

[2-Hydroxy-N'-[1-(2-oxidophenyl)ethylidene]benzohydrazidato}morpholine-copper(II)

Song-Zhu Lin,* Ruo-Kun Jia, Yan-Lin Yuan and Peng Zhan

Chemical Engineering Institute, Northeast Dianli University, Jilin, Jilin 132012, People's Republic of China
Correspondence e-mail: songzhulin@163.com

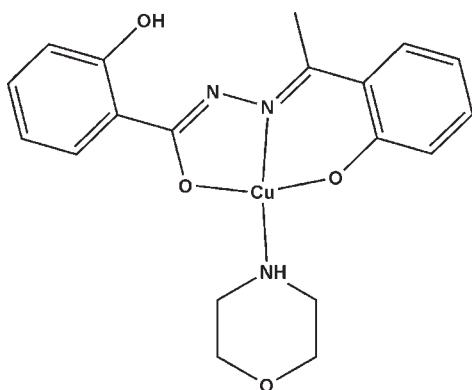
Received 16 October 2009; accepted 18 October 2009

Key indicators: single-crystal X-ray study; $T = 293\text{ K}$; mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$; R factor = 0.034; wR factor = 0.089; data-to-parameter ratio = 16.4.

The Cu^{II} ion in the title complex, $[\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3)(\text{C}_4\text{H}_9\text{NO})]$, is coordinated by one carbonyl O atom, one hydrazine N atom and one phenolate O atom from the doubly deprotonated tridentate ligand and one N atom from a morpholine molecule, forming a distorted *trans*- CuN_2O_2 square-planar coordination geometry. An intramolecular O—H···N hydrogen bond occurs within the ligand, generating an *S*(6) ring.

Related literature

For background to arylhydrazone derivatives, see: Singh (1992); Liu *et al.* (2003); Bai *et al.* (2005). For related structures, see: Gatto *et al.* (2004); Huo *et al.* (2004); Chen *et al.* (2009).



Experimental

Crystal data

$[\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3)(\text{C}_4\text{H}_9\text{NO})]$

$M_r = 418.93$

Monoclinic, $P2_1/n$

$a = 9.220 (4)\text{ \AA}$

$b = 17.616 (9)\text{ \AA}$

$c = 12.023 (6)\text{ \AA}$

$\beta = 112.257 (14)^\circ$

$V = 1807.4 (15)\text{ \AA}^3$

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.24\text{ mm}^{-1}$

$T = 293\text{ K}$
 $0.26 \times 0.17 \times 0.14\text{ mm}$

Data collection

Rigaku Weissenberg IP diffractometer
Absorption correction: multi-scan (*TEXRAY*; Molecular Structure Corporation, 1999)
 $T_{\min} = 0.769$, $T_{\max} = 0.837$

16528 measured reflections
4032 independent reflections
3273 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.089$
 $S = 1.05$
4032 reflections

246 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.35\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.47\text{ e \AA}^{-3}$

Table 1
Selected bond lengths (\AA).

| | | | |
|-----------------|-------------|-----------------|-------------|
| Cu1—O3 | 1.8702 (17) | Cu1—N2 | 1.9409 (18) |
| Cu1—O2 | 1.9208 (16) | Cu1—N3 | 2.0308 (19) |

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

| $D—H\cdots A$ | $D—H$ | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|--------------------------------|-------|-------------|-------------|---------------|
| $\text{O1—H1A}\cdots\text{N1}$ | 0.82 | 1.87 | 2.588 (3) | 146 |

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

We thank the Northeast Dianli University for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5147).

References

- Bai, Y., Dang, D. B., Duan, C. Y., Song, Y. & Meng, Q. J. (2005). *Inorg. Chem.* **44**, 5972–5974.
- Chen, X.-H., Wu, Q.-J., Liang, Z.-Y., Zhan, C.-R. & Liu, J.-B. (2009). *Acta Cryst. C* **65**, m190–m194.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gatto, C. C., Schulz-Lang, E., Kupfer, A., Hagenbach, A. & Abram, U. (2004). *Z. Anorg. Allg. Chem.* **630**, 1286–1295.
- Huo, L.-H., Lu, Z.-Z., Gao, S., Zhao, H. & Zhao, J.-G. (2004). *Acta Cryst. E* **60**, m1636–m1638.
- Liu, L., Ji, Y.-L., Jia, D.-Z. & Yu, K.-B. (2003). *Chin. J. Struct. Chem.* **22**, 568–572.
- Molecular Structure Corporation (1999). *TEXRAY* and *TEXSAN*. MSC, The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Singh, G. (1992). *Synth. React. Inorg. Met.-Org. Chem.* **22**, 1605–1618.

supplementary materials

Acta Cryst. (2009). E65, m1422 [doi:10.1107/S1600536809042810]

{2-Hydroxy-N'-[1-(2-oxidophenyl)ethylidene]benzohydrazidato}morpholinecopper(II)

S.-Z. Lin, R.-K. Jia, Y.-L. Yuan and P. Zhan

Comment

In the past decade, much attention has been focused on the study of arylhydrazone derivative with aryl, aroyl and heteroaroyl Schiff bases due to their coordination abilities to metal ions (Singh *et al.*, 1992; Liu *et al.*, 2003; Bai *et al.*, 2005). Ongoing the study of arylhydrazone complexes, we report here the synthesis and crystal structure of a new complex with 2-hydroxy-N'-(2-oxyphenyl-ethylidene)benzohydrazide(2-) ligand (Fig. 1).

The title complex, (I), contains one copper(II) center having distorted quadrilateral coordination environment, one *O,N,O'*-tridentate ligand molecule and one coordinated morpholine molecule. There exists one intramolecular phenol-hydrazone O—H···N hydrogen bond in each ligand, forming a six-membered ring.

Experimental

The ligand was prepared by the reaction of 2-hydroxyacetophenone and salicylhydrazine in a molar ratio of 1:1 under reflux in ethanol for 2 h. The white precipitate was collected, washed several times with ethanol and dried in *vacuo* (yield 79%). Morpholine (3 ml) was dropped into the mixture of 2-hydroxy-N'-(2-oxyphenyl- ethylidene)benzohydrazide (27 mg, 0.1 mmol) and Cu(Ac)₂·2H₂O (21 mg, 0.1 mmol) in methanol (10 ml). After stirring for 5 h, the reaction mixture was filtered and left to stand at room temperature. Green prisms of (I) were obtained by slow evaporation after 10 d. Analysis calculated for C₁₉H₂₁N₃O₄Cu: C 54.47, H 5.05, N 10.03%; found: C 53.99, H 5.01, N 10.29%.

Refinement

H atoms bonded to phenolate O and morpholine N atoms were located in difference Fourier maps and were refined isotropically with O—H and N—H distance restraints of 0.82 and 0.91 Å, respectively. All other H atoms were placed in idealized positions and refined using a riding model [C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the methylene H atoms].

Figures

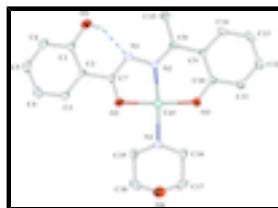


Fig. 1. The molecular structure of (I), showing displacement ellipsoids at the 30% probability level for non-H atoms. Dashed lines indicate hydrogen bonding. Only H atoms involved in hydrogen bonds have been included.

supplementary materials

{2-Hydroxy-*N'*-[1-(2-oxidophenyl)ethylidene]benzohydrazidato}morpholinecopper(II)

Crystal data

| | |
|--|---|
| [Cu(C ₁₅ H ₁₂ N ₂ O ₃)(C ₄ H ₉ NO)] | $F_{000} = 868$ |
| $M_r = 418.93$ | $D_x = 1.540 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: -P 2yn | Cell parameters from 4032 reflections |
| $a = 9.220 (4) \text{ \AA}$ | $\theta = 3.3\text{--}27.5^\circ$ |
| $b = 17.616 (9) \text{ \AA}$ | $\mu = 1.24 \text{ mm}^{-1}$ |
| $c = 12.023 (6) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $\beta = 112.257 (14)^\circ$ | Prism, green |
| $V = 1807.4 (15) \text{ \AA}^3$ | $0.26 \times 0.17 \times 0.14 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Rigaku Weissenberg IP diffractometer | 4032 independent reflections |
| Radiation source: fine-focus sealed tube | 3273 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.049$ |
| $T = 293 \text{ K}$ | $\theta_{\text{max}} = 27.5^\circ$ |
| ω scans | $\theta_{\text{min}} = 3.3^\circ$ |
| Absorption correction: multi-scan (TEXRAY; Molecular Structure Corporation, 1999) | $h = -11 \rightarrow 10$ |
| $T_{\text{min}} = 0.769$, $T_{\text{max}} = 0.837$ | $k = -22 \rightarrow 22$ |
| 16528 measured reflections | $l = -14 \rightarrow 15$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | H-atom parameters constrained |
| $wR(F^2) = 0.089$ | $w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.6843P]$ |
| $S = 1.05$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4032 reflections | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 246 parameters | $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$ |
| | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|--------------|----------------------------------|
| Cu1 | 0.35584 (3) | 0.512750 (15) | 0.55888 (2) | 0.03343 (10) |
| O1 | -0.2016 (2) | 0.39749 (11) | 0.30393 (17) | 0.0635 (5) |
| H1A | -0.1404 | 0.4330 | 0.3147 | 0.064 (9)* |
| O2 | 0.24346 (16) | 0.42406 (8) | 0.57392 (13) | 0.0392 (4) |
| O3 | 0.46114 (18) | 0.59329 (10) | 0.52104 (14) | 0.0479 (4) |
| O4 | 0.7081 (2) | 0.51533 (12) | 0.97389 (16) | 0.0626 (5) |
| N1 | 0.06587 (19) | 0.46639 (10) | 0.39142 (17) | 0.0373 (4) |
| N2 | 0.17322 (19) | 0.52585 (9) | 0.41154 (16) | 0.0334 (4) |
| N3 | 0.5322 (2) | 0.49568 (9) | 0.72070 (16) | 0.0343 (4) |
| H3B | 0.5980 | 0.4618 | 0.7068 | 0.042 (6)* |
| C1 | -0.1317 (3) | 0.34097 (13) | 0.3828 (2) | 0.0438 (5) |
| C2 | 0.0206 (2) | 0.34834 (12) | 0.4699 (2) | 0.0369 (5) |
| C3 | 0.0825 (3) | 0.28792 (13) | 0.5489 (2) | 0.0428 (5) |
| H3A | 0.1829 | 0.2921 | 0.6075 | 0.051* |
| C4 | -0.0011 (3) | 0.22263 (14) | 0.5418 (3) | 0.0534 (6) |
| H4A | 0.0428 | 0.1827 | 0.5946 | 0.064* |
| C5 | -0.1511 (3) | 0.21633 (16) | 0.4560 (3) | 0.0618 (7) |
| H5A | -0.2085 | 0.1722 | 0.4513 | 0.074* |
| C6 | -0.2160 (3) | 0.27518 (16) | 0.3775 (3) | 0.0583 (7) |
| H6A | -0.3174 | 0.2707 | 0.3205 | 0.070* |
| C7 | 0.1169 (2) | 0.41671 (12) | 0.4806 (2) | 0.0356 (5) |
| C8 | 0.1354 (2) | 0.58214 (12) | 0.33475 (19) | 0.0362 (5) |
| C9 | 0.2478 (2) | 0.64281 (12) | 0.34607 (19) | 0.0361 (5) |
| C10 | 0.4016 (3) | 0.64486 (12) | 0.43607 (19) | 0.0370 (5) |
| C11 | 0.5022 (3) | 0.70507 (13) | 0.4351 (2) | 0.0482 (6) |
| H11A | 0.6018 | 0.7072 | 0.4952 | 0.058* |
| C12 | 0.4580 (3) | 0.76027 (14) | 0.3488 (3) | 0.0570 (7) |
| H12A | 0.5275 | 0.7987 | 0.3494 | 0.068* |
| C13 | 0.3082 (4) | 0.75849 (15) | 0.2602 (3) | 0.0619 (7) |
| H13A | 0.2771 | 0.7958 | 0.2011 | 0.074* |
| C14 | 0.2067 (3) | 0.70213 (14) | 0.2596 (2) | 0.0503 (6) |
| H14A | 0.1065 | 0.7025 | 0.2002 | 0.060* |
| C15 | -0.0237 (3) | 0.58277 (16) | 0.2353 (2) | 0.0536 (6) |
| H15A | -0.0490 | 0.5326 | 0.2024 | 0.080* |
| H15B | -0.0235 | 0.6172 | 0.1735 | 0.080* |
| H15C | -0.1004 | 0.5989 | 0.2665 | 0.080* |
| C16 | 0.6283 (3) | 0.56298 (15) | 0.7719 (2) | 0.0539 (7) |
| H16A | 0.5626 | 0.6022 | 0.7849 | 0.065* |

supplementary materials

| | | | | |
|------|------------|--------------|------------|-------------|
| H16B | 0.6706 | 0.5824 | 0.7149 | 0.065* |
| C17 | 0.7606 (3) | 0.5460 (2) | 0.8884 (2) | 0.0656 (8) |
| H17A | 0.8319 | 0.5104 | 0.8740 | 0.079* |
| H17B | 0.8182 | 0.5924 | 0.9200 | 0.079* |
| C18 | 0.6243 (4) | 0.44769 (19) | 0.9289 (2) | 0.0773 (10) |
| H18A | 0.5881 | 0.4268 | 0.9885 | 0.093* |
| H18B | 0.6941 | 0.4108 | 0.9153 | 0.093* |
| C19 | 0.4852 (3) | 0.46037 (18) | 0.8129 (2) | 0.0630 (8) |
| H19A | 0.4348 | 0.4121 | 0.7832 | 0.076* |
| H19B | 0.4098 | 0.4928 | 0.8282 | 0.076* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| Cu1 | 0.02910 (14) | 0.03649 (15) | 0.02903 (15) | -0.00266 (10) | 0.00461 (11) | 0.00205 (10) |
| O1 | 0.0410 (9) | 0.0587 (11) | 0.0667 (12) | -0.0113 (8) | -0.0069 (9) | 0.0105 (9) |
| O2 | 0.0315 (8) | 0.0406 (8) | 0.0368 (8) | -0.0046 (6) | 0.0032 (7) | 0.0024 (6) |
| O3 | 0.0385 (8) | 0.0521 (10) | 0.0427 (9) | -0.0085 (7) | 0.0035 (7) | 0.0171 (7) |
| O4 | 0.0669 (12) | 0.0777 (13) | 0.0314 (9) | -0.0159 (10) | 0.0053 (9) | -0.0069 (8) |
| N1 | 0.0294 (9) | 0.0389 (10) | 0.0378 (10) | -0.0020 (7) | 0.0060 (8) | -0.0014 (8) |
| N2 | 0.0295 (8) | 0.0347 (10) | 0.0316 (9) | 0.0004 (7) | 0.0067 (7) | -0.0024 (7) |
| N3 | 0.0321 (9) | 0.0344 (9) | 0.0314 (9) | 0.0001 (7) | 0.0065 (8) | -0.0045 (7) |
| C1 | 0.0394 (12) | 0.0444 (13) | 0.0434 (13) | -0.0061 (9) | 0.0111 (10) | -0.0073 (10) |
| C2 | 0.0326 (10) | 0.0384 (11) | 0.0383 (11) | -0.0029 (8) | 0.0118 (9) | -0.0091 (9) |
| C3 | 0.0402 (12) | 0.0424 (12) | 0.0438 (13) | -0.0020 (9) | 0.0138 (11) | -0.0039 (10) |
| C4 | 0.0618 (16) | 0.0403 (13) | 0.0558 (15) | -0.0078 (11) | 0.0197 (13) | -0.0032 (11) |
| C5 | 0.0701 (18) | 0.0481 (15) | 0.0636 (17) | -0.0251 (13) | 0.0212 (15) | -0.0121 (13) |
| C6 | 0.0494 (15) | 0.0606 (16) | 0.0532 (15) | -0.0206 (12) | 0.0063 (13) | -0.0138 (13) |
| C7 | 0.0297 (10) | 0.0382 (11) | 0.0377 (11) | 0.0000 (8) | 0.0115 (9) | -0.0047 (9) |
| C8 | 0.0335 (11) | 0.0416 (12) | 0.0304 (10) | 0.0084 (8) | 0.0087 (9) | -0.0003 (8) |
| C9 | 0.0391 (11) | 0.0350 (11) | 0.0341 (11) | 0.0086 (8) | 0.0139 (9) | 0.0012 (8) |
| C10 | 0.0416 (11) | 0.0356 (11) | 0.0345 (11) | 0.0025 (8) | 0.0151 (10) | 0.0017 (9) |
| C11 | 0.0489 (13) | 0.0413 (13) | 0.0524 (14) | -0.0024 (10) | 0.0170 (12) | 0.0038 (10) |
| C12 | 0.0651 (17) | 0.0374 (13) | 0.0692 (17) | -0.0018 (11) | 0.0262 (15) | 0.0089 (12) |
| C13 | 0.0736 (18) | 0.0452 (15) | 0.0617 (17) | 0.0103 (13) | 0.0196 (15) | 0.0198 (13) |
| C14 | 0.0526 (14) | 0.0436 (14) | 0.0478 (14) | 0.0109 (11) | 0.0112 (12) | 0.0126 (11) |
| C15 | 0.0411 (13) | 0.0613 (16) | 0.0451 (14) | 0.0045 (11) | 0.0014 (11) | 0.0107 (11) |
| C16 | 0.0597 (15) | 0.0538 (15) | 0.0383 (12) | -0.0212 (12) | 0.0072 (12) | -0.0059 (10) |
| C17 | 0.0515 (15) | 0.092 (2) | 0.0416 (14) | -0.0220 (15) | 0.0043 (13) | -0.0141 (14) |
| C18 | 0.100 (2) | 0.068 (2) | 0.0369 (14) | -0.0222 (17) | -0.0044 (16) | 0.0128 (13) |
| C19 | 0.0653 (17) | 0.0730 (18) | 0.0367 (13) | -0.0284 (14) | 0.0036 (13) | 0.0081 (12) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-------------|--------|-----------|
| Cu1—O3 | 1.8702 (17) | C6—H6A | 0.9300 |
| Cu1—O2 | 1.9208 (16) | C8—C9 | 1.459 (3) |
| Cu1—N2 | 1.9409 (18) | C8—C15 | 1.501 (3) |
| Cu1—N3 | 2.0308 (19) | C9—C14 | 1.421 (3) |
| O1—C1 | 1.357 (3) | C9—C10 | 1.421 (3) |

| | | | |
|------------|-------------|---------------|-------------|
| O1—H1A | 0.8200 | C10—C11 | 1.412 (3) |
| O2—C7 | 1.283 (3) | C11—C12 | 1.366 (3) |
| O3—C10 | 1.321 (3) | C11—H11A | 0.9300 |
| O4—C17 | 1.399 (4) | C12—C13 | 1.389 (4) |
| O4—C18 | 1.412 (4) | C12—H12A | 0.9300 |
| N1—C7 | 1.325 (3) | C13—C14 | 1.362 (4) |
| N1—N2 | 1.398 (2) | C13—H13A | 0.9300 |
| N2—C8 | 1.309 (3) | C14—H14A | 0.9300 |
| N3—C16 | 1.468 (3) | C15—H15A | 0.9600 |
| N3—C19 | 1.472 (3) | C15—H15B | 0.9600 |
| N3—H3B | 0.9100 | C15—H15C | 0.9600 |
| C1—C6 | 1.384 (3) | C16—C17 | 1.499 (4) |
| C1—C2 | 1.404 (3) | C16—H16A | 0.9700 |
| C2—C3 | 1.397 (3) | C16—H16B | 0.9700 |
| C2—C7 | 1.473 (3) | C17—H17A | 0.9700 |
| C3—C4 | 1.370 (3) | C17—H17B | 0.9700 |
| C3—H3A | 0.9300 | C18—C19 | 1.512 (4) |
| C4—C5 | 1.381 (4) | C18—H18A | 0.9700 |
| C4—H4A | 0.9300 | C18—H18B | 0.9700 |
| C5—C6 | 1.377 (4) | C19—H19A | 0.9700 |
| C5—H5A | 0.9300 | C19—H19B | 0.9700 |
| O3—Cu1—O2 | 171.23 (7) | C10—C9—C8 | 123.93 (19) |
| O3—Cu1—N2 | 92.21 (7) | O3—C10—C11 | 116.2 (2) |
| O2—Cu1—N2 | 82.54 (7) | O3—C10—C9 | 125.0 (2) |
| O3—Cu1—N3 | 92.53 (7) | C11—C10—C9 | 118.8 (2) |
| O2—Cu1—N3 | 93.11 (7) | C12—C11—C10 | 122.2 (2) |
| N2—Cu1—N3 | 174.38 (8) | C12—C11—H11A | 118.9 |
| C1—O1—H1A | 109.5 | C10—C11—H11A | 118.9 |
| C7—O2—Cu1 | 110.14 (14) | C11—C12—C13 | 119.4 (2) |
| C10—O3—Cu1 | 127.42 (14) | C11—C12—H12A | 120.3 |
| C17—O4—C18 | 109.6 (2) | C13—C12—H12A | 120.3 |
| C7—N1—N2 | 110.10 (17) | C14—C13—C12 | 120.1 (2) |
| C8—N2—N1 | 117.62 (17) | C14—C13—H13A | 119.9 |
| C8—N2—Cu1 | 129.87 (15) | C12—C13—H13A | 119.9 |
| N1—N2—Cu1 | 112.43 (13) | C13—C14—C9 | 122.7 (2) |
| C16—N3—C19 | 109.2 (2) | C13—C14—H14A | 118.7 |
| C16—N3—Cu1 | 114.77 (15) | C9—C14—H14A | 118.7 |
| C19—N3—Cu1 | 115.24 (15) | C8—C15—H15A | 109.5 |
| C16—N3—H3B | 105.6 | C8—C15—H15B | 109.5 |
| C19—N3—H3B | 105.6 | H15A—C15—H15B | 109.5 |
| Cu1—N3—H3B | 105.6 | C8—C15—H15C | 109.5 |
| O1—C1—C6 | 118.2 (2) | H15A—C15—H15C | 109.5 |
| O1—C1—C2 | 122.0 (2) | H15B—C15—H15C | 109.5 |
| C6—C1—C2 | 119.8 (2) | N3—C16—C17 | 112.2 (2) |
| C3—C2—C1 | 118.2 (2) | N3—C16—H16A | 109.2 |
| C3—C2—C7 | 119.06 (19) | C17—C16—H16A | 109.2 |
| C1—C2—C7 | 122.7 (2) | N3—C16—H16B | 109.2 |
| C4—C3—C2 | 121.5 (2) | C17—C16—H16B | 109.2 |
| C4—C3—H3A | 119.3 | H16A—C16—H16B | 107.9 |

supplementary materials

| | | | |
|---------------|--------------|-----------------|--------------|
| C2—C3—H3A | 119.3 | O4—C17—C16 | 112.2 (2) |
| C3—C4—C5 | 119.7 (3) | O4—C17—H17A | 109.2 |
| C3—C4—H4A | 120.2 | C16—C17—H17A | 109.2 |
| C5—C4—H4A | 120.2 | O4—C17—H17B | 109.2 |
| C6—C5—C4 | 120.2 (2) | C16—C17—H17B | 109.2 |
| C6—C5—H5A | 119.9 | H17A—C17—H17B | 107.9 |
| C4—C5—H5A | 119.9 | O4—C18—C19 | 112.3 (2) |
| C5—C6—C1 | 120.6 (2) | O4—C18—H18A | 109.2 |
| C5—C6—H6A | 119.7 | C19—C18—H18A | 109.2 |
| C1—C6—H6A | 119.7 | O4—C18—H18B | 109.2 |
| O2—C7—N1 | 124.6 (2) | C19—C18—H18B | 109.2 |
| O2—C7—C2 | 118.6 (2) | H18A—C18—H18B | 107.9 |
| N1—C7—C2 | 116.84 (19) | N3—C19—C18 | 111.6 (2) |
| N2—C8—C9 | 119.94 (18) | N3—C19—H19A | 109.3 |
| N2—C8—C15 | 119.1 (2) | C18—C19—H19A | 109.3 |
| C9—C8—C15 | 121.0 (2) | N3—C19—H19B | 109.3 |
| C14—C9—C10 | 116.8 (2) | C18—C19—H19B | 109.3 |
| C14—C9—C8 | 119.2 (2) | H19A—C19—H19B | 108.0 |
| O3—Cu1—O2—C7 | -49.8 (5) | N2—N1—C7—C2 | -176.95 (18) |
| N2—Cu1—O2—C7 | 3.75 (14) | C3—C2—C7—O2 | -11.5 (3) |
| N3—Cu1—O2—C7 | -179.83 (14) | C1—C2—C7—O2 | 168.8 (2) |
| O2—Cu1—O3—C10 | 65.8 (5) | C3—C2—C7—N1 | 168.0 (2) |
| N2—Cu1—O3—C10 | 12.8 (2) | C1—C2—C7—N1 | -11.7 (3) |
| N3—Cu1—O3—C10 | -164.2 (2) | N1—N2—C8—C9 | -175.30 (18) |
| C7—N1—N2—C8 | -176.03 (19) | Cu1—N2—C8—C9 | 8.3 (3) |
| C7—N1—N2—Cu1 | 1.0 (2) | N1—N2—C8—C15 | 4.2 (3) |
| O3—Cu1—N2—C8 | -13.1 (2) | Cu1—N2—C8—C15 | -172.20 (17) |
| O2—Cu1—N2—C8 | 173.9 (2) | N2—C8—C9—C14 | 177.9 (2) |
| N3—Cu1—N2—C8 | 134.4 (7) | C15—C8—C9—C14 | -1.6 (3) |
| O3—Cu1—N2—N1 | 170.31 (14) | N2—C8—C9—C10 | 1.1 (3) |
| O2—Cu1—N2—N1 | -2.64 (14) | C15—C8—C9—C10 | -178.4 (2) |
| N3—Cu1—N2—N1 | -42.2 (8) | Cu1—O3—C10—C11 | 172.81 (17) |
| O3—Cu1—N3—C16 | 25.97 (19) | Cu1—O3—C10—C9 | -8.7 (3) |
| O2—Cu1—N3—C16 | -160.75 (18) | C14—C9—C10—O3 | -177.8 (2) |
| N2—Cu1—N3—C16 | -121.6 (7) | C8—C9—C10—O3 | -0.9 (4) |
| O3—Cu1—N3—C19 | 154.11 (19) | C14—C9—C10—C11 | 0.6 (3) |
| O2—Cu1—N3—C19 | -32.60 (19) | C8—C9—C10—C11 | 177.5 (2) |
| N2—Cu1—N3—C19 | 6.6 (8) | O3—C10—C11—C12 | 176.9 (2) |
| O1—C1—C2—C3 | 178.8 (2) | C9—C10—C11—C12 | -1.7 (4) |
| C6—C1—C2—C3 | 0.3 (4) | C10—C11—C12—C13 | 1.4 (4) |
| O1—C1—C2—C7 | -1.4 (4) | C11—C12—C13—C14 | 0.0 (4) |
| C6—C1—C2—C7 | -180.0 (2) | C12—C13—C14—C9 | -1.0 (4) |
| C1—C2—C3—C4 | 0.6 (4) | C10—C9—C14—C13 | 0.7 (4) |
| C7—C2—C3—C4 | -179.1 (2) | C8—C9—C14—C13 | -176.3 (3) |
| C2—C3—C4—C5 | -0.9 (4) | C19—N3—C16—C17 | 51.4 (3) |
| C3—C4—C5—C6 | 0.3 (4) | Cu1—N3—C16—C17 | -177.45 (19) |
| C4—C5—C6—C1 | 0.6 (5) | C18—O4—C17—C16 | 59.0 (4) |
| O1—C1—C6—C5 | -179.5 (3) | N3—C16—C17—O4 | -56.9 (3) |
| C2—C1—C6—C5 | -0.9 (4) | C17—O4—C18—C19 | -58.7 (4) |

supplementary materials

| | | | |
|--------------|-------------|----------------|-----------|
| Cu1—O2—C7—N1 | −4.7 (3) | C16—N3—C19—C18 | −50.8 (3) |
| Cu1—O2—C7—C2 | 174.76 (15) | Cu1—N3—C19—C18 | 178.3 (2) |
| N2—N1—C7—O2 | 2.6 (3) | O4—C18—C19—N3 | 55.9 (4) |

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> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1A···N1 | 0.82 | 1.87 | 2.588 (3) | 146 |

supplementary materials

Fig. 1

