99 (2)	C29—C30	1.382 (3)
O2—C3	1.4204 (19)	C29—H29	0.9500
O2—H2A	0.99 (3)	C30—C31	1.392 (3)
N1—C1	1.3593 (19)	C30—H30	0.9500
N1—C4	1.3618 (19)	C31—C32	1.389 (2)
N2—C6	1.3661 (18)	C31—H31	0.9500
N2—C9	1.3865 (18)	C32—H32	0.9500
N3—C14	1.3716 (18)	C33—C34	1.397 (2)
N3—C11	1.3731 (18)	C33—C38	1.397 (2)
N4—C19	1.3654 (18)	C34—C35	1.393 (2)
N4—C16	1.3863 (18)	C34—H34	0.9500
C1—C20	1.382 (2)	C35—C36	1.384 (2)
C1—C2	1.5257 (19)	C35—H35	0.9500
C2—C3	1.544 (2)	C36—C37	1.383 (3)
C2—H2	1.0000	C36—H36	0.9500
C3—C4	1.5292 (19)	C37—C38	1.393 (2)
C3—H3	1.0000	C37—H37	0.9500
C4—C5	1.383 (2)	C38—H38	0.9500
C5—C6	1.417 (2)	C39—C44	1.395 (2)
C5—C21	1.500 (2)	C39—C40	1.395 (2)
C6—C7	1.442 (2)	C40—C41	1.389 (2)
C7—C8	1.356 (2)	C40—H40	0.9500
C7—H7	0.9500	C41—C42	1.389 (3)
C8—C9	1.438 (2)	C41—H41	0.9500
C8—H8	0.9500	C42—C43	1.372 (3)

C9—C10	1.394 (2)	C42—H42	0.9500
C10—C11	1.411 (2)	C43—C44	1.396 (2)
C10—C27	1.4990 (19)	C43—H43	0.9500
C11—C12	1.434 (2)	C44—H44	0.9500
C12—C13	1.359 (2)	N5—C45	1.486 (2)
C12—H12	0.9500	N5—H5A	0.884 (15)
C13—C14	1.4364 (19)	N5—H5B	0.882 (15)
C13—H13	0.9500	C45—C46B	1.498 (3)
C14—C15	1.414 (2)	C45—C46	1.498 (3)
C15—C16	1.401 (2)	C45—H45A	0.9900
C15—C33	1.4960 (19)	C45—H45B	0.9900
C16—C17	1.439 (2)	C46—N6	1.463 (2)
C17—C18	1.354 (2)	C46—H46A	0.9900
C17—H17	0.9500	C46—H46B	0.9900
C18—C19	1.441 (2)	N6—H6A	0.898 (16)
C18—H18	0.9500	N6—H6B	0.853 (16)
C19—C20	1.421 (2)	C46B—N6B	1.479 (14)
C20—C39	1.5001 (19)	C46B—H46C	0.9900
C21—C22	1.385 (2)	C46B—H46D	0.9900
C21—C26	1.387 (2)	N6B—H6C	0.88 (2)
C22—C23	1.383 (3)	N6B—H6D	0.89 (2)
C22—H22	0.9500	O3—C47	1.35 (2)
C23—C24	1.382 (3)	O3—H3O	0.8400
C23—H23	0.9500	C47—H47A	0.9800
C24—C25	1.372 (3)	C47—H47B	0.9800
C24—H24	0.9500	C47—H47C	0.9800
C25—C26	1.394 (3)		

N2—Zn1—N4	155.81 (5)	C25—C24—H24	120.1
N2—Zn1—N3	88.38 (5)	C23—C24—H24	120.1
N4—Zn1—N3	87.85 (5)	C24—C25—C26	120.1 (2)
N2—Zn1—N5	102.59 (5)	C24—C25—H25	120.0
N4—Zn1—N5	101.54 (5)	C26—C25—H25	120.0
N3—Zn1—N5	102.84 (5)	C21—C26—C25	120.47 (18)
N2—Zn1—N1	88.29 (5)	C21—C26—H26	119.8
N4—Zn1—N1	88.25 (5)	C25—C26—H26	119.8
N3—Zn1—N1	162.66 (5)	C32—C27—C28	118.52 (14)
N5—Zn1—N1	94.49 (5)	C32—C27—C10	120.79 (13)
C2—O1—H1	109.5	C28—C27—C10	120.69 (13)
C3—O2—H2A	109.5	C29—C28—C27	120.48 (15)
C1—N1—C4	110.22 (12)	C29—C28—H28	119.8
C1—N1—Zn1	124.07 (10)	C27—C28—H28	119.8
C4—N1—Zn1	124.07 (9)	C30—C29—C28	120.72 (15)
C6—N2—C9	106.70 (12)	C30—C29—H29	119.6
C6—N2—Zn1	126.63 (10)	C28—C29—H29	119.6
C9—N2—Zn1	126.20 (10)	C29—C30—C31	119.17 (15)
C14—N3—C11	106.58 (11)	C29—C30—H30	120.4
C14—N3—Zn1	125.90 (9)	C31—C30—H30	120.4

712	C11—N3—Zn1	124.72 (9)	C32—C31—C30	120.32 (16)
713	C19—N4—C16	106.72 (12)	C32—C31—H31	119.8
714	C19—N4—Zn1	126.30 (10)	C30—C31—H31	119.8
715	C16—N4—Zn1	126.97 (9)	C31—C32—C27	120.76 (15)
716	N1—C1—C20	125.66 (13)	C31—C32—H32	119.6
717	N1—C1—C2	111.54 (12)	C27—C32—H32	119.6
718	C20—C1—C2	122.79 (13)	C34—C33—C38	118.04 (13)
719	O1—C2—C1	109.69 (12)	C34—C33—C15	120.58 (13)
720	O1—C2—C3	112.41 (12)	C38—C33—C15	121.37 (13)
721	C1—C2—C3	103.15 (12)	C35—C34—C33	121.16 (14)
722	O1—C2—H2	110.5	C35—C34—H34	119.4
723	C1—C2—H2	110.5	C33—C34—H34	119.4
724	C3—C2—H2	110.5	C36—C35—C34	119.99 (15)
725	O2—C3—C4	113.06 (12)	C36—C35—H35	120.0
726	O2—C3—C2	114.25 (13)	C34—C35—H35	120.0
727	C4—C3—C2	102.83 (12)	C37—C36—C35	119.65 (14)
728	O2—C3—H3	108.8	C37—C36—H36	120.2
729	C4—C3—H3	108.8	C35—C36—H36	120.2
730	C2—C3—H3	108.8	C36—C37—C38	120.50 (15)
731	N1—C4—C5	125.69 (13)	C36—C37—H37	119.7
732	N1—C4—C3	111.67 (12)	C38—C37—H37	119.7
733	C5—C4—C3	122.63 (13)	C37—C38—C33	120.65 (15)
734	C4—C5—C6	125.81 (13)	C37—C38—H38	119.7
735	C4—C5—C21	118.21 (13)	C33—C38—H38	119.7
736	C6—C5—C21	115.86 (13)	C44—C39—C40	118.47 (14)
737	N2—C6—C5	126.18 (13)	C44—C39—C20	121.42 (14)
738	N2—C6—C7	109.70 (12)	C40—C39—C20	120.03 (14)
739	C5—C6—C7	124.10 (13)	C41—C40—C39	120.89 (17)
740	C8—C7—C6	107.13 (13)	C41—C40—H40	119.6
741	C8—C7—H7	126.4	C39—C40—H40	119.6
742	C6—C7—H7	126.4	C42—C41—C40	119.91 (18)
743	C7—C8—C9	107.28 (13)	C42—C41—H41	120.0
744	C7—C8—H8	126.4	C40—C41—H41	120.0
745	C9—C8—H8	126.4	C43—C42—C41	119.83 (16)
746	N2—C9—C10	125.87 (13)	C43—C42—H42	120.1
747	N2—C9—C8	109.15 (13)	C41—C42—H42	120.1
748	C10—C9—C8	124.93 (13)	C42—C43—C44	120.60 (17)
749	C9—C10—C11	125.20 (13)	C42—C43—H43	119.7
750	C9—C10—C27	117.69 (13)	C44—C43—H43	119.7
751	C11—C10—C27	117.08 (13)	C39—C44—C43	120.28 (17)
752	N3—C11—C10	124.71 (13)	C39—C44—H44	119.9
753	N3—C11—C12	109.73 (12)	C43—C44—H44	119.9
754	C10—C11—C12	125.48 (13)	C45—N5—Zn1	117.93 (11)
755	C13—C12—C11	106.91 (13)	C45—N5—H5A	111.4 (15)
756	C13—C12—H12	126.5	Zn1—N5—H5A	110.1 (15)
757	C11—C12—H12	126.5	C45—N5—H5B	108.8 (14)
758	C12—C13—C14	107.17 (13)	Zn1—N5—H5B	105.3 (14)
759	C12—C13—H13	126.4	H5A—N5—H5B	101.8 (18)

C14—C13—H13	126.4	N5—C45—C46B	112.77 (14)
N3—C14—C15	124.61 (12)	N5—C45—C46	112.77 (14)
N3—C14—C13	109.49 (12)	N5—C45—H45A	109.0
C15—C14—C13	125.79 (13)	C46—C45—H45A	109.0
C16—C15—C14	124.48 (13)	N5—C45—H45B	109.0
C16—C15—C33	117.67 (13)	C46—C45—H45B	109.0
C14—C15—C33	117.82 (12)	H45A—C45—H45B	107.8
N4—C16—C15	125.85 (13)	N6—C46—C45	111.44 (17)
N4—C16—C17	109.14 (12)	N6—C46—H46A	109.3
C15—C16—C17	124.99 (13)	C45—C46—H46A	109.3
C18—C17—C16	107.17 (13)	N6—C46—H46B	109.3
C18—C17—H17	126.4	C45—C46—H46B	109.3
C16—C17—H17	126.4	H46A—C46—H46B	108.0
C17—C18—C19	107.31 (13)	C46—N6—H6A	109.2 (15)
C17—C18—H18	126.3	C46—N6—H6B	114.0 (16)
C19—C18—H18	126.3	H6A—N6—H6B	104 (2)
N4—C19—C20	126.10 (13)	N6B—C46B—C45	116.8 (7)
N4—C19—C18	109.61 (13)	N6B—C46B—H46C	108.1
C20—C19—C18	124.29 (13)	C45—C46B—H46C	108.1
C1—C20—C19	125.69 (13)	N6B—C46B—H46D	108.1
C1—C20—C39	119.08 (13)	C45—C46B—H46D	108.1
C19—C20—C39	115.23 (13)	H46C—C46B—H46D	107.3
C22—C21—C26	118.74 (15)	C46B—N6B—H6C	110 (3)
C22—C21—C5	121.41 (15)	C46B—N6B—H6D	109 (3)
C26—C21—C5	119.76 (14)	H6C—N6B—H6D	102 (4)
C23—C22—C21	120.74 (18)	C47—O3—H3O	109.5
C23—C22—H22	119.6	O3—C47—H47A	109.5
C21—C22—H22	119.6	O3—C47—H47B	109.5
C24—C23—C22	120.11 (19)	H47A—C47—H47B	109.5
C24—C23—H23	119.9	O3—C47—H47C	109.5
C22—C23—H23	119.9	H47A—C47—H47C	109.5
C25—C24—C23	119.88 (17)	H47B—C47—H47C	109.5

C4—N1—C1—C20	−172.69 (14)	C14—C15—C16—C17	−173.90 (15)
Zn1—N1—C1—C20	21.5 (2)	C33—C15—C16—C17	4.1 (2)
C4—N1—C1—C2	8.29 (16)	N4—C16—C17—C18	1.83 (19)
Zn1—N1—C1—C2	−157.56 (10)	C15—C16—C17—C18	−176.45 (15)
N1—C1—C2—O1	113.02 (14)	C16—C17—C18—C19	−0.5 (2)
C20—C1—C2—O1	−66.03 (18)	C16—N4—C19—C20	−177.20 (14)
N1—C1—C2—C3	−6.94 (16)	Zn1—N4—C19—C20	3.4 (2)
C20—C1—C2—C3	174.00 (14)	C16—N4—C19—C18	2.20 (17)
O1—C2—C3—O2	7.86 (17)	Zn1—N4—C19—C18	−177.24 (11)
C1—C2—C3—O2	125.94 (13)	C17—C18—C19—N4	−1.09 (19)
O1—C2—C3—C4	−115.04 (13)	C17—C18—C19—C20	178.32 (15)
C1—C2—C3—C4	3.04 (15)	N1—C1—C20—C19	−3.6 (2)
C1—N1—C4—C5	173.14 (14)	C2—C1—C20—C19	175.28 (14)
Zn1—N1—C4—C5	−21.0 (2)	N1—C1—C20—C39	175.45 (13)
C1—N1—C4—C3	−6.09 (17)	C2—C1—C20—C39	−5.6 (2)

Zn1—N1—C4—C3	159.75 (10)	N4—C19—C20—C1	−10.3 (2)
O2—C3—C4—N1	−122.20 (14)	C18—C19—C20—C1	170.36 (15)
C2—C3—C4—N1	1.50 (16)	N4—C19—C20—C39	170.55 (14)
O2—C3—C4—C5	58.54 (19)	C18—C19—C20—C39	−8.8 (2)
C2—C3—C4—C5	−177.76 (13)	C4—C5—C21—C22	−108.81 (18)
N1—C4—C5—C6	7.8 (2)	C6—C5—C21—C22	74.97 (19)
C3—C4—C5—C6	−173.08 (14)	C4—C5—C21—C26	74.7 (2)
N1—C4—C5—C21	−168.03 (14)	C6—C5—C21—C26	−101.57 (18)
C3—C4—C5—C21	11.1 (2)	C26—C21—C22—C23	0.7 (3)
C9—N2—C6—C5	176.68 (14)	C5—C21—C22—C23	−175.87 (17)
Zn1—N2—C6—C5	4.2 (2)	C21—C22—C23—C24	−0.1 (3)
C9—N2—C6—C7	−1.77 (16)	C22—C23—C24—C25	−0.6 (3)
Zn1—N2—C6—C7	−174.29 (10)	C23—C24—C25—C26	0.7 (4)
C4—C5—C6—N2	1.8 (2)	C22—C21—C26—C25	−0.6 (3)
C21—C5—C6—N2	177.74 (14)	C5—C21—C26—C25	176.01 (18)
C4—C5—C6—C7	−179.92 (15)	C24—C25—C26—C21	−0.1 (3)
C21—C5—C6—C7	−4.0 (2)	C9—C10—C27—C32	110.01 (18)
N2—C6—C7—C8	0.94 (18)	C11—C10—C27—C32	−68.0 (2)
C5—C6—C7—C8	−177.54 (15)	C9—C10—C27—C28	−69.78 (19)
C6—C7—C8—C9	0.26 (18)	C11—C10—C27—C28	112.19 (17)
C6—N2—C9—C10	−175.80 (14)	C32—C27—C28—C29	0.5 (2)
Zn1—N2—C9—C10	−3.2 (2)	C10—C27—C28—C29	−179.74 (14)
C6—N2—C9—C8	1.93 (16)	C27—C28—C29—C30	−1.6 (2)
Zn1—N2—C9—C8	174.49 (10)	C28—C29—C30—C31	1.3 (3)
C7—C8—C9—N2	−1.36 (18)	C29—C30—C31—C32	0.1 (3)
C7—C8—C9—C10	176.39 (15)	C30—C31—C32—C27	−1.2 (3)
N2—C9—C10—C11	−5.4 (2)	C28—C27—C32—C31	0.9 (3)
C8—C9—C10—C11	177.25 (15)	C10—C27—C32—C31	−178.87 (16)
N2—C9—C10—C27	176.78 (13)	C16—C15—C33—C34	−123.99 (15)
C8—C9—C10—C27	−0.6 (2)	C14—C15—C33—C34	54.12 (19)
C14—N3—C11—C10	−173.52 (14)	C16—C15—C33—C38	55.03 (19)
Zn1—N3—C11—C10	24.5 (2)	C14—C15—C33—C38	−126.86 (15)
C14—N3—C11—C12	3.29 (16)	C38—C33—C34—C35	0.5 (2)
Zn1—N3—C11—C12	−158.64 (10)	C15—C33—C34—C35	179.57 (14)
C9—C10—C11—N3	−6.2 (2)	C33—C34—C35—C36	−0.4 (2)
C27—C10—C11—N3	171.62 (13)	C34—C35—C36—C37	−0.2 (3)
C9—C10—C11—C12	177.44 (15)	C35—C36—C37—C38	0.6 (3)
C27—C10—C11—C12	−4.7 (2)	C36—C37—C38—C33	−0.4 (3)
N3—C11—C12—C13	−1.97 (17)	C34—C33—C38—C37	−0.1 (2)
C10—C11—C12—C13	174.82 (15)	C15—C33—C38—C37	−179.16 (14)
C11—C12—C13—C14	−0.14 (17)	C1—C20—C39—C44	−65.50 (19)
C11—N3—C14—C15	173.12 (13)	C19—C20—C39—C44	113.68 (16)
Zn1—N3—C14—C15	−25.2 (2)	C1—C20—C39—C40	117.69 (17)
C11—N3—C14—C13	−3.37 (16)	C19—C20—C39—C40	−63.13 (19)
Zn1—N3—C14—C13	158.29 (10)	C44—C39—C40—C41	−0.9 (2)
C12—C13—C14—N3	2.20 (17)	C20—C39—C40—C41	176.05 (15)
C12—C13—C14—C15	−174.24 (14)	C39—C40—C41—C42	1.1 (3)
N3—C14—C15—C16	7.9 (2)	C40—C41—C42—C43	−0.2 (3)

C13—C14—C15—C16	−176.19 (14)	C41—C42—C43—C44	−0.8 (3)
N3—C14—C15—C33	−170.08 (13)	C40—C39—C44—C43	−0.2 (2)
C13—C14—C15—C33	5.8 (2)	C20—C39—C44—C43	−177.06 (14)
C19—N4—C16—C15	175.79 (14)	C42—C43—C44—C39	1.0 (2)
Zn1—N4—C16—C15	−4.8 (2)	Zn1—N5—C45—C46B	−78.92 (16)
C19—N4—C16—C17	−2.47 (17)	Zn1—N5—C45—C46	−78.92 (16)
Zn1—N4—C16—C17	176.96 (11)	N5—C45—C46—N6	−69.5 (3)
C14—C15—C16—N4	8.1 (2)	N5—C45—C46B—N6B	−38.3 (15)
C33—C15—C16—N4	−173.93 (13)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N6^{i}	0.99	1.73	2.710 (3)	168
O1—H1···N6*B*^{i}	0.99	1.54	2.510 (17)	165
O2—H2*A*···O1^{i}	0.99	1.82	2.8056 (18)	171
C2—H2···O3^{i}	1.00	2.53	3.460 (14)	155
N5—H5*A*···O1^{i}	0.88 (2)	2.38 (2)	3.2442 (18)	166 (2)
C46—H46*A*···N2	0.99	2.49	3.368 (2)	148
N6—H6*A*···O3	0.90 (2)	2.08 (2)	2.932 (14)	159 (3)
C46*B*—H46*C*···N2	0.99	2.68	3.368 (2)	126
O3—H3*O*···N4^{ii}	0.84	2.20	2.992 (14)	157

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

other supporting information

The following files will be made available to readers when your article is published. Unless otherwise stated, these files will be the same as those submitted during the review process.

Crystal structure: contains datablocks 2PhH2, 2PhZn. dj2044sup1.cif

Structure factors: contains datablock 2PhH2. dj20442PhH2sup2.hkl

Structure factors: contains datablock 2PhZn. dj20442PhZnsup3.hkl

Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN: 2056-9890

ORDER FORM

YOU WILL AUTOMATICALLY BE SENT DETAILS OF HOW TO DOWNLOAD AN ELECTRONIC REPRINT OF YOUR PAPER, FREE OF CHARGE. PRINTED REPRINTS MAY BE PURCHASED USING THIS FORM.

Please scan your order and send to checkin@iucr.org

INTERNATIONAL UNION OF CRYSTALLOGRAPHY
5 Abbey Square
Chester CH1 2HU, England.

VAT No. GB 161 9034 76

Article No.: E220272-DJ2044

Title of article Crystal structure of *cis*-7,8-dihydroxy-5,10,15,20-tetraphenylchlorin and its zinc(II)–ethylenediamine complex

Name Christian Bruckner

Address Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060, USA,

E-mail address (for electronic reprints) c.bruckner@uconn.edu

DIGITAL PRINTED REPRINTS

I wish to order . . . . . paid reprints

These reprints will be sent to the address given above. If the above address or e-mail address is not correct, please indicate an alternative:

PAYMENT

☐ An official purchase order made out to **INTERNATIONAL UNION OF CRYSTALLOGRAPHY** ☐ is enclosed ☐ will follow

Purchase order No.

☐ Please invoice me

☐ I wish to pay by credit card

EU authors only: VAT No:

Date | Signature

DIGITAL PRINTED REPRINTS

An electronic reprint is supplied free of charge.

Printed reprints without limit of number may be purchased at the prices given in the table below. The requirements of all joint authors, if any, and of their laboratories should be included in a single order, specifically ordered on the form overleaf. All orders for reprints must be submitted promptly.

Prices for reprints are given below in **United States dollars** and include postage.

	Size of paper (in printed pages)				
Number of reprints required	1–2	3–4	5–8	9–16	Additional 8's
50	184	268	372	560	246
100	278	402	556	842	370
150	368	534	740	1122	490
200	456	664	920	1400	610
Additional 50's	86	128	178	276	116

PAYMENT AND ORDERING

Official purchase orders should be made out to **INTERNATIONAL UNION OF CRYSTALLOGRAPHY**.

Orders should be returned by email to checkin@iucr.org

ENQUIRIES

Enquiries concerning reprints should be sent to support@iucr.org.