

# Bis(1-methyl-1*H*-imidazole- $\kappa$ N<sup>3</sup>)bis[2-(naphthalen-1-yl)acetato- $\kappa$ O]copper(II) monohydrate

Fu-Jun Yin,<sup>a\*</sup> Li-Jun Han,<sup>b</sup> Shu-Ping Yang,<sup>c</sup> Xing-You Xu<sup>d</sup> and Yu Gu<sup>e</sup>

<sup>a</sup>Jiangsu Marine Resources Development, Research Institute, Huaihai Institute of Technology, Lianyungang 222005, People's Republic of China, <sup>b</sup>Department of Mathematics and Science, Huaihai Institute of Technology, Lianyungang 222005, People's Republic of China, <sup>c</sup>Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, People's Republic of China, <sup>d</sup>Department of Chemical Engineering, Huaiyin Institute of Technology, Huaiyin 223003, People's Republic of China, and <sup>e</sup>Qian'an College, Hebei United University, Tangshan 063009, People's Republic of China

Correspondence e-mail: yfj1999@126.com

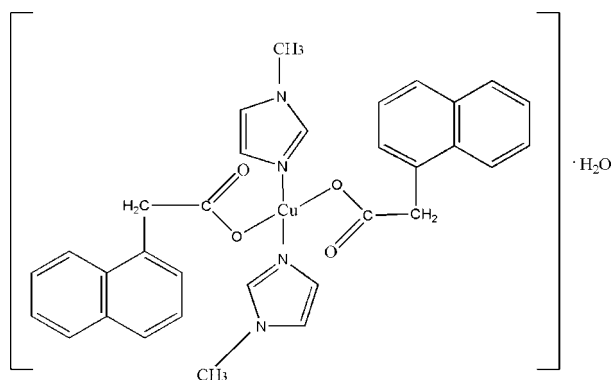
Received 10 November 2011; accepted 19 November 2011

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.102; data-to-parameter ratio = 13.4.

In the crystal structure of the title compound,  $[\text{Cu}(\text{C}_{12}\text{H}_9\text{O}_2)_2(\text{C}_4\text{H}_6\text{N}_2)_2]\cdot\text{H}_2\text{O}$ , the  $\text{Cu}^{\text{II}}$  atom is coordinated by two 2-(naphthalen-1-yl)acetate anions and two 1-methylimidazole ligands, giving monomeric complexes with a square-planar coordination environment. Two complex molecules and two water molecules form a centrosymmetric ring system *via*  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the pharmacological potential of metal complexes with imidazole, see: Boiani & Gonzales (2005); Parshina & Trofimov (2011). For the coordination chemistry of 1-naphthylacetate ligands, see: Yin *et al.* (2010); Chen *et al.* (2004); Yang *et al.* (2008); Tang *et al.* (2006); Ji *et al.* (2011).



## Experimental

### Crystal data

$[\text{Cu}(\text{C}_{12}\text{H}_9\text{O}_2)_2(\text{C}_4\text{H}_6\text{N}_2)_2]\cdot\text{H}_2\text{O}$   
 $M_r = 616.16$   
 Triclinic,  $P\bar{1}$   
 $a = 8.7213$  (10) Å  
 $b = 12.8689$  (14) Å  
 $c = 13.5787$  (15) Å  
 $\alpha = 107.223$  (1)°  
 $\beta = 90.295$  (2)°  
 $\gamma = 90.931$  (1)°  
 $V = 1455.4$  (3) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.80$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.20 \times 0.20 \times 0.20$  mm

### Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.843$ ,  $T_{\text{max}} = 0.843$   
 11175 measured reflections  
 5094 independent reflections  
 3534 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.102$   
 $S = 1.03$   
 5094 reflections  
 381 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{O1}$	0.85	1.97	2.789 (3)	163
$\text{O1W}-\text{H1WB}\cdots\text{O3}^i$	0.85	2.07	2.904 (3)	167

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

Data collection: *APEX2* (Bruker 2007); cell refinement: *SAINT* (Bruker 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2340).

## References

- Boiani, M. & Gonzales, M. (2005). *Mini Rev. Med. Chem.* **5**, 409–424.  
 Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Chen, L.-F., Zhang, J., Song, L.-J., Wang, W.-G. & Ju, Z.-F. (2004). *Acta Cryst.* **E60**, m1032–m1034.  
 Ji, L.-L., Liu, J.-S. & Song, W.-D. (2011). *Acta Cryst.* **E67**, m606.  
 Parshina, L. N. & Trofimov, B. A. (2011). *Russ. Chem. Bull.* **60**, 601–614.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Tang, D.-X., Feng, L.-X. & Zhang, X.-Q. (2006). *Chin. J. Inorg. Chem.* **22**, 1891–1894.  
 Yang, Y.-Q., Li, C.-H. L. W. & Kuang, Y.-F. (2008). *Chin. J. Struct. Chem.* **30**, 4524–4530.  
 Yin, F.-J., Zhao, H. & Hu, X.-L. (2010). *Synth. React. Inorg. Met. Org. Nano-Metal Chem.* **40**, 606–612.

**supplementary materials**

*Acta Cryst.* (2011). E67, m1821 [ doi:10.1107/S1600536811049439 ]

## Bis(1-methyl-1*H*-imidazole- $\kappa N^3$ )bis[2-(naphthalen-1-yl)acetato- $\kappa O$ ]copper(II) monohydrate

F.-J. Yin, L.-J. Han, S.-P. Yang, X.-Y. Xu and Y. Gu

### Comment

Self-assembly of supramolecular architectures based on naphthalene-1-yl-acetate ligands has attracted much attention during recent decades (Yin *et al.*, 2010; Chen *et al.*, 2004; Yang *et al.*, 2008; Tang *et al.*, 2006; Ji *et al.*, 2011). Recent studies reveal that metal complexes with substituted imidazole and carboxylate ligands are interesting for medicinal chemists who explore their various pharmacological potentials (Boiani & Gonzales, 2005; Parshina & Trofimov, 2011). The crystal structure of the title compound was determined as part of an ongoing study on the properties of copper complexes containing imidazole ligands.

In the crystal structure of the title compound  $[\text{Cu}(\text{C}_{12}\text{H}_9\text{O}_2)_2(\text{C}_4\text{H}_6\text{N}_2)_2]\text{H}_2\text{O}$ , each copper cation is coordinated by two N atoms of different 1-methylimidazole ligands and by two carboxyl O atoms of distinct naphthalene-1-yl-acetate anions within a square planar coordination sphere (Fig. 1). The Cu—N and Cu—O bond lengths are 1.985 (3) and 1.974 (2) Å, respectively. The asymmetric unit consists of one  $\text{Cu}^{\text{II}}$  cation, two neutral imidazole ligands, two anionic carboxylate ligands and one lattice water in general positions. It is noteworthy that there exist strong hydrogen-bonding interactions (Table 1, Fig.2) involving the carboxy group oxygen atoms of 1-naphthylacetate ligands as well as water molecules. The molecules form centrosymmetric ring systems by O—H $\cdots$ O hydrogen bonds

### Experimental

The title compound was synthesized by the reaction of  $\text{Cu}(\text{NO}_3)_2 \times 3 \text{H}_2\text{O}$  (72.3 mg, 0.3 mmol), naphthalene-1-yl-acetic acid (93 mg, 0.5 mmol), 1-methylimidazole (32.8 mg, 0.4 mmol) and NaOH (20 mg, 0.5 mmol) in 6 mL of a water-ethanol (2:1) mixture under solvothermal conditions. The mixture was homogenized and transferred into a sealed Teflon-lined solvothermal bomb (volume: 25 ml) and heated to 140°C for three days. After cooling green crystals of the title compound were obtained, which were washed with distilled water and absolute ethanol (yield: 38.7% based on  $\text{Cu}(\text{NO}_3)_2 \times 3 \text{H}_2\text{O}$ ).

### Refinement

H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and included in the final cycles of refinement using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ . Water H atoms were located in Fourier difference maps and refined isotropically.

### Figures

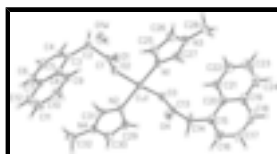


Fig. 1. Crystal structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

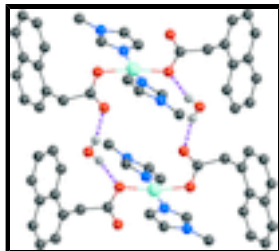


Fig. 2. Centrosymmetric ring system of the title compound including lattice water molecules. Hydrogen bonds are shown as dashed lines, and H atoms not involved in hydrogen bonding are omitted for clarity.

## Bis(1-methyl-1*H*-imidazole- $\kappa$ N<sup>3</sup>)bis[2-(naphthalen-1-yl)acetato- $\kappa$ O]copper(II) monohydrate

### Crystal data

[Cu(C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>2</sub>].H<sub>2</sub>O

$M_r = 616.16$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 8.7213$  (10) Å

$b = 12.8689$  (14) Å

$c = 13.5787$  (15) Å

$\alpha = 107.223$  (1)°

$\beta = 90.295$  (2)°

$\gamma = 90.931$  (1)°

$V = 1455.4$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 642$

$D_x = 1.406$  Mg m<sup>-3</sup>

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

Cell parameters from 1644 reflections

$\theta = 2.3$ – $19.2$ °

$\mu = 0.80$  mm<sup>-1</sup>

$T = 298$  K

Prism, green

$0.20 \times 0.20 \times 0.20$  mm

### Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.843$ ,  $T_{\max} = 0.843$

11175 measured reflections

5094 independent reflections

3534 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 25.0$ °,  $\theta_{\min} = 2.3$ °

$h = -10 \rightarrow 10$

$k = -15 \rightarrow 15$

$l = -15 \rightarrow 16$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.102$

$S = 1.03$

5094 reflections

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

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.1784P]$

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

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

381 parameters

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

### 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.

**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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7153 (4)	0.7870 (3)	0.6104 (3)	0.0395 (8)
C2	0.7391 (4)	0.6657 (2)	0.5639 (3)	0.0490 (9)
H2A	0.6505	0.6333	0.5219	0.059*
H2B	0.7486	0.6320	0.6187	0.059*
C3	0.8829 (4)	0.6438 (2)	0.4976 (3)	0.0444 (8)
C4	0.8703 (4)	0.6226 (3)	0.3940 (3)	0.0500 (9)
H4	0.7735	0.6199	0.3643	0.060*
C5	0.9998 (5)	0.6045 (3)	0.3301 (3)	0.0630 (11)
H5	0.9880	0.5891	0.2590	0.076*
C6	1.1423 (5)	0.6098 (3)	0.3728 (3)	0.0587 (10)
H6	1.2279	0.5991	0.3307	0.070*
C7	1.1612 (4)	0.6314 (3)	0.4797 (3)	0.0470 (9)
C8	1.0292 (4)	0.6489 (2)	0.5452 (3)	0.0435 (8)
C9	1.0541 (4)	0.6709 (3)	0.6524 (3)	0.0479 (9)
H9	0.9703	0.6810	0.6960	0.058*
C10	1.1973 (5)	0.6777 (3)	0.6928 (3)	0.0639 (11)
H10	1.2109	0.6938	0.7637	0.077*
C11	1.3237 (5)	0.6609 (3)	0.6291 (4)	0.0746 (13)
H11	1.4216	0.6652	0.6577	0.090*
C12	1.3065 (4)	0.6384 (3)	0.5264 (4)	0.0653 (11)
H12	1.3932	0.6273	0.4852	0.078*
C13	0.7022 (4)	1.1979 (3)	0.8398 (3)	0.0435 (8)
C14	0.6624 (4)	1.3180 (2)	0.8668 (2)	0.0486 (9)
H14A	0.7555	1.3604	0.8673	0.058*
H14B	0.5946	1.3286	0.8139	0.058*
C15	0.5856 (4)	1.3596 (3)	0.9707 (3)	0.0461 (9)
C16	0.6705 (5)	1.4139 (3)	1.0546 (3)	0.0587 (10)
H16	0.7744	1.4269	1.0472	0.070*
C17	0.6043 (6)	1.4509 (3)	1.1527 (3)	0.0729 (13)
H17	0.6643	1.4883	1.2093	0.088*

## supplementary materials

---

C18	0.4542 (6)	1.4321 (3)	1.1650 (3)	0.0736 (13)
H18	0.4120	1.4561	1.2304	0.088*
C19	0.3595 (5)	1.3768 (3)	1.0802 (3)	0.0572 (10)
C20	0.4261 (4)	1.3412 (3)	0.9806 (3)	0.0448 (9)
C21	0.3277 (5)	1.2891 (3)	0.8967 (3)	0.0597 (10)
H21	0.3683	1.2649	0.8308	0.072*
C22	0.1773 (5)	1.2735 (4)	0.9093 (4)	0.0807 (13)
H22	0.1156	1.2400	0.8524	0.097*
C23	0.1130 (6)	1.3074 (4)	1.0074 (5)	0.0928 (16)
H23	0.0093	1.2948	1.0157	0.111*
C24	0.2010 (6)	1.3585 (4)	1.0903 (4)	0.0837 (15)
H24	0.1565	1.3820	1.1551	0.100*
C25	0.5448 (4)	0.8706 (3)	0.8592 (3)	0.0524 (9)
H25	0.6224	0.8212	0.8566	0.063*
C26	0.4117 (4)	0.8717 (3)	0.9070 (3)	0.0579 (10)
H26	0.3797	0.8238	0.9427	0.069*
C27	0.4195 (4)	1.0032 (3)	0.8372 (3)	0.0518 (9)
H27	0.3913	1.0633	0.8169	0.062*
C28	0.1776 (4)	0.9878 (4)	0.9308 (3)	0.0884 (15)
H28A	0.1519	1.0545	0.9172	0.133*
H28B	0.1746	0.9981	1.0037	0.133*
H28C	0.1050	0.9318	0.8964	0.133*
C29	0.9660 (4)	1.1131 (3)	0.6535 (3)	0.0530 (10)
H29	0.9081	1.1756	0.6656	0.064*
C30	1.1062 (4)	1.1006 (3)	0.6125 (3)	0.0574 (10)
H30	1.1621	1.1517	0.5906	0.069*
C31	1.0373 (4)	0.9532 (3)	0.6472 (3)	0.0486 (9)
H31	1.0398	0.8832	0.6536	0.058*
C32	1.2957 (4)	0.9490 (3)	0.5669 (3)	0.0702 (12)
H32A	1.2955	0.8747	0.5679	0.105*
H32B	1.3799	0.9881	0.6081	0.105*
H32C	1.3064	0.9513	0.4973	0.105*
Cu1	0.72561 (4)	0.98739 (3)	0.73588 (3)	0.03873 (15)
N1	0.5513 (3)	0.9531 (2)	0.8147 (2)	0.0434 (7)
N2	0.9208 (3)	1.0192 (2)	0.67509 (19)	0.0403 (7)
N3	0.3314 (3)	0.9560 (2)	0.8930 (2)	0.0527 (8)
N4	1.1514 (3)	0.9992 (2)	0.6089 (2)	0.0461 (7)
O1	0.6406 (3)	0.83829 (19)	0.56361 (17)	0.0543 (6)
O2	0.7793 (2)	0.83265 (16)	0.69796 (17)	0.0433 (6)
O3	0.6513 (2)	1.13568 (16)	0.75272 (17)	0.0444 (6)
O4	0.7809 (3)	1.16518 (18)	0.89921 (18)	0.0540 (6)
O1W	0.5269 (3)	0.7509 (2)	0.36319 (19)	0.0803 (9)
H1WA	0.5433	0.7839	0.4266	0.120*
H1WB	0.4770	0.7933	0.3378	0.120*

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

$U^{11}$

$U^{22}$

$U^{33}$

$U^{12}$

$U^{13}$

$U^{23}$

C1	0.0288 (18)	0.0333 (19)	0.053 (2)	0.0010 (15)	0.0151 (17)	0.0078 (17)
C2	0.0364 (19)	0.0341 (19)	0.068 (2)	0.0010 (16)	0.0061 (17)	0.0025 (17)
C3	0.043 (2)	0.0273 (18)	0.057 (2)	0.0033 (15)	0.0049 (18)	0.0016 (16)
C4	0.050 (2)	0.0354 (19)	0.053 (2)	0.0078 (17)	-0.0026 (18)	-0.0050 (17)
C5	0.082 (3)	0.046 (2)	0.054 (2)	0.016 (2)	0.010 (2)	0.0012 (19)
C6	0.057 (3)	0.047 (2)	0.072 (3)	0.0129 (19)	0.023 (2)	0.016 (2)
C7	0.039 (2)	0.0324 (19)	0.072 (3)	0.0081 (16)	0.0143 (19)	0.0175 (18)
C8	0.040 (2)	0.0250 (17)	0.066 (3)	0.0041 (15)	0.0048 (18)	0.0145 (17)
C9	0.048 (2)	0.041 (2)	0.057 (2)	0.0063 (17)	0.0068 (18)	0.0174 (18)
C10	0.061 (3)	0.064 (3)	0.073 (3)	0.005 (2)	-0.011 (2)	0.029 (2)
C11	0.045 (3)	0.081 (3)	0.109 (4)	0.003 (2)	-0.009 (3)	0.046 (3)
C12	0.040 (2)	0.071 (3)	0.094 (3)	0.011 (2)	0.013 (2)	0.037 (3)
C13	0.049 (2)	0.038 (2)	0.045 (2)	0.0085 (17)	0.0225 (18)	0.0130 (18)
C14	0.060 (2)	0.0341 (19)	0.050 (2)	0.0078 (17)	0.0128 (18)	0.0092 (17)
C15	0.065 (3)	0.0293 (18)	0.044 (2)	0.0163 (18)	0.0044 (19)	0.0098 (17)
C16	0.069 (3)	0.039 (2)	0.063 (3)	0.0108 (19)	-0.006 (2)	0.007 (2)
C17	0.110 (4)	0.048 (2)	0.051 (3)	0.023 (3)	-0.017 (3)	-0.001 (2)
C18	0.125 (4)	0.054 (3)	0.043 (3)	0.044 (3)	0.017 (3)	0.014 (2)
C19	0.077 (3)	0.047 (2)	0.052 (3)	0.029 (2)	0.019 (2)	0.020 (2)
C20	0.058 (2)	0.0325 (19)	0.044 (2)	0.0147 (17)	0.0094 (18)	0.0109 (16)
C21	0.062 (3)	0.049 (2)	0.065 (3)	0.009 (2)	0.000 (2)	0.010 (2)
C22	0.063 (3)	0.074 (3)	0.102 (4)	0.007 (3)	-0.009 (3)	0.022 (3)
C23	0.061 (3)	0.092 (4)	0.135 (5)	0.022 (3)	0.020 (3)	0.047 (4)
C24	0.088 (4)	0.081 (3)	0.095 (4)	0.040 (3)	0.049 (3)	0.043 (3)
C25	0.060 (2)	0.048 (2)	0.055 (2)	0.0086 (19)	0.0147 (19)	0.0227 (19)
C26	0.071 (3)	0.055 (2)	0.052 (2)	-0.001 (2)	0.015 (2)	0.022 (2)
C27	0.054 (2)	0.045 (2)	0.061 (2)	0.0096 (19)	0.0161 (19)	0.0212 (19)
C28	0.052 (3)	0.114 (4)	0.106 (4)	0.012 (3)	0.039 (3)	0.042 (3)
C29	0.061 (2)	0.035 (2)	0.066 (3)	0.0124 (18)	0.022 (2)	0.0186 (19)
C30	0.062 (3)	0.047 (2)	0.065 (3)	-0.001 (2)	0.017 (2)	0.021 (2)
C31	0.050 (2)	0.038 (2)	0.059 (2)	0.0021 (18)	0.0131 (19)	0.0160 (18)
C32	0.047 (2)	0.068 (3)	0.097 (3)	0.014 (2)	0.023 (2)	0.025 (2)
Cu1	0.0421 (3)	0.0321 (2)	0.0417 (3)	0.00717 (17)	0.00974 (18)	0.00997 (18)
N1	0.0499 (18)	0.0345 (15)	0.0460 (17)	0.0054 (14)	0.0122 (14)	0.0116 (13)
N2	0.0433 (17)	0.0325 (15)	0.0437 (17)	0.0034 (13)	0.0083 (13)	0.0089 (13)
N3	0.0475 (18)	0.0539 (19)	0.0560 (19)	0.0007 (16)	0.0189 (15)	0.0150 (16)
N4	0.0430 (17)	0.0433 (17)	0.0508 (18)	0.0046 (14)	0.0133 (14)	0.0118 (14)
O1	0.0524 (15)	0.0514 (15)	0.0562 (16)	0.0112 (12)	0.0009 (12)	0.0111 (13)
O2	0.0456 (14)	0.0348 (13)	0.0479 (15)	0.0066 (11)	0.0114 (11)	0.0092 (11)
O3	0.0512 (14)	0.0351 (13)	0.0468 (15)	0.0091 (11)	0.0119 (11)	0.0113 (11)
O4	0.0604 (16)	0.0506 (15)	0.0530 (16)	0.0123 (13)	0.0076 (13)	0.0177 (13)
O1W	0.091 (2)	0.085 (2)	0.0606 (18)	0.0234 (17)	-0.0078 (15)	0.0132 (15)

*Geometric parameters (Å, °)*

C1—O1	1.233 (4)	C19—C20	1.423 (5)
C1—O2	1.280 (4)	C20—C21	1.416 (5)
C1—C2	1.519 (4)	C21—C22	1.343 (5)
C2—C3	1.528 (4)	C21—H21	0.9300

## supplementary materials

---

C2—H2A	0.9700	C22—C23	1.396 (6)
C2—H2B	0.9700	C22—H22	0.9300
C3—C4	1.355 (4)	C23—C24	1.351 (6)
C3—C8	1.419 (4)	C23—H23	0.9300
C4—C5	1.408 (5)	C24—H24	0.9300
C4—H4	0.9300	C25—C26	1.331 (4)
C5—C6	1.360 (5)	C25—N1	1.369 (4)
C5—H5	0.9300	C25—H25	0.9300
C6—C7	1.403 (5)	C26—N3	1.360 (4)
C6—H6	0.9300	C26—H26	0.9300
C7—C12	1.404 (5)	C27—N1	1.319 (4)
C7—C8	1.438 (4)	C27—N3	1.341 (4)
C8—C9	1.413 (4)	C27—H27	0.9300
C9—C10	1.353 (4)	C28—N3	1.460 (4)
C9—H9	0.9300	C28—H28A	0.9600
C10—C11	1.385 (5)	C28—H28B	0.9600
C10—H10	0.9300	C28—H28C	0.9600
C11—C12	1.345 (5)	C29—C30	1.338 (4)
C11—H11	0.9300	C29—N2	1.377 (4)
C12—H12	0.9300	C29—H29	0.9300
C13—O4	1.226 (4)	C30—N4	1.356 (4)
C13—O3	1.288 (4)	C30—H30	0.9300
C13—C14	1.525 (4)	C31—N2	1.319 (4)
C14—C15	1.517 (4)	C31—N4	1.334 (4)
C14—H14A	0.9700	C31—H31	0.9300
C14—H14B	0.9700	C32—N4	1.463 (4)
C15—C16	1.356 (5)	C32—H32A	0.9600
C15—C20	1.421 (5)	C32—H32B	0.9600
C16—C17	1.406 (5)	C32—H32C	0.9600
C16—H16	0.9300	Cu1—O2	1.969 (2)
C17—C18	1.348 (6)	Cu1—O3	1.974 (2)
C17—H17	0.9300	Cu1—N1	1.981 (3)
C18—C19	1.415 (5)	Cu1—N2	1.985 (3)
C18—H18	0.9300	O1W—H1WA	0.8500
C19—C24	1.413 (6)	O1W—H1WB	0.8501
O1—C1—O2	122.5 (3)	C15—C20—C19	118.9 (3)
O1—C1—C2	120.6 (3)	C22—C21—C20	122.0 (4)
O2—C1—C2	116.9 (3)	C22—C21—H21	119.0
C1—C2—C3	111.2 (3)	C20—C21—H21	119.0
C1—C2—H2A	109.4	C21—C22—C23	120.5 (5)
C3—C2—H2A	109.4	C21—C22—H22	119.8
C1—C2—H2B	109.4	C23—C22—H22	119.8
C3—C2—H2B	109.4	C24—C23—C22	120.3 (5)
H2A—C2—H2B	108.0	C24—C23—H23	119.9
C4—C3—C8	120.3 (3)	C22—C23—H23	119.9
C4—C3—C2	119.8 (3)	C23—C24—C19	121.0 (4)
C8—C3—C2	119.8 (3)	C23—C24—H24	119.5
C3—C4—C5	121.9 (3)	C19—C24—H24	119.5
C3—C4—H4	119.1	C26—C25—N1	110.2 (3)



C5—C4—H4	119.1	C26—C25—H25	125.0
C6—C5—C4	119.6 (4)	N1—C25—H25	124.8
C6—C5—H5	120.2	C25—C26—N3	106.7 (3)
C4—C5—H5	120.2	C25—C26—H26	126.6
C5—C6—C7	120.7 (4)	N3—C26—H26	126.7
C5—C6—H6	119.7	N1—C27—N3	111.1 (3)
C7—C6—H6	119.7	N1—C27—H27	124.5
C6—C7—C12	122.1 (3)	N3—C27—H27	124.4
C6—C7—C8	119.9 (3)	N3—C28—H28A	109.5
C12—C7—C8	118.0 (4)	N3—C28—H28B	109.5
C9—C8—C3	124.6 (3)	H28A—C28—H28B	109.5
C9—C8—C7	117.8 (3)	N3—C28—H28C	109.5
C3—C8—C7	117.6 (3)	H28A—C28—H28C	109.5
C10—C9—C8	121.4 (3)	H28B—C28—H28C	109.5
C10—C9—H9	119.3	C30—C29—N2	109.5 (3)
C8—C9—H9	119.3	C30—C29—H29	125.2
C9—C10—C11	120.3 (4)	N2—C29—H29	125.2
C9—C10—H10	119.8	C29—C30—N4	107.0 (3)
C11—C10—H10	119.8	C29—C30—H30	126.6
C12—C11—C10	120.8 (4)	N4—C30—H30	126.4
C12—C11—H11	119.6	N2—C31—N4	111.6 (3)
C10—C11—H11	119.6	N2—C31—H31	124.2
C11—C12—C7	121.7 (4)	N4—C31—H31	124.1
C11—C12—H12	119.1	N4—C32—H32A	109.5
C7—C12—H12	119.1	N4—C32—H32B	109.5
O4—C13—O3	123.2 (3)	H32A—C32—H32B	109.5
O4—C13—C14	120.0 (3)	N4—C32—H32C	109.5
O3—C13—C14	116.7 (3)	H32A—C32—H32C	109.5
C15—C14—C13	112.8 (3)	H32B—C32—H32C	109.5
C15—C14—H14A	109.0	O2—Cu1—O3	170.52 (10)
C13—C14—H14A	109.0	O2—Cu1—N1	88.15 (10)
C15—C14—H14B	109.0	O3—Cu1—N1	92.02 (10)
C13—C14—H14B	109.0	O2—Cu1—N2	89.41 (9)
H14A—C14—H14B	107.8	O3—Cu1—N2	91.82 (9)
C16—C15—C20	120.1 (3)	N1—Cu1—N2	170.95 (11)
C16—C15—C14	119.5 (3)	C27—N1—C25	105.1 (3)
C20—C15—C14	120.5 (3)	C27—N1—Cu1	128.9 (2)
C15—C16—C17	121.1 (4)	C25—N1—Cu1	126.0 (2)
C15—C16—H16	119.4	C31—N2—C29	104.9 (3)
C17—C16—H16	119.4	C31—N2—Cu1	126.5 (2)
C18—C17—C16	120.2 (4)	C29—N2—Cu1	128.7 (2)
C18—C17—H17	119.9	C27—N3—C26	107.0 (3)
C16—C17—H17	119.9	C27—N3—C28	126.8 (3)
C17—C18—C19	121.2 (4)	C26—N3—C28	126.2 (3)
C17—C18—H18	119.4	C31—N4—C30	107.0 (3)
C19—C18—H18	119.4	C31—N4—C32	126.9 (3)
C24—C19—C18	122.4 (4)	C30—N4—C32	126.1 (3)
C24—C19—C20	119.1 (4)	C1—O2—Cu1	106.53 (19)
C18—C19—C20	118.5 (4)	C13—O3—Cu1	108.00 (19)

## supplementary materials

---

C21—C20—C15	123.9 (3)	H1WA—O1W—H1WB	107.7
C21—C20—C19	117.3 (4)		
O1—C1—C2—C3	89.1 (4)	C20—C21—C22—C23	-0.9 (6)
O2—C1—C2—C3	-89.1 (4)	C21—C22—C23—C24	1.5 (7)
C1—C2—C3—C4	-97.6 (4)	C22—C23—C24—C19	-1.2 (7)
C1—C2—C3—C8	80.5 (4)	C18—C19—C24—C23	178.5 (4)
C8—C3—C4—C5	0.3 (5)	C20—C19—C24—C23	0.4 (6)
C2—C3—C4—C5	178.4 (3)	N1—C25—C26—N3	0.1 (4)
C3—C4—C5—C6	-1.0 (5)	N2—C29—C30—N4	-0.6 (4)
C4—C5—C6—C7	1.0 (5)	N3—C27—N1—C25	-0.2 (4)
C5—C6—C7—C12	-179.4 (3)	N3—C27—N1—Cu1	-179.4 (2)
C5—C6—C7—C8	-0.4 (5)	C26—C25—N1—C27	0.1 (4)
C4—C3—C8—C9	179.7 (3)	C26—C25—N1—Cu1	179.3 (2)
C2—C3—C8—C9	1.5 (5)	O2—Cu1—N1—C27	-153.0 (3)
C4—C3—C8—C7	0.3 (5)	O3—Cu1—N1—C27	17.5 (3)
C2—C3—C8—C7	-177.9 (3)	N2—Cu1—N1—C27	132.6 (6)
C6—C7—C8—C9	-179.7 (3)	O2—Cu1—N1—C25	27.9 (3)
C12—C7—C8—C9	-0.7 (4)	O3—Cu1—N1—C25	-161.5 (3)
C6—C7—C8—C3	-0.2 (4)	N2—Cu1—N1—C25	-46.5 (8)
C12—C7—C8—C3	178.8 (3)	N4—C31—N2—C29	-0.6 (4)
C3—C8—C9—C10	-178.0 (3)	N4—C31—N2—Cu1	180.0 (2)
C7—C8—C9—C10	1.4 (5)	C30—C29—N2—C31	0.7 (4)
C8—C9—C10—C11	-1.3 (5)	C30—C29—N2—Cu1	-179.8 (2)
C9—C10—C11—C12	0.5 (6)	O2—Cu1—N2—C31	-12.6 (3)
C10—C11—C12—C7	0.2 (6)	O3—Cu1—N2—C31	176.8 (3)
C6—C7—C12—C11	178.9 (4)	N1—Cu1—N2—C31	61.7 (8)
C8—C7—C12—C11	-0.1 (5)	O2—Cu1—N2—C29	168.0 (3)
O4—C13—C14—C15	-55.1 (4)	O3—Cu1—N2—C29	-2.6 (3)
O3—C13—C14—C15	125.9 (3)	N1—Cu1—N2—C29	-117.6 (7)
C13—C14—C15—C16	98.1 (4)	N1—C27—N3—C26	0.2 (4)
C13—C14—C15—C20	-81.3 (4)	N1—C27—N3—C28	-179.1 (3)
C20—C15—C16—C17	1.3 (5)	C25—C26—N3—C27	-0.1 (4)
C14—C15—C16—C17	-178.1 (3)	C25—C26—N3—C28	179.2 (4)
C15—C16—C17—C18	0.4 (6)	N2—C31—N4—C30	0.2 (4)
C16—C17—C18—C19	-0.9 (6)	N2—C31—N4—C32	-177.6 (3)
C17—C18—C19—C24	-178.3 (4)	C29—C30—N4—C31	0.3 (4)
C17—C18—C19—C20	-0.2 (5)	C29—C30—N4—C32	178.0 (3)
C16—C15—C20—C21	177.5 (3)	O1—C1—O2—Cu1	2.0 (3)
C14—C15—C20—C21	-3.1 (5)	C2—C1—O2—Cu1	-179.8 (2)
C16—C15—C20—C19	-2.4 (5)	O3—Cu1—O2—C1	3.1 (6)
C14—C15—C20—C19	177.0 (3)	N1—Cu1—O2—C1	94.28 (19)
C24—C19—C20—C21	0.1 (5)	N2—Cu1—O2—C1	-94.44 (19)
C18—C19—C20—C21	-178.0 (3)	O4—C13—O3—Cu1	-1.0 (4)
C24—C19—C20—C15	-179.9 (3)	C14—C13—O3—Cu1	178.0 (2)
C18—C19—C20—C15	1.9 (5)	O2—Cu1—O3—C13	176.3 (5)
C15—C20—C21—C22	-179.8 (3)	N1—Cu1—O3—C13	85.4 (2)
C19—C20—C21—C22	0.1 (5)	N2—Cu1—O3—C13	-86.4 (2)

*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>
O1W—H1WA···O1	0.85	1.97	2.789 (3)	163
O1W—H1WB···O3 <sup>i</sup>	0.85	2.07	2.904 (3)	167

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

Fig. 1

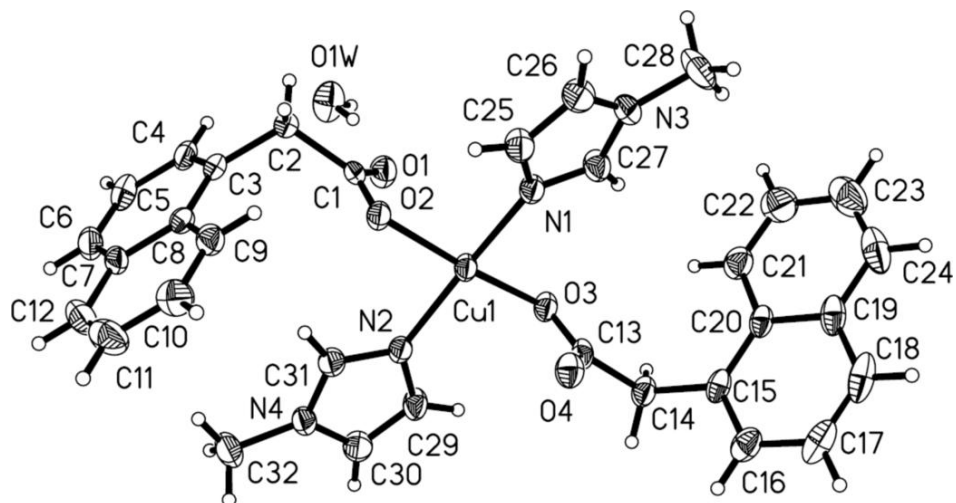


Fig. 2

