A synchrotron study of [5,10,15,20-tetrakis(3-cyanophenyl)porphyrinato- $\kappa^4 N^5, N^{10}, N^{15}, N^{20}$]copper(II) nitrobenzene trisolvate at 80 K

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A synchrotron study of [5,10,15,20-tetrakis(3-cyanophenyl)porphyrinato- $\kappa^4 N^5, N^{10}, N^{15}, N^{20}$]-copper(II) nitrobenzene trisolvate at 80 K¹

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¹ Dedicated to Professor Wolfgang Seidel on the occasion of his 85th birthday.

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Porphyrin assemblies display interesting photophysical properties and a relatively high thermal stability. Moreover, *meso*-functionalized porphyrins with virtually fourfold symmetry can be relatively readily synthesized from pyrrole and the appropriate aldehyde. A number of metallo derivatives of 5,10,15,20-tetrakis(4-cyanophenyl)porphyrin, where the N atom of the linear cyano group can act both as a donor for coordination bonds or as an acceptor for hydrogen bonds, have been structurally characterized by single-crystal X-ray analysis. The supramolecular and structural chemistry of the corresponding 2- and 3-cyanophenyl isomers of the parent porphyrin, however, has remained largely unexplored. The crystal structure of [5,10,15,20-tetrakis(3-cyanophenyl)porphyrinato]copper(II) (CuTCNPP) nitrobenzene trisolvate, [Cu(C₄₈H₂₄N₈)]·3C₆H₅NO₂, has been determined at 80 K by synchrotron single-crystal X-ray diffraction. CuTCNPP exhibits a C_{2h}-symmetric $\alpha\alpha\beta\beta$ conformation, despite an unsymmetrical crystal environment, and is situated on a crystallographic centre of symmetry. The Cu^{II} ion adopts a genuine square-planar coordination by the four pyrrole N atoms. The 24-membered porphyrin ring system shows no marked deviation from planarity. In the crystal, the CuTCNPP molecules and two nitrobenzene molecules are face-to-face stacked in an alternating fashion, resulting in corrugated layers. The remaining nitrobenzene guest molecule per CuTCNPP resides in the region between four neighbouring columnar stacks of CuTCNPP and sandwiched nitrobenzene molecules, and is disordered over four positions about a centre of symmetry.

1. Introduction

Solid-state supramolecular porphyrin assemblies have attracted ongoing interest in numerous research fields, such as heterogeneous catalysis, sensing, separation, light harvesting, artificial photosynthesis and carbon dioxide capture. A relatively rigid planar structure, interesting photophysical properties (*i.e.* intense light absorption and fluorescence in the visible region) and a relatively high thermal stability make the porphyrin skeleton useful for these applications (for recent reviews, see, Gao *et al.*, 2014; Guo & Chen, 2015; Huh *et al.*, 2016; Ishihara *et al.*, 2014; Kumar, Bansal *et al.*, 2015; Kumar, Deep & Kim, 2015; Kumar, Wani *et al.*, 2015; So *et al.*, 2015; Zhang & Lin, 2014; Zha *et al.*, 2014). Moreover, *meso*-functionalized porphyrins with virtually fourfold symmetry can be relatively readily synthesized from pyrrole and the appropriate aldehyde.

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The N atom of the linear cyano group can act both as a donor for coordination bonds or as an acceptor for hydrogen bonds. In a seminal work, Robson and co-workers utilized the *meso*-functionalized metalloporphyrin [5,10,15,20-tetrakis(4-cyanophenyl)porphyrinato]copper(II) as a square-planar building block to form a PtS-related three-dimensional coordination polymer with Cu^{I} ions as tetrahedral nodes (Abrahams *et al.*, 1994). Whereas a number of metallo derivatives of 5,10,15,20-tetrakis(4-cyanophenyl)porphyrin have been structurally characterized by single-crystal X-ray analysis since (Cao *et al.*, 2015; Dong & Jiang, 2011; He *et al.*, 2008; Kumar *et al.*, 1998; Wang *et al.*, 2001, 2009), the supramolecular and structural chemistry of the corresponding 2- and 3-cyanophenyl isomers of the parent porphyrin has remained largely unexplored.

In contrast to the 4-cyanophenyl isomer, [5,10,15,20-tetrakis(3-cyanophenyl)porphyrinato]copper(II) (CuTCNPP) can occur as four possible minimum-energy conformational isomers (Tomé *et al.*, 2011), depending on the orientations of

Figure 1
The four possible minimum-energy conformations of CuTCNPP.

the 3-cyanophenyl groups relative to the porphyrin plane [*i.e.* above (α) or below (β)], as illustrated in Fig. 1. For [5,10,15,20-tetrakis(2-cyanophenyl)porphyrinato]zinc(II), the four atropisomers resulting from restricted rotation of the 2-cyanophenyl groups about the porphyrin plane could be isolated and a crystal structure containing the $\alpha\beta\alpha\beta$ -atropisomer [refcode FUPCEY in the Cambridge Structural Database (CSD); Groom *et al.*, 2016] has been determined (Hatano *et al.*, 1987). Kirichenko *et al.* (2011) have described a discrete metallosupramolecular assembly consisting of two $\alpha\alpha\alpha\alpha$ -conformational isomers of [5,10,15,20-tetrakis(3-cyanophenyl)porphyrinato]zinc(II) linked by four PdCl_2 units through coordination bonds between the peripheral cyano groups and the Pd^{II} atoms, which was studied by ^1H NMR and visible spectroscopy in solution. To the best of our knowledge, and based on a search of the CSD via the WebCSD interface (Thomas *et al.*, 2010) in July 2016, a crystal structure containing 5,10,15,20-tetrakis(3-cyanophenyl)porphyrin has not been reported so far. In this contribution, we report the synthesis of CuTCNPP and the crystal structure of its nitrobenzene trisolvate, *i.e.* the title compound, (I).

2. Experimental

2.1. Synthesis and crystallization

The chemicals used were of reagent grade and were obtained from commercial sources. The solvents used for chromatographic, mass spectrometric and spectroscopic analyses were of analytical grade. High-resolution electron-spray ionization mass spectrometry was performed using a Thermo LTQ-FT Ultra mass spectrometer. The UV-Vis spectrum of CuTCNPP was recorded on a Shimadzu UV-1650PC spectrophotometer and the IR spectrum was recorded on a Bruker Alpha Platinum-ATR spectrometer.

2.1.1. Preparation of H_2TCNPP . A solution of 3-cyanobenzaldehyde (9.70 g, 0.074 mol) and freshly distilled pyrrole (0.074 mol, 5.1 ml) was stirred at 403 K in propionic acid (260 ml) for 2 h. After the reaction mixture was cooled to 323–333 K, a first crop of the product was isolated by filtration over a sintered glass funnel. A second crop was obtained by filtration over a fresh funnel after cooling to room temperature. Another crop of product was isolated after evaporation of half of the propionic acid solvent. The precipitates were washed with methanol, followed by water, and then methanol again until the filtrate remained colourless. After washing, the combined precipitates were dried in high vacuum at 453 K for 3 h (yield: 9.52 g, 0.013 mol, 18%). The physical properties agreed with those reported in the literature (Kirichenko *et al.*, 2011).

2.1.2. Synthesis of CuTCNPP. A solution of copper(II) acetate monohydrate (100 mg, 0.5 mmol) in methanol (25 ml) was added to a solution of H_2TCNPP (357 mg, 0.5 mmol) in dichloromethane (25 ml). The mixture was stirred overnight and the solvents were subsequently removed under reduced pressure. The residue was taken up in ethyl acetate. The solution was washed three times with water, dried on

Table 1
Experimental details.

Crystal data	
Chemical formula	[Cu(C ₄₈ H ₂₄ N ₈)]·3C ₆ H ₅ NO ₂
<i>M_r</i>	1145.62
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	80
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.234 (4), 11.872 (9), 14.212 (7)
α , β , γ (°)	104.37 (3), 94.85 (10), 96.85 (8)
<i>V</i> (Å ³)	1326.8 (14)
<i>Z</i>	1
Radiation type	Synchrotron, λ = 0.56305 Å
μ (mm ⁻¹)	0.26
Crystal size (mm)	0.04 × 0.01 × 0.01
Data collection	
Diffractometer	P11 beamline at PETRA III with a Pilatus 6M detector (Kraft <i>et al.</i> , 2009)
Absorption correction	Multi-scan (<i>XDS</i> ; Kabsch, 2010)
<i>T_{min}</i> , <i>T_{max}</i>	0.918, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	43137, 7802, 7176
<i>R_{int}</i>	0.038
(sin θ/λ) _{max} (Å ⁻¹)	0.715
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.130, 1.05
No. of reflections	7802
No. of parameters	389
No. of restraints	60
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.97, -1.13

Computer programs: P11 Crystallography Control (Meents *et al.*, 2013), *XDS* (Kabsch, 2010), *SUPERFLIP* (Palatinus & Chapuis, 2007), *EDMA* (Palatinus *et al.*, 2012), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2014) and *enCIFer* (Allen *et al.*, 2004).

magnesium sulfate and evaporated to dryness. The product was dried in a vacuum desiccator over calcium chloride (yield: 239 mg, 0.308 mmol, 62%). The material thus obtained was used for crystallization (see below) without further purification. For UV–Vis and IR spectroscopic analyses, a small amount of the product was purified (purity 99.7 area%) by semipreparative HPLC (see *Supporting information*). HRMS (ESI⁺): calculated for [C₄₈H₂₄CuNaN₈]⁺: *m/z* 798.131200; found: *m/z* 798.131550. IR (ATR): 2229 (C≡N) cm⁻¹. UV–Vis (CH₂Cl₂): $\lambda_{\max}$ = 223, 309, 415, 538, 574 nm.

Tiny purple crystals of (I) suitable for synchrotron single-crystal X-ray diffraction were obtained from a solution of CuTCNPP in acetone containing a few drops of nitrobenzene. The solvents were allowed to evaporate slowly at room temperature.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. A nitrobenzene solvent molecule was found to be disordered over four positions about a centre of symmetry. The occupancies of the components of the asymmetric half were refined by means of a free variable, affording occupancies of 0.261 (5) and 0.239 (5). The disordered nitrobenzene molecule was modelled with isotropic atomic displacement parameters and standard similar distance restraints with effective standard deviations of 0.02 Å for 1,2-

distances and 0.04 Å for 1,3-distances. H-atom positions were calculated geometrically (C–H = 0.95 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

3. Results and discussion

The corresponding free-base porphyrin (H₂TCNPP) was prepared using the Adler–Longo method (Lindsey, 2000) and copper(II) was inserted into the porphyrin macrocycle by treatment of H₂TCNPP with copper(II) acetate to give CuTCNPP. The electronic spectrum of CuTCNPP (Fig. S1 in the *Supporting information*) in the visible region shows the three bands characteristic of a metallocporphyrin with virtual *D*_{4h} symmetry (Buchler, 1975). The intense Soret band (or B band) is observed at 415 nm, and weak β and α bands in the Q-band region appear at 538 and 574 nm, respectively. The band at 2229 cm⁻¹ in the IR spectrum (Fig. S2 in the *Supporting information*) is characteristic of the C≡N stretching vibration of aromatic nitrile groups (Coates, 2000).

Crystallization from a solution of CuTCNPP in acetone containing a small amount of nitrobenzene yielded tiny crystals of (I). X-ray diffraction data were collected from a single crystal at beamline P11 of the PETRA III synchrotron facility at DESY, Hamburg (Burkhardt *et al.*, 2016). Fig. 2 shows the molecular structure of CuTCNPP in (I). The molecule adopts the $\alpha\alpha\beta\beta$ conformation (Fig. 1) in the crystal. CuTCNPP is situated on a crystallographic centre of symmetry and exhibits an r.m.s. deviation from exact molecular *C*_{2h} point group symmetry of 0.047 Å, as calculated with MOLSYM in PLATON (Spek, 2009). Opposite 3-cyanophenyl moieties are

Figure 2
The molecular structure of CuTCNPP in (I). Displacement ellipsoids are drawn at the 70% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

virtually coplanar. The porphyrin macrocycle is approximately planar, with an r.m.s. deviation of 0.036 Å for the 24 fitted non-H atoms. The displacements of individual atoms from the least-squares mean plane indicate a slight *wav* deformation, with two opposite pyrrole rings lying above and below the porphyrin mean plane (Jentzen *et al.*, 1997). The largest displacements are observed for atom N22 [0.072 (1) Å] and the corresponding symmetry-related N22ⁱ atom [−0.072 (1) Å; symmetry code: (i) $-x, -y + 1, -z + 1$]. The dihedral angles between the mean plane of the porphyrin macrocycle and the mean planes of the arene rings are 62.9 (1)° for C51–C56 and 65.7 (1)° for C101–C107. The central Cu1 atom lies perfectly in the mean plane through the porphyrin ring system, as required by the site symmetry. The bond lengths and angles around the Cu1 atom are listed in Table 2. The sum of the N–Cu–N angles confirms the square coordination of the Cu^{II} ion by the four pyrrole N atoms, as required by crystallographic symmetry. The Cu–N bond lengths are as expected for copper(II) porphyrins (Hoard, 1975).

In the crystal, the CuTCNPP molecules are stacked, together with two sandwiched nitrobenzene molecules, along the *a*-axis direction, in such a way that the CuTCNPP molecules and nitrobenzene molecules in adjacent stacks form corrugated layers. Another nitrobenzene guest molecule per metalloporphyrin resides in the region between four neighbouring columnar stacks of CuTCNPP and sandwiched nitrobenzene molecules, and is disordered over four positions about a centre of symmetry (Fig. 3). Of the four minimum-energy conformations of CuTCNPP, only the $\alpha\alpha\beta\beta$ confor-

Table 2
Selected geometric parameters (Å, °).

Cu1–N21	1.9977 (17)	Cu1–N22	2.021 (2)
N21–Cu1–N21 ⁱ	180.0	N21–Cu1–N22	89.84 (8)
N21–Cu1–N22 ⁱ	90.16 (8)	N22–Cu1–N22 ⁱ	180.0

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

mation is compatible with a centrosymmetric triclinic unit cell with $Z = 1$. This arrangement resembles the typical triclinic porphyrin-based framework of solvated *meso*-tetraarylporphyrins, which is maintained in the solvates they form (Byrn *et al.*, 1993). The two sandwiched nondisordered nitrobenzene guest molecules per metalloporphyrin exhibit a centrosymmetric antiparallel alignment face-to-face stacked between the porphyrin macrocycles along the *a*-axis direction (Fig. 4). The separation between the mean planes through the porphyrin ring systems is 7.35 Å, allowing the accommodation of flat aromatic guest molecules *via* face-to-face stacking. It is worth noting that the sandwiched nitrobenzene molecules are not symmetrically placed between adjacent porphyrin rings, but each is slightly tilted and closest to the nearest Cu^{II} atom. The total solvent-accessible volume per unit-cell volume, as calculated with SOLV in PLATON (Spek, 2009) using default options (probe radius 1.2 Å), is 42.7%. Nitrobenzene has been recognised as a crystallization template for porphyrins (Diskin-Posner & Goldberg, 1999; Diskin-Posner *et al.*, 2002; Vinodu & Goldberg, 2005) since the pioneering work of Abrahams *et al.* (1994). A face-to-face arrangement of nitro-

Figure 3

Packing diagram of (I), viewed along the *a* axis. Nitrobenzene guest molecules in the interstices are shown in space-filling representation. For the sake of clarity, disorder of the nitrobenzene molecules is not shown. The nondisordered nitrobenzene molecules sandwiched between the porphyrin macrocycles and the H atoms of CuTCNPP have also been omitted for clarity.

benzene guest molecules and porphyrin macrocycles as in (I) is not always the case. Previously, we observed genuine edge-to-face stacking of porphyrin macrocycles and nitrobenzene guest molecules, while the nitrobenzene guest molecules are face-to-face stacked with respect to one another (Seidel *et al.*, 2014).

In summary, we have achieved the first structural analysis of a solvated 5,10,15,20-tetrakis(3-cyanophenyl)porphyrin derivative from a tiny crystal by synchrotron single-crystal X-ray diffraction at 80 K. The crystal structure features an essentially flat porphyrin ring system in CuTCNPP. The orientation of the 3-cyanophenyl groups in the *meso*-positions of the porphyrin in the solid-state represents a centrosymmetric $\alpha\alpha\beta\beta$ conformation. Nitrobenzene was successfully used as a crystallization template and was found to interact with the porphyrin molecules *via* face-to-face stacking in the crystal, as well as occupying interstitial spaces. The results described in this contribution are an important addition to the increasing library of crystalline porphyrin-based solids and reveal several novel subtleties in crystal packing.

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Figure 4

View of the triclinic unit cell of (I) along the [011] direction, showing the nondisordered nitrobenzene molecules sandwiched between CuTCNPP molecules. The H atoms of CuTCNPP and the disordered nitrobenzene guest molecules residing at $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, 1, 0)$, $(\frac{1}{2}, 0, 1)$ and $(\frac{1}{2}, 1, 1)$ have been omitted for clarity.

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A synchrotron study of [5,10,15,20-tetrakis(3-cyanophenyl)porphyrinato- $\kappa^4 N^5, N^{10}, N^{15}, N^{20}$]copper(II) nitrobenzene trisolvate at 80 K

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Computing details

Data collection: P11 Crystallography Control (Meents *et al.*, 2013); cell refinement: XDS (Kabsch, 2010); data reduction: XDS (Kabsch, 2010); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007) and EDMA (Palatinus *et al.*, 2012); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2014); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

5,10,15,20-tetrakis(3-cyanophenyl)porphyrinatocopper(II) nitrobenzene trisolvate

Crystal data

[Cu(C₄₈H₂₄N₈)]·3C₆H₅NO₂

$M_r = 1145.62$

Triclinic, $P\bar{1}$

$a = 8.234$ (4) Å

$b = 11.872$ (9) Å

$c = 14.212$ (7) Å

$\alpha = 104.37$ (3)°

$\beta = 94.85$ (10)°

$\gamma = 96.85$ (8)°

$V = 1326.8$ (14) Å³

$Z = 1$

$F(000) = 589$

$D_x = 1.434$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.56305$ Å

Cell parameters from 34070 reflections

$\theta = 1.2$ – 23.7°

$\mu = 0.26$ mm⁻¹

$T = 80$ K

Prism, purple

$0.04 \times 0.01 \times 0.01$ mm

Data collection

P11 beamline at PETRA III with Pilatus 6M detector (Kraft *et al.*, 2009)

diffractometer

Radiation source: synchrotron

Detector resolution: 5.81 pixels mm⁻¹

φ scans

Absorption correction: multi-scan (XDS; Kabsch, 2010)

$T_{\min} = 0.918$, $T_{\max} = 1.000$

43137 measured reflections

7802 independent reflections

7176 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 23.7^\circ$, $\theta_{\min} = 1.2^\circ$

$h = -11 \rightarrow 11$

$k = -16 \rightarrow 16$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.130$

$S = 1.05$

7802 reflections

389 parameters

60 restraints

Primary atom site location: iterative

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 2.9063P]$

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

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

$$\Delta\rho_{\max} = 0.97 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.13 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.0000	0.5000	0.5000	0.00671 (8)	
N1	0.6994 (2)	0.32906 (15)	0.95871 (12)	0.0144 (3)	
N2	0.5750 (2)	−0.08604 (15)	0.23767 (14)	0.0190 (3)	
N21	0.02618 (18)	0.58412 (12)	0.64199 (10)	0.0059 (2)	
N22	0.09972 (18)	0.36511 (12)	0.53325 (10)	0.0066 (2)	
C1	−0.0107 (2)	0.69490 (14)	0.68306 (12)	0.0070 (3)	
C2	0.0317 (2)	0.72614 (15)	0.78785 (12)	0.0105 (3)	
H2	0.0167	0.7971	0.8327	0.013*	
C3	0.0970 (2)	0.63481 (15)	0.81011 (12)	0.0093 (3)	
H3	0.1386	0.6304	0.8733	0.011*	
C4	0.0909 (2)	0.54588 (14)	0.71940 (11)	0.0065 (3)	
C5	0.1438 (2)	0.43677 (14)	0.71330 (11)	0.0061 (3)	
C6	0.1465 (2)	0.35264 (14)	0.62531 (12)	0.0073 (3)	
C7	0.1955 (2)	0.23842 (15)	0.61857 (13)	0.0114 (3)	
H7	0.2324	0.2086	0.6715	0.014*	
C8	0.1785 (2)	0.18180 (15)	0.52180 (13)	0.0121 (3)	
H8	0.2018	0.1048	0.4942	0.014*	
C9	0.1184 (2)	0.26042 (14)	0.46891 (12)	0.0081 (3)	
C10	0.0780 (2)	0.23160 (14)	0.36749 (12)	0.0071 (3)	
C51	0.3989 (2)	0.36336 (14)	0.91937 (12)	0.0074 (3)	
C52	0.3537 (2)	0.38807 (14)	0.83029 (12)	0.0077 (3)	
H52	0.4323	0.3912	0.7854	0.009*	
C53	0.1939 (2)	0.40814 (13)	0.80724 (11)	0.0063 (3)	
C54	0.0792 (2)	0.40126 (14)	0.87430 (12)	0.0074 (3)	
H54	−0.0307	0.4138	0.8591	0.009*	
C55	0.1251 (2)	0.37619 (15)	0.96280 (12)	0.0090 (3)	
H55	0.0461	0.3717	1.0072	0.011*	
C56	0.2850 (2)	0.35780 (15)	0.98655 (12)	0.0094 (3)	
H56	0.3166	0.3418	1.0472	0.011*	
C57	0.5659 (2)	0.34414 (15)	0.94157 (12)	0.0101 (3)	
C101	0.2809 (2)	−0.02879 (14)	0.24570 (12)	0.0085 (3)	
C102	0.2607 (2)	0.08212 (14)	0.30248 (12)	0.0082 (3)	
H102	0.3541	0.1363	0.3363	0.010*	
C103	0.1031 (2)	0.11283 (14)	0.30923 (12)	0.0074 (3)	
C104	−0.0328 (2)	0.03053 (14)	0.25935 (12)	0.0090 (3)	
H104	−0.1408	0.0502	0.2644	0.011*	

C105	−0.0118 (2)	−0.07955 (15)	0.20254 (13)	0.0104 (3)	
H105	−0.1053	−0.1341	0.1693	0.012*	
C106	0.1452 (2)	−0.10993 (14)	0.19439 (13)	0.0099 (3)	
H106	0.1603	−0.1843	0.1548	0.012*	
C107	0.4445 (2)	−0.06028 (15)	0.24046 (14)	0.0124 (3)	
O1	0.3979 (3)	0.43185 (19)	0.34409 (16)	0.0379 (5)	
O2	0.2887 (2)	0.50260 (17)	0.23127 (13)	0.0279 (4)	
N3	0.3365 (2)	0.50953 (18)	0.31689 (15)	0.0236 (4)	
C11	0.3205 (3)	0.6179 (2)	0.39096 (16)	0.0206 (4)	
C12	0.3550 (3)	0.6213 (2)	0.48943 (17)	0.0260 (5)	
H12	0.3869	0.5552	0.5086	0.031*	
C13	0.3415 (3)	0.7241 (3)	0.55864 (17)	0.0302 (6)	
H13	0.3645	0.7289	0.6263	0.036*	
C14	0.2944 (3)	0.8202 (2)	0.52978 (18)	0.0308 (5)	
H14	0.2863	0.8905	0.5776	0.037*	
C15	0.2591 (3)	0.8136 (2)	0.43061 (18)	0.0288 (5)	
H15	0.2259	0.8793	0.4112	0.035*	
C16	0.2721 (3)	0.7120 (2)	0.36030 (16)	0.0232 (4)	
H16	0.2483	0.7070	0.2927	0.028*	
O3	0.2297 (14)	0.1246 (8)	0.0730 (7)	0.054 (3)*	0.261 (5)
O4	0.1129 (11)	−0.0405 (8)	−0.0211 (7)	0.047 (2)*	0.261 (5)
N4	0.2302 (11)	0.0300 (8)	0.0159 (7)	0.032 (2)*	0.261 (5)
C21	0.3953 (6)	−0.0015 (6)	−0.0055 (5)	0.0237 (19)*	0.261 (5)
C22	0.4071 (6)	−0.1080 (5)	−0.0709 (4)	0.0148 (16)*	0.261 (5)
H22	0.3100	−0.1594	−0.1029	0.018*	0.261 (5)
C23	0.5609 (9)	−0.1392 (5)	−0.0897 (4)	0.0233 (18)*	0.261 (5)
H23	0.5689	−0.2119	−0.1344	0.028*	0.261 (5)
C24	0.7029 (6)	−0.0639 (7)	−0.0430 (6)	0.0197 (18)*	0.261 (5)
H24	0.8080	−0.0853	−0.0558	0.024*	0.261 (5)
C25	0.6912 (7)	0.0425 (7)	0.0225 (5)	0.034 (2)*	0.261 (5)
H25	0.7883	0.0939	0.0545	0.041*	0.261 (5)
C26	0.5374 (10)	0.0737 (5)	0.0413 (5)	0.035 (2)*	0.261 (5)
H26	0.5294	0.1464	0.0860	0.042*	0.261 (5)
O3′	0.8337 (16)	−0.0624 (14)	−0.0272 (11)	0.077 (4)*	0.239 (5)
O4′	0.6299 (16)	−0.1808 (11)	−0.1247 (9)	0.067 (4)*	0.239 (5)
N4′	0.6860 (16)	−0.0956 (14)	−0.0589 (12)	0.050 (5)*	0.239 (5)
C21′	0.5619 (9)	−0.0248 (7)	−0.0149 (7)	0.029 (2)*	0.239 (5)
C22′	0.6144 (8)	0.0833 (8)	0.0522 (7)	0.026 (3)*	0.239 (5)
H22′	0.7288	0.1111	0.0692	0.031*	0.239 (5)
C23′	0.4994 (12)	0.1506 (6)	0.0943 (6)	0.041 (3)*	0.239 (5)
H23′	0.5353	0.2245	0.1401	0.049*	0.239 (5)
C24′	0.3321 (11)	0.1099 (8)	0.0694 (7)	0.026 (3)*	0.239 (5)
H24′	0.2535	0.1560	0.0982	0.031*	0.239 (5)
C25′	0.2796 (8)	0.0019 (8)	0.0023 (6)	0.024 (2)*	0.239 (5)
H25′	0.1652	−0.0259	−0.0147	0.029*	0.239 (5)
C26′	0.3945 (11)	−0.0655 (6)	−0.0398 (5)	0.020 (2)*	0.239 (5)
H26′	0.3587	−0.1394	−0.0857	0.024*	0.239 (5)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01073 (15)	0.00465 (13)	0.00523 (13)	0.00414 (10)	0.00089 (10)	0.00079 (9)
N1	0.0142 (8)	0.0152 (7)	0.0120 (7)	0.0067 (6)	−0.0017 (6)	−0.0006 (6)
N2	0.0131 (8)	0.0146 (7)	0.0282 (9)	0.0054 (6)	0.0026 (6)	0.0016 (7)
N21	0.0107 (6)	0.0038 (5)	0.0037 (5)	0.0046 (5)	0.0003 (5)	0.0004 (4)
N22	0.0120 (7)	0.0041 (6)	0.0042 (6)	0.0043 (5)	0.0003 (5)	0.0006 (4)
C1	0.0116 (7)	0.0042 (6)	0.0054 (6)	0.0040 (5)	0.0007 (5)	0.0003 (5)
C2	0.0189 (9)	0.0070 (7)	0.0048 (7)	0.0055 (6)	0.0000 (6)	−0.0011 (5)
C3	0.0160 (8)	0.0075 (7)	0.0044 (6)	0.0051 (6)	−0.0002 (5)	0.0004 (5)
C4	0.0096 (7)	0.0058 (6)	0.0047 (6)	0.0036 (5)	0.0007 (5)	0.0015 (5)
C5	0.0087 (7)	0.0055 (6)	0.0049 (6)	0.0032 (5)	0.0005 (5)	0.0021 (5)
C6	0.0114 (7)	0.0060 (6)	0.0054 (6)	0.0046 (5)	0.0005 (5)	0.0020 (5)
C7	0.0201 (9)	0.0078 (7)	0.0080 (7)	0.0084 (6)	0.0004 (6)	0.0024 (6)
C8	0.0221 (9)	0.0071 (7)	0.0083 (7)	0.0092 (6)	0.0004 (6)	0.0014 (6)
C9	0.0132 (8)	0.0047 (6)	0.0070 (7)	0.0057 (5)	0.0008 (5)	0.0007 (5)
C10	0.0111 (7)	0.0040 (6)	0.0061 (6)	0.0042 (5)	0.0008 (5)	0.0001 (5)
C51	0.0091 (7)	0.0060 (6)	0.0068 (6)	0.0040 (5)	−0.0010 (5)	0.0001 (5)
C52	0.0098 (7)	0.0071 (7)	0.0069 (6)	0.0033 (5)	0.0014 (5)	0.0018 (5)
C53	0.0103 (7)	0.0043 (6)	0.0048 (6)	0.0037 (5)	0.0007 (5)	0.0011 (5)
C54	0.0091 (7)	0.0060 (6)	0.0073 (7)	0.0032 (5)	0.0012 (5)	0.0009 (5)
C55	0.0124 (8)	0.0083 (7)	0.0070 (7)	0.0037 (6)	0.0036 (6)	0.0016 (5)
C56	0.0150 (8)	0.0082 (7)	0.0054 (6)	0.0044 (6)	0.0008 (6)	0.0014 (5)
C57	0.0137 (8)	0.0090 (7)	0.0069 (7)	0.0045 (6)	−0.0007 (6)	−0.0002 (5)
C101	0.0098 (7)	0.0058 (6)	0.0101 (7)	0.0042 (5)	0.0014 (6)	0.0010 (5)
C102	0.0109 (7)	0.0048 (6)	0.0082 (7)	0.0030 (5)	0.0000 (5)	−0.0002 (5)
C103	0.0126 (8)	0.0039 (6)	0.0057 (6)	0.0042 (5)	0.0009 (5)	−0.0002 (5)
C104	0.0100 (7)	0.0063 (7)	0.0106 (7)	0.0039 (6)	0.0013 (6)	0.0004 (5)
C105	0.0108 (8)	0.0062 (7)	0.0123 (7)	0.0018 (6)	0.0003 (6)	−0.0008 (6)
C106	0.0127 (8)	0.0049 (6)	0.0114 (7)	0.0038 (6)	0.0021 (6)	−0.0004 (5)
C107	0.0131 (8)	0.0076 (7)	0.0152 (8)	0.0028 (6)	0.0009 (6)	0.0001 (6)
O1	0.0328 (10)	0.0391 (11)	0.0457 (12)	0.0103 (8)	−0.0022 (9)	0.0180 (9)
O2	0.0235 (8)	0.0377 (10)	0.0225 (8)	0.0011 (7)	0.0044 (6)	0.0088 (7)
N3	0.0139 (8)	0.0305 (10)	0.0277 (9)	−0.0015 (7)	0.0028 (7)	0.0122 (8)
C11	0.0135 (9)	0.0290 (11)	0.0193 (9)	−0.0047 (8)	0.0001 (7)	0.0104 (8)
C12	0.0147 (9)	0.0417 (13)	0.0239 (10)	−0.0056 (9)	−0.0021 (8)	0.0186 (10)
C13	0.0200 (10)	0.0498 (15)	0.0168 (10)	−0.0131 (10)	−0.0024 (8)	0.0113 (10)
C14	0.0297 (12)	0.0363 (13)	0.0199 (10)	−0.0125 (10)	0.0039 (9)	0.0030 (9)
C15	0.0359 (13)	0.0262 (11)	0.0236 (11)	−0.0056 (9)	0.0041 (9)	0.0098 (9)
C16	0.0242 (11)	0.0280 (11)	0.0176 (9)	−0.0040 (8)	0.0006 (8)	0.0109 (8)

Geometric parameters ($\text{\AA}$, $^\circ$)

Cu1—N21 ⁱ	1.9977 (17)	C105—C106	1.390 (3)
Cu1—N21	1.9977 (17)	C105—H105	0.9500
Cu1—N22 ⁱ	2.021 (2)	C106—H106	0.9500
Cu1—N22	2.021 (2)	O1—N3	1.229 (3)

N1—C57	1.150 (3)	O2—N3	1.226 (3)
N2—C107	1.153 (3)	N3—C11	1.474 (3)
N21—C1	1.381 (2)	C11—C16	1.385 (3)
N21—C4	1.381 (2)	C11—C12	1.394 (3)
N22—C6	1.381 (2)	C12—C13	1.387 (4)
N22—C9	1.382 (2)	C12—H12	0.9500
C1—C10 ⁱ	1.394 (2)	C13—C14	1.389 (4)
C1—C2	1.444 (2)	C13—H13	0.9500
C2—C3	1.358 (2)	C14—C15	1.396 (3)
C2—H2	0.9500	C14—H14	0.9500
C3—C4	1.442 (2)	C15—C16	1.384 (4)
C3—H3	0.9500	C15—H15	0.9500
C4—C5	1.400 (2)	C16—H16	0.9500
C5—C6	1.397 (2)	O3—N4	1.212 (11)
C5—C53	1.495 (2)	O4—N4	1.188 (11)
C6—C7	1.443 (2)	N4—C21	1.489 (9)
C7—C8	1.360 (2)	C21—C22	1.3900
C7—H7	0.9500	C21—C26	1.3900
C8—C9	1.441 (2)	C22—C23	1.3900
C8—H8	0.9500	C22—H22	0.9500
C9—C10	1.397 (2)	C23—C24	1.3900
C10—C1 ⁱ	1.394 (2)	C23—H23	0.9500
C10—C103	1.495 (2)	C24—C25	1.3900
C51—C52	1.400 (2)	C24—H24	0.9500
C51—C56	1.402 (3)	C25—C26	1.3900
C51—C57	1.442 (3)	C25—H25	0.9500
C52—C53	1.391 (2)	C26—H26	0.9500
C52—H52	0.9500	O3'—N4'	1.242 (13)
C53—C54	1.407 (3)	O4'—N4'	1.207 (14)
C54—C55	1.395 (2)	N4'—C21'	1.481 (11)
C54—H54	0.9500	C21'—C22'	1.3900
C55—C56	1.387 (3)	C21'—C26'	1.3900
C55—H55	0.9500	C22'—C23'	1.3900
C56—H56	0.9500	C22'—H22'	0.9500
C101—C102	1.400 (2)	C23'—C24'	1.3900
C101—C106	1.402 (3)	C23'—H23'	0.9500
C101—C107	1.444 (3)	C24'—C25'	1.3900
C102—C103	1.393 (2)	C24'—H24'	0.9500
C102—H102	0.9500	C25'—C26'	1.3900
C103—C104	1.404 (3)	C25'—H25'	0.9500
C104—C105	1.394 (2)	C26'—H26'	0.9500
C104—H104	0.9500		
N21—Cu1—N21 ⁱ	180.0	C103—C104—H104	119.5
N21 ⁱ —Cu1—N22 ⁱ	89.84 (8)	C106—C105—C104	120.29 (18)
N21—Cu1—N22 ⁱ	90.16 (8)	C106—C105—H105	119.9
N21 ⁱ —Cu1—N22	90.16 (8)	C104—C105—H105	119.9
N21—Cu1—N22	89.84 (8)	C105—C106—C101	118.74 (16)

N22—Cu1—N22 ⁱ	180.0	C105—C106—H106	120.6
C1—N21—C4	105.46 (14)	C101—C106—H106	120.6
C1—N21—Cu1	127.15 (11)	N2—C107—C101	178.9 (2)
C4—N21—Cu1	127.35 (12)	O2—N3—O1	123.8 (2)
C6—N22—C9	105.52 (14)	O2—N3—C11	117.9 (2)
C6—N22—Cu1	127.29 (11)	O1—N3—C11	118.4 (2)
C9—N22—Cu1	126.86 (12)	C16—C11—C12	122.6 (2)
N21—C1—C10 ⁱ	126.02 (15)	C16—C11—N3	119.0 (2)
N21—C1—C2	110.28 (14)	C12—C11—N3	118.5 (2)
C10 ⁱ —C1—C2	123.70 (15)	C13—C12—C11	118.1 (2)
C3—C2—C1	106.98 (15)	C13—C12—H12	121.0
C3—C2—H2	126.5	C11—C12—H12	121.0
C1—C2—H2	126.5	C12—C13—C14	120.5 (2)
C2—C3—C4	106.81 (15)	C12—C13—H13	119.8
C2—C3—H3	126.6	C14—C13—H13	119.8
C4—C3—H3	126.6	C13—C14—C15	120.1 (2)
N21—C4—C5	126.06 (15)	C13—C14—H14	120.0
N21—C4—C3	110.45 (15)	C15—C14—H14	120.0
C5—C4—C3	123.49 (15)	C16—C15—C14	120.4 (2)
C6—C5—C4	123.85 (15)	C16—C15—H15	119.8
C6—C5—C53	118.75 (15)	C14—C15—H15	119.8
C4—C5—C53	117.36 (14)	C15—C16—C11	118.4 (2)
N22—C6—C5	125.38 (15)	C15—C16—H16	120.8
N22—C6—C7	110.42 (14)	C11—C16—H16	120.8
C5—C6—C7	124.18 (15)	O4—N4—O3	126.3 (11)
C8—C7—C6	106.68 (15)	O4—N4—C21	117.8 (8)
C8—C7—H7	126.7	O3—N4—C21	115.9 (9)
C6—C7—H7	126.7	C22—C21—C26	120.0
C7—C8—C9	107.17 (16)	C22—C21—N4	119.6 (6)
C7—C8—H8	126.4	C26—C21—N4	120.3 (6)
C9—C8—H8	126.4	C23—C22—C21	120.0
N22—C9—C10	125.42 (15)	C23—C22—H22	120.0
N22—C9—C8	110.20 (15)	C21—C22—H22	120.0
C10—C9—C8	124.30 (15)	C22—C23—C24	120.0
C1 ⁱ —C10—C9	124.28 (15)	C22—C23—H23	120.0
C1 ⁱ —C10—C103	117.53 (15)	C24—C23—H23	120.0
C9—C10—C103	118.16 (15)	C25—C24—C23	120.0
C52—C51—C56	120.95 (16)	C25—C24—H24	120.0
C52—C51—C57	118.88 (17)	C23—C24—H24	120.0
C56—C51—C57	120.17 (16)	C26—C25—C24	120.0
C53—C52—C51	120.19 (17)	C26—C25—H25	120.0
C53—C52—H52	119.9	C24—C25—H25	120.0
C51—C52—H52	119.9	C25—C26—C21	120.0
C52—C53—C54	118.77 (16)	C25—C26—H26	120.0
C52—C53—C5	121.07 (16)	C21—C26—H26	120.0
C54—C53—C5	120.16 (15)	O4'—N4'—O3'	126.6 (14)
C55—C54—C53	120.69 (16)	O4'—N4'—C21'	114.6 (12)
C55—C54—H54	119.7	O3'—N4'—C21'	118.8 (13)

C53—C54—H54	119.7	C22'—C21'—C26'	120.0
C56—C55—C54	120.64 (17)	C22'—C21'—N4'	119.3 (8)
C56—C55—H55	119.7	C26'—C21'—N4'	120.7 (8)
C54—C55—H55	119.7	C21'—C22'—C23'	120.0
C55—C56—C51	118.75 (16)	C21'—C22'—H22'	120.0
C55—C56—H56	120.6	C23'—C22'—H22'	120.0
C51—C56—H56	120.6	C22'—C23'—C24'	120.0
N1—C57—C51	179.5 (2)	C22'—C23'—H23'	120.0
C102—C101—C106	121.22 (17)	C24'—C23'—H23'	120.0
C102—C101—C107	119.30 (18)	C23'—C24'—C25'	120.0
C106—C101—C107	119.48 (16)	C23'—C24'—H24'	120.0
C103—C102—C101	119.80 (18)	C25'—C24'—H24'	120.0
C103—C102—H102	120.1	C26'—C25'—C24'	120.0
C101—C102—H102	120.1	C26'—C25'—H25'	120.0
C102—C103—C104	118.85 (16)	C24'—C25'—H25'	120.0
C102—C103—C10	121.02 (17)	C25'—C26'—C21'	120.0
C104—C103—C10	120.12 (16)	C25'—C26'—H26'	120.0
C105—C104—C103	121.07 (17)	C21'—C26'—H26'	120.0
C105—C104—H104	119.5		

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

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 $\cdots$ N1 ⁱⁱ	0.95	2.54	3.463 (4)	164
C7—H7 $\cdots$ N2 ⁱⁱⁱ	0.95	2.73	3.608 (4)	155
C55—H55 $\cdots$ N1 ^{iv}	0.95	2.83	3.477 (3)	126
C104—H104 $\cdots$ N2 ^{iv}	0.95	2.62	3.316 (3)	130
C105—H105 $\cdots$ N2 ^{iv}	0.95	2.95	3.475 (3)	116
C106—H106 $\cdots$ N1 ⁱⁱⁱ	0.95	2.51	3.405 (3)	157

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