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# Redetermination of *cyclo*-tetrakis(*μ*-5,10,15,20-tetra-4-pyridylporphyrinato)-tetrazinc(II) dimethylformamide octasolvate trihydrate at 100 K

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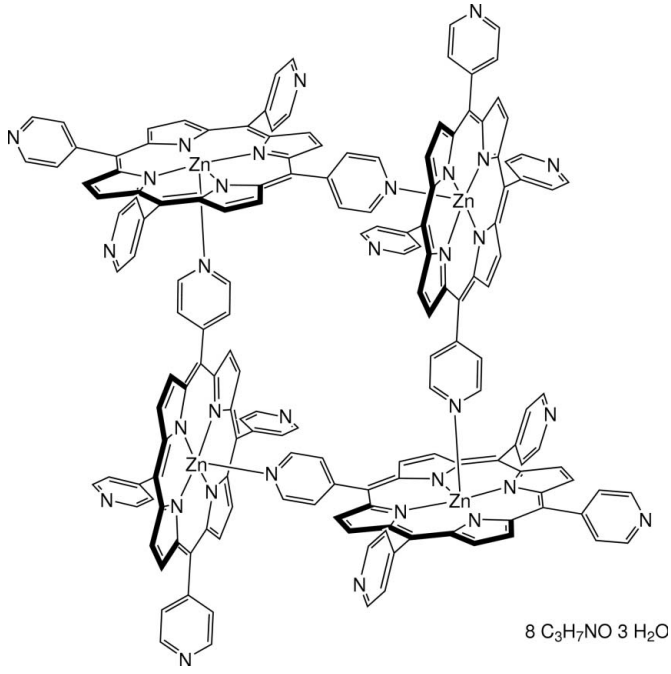
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; some non-H atoms missing; $R$ factor = 0.042; $wR$ factor = 0.108; data-to-parameter ratio = 17.5.

The structure of the title compound, $[Zn_4(C_{40}H_{24}N_8)_4]\cdot 8C_3H_7NO\cdot 3H_2O$, has been redetermined at 100 K. The redetermination is of significantly higher precision and gives further insight into the disorder of pyridyl groups and solvent molecules. The molecules of (5,10,15,20-tetra-4-pyridylporphyrinato)zinc(II) (ZnTPyP) form homomolecular cyclic tetramers by coordination of a peripheral pyridyl group to the central Zn atom of an adjacent symmetry-related molecule. The tetramer so formed exhibits molecular $S_4$ symmetry and is located about a crystallographic fourfold rotoinversion axis. Severely disordered dimethylformamide and water molecules are present in the crystal, the contributions of which were omitted from refinement. Intermolecular C—H···N hydrogen bonding is observed.

## Related literature

For the structure at 200 K, see: Seidel *et al.* (2010). For the 2-chlorophenol solvate of cyclic tetrameric ZnTPyP, see: Lipstman & Goldberg (2010). For a review article on structural motifs in coordination polymers of the 5,10,15,20-tetra4-pyridylporphyrin ligand, see: DeVries & Choe (2009). For the supramolecular chemistry of ZnTPyP in the solid-state, see: Lipstman & Goldberg (2010); Seidel *et al.* (2010) and references cited therein. For a description of the I$\mu$S microfocus X-ray source used in the present study, see: Graf (2008); Schulz *et al.* (2009). For *PLATON* / *SQUEEZE*, see: van der Sluis & Spek (1990); Spek (2009). For a description of the program *COOT*, see: Emsley *et al.* (2010).




## Experimental

### Crystal data

$[Zn_4(C_{40}H_{24}N_8)_4]\cdot 8C_3H_7NO\cdot 3H_2O$
$M_r$ = 3366.98
Tetragonal, $P4_2/n$
$a$ = 23.6897 (5) Å
$c$ = 14.9876 (7) Å
$V$ = 8411.1 (5) Å$^3$
$Z$ = 2
Cu $K\alpha$ radiation
$\mu$ = 1.24 mm$^{-1}$
$T$ = 100 K
0.16 × 0.04 × 0.02 mm

### Data collection

Bruker X8 PROSPECTOR diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.827, $T_{max}$ = 0.976
44415 measured reflections
7723 independent reflections
6768 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.108
$S$ = 1.04
7723 reflections
442 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N24 | 2.0684 (15) | Zn1—N23 | 2.0747 (16) |
| Zn1—N21 | 2.0695 (16) | Zn1—N101$^{i}$ | 2.1385 (16) |
| Zn1—N22 | 2.0695 (17) | | |
| N24—Zn1—N21 | 162.77 (7) | N22—Zn1—N23 | 161.70 (7) |
| N24—Zn1—N22 | 88.42 (6) | N24—Zn1—N101$^{i}$ | 95.10 (6) |
| N21—Zn1—N22 | 88.84 (7) | N21—Zn1—N101$^{i}$ | 102.11 (6) |
| N24—Zn1—N23 | 89.34 (6) | N22—Zn1—N101$^{i}$ | 102.00 (6) |
| N21—Zn1—N23 | 87.94 (6) | N23—Zn1—N101$^{i}$ | 96.29 (6) |

Symmetry code: (i) $y, -x+\frac{1}{2}, -z+\frac{1}{2}$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C7—H7···N151$^{ii}$ | 0.95 | 2.65 | 3.583 (4) | 167 |
| C17—H17···N51$^{iii}$ | 0.95 | 2.66 | 3.583 (3) | 165 |

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2170).

## References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Brandenburg, K. (2010). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2008). *APEX2* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2010). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
DeVries, L. D. & Choe, W. (2009). *J. Chem. Crystallogr.* **39**, 229–240.
Emsley, P., Lohkamp, B., Scott, W. G. & Cowtan, K. (2010). *Acta Cryst.* D**66**, 486–501.
Graf, J. (2008). *Nachr. Chem.* **56**, 1050–1052.
Lipstman, S. & Goldberg, I. (2010). *CrystEngComm*, **12**, 52–54.
Schulz, T., Meindl, K., Leusser, D., Stern, D., Graf, J., Michaelsen, C., Ruf, M., Sheldrick, G. M. & Stalke, D. (2009). *J. Appl. Cryst.* **42**, 885–891.
Seidel, R. W., Goddard, R., Föcker, K. & Oppel, I. M. (2010). *CrystEngComm*, **12**, 387–394.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* A**46**, 194–201.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

# supporting information

*Acta Cryst.* (2011). E**67**, m236–m237 [doi:10.1107/S1600536811002054]

# Redetermination of *cyclo*-tetrakis(*μ*-5,10,15,20-tetra-4-pyridyl-porphyrinato)tetrazinc(II) dimethylformamide octasolvate trihydrate at 100 K

**Rüdiger W. Seidel, Jürgen Graf, Richard Goddard and Iris M. Oppel**

## S1. Comment

5,10,15,20-Tetra(4-pyridyl)porphyrin has been widely used as ligand for the construction of coordination polymers (DeVries & Choe, 2009). We and others have reported on the solid-state supramolecular chemistry of the self-complementary [5,10,15,20-tetra(4-pyridyl)porphyrinato]zinc(II) (ZnTPyP) building block (Lipstman & Goldberg, 2010; Seidel *et al.*, 2010 and references cited therein). Recently, we reported the title structure of $[ZnTPyP]_4$.

The small dark red plate-shaped crystals of the title compound were subjected to diffraction experiments using a Bruker AXS X8 PROSPECTOR diffractometer equipped with an INCOATEC microfocus X-ray source (I$\mu$S) for Cu radiation (Graf, 2008). Such microfocus X-ray sources use multilayer mirrors to focus the X-ray beam onto the crystal and, therefore, lead to a significant reduction of the background and an increase in diffracted intensities. It has already been demonstrated that the Mo I$\mu$S gives data of significantly higher quality than a 2 kW Mo fine focus sealed tube, when small crystals are examined (Schulz *et al.*, 2009). The data collection presented here, using the Cu I$\mu$S, resulted in intensity data of surprisingly good quality and, hence, indicated a re-refinement of the crystal structure. The crystals investigated in the original work were significantly larger than those examined in the present study and split on cooling to 100 K. For this reason, the data were collected at 200 K with a Cu rotating anode system at that time. Using small crystals has the advantage that these are less likely to split on flash cooling.

The molecular structure of $[ZnTPyP]_4$ is depicted in Fig. 1. The asymmetric unit contains one ZnTPyP unit (Fig 2.) and the $S_4$ symmetric tetramer is generated by crystallographic fourfold rotoinversion symmetry. One peripheral pyridyl group binds to the central Zn atom of an adjacent symmetry related ZnTPyP unit. Zn1 is pentacoordinated and is displaced from the $N_4$ mean plane by 0.3196 (9) Å. The coordination geometry parameters about Zn1 are given in Table 1. The three remaining pyridyl groups are non-coordinating. Even at 100 K, the pyridyl groups attached to C5 and C15 show elongated ellipsoids, which cause a checkCIF B level alert (Spek, 2009) due to large $U_{eq}$(max)/$U_{eq}$(min) ratio. This reveals that the disorder is rather of static than dynamic nature. Attempts were made to describe the electron density of the pyridyl ring attached to C15 (Fig. 3) by a split model. However, the refinement results could not be improved thereby. Thus, both pyridyl rings were finally described with large displacement parameters.

In the crystal, the $[ZnTPyP]_4$ entities are stacked into columns located at $x$ = 1/4, $y$ = 1/4 and $x$ = 3/4, $y$ = 3/4 (Fig 4). The stacking propagates *via* $C_{\beta}$—H···$N_{py}$ interactions (see Table 2) by translational symmetry in the $c$ axis direction. Within a column, the distance between the centroids of the pyridyl rings attached to C5 and C15$^{iii}$ is 4.0714 (1) Å. Adjacent columns of $[ZnTPyP]_4$ are arranged with an offset of $c$/2 (*ca* 7.49 Å). Interstitial channels are formed parallel to the $c$ axis direction centred at $x$ = 1/4, $y$ = 3/4 and $x$ = 3/4, $y$ = 1/4 (Fig 5). The potential solvent accessible void estimated with *PLATON* / *SOLV* (Spek, 2009) is 33.2% of the unit cell volume. On cooling to 100 K, the $a$ lattice vector is shortened by approximately 0.27 Å in comparison to the tetragonal unit cell at 200 K ($a$ = 23.958 (2) Å), whereas the

length of *c* lattice vector remains relatively unaffected (*c* = 15.0646 (16) Å at 200 K; Seidel *et al.*, 2010).

Despite intensive efforts, the disordered solvent molecules filling the voids within the columns of $[ZnTPyP]_4$ and the interstitial channels could not be modeled reasonably with the data collected at 100 K. Nevertheless, residual electron density was visible in a difference Fourier synthesis calculated for the solvent regions (Fig. 6) with phases based on the model using *COOT* (Emsley *et al.*, 2010). For the visualization of the surface of the (difference) electron density using a three-dimensional mesh, the electron densities should be read into *COOT* in terms of structure factors. To obtain a structure factor (.fcf) file containg the informations necessary for the calculation of electron density maps and suitable for *COOT*, the LIST 6 instruction of *SHELXL-97* was used. The atomic model of the framework was read into *COOT* by means of the *SHELXL-97*. res file. The visual inspection of the difference electron density map indicates that four molecules of dimethylformamide (DMF) plus one water molecule are located within the voids in the columns approximately centred at (1/4,1/4,0), whereas another four molecules of DMF and two water molecules are clustered around the $4_2$ screw axes running through the interstitial channels parallel to the *c* axis direction. The compound can, therefore, probably best be described as $[ZnTPyP]_4$. 8 DMF. 3 $H_2O$. The compound was originally formulated as being a pure DMF solvate (Seidel *et al.*, 2010). To improve the fit of the model to the data and, hence, the precision of the main part of the structure, the contributions of the disordered solvent molecules were removed from the diffraction data with *PLATON* / *SQUEEZE* (van der Sluis & Spek, 1990; Spek, 2009). *SQUEEZE* estimated the electron counts in the voids within the columns and interstitial channels of $[ZnTPyP]_4$ to be 182 and 207, respectively. These values are relatively close to those based on the proposed chemical formula (178 and 196).

## S2. Experimental

Small dark red plate-shaped crystals of the title compound were obtained similarly as reported previously (Seidel *et al.*, 2010); 12 mg of ZnTPyP (Aldrich) and 11 mg of $[Pd(NO_3)_2(en)]$ (en = 1,2-diaminoethane) were placed in an ampoule and 4 ml of DMF were added. The ampoule was sealed and placed in a heater. The sample was heated to 150 °C in 24 h and held for five days at this temperature. Subsequently, the sample was cooled down to room temperature in 100 h. Noteworthy, the crystals of the title compound were accompanied by crystals of the triclinic phase, containing a polymeric one-dimensional ladder structure of ZnTPyP, as observed previously (Seidel *et al.*, 2010).

## S3. Refinement

For the final refinement, the contributions of severely disordered DMF and water molecules of crystallization were removed from the diffraction data with *PLATON* / *SQUEEZE* (van der Sluis & Spek, 1990; Spek, 2009), see comment. H atoms were placed at geometrically calculated positions and refined with constrained C—H bond length of 0.95 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$ allowing them to ride on the parent C atom.

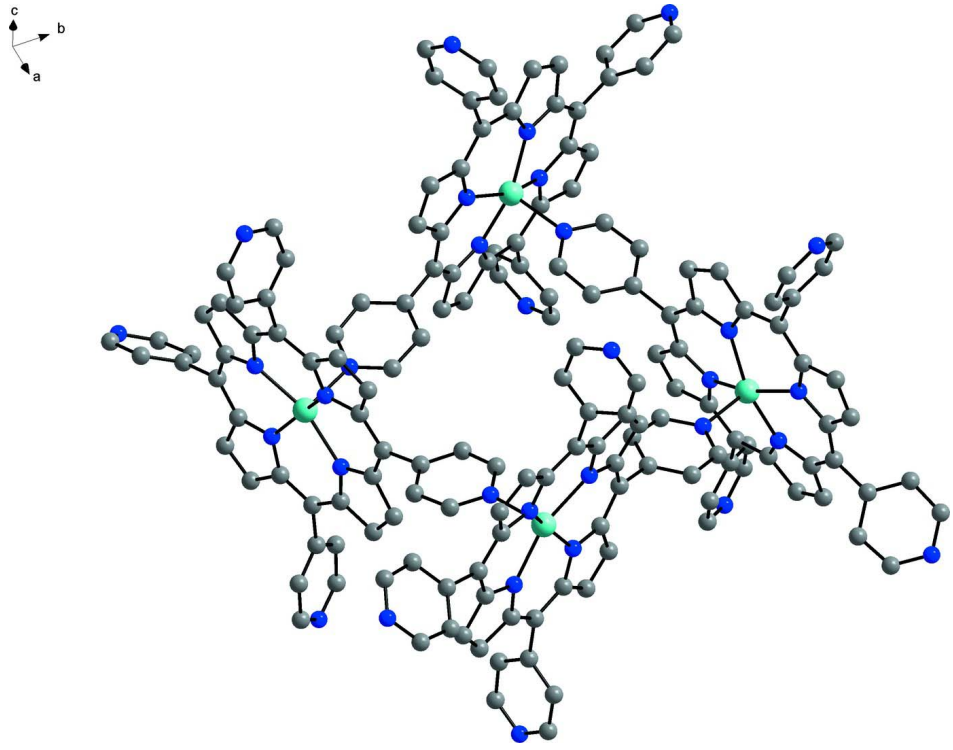


**Figure 1**

Molecular structure of the title compound. H atoms are omitted for clarity.

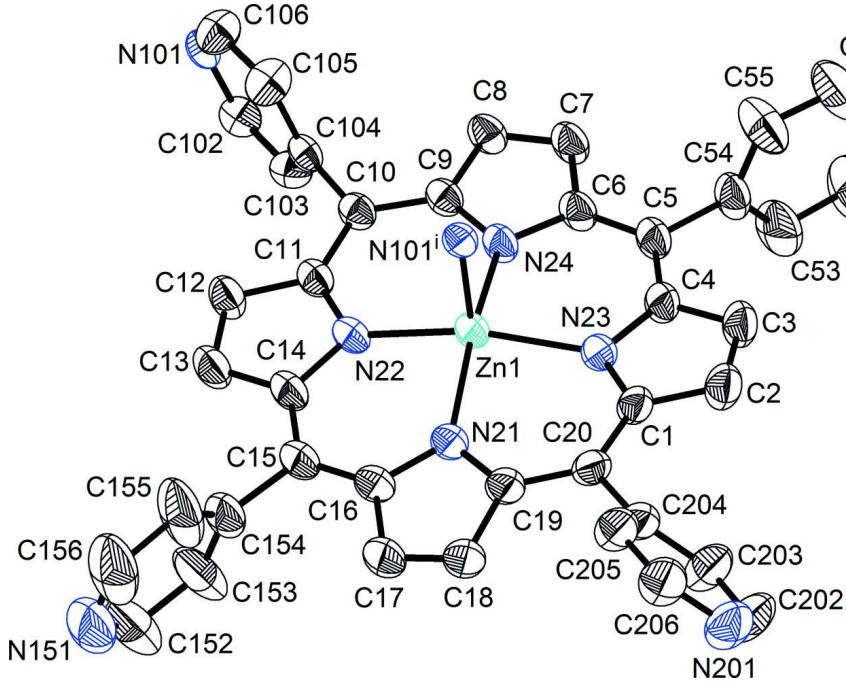


**Figure 2**

Displacement ellipsoid plot of one repeat unit of cyclic $[ZnTPyP]_4$ drawn at 50% probability. H atoms are omitted for clarity. Symmetry code: (i) *y*, -*x* + 1/2, -*z* + 1/2.

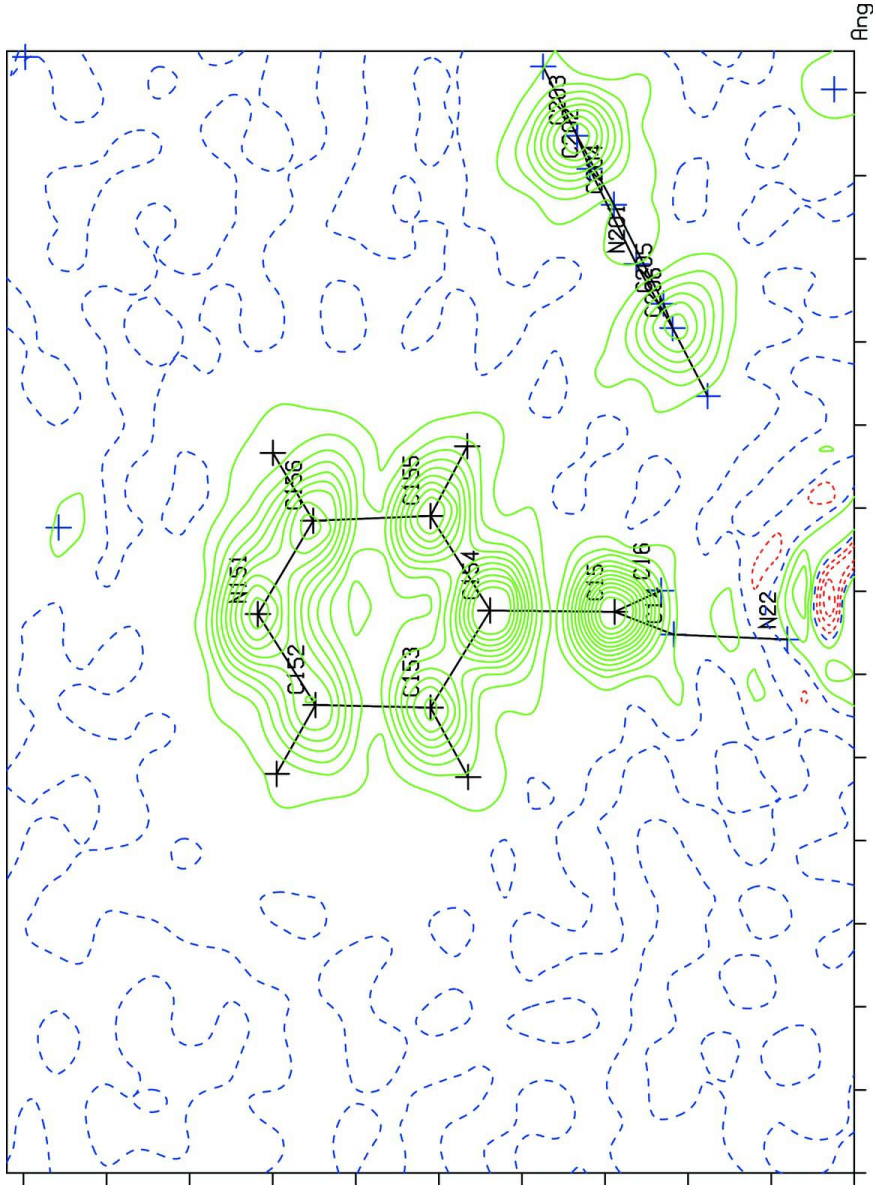


**Figure 3**

Contour plot of the $F_o$ electron density map in the plane of the pyridyl group attached to C15, calculated with phases from $F_c$. Contours are drawn at 0.50 e Å$^{-3}$ starting at 6.00 e Å$^{-3}$. The contour plot was generated with *PLATON* (Spek, 2009).

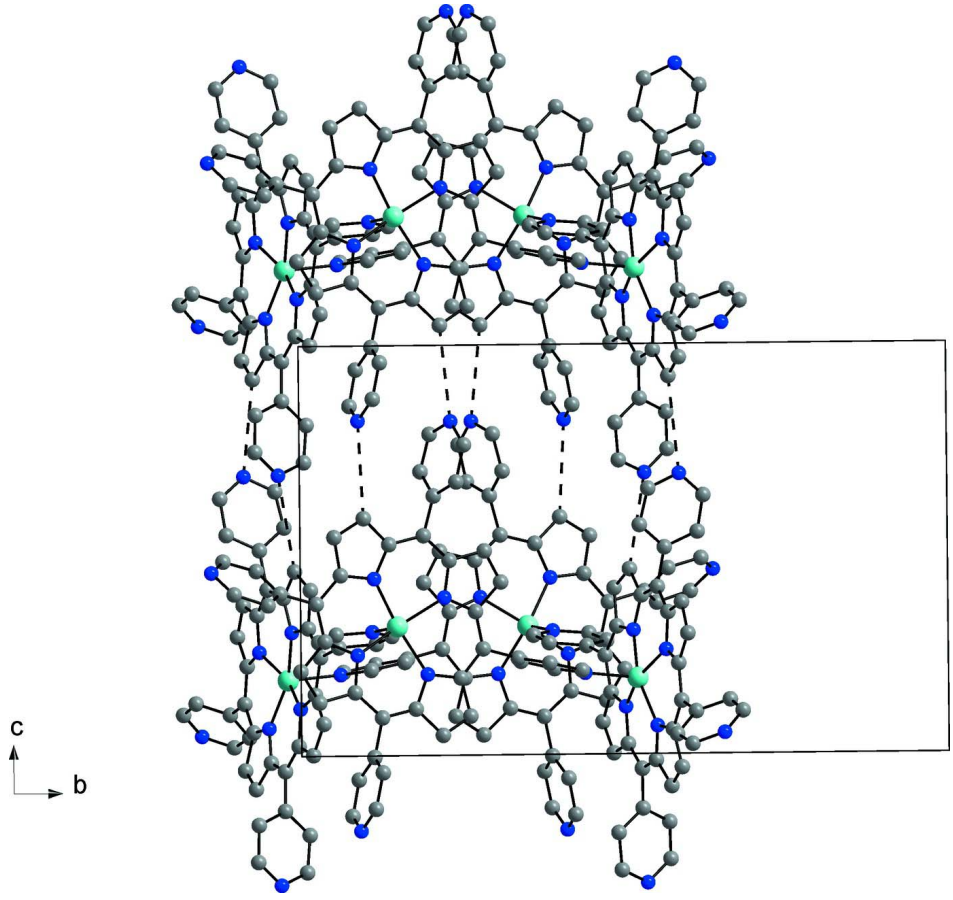


**Figure 4**

Stacking of the $[ZnTPyP]_4$ entities viewed along the a axis direction. H atoms are omitted for clarity. $C_{\beta}$—H···$N_{py}$ interactions are represented by dashed lines.

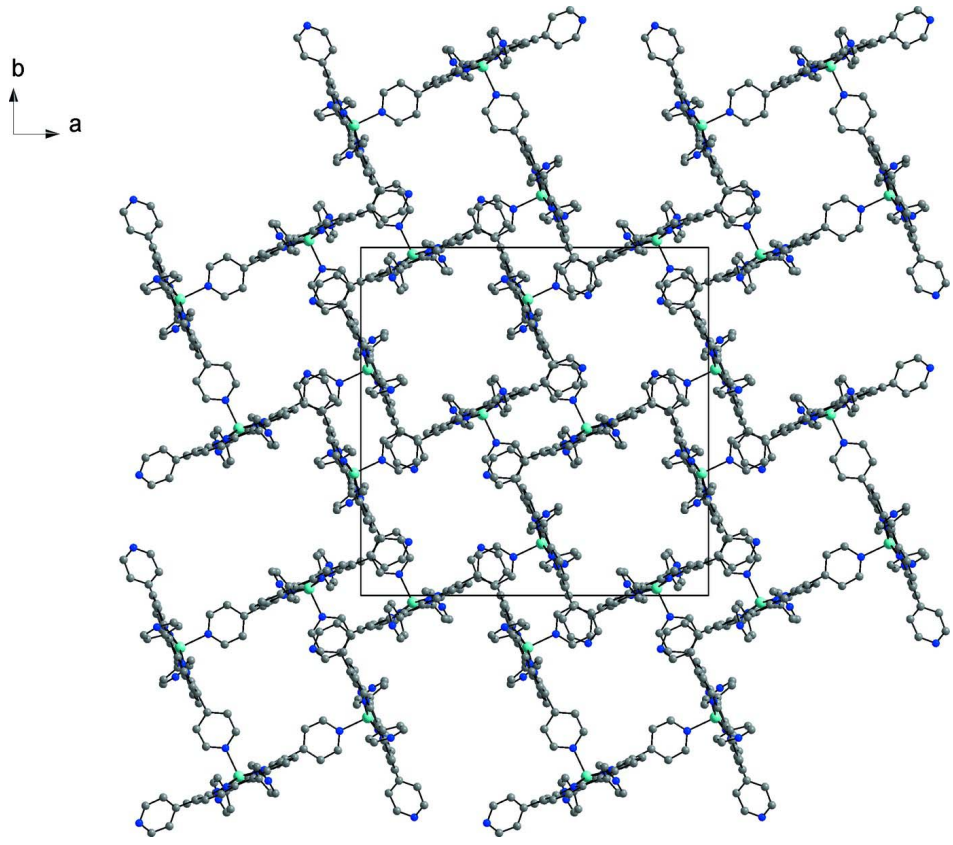


**Figure 5**

Packing diagram of the title compound projected along the *c* axis direction. H atoms are omitted for clarity.

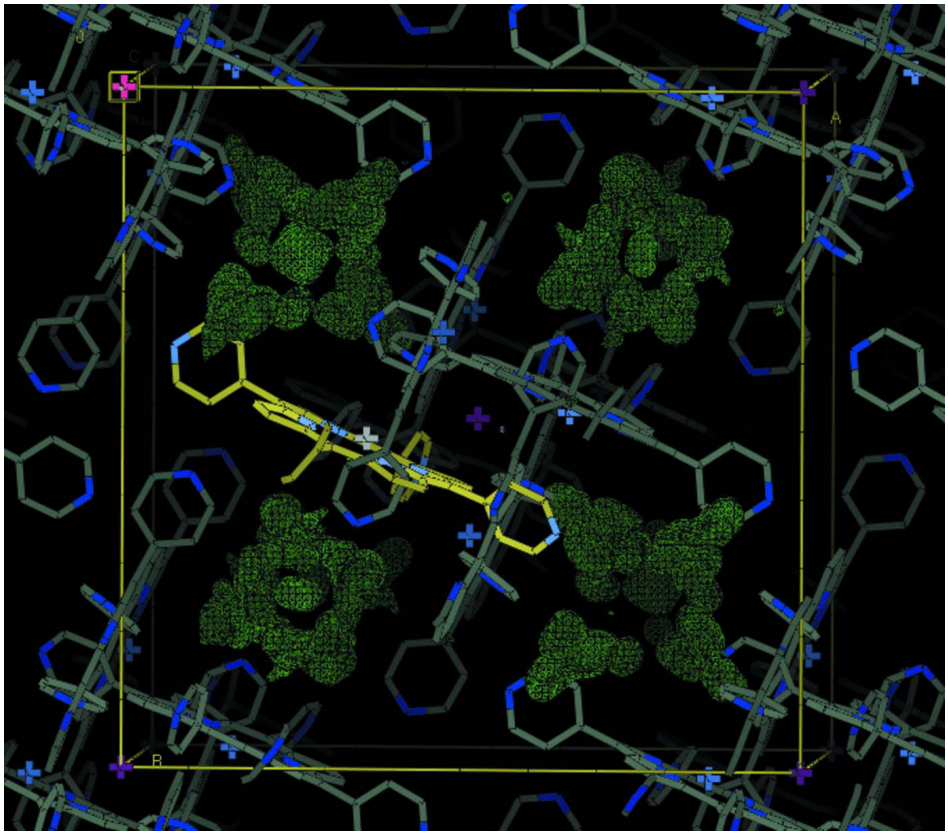

**Figure 6**

The tetragonal unit cell of the title compound viewed approximately along the *c* axis direction showing the $F_o$-$F_c$ map of the disordered solvent regions (contoured at 3.0$\sigma$ level). The figure was created with *COOT* (Emsley *et al.*, 2010) using $F_o$ including the contributions of the disordered solvent with phases from $F_c$ based on the model.

### *cyclo*-tetrakis(*μ*-5,10,15,20-tetra-4-pyridylporphyrinato)tetrazinc(II) dimethylformamide octasolvate

*Crystal data*

$[Zn_4(C_{40}H_{24}N_8)_4]\cdot 8C_3H_7NO\cdot 3H_2O$
$M_r$ = 3366.98
Tetragonal, $P4_2/n$
Hall symbol: -P 4bc
$a$ = 23.6897 (5) Å
$c$ = 14.9876 (7) Å
$V$ = 8411.1 (5) Å$^3$
$Z$ = 2
$F$(000) = 3500
$D_x$ = 1.329 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 130 reflections
$\theta$ = 3.5–31.5°
$\mu$ = 1.24 mm$^{-1}$
$T$ = 100 K
Plate, dark red
0.16 × 0.04 × 0.02 mm

*Data collection*

Bruker X8 PROSPECTOR goniometer diffractometer
Radiation source: Incoatec I$\mu$S microfocus X-ray source
Incoatec Quazar Multilayer Mirror monochromator
Detector resolution: 8.33 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.827, $T_{max}$ = 0.976
44415 measured reflections
7723 independent reflections
6768 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018
$\theta_{max}$ = 69.2°, $\theta_{min}$ = 2.6°

$h = -28 \rightarrow 25$
$k = -24 \rightarrow 28$
$l = -17 \rightarrow 14$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.108$
$S = 1.04$
7723 reflections
442 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 5.0454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.59$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ 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**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.350673 (11) | 0.520064 (11) | 0.185590 (16) | 0.03823 (9) |
| N21 | 0.38601 (8) | 0.54998 (7) | 0.06850 (10) | 0.0433 (4) |
| N22 | 0.27781 (7) | 0.50134 (7) | 0.11541 (10) | 0.0404 (4) |
| N23 | 0.41242 (7) | 0.56428 (7) | 0.25451 (10) | 0.0404 (4) |
| N24 | 0.30440 (7) | 0.51392 (7) | 0.30222 (10) | 0.0377 (4) |
| C1 | 0.46288 (9) | 0.58336 (8) | 0.22081 (13) | 0.0420 (4) |
| C2 | 0.50033 (10) | 0.59793 (10) | 0.29314 (14) | 0.0532 (6) |
| H2 | 0.5379 | 0.6115 | 0.2880 | 0.064* |
| C3 | 0.47175 (10) | 0.58861 (10) | 0.36945 (15) | 0.0534 (6) |
| H3 | 0.4853 | 0.5949 | 0.4283 | 0.064* |
| C4 | 0.41675 (9) | 0.56739 (9) | 0.34544 (13) | 0.0428 (5) |
| C5 | 0.37497 (9) | 0.55138 (9) | 0.40720 (13) | 0.0442 (5) |
| C6 | 0.32280 (9) | 0.52641 (9) | 0.38657 (12) | 0.0411 (4) |
| C7 | 0.28126 (9) | 0.50864 (9) | 0.45108 (13) | 0.0451 (5) |
| H7 | 0.2835 | 0.5130 | 0.5140 | 0.054* |
| C8 | 0.23852 (9) | 0.48459 (9) | 0.40491 (13) | 0.0422 (4) |
| H8 | 0.2052 | 0.4684 | 0.4292 | 0.051* |
| C9 | 0.25323 (8) | 0.48825 (8) | 0.31165 (12) | 0.0362 (4) |
| C10 | 0.21846 (8) | 0.46994 (8) | 0.24113 (12) | 0.0360 (4) |
| C11 | 0.22974 (8) | 0.47834 (8) | 0.14991 (12) | 0.0376 (4) |
| C12 | 0.19052 (9) | 0.46543 (9) | 0.07858 (13) | 0.0460 (5) |
| H12 | 0.1543 | 0.4486 | 0.0845 | 0.055* |
| C13 | 0.21544 (10) | 0.48202 (10) | 0.00230 (14) | 0.0526 (6) |

| | | | | |
|---|---|---|---|---|
| H13 | 0.1998 | 0.4794 | −0.0559 | 0.063* |
| C14 | 0.26979 (9) | 0.50435 (10) | 0.02480 (13) | 0.0477 (5) |
| C15 | 0.30923 (11) | 0.52569 (10) | −0.03612 (14) | 0.0545 (6) |
| C16 | 0.36281 (10) | 0.54737 (10) | −0.01508 (13) | 0.0515 (5) |
| C17 | 0.40164 (12) | 0.57099 (11) | −0.07905 (15) | 0.0636 (7) |
| H17 | 0.3959 | 0.5743 | −0.1416 | 0.076* |
| C18 | 0.44735 (11) | 0.58736 (10) | −0.03328 (15) | 0.0581 (6) |
| H18 | 0.4801 | 0.6046 | −0.0575 | 0.070* |
| C19 | 0.43790 (9) | 0.57411 (9) | 0.05937 (13) | 0.0455 (5) |
| C20 | 0.47569 (9) | 0.58754 (8) | 0.12914 (13) | 0.0429 (5) |
| N51 | 0.40921 (10) | 0.58630 (15) | 0.68340 (15) | 0.0812 (8) |
| C52 | 0.38597 (16) | 0.62318 (17) | 0.6300 (2) | 0.0945 (11) |
| H52 | 0.3762 | 0.6589 | 0.6542 | 0.113* |
| C53 | 0.37466 (15) | 0.61389 (13) | 0.54115 (18) | 0.0816 (9) |
| H53 | 0.3581 | 0.6429 | 0.5060 | 0.098* |
| C54 | 0.38735 (9) | 0.56279 (11) | 0.50349 (14) | 0.0513 (5) |
| C55 | 0.41194 (13) | 0.52451 (15) | 0.55825 (18) | 0.0792 (8) |
| H55 | 0.4222 | 0.4884 | 0.5360 | 0.095* |
| C56 | 0.42214 (14) | 0.53814 (18) | 0.6469 (2) | 0.0885 (10) |
| H56 | 0.4397 | 0.5105 | 0.6834 | 0.106* |
| N101 | 0.06117 (6) | 0.38923 (7) | 0.30189 (10) | 0.0355 (3) |
| C102 | 0.06574 (8) | 0.44515 (8) | 0.29549 (13) | 0.0403 (4) |
| H102 | 0.0327 | 0.4673 | 0.3038 | 0.048* |
| C103 | 0.11567 (8) | 0.47254 (8) | 0.27747 (13) | 0.0406 (4) |
| H103 | 0.1167 | 0.5126 | 0.2740 | 0.049* |
| C104 | 0.16441 (8) | 0.44146 (8) | 0.26451 (11) | 0.0339 (4) |
| C105 | 0.16034 (9) | 0.38345 (9) | 0.27246 (17) | 0.0506 (5) |
| H105 | 0.1928 | 0.3604 | 0.2652 | 0.061* |
| C106 | 0.10845 (9) | 0.35925 (9) | 0.29112 (16) | 0.0490 (5) |
| H106 | 0.1064 | 0.3194 | 0.2965 | 0.059* |
| N151 | 0.2660 (2) | 0.5329 (2) | −0.3142 (2) | 0.1294 (17) |
| C152 | 0.2458 (3) | 0.5685 (2) | −0.2569 (3) | 0.155 (2) |
| H152 | 0.2211 | 0.5972 | −0.2780 | 0.185* |
| C153 | 0.2581 (2) | 0.56707 (18) | −0.1666 (2) | 0.1290 (18) |
| H153 | 0.2421 | 0.5945 | −0.1278 | 0.155* |
| C154 | 0.29319 (12) | 0.52625 (14) | −0.13291 (16) | 0.0729 (8) |
| C155 | 0.31337 (15) | 0.4886 (2) | −0.19209 (18) | 0.1009 (13) |
| H155 | 0.3375 | 0.4591 | −0.1726 | 0.121* |
| C156 | 0.29872 (18) | 0.4931 (2) | −0.2832 (2) | 0.1174 (17) |
| H156 | 0.3133 | 0.4659 | −0.3237 | 0.141* |
| N201 | 0.63736 (10) | 0.65387 (10) | 0.05085 (15) | 0.0695 (6) |
| C202 | 0.60235 (13) | 0.68222 (12) | 0.1038 (2) | 0.0742 (8) |
| H202 | 0.6140 | 0.7184 | 0.1241 | 0.089* |
| C203 | 0.55016 (12) | 0.66270 (10) | 0.13114 (18) | 0.0635 (7) |
| H203 | 0.5271 | 0.6852 | 0.1689 | 0.076* |
| C204 | 0.53176 (10) | 0.61002 (9) | 0.10312 (14) | 0.0474 (5) |
| C205 | 0.56798 (10) | 0.58046 (10) | 0.04725 (15) | 0.0548 (6) |
| H205 | 0.5577 | 0.5442 | 0.0255 | 0.066* |

| | | | | |
|---|---|---|---|---|
| C206 | 0.61911 (11) | 0.60416 (12) | 0.02354 (17) | 0.0645 (7) |
| H206 | 0.6429 | 0.5831 | −0.0153 | 0.077* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.04778 (16) | 0.04374 (16) | 0.02318 (14) | −0.00756 (11) | 0.00168 (10) | −0.00080 (10) |
| N21 | 0.0579 (10) | 0.0455 (9) | 0.0266 (8) | −0.0116 (8) | 0.0027 (7) | 0.0007 (7) |
| N22 | 0.0485 (9) | 0.0476 (9) | 0.0251 (8) | −0.0020 (7) | −0.0005 (7) | 0.0025 (7) |
| N23 | 0.0531 (10) | 0.0414 (9) | 0.0266 (8) | −0.0084 (7) | 0.0028 (7) | −0.0033 (6) |
| N24 | 0.0438 (9) | 0.0446 (9) | 0.0247 (8) | −0.0010 (7) | 0.0004 (6) | −0.0035 (6) |
| C1 | 0.0521 (12) | 0.0395 (10) | 0.0342 (10) | −0.0129 (9) | 0.0034 (8) | −0.0050 (8) |
| C2 | 0.0581 (14) | 0.0608 (14) | 0.0408 (12) | −0.0204 (11) | 0.0039 (10) | −0.0108 (10) |
| C3 | 0.0599 (14) | 0.0649 (14) | 0.0354 (11) | −0.0209 (11) | −0.0001 (10) | −0.0111 (10) |
| C4 | 0.0522 (12) | 0.0473 (11) | 0.0290 (10) | −0.0094 (9) | 0.0010 (8) | −0.0072 (8) |
| C5 | 0.0520 (12) | 0.0531 (12) | 0.0275 (10) | −0.0066 (9) | −0.0019 (8) | −0.0055 (8) |
| C6 | 0.0479 (11) | 0.0494 (11) | 0.0259 (10) | 0.0000 (9) | 0.0024 (8) | −0.0038 (8) |
| C7 | 0.0494 (12) | 0.0603 (13) | 0.0256 (10) | −0.0036 (10) | 0.0010 (8) | −0.0026 (9) |
| C8 | 0.0458 (11) | 0.0528 (12) | 0.0279 (10) | 0.0012 (9) | 0.0035 (8) | −0.0002 (8) |
| C9 | 0.0410 (10) | 0.0403 (10) | 0.0274 (9) | 0.0045 (8) | 0.0019 (7) | −0.0024 (7) |
| C10 | 0.0421 (10) | 0.0373 (10) | 0.0286 (9) | 0.0047 (8) | 0.0014 (7) | −0.0020 (7) |
| C11 | 0.0428 (10) | 0.0414 (10) | 0.0287 (10) | 0.0024 (8) | −0.0018 (8) | −0.0010 (8) |
| C12 | 0.0457 (11) | 0.0623 (13) | 0.0300 (10) | −0.0037 (10) | −0.0036 (8) | −0.0017 (9) |
| C13 | 0.0565 (13) | 0.0725 (15) | 0.0289 (11) | −0.0093 (11) | −0.0068 (9) | 0.0036 (10) |
| C14 | 0.0566 (13) | 0.0600 (13) | 0.0264 (10) | −0.0071 (10) | −0.0044 (9) | 0.0036 (9) |
| C15 | 0.0687 (15) | 0.0670 (15) | 0.0279 (11) | −0.0171 (12) | −0.0035 (10) | 0.0076 (9) |
| C16 | 0.0697 (15) | 0.0574 (13) | 0.0273 (10) | −0.0158 (11) | 0.0024 (9) | 0.0052 (9) |
| C17 | 0.0816 (18) | 0.0817 (17) | 0.0276 (11) | −0.0288 (14) | 0.0023 (11) | 0.0087 (11) |
| C18 | 0.0723 (16) | 0.0672 (15) | 0.0347 (12) | −0.0260 (12) | 0.0053 (10) | 0.0071 (10) |
| C19 | 0.0595 (13) | 0.0455 (11) | 0.0314 (10) | −0.0118 (9) | 0.0050 (9) | 0.0012 (8) |
| C20 | 0.0570 (12) | 0.0366 (10) | 0.0351 (10) | −0.0118 (9) | 0.0066 (9) | −0.0009 (8) |
| N51 | 0.0633 (14) | 0.145 (3) | 0.0359 (12) | −0.0305 (15) | −0.0006 (10) | −0.0144 (14) |
| C52 | 0.126 (3) | 0.113 (3) | 0.0447 (17) | −0.011 (2) | −0.0056 (17) | −0.0286 (17) |
| C53 | 0.126 (3) | 0.0787 (19) | 0.0403 (14) | −0.0017 (18) | −0.0102 (15) | −0.0181 (13) |
| C54 | 0.0499 (12) | 0.0755 (16) | 0.0286 (11) | −0.0147 (11) | 0.0009 (9) | −0.0067 (10) |
| C55 | 0.096 (2) | 0.100 (2) | 0.0419 (15) | 0.0139 (17) | −0.0143 (14) | −0.0037 (14) |
| C56 | 0.082 (2) | 0.135 (3) | 0.0486 (17) | 0.002 (2) | −0.0152 (14) | 0.0081 (18) |
| N101 | 0.0379 (8) | 0.0442 (9) | 0.0244 (8) | 0.0040 (7) | −0.0013 (6) | −0.0035 (6) |
| C102 | 0.0418 (11) | 0.0434 (11) | 0.0358 (10) | 0.0092 (8) | 0.0059 (8) | −0.0024 (8) |
| C103 | 0.0466 (11) | 0.0392 (10) | 0.0360 (10) | 0.0058 (8) | 0.0063 (8) | 0.0009 (8) |
| C104 | 0.0386 (10) | 0.0412 (10) | 0.0218 (8) | 0.0052 (8) | −0.0005 (7) | −0.0033 (7) |
| C105 | 0.0376 (11) | 0.0436 (12) | 0.0707 (15) | 0.0078 (9) | 0.0018 (10) | −0.0042 (10) |
| C106 | 0.0422 (11) | 0.0384 (11) | 0.0665 (15) | 0.0038 (9) | −0.0002 (10) | −0.0022 (10) |
| N151 | 0.157 (4) | 0.182 (4) | 0.0499 (18) | −0.092 (3) | −0.022 (2) | 0.029 (2) |
| C152 | 0.267 (7) | 0.130 (4) | 0.067 (3) | −0.043 (4) | −0.074 (3) | 0.028 (3) |
| C153 | 0.218 (5) | 0.105 (3) | 0.064 (2) | −0.016 (3) | −0.068 (3) | 0.026 (2) |
| C154 | 0.0797 (18) | 0.108 (2) | 0.0312 (13) | −0.0441 (16) | −0.0058 (12) | 0.0136 (13) |
| C155 | 0.088 (2) | 0.180 (4) | 0.0349 (15) | −0.029 (2) | 0.0018 (13) | −0.0193 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C156 | 0.098 (3) | 0.210 (5) | 0.0446 (19) | −0.059 (3) | 0.0097 (17) | −0.011 (2) |
| N201 | 0.0714 (14) | 0.0754 (15) | 0.0616 (13) | −0.0299 (12) | 0.0153 (11) | −0.0022 (11) |
| C202 | 0.0847 (19) | 0.0592 (15) | 0.0786 (19) | −0.0325 (14) | 0.0173 (16) | −0.0085 (14) |
| C203 | 0.0751 (17) | 0.0495 (13) | 0.0658 (16) | −0.0190 (12) | 0.0165 (13) | −0.0104 (11) |
| C204 | 0.0627 (13) | 0.0454 (11) | 0.0340 (11) | −0.0135 (10) | 0.0057 (9) | 0.0004 (8) |
| C205 | 0.0693 (15) | 0.0540 (13) | 0.0410 (12) | −0.0153 (11) | 0.0148 (10) | −0.0076 (10) |
| C206 | 0.0700 (16) | 0.0752 (17) | 0.0482 (14) | −0.0173 (13) | 0.0177 (12) | −0.0064 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—N24 | 2.0684 (15) | C19—C20 | 1.413 (3) |
| Zn1—N21 | 2.0695 (16) | C20—C204 | 1.483 (3) |
| Zn1—N22 | 2.0695 (17) | N51—C56 | 1.302 (5) |
| Zn1—N23 | 2.0747 (16) | N51—C52 | 1.306 (5) |
| Zn1—N101$^{i}$ | 2.1385 (16) | C52—C53 | 1.376 (4) |
| N21—C19 | 1.363 (3) | C52—H52 | 0.9500 |
| N21—C16 | 1.369 (3) | C53—C54 | 1.369 (4) |
| N22—C11 | 1.364 (3) | C53—H53 | 0.9500 |
| N22—C14 | 1.373 (2) | C54—C55 | 1.355 (4) |
| N23—C4 | 1.369 (3) | C55—C56 | 1.389 (4) |
| N23—C1 | 1.374 (3) | C55—H55 | 0.9500 |
| N24—C9 | 1.363 (3) | C56—H56 | 0.9500 |
| N24—C6 | 1.370 (2) | N101—C102 | 1.333 (3) |
| C1—C20 | 1.411 (3) | N101—C106 | 1.336 (3) |
| C1—C2 | 1.443 (3) | N101—Zn1$^{ii}$ | 2.1385 (16) |
| C2—C3 | 1.347 (3) | C102—C103 | 1.376 (3) |
| C2—H2 | 0.9500 | C102—H102 | 0.9500 |
| C3—C4 | 1.442 (3) | C103—C104 | 1.383 (3) |
| C3—H3 | 0.9500 | C103—H103 | 0.9500 |
| C4—C5 | 1.407 (3) | C104—C105 | 1.383 (3) |
| C5—C6 | 1.404 (3) | C105—C106 | 1.385 (3) |
| C5—C54 | 1.497 (3) | C105—H105 | 0.9500 |
| C6—C7 | 1.442 (3) | C106—H106 | 0.9500 |
| C7—C8 | 1.352 (3) | N151—C152 | 1.294 (7) |
| C7—H7 | 0.9500 | N151—C156 | 1.307 (6) |
| C8—C9 | 1.443 (3) | C152—C153 | 1.385 (5) |
| C8—H8 | 0.9500 | C152—H152 | 0.9500 |
| C9—C10 | 1.408 (3) | C153—C154 | 1.372 (5) |
| C10—C11 | 1.407 (3) | C153—H153 | 0.9500 |
| C10—C104 | 1.489 (3) | C154—C155 | 1.345 (5) |
| C11—C12 | 1.449 (3) | C155—C156 | 1.413 (5) |
| C12—C13 | 1.345 (3) | C155—H155 | 0.9500 |
| C12—H12 | 0.9500 | C156—H156 | 0.9500 |
| C13—C14 | 1.432 (3) | N201—C206 | 1.320 (3) |
| C13—H13 | 0.9500 | N201—C202 | 1.330 (4) |
| C14—C15 | 1.401 (3) | C202—C203 | 1.382 (4) |
| C15—C16 | 1.405 (3) | C202—H202 | 0.9500 |
| C15—C154 | 1.500 (3) | C203—C204 | 1.387 (3) |

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|---|---|---|---|
| C16—C17 | 1.442 (3) | C203—H203 | 0.9500 |
| C17—C18 | 1.339 (3) | C204—C205 | 1.388 (3) |
| C17—H17 | 0.9500 | C205—C206 | 1.382 (3) |
| C18—C19 | 1.441 (3) | C205—H205 | 0.9500 |
| C18—H18 | 0.9500 | C206—H206 | 0.9500 |
| | | | |
| N24—Zn1—N21 | 162.77 (7) | C17—C18—H18 | 126.1 |
| N24—Zn1—N22 | 88.42 (6) | C19—C18—H18 | 126.1 |
| N21—Zn1—N22 | 88.84 (7) | N21—C19—C20 | 126.29 (18) |
| N24—Zn1—N23 | 89.34 (6) | N21—C19—C18 | 109.15 (18) |
| N21—Zn1—N23 | 87.94 (6) | C20—C19—C18 | 124.46 (19) |
| N22—Zn1—N23 | 161.70 (7) | C1—C20—C19 | 124.66 (19) |
| N24—Zn1—N101$^{i}$ | 95.10 (6) | C1—C20—C204 | 118.30 (18) |
| N21—Zn1—N101$^{i}$ | 102.11 (6) | C19—C20—C204 | 116.97 (18) |
| N22—Zn1—N101$^{i}$ | 102.00 (6) | C56—N51—C52 | 115.3 (3) |
| N23—Zn1—N101$^{i}$ | 96.29 (6) | N51—C52—C53 | 124.6 (3) |
| C19—N21—C16 | 106.82 (16) | N51—C52—H52 | 117.7 |
| C19—N21—Zn1 | 126.42 (13) | C53—C52—H52 | 117.7 |
| C16—N21—Zn1 | 126.72 (14) | C54—C53—C52 | 119.8 (3) |
| C11—N22—C14 | 106.27 (17) | C54—C53—H53 | 120.1 |
| C11—N22—Zn1 | 126.10 (13) | C52—C53—H53 | 120.1 |
| C14—N22—Zn1 | 127.37 (14) | C55—C54—C53 | 115.9 (2) |
| C4—N23—C1 | 106.45 (16) | C55—C54—C5 | 123.2 (2) |
| C4—N23—Zn1 | 125.15 (13) | C53—C54—C5 | 120.9 (2) |
| C1—N23—Zn1 | 126.61 (13) | C54—C55—C56 | 119.9 (3) |
| C9—N24—C6 | 106.48 (15) | C54—C55—H55 | 120.0 |
| C9—N24—Zn1 | 126.17 (12) | C56—C55—H55 | 120.0 |
| C6—N24—Zn1 | 126.59 (13) | N51—C56—C55 | 124.4 (3) |
| N23—C1—C20 | 124.64 (18) | N51—C56—H56 | 117.8 |
| N23—C1—C2 | 109.72 (17) | C55—C56—H56 | 117.8 |
| C20—C1—C2 | 125.64 (19) | C102—N101—C106 | 116.85 (17) |
| C3—C2—C1 | 106.8 (2) | C102—N101—Zn1$^{ii}$ | 120.26 (13) |
| C3—C2—H2 | 126.6 | C106—N101—Zn1$^{ii}$ | 122.55 (14) |
| C1—C2—H2 | 126.6 | N101—C102—C103 | 123.56 (18) |
| C2—C3—C4 | 107.42 (19) | N101—C102—H102 | 118.2 |
| C2—C3—H3 | 126.3 | C103—C102—H102 | 118.2 |
| C4—C3—H3 | 126.3 | C102—C103—C104 | 119.61 (18) |
| N23—C4—C5 | 126.00 (18) | C102—C103—H103 | 120.2 |
| N23—C4—C3 | 109.56 (18) | C104—C103—H103 | 120.2 |
| C5—C4—C3 | 124.42 (18) | C105—C104—C103 | 117.31 (18) |
| C6—C5—C4 | 125.98 (18) | C105—C104—C10 | 122.03 (17) |
| C6—C5—C54 | 117.43 (18) | C103—C104—C10 | 120.65 (17) |
| C4—C5—C54 | 116.59 (18) | C104—C105—C106 | 119.38 (19) |
| N24—C6—C5 | 125.05 (18) | C104—C105—H105 | 120.3 |
| N24—C6—C7 | 109.78 (17) | C106—C105—H105 | 120.3 |
| C5—C6—C7 | 125.15 (18) | N101—C106—C105 | 123.3 (2) |
| C8—C7—C6 | 106.91 (17) | N101—C106—H106 | 118.4 |
| C8—C7—H7 | 126.5 | C105—C106—H106 | 118.4 |

| | | | |
|---|---|---|---|
| C6—C7—H7 | 126.5 | C152—N151—C156 | 117.0 (4) |
| C7—C8—C9 | 106.83 (18) | N151—C152—C153 | 123.7 (5) |
| C7—C8—H8 | 126.6 | N151—C152—H152 | 118.2 |
| C9—C8—H8 | 126.6 | C153—C152—H152 | 118.2 |
| N24—C9—C10 | 125.42 (17) | C154—C153—C152 | 120.3 (5) |
| N24—C9—C8 | 110.00 (16) | C154—C153—H153 | 119.9 |
| C10—C9—C8 | 124.54 (18) | C152—C153—H153 | 119.9 |
| C11—C10—C9 | 125.06 (18) | C155—C154—C153 | 116.1 (3) |
| C11—C10—C104 | 117.12 (16) | C155—C154—C15 | 122.8 (3) |
| C9—C10—C104 | 117.77 (16) | C153—C154—C15 | 121.1 (3) |
| N22—C11—C10 | 125.68 (17) | C154—C155—C156 | 120.0 (4) |
| N22—C11—C12 | 109.87 (17) | C154—C155—H155 | 120.0 |
| C10—C11—C12 | 124.42 (18) | C156—C155—H155 | 120.0 |
| C13—C12—C11 | 106.50 (19) | N151—C156—C155 | 122.9 (5) |
| C13—C12—H12 | 126.7 | N151—C156—H156 | 118.6 |
| C11—C12—H12 | 126.7 | C155—C156—H156 | 118.6 |
| C12—C13—C14 | 107.59 (19) | C206—N201—C202 | 115.6 (2) |
| C12—C13—H13 | 126.2 | N201—C202—C203 | 124.5 (2) |
| C14—C13—H13 | 126.2 | N201—C202—H202 | 117.8 |
| N22—C14—C15 | 124.8 (2) | C203—C202—H202 | 117.8 |
| N22—C14—C13 | 109.76 (18) | C202—C203—C204 | 119.5 (2) |
| C15—C14—C13 | 125.41 (19) | C202—C203—H203 | 120.3 |
| C14—C15—C16 | 126.03 (19) | C204—C203—H203 | 120.3 |
| C14—C15—C154 | 117.7 (2) | C203—C204—C205 | 116.2 (2) |
| C16—C15—C154 | 116.28 (19) | C203—C204—C20 | 121.7 (2) |
| N21—C16—C15 | 125.76 (19) | C205—C204—C20 | 122.07 (19) |
| N21—C16—C17 | 109.5 (2) | C206—C205—C204 | 119.5 (2) |
| C15—C16—C17 | 124.7 (2) | C206—C205—H205 | 120.3 |
| C18—C17—C16 | 106.7 (2) | C204—C205—H205 | 120.3 |
| C18—C17—H17 | 126.6 | N201—C206—C205 | 124.8 (2) |
| C16—C17—H17 | 126.6 | N201—C206—H206 | 117.6 |
| C17—C18—C19 | 107.8 (2) | C205—C206—H206 | 117.6 |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C7—H7···N151$^{iii}$ | 0.95 | 2.65 | 3.583 (4) | 167 |
| C17—H17···N51$^{iv}$ | 0.95 | 2.66 | 3.583 (3) | 165 |

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