A bis-chelate o-vanillin-2-ethanolamine copper(II) complex bearing both imine and amine forms of the ligand

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The molecular bis-chelate complex (2-[[2-hydroxyethyl-κO]amino-κN[methyl]-6-methoxyphenolato-κO](2-[[2-hydroxyethyl]imino-κN[methyl]-6-methoxyphenolato-κO])copper(II), [Cu(C_{10}H_{14}NO_{3})(C_{10}H_{12}NO_{3})] or [Cu(HL^{im})(HL^{am})]; HL^{im} = C_{10}H_{14}NO_{3}; HL^{am} = C_{10}H_{12}NO_{3}, represents the first compound containing a salicylidene-2-ethanolamine type ligand in both imino HL^{im} (Schiff base) and amino HL^{am} (reduced Schiff base) forms that has been structurally characterized on the basis of X-ray data. Two molecules of the monodeprotonated ligands coordinate the Cu^{II} ion in an (N,Ophen)-bidentate and an (N,Ophen,Oal)-tridentate fashion in the case of the imino and amino forms, respectively. The shape of the CuN_{2}O_{3} coordination polyhedron is a distorted square-pyramid (geometry index τ = 0.26). Intermolecular N—H···O and O—H···O hydrogen bonds, involving H atoms of the amino and hydroxyethyl groups, create a two-dimensional supramolecular array extending parallel to (010).

1. Chemical context

Over the last decade, research on transition-metal complexes with salicylidene-type Schiff bases (SB) gained a new impetus after a number of highly effective and simple M-(SB) catalysts were obtained, where M = Cu, Co, Al, etc (Payne et al., 2020; Mitra et al., 2015; Fei et al., 2014; Saha et al., 2013). It has been shown that incorporation of partially or fully reduced Schiff bases (RSB) into the coordination spheres of metal cations can significantly increase their catalytic activities (Liu et al., 2020; Huo et al., 2021; Adão et al., 2014; Sreenivasulu et al., 2005). Despite the fact that complexes with RSB ligands are supposed to be very promising objects for the creation of new catalysts, information about their syntheses and structures is rather limited. Continuing our work on the elaboration of alternative methods for the synthesis of coordination compounds (Kokozay et al., 2018), we have investigated the following system: zinc (powder) – copper (powder) – H_{2}L – ammonium thiocyanate – methanol, to prepare heterometallic Cu/Zn complexes with the Schiff base H_{2}L^{im}, which is formed in situ upon condensation of o-vanillin and 2-aminooethanol. The complex [Cu(HL^{im})(HL^{am})] (where H_{2}L^{im} = 2-[(2-hydroxyethyl)iminomethyl]-6-methoxyphenol; H_{2}L^{am} = 2-[(2-hydroxyethyl)aminomethyl]-6-methoxyphenol) was formed in the reaction mixture as an unintended by-product for which only a few crystals suitable for X-ray analysis were isolated.
Herein, we report the crystal structure of the title compound, [Cu(HL\textsuperscript{im})(HL\textsuperscript{am})] (I), which represents the first example of a mixed (SB/RSB) complex derived from salicylidene-2-aminoethanol type ligands.

2. Structural commentary

The asymmetric unit of (I) comprises one neutral molecular complex [Cu(HL\textsuperscript{im})(HL\textsuperscript{am})] (Fig. 1). The copper(II) ion has an O\textsubscript{3}N\textsubscript{2} coordination set defined by two monodeprotonated molecules of the organic ligands realizing their bidentate (N,O) and tridentate (O,N,O) functions for the SB and RSB forms, respectively. This difference in coordination behavior of the ligands can be explained by a higher flexibility of the amine ligand, and is observed in similar bis-chelate copper(II) complexes with salicylidene-2-aminoethanol type ligands. Usually, [Cu(SB)\textsubscript{2}] complexes are square-planar and [Cu(RSB)\textsubscript{2}] complexes are octahedral. For the corresponding imine complexes, see: Li \textit{et al.} (2005); Zabierowski \textit{et al.} (2013, 2014); Xin \textit{et al.} (2019); for amine complexes, see: Xie \textit{et al.} (2000). It is worth noting that such a dependence was not found for similar Ni\textsuperscript{II} complexes, which have an octahedral shape via both tridentate imino and amino ligands. For [Ni(RSB)\textsubscript{2}], see: Zhang \textit{et al.} (2007). The shape of the coordination polyhedron of the Cu\textsuperscript{II} ion in (I) can be described as distorted [4 + 1] square-pyramidal. The equatorial Cu—O(N) bond lengths vary from 1.923 (2) to 2.030 (3) Å and are in accordance with those found in related complexes (Stetsiuk \textit{et al.}, 2018; Xie \textit{et al.}, 2000; Zabierowski \textit{et al.}, 2013). The length of the long apical Cu—O bond of 2.432 (3) Å lies within the range of Cu\textsuperscript{II}—O bond lengths extending up to ca 2.70 Å (Alvarez, 2013). The deviations in cis and trans [O—Cu—O(N)] angles [80.08 (10)—108.36 (10)° and 157.96 (12)—173.44 (11)°, respectively] are caused by the steric hindrances that are typical for chelate rings. According to the τ criterion for five-coordinate complexes (Addison \textit{et al.}, 1984; O’Sullivan \textit{et al.}, 1999), the distortion of the Cu\textsubscript{N\textsubscript{2}O\textsubscript{3}} coordination polyhedron is about 26% along the pathway from regular square-pyramidal to regular trigonal–bipyramidal. The bond-valence sums calculated for Cu\textsuperscript{II} with CN = 4 (1.86 valence units) and CN = 5 (1.99 valence units) (Allmann, 1975; Shields \textit{et al.}, 2000) can serve as an additional argument in favor of the coordination number of 5 for Cu\textsuperscript{II} in (I).

3. Supramolecular features

Each molecule of (I) forms six intermolecular hydrogen bonds with four adjacent molecules whereby the following groups take part: non-coordinating hydroxyethyl and amino groups (as H-atom donors), half of the phenolato and methoxy groups (as H-atom acceptors) and the coordinating hydroxyethyl groups (both as H-atom donors and acceptors). Chains based on two hydrogen bonds O6—H6…O1\textsuperscript{ii} and \textsuperscript{ii}O6—H2…N2 (Table 1, Fig. 2) are formed along [001]. These

| Symmetry codes: (i) \( -x+2, -y+1, z+\frac{1}{2} \); (ii) \( -x+1, -y+1, z+\frac{1}{2} \); (iii) \( -x+1, -y+1, z-\frac{1}{2} \). |
chains are linked by \( \text{O}^3 - \text{H}^3 \cdot \cdot \cdot \text{O}^4 \) bonds (Table 1) into supramolecular sheets extending parallel to (010) (Fig. 3).

4. Database survey

Among the 33 deposited crystal structures of bis-complexes with a salicylidene-2-aminoethanol-type ligand (CSD, version 5.42, last update February 2021; Groom et al., 2016), there are 30 hits for complexes with SBs and three hits for complexes with RSBs (Xie et al., 2000, 2003; Zhang et al., 2007). \( M(SB)(RSB) \) complexes including both forms of a ligand are not known up to now.

5. Synthesis and crystallization

\( \alpha \)-Vanillin (0.3 g, 0.002 mol) and 2-aminoethanol (0.12 ml, 0.002 mol) were dissolved in methanol and then stirred magnetically at 323–333 K for 20 mins. Copper powder (0.06 g, 0.001 mol), zinc powder (0.07 g, 0.001 mol) and \( \text{NH}_4 \text{SCN} \) (0.15 g, 0.002 mol) were added to the hot yellow solution with further stirring until total dissolution of powder was observed (about 4 h). The resulting brown solution was filtered and left for 1 d. A green powdery precipitate with a few green crystals available for X-ray crystallographic analysis was collected by filtration.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carbon-bound H atoms were placed in idealized positions and refined using a riding model. H atoms of the NH and OH groups were located in a difference-Fourier map. For the final model they were also treated as riding on their parent atoms.

| Table 2 Experimental details. |
|-------------------------------|
| **Crystal data**              |
| Chemical formula: [Cu(C_{10}H_{14}NO_{3})(C_{10}H_{12}NO_{3})] |
| \( \text{M} \)                   | 453.97 |
| Crystal system, space group: Orthorhombic, \( \text{Pna}_2_1 \) |
| Temperature (K): 150 |
| \( \text{a} \), \( \text{b} \), \( \text{c} \) (\( \text{Å} \)): 8.3068 (9), 24.3280 (19), 10.1370 (9) |
| \( \text{V} \) (\( \text{Å}^3 \)): 2048.6 (3) |
| \( \text{Z} \): 4 |
| Radiation type: Mo \( \text{K} \alpha \) |
| \( \mu \) (\( \text{mm}^{-1} \)): 1.11 |
| Crystal size (mm): 0.31 \( \times \) 0.15 \( \times \) 0.05 |

| **Data collection**             |
| Diffractometer: New Gemini, Dual, Cu at zero, Atlas |
| Absorption correction: Analytical (\( \text{CrysAlis PRO} \), Rigaku OD, 2015) |
| \( T_{\text{min}}, T_{\text{max}} \): 0.509, 0.855 |
| No. of measured, independent and observed \( |F| > 2\sigma(|F|) \) reflections: 10546, 3777, 3539 |
| \( R_{\text{int}} \): 0.036 |

| **Refinement**                  |
| \( R_{1}[F^2 > 2\sigma(F^2)], wR(F^2), \) \( S \): 0.032, 0.079, 1.06 |
| No. of reflections: 3777 |
| No. of parameters: 268 |
| No. of restraints: 1 |
| \( H \)-atom treatment: H atoms treated by a mixture of independent and constrained refinement |

| **Absolute structure**               |
| \( \Delta_{\text{phi}} \), \( \Delta_{\text{omega}} \) (\( e \text{ Å}^{-3} \)): 0.31, –0.38 |
| Absolute structure parameter: Classical Flack method preferred over Parsons because s.u. lower –0.011 (15) |

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2015); cell refinement: CrysAlis PRO (Rigaku OD, 2015); data reduction: CrysAlis PRO (Rigaku OD, 2015); program(s) used to solve structure: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: publCIF (Westrip, 2010).

(2-[(2-Hydroxyethyl-κO)amino-κN[methyl]-6-methoxyphenolato-κO](2-[(2-hydroxyethyl)imino-κN[methyl]-6-methoxyphenolato-κO])copper(II)

Crystal data

\[
\text{[Cu(C}_{10}\text{H}_{14}\text{NO}_{3})(\text{C}_{10}\text{H}_{12}\text{NO}_{3})]\]

\(D_c = 1.472\ \text{Mg m}^{-3}\)

\(M_r = 453.97\)

Orthorhombic, \(Pna2_1\)

Cell parameters from 4616 reflections

\(a = 8.3068 (9)\ \text{Å}\)

\(b = 24.3280 (19)\ \text{Å}\)

\(c = 10.1370 (9)\ \text{Å}\)

\(V = 2048.6 (3)\ \text{Å}^3\)

\(Z = 4\)

\(F(000) = 948\)

\(T = 150\ \text{K}\)

Plate, green

\(\mu = 1.11\ \text{mm}^{-1}\)

\(\theta = 4.1–28.6^\circ\)

\(\omega\) scans

\(h = -10\rightarrow9\)

\(k = -31\rightarrow31\)

\(l = -13\rightarrow12\)

Refinement

Refinement on \(F^2\)

\(R[F^2 > 2\sigma(F^2)] = 0.032\)

\(wR(F^2) = 0.079\)

\(S = 1.06\)

3777 reflections

268 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

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**Supporting Information**

$$w = \frac{1}{\sigma^2(F_o^2) + (0.0466P)^2 + 0.2171P}$$

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

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta \rho_{\text{max}} = 0.31 \text{ e Å}^{-3}$

$\Delta \rho_{\text{min}} = -0.38 \text{ e Å}^{-3}$

**Absolute structure:** Classical Flack method preferred over Parsons because s.u. lower

**Absolute structure parameter:** $-0.011 \pm 0.015$

**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.**

1. Fixed $U_{iso}$ At 1.2 times of: All C(H) groups, All C(H,H) groups, All N(H) groups At 1.5 times of: All C(H,H,H) groups, All O(H) groups

2.a Ternary CH refined with riding coordinates: N2(H2)

2.b Secondary CH2 refined with riding coordinates: C9(H9A,H9B), C10(H10A,H10B), C18(H18A,H18B), C19(H19A,H19B), C20(H20A,H20B)

2.c Aromatic/amide H refined with riding coordinates: C3(H3A), C4(H4), C5(H5), C8(H8), C13(H13), C14(H14), C15(H15)

2.d Idealised Me refined as rotating group: C1(H1A,H1B,H1C), C11(H11A,H11B,H11C)

2.e Idealised tetrahedral OH refined as rotating group: O3(H3)

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

| Atom | x     | y     | z     | $U_{iso}$/$U_{eq}$ |
|------|-------|-------|-------|-------------------|
| Cu1  | 0.71596 (4) | 0.50706 (2) | 0.41167 (6) | 0.01347 (11) |
| O1   | 0.3846 (3)  | 0.37604 (10) | 0.2532 (3)  | 0.0268 (6)   |
| O2   | 0.5899 (3)  | 0.44465 (9)  | 0.3556 (2)  | 0.0194 (5)   |
| O3   | 0.8418 (3)  | 0.47888 (13) | 0.8013 (3)  | 0.0303 (6)   |
| H3   | 0.910708 (5)| 0.461250     | 0.840828    | 0.045*       |
| O4   | 1.0725 (3)  | 0.63655 (10) | 0.5057 (3)  | 0.0219 (5)   |
| O5   | 0.8755 (2)  | 0.56419 (8)  | 0.4016 (3)  | 0.0176 (5)   |
| O6   | 0.5411 (3)  | 0.52613 (11) | 0.5985 (3)  | 0.0187 (5)   |
| H6   | 0.567 (5)   | 0.5466 (18)  | 0.649 (5)   | 0.028*       |
| N1   | 0.8651 (3)  | 0.46065 (12) | 0.5178 (3)  | 0.0154 (6)   |
| N2   | 0.5490 (3)  | 0.55538 (11) | 0.3227 (3)  | 0.0155 (6)   |
| H2   | 0.475620    | 0.530360     | 0.276506    | 0.019*       |
| C1   | 0.2700 (6)  | 0.33956 (19) | 0.1958 (5)  | 0.0428 (12)  |
| H1A  | 0.200504    | 0.359757     | 0.137664    | 0.064*       |
| H1B  | 0.206937    | 0.322833     | 0.264295    | 0.064*       |
| H1C  | 0.325208    | 0.311543     | 0.146868    | 0.064*       |
| C2   | 0.4986 (4)  | 0.35356 (15) | 0.3365 (3)  | 0.0196 (7)   |
| C3   | 0.5087 (5)  | 0.29840 (15) | 0.3675 (3)  | 0.0245 (8)   |
| H3A  | 0.434851    | 0.273654     | 0.332428    | 0.029*       |
| C4   | 0.6303 (5)  | 0.27994 (15) | 0.4515 (4)  | 0.0303 (9)   |
| H4   | 0.636593    | 0.242899     | 0.473592    | 0.036*       |
| C5   | 0.7397 (5)  | 0.31605 (16) | 0.5012 (4)  | 0.0255 (8)   |
| H5   | 0.821347    | 0.303071     | 0.555711    | 0.031*       |
| C6   | 0.7321 (4)  | 0.37315 (15) | 0.4720 (3)  | 0.0187 (7)   |
| C7   | 0.6087 (4)  | 0.39289 (12) | 0.3878 (3)  | 0.0155 (7)   |
| C8   | 0.8504 (4)  | 0.40836 (15) | 0.5316 (3)  | 0.0184 (7)   |
| H8   | 0.924904    | 0.391349     | 0.586611    | 0.022*       |
| C9   | 0.9906 (5)  | 0.48739 (15) | 0.5970 (4)  | 0.0208 (8)   |
| H9A  | 1.048384    | 0.513686     | 0.542842    | 0.025*       |
**Atomic displacement parameters (Å\(^2\))**

|   | \(U^{11}\)  | \(U^{22}\)  | \(U^{33}\)  | \(U^{12}\)  | \(U^{13}\)  | \(U^{23}\)  |
|---|---|---|---|---|---|---|
| Cu1 | 0.0124 (19) | 0.01677 (18) | 0.01119 (17) | 0.00087 (13) | −0.0031 (2) | 0.0002 (3) |
| O1 | 0.0330 (15) | 0.0203 (12) | 0.0270 (14) | −0.0059 (11) | −0.0155 (11) | 0.0038 (11) |
| O2 | 0.0223 (13) | 0.0170 (11) | 0.0191 (11) | 0.0016 (10) | −0.0084 (10) | 0.0035 (10) |
| O3 | 0.0191 (13) | 0.0263 (18) | 0.0155 (12) | 0.0059 (14) | −0.0001 (11) | 0.0035 (13) |
| O4 | 0.0167 (12) | 0.0237 (12) | 0.0254 (12) | −0.0012 (10) | −0.0079 (11) | −0.0016 (11) |
| O5 | 0.0133 (10) | 0.0172 (9)  | 0.0224 (11) | 0.013 (8)  | −0.0023 (12) | 0.0018 (13) |
| O6 | 0.0148 (13) | 0.0261 (13) | 0.0152 (11) | 0.0016 (10) | −0.0013 (10) | −0.0025 (11) |
| N1 | 0.0091 (13) | 0.0265 (15) | 0.0107 (12) | 0.0014 (11) | −0.0009 (10) | 0.0005 (12) |
| N2 | 0.0123 (13) | 0.0199 (14) | 0.0143 (12) | −0.0019 (11) | −0.0028 (11) | −0.0014 (12) |
| C1 | 0.047 (3)  | 0.032 (2)  | 0.049 (3)  | −0.017 (2)  | −0.029 (2)  | 0.006 (2)  |
| C2 | 0.0239 (19) | 0.0221 (17) | 0.0126 (15) | 0.0020 (14) | −0.0013 (14) | 0.0024 (14) |
| C3 | 0.030 (2)  | 0.0193 (16) | 0.0239 (17) | −0.0026 (15) | −0.0004 (15) | −0.0018 (15) |
| C4 | 0.037 (2)  | 0.0180 (17) | 0.036 (2)  | 0.0062 (16) | −0.0021 (17) | 0.0066 (16) |
| C5 | 0.028 (2)  | 0.0234 (19) | 0.0253 (18) | 0.0093 (15) | −0.0033 (16) | 0.0062 (17) |
| C6 | 0.0193 (18) | 0.0226 (18) | 0.0143 (17) | 0.0049 (14) | 0.0016 (13) | 0.0019 (15) |
| C7 | 0.0187 (16) | 0.0168 (13) | 0.0109 (17) | 0.0015 (12) | 0.0027 (12) | 0.0024 (13) |
| C8 | 0.0133 (17) | 0.0290 (19) | 0.0131 (15) | 0.0095 (14) | 0.0000 (13) | 0.0046 (15) |
| C9 | 0.0138 (18) | 0.033 (2)  | 0.0157 (16) | −0.0009 (15) | −0.0048 (15) | 0.0074 (16) |

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**sup-3**

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### Geometric parameters (Å, °)

| Bond/Distance | Length/Å | Angle/° |
|--------------|---------|--------|
| Cu1—O2      | 1.930 (2) | C5—C6 1.422 (5) |
| Cu1—O5      | 1.923 (2) | C6—C7 1.417 (5) |
| Cu1—O6      | 2.432 (3) | C6—C8 1.437 (5) |
| Cu1—N1      | 1.992 (3) | C8—H8 0.9300 |
| Cu1—N2      | 2.030 (3) | C9—H9A 0.9700 |
| O1—C1       | 1.426 (5) | C9—H9B 0.9700 |
| O1—C2       | 1.382 (4) | C9—C10 1.508 (5) |
| O2—C7       | 1.310 (4) | C10—H10A 0.9700 |
| O3—H3       | 0.8200 | C10—H10B 0.9700 |
| O3—C10      | 1.420 (5) | C11—H11A 0.9600 |
| O4—C11      | 1.425 (4) | C11—H11B 0.9600 |
| O4—C12      | 1.379 (4) | C11—H11C 0.9600 |
| O5—C17      | 1.332 (4) | C12—C13 1.392 (5) |
| O6—H6       | 0.75 (5) | C12—C17 1.417 (5) |
| O6—C20      | 1.432 (4) | C13—H13 0.9300 |
| N1—C8       | 1.286 (5) | C13—C14 1.390 (5) |
| N1—C9       | 1.467 (5) | C14—H14 0.9300 |
| N2—H2       | 0.9800 | C14—C15 1.381 (6) |
| N2—C18      | 1.491 (4) | C15—H15 0.9300 |
| N2—C19      | 1.476 (4) | C15—C16 1.397 (5) |
| C1—H1A      | 0.9600 | C16—C17 1.402 (5) |
| C1—H1B      | 0.9600 | C16—C18 1.518 (5) |
| C1—H1C      | 0.9600 | C18—H18A 0.9700 |
| C2—C3       | 1.381 (5) | C18—H18B 0.9700 |
| C2—C7       | 1.422 (5) | C19—H19A 0.9700 |
| C3—H3A      | 0.9300 | C19—H19B 0.9700 |
| C3—C4       | 1.396 (5) | C19—C20 1.519 (5) |
| C4—H4       | 0.9300 | C20—H20A 0.9700 |
| C4—C5       | 1.360 (6) | C20—H20B 0.9700 |
| C5—H5       | 0.9300 |  |  |

| Distance | Length/Å |
|----------|----------|
| O2—Cu1—O6 | 93.16 (10) |
| O2—Cu1—N1  | 92.92 (11) |
| O2—Cu1—N2  | 87.35 (11) |

| Distance | Length/Å |
|----------|----------|
| Cu1—O6   | 2.432 (3) |
| Cu1—N1   | 1.992 (3) |
| Cu1—N2   | 2.030 (3) |
| O1—C1    | 1.426 (5) |
| O1—C2    | 1.382 (4) |
| O2—C7    | 1.310 (4) |
| O3—H3    | 0.8200 |
| O3—C10   | 1.420 (5) |
| O4—C11   | 1.425 (4) |
| O4—C12   | 1.379 (4) |
| O5—C17   | 1.332 (4) |
| O6—H6    | 0.75 (5) |
| O6—C20   | 1.432 (4) |
| N1—C8    | 1.286 (5) |
| N1—C9    | 1.467 (5) |
| N2—H2    | 0.9800 |
| N2—C18   | 1.491 (4) |
| N2—C19   | 1.476 (4) |
| C1—H1A   | 0.9600 |
| C1—H1B   | 0.9600 |
| C1—H1C   | 0.9600 |
| C2—C3    | 1.381 (5) |
| C2—C7    | 1.422 (5) |
| C3—H3A   | 0.9300 |
| C3—C4    | 1.396 (5) |
| C4—H4    | 0.9300 |
| C4—C5    | 1.360 (6) |
| C5—H5    | 0.9300 |
| Bond                  | Length (Å) | Angle (°) |
|----------------------|------------|-----------|
| O5—Cu1—O2           | 157.96 (12) | H9A—C9—H9B 108.1 |
| O5—Cu1—O6           | 108.36 (10) | C10—C9—H9A 109.5 |
| O5—Cu1—N1           | 90.55 (10)  | C10—C9—H9B 109.5 |
| O5—Cu1—N2           | 91.65 (10)  | O3—C10—C9 111.5 (3) |
| N1—Cu1—O6           | 93.37 (10)  | O3—C10—H10A 109.3 |
| N1—Cu1—N2           | 173.44 (11) | O3—C10—H10B 109.3 |
| N2—Cu1—O6           | 80.08 (10)  | C9—C10—H10A 109.3 |
| C2—O1—C1            | 117.4 (3)   | C9—C10—H10B 109.3 |
| C7—O2—Cu1           | 128.1 (2)   | H10A—C10—H10B 108.0 |
| C10—O3—H3           | 109.5       | O4—C11—H11A 109.5 |
| C12—O4—C11          | 116.8 (3)   | O4—C11—H11B 109.5 |
| C17—O5—Cu1          | 128.2 (2)   | O4—C11—H11C 109.5 |
| Cu1—O6—H6           | 119 (3)     | H11A—C11—H11B 109.5 |
| C20—O6—Cu1          | 99.2 (2)    | H11A—C11—H11C 109.5 |
| C20—O6—H6           | 111 (3)     | H11B—C11—H11C 109.5 |
| C8—N1—Cu1           | 124.1 (2)   | O4—C12—C13 123.9 (3) |
| C8—N1—C9            | 116.5 (3)   | O4—C12—C17 114.8 (3) |
| C9—N1—Cu1           | 119.1 (2)   | C13—C12—C17 121.2 (3) |
| Cu1—N2—H2           | 106.1       | C12—C13—H13 120.3 |
| C18—N2—Cu1          | 113.8 (2)   | C14—C13—C12 119.5 (3) |
| C18—N2—H2           | 106.1       | C14—C13—H13 120.3 |
| C19—N2—Cu1          | 111.4 (2)   | C13—C14—H14 119.9 |
| C19—N2—H2           | 106.1       | C15—C14—C13 120.1 (3) |
| C19—N2—C18          | 112.6 (3)   | C15—C14—H14 119.9 |
| O1—C1—H1A           | 109.5       | C14—C15—C18 119.8 (3) |
| O1—C1—H1B           | 109.5       | C14—C15—C16 121.1 (3) |
| O1—C1—H1C           | 109.5       | C16—C15—H15 119.4 |
| H1A—C1—H1B          | 109.5       | C15—C16—C17 119.9 (3) |
| H1A—C1—H1C          | 109.5       | C15—C16—C18 119.8 (3) |
| H1B—C1—H1C          | 109.5       | C17—C16—C18 120.2 (3) |
| O1—C2—C7            | 113.5 (3)   | O5—C17—C12 118.1 (3) |
| C3—C2—O1            | 124.4 (3)   | O5—C17—C16 123.8 (3) |
| C3—C2—C7            | 122.1 (3)   | C16—C17—C12 118.1 (3) |
| C2—C3—H3A           | 120.2       | N2—C18—C16 112.7 (3) |
| C2—C3—C4            | 119.7 (3)   | N2—C18—H18A 109.1 |
| C4—C3—H3A           | 120.2       | N2—C18—H18B 109.1 |
| C3—C4—H4            | 119.9       | C16—C18—H18A 109.1 |
| C5—C4—C3            | 120.1 (3)   | C16—C18—H18B 109.1 |
| C5—C4—H4            | 119.9       | H18A—C18—H18B 107.8 |
| C4—C5—H5            | 119.2       | N2—C19—H19A 109.9 |
| C4—C5—C6            | 121.6 (4)   | N2—C19—H19B 109.9 |
| C6—C5—H5            | 119.2       | N2—C19—C20 108.7 (3) |
| C5—C6—C8            | 117.7 (3)   | H19A—C19—H19B 108.3 |
| C7—C6—C5            | 119.2 (3)   | C20—C19—H19A 109.9 |
| C7—C6—C8            | 123.1 (3)   | C20—C19—H19B 109.9 |
| O2—C7—C2            | 118.6 (3)   | O6—C20—C19 110.6 (3) |
| O2—C7—C6            | 124.2 (3)   | O6—C20—H20A 109.5 |
| C6—C7—C2            | 117.2 (3)   | O6—C20—H20B 109.5 |
| Bond               | Angle/Distance         | Bond               | Angle/Distance         |
|--------------------|------------------------|--------------------|------------------------|
| N1—C8—C6          | 127.5 (3)              | C19—C20—H20A      | 109.5                  |
| N1—C8—H8          | 116.2                  | C19—C20—H20B      | 109.5                  |
| C6—C8—H8          | 116.2                  | H20A—C20—H20B     | 108.1                  |
| Cu1—O2—C7—C2      | 178.7 (2)              | C5—C6—C7—C2      | −0.3 (5)               |
| Cu1—O2—C7—C6      | −0.9 (5)               | C5—C6—C8—N1      | 179.7 (3)              |
| Cu1—O5—C17—C12    | 153.4 (3)              | C7—C2—C3—C4      | −0.1 (5)               |
| Cu1—O5—C17—C16    | −27.4 (5)              | C7—C6—C8—N1      | −1.2 (6)               |
| Cu1—O6—C20—C19    | −44.8 (3)              | C8—N1—C9—C10     | −102.7 (3)             |
| Cu1—N1—C8—C6      | 2.6 (5)                | C8—C6—C7—O2      | 0.2 (5)                |
| Cu1—N1—C9—C10     | 71.2 (3)               | C8—C6—C7—C2      | −179.4 (3)             |
| Cu1—N2—C18—C16    | −62.6 (3)              | C9—N1—C8—C6      | 176.1 (3)              |
| Cu1—N2—C19—C20    | −44.5 (3)              | C9—N1—C8—C6      | 176.1 (3)              |
| O1—C2—C3—C4      | 179.1 (3)              | C11—O4—C12—C13   | 9.3 (5)                |
| O1—C2—C7—O2      | 1.8 (4)                | C11—O4—C12—C17   | −169.1 (3)             |
| O1—C2—C7—C6      | −178.6 (3)             | C12—C13—C14—C15 | 2.2 (6)                |
| O4—C12—C13—C14   | −178.6 (3)             | C13—C12—C17—O5   | 177.7 (3)              |
| O4—C12—C17—O5    | −3.9 (5)               | C13—C12—C17—C16 | −1.6 (5)               |
| O4—C12—C17—C16   | 176.9 (3)              | C13—C14—C15—C16 | −2.2 (6)               |
| N1—C9—C10—O3     | 63.7 (4)               | C14—C15—C16—C17 | 0.3 (6)                |
| N2—C19—C20—O6    | 63.9 (4)               | C14—C15—C16—C18 | −179.0 (3)             |
| C1—O1—C2—C3      | 0.1 (5)                | C15—C16—C17—C12 | 1.5 (5)                |
| C1—O1—C2—C7      | 179.4 (4)              | C15—C16—C18—N2   | −134.9 (3)             |
| C2—C3—C4—C5      | −0.9 (6)               | C17—C12—C13—C14 | −0.3 (6)               |
| C3—C2—C7—O2      | −178.9 (3)             | C17—C16—C18—N2   | 45.8 (4)               |
| C3—C2—C7—C6      | 0.7 (5)                | C18—N2—C19—C20   | −173.8 (3)             |
| C3—C4—C5—C6      | 1.3 (6)                | C18—C16—C17—O5   | 1.6 (5)                |
| C4—C5—C6—C7      | −0.7 (6)               | C18—C16—C17—C12 | −179.2 (3)             |
| C4—C5—C6—C8      | 178.5 (4)              | C19—N2—C18—C16   | 65.4 (3)               |
| C5—C6—C7—O2      | 179.3 (3)              |                      |                        |

**Hydrogen-bond geometry (Å, °)**

| D—H···A           | D—H  | H···A | D···A  | D—H···A |
|-------------------|------|-------|-------|---------|
| O3—H3···O5       | 0.82 | 1.98  | 2.766 (3) | 161     |
| O6—H6···O1       | 0.75 (5) | 2.19 (5) | 2.916 (4) | 163 (5) |
| N2—H2···O6       | 0.98 | 2.27  | 3.107 (4) | 142     |

Symmetry codes: (i) −x+2, −y+1, z+1/2; (ii) −x+1, −y+1, z+1/2; (iii) −x+1, −y+1, z−1/2.