

{6,6'-Dimethoxy-2,2'-[6-bromopyridine-2,3-diylbis(nitrilomethylidene)]diphenolato}copper(II) methanol solvate

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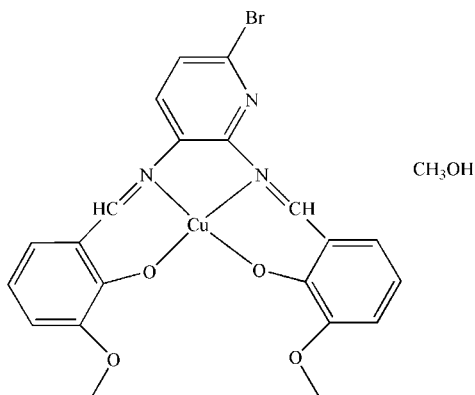
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.043; wR factor = 0.139; data-to-parameter ratio = 12.6.

In the title compound, $[\text{Cu}(\text{C}_{21}\text{H}_{16}\text{BrN}_3\text{O}_4)] \cdot \text{CH}_3\text{OH}$, the Cu^{II} ion is coordinated by two N [$\text{Cu}-\text{N} = 1.814$ (3) and 1.917 (3) Å] and two O [$\text{Cu}-\text{O} = 1.805$ (3) and 1.893 (3) Å] atoms from the tetradentate Schiff base ligand in a distorted square-planar geometry. In the crystal structure, the approximately planar Cu complex molecules are paired into centrosymmetric dimers with short intermolecular $\text{Cu} \cdots \text{N}$ distances of 3.162 (3) Å. Weak $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds may help to stabilize the structure.

Related literature

For a related crystal structure, see Saha *et al.* (2007). For general background, see: Ghosh *et al.* (2006); Nayak *et al.* (2006); Singh *et al.* (2007); Yu *et al.* (2007).



Experimental

Crystal data

| | |
|---|-----------------------------------|
| $[\text{Cu}(\text{C}_{21}\text{H}_{16}\text{BrN}_3\text{O}_4)] \cdot \text{CH}_4\text{O}$ | $\gamma = 96.531$ (2) $^\circ$ |
| $M_r = 549.86$ | $V = 1059.9$ (2) Å ³ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 7.4520$ (8) Å | Mo $K\alpha$ radiation |
| $b = 11.5402$ (13) Å | $\mu = 2.96$ mm ⁻¹ |
| $c = 12.9432$ (14) Å | $T = 293$ (2) K |
| $\alpha = 104.345$ (2) $^\circ$ | $0.15 \times 0.13 \times 0.11$ mm |
| $\beta = 96.467$ (2) $^\circ$ | |

Data collection

| | |
|---|--|
| Bruker APEXII CCD area-detector diffractometer | 5332 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2003) | 3705 independent reflections |
| $T_{\min} = 0.665$, $T_{\max} = 0.737$ | 2885 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.019$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | 293 parameters |
| $wR(F^2) = 0.139$ | H-atom parameters constrained |
| $S = 1.06$ | $\Delta\rho_{\text{max}} = 0.73$ e Å ⁻³ |
| 3705 reflections | $\Delta\rho_{\text{min}} = -0.45$ e Å ⁻³ |

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| $\text{O5}-\text{H5} \cdots \text{O1}$ | 0.82 | 2.24 | 3.033 (5) | 163 |
| $\text{O5}-\text{H5} \cdots \text{O3}$ | 0.82 | 2.63 | 3.165 (5) | 124 |

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP (Sheldrick, 1998); software used to prepare material for publication: XP.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2514).

References

- Bruker (2001). SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2004). APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.
 Ghosh, R., Rahaman, S. H., Lin, C. N., Lu, T. H. & Ghosh, B. K. (2006). *Polyhedron*, **25**, 3104–3112.
 Nayak, M., Koner, R., Lin, H. H., Flörke, U., Wei, H. H. & Mohanta, S. (2006). *Inorg. Chem.* **45**, 10764–10773.
 Saha, P. K., Dutta, B., Jana, S., Bera, R., Saha, S., Okamoto, K. & Koner, S. (2007). *Polyhedron*, **26**, 563–571.
 Sheldrick, G. M. (1998). XP. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (2003). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Singh, K., Barwa, M. S. & Tyagi, P. (2007). *Eur. J. Med. Chem.* **42**, 394–402.
 Yu, T. Z., Zhang, K., Zhao, Y. L., Yang, C. H., Zhang, H., Fan, D. W. & Dong, W. K. (2007). *Inorg. Chem. Commun.* **10**, 401–403.

supplementary materials

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**{6,6'-Dimethoxy-2,2'-[6-bromopyridine-2,3-diylbis(nitrilomethylidene)]diphenolato}copper(II)
methanol solvate**

Z. Jia

Comment

Schiff bases play an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals, in which some could exhibit interesting properties (Yu *et al.*, 2007; Ghosh *et al.*, 2006; Singh *et al.*, 2007; Nayak *et al.*, 2006). Here, we report a new Cu^{II} complex based on the tetradentate Schiff-base ligand 6-bromo-2,3-diaminopyridine-*N,N'*-bis (3-methoxysalicylideneimine).

The geometry and labeling scheme for the crystal structure of the title complex are shown in Figure 1. The coordination sphere for the Cu^{II} ion in the title complex is a slightly distorted square planar, in which the four positions are occupied by two N atoms and two O atoms of the Schiff-base ligand. The mean deviation from the plane formed by the two N atoms, two O atoms and the Cu ion is only 0.0329 Å, indicative of that these five atoms are nearly coplanar. The average bond lengths of Cu—N and Cu—O are 1.866 and 1.849 Å, respectively, which are slightly shorter than the corresponding distances in aqua-(*N,N'*-ethylenebis(3-methoxysalicylaldiminato)-*N,N',O,O'*)copper(II) (Saha, *et al.*, 2007).

Experimental

The Schiff base ligand was synthesized by condensation 6-bromo-2,3-diaminopyridine and 2-hydroxy-3-methoxybenzaldehyde with the ratio 1:2 in ethanol. The synthesis of the title complex was carried out by reacting Cu(ClO₄)₂·6H₂O, and the Schiff-base ligand (1:1, molar ratio) in methanol. After the stirring process was continued for about 30 min at room temperature, the mixture was filtered and the filtrate was allowed to partial evaporate in air for several days to produce crystals suitable for X-ray diffraction with a yield about 60%.

Refinement

All H atoms were geometrically positioned (C—H 0.93, 0.96 Å and O—H 0.82 Å), and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C}, \text{O})$.

Figures

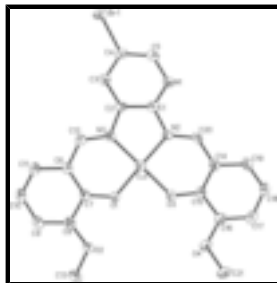


Fig. 1. View of the title compound with the atom-labelling scheme and displacement ellipsoids drawn at the 30% probability level. All H-atoms and the methanol molecule are omitted for clarity.

supplementary materials

{6,6'-Dimethoxy-2,2'-[6-bromopyridine-2,3- diylbis(nitrilomethylidyne)]diphenolato}copper(II) methanol solvate

Crystal data

[Cu(C₂₁H₁₆BrN₃O₄)]·CH₄O

$M_r = 549.86$

Triclinic, $P\bar{1}$

$a = 7.4520$ (8) Å

$b = 11.5402$ (13) Å

$c = 12.9432$ (14) Å

$\alpha = 104.345$ (2)°

$\beta = 96.467$ (2)°

$\gamma = 96.531$ (2)°

$V = 1059.9$ (2) Å³

$Z = 2$

$F_{000} = 554$

$D_x = 1.723$ Mg m⁻³

$D_m = 1.723$ Mg m⁻³

D_m measured by not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1770 reflections

$\theta = 3.0$ – 24.5 °

$\mu = 2.96$ mm⁻¹

$T = 293$ K

Block, blue

$0.15 \times 0.13 \times 0.11$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.665$, $T_{\max} = 0.737$

5332 measured reflections

3705 independent reflections

2885 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 25.0$ °

$\theta_{\min} = 1.8$ °

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 9$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.139$

$S = 1.06$

3705 reflections

293 parameters

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

$$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 0.2066P]$$

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

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

$\Delta\rho_{\max} = 0.73$ e Å⁻³

$\Delta\rho_{\min} = -0.45$ e Å⁻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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|-------------|----------------------------------|
| Cu1 | 0.36241 (7) | -0.01108 (4) | 0.60230 (4) | 0.03577 (19) |
| Br1 | 0.23295 (10) | -0.51353 (5) | 0.16747 (4) | 0.0761 (3) |
| O1 | 0.2903 (4) | 0.1323 (3) | 0.5995 (2) | 0.0383 (7) |
| O2 | 0.2316 (5) | 0.3501 (3) | 0.6365 (3) | 0.0485 (8) |
| O3 | 0.4745 (4) | 0.0684 (3) | 0.7448 (2) | 0.0405 (7) |
| O4 | 0.6350 (5) | 0.2207 (3) | 0.9307 (3) | 0.0634 (10) |
| O5 | 0.1419 (5) | 0.2035 (3) | 0.8114 (3) | 0.0625 (10) |
| H5 | 0.2014 | 0.1945 | 0.7612 | 0.075* |
| N1 | 0.4117 (5) | -0.3542 (3) | 0.4995 (3) | 0.0425 (9) |
| N2 | 0.4290 (4) | -0.1555 (3) | 0.6099 (3) | 0.0332 (8) |
| N3 | 0.2583 (4) | -0.0873 (3) | 0.4554 (3) | 0.0314 (7) |
| C1 | 0.3764 (5) | -0.2447 (4) | 0.5091 (3) | 0.0360 (9) |
| C2 | 0.2886 (5) | -0.2069 (3) | 0.4228 (3) | 0.0334 (9) |
| C3 | 0.2440 (6) | -0.2854 (4) | 0.3183 (4) | 0.0451 (11) |
| H3 | 0.1896 | -0.2613 | 0.2603 | 0.054* |
| C4 | 0.2859 (6) | -0.3987 (4) | 0.3081 (4) | 0.0450 (11) |
| C5 | 0.3641 (6) | -0.4313 (4) | 0.3988 (4) | 0.0465 (11) |
| H5A | 0.3850 | -0.5109 | 0.3896 | 0.056* |
| C6 | 0.1301 (5) | 0.0772 (4) | 0.4117 (3) | 0.0359 (9) |
| C7 | 0.1961 (5) | 0.1589 (4) | 0.5164 (3) | 0.0342 (9) |
| C8 | 0.1615 (6) | 0.2776 (4) | 0.5331 (4) | 0.0397 (10) |
| C9 | 0.0664 (6) | 0.3116 (4) | 0.4483 (4) | 0.0478 (12) |
| H9 | 0.0452 | 0.3913 | 0.4597 | 0.057* |
| C10 | 0.0008 (6) | 0.2296 (5) | 0.3456 (4) | 0.0501 (12) |
| H10 | -0.0619 | 0.2564 | 0.2919 | 0.060* |
| C11 | 0.0288 (6) | 0.1147 (4) | 0.3262 (4) | 0.0443 (11) |
| H11 | -0.0153 | 0.0602 | 0.2598 | 0.053* |
| C12 | 0.1635 (5) | -0.0414 (4) | 0.3872 (3) | 0.0366 (10) |
| H12 | 0.1166 | -0.0913 | 0.3191 | 0.044* |
| C13 | 0.2030 (8) | 0.4705 (4) | 0.6604 (4) | 0.0583 (14) |
| H13A | 0.2575 | 0.5096 | 0.6117 | 0.087* |
| H13B | 0.2576 | 0.5108 | 0.7331 | 0.087* |
| H13C | 0.0743 | 0.4741 | 0.6527 | 0.087* |

supplementary materials

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|------|-------------|-------------|------------|-------------|
| C14 | 0.5858 (6) | -0.0953 (4) | 0.7995 (3) | 0.0379 (10) |
| C15 | 0.5660 (6) | 0.0254 (4) | 0.8168 (3) | 0.0372 (10) |
| C16 | 0.6525 (6) | 0.1045 (4) | 0.9197 (4) | 0.0446 (11) |
| C17 | 0.7470 (7) | 0.0636 (5) | 1.0005 (4) | 0.0547 (13) |
| H17 | 0.7998 | 0.1177 | 1.0657 | 0.066* |
| C18 | 0.7609 (7) | -0.0570 (5) | 0.9823 (4) | 0.0546 (13) |
| H18 | 0.8209 | -0.0859 | 1.0356 | 0.066* |
| C19 | 0.6857 (7) | -0.1340 (5) | 0.8852 (4) | 0.0501 (12) |
| H19 | 0.6988 | -0.2152 | 0.8731 | 0.060* |
| C20 | 0.5175 (6) | -0.1781 (4) | 0.6964 (3) | 0.0380 (10) |
| H20 | 0.5376 | -0.2576 | 0.6890 | 0.046* |
| C21 | 0.7138 (11) | 0.3026 (5) | 1.0320 (5) | 0.088 (2) |
| H21A | 0.6589 | 0.2793 | 1.0888 | 0.132* |
| H21B | 0.6927 | 0.3831 | 1.0316 | 0.132* |
| H21C | 0.8428 | 0.3006 | 1.0435 | 0.132* |
| C22 | 0.2129 (10) | 0.3101 (5) | 0.8876 (5) | 0.0784 (18) |
| H22A | 0.2649 | 0.2925 | 0.9523 | 0.118* |
| H22B | 0.1175 | 0.3582 | 0.9032 | 0.118* |
| H22C | 0.3060 | 0.3538 | 0.8604 | 0.118* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|-------------|
| Cu1 | 0.0395 (3) | 0.0311 (3) | 0.0352 (3) | 0.0046 (2) | 0.0021 (2) | 0.0076 (2) |
| Br1 | 0.1168 (6) | 0.0451 (3) | 0.0517 (4) | 0.0169 (3) | -0.0020 (3) | -0.0105 (3) |
| O1 | 0.0485 (17) | 0.0308 (15) | 0.0337 (15) | 0.0054 (13) | -0.0022 (13) | 0.0085 (12) |
| O2 | 0.066 (2) | 0.0302 (16) | 0.0483 (19) | 0.0142 (15) | 0.0021 (16) | 0.0084 (14) |
| O3 | 0.0484 (17) | 0.0341 (16) | 0.0364 (16) | 0.0062 (13) | -0.0035 (14) | 0.0086 (13) |
| O4 | 0.092 (3) | 0.039 (2) | 0.047 (2) | 0.0006 (18) | -0.0166 (19) | 0.0059 (16) |
| O5 | 0.071 (2) | 0.062 (2) | 0.048 (2) | 0.0059 (19) | 0.0110 (18) | 0.0016 (18) |
| N1 | 0.045 (2) | 0.032 (2) | 0.050 (2) | 0.0079 (16) | 0.0042 (18) | 0.0097 (18) |
| N2 | 0.0338 (18) | 0.0295 (18) | 0.0352 (19) | 0.0026 (14) | 0.0053 (15) | 0.0074 (15) |
| N3 | 0.0306 (17) | 0.0291 (18) | 0.0335 (18) | 0.0022 (14) | 0.0043 (14) | 0.0078 (15) |
| C1 | 0.032 (2) | 0.035 (2) | 0.039 (2) | 0.0020 (18) | 0.0081 (18) | 0.0070 (19) |
| C2 | 0.033 (2) | 0.028 (2) | 0.036 (2) | -0.0014 (17) | 0.0079 (18) | 0.0032 (18) |
| C3 | 0.050 (3) | 0.038 (3) | 0.045 (3) | 0.007 (2) | 0.002 (2) | 0.007 (2) |
| C4 | 0.054 (3) | 0.034 (2) | 0.039 (2) | 0.006 (2) | 0.007 (2) | -0.003 (2) |
| C5 | 0.051 (3) | 0.034 (2) | 0.054 (3) | 0.011 (2) | 0.014 (2) | 0.006 (2) |
| C6 | 0.030 (2) | 0.043 (3) | 0.037 (2) | 0.0034 (18) | 0.0054 (18) | 0.017 (2) |
| C7 | 0.032 (2) | 0.034 (2) | 0.039 (2) | 0.0039 (17) | 0.0082 (18) | 0.0132 (19) |
| C8 | 0.038 (2) | 0.039 (2) | 0.043 (3) | 0.0040 (19) | 0.005 (2) | 0.014 (2) |
| C9 | 0.045 (3) | 0.048 (3) | 0.059 (3) | 0.015 (2) | 0.009 (2) | 0.024 (2) |
| C10 | 0.047 (3) | 0.059 (3) | 0.050 (3) | 0.015 (2) | -0.002 (2) | 0.026 (3) |
| C11 | 0.040 (2) | 0.051 (3) | 0.041 (3) | 0.005 (2) | 0.001 (2) | 0.015 (2) |
| C12 | 0.035 (2) | 0.040 (2) | 0.033 (2) | -0.0013 (18) | 0.0057 (18) | 0.0082 (19) |
| C13 | 0.077 (4) | 0.034 (3) | 0.066 (3) | 0.015 (2) | 0.011 (3) | 0.014 (2) |
| C14 | 0.037 (2) | 0.043 (3) | 0.036 (2) | 0.0122 (19) | 0.0084 (19) | 0.011 (2) |
| C15 | 0.037 (2) | 0.041 (2) | 0.035 (2) | 0.0035 (18) | 0.0057 (18) | 0.0137 (19) |

| | | | | | | |
|-----|-----------|-----------|-----------|-------------|------------|------------|
| C16 | 0.046 (3) | 0.045 (3) | 0.040 (3) | 0.002 (2) | 0.000 (2) | 0.010 (2) |
| C17 | 0.053 (3) | 0.065 (3) | 0.040 (3) | 0.001 (2) | -0.005 (2) | 0.011 (2) |
| C18 | 0.063 (3) | 0.059 (3) | 0.042 (3) | 0.020 (3) | -0.007 (2) | 0.017 (2) |
| C19 | 0.057 (3) | 0.052 (3) | 0.049 (3) | 0.020 (2) | 0.006 (2) | 0.022 (2) |
| C20 | 0.040 (2) | 0.035 (2) | 0.043 (2) | 0.0151 (19) | 0.009 (2) | 0.014 (2) |
| C21 | 0.139 (6) | 0.042 (3) | 0.060 (4) | -0.012 (3) | -0.032 (4) | 0.002 (3) |
| C22 | 0.104 (5) | 0.064 (4) | 0.053 (3) | 0.016 (3) | -0.008 (3) | -0.004 (3) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|---------------|-----------|
| Cu1—O1 | 1.805 (3) | C7—C8 | 1.392 (6) |
| Cu1—N2 | 1.814 (3) | C8—C9 | 1.400 (6) |
| Cu1—O3 | 1.893 (3) | C9—C10 | 1.423 (7) |
| Cu1—N3 | 1.917 (3) | C9—H9 | 0.9300 |
| Br1—C4 | 1.936 (4) | C10—C11 | 1.332 (6) |
| O1—C7 | 1.337 (5) | C10—H10 | 0.9300 |
| O2—C13 | 1.393 (5) | C11—H11 | 0.9300 |
| O2—C8 | 1.398 (5) | C12—H12 | 0.9300 |
| O3—C15 | 1.320 (5) | C13—H13A | 0.9600 |
| O4—C16 | 1.335 (6) | C13—H13B | 0.9600 |
| O4—C21 | 1.430 (6) | C13—H13C | 0.9600 |
| O5—C22 | 1.378 (6) | C14—C15 | 1.382 (6) |
| O5—H5 | 0.8200 | C14—C20 | 1.434 (6) |
| N1—C1 | 1.298 (5) | C14—C19 | 1.456 (6) |
| N1—C5 | 1.366 (6) | C15—C16 | 1.447 (6) |
| N2—C20 | 1.331 (5) | C16—C17 | 1.402 (6) |
| N2—C1 | 1.430 (5) | C17—C18 | 1.371 (7) |
| N3—C12 | 1.317 (5) | C17—H17 | 0.9300 |
| N3—C2 | 1.392 (5) | C18—C19 | 1.364 (7) |
| C1—C2 | 1.417 (6) | C18—H18 | 0.9300 |
| C2—C3 | 1.408 (6) | C19—H19 | 0.9300 |
| C3—C4 | 1.356 (6) | C20—H20 | 0.9300 |
| C3—H3 | 0.9300 | C21—H21A | 0.9600 |
| C4—C5 | 1.405 (7) | C21—H21B | 0.9600 |
| C5—H5A | 0.9300 | C21—H21C | 0.9600 |
| C6—C12 | 1.385 (6) | C22—H22A | 0.9600 |
| C6—C7 | 1.441 (6) | C22—H22B | 0.9600 |
| C6—C11 | 1.451 (6) | C22—H22C | 0.9600 |
| O1—Cu1—N2 | 177.45 (14) | C9—C10—H10 | 119.9 |
| O1—Cu1—O3 | 85.51 (12) | C10—C11—C6 | 118.1 (4) |
| N2—Cu1—O3 | 93.31 (13) | C10—C11—H11 | 121.0 |
| O1—Cu1—N3 | 93.72 (13) | C6—C11—H11 | 121.0 |
| N2—Cu1—N3 | 87.57 (14) | N3—C12—C6 | 123.4 (4) |
| O3—Cu1—N3 | 177.17 (13) | N3—C12—H12 | 118.3 |
| C7—O1—Cu1 | 127.0 (3) | C6—C12—H12 | 118.3 |
| C13—O2—C8 | 117.2 (4) | O2—C13—H13A | 109.5 |
| C15—O3—Cu1 | 129.7 (3) | O2—C13—H13B | 109.5 |
| C16—O4—C21 | 116.2 (4) | H13A—C13—H13B | 109.5 |
| C22—O5—H5 | 109.5 | O2—C13—H13C | 109.5 |

supplementary materials

| | | | |
|-------------|-----------|---------------|-----------|
| C1—N1—C5 | 115.7 (4) | H13A—C13—H13C | 109.5 |
| C20—N2—C1 | 123.0 (3) | H13B—C13—H13C | 109.5 |
| C20—N2—Cu1 | 125.7 (3) | C15—C14—C20 | 119.8 (4) |
| C1—N2—Cu1 | 111.3 (3) | C15—C14—C19 | 118.7 (4) |
| C12—N3—C2 | 119.4 (3) | C20—C14—C19 | 121.3 (4) |
| C12—N3—Cu1 | 128.3 (3) | O3—C15—C14 | 123.0 (4) |
| C2—N3—Cu1 | 112.3 (3) | O3—C15—C16 | 120.7 (4) |
| N1—C1—C2 | 123.0 (4) | C14—C15—C16 | 116.2 (4) |
| N1—C1—N2 | 120.0 (4) | O4—C16—C17 | 122.9 (4) |
| C2—C1—N2 | 116.9 (4) | O4—C16—C15 | 113.8 (4) |
| N3—C2—C3 | 127.0 (4) | C17—C16—C15 | 123.3 (4) |
| N3—C2—C1 | 111.8 (3) | C18—C17—C16 | 119.3 (5) |
| C3—C2—C1 | 121.3 (4) | C18—C17—H17 | 120.3 |
| C4—C3—C2 | 115.3 (4) | C16—C17—H17 | 120.3 |
| C4—C3—H3 | 122.4 | C19—C18—C17 | 119.1 (4) |
| C2—C3—H3 | 122.4 | C19—C18—H18 | 120.4 |
| C3—C4—C5 | 120.1 (4) | C17—C18—H18 | 120.4 |
| C3—C4—Br1 | 118.7 (4) | C18—C19—C14 | 123.2 (4) |
| C5—C4—Br1 | 121.2 (3) | C18—C19—H19 | 118.4 |
| N1—C5—C4 | 124.5 (4) | C14—C19—H19 | 118.4 |
| N1—C5—H5A | 117.7 | N2—C20—C14 | 128.2 (4) |
| C4—C5—H5A | 117.7 | N2—C20—H20 | 115.9 |
| C12—C6—C7 | 121.2 (4) | C14—C20—H20 | 115.9 |
| C12—C6—C11 | 116.5 (4) | O4—C21—H21A | 109.5 |
| C7—C6—C11 | 122.3 (4) | O4—C21—H21B | 109.5 |
| O1—C7—C8 | 116.2 (4) | H21A—C21—H21B | 109.5 |
| O1—C7—C6 | 126.3 (4) | O4—C21—H21C | 109.5 |
| C8—C7—C6 | 117.5 (4) | H21A—C21—H21C | 109.5 |
| C7—C8—O2 | 113.3 (4) | H21B—C21—H21C | 109.5 |
| C7—C8—C9 | 118.9 (4) | O5—C22—H22A | 109.5 |
| O2—C8—C9 | 127.8 (4) | O5—C22—H22B | 109.5 |
| C8—C9—C10 | 123.0 (4) | H22A—C22—H22B | 109.5 |
| C8—C9—H9 | 118.5 | O5—C22—H22C | 109.5 |
| C10—C9—H9 | 118.5 | H22A—C22—H22C | 109.5 |
| C11—C10—C9 | 120.3 (4) | H22B—C22—H22C | 109.5 |
| C11—C10—H10 | 119.9 | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------|-------|-------------|-------------|---------------|
| O5—H5 \cdots O1 | 0.82 | 2.24 | 3.033 (5) | 163 |
| O5—H5 \cdots O3 | 0.82 | 2.63 | 3.165 (5) | 124 |

Fig. 1

