

Crystal structure of (diethyl ether- κ O)[5,10,15,20-tetrakis(2-isothiocyanatophenyl)porphyrinato- κ^4 N]zinc diethyl ether solvate

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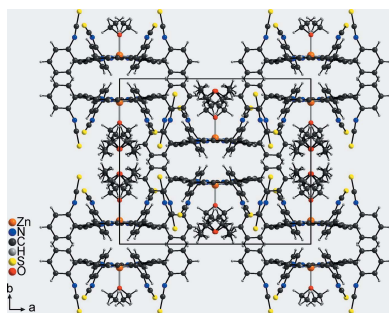
Edited by M. Weil, Vienna University of
Technology, Austria**Keywords:** crystal structure; picket fence
porphyrin; zinc(II) porphyrin; atropisomer; iso-
thiocyanate.**CCDC reference:** 1872076**Supporting information:** this article has
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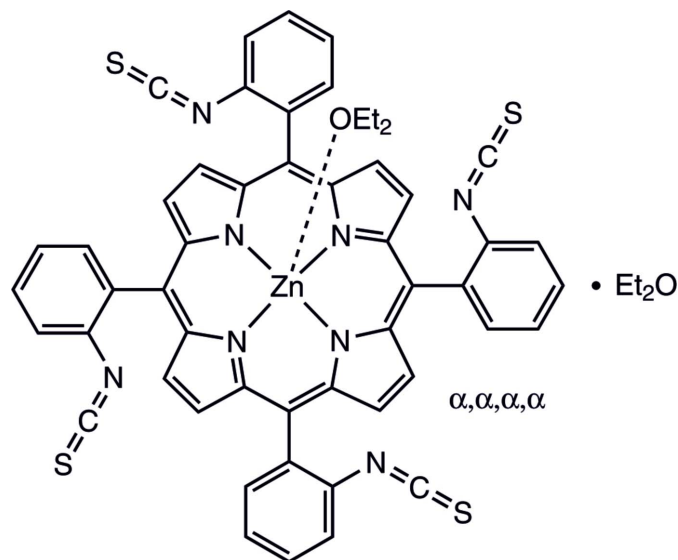
The crystal structure of the title compound, $[\text{Zn}(\text{C}_{48}\text{H}_{24}\text{N}_8\text{S}_4)(\text{C}_4\text{H}_{10}\text{O})]\cdot\text{C}_4\text{H}_{10}\text{O}$, consists of discrete porphyrin complexes that are located on a twofold rotation axis. The Zn^{II} cation is fivefold coordinated by four N atoms of the porphyrin moiety and one O atom of a diethyl ether molecule in a slightly distorted square-pyramidal environment with the diethyl ether molecule in the apical position. The porphyrin backbone is nearly planar with the metal cation slightly shifted out of the plane towards the coordinating diethyl ether molecule. All four isothiocyanato groups of the phenyl substituents at the *meso*-positions face the same side of the porphyrin, as is characteristic for picket fence porphyrins. In the crystal structure, the discrete porphyrin complexes are arranged in such a way that cavities are formed in which additional diethyl ether solvate molecules are located around a twofold rotation axis. The O atom of the solvent molecule is not positioned exactly on the twofold rotation axis, thus making the whole molecule equally disordered over two symmetry-related positions.

1. Chemical context

Isothiocyanates serve as versatile starting materials for a variety of functional groups (Batey & Powell, 2000; Ding *et al.*, 2011; Serra *et al.*, 2014; Guo *et al.*, 2010; Shin *et al.*, 2000; Kosurkar *et al.*, 2014; Alizadeh *et al.*, 2016; Rao *et al.*, 2015). Included in porphyrin scaffolds, isothiocyanates may serve as precursors for the synthesis of tetrapic ligands with fourfold symmetry. In the case where all four *ortho*-substituents of the *meso*-phenyl groups face the same side of the porphyrin plane, these porphyrins are denominated picket fence porphyrins. These compounds are widely used as model compounds for hemoproteins (Collman *et al.*, 1975; Tabushi *et al.*, 1985; Schappacher *et al.*, 1989). With a bulky *ortho*-substituent and Zn^{II} as the central metal cation, the rotational barriers are sufficiently high to isolate the different atropisomers (Freitag & Whitten, 1983). A variety of picket fence porphyrins has been reported (Collman *et al.*, 1975; Mansour *et al.*, 2017; Cormode *et al.*, 2006; Le Maux *et al.*, 1993; Wuenschell *et al.*, 1992). In most cases, amides are used as functional groups in the *ortho*-positions of the *meso*-phenyl groups, which hampers further functionalization. The title compound now opens new avenues for the synthesis of functionalized picket fence porphyrins and is a promising starting material for the design of anion binding ligands. The title compound can be obtained in one step using a method reported by Jha *et al.* (Fig. 1), starting from the all- α isomer of the amino derivative we have



published previously (Jha *et al.*, 2007; Leben *et al.*, 2018). It is important to note that the reaction has to be carried out at 273 K, because at room temperature a mixture of the atropisomers is obtained. After dissolving the tetrakis(isothiocyanatophenyl) porphyrin in acetone and precipitating with diethyl ether, single crystals were obtained, which were characterized by single crystal X-ray diffraction.



2. Structural commentary

The asymmetric unit of the title compound, $\text{Zn}(\text{C}_{48}\text{H}_{24}\text{N}_8\text{S}_4)(\text{C}_4\text{H}_{10}\text{O})\cdot\text{C}_4\text{H}_{10}\text{O}$, comprises one Zn^{II} cation, one half of the porphyrin molecule and one half of a coordinating diethyl ether molecule as well as one half of a diethyl ether solvate molecule. The complex porphyrin molecule and the coordinating diethyl ether molecule are located on a twofold rotation axis whereas the solvent diethyl ether molecule is in a general position and is equally disordered around a twofold rotation axis (Fig. 2). The four isothiocyanate substituents of the phenyl groups at the *meso*-positions point to the same side of the porphyrin moiety, which proves that the tetra- α isomer has formed. The porphyrin plane is close to planar with a maximum deviation from the mean plane of 0.276 (3) Å. The phenyl rings are rotated out of the porphyrin plane by 63.16 (5) and 82.06 (6)°. The Zn^{II} cation is fivefold coordinated by the four N atoms of the porphyrin molecule in the basal positions and by one O atom of a diethyl ether

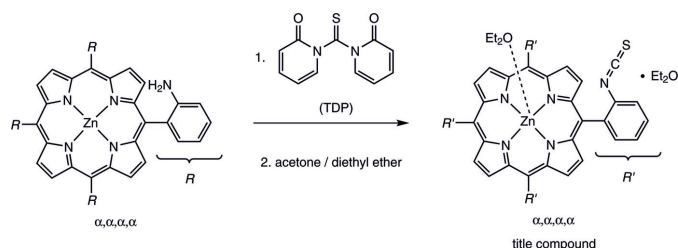


Figure 1
Reaction scheme for the synthesis of the title compound.

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	2.0622 (13)	Zn1—N1	2.0685 (14)
Zn1—N2 ⁱ	2.0622 (13)	Zn1—O1	2.1352 (19)
Zn1—N1 ⁱ	2.0684 (14)		
N2—Zn1—N2 ⁱ	164.44 (8)	N1 ⁱ —Zn1—N1	160.61 (8)
N2—Zn1—N1 ⁱ	88.85 (6)	N2 ⁱ —Zn1—O1	97.78 (4)
N2 ⁱ —Zn1—N1 ⁱ	88.54 (6)	N1 ⁱ —Zn1—O1	99.69 (4)
N2—Zn1—N1	88.54 (6)	N1—Zn1—O1	99.69 (4)
N2 ⁱ —Zn1—N1	88.85 (6)		

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

molecule in the apical position, leading to a distorted square-pyramidal coordination environment (Table 1, Fig. 3). The Zn—N distances of 2.0622 (13) and 2.0684 (14) Å and the Zn—O distance of 2.1352 (19) Å are in characteristic ranges. The angles around the Zn^{II} cation range from 88.54 (6) to 99.69 (4)° for the basal N_4 plane and from 160.61 (8) to 164.44 (8)° involving the apical O atom, demonstrating that the square pyramid is slightly distorted (Table 1). The Zn^{II} cation is located 0.4052 (9) Å out of the mean porphyrin plane and is shifted towards the coordinating diethyl ether molecule (Fig. 4).

3. Supramolecular features

In the crystal structure of the title compound, each two discrete complexes form centrosymmetric pairs with the coordinating diethyl ether molecules pointing in opposite directions (Fig. 5). The complexes are arranged into columns along [001]. This arrangement leads to the formation of cavities between two neighbouring coordinating diethyl ether

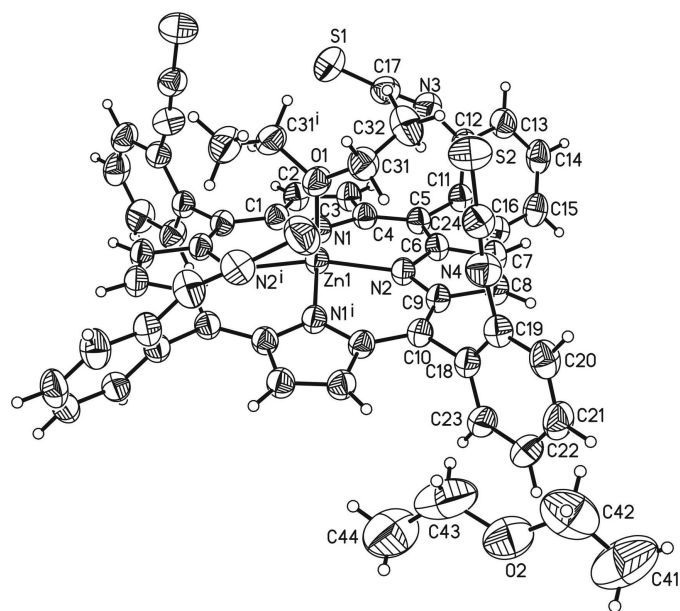


Figure 2
The molecular entities of the title compound with the atom labelling and displacement ellipsoids drawn at the 50% probability level. Only one orientation of the disordered diethyl ether solvent is given. [Symmetry code: (i) $-x + 2, y, -z + \frac{3}{2}$.]

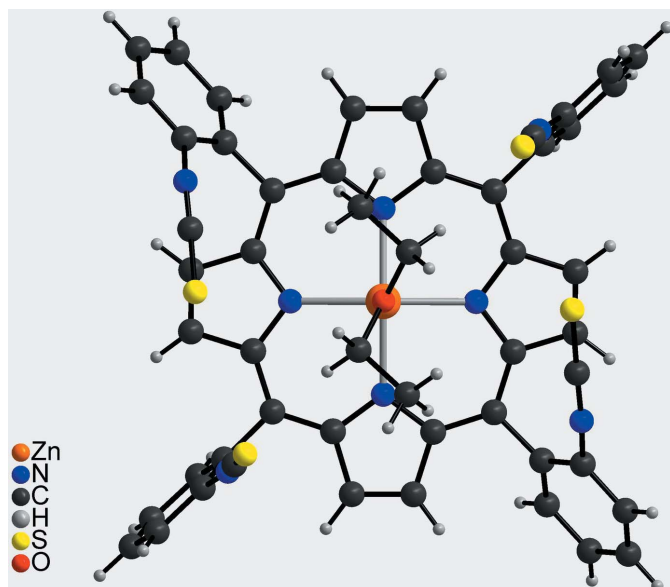


Figure 3
Molecular structure of the discrete complex in a view onto the porphyrin plane.

molecules, in which the disordered diethyl ether solvate molecules are embedded (Fig. 5). There are no notable intermolecular interactions between the molecular moieties in the crystal structure.

4. Database survey

The synthesis of the metal-free oxygen derivative 5,10,15,20-tetrakis $\alpha,\alpha,\alpha,\alpha$ 2-isocyanatophenyl porphyrin has been known for several years (Collman *et al.*, 1998). However, the crystal structure of this compound has not yet been reported. A CSD database search (Version 5.39; Groom *et al.*, 2016) revealed the crystal structures of several metal porphyrins with isothiocyanate entities as axial ligands (Dhifet *et al.*, 2010; Scheidt *et al.*, 1982; Ezzayani *et al.*, 2014; Denden *et al.*, 2015). In addition, the crystal structure of a *para*-isothiocyanato-

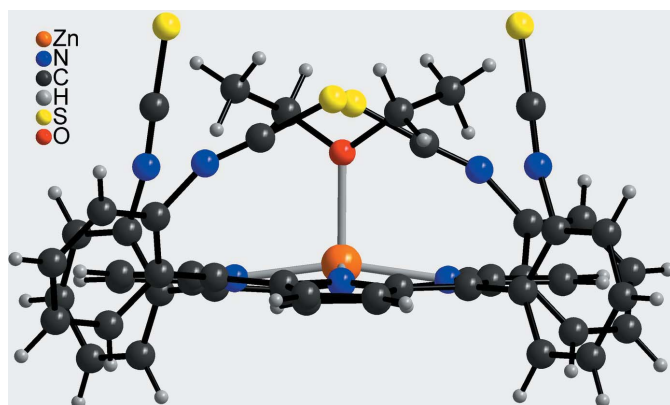


Figure 4
Molecular structure of the discrete complex in a view parallel to the porphyrin plane.

phenyl porphyrin has been reported (Sibrian-Vazquez *et al.*, 2005).

5. Synthesis and crystallization

The metal-free all- α isomer of 2-aminophenyl porphyrin was synthesized according to reported procedures (Collman *et al.*, 1975; Lindsey, 1980). Metallation followed standard metallation conditions as reported previously (Strohmeier *et al.*, 1997; Leben *et al.*, 2018). For the introduction of the isothiocyanato groups, a modified synthesis was used (Jha *et al.*, 2007). 5,10,15,20-Tetrakis($\alpha,\alpha,\alpha,\alpha$ 2-aminophenyl)zinc(II) porphyrin (150 mg, 203 μmol) was dissolved in 30 ml of dichloromethane and cooled to 273 K. 1,1'-Thiocarbonyldi-2,2'-pyridone (TDP, 377 mg, 1.62 mmol) was added and the mixture stirred for 50 minutes at 273 K. Removing the solvent and filtration over silica gel (cyclohexane/ethyl acetate, $v:v = 1:1$) gave the title compound in quantitative yield. For crystallization, a small amount was dissolved in acetone and crystallized by adding diethyl ether.

^1H NMR (500 MHz, CDCl_3 , 300 K): $\delta = 8.80$ (s, 8H, H- β), 8.21 (dd, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz, 4H, H-6), 7.78 (dt, $^3J = 7.9$ Hz, $^4J = 1.5$ Hz, 4H, H-4), 7.68 (dt, $^3J = 7.6$ Hz, $^4J = 1.3$ Hz, 4H, H-5), 7.61 (dd, $^3J = 8.2$ Hz, $^4J = 1.0$ Hz, 4H, H-3) ppm. ^{13}C NMR (125 MHz, CDCl_3 , 300 K): $\delta = 149.9$ (C- α), 141.0 (C1), 134.8 (C6), 134.5 (C2), 131.6 (C- β), 129.3 (C4), 125.7 (C5), 124.4 (C3), 115.7 (C-*meso*) ppm. EI-MS (70 eV): m/z (%) = 904.1 (100) [M] $^+$.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C–H hydrogen atoms were positioned with idealized geometries (C–H = 0.95–0.99 Å; methyl H atoms of the coordinating diethyl ether molecule were allowed to rotate but not to tip) and were refined with

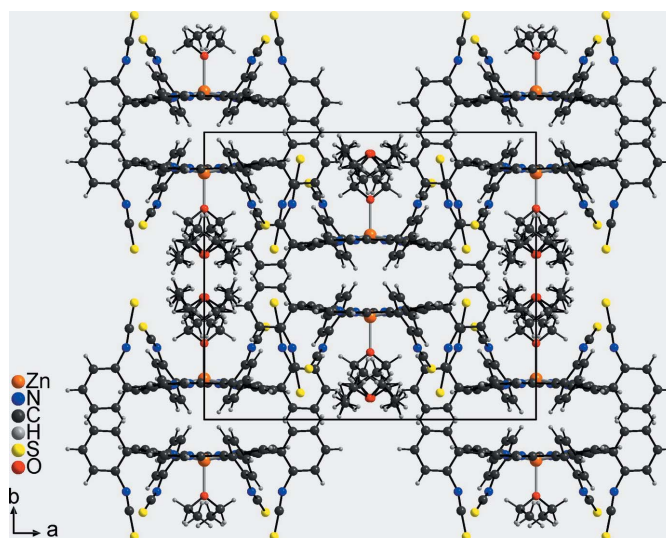


Figure 5
Crystal structure of the title compound viewed along [001].

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model. The O atom of the diethyl ether solvate molecule is not located exactly on the twofold rotation axis and thus the complete molecule is equally disordered over two sets of sites because of symmetry. Therefore for each atom the occupancy was set to 0.5, and atoms were treated with SADI and SIMU commands (Sheldrick, 2015*b*) to achieve similar displacement ellipsoids.

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Table 2
Experimental details.

Crystal data	
Chemical formula	[Zn(C ₄₈ H ₂₄ N ₈ S ₄)(C ₄ H ₁₀ O)]·C ₄ H ₁₀ O
M_r	1054.60
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	200
a, b, c (Å)	19.8830 (4), 17.1781 (3), 14.8684 (3)
β (°)	91.667 (1)
V (Å ³)	5076.18 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.70
Crystal size (mm)	0.14 × 0.11 × 0.07
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (<i>X-RED</i> and <i>X-SHAPE</i> ; Stoe, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.807, 0.951
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39705, 5530, 5042
R_{int}	0.039
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.103, 1.05
No. of reflections	5530
No. of parameters	346
No. of restraints	26
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.39, -0.35

Computer programs: *X-AREA* (Stoe, 2008), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *XP* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2014) and *pubCIF* (Westrip, 2010).

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supporting information

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Crystal structure of (diethyl ether- κ O)[5,10,15,20-tetrakis(2-isothiocyanatophenyl)porphyrinato- κ^4 N]zinc diethyl ether solvate

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Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-AREA* (Stoe, 2008); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(Diethyl ether- κ O)[5,10,15,20-tetrakis(2-isothiocyanatophenyl)porphyrinato- κ^4 N]zinc diethyl ether solvate

Crystal data

[Zn(C₄₈H₂₄N₈S₄)(C₄H₁₀O)]·C₄H₁₀O

$M_r = 1054.60$

Monoclinic, *C2/c*

$a = 19.8830$ (4) Å

$b = 17.1781$ (3) Å

$c = 14.8684$ (3) Å

$\beta = 91.667$ (1)°

$V = 5076.18$ (17) Å³

$Z = 4$

$F(000) = 2184$

$D_x = 1.380$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 39705 reflections

$\theta = 1.6$ – 27.0 °

$\mu = 0.70$ mm⁻¹

$T = 200$ K

Block, red

$0.14 \times 0.11 \times 0.07$ mm

Data collection

Stoe IPDS-2
diffractometer

ω scans

Absorption correction: numerical
(X-Red and X-Shape; Stoe, 2008)

$T_{\min} = 0.807$, $T_{\max} = 0.951$

39705 measured reflections

5530 independent reflections

5042 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.0$ °, $\theta_{\min} = 1.6$ °

$h = -25 \rightarrow 25$

$k = -21 \rightarrow 21$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.103$

$S = 1.05$

5530 reflections

346 parameters

26 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 2.7141P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.39$ e Å⁻³

$\Delta\rho_{\min} = -0.35$ e Å⁻³

Extinction correction: SHELXL,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0011 (2)

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.5000	0.64166 (2)	0.7500	0.03835 (10)	
N1	0.40708 (7)	0.62138 (9)	0.68826 (9)	0.0400 (3)	
N2	0.54332 (7)	0.62541 (9)	0.62706 (9)	0.0392 (3)	
C1	0.34674 (8)	0.61377 (10)	0.72962 (11)	0.0405 (3)	
C2	0.29355 (9)	0.60302 (11)	0.66268 (12)	0.0460 (4)	
H2	0.2471	0.5962	0.6736	0.055*	
C3	0.32240 (9)	0.60449 (12)	0.58175 (12)	0.0464 (4)	
H3	0.3001	0.5983	0.5248	0.056*	
C4	0.39333 (8)	0.61718 (10)	0.59772 (11)	0.0407 (3)	
C5	0.44062 (9)	0.62460 (10)	0.53022 (11)	0.0408 (3)	
C6	0.51067 (9)	0.62744 (10)	0.54465 (11)	0.0405 (3)	
C7	0.55953 (9)	0.62818 (12)	0.47508 (12)	0.0472 (4)	
H7	0.5503	0.6310	0.4121	0.057*	
C8	0.62118 (9)	0.62418 (12)	0.51605 (12)	0.0473 (4)	
H8	0.6632	0.6226	0.4873	0.057*	
C9	0.61077 (8)	0.62273 (10)	0.61146 (11)	0.0407 (3)	
C10	0.66219 (8)	0.61682 (10)	0.67757 (11)	0.0406 (3)	
C11	0.41493 (9)	0.62820 (11)	0.43487 (11)	0.0423 (4)	
C12	0.37604 (9)	0.69080 (12)	0.40320 (12)	0.0479 (4)	
C13	0.35525 (11)	0.69580 (14)	0.31334 (13)	0.0578 (5)	
H13	0.3294	0.7392	0.2928	0.069*	
C14	0.37198 (10)	0.63815 (14)	0.25443 (13)	0.0578 (5)	
H14	0.3579	0.6417	0.1929	0.069*	
C15	0.40929 (10)	0.57473 (13)	0.28425 (13)	0.0539 (5)	
H15	0.4204	0.5345	0.2435	0.065*	
C16	0.43038 (9)	0.57010 (12)	0.37372 (12)	0.0474 (4)	
H16	0.4559	0.5263	0.3937	0.057*	
N3	0.35733 (9)	0.75046 (11)	0.46079 (11)	0.0581 (4)	
C17	0.33979 (10)	0.77941 (12)	0.52739 (14)	0.0531 (4)	
S1	0.31534 (3)	0.82304 (4)	0.61376 (4)	0.07149 (18)	
C18	0.73280 (8)	0.61190 (11)	0.64634 (11)	0.0422 (4)	
C19	0.76769 (9)	0.67895 (11)	0.62281 (12)	0.0456 (4)	
C20	0.83405 (10)	0.67559 (14)	0.59531 (14)	0.0564 (5)	
H20	0.8569	0.7217	0.5787	0.068*	
C21	0.86599 (10)	0.60474 (15)	0.59256 (15)	0.0617 (5)	
H21	0.9114	0.6020	0.5748	0.074*	
C22	0.83267 (11)	0.53773 (14)	0.61539 (16)	0.0629 (5)	
H22	0.8551	0.4890	0.6131	0.075*	
C23	0.76637 (10)	0.54120 (12)	0.64176 (14)	0.0529 (4)	

H23	0.7436	0.4946	0.6569	0.063*	
N4	0.73517 (9)	0.75053 (11)	0.62762 (13)	0.0587 (4)	
C24	0.72587 (9)	0.81716 (12)	0.63222 (14)	0.0510 (4)	
S2	0.71060 (3)	0.90666 (3)	0.63860 (5)	0.07015 (18)	
O1	0.5000	0.76596 (11)	0.7500	0.0511 (4)	
C31	0.54792 (10)	0.81107 (12)	0.70173 (15)	0.0555 (5)	
H31A	0.5892	0.7798	0.6939	0.067*	
H31B	0.5604	0.8578	0.7374	0.067*	
C32	0.52032 (14)	0.83590 (17)	0.61075 (17)	0.0761 (7)	
H32A	0.5068	0.7898	0.5759	0.114*	
H32B	0.5550	0.8644	0.5788	0.114*	
H32C	0.4812	0.8697	0.6184	0.114*	
O2	0.9968 (9)	0.5749 (3)	0.7693 (6)	0.092 (3)	0.5
C41	1.0756 (8)	0.5710 (9)	0.6491 (11)	0.155 (6)	0.5
H41A	1.0997	0.6007	0.6059	0.233*	0.5
H41B	1.1070	0.5431	0.6873	0.233*	0.5
H41C	1.0464	0.5346	0.6182	0.233*	0.5
C42	1.0345 (7)	0.6237 (9)	0.7061 (9)	0.114 (4)	0.5
H42A	1.0636	0.6605	0.7364	0.136*	0.5
H42B	1.0035	0.6521	0.6679	0.136*	0.5
C43	0.9492 (8)	0.6115 (8)	0.8328 (10)	0.124 (5)	0.5
H43A	0.9091	0.6246	0.7988	0.148*	0.5
H43B	0.9660	0.6586	0.8600	0.148*	0.5
C44	0.9249 (6)	0.5580 (6)	0.8994 (8)	0.117 (3)	0.5
H44A	0.8920	0.5822	0.9363	0.176*	0.5
H44B	0.9064	0.5111	0.8736	0.176*	0.5
H44C	0.9642	0.5455	0.9356	0.176*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03477 (15)	0.04689 (17)	0.03351 (15)	0.000	0.00291 (10)	0.000
N1	0.0356 (7)	0.0494 (8)	0.0350 (7)	-0.0013 (6)	0.0024 (5)	0.0005 (6)
N2	0.0361 (7)	0.0477 (8)	0.0339 (7)	0.0002 (6)	0.0028 (5)	0.0001 (5)
C1	0.0360 (8)	0.0453 (9)	0.0404 (8)	-0.0008 (6)	0.0033 (6)	0.0012 (7)
C2	0.0384 (8)	0.0556 (10)	0.0440 (9)	-0.0045 (7)	0.0012 (7)	-0.0001 (8)
C3	0.0407 (9)	0.0590 (11)	0.0394 (8)	-0.0046 (7)	-0.0009 (7)	-0.0013 (7)
C4	0.0387 (8)	0.0468 (9)	0.0364 (8)	-0.0011 (7)	-0.0008 (6)	-0.0003 (7)
C5	0.0408 (8)	0.0458 (9)	0.0359 (8)	-0.0009 (7)	0.0016 (6)	-0.0009 (6)
C6	0.0419 (8)	0.0465 (9)	0.0332 (8)	-0.0009 (7)	0.0032 (6)	0.0005 (6)
C7	0.0429 (9)	0.0639 (11)	0.0350 (8)	-0.0039 (8)	0.0049 (7)	0.0007 (7)
C8	0.0408 (9)	0.0634 (11)	0.0382 (9)	-0.0031 (8)	0.0074 (7)	-0.0001 (8)
C9	0.0384 (8)	0.0464 (9)	0.0377 (8)	-0.0012 (7)	0.0066 (6)	-0.0003 (7)
C10	0.0380 (8)	0.0440 (8)	0.0401 (8)	-0.0010 (6)	0.0052 (6)	-0.0005 (7)
C11	0.0395 (8)	0.0507 (10)	0.0365 (8)	-0.0032 (7)	0.0013 (6)	-0.0006 (7)
C12	0.0472 (9)	0.0573 (11)	0.0393 (8)	0.0030 (8)	0.0031 (7)	-0.0016 (7)
C13	0.0524 (11)	0.0778 (14)	0.0431 (10)	0.0109 (10)	-0.0023 (8)	0.0054 (9)
C14	0.0482 (10)	0.0903 (16)	0.0346 (9)	0.0001 (10)	-0.0016 (7)	-0.0027 (9)

C15	0.0495 (10)	0.0705 (13)	0.0418 (9)	-0.0087 (9)	0.0040 (7)	-0.0132 (9)
C16	0.0465 (9)	0.0516 (10)	0.0443 (9)	-0.0033 (7)	0.0032 (7)	-0.0037 (7)
N3	0.0655 (10)	0.0604 (10)	0.0485 (9)	0.0124 (8)	0.0023 (7)	-0.0006 (8)
C17	0.0506 (10)	0.0545 (11)	0.0540 (11)	0.0066 (8)	-0.0021 (8)	0.0003 (9)
S1	0.0758 (4)	0.0729 (4)	0.0663 (4)	0.0059 (3)	0.0115 (3)	-0.0197 (3)
C18	0.0377 (8)	0.0522 (9)	0.0368 (8)	-0.0008 (7)	0.0036 (6)	-0.0005 (7)
C19	0.0423 (9)	0.0526 (10)	0.0417 (8)	-0.0045 (7)	-0.0004 (7)	-0.0002 (7)
C20	0.0430 (9)	0.0734 (13)	0.0529 (10)	-0.0128 (9)	0.0049 (8)	0.0062 (9)
C21	0.0389 (9)	0.0876 (16)	0.0592 (12)	0.0013 (10)	0.0104 (8)	0.0032 (11)
C22	0.0483 (10)	0.0702 (14)	0.0707 (13)	0.0137 (10)	0.0129 (9)	0.0031 (11)
C23	0.0463 (10)	0.0548 (11)	0.0579 (11)	0.0035 (8)	0.0105 (8)	0.0038 (8)
N4	0.0569 (10)	0.0526 (10)	0.0665 (11)	-0.0068 (8)	0.0004 (8)	0.0012 (8)
C24	0.0418 (9)	0.0569 (12)	0.0543 (10)	-0.0058 (8)	0.0004 (7)	0.0018 (8)
S2	0.0700 (4)	0.0529 (3)	0.0870 (4)	0.0033 (2)	-0.0071 (3)	-0.0033 (3)
O1	0.0499 (10)	0.0455 (10)	0.0586 (11)	0.000	0.0160 (8)	0.000
C31	0.0510 (10)	0.0541 (11)	0.0620 (12)	-0.0087 (8)	0.0112 (9)	0.0022 (9)
C32	0.0862 (18)	0.0802 (16)	0.0623 (14)	-0.0162 (14)	0.0082 (12)	0.0123 (12)
O2	0.073 (3)	0.087 (2)	0.116 (8)	0.005 (3)	-0.004 (7)	-0.006 (3)
C41	0.152 (10)	0.135 (10)	0.179 (13)	0.050 (8)	-0.008 (10)	-0.063 (9)
C42	0.091 (7)	0.125 (8)	0.122 (9)	-0.016 (5)	-0.039 (6)	0.025 (7)
C43	0.125 (11)	0.099 (8)	0.145 (13)	0.046 (7)	-0.036 (9)	-0.035 (8)
C44	0.108 (6)	0.071 (5)	0.175 (11)	-0.013 (4)	0.030 (7)	-0.002 (6)

Geometric parameters (Å, °)

Zn1—N2	2.0622 (13)	C20—C21	1.374 (3)
Zn1—N2 ⁱ	2.0622 (13)	C20—H20	0.9500
Zn1—N1 ⁱ	2.0684 (14)	C21—C22	1.376 (3)
Zn1—N1	2.0685 (14)	C21—H21	0.9500
Zn1—O1	2.1352 (19)	C22—C23	1.387 (3)
N1—C4	1.368 (2)	C22—H22	0.9500
N1—C1	1.370 (2)	C23—H23	0.9500
N2—C9	1.368 (2)	N4—C24	1.162 (3)
N2—C6	1.370 (2)	C24—S2	1.571 (2)
C1—C10 ⁱ	1.397 (2)	O1—C31	1.436 (2)
C1—C2	1.443 (2)	O1—C31 ⁱ	1.436 (2)
C2—C3	1.348 (2)	C31—C32	1.507 (3)
C2—H2	0.9500	C31—H31A	0.9900
C3—C4	1.440 (2)	C31—H31B	0.9900
C3—H3	0.9500	C32—H32A	0.9800
C4—C5	1.401 (2)	C32—H32B	0.9800
C5—C6	1.404 (2)	C32—H32C	0.9800
C5—C11	1.494 (2)	O2—C42 ⁱⁱ	1.11 (2)
C6—C7	1.440 (2)	O2—C42	1.479 (12)
C7—C8	1.355 (3)	O2—C43	1.495 (11)
C7—H7	0.9500	O2—C41 ⁱⁱ	1.912 (18)
C8—C9	1.440 (2)	C41—C44 ⁱⁱ	0.755 (17)
C8—H8	0.9500	C41—C43 ⁱⁱ	0.900 (18)

C9—C10	1.401 (2)	C41—C42	1.499 (14)
C10—C1 ⁱ	1.397 (2)	C41—O2 ⁱⁱ	1.912 (18)
C10—C18	1.494 (2)	C41—H41A	0.9600
C11—C16	1.391 (3)	C41—H41B	0.9599
C11—C12	1.398 (3)	C41—H41C	0.9600
C12—C13	1.390 (3)	C42—C43 ⁱⁱ	0.703 (16)
C12—N3	1.393 (2)	C42—O2 ⁱⁱ	1.11 (2)
C13—C14	1.370 (3)	C42—C42 ⁱⁱ	1.92 (3)
C13—H13	0.9500	C42—H42A	0.9601
C14—C15	1.384 (3)	C42—H42B	0.9599
C14—H14	0.9500	C43—C42 ⁱⁱ	0.703 (16)
C15—C16	1.385 (3)	C43—C41 ⁱⁱ	0.900 (18)
C15—H15	0.9500	C43—C44	1.446 (14)
C16—H16	0.9500	C43—H43A	0.9599
N3—C17	1.170 (3)	C43—H43B	0.9600
C17—S1	1.576 (2)	C44—C41 ⁱⁱ	0.755 (17)
C18—C23	1.389 (3)	C44—H44A	0.9600
C18—C19	1.394 (3)	C44—H44B	0.9600
C19—N4	1.392 (3)	C44—H44C	0.9599
C19—C20	1.394 (3)		
N2—Zn1—N2 ⁱ	164.44 (8)	C31—O1—Zn1	122.65 (11)
N2—Zn1—N1 ⁱ	88.85 (6)	C31 ⁱ —O1—Zn1	122.65 (11)
N2 ⁱ —Zn1—N1 ⁱ	88.54 (6)	O1—C31—C32	111.82 (17)
N2—Zn1—N1	88.54 (6)	O1—C31—H31A	109.3
N2 ⁱ —Zn1—N1	88.85 (6)	C32—C31—H31A	109.3
N1 ⁱ —Zn1—N1	160.61 (8)	O1—C31—H31B	109.3
N2—Zn1—O1	97.78 (4)	C32—C31—H31B	109.3
N2 ⁱ —Zn1—O1	97.78 (4)	H31A—C31—H31B	107.9
N1 ⁱ —Zn1—O1	99.69 (4)	C31—C32—H32A	109.5
N1—Zn1—O1	99.69 (4)	C31—C32—H32B	109.5
C4—N1—C1	106.50 (14)	H32A—C32—H32B	109.5
C4—N1—Zn1	126.59 (11)	C31—C32—H32C	109.5
C1—N1—Zn1	126.82 (11)	H32A—C32—H32C	109.5
C9—N2—C6	106.88 (13)	H32B—C32—H32C	109.5
C9—N2—Zn1	126.26 (11)	C42 ⁱⁱ —O2—C42	94.7 (13)
C6—N2—Zn1	126.16 (11)	C42 ⁱⁱ —O2—C43	26.4 (9)
N1—C1—C10 ⁱ	125.29 (15)	C42—O2—C43	120.3 (9)
N1—C1—C2	109.66 (14)	C42 ⁱⁱ —O2—C41 ⁱⁱ	51.6 (8)
C10 ⁱ —C1—C2	125.05 (16)	C42—O2—C41 ⁱⁱ	146.0 (10)
C3—C2—C1	106.91 (15)	C43—O2—C41 ⁱⁱ	27.3 (8)
C3—C2—H2	126.5	C44 ⁱⁱ —C41—C43 ⁱⁱ	122 (3)
C1—C2—H2	126.5	C44 ⁱⁱ —C41—C42	137 (3)
C2—C3—C4	107.20 (15)	C43 ⁱⁱ —C41—C42	18.1 (13)
C2—C3—H3	126.4	C44 ⁱⁱ —C41—O2 ⁱⁱ	129 (2)
C4—C3—H3	126.4	C43 ⁱⁱ —C41—O2 ⁱⁱ	49.6 (12)
N1—C4—C5	125.53 (15)	C42—C41—O2 ⁱⁱ	35.6 (7)
N1—C4—C3	109.70 (14)	C44 ⁱⁱ —C41—H41A	60.7

C5—C4—C3	124.76 (16)	C43 ⁱⁱ —C41—H41A	94.4
C4—C5—C6	125.25 (16)	C42—C41—H41A	110.3
C4—C5—C11	117.74 (15)	O2 ⁱⁱ —C41—H41A	143.7
C6—C5—C11	116.99 (15)	C44 ⁱⁱ —C41—H41B	114.2
N2—C6—C5	125.30 (15)	C43 ⁱⁱ —C41—H41B	124.1
N2—C6—C7	109.32 (15)	C42—C41—H41B	108.7
C5—C6—C7	125.28 (16)	O2 ⁱⁱ —C41—H41B	97.5
C8—C7—C6	107.28 (16)	H41A—C41—H41B	109.5
C8—C7—H7	126.4	C44 ⁱⁱ —C41—H41C	50.2
C6—C7—H7	126.4	C43 ⁱⁱ —C41—H41C	108.5
C7—C8—C9	106.85 (15)	C42—C41—H41C	109.4
C7—C8—H8	126.6	O2 ⁱⁱ —C41—H41C	82.6
C9—C8—H8	126.6	H41A—C41—H41C	109.5
N2—C9—C10	125.61 (15)	H41B—C41—H41C	109.5
N2—C9—C8	109.64 (15)	C43 ⁱⁱ —C42—O2 ⁱⁱ	109 (2)
C10—C9—C8	124.73 (16)	C43 ⁱⁱ —C42—O2	127 (2)
C1 ⁱ —C10—C9	125.76 (16)	O2 ⁱⁱ —C42—O2	20.8 (8)
C1 ⁱ —C10—C18	116.90 (15)	C43 ⁱⁱ —C42—C41	23 (2)
C9—C10—C18	117.33 (15)	O2 ⁱⁱ —C42—C41	92.9 (12)
C16—C11—C12	117.55 (16)	O2—C42—C41	108.1 (13)
C16—C11—C5	120.98 (17)	C43 ⁱⁱ —C42—C42 ⁱⁱ	156 (3)
C12—C11—C5	121.45 (16)	O2 ⁱⁱ —C42—C42 ⁱⁱ	50.1 (8)
C13—C12—N3	117.92 (18)	O2—C42—C42 ⁱⁱ	35.3 (7)
C13—C12—C11	121.16 (18)	C41—C42—C42 ⁱⁱ	142.7 (10)
N3—C12—C11	120.92 (16)	C43 ⁱⁱ —C42—H42A	107.4
C14—C13—C12	119.9 (2)	O2 ⁱⁱ —C42—H42A	132.6
C14—C13—H13	120.0	O2—C42—H42A	112.6
C12—C13—H13	120.0	C41—C42—H42A	109.5
C13—C14—C15	120.15 (18)	C42 ⁱⁱ —C42—H42A	96.5
C13—C14—H14	119.9	C43 ⁱⁱ —C42—H42B	88.1
C15—C14—H14	119.9	O2 ⁱⁱ —C42—H42B	102.7
C14—C15—C16	119.83 (18)	O2—C42—H42B	109.6
C14—C15—H15	120.1	C41—C42—H42B	108.8
C16—C15—H15	120.1	C42 ⁱⁱ —C42—H42B	86.7
C15—C16—C11	121.34 (19)	H42A—C42—H42B	108.1
C15—C16—H16	119.3	C42 ⁱⁱ —C43—C41 ⁱⁱ	138 (3)
C11—C16—H16	119.3	C42 ⁱⁱ —C43—C44	158 (2)
C17—N3—C12	157.6 (2)	C41 ⁱⁱ —C43—C44	26.4 (16)
N3—C17—S1	176.6 (2)	C42 ⁱⁱ —C43—O2	44.9 (18)
C23—C18—C19	117.82 (16)	C41 ⁱⁱ —C43—O2	103.2 (17)
C23—C18—C10	121.48 (16)	C44—C43—O2	113.4 (10)
C19—C18—C10	120.68 (17)	C42 ⁱⁱ —C43—H43A	83.7
N4—C19—C20	119.79 (18)	C41 ⁱⁱ —C43—H43A	83.3
N4—C19—C18	118.78 (16)	C44—C43—H43A	102.7
C20—C19—C18	121.44 (19)	O2—C43—H43A	107.3
C21—C20—C19	119.2 (2)	C42 ⁱⁱ —C43—H43B	86.1
C21—C20—H20	120.4	C41 ⁱⁱ —C43—H43B	135.5
C19—C20—H20	120.4	C44—C43—H43B	111.5

C20—C21—C22	120.49 (18)	O2—C43—H43B	113.6
C20—C21—H21	119.8	H43A—C43—H43B	107.3
C22—C21—H21	119.8	C41 ⁱⁱ —C44—C43	32.0 (18)
C21—C22—C23	120.1 (2)	C41 ⁱⁱ —C44—H44A	115.3
C21—C22—H22	119.9	C43—C44—H44A	111.3
C23—C22—H22	119.9	C41 ⁱⁱ —C44—H44B	82.6
C22—C23—C18	120.90 (19)	C43—C44—H44B	113.0
C22—C23—H23	119.5	H44A—C44—H44B	109.5
C18—C23—H23	119.5	C41 ⁱⁱ —C44—H44C	126.1
C24—N4—C19	161.5 (2)	C43—C44—H44C	104.0
N4—C24—S2	178.01 (19)	H44A—C44—H44C	109.5
C31—O1—C31 ⁱ	114.7 (2)	H44B—C44—H44C	109.5

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $-x+2, y, -z+3/2$.