

## (Acetato- $\kappa$ O)(2-{[2-(dimethylamino)-ethylimino](phenyl)methyl}-5-methoxyphenolato- $\kappa^3$ N,N',O<sup>1</sup>)copper(II)

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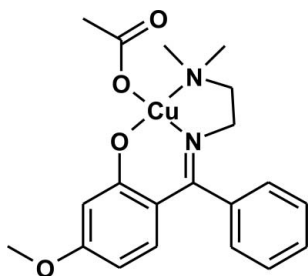
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}—\text{C}) = 0.005$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.103; data-to-parameter ratio = 15.7.

The Cu<sup>II</sup> atom in the title complex,  $[\text{Cu}(\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2)(\text{C}_2\text{H}_3\text{O}_2)]$ , is tetracoordinated by two N atoms and two O atoms, of which one O atom is attributed to the acetate group and the other atoms are from the tridentate salicylideneimine ligand, forming a slight distorted square-planar environment. The other acetate O atom exhibits a very weak intramolecular interaction toward the Cu atom, the Cu—O distance of 2.771 (2) Å being shorter than the van der Waals radii for Cu and O atoms (2.92 Å). Furthermore, there are weak intermolecular interactions, in which the bonding O atom of the acetate group can bridge to the Cu atom of another complex, and the distance of 2.523 (2) Å is about 0.4 Å shorter than the van der Waals Cu—O distance in other crystal structures.

### Related literature

For general background, see: Coates & Moore (2004); Darensbourg *et al.* (2001); Inoue *et al.* (1969); Shen *et al.* (2003). For related structures, see: Chen *et al.* (2006); Luo *et al.* (1998, 1999).



### Experimental

#### Crystal data

$[\text{Cu}(\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2)(\text{C}_2\text{H}_3\text{O}_2)]$   
 $M_r = 419.96$   
 Monoclinic,  $P2_1/c$   
 $a = 11.9721$  (16) Å  
 $b = 15.674$  (2) Å  
 $c = 10.6346$  (14) Å  
 $\beta = 102.655$  (3)°

$V = 1947.1$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.15$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
 $0.40 \times 0.30 \times 0.20$  mm

#### Data collection

Bruker SMART 1000 CCD  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.656$ ,  $T_{\max} = 0.803$

11008 measured reflections  
 3822 independent reflections  
 2673 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.103$   
 $S = 1.02$   
 3822 reflections

244 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.47$  e Å<sup>−3</sup>  
 $\Delta\rho_{\text{min}} = -0.40$  e Å<sup>−3</sup>

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2108).

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**supplementary materials**

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**(Acetato- $\kappa O$ )(2-{[2-(dimethylamino)ethylimino](phenyl)methyl}-5-methoxyphenolato- $\kappa^3 N, N', O^1$ )copper(II)**

**C.-S. Lin, C.-H. Lin, J.-H. Huang and B.-T. Ko**

**Comment**

Carbon dioxide is the most abundant carbon resource in the atmosphere and is used by green plants and anaerobic bacteria for chemical production on a massive scale. In contrast, industrial and laboratory utilization of CO<sub>2</sub> as a chemical feedstock is rare. The reuse and recovery of CO<sub>2</sub> have received much attention from the viewpoint of carbon resources and environmental problems during the last two decades of the twentieth century. In particular, the catalytic coupling of CO<sub>2</sub> with heterocycles has been discovered and investigated over the past 35 years (Inoue *et al.*, 1969). One of the major successes is the utilization of epoxides and CO<sub>2</sub> as starting materials to prepare the polycarbonates and/or cyclic carbonates in the presence of a transition metal catalyst. However, only a few metals, including Al, Cr, Co, Mg, Li, Zn, Cu, and Cd (Coates & Moore, 2004) are active for the coupling of epoxides and CO<sub>2</sub>. Recently, Darensbourg *et al.*, (2001) disclosed the synthesis, characterization and catalytic studies of a number of bis(salicylaldiminato)zinc complexes, in which the most active catalyst for co-polymerization of cyclohexene oxide and CO<sub>2</sub> giving poly(cyclohexene carbonate) (>99% carbonate linkages,  $M_n = 41000 \text{ g mol}^{-1}$ ,  $M_w/M_n = 10.3$ ) with a turnover frequency of  $6.9 \text{ h}^{-1}$ . In addition, Shen *et al.* (2003) reported that binaphthyldiaminosalen-type Zn, Cu, and Co complexes efficiently catalyzed reactions of epoxides with CO<sub>2</sub> to achieve five-membered ring cyclic carbonates in the presence of various catalytic amounts of organic bases. Most recently, Chen *et al.*, (2006) has synthesized a series of Schiff base zinc complexes which have shown high activity in the ring-opening polymerization of lactide (Chen *et al.*, 2006). We report herein the synthesis and crystal structure study of a *N,N,O*-tridentate Schiff base Cu<sup>II</sup> complex (**I**), a potential catalyst for CO<sub>2</sub>/epoxide coupling copolymerization (Fig. 1).

The solid structure of **I** reveals a monomeric Cu<sup>II</sup> complex (Fig. 1) containing a six-member and five-member ring coordinated from the tridentate salicylideneimine ligand. The geometry around Cu atom is tetracoordinated with a slight distorted square planar environment in which two nitrogen atoms and two oxygen atoms are almost coplanar. The sums of bond angles around Cu center are  $359.7 (1)^\circ$ . The distances between the Cu atom and O1, O3, N1 and N2 are 1.908 (2), 1.968 (2), 2.073 (3), 1.969 (3) Å, respectively. These bond distances are similar to those found in other Schiff base Cu<sup>II</sup> complexes (Luo *et al.*, 1998). The other acetate's oxygen, O4 shows very weak intramolecular contact with Cu (Cu...O4 = 2.771 (2) Å) in comparison with Van der Waals contact (2.92 Å) for Cu...O. In addition, there are weak intermolecular interactions, in which the bonding oxygen (O3) of acetate group can be bridged to the Cu atom of another complex and the distance (2.523 (2) Å) is about 0.4 Å shorter than Van der Waals contact of Cu...O in the other crystal structure.

**Experimental**

The ligand, 5-methoxy-2-{1-[2-(dimethylamino)ethylimino]benzyl}phenol was prepared by the reaction in which 2-dimethylaminoethylamine (1.95 g, 22.1 mmol) and 5-methoxy-2-hydroxybenzophenone (4.60 g, 20.2 mmol) in refluxed ethanol (30 ml) for 24 h (Fig. 2). Volatile materials were removed under vacuum and the resulting solid was recrystallized from slowly cooling a hot hexane (40 ml) solution giving yellow powders (yield: 71%). The title complex was syntheses-

ized by the following procedures: 5-methoxy-2-{1-[2-(dimethylamino)ethylimino]benzyl}phenol (0.597 g, 2.0 mmol) and  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.398 g, 2.0 mmol) was refluxed in *EtOH* (30 ml) for 3 h and the volatile materials were removed under vacuum giving green crystalline solid (Fig. 2). The resulting precipitate was crystallized from *EtOH* to yield green crystals.

## Refinement

The C-bound H atoms were placed in calculated positions ( $\text{C}-\text{H} = 0.93\text{--}0.96 \text{ \AA}$ ) and included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C})$ .

## Figures

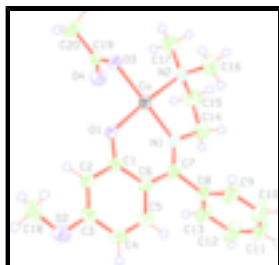


Fig. 1. A view of the molecular structure of **I** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

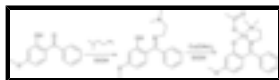


Fig. 2. The synthetic route of the title Cu complex.

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### Crystal data

$[\text{Cu}(\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2)(\text{C}_2\text{H}_3\text{O}_2)]$

$M_r = 419.96$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 11.9721 (16) \text{ \AA}$

$b = 15.674 (2) \text{ \AA}$

$c = 10.6346 (14) \text{ \AA}$

$\beta = 102.655 (3)^\circ$

$V = 1947.1 (4) \text{ \AA}^3$

$Z = 4$

$F_{000} = 876$

$D_x = 1.433 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3118 reflections

$\theta = 2.2\text{--}25.4^\circ$

$\mu = 1.15 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism, green

$0.40 \times 0.30 \times 0.20 \text{ mm}$

### Data collection

Bruker SMART 1000 CCD  
diffractometer

Radiation source: Fine-focus sealed tube

Monochromator: Graphite

$T = 298(2) \text{ K}$

$\varphi$  and  $\omega$  scans

3822 independent reflections

2673 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 2.2^\circ$

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

$T_{\min} = 0.656$ ,  $T_{\max} = 0.803$

11008 measured reflections

$h = -14 \rightarrow 14$

$k = -18 \rightarrow 19$

$l = -8 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: Full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.103$

$S = 1.02$

3822 reflections

244 parameters

Primary atom site location: Direct

Secondary atom site location: Difmap

Hydrogen site location: Geom

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$

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

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

$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

### Special details

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 ( $\text{\AA}^2$ )

|     | <i>x</i>     | <i>y</i>      | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|-------------|----------------------------------|
| Cu  | 0.93747 (3)  | 0.10053 (2)   | 0.02371 (4) | 0.02773 (13)                     |
| O1  | 0.92068 (16) | 0.06311 (14)  | 0.1893 (2)  | 0.0332 (5)                       |
| O2  | 0.7404 (2)   | −0.04350 (17) | 0.5113 (2)  | 0.0474 (6)                       |
| O3  | 1.09237 (16) | 0.05131 (13)  | 0.0552 (2)  | 0.0303 (5)                       |
| O4  | 1.1426 (2)   | 0.17945 (16)  | 0.1343 (2)  | 0.0467 (6)                       |
| N1  | 0.7889 (2)   | 0.15948 (18)  | −0.0052 (3) | 0.0379 (7)                       |
| N2  | 0.9457 (2)   | 0.15348 (17)  | −0.1526 (3) | 0.0333 (6)                       |
| C1  | 0.8276 (2)   | 0.05790 (19)  | 0.2325 (3)  | 0.0268 (7)                       |
| C2  | 0.8331 (3)   | 0.0119 (2)    | 0.3478 (3)  | 0.0327 (7)                       |
| H2A | 0.9021       | −0.0132       | 0.3880      | 0.039*                           |
| C3  | 0.7400 (3)   | 0.0029 (2)    | 0.4025 (3)  | 0.0355 (8)                       |
| C4  | 0.6361 (3)   | 0.0424 (2)    | 0.3444 (3)  | 0.0434 (9)                       |
| H4A | 0.5733       | 0.0386        | 0.3825      | 0.052*                           |
| C5  | 0.6277 (3)   | 0.0858 (2)    | 0.2337 (4)  | 0.0392 (8)                       |
| H5A | 0.5581       | 0.1112        | 0.1967      | 0.047*                           |
| C6  | 0.7199 (2)   | 0.0949 (2)    | 0.1702 (3)  | 0.0290 (7)                       |

## supplementary materials

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|      |            |             |             |             |
|------|------------|-------------|-------------|-------------|
| C7   | 0.7052 (3) | 0.1444 (2)  | 0.0533 (3)  | 0.0321 (7)  |
| C8   | 0.5879 (2) | 0.1779 (2)  | −0.0065 (3) | 0.0348 (8)  |
| C9   | 0.5162 (3) | 0.1296 (3)  | −0.0985 (4) | 0.0603 (12) |
| H9A  | 0.5396     | 0.0757      | −0.1189     | 0.072*      |
| C10  | 0.4106 (3) | 0.1598 (3)  | −0.1607 (4) | 0.0675 (13) |
| H10A | 0.3635     | 0.1267      | −0.2232     | 0.081*      |
| C11  | 0.3748 (3) | 0.2386 (3)  | −0.1307 (4) | 0.0581 (11) |
| H11A | 0.3038     | 0.2593      | −0.1733     | 0.070*      |
| C12  | 0.4432 (3) | 0.2866 (3)  | −0.0384 (4) | 0.0635 (12) |
| H12A | 0.4181     | 0.3397      | −0.0169     | 0.076*      |
| C13  | 0.5505 (3) | 0.2568 (3)  | 0.0241 (4)  | 0.0527 (10) |
| H13A | 0.5970     | 0.2902      | 0.0868      | 0.063*      |
| C14  | 0.7695 (3) | 0.2182 (3)  | −0.1169 (4) | 0.0592 (12) |
| H14A | 0.7370     | 0.2715      | −0.0952     | 0.071*      |
| H14B | 0.7167     | 0.1929      | −0.1896     | 0.071*      |
| C15  | 0.8852 (3) | 0.2344 (2)  | −0.1512 (4) | 0.0535 (10) |
| H15A | 0.8737     | 0.2613      | −0.2352     | 0.064*      |
| H15B | 0.9306     | 0.2726      | −0.0883     | 0.064*      |
| C16  | 0.8860 (3) | 0.0981 (3)  | −0.2608 (4) | 0.0561 (11) |
| H16A | 0.8906     | 0.1237      | −0.3415     | 0.084*      |
| H16B | 0.8071     | 0.0918      | −0.2567     | 0.084*      |
| H16C | 0.9219     | 0.0430      | −0.2539     | 0.084*      |
| C17  | 1.0606 (3) | 0.1696 (3)  | −0.1764 (4) | 0.0522 (10) |
| H17A | 1.0535     | 0.1941      | −0.2606     | 0.078*      |
| H17B | 1.1020     | 0.1169      | −0.1717     | 0.078*      |
| H17C | 1.1011     | 0.2084      | −0.1126     | 0.078*      |
| C18  | 0.8349 (3) | −0.1007 (3) | 0.5543 (4)  | 0.0537 (10) |
| H18A | 0.8254     | −0.1296     | 0.6309      | 0.081*      |
| H18B | 0.9050     | −0.0688     | 0.5726      | 0.081*      |
| H18C | 0.8372     | −0.1418     | 0.4881      | 0.081*      |
| C19  | 1.1673 (3) | 0.1069 (2)  | 0.1073 (3)  | 0.0329 (7)  |
| C20  | 1.2906 (3) | 0.0780 (3)  | 0.1325 (4)  | 0.0571 (12) |
| H20A | 1.3396     | 0.1237      | 0.1713      | 0.086*      |
| H20B | 1.3096     | 0.0620      | 0.0525      | 0.086*      |
| H20C | 1.3008     | 0.0298      | 0.1896      | 0.086*      |

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

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| Cu | 0.0244 (2)  | 0.0309 (2)  | 0.0274 (2)  | 0.00498 (16) | 0.00454 (14) | 0.00588 (17) |
| O1 | 0.0233 (11) | 0.0480 (14) | 0.0286 (13) | 0.0067 (10)  | 0.0060 (9)   | 0.0079 (10)  |
| O2 | 0.0479 (14) | 0.0579 (18) | 0.0401 (15) | −0.0047 (12) | 0.0181 (11)  | 0.0103 (13)  |
| O3 | 0.0234 (10) | 0.0327 (13) | 0.0332 (13) | −0.0008 (9)  | 0.0027 (9)   | 0.0013 (10)  |
| O4 | 0.0470 (15) | 0.0407 (16) | 0.0502 (17) | 0.0011 (12)  | 0.0061 (12)  | −0.0130 (12) |
| N1 | 0.0352 (15) | 0.0444 (19) | 0.0333 (17) | 0.0152 (13)  | 0.0055 (12)  | 0.0123 (13)  |
| N2 | 0.0354 (15) | 0.0289 (16) | 0.0344 (17) | 0.0033 (12)  | 0.0053 (12)  | 0.0072 (12)  |
| C1 | 0.0257 (15) | 0.0265 (17) | 0.0271 (18) | −0.0019 (12) | 0.0034 (13)  | −0.0033 (13) |
| C2 | 0.0295 (16) | 0.037 (2)   | 0.0309 (19) | 0.0011 (14)  | 0.0042 (13)  | 0.0023 (14)  |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C3  | 0.0411 (19) | 0.035 (2)   | 0.032 (2)   | −0.0092 (15) | 0.0106 (15)  | −0.0030 (15) |
| C4  | 0.0347 (19) | 0.050 (2)   | 0.052 (2)   | 0.0000 (16)  | 0.0217 (16)  | 0.0017 (19)  |
| C5  | 0.0282 (17) | 0.040 (2)   | 0.050 (2)   | 0.0031 (14)  | 0.0106 (15)  | 0.0002 (17)  |
| C6  | 0.0242 (15) | 0.0284 (18) | 0.0334 (18) | 0.0011 (13)  | 0.0039 (13)  | −0.0032 (14) |
| C7  | 0.0293 (16) | 0.0291 (19) | 0.036 (2)   | 0.0068 (13)  | 0.0024 (14)  | −0.0061 (15) |
| C8  | 0.0277 (17) | 0.041 (2)   | 0.033 (2)   | 0.0092 (14)  | 0.0008 (14)  | 0.0031 (15)  |
| C9  | 0.041 (2)   | 0.059 (3)   | 0.071 (3)   | 0.0148 (19)  | −0.011 (2)   | −0.026 (2)   |
| C10 | 0.043 (2)   | 0.077 (3)   | 0.069 (3)   | 0.013 (2)    | −0.017 (2)   | −0.021 (2)   |
| C11 | 0.0314 (19) | 0.070 (3)   | 0.065 (3)   | 0.0144 (19)  | −0.0067 (18) | 0.011 (2)    |
| C12 | 0.045 (2)   | 0.049 (3)   | 0.090 (3)   | 0.0256 (19)  | 0.002 (2)    | −0.003 (2)   |
| C13 | 0.038 (2)   | 0.047 (2)   | 0.065 (3)   | 0.0128 (17)  | −0.0054 (18) | −0.011 (2)   |
| C14 | 0.059 (2)   | 0.071 (3)   | 0.053 (3)   | 0.034 (2)    | 0.0219 (19)  | 0.034 (2)    |
| C15 | 0.068 (3)   | 0.041 (2)   | 0.055 (3)   | 0.0165 (19)  | 0.022 (2)    | 0.0177 (19)  |
| C16 | 0.070 (3)   | 0.053 (3)   | 0.041 (2)   | −0.003 (2)   | 0.0019 (19)  | 0.0058 (19)  |
| C17 | 0.048 (2)   | 0.062 (3)   | 0.051 (3)   | 0.0074 (19)  | 0.0203 (18)  | 0.021 (2)    |
| C18 | 0.058 (2)   | 0.062 (3)   | 0.041 (2)   | −0.005 (2)   | 0.0095 (18)  | 0.015 (2)    |
| C19 | 0.0274 (16) | 0.045 (2)   | 0.0265 (18) | −0.0012 (15) | 0.0061 (13)  | −0.0016 (16) |
| C20 | 0.0288 (19) | 0.063 (3)   | 0.076 (3)   | 0.0009 (17)  | 0.0047 (18)  | −0.011 (2)   |

*Geometric parameters (Å, °)*

|          |            |             |           |
|----------|------------|-------------|-----------|
| Cu—O1    | 1.908 (2)  | C9—C10      | 1.377 (5) |
| Cu—N1    | 1.968 (3)  | C9—H9A      | 0.9300    |
| Cu—O3    | 1.968 (2)  | C10—C11     | 1.368 (6) |
| Cu—N2    | 2.073 (3)  | C10—H10A    | 0.9300    |
| O1—C1    | 1.298 (3)  | C11—C12     | 1.359 (5) |
| O2—C3    | 1.366 (4)  | C11—H11A    | 0.9300    |
| O2—C18   | 1.437 (4)  | C12—C13     | 1.392 (5) |
| O3—C19   | 1.287 (4)  | C12—H12A    | 0.9300    |
| O4—C19   | 1.224 (4)  | C13—H13A    | 0.9300    |
| N1—C7    | 1.312 (4)  | C14—C15     | 1.529 (5) |
| N1—C14   | 1.481 (4)  | C14—H14A    | 0.9700    |
| N2—C15   | 1.463 (4)  | C14—H14B    | 0.9700    |
| N2—C17   | 1.475 (4)  | C15—H15A    | 0.9700    |
| N2—C16   | 1.493 (4)  | C15—H15B    | 0.9700    |
| C1—C2    | 1.412 (4)  | C16—H16A    | 0.9600    |
| C1—C6    | 1.436 (4)  | C16—H16B    | 0.9600    |
| C2—C3    | 1.374 (4)  | C16—H16C    | 0.9600    |
| C2—H2A   | 0.9300     | C17—H17A    | 0.9600    |
| C3—C4    | 1.405 (5)  | C17—H17B    | 0.9600    |
| C4—C5    | 1.345 (5)  | C17—H17C    | 0.9600    |
| C4—H4A   | 0.9300     | C18—H18A    | 0.9600    |
| C5—C6    | 1.421 (4)  | C18—H18B    | 0.9600    |
| C5—H5A   | 0.9300     | C18—H18C    | 0.9600    |
| C6—C7    | 1.443 (4)  | C19—C20     | 1.510 (4) |
| C7—C8    | 1.505 (4)  | C20—H20A    | 0.9600    |
| C8—C13   | 1.378 (5)  | C20—H20B    | 0.9600    |
| C8—C9    | 1.378 (5)  | C20—H20C    | 0.9600    |
| O1—Cu—N1 | 90.82 (10) | C10—C11—C12 | 119.9 (3) |

## supplementary materials

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|              |             |               |           |
|--------------|-------------|---------------|-----------|
| O1—Cu—O3     | 90.49 (8)   | C10—C11—H11A  | 120.0     |
| N1—Cu—O3     | 175.05 (11) | C12—C11—H11A  | 120.0     |
| O1—Cu—N2     | 173.51 (10) | C13—C12—C11   | 120.4 (4) |
| N1—Cu—N2     | 83.74 (11)  | C13—C12—H12A  | 119.8     |
| O3—Cu—N2     | 94.64 (9)   | C11—C12—H12A  | 119.8     |
| C1—O1—Cu     | 128.17 (19) | C8—C13—C12    | 120.1 (3) |
| C3—O2—C18    | 117.2 (3)   | C8—C13—H13A   | 119.9     |
| C19—O3—Cu    | 110.5 (2)   | C12—C13—H13A  | 119.9     |
| C7—N1—C14    | 119.4 (3)   | N1—C14—C15    | 107.7 (3) |
| C7—N1—Cu     | 126.8 (2)   | N1—C14—H14A   | 110.2     |
| C14—N1—Cu    | 113.3 (2)   | C15—C14—H14A  | 110.2     |
| C15—N2—C17   | 109.6 (3)   | N1—C14—H14B   | 110.2     |
| C15—N2—C16   | 111.0 (3)   | C15—C14—H14B  | 110.2     |
| C17—N2—C16   | 105.9 (3)   | H14A—C14—H14B | 108.5     |
| C15—N2—Cu    | 102.5 (2)   | N2—C15—C14    | 109.6 (3) |
| C17—N2—Cu    | 117.1 (2)   | N2—C15—H15A   | 109.8     |
| C16—N2—Cu    | 110.8 (2)   | C14—C15—H15A  | 109.8     |
| O1—C1—C2     | 117.3 (3)   | N2—C15—H15B   | 109.8     |
| O1—C1—C6     | 124.4 (3)   | C14—C15—H15B  | 109.8     |
| C2—C1—C6     | 118.3 (3)   | H15A—C15—H15B | 108.2     |
| C3—C2—C1     | 122.2 (3)   | N2—C16—H16A   | 109.5     |
| C3—C2—H2A    | 118.9       | N2—C16—H16B   | 109.5     |
| C1—C2—H2A    | 118.9       | H16A—C16—H16B | 109.5     |
| O2—C3—C2     | 124.1 (3)   | N2—C16—H16C   | 109.5     |
| O2—C3—C4     | 116.5 (3)   | H16A—C16—H16C | 109.5     |
| C2—C3—C4     | 119.4 (3)   | H16B—C16—H16C | 109.5     |
| C5—C4—C3     | 119.8 (3)   | N2—C17—H17A   | 109.5     |
| C5—C4—H4A    | 120.1       | N2—C17—H17B   | 109.5     |
| C3—C4—H4A    | 120.1       | H17A—C17—H17B | 109.5     |
| C4—C5—C6     | 123.4 (3)   | N2—C17—H17C   | 109.5     |
| C4—C5—H5A    | 118.3       | H17A—C17—H17C | 109.5     |
| C6—C5—H5A    | 118.3       | H17B—C17—H17C | 109.5     |
| C7—C6—C5     | 120.2 (3)   | O2—C18—H18A   | 109.5     |
| C7—C6—C1     | 122.8 (3)   | O2—C18—H18B   | 109.5     |
| C5—C6—C1     | 116.9 (3)   | H18A—C18—H18B | 109.5     |
| N1—C7—C6     | 123.0 (3)   | O2—C18—H18C   | 109.5     |
| N1—C7—C8     | 118.4 (3)   | H18A—C18—H18C | 109.5     |
| C6—C7—C8     | 118.6 (3)   | H18B—C18—H18C | 109.5     |
| C13—C8—C9    | 118.5 (3)   | O4—C19—O3     | 123.3 (3) |
| C13—C8—C7    | 122.3 (3)   | O4—C19—C20    | 120.9 (3) |
| C9—C8—C7     | 119.1 (3)   | O3—C19—C20    | 115.8 (3) |
| C10—C9—C8    | 121.0 (4)   | C19—C20—H20A  | 109.5     |
| C10—C9—H9A   | 119.5       | C19—C20—H20B  | 109.5     |
| C8—C9—H9A    | 119.5       | H20A—C20—H20B | 109.5     |
| C11—C10—C9   | 120.0 (4)   | C19—C20—H20C  | 109.5     |
| C11—C10—H10A | 120.0       | H20A—C20—H20C | 109.5     |
| C9—C10—H10A  | 120.0       | H20B—C20—H20C | 109.5     |





Fig. 2

