

Received 13 January 2015

Accepted 19 January 2015

Edited by M. Weil, Vienna University of
Technology, Austria

Keywords: Crystal structure; azamacrocyclic ligand; Jahn–Teller distortion; isonicotinic acid; offset π – π interaction; hydrogen bonds; synchrotron data

CCDC reference: 1044260

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

Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(isonicotinato- κO)copper(II) from synchrotron data

Jong Won Shin, Dae-Woong Kim, Jin Hong Kim and Dohyun Moon*

Beamline Department, Pohang Accelerator Laboratory, 80 Jigokro-127-beongil, Nam-Gu Pohang, Gyeongbuk 790-784, South Korea. *Correspondence e-mail: dmoon@postech.ac.kr

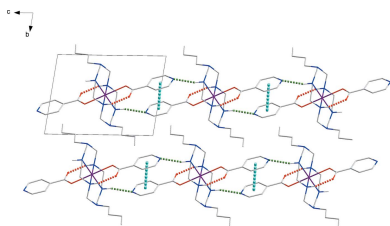
The title compound, $[\text{Cu}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{C}_{16}\text{H}_{38}\text{N}_6)]$ has been synthesized and characterized by structure analysis based on synchrotron data and by FT–IR spectroscopy. The asymmetric unit consists of half of the Cu^{II} complex, the other half being completed by inversion symmetry. The Cu^{II} ion has a tetragonally distorted octahedral coordination sphere with four secondary N atoms of the azamacrocyclic ligand in the equatorial plane [$\text{Cu}–\text{N}_{\text{eq}} = 2.018(12) \text{ \AA}$] and two O atoms of the isonicotinate anions at the axial positions [$\text{Cu}–\text{O}_{\text{ax}} = 2.4100(11) \text{ \AA}$]. Intramolecular $\text{N}–\text{H} \cdots \text{O}$ hydrogen bonds between one of the secondary amine N–H groups of the azamacrocyclic ligand and the non-coordinating O atom of the isonicotinate ions stabilize the molecular structure. Intermolecular $\text{N}–\text{H} \cdots \text{N}$ hydrogen bonds between the other macrocyclic N–H group and the pyridine N atom of an adjacent isonicotinate anion as well as π – π interactions [centroid-to-centroid distance $3.711(2) \text{ \AA}$] lead to the formation of rods parallel to $[001]$.

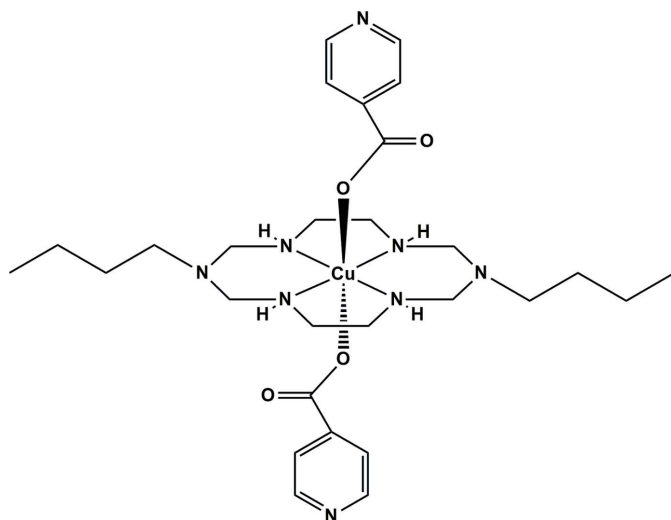
1. Chemical context

The coordination chemistry of macrocyclic ligands has attracted extensive interest due to their potential applications in material science, chemistry and metalloenzymes (Lehn, 1995; Carnes *et al.*, 2014). In particular, Cu^{II} macrocyclic complexes involving vacant sites in an axial position are feasible candidates for assembling supramolecular materials, with potential applications as gas-storage materials (Suh *et al.*, 2012) as well as catalysts for co-polymerization of carbon dioxide and cyclohexene oxide (Tsai *et al.*, 2014). Moreover, Cu^{II} complexes with tetraazamacrocyclic ligands involving alkyl moieties have been investigated as magnetic materials with various auxiliary ligands such as metal cyanide, azide, and dicyanamide (Bi *et al.*, 2012).

Isonicotinic acid is a versatile anion which can easily bind to transition metals *via* the carboxyl group or the pyridine N atom, thus allowing the assembly of multidimensionally structured compounds or heterometallic complexes (Liu *et al.*, 2006).

Here, we report on the synthesis and crystal structure of a Cu^{II} azamacrocyclic complex with two isonicotinato coligands, *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(isonicotinato- κO)copper(II), (I).





2. Structural commentary

In compound (I), the Cu^{II} ion lies on an inversion center and is coordinated by the four secondary amine N atoms of the azamacrocyclic ligand in the equatorial plane and by two O atoms from the isonicotinate anions at the axial positions, resulting in a tetragonally distorted octahedral geometry, as shown in Fig. 1. The average Cu–N_{eq} bond length is 2.018 (12) and the Cu–O_{ax} bond length is 2.4100 (11) Å. This difference can be attributed either to a large Jahn–Teller distortion effect of the Cu^{II} ion and/or to a ring contraction of the azamacrocyclic ligand (Halcrow, 2013). The six-membered chelate ring (Cu1–N1–C2–N3–C3–N2) adopts a chair confor-

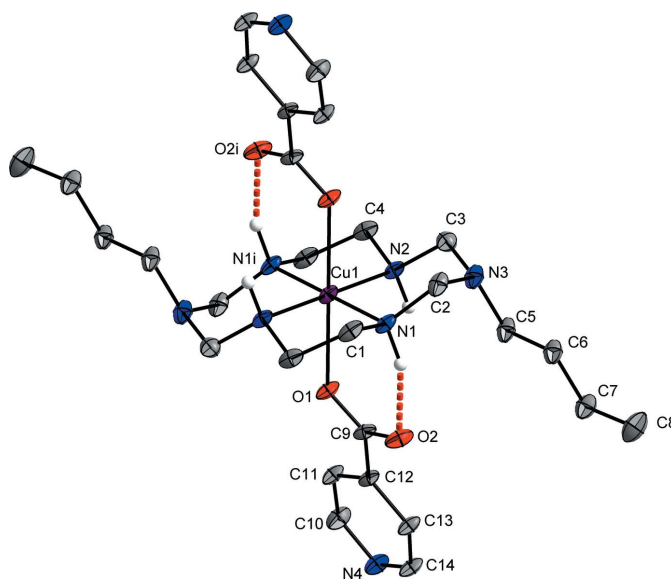


Figure 1

The molecular structure of (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. Intramolecular N–H...O hydrogen bonds are shown as red dashed lines. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1...O2	1.00	1.98	2.9179 (16)	155
N2–H2...N4 ⁱ	1.00	2.21	3.1160 (16)	150

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

mation and the five-membered chelate ring (Cu1–N1–C1–C4–N2) a *gauche* conformation (Min & Suh, 2001). The two C–O bond lengths of the carboxylate group are 1.255 (2) and 1.258 (2) Å, indicating that this group is fully delocalized with a bond angle (O1–C9–O2) of 126.8 (1)°. Intramolecular N1–H1...O2 hydrogen bonds between one of the secondary amine groups of the azamacrocyclic ligand and the O atoms of a coordinating isonicotinate anion stabilize the molecular structure (Fig. 1 and Table 1).

3. Supramolecular features

The N atoms of the isonicotinate ions form intermolecular N2–H2...N4 hydrogen bonds (Steed & Atwood, 2009) with the adjacent secondary amine group of the azamacrocyclic ligand (Fig. 2 and Table 1). The pyridine rings of the isonicotinate co-ligand are involved in π – π stacking interactions [centroid-to-centroid distance 3.711 (2) Å]. The interplanar separation and dihedral angle between the pyridine rings in adjacent isonicotinate anions are 3.522 (2) Å and 0.0°, respectively, implying a parallel assignment to each other (Hunter & Sanders, 1990). The hydrogen-bonding and π – π interactions generate rods of interacting molecules parallel to [001].

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, May 2014 with three updates; Groom & Allen, 2014) indicate that only one Cu^{II} azamacrocyclic complex having butyl pendant groups has been reported (Kim *et al.*, 2015).

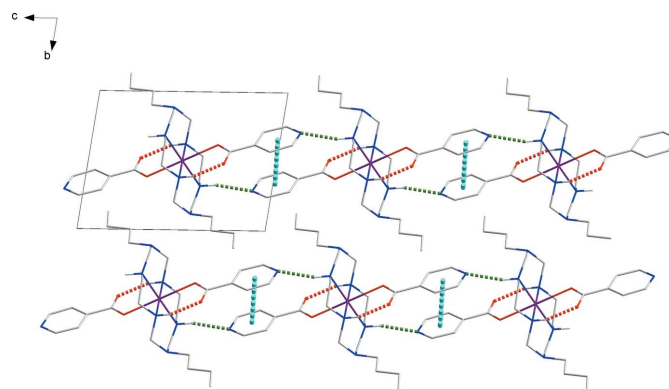


Figure 2

View of the crystal packing of (I), with N–H...O hydrogen bonds and π – π interactions shown as dashed lines (red: intramolecular hydrogen bonds, green: intermolecular hydrogen bonds, cyan: π – π interactions).

Table 2
Experimental details.

Crystal data	
Chemical formula	[Cu(C ₆ H ₄ NO ₂) ₂ (C ₁₆ H ₃₈ N ₆)]
<i>M</i> _r	622.27
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.0490 (16), 8.3000 (17), 11.175 (2)
α , β , γ (°)	81.16 (3), 87.14 (3), 86.68 (3)
<i>V</i> (Å ³)	735.8 (3)
<i>Z</i>	1
Radiation type	Synchrotron, $\lambda = 0.630$ Å
μ (mm ⁻¹)	0.57
Crystal size (mm)	0.08 × 0.03 × 0.03
Data collection	
Diffractometer	ADSC Q210 CCD area detector
Absorption correction	Empirical (using intensity measurements) (<i>HKL3000sm SCALEPACK</i> ; Otwinowski & Minor, 1997)
<i>T</i> _{min} , <i>T</i> _{max}	0.958, 0.983
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7574, 3882, 3608
<i>R</i> _{int}	0.018
(sin θ/λ) _{max} (Å ⁻¹)	0.696
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.086, 1.09
No. of reflections	3882
No. of parameters	188
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.43, -0.62

Computer programs: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2008, 2015b), *DIAMOND4* (Putz & Brandenburg, 2014) and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

Compound (I) was prepared as follows. The starting complex, [Cu(C₁₆H₃₈N₆)(ClO₄)₂], was obtained by a slight modification of the reported method (Kim *et al.*, 2015). To an MeCN (10 mL) solution of [Cu(C₁₆H₃₈N₆)(ClO₄)₂] (0.15 g, 0.26 mmol) was slowly added an MeCN solution (5 mL) containing isonicotinic acid (0.064 g, 0.52 mmol) and excess triethylamine (0.06 g, 0.60 mmol) at room temperature. The formed purple precipitate was filtered off, washed with MeCN, and diethyl ether, and dried in air. Single crystals of the title compound were obtained by layering a MeCN solution of isonicotinic acid on the MeCN solution of [Cu(C₁₆H₃₈N₆)(ClO₄)₂] for several days. Yield: 0.087 g (54%). FT-IR (ATR, cm⁻¹): 3197, 3097, 2954, 2929, 1596, 1544, 1365, 1280, 1016, 964.

Safety note: Although we have experienced no problem with the compounds involved in this study, perchlorate salts of metal complexes are often explosive and should be handled with great caution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (ring H atoms) or 0.98–0.99 Å (open-chain H atoms) and an N—H distance of 1.0 Å with *U*_{iso}(H) values of 1.2 or 1.5*U*_{eq} of the parent atoms.

Acknowledgements

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2014R1A1A2058815) and supported by the Institute for Basic Science (IBS, IBS-R007-D1-2014-a01). The X-ray crystallography 2D-SMC beamline and FT-IR experiment at PLS-II were supported in part by MSIP and POSTECH.

References

- Arvai, A. J. & Nielsen, C. (1983). *ADSC Quantum-210 ADX*. Area Detector System Corporation, Poway, CA, USA.
- Bi, J.-H., Bi, W.-T. & Hu, N.-L. (2012). *Asian J. Chem.* **24**, 943–944.
- Carnes, M. E., Collins, M. S. & Johnson, D. W. (2014). *Chem. Soc. Rev.* **43**, 1825–1834.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Halcrow, M. A. (2013). *Chem. Soc. Rev.* **42**, 1784–1795.
- Hunter, C. A. & Sanders, K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
- Kim, D.-W., Shin, J. W. & Moon, D. (2015). *Acta Cryst.* **E71**, 136–138.
- Lehn, J.-M. (1995). *Supramolecular Chemistry; Concepts and Perspectives*. Weinheim: VCH.
- Liu, F.-C., Zeng, Y.-F., Jiao, J., Li, J.-R., Bu, X.-H., Ribas, J. & Batten, S. R. (2006). *Inorg. Chem.* **45**, 6129–6131.
- Min, K. S. & Suh, M. P. (2001). *Chem. Eur. J.* **7**, 303–313.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. Academic Press, New York.
- Putz, H. & Brandenburg, K. (2014). *DIAMOND4*. Crystal Impact GbR, Bonn, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Steed, J. W. & Atwood, J. L. (2009). *Supramolecular Chemistry*, 2nd ed., John Wiley & Sons, Ltd, Chichester.
- Suh, M. P., Park, H. J., Prasad, T. K. & Lim, D.-W. (2012). *Chem. Rev.* **112**, 782–835.
- Tsai, C.-Y., Huang, B.-H., Hsiao, M.-W., Lin, C.-C. & Ko, B.-T. (2014). *Inorg. Chem.* **53**, 5109–5116.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2015). E71, 203-205 [doi:10.1107/S2056989015001115]

Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(isonicotinato- κO)copper(II) from synchrotron data

Jong Won Shin, Dae-Woong Kim, Jin Hong Kim and Dohyun Moon

Computing details

Data collection: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2008, 2015b); molecular graphics: *DIAMOND4* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-(1,8-Dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(isonicotinato- κO)copper(II)

Crystal data

[Cu(C₆H₄NO₂)₂(C₁₆H₃₈N₆)]

$M_r = 622.27$

Triclinic, $P\bar{1}$

$a = 8.0490$ (16) Å

$b = 8.3000$ (17) Å

$c = 11.175$ (2) Å

$\alpha = 81.16$ (3)°

$\beta = 87.14$ (3)°

$\gamma = 86.68$ (3)°

$V = 735.8$ (3) Å³

$Z = 1$

$F(000) = 331$

$D_x = 1.404$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.630$ Å

Cell parameters from 21514 reflections

$\theta = 0.4$ – 33.6 °

$\mu = 0.57$ mm⁻¹

$T = 100$ K

Needle, purple

$0.08 \times 0.03 \times 0.03$ mm

Data collection

ADSC Q210 CCD area detector
diffractometer

Radiation source: PLSII 2D bending magnet

ω scan

Absorption correction: empirical (using
intensity measurements)

(*HKL3000sm SCALEPACK*; Otwinowski &
Minor, 1997)

$T_{\min} = 0.958$, $T_{\max} = 0.983$

7574 measured reflections

3882 independent reflections

3608 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.7$ °

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.086$

$S = 1.09$

3882 reflections

188 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.1939P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$$

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.01489 (8)
O1	0.43502 (12)	0.38249 (14)	0.32476 (8)	0.0228 (2)
O2	0.19078 (12)	0.51588 (15)	0.27708 (9)	0.0250 (2)
N1	0.27675 (13)	0.62129 (14)	0.50255 (9)	0.0174 (2)
H1	0.2211	0.6111	0.4262	0.021*
N2	0.60724 (13)	0.68104 (14)	0.38483 (9)	0.0174 (2)
H2	0.5757	0.6720	0.3008	0.021*
N3	0.37958 (16)	0.88517 (15)	0.40936 (10)	0.0241 (2)
N4	0.36803 (15)	0.28785 (16)	-0.10314 (10)	0.0234 (2)
C1	0.17805 (15)	0.53580 (19)	0.60560 (11)	0.0208 (3)
H1A	0.0580	0.5652	0.5960	0.025*
H1B	0.2109	0.5678	0.6825	0.025*
C2	0.28664 (18)	0.79685 (18)	0.50926 (11)	0.0231 (3)
H2A	0.1722	0.8471	0.5123	0.028*
H2B	0.3389	0.8084	0.5856	0.028*
C3	0.55623 (18)	0.84773 (18)	0.40891 (12)	0.0239 (3)
H3A	0.5973	0.8617	0.4885	0.029*
H3B	0.6110	0.9276	0.3466	0.029*
C4	0.78914 (16)	0.64587 (18)	0.39220 (11)	0.0211 (3)
H4A	0.8291	0.6792	0.4666	0.025*
H4B	0.8484	0.7070	0.3212	0.025*
C5	0.30584 (19)	0.90191 (18)	0.29031 (12)	0.0241 (3)
H5A	0.2879	0.7920	0.2709	0.029*
H5B	0.3848	0.9552	0.2279	0.029*
C6	0.13998 (19)	1.00201 (18)	0.28563 (12)	0.0241 (3)
H6A	0.0599	0.9481	0.3470	0.029*
H6B	0.1572	1.1119	0.3056	0.029*
C7	0.06801 (19)	1.0188 (2)	0.16070 (13)	0.0270 (3)
H7A	0.0460	0.9091	0.1425	0.032*
H7B	0.1505	1.0676	0.0990	0.032*
C8	-0.0932 (2)	1.1251 (2)	0.15327 (15)	0.0373 (4)
H8A	-0.1767	1.0745	0.2119	0.056*
H8B	-0.1347	1.1357	0.0713	0.056*
H8C	-0.0720	1.2335	0.1719	0.056*
C9	0.31897 (15)	0.43043 (17)	0.25450 (10)	0.0177 (2)
C10	0.48401 (17)	0.2439 (2)	-0.02071 (12)	0.0246 (3)

H10	0.5792	0.1802	-0.0429	0.029*
C11	0.47339 (16)	0.28583 (18)	0.09515 (11)	0.0204 (3)
H11	0.5587	0.2502	0.1504	0.024*
C12	0.33664 (14)	0.38038 (16)	0.12895 (10)	0.0157 (2)
C13	0.21551 (16)	0.42803 (18)	0.04430 (11)	0.0198 (2)
H13	0.1201	0.4935	0.0636	0.024*
C14	0.23614 (17)	0.37841 (19)	-0.06890 (11)	0.0223 (3)
H14	0.1517	0.4106	-0.1254	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01176 (11)	0.02337 (13)	0.00843 (10)	0.00026 (7)	0.00131 (6)	0.00020 (7)
O1	0.0233 (5)	0.0349 (6)	0.0105 (4)	0.0010 (4)	-0.0053 (3)	-0.0035 (4)
O2	0.0172 (4)	0.0447 (6)	0.0148 (4)	0.0016 (4)	0.0002 (3)	-0.0113 (4)
N1	0.0156 (5)	0.0287 (6)	0.0070 (4)	0.0019 (4)	0.0007 (3)	-0.0012 (4)
N2	0.0161 (5)	0.0262 (6)	0.0094 (4)	-0.0021 (4)	0.0000 (3)	-0.0002 (4)
N3	0.0318 (6)	0.0249 (6)	0.0143 (5)	0.0043 (5)	-0.0003 (4)	-0.0009 (4)
N4	0.0251 (6)	0.0351 (7)	0.0098 (4)	0.0011 (5)	0.0002 (4)	-0.0042 (4)
C1	0.0136 (5)	0.0381 (7)	0.0095 (5)	0.0004 (5)	0.0026 (4)	-0.0016 (5)
C2	0.0297 (7)	0.0266 (7)	0.0116 (5)	0.0075 (5)	0.0013 (5)	-0.0026 (5)
C3	0.0306 (7)	0.0231 (6)	0.0182 (6)	-0.0035 (5)	-0.0010 (5)	-0.0029 (5)
C4	0.0154 (5)	0.0353 (7)	0.0120 (5)	-0.0057 (5)	0.0016 (4)	-0.0009 (5)
C5	0.0326 (7)	0.0241 (7)	0.0136 (5)	0.0050 (5)	0.0005 (5)	0.0003 (5)
C6	0.0310 (7)	0.0232 (6)	0.0166 (6)	0.0032 (5)	0.0005 (5)	-0.0004 (5)
C7	0.0299 (7)	0.0314 (7)	0.0182 (6)	0.0027 (6)	-0.0001 (5)	-0.0010 (5)
C8	0.0307 (8)	0.0520 (10)	0.0250 (7)	0.0082 (7)	0.0013 (6)	0.0032 (7)
C9	0.0163 (5)	0.0290 (7)	0.0080 (5)	-0.0057 (4)	0.0003 (4)	-0.0022 (4)
C10	0.0233 (6)	0.0365 (8)	0.0135 (5)	0.0061 (5)	0.0009 (5)	-0.0057 (5)
C11	0.0186 (6)	0.0314 (7)	0.0104 (5)	0.0025 (5)	-0.0020 (4)	-0.0014 (5)
C12	0.0146 (5)	0.0254 (6)	0.0069 (4)	-0.0034 (4)	0.0005 (4)	-0.0007 (4)
C13	0.0170 (5)	0.0326 (7)	0.0094 (5)	0.0023 (5)	-0.0008 (4)	-0.0027 (5)
C14	0.0216 (6)	0.0362 (7)	0.0088 (5)	0.0015 (5)	-0.0031 (4)	-0.0029 (5)

Geometric parameters (Å, °)

Cu1—N1 ⁱ	2.0093 (12)	C3—H3B	0.9900
Cu1—N1	2.0093 (12)	C4—C1 ⁱ	1.512 (2)
Cu1—N2	2.0260 (13)	C4—H4A	0.9900
Cu1—N2 ⁱ	2.0261 (13)	C4—H4B	0.9900
Cu1—O1 ⁱ	2.4100 (11)	C5—C6	1.530 (2)
Cu1—O1	2.4100 (11)	C5—H5A	0.9900
O1—C9	1.2576 (16)	C5—H5B	0.9900
O2—C9	1.2551 (17)	C6—C7	1.522 (2)
N1—C2	1.4775 (19)	C6—H6A	0.9900
N1—C1	1.4778 (16)	C6—H6B	0.9900
N1—H1	1.0000	C7—C8	1.525 (2)
N2—C4	1.4801 (16)	C7—H7A	0.9900

N2—C3	1.4807 (19)	C7—H7B	0.9900
N2—H2	1.0000	C8—H8A	0.9800
N3—C3	1.4377 (19)	C8—H8B	0.9800
N3—C2	1.4394 (19)	C8—H8C	0.9800
N3—C5	1.4676 (18)	C9—C12	1.5211 (17)
N4—C14	1.3393 (18)	C10—C11	1.3888 (18)
N4—C10	1.3402 (18)	C10—H10	0.9500
C1—C4 ⁱ	1.512 (2)	C11—C12	1.3855 (18)
C1—H1A	0.9900	C11—H11	0.9500
C1—H1B	0.9900	C12—C13	1.3908 (16)
C2—H2A	0.9900	C13—C14	1.3887 (17)
C2—H2B	0.9900	C13—H13	0.9500
C3—H3A	0.9900	C14—H14	0.9500
N1 ⁱ —Cu1—N1	180.0	H3A—C3—H3B	107.6
N1 ⁱ —Cu1—N2	86.38 (5)	N2—C4—C1 ⁱ	107.66 (11)
N1—Cu1—N2	93.62 (5)	N2—C4—H4A	110.2
N1 ⁱ —Cu1—N2 ⁱ	93.62 (5)	C1 ⁱ —C4—H4A	110.2
N1—Cu1—N2 ⁱ	86.38 (5)	N2—C4—H4B	110.2
N2—Cu1—N2 ⁱ	180.00 (5)	C1 ⁱ —C4—H4B	110.2
N1 ⁱ —Cu1—O1 ⁱ	91.88 (5)	H4A—C4—H4B	108.5
N1—Cu1—O1 ⁱ	88.12 (5)	N3—C5—C6	112.45 (12)
N2—Cu1—O1 ⁱ	92.34 (4)	N3—C5—H5A	109.1
N2 ⁱ —Cu1—O1 ⁱ	87.66 (4)	C6—C5—H5A	109.1
N1 ⁱ —Cu1—O1	88.12 (5)	N3—C5—H5B	109.1
N1—Cu1—O1	91.88 (5)	C6—C5—H5B	109.1
N2—Cu1—O1	87.66 (4)	H5A—C5—H5B	107.8
N2 ⁱ —Cu1—O1	92.34 (4)	C7—C6—C5	111.11 (12)
O1 ⁱ —Cu1—O1	180.0	C7—C6—H6A	109.4
C9—O1—Cu1	126.16 (9)	C5—C6—H6A	109.4
C2—N1—C1	112.34 (10)	C7—C6—H6B	109.4
C2—N1—Cu1	113.64 (9)	C5—C6—H6B	109.4
C1—N1—Cu1	106.52 (8)	H6A—C6—H6B	108.0
C2—N1—H1	108.0	C6—C7—C8	111.54 (13)
C1—N1—H1	108.0	C6—C7—H7A	109.3
Cu1—N1—H1	108.0	C8—C7—H7A	109.3
C4—N2—C3	112.40 (11)	C6—C7—H7B	109.3
C4—N2—Cu1	105.83 (8)	C8—C7—H7B	109.3
C3—N2—Cu1	114.38 (8)	H7A—C7—H7B	108.0
C4—N2—H2	108.0	C7—C8—H8A	109.5
C3—N2—H2	108.0	C7—C8—H8B	109.5
Cu1—N2—H2	108.0	H8A—C8—H8B	109.5
C3—N3—C2	114.61 (11)	C7—C8—H8C	109.5
C3—N3—C5	114.92 (11)	H8A—C8—H8C	109.5
C2—N3—C5	116.23 (12)	H8B—C8—H8C	109.5
C14—N4—C10	116.32 (12)	O2—C9—O1	126.75 (12)
N1—C1—C4 ⁱ	108.03 (10)	O2—C9—C12	116.76 (11)
N1—C1—H1A	110.1	O1—C9—C12	116.49 (11)

C4 ⁱ —C1—H1A	110.1	N4—C10—C11	123.95 (13)
N1—C1—H1B	110.1	N4—C10—H10	118.0
C4 ⁱ —C1—H1B	110.1	C11—C10—H10	118.0
H1A—C1—H1B	108.4	C12—C11—C10	119.03 (12)
N3—C2—N1	114.08 (11)	C12—C11—H11	120.5
N3—C2—H2A	108.7	C10—C11—H11	120.5
N1—C2—H2A	108.7	C11—C12—C13	117.81 (11)
N3—C2—H2B	108.7	C11—C12—C9	121.25 (11)
N1—C2—H2B	108.7	C13—C12—C9	120.94 (11)
H2A—C2—H2B	107.6	C14—C13—C12	118.98 (12)
N3—C3—N2	114.67 (12)	C14—C13—H13	120.5
N3—C3—H3A	108.6	C12—C13—H13	120.5
N2—C3—H3A	108.6	N4—C14—C13	123.90 (12)
N3—C3—H3B	108.6	N4—C14—H14	118.1
N2—C3—H3B	108.6	C13—C14—H14	118.1
C2—N1—C1—C4 ⁱ	-166.01 (10)	C5—C6—C7—C8	-177.30 (14)
Cu1—N1—C1—C4 ⁱ	-40.98 (11)	Cu1—O1—C9—O2	-20.4 (2)
C3—N3—C2—N1	-70.73 (16)	Cu1—O1—C9—C12	159.19 (8)
C5—N3—C2—N1	67.19 (15)	C14—N4—C10—C11	0.4 (2)
C1—N1—C2—N3	-179.05 (10)	N4—C10—C11—C12	-0.8 (2)
Cu1—N1—C2—N3	59.93 (13)	C10—C11—C12—C13	0.3 (2)
C2—N3—C3—N2	68.49 (15)	C10—C11—C12—C9	-179.76 (13)
C5—N3—C3—N2	-69.99 (15)	O2—C9—C12—C11	-179.88 (13)
C4—N2—C3—N3	-176.79 (10)	O1—C9—C12—C11	0.48 (19)
Cu1—N2—C3—N3	-56.07 (13)	O2—C9—C12—C13	0.02 (19)
C3—N2—C4—C1 ⁱ	167.50 (10)	O1—C9—C12—C13	-179.62 (12)
Cu1—N2—C4—C1 ⁱ	41.99 (10)	C11—C12—C13—C14	0.4 (2)
C3—N3—C5—C6	-158.17 (12)	C9—C12—C13—C14	-179.48 (12)
C2—N3—C5—C6	64.03 (16)	C10—N4—C14—C13	0.4 (2)
N3—C5—C6—C7	179.31 (12)	C12—C13—C14—N4	-0.8 (2)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O2	1.00	1.98	2.9179 (16)	155
N2—H2 \cdots N4 ⁱⁱ	1.00	2.21	3.1160 (16)	150

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