



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

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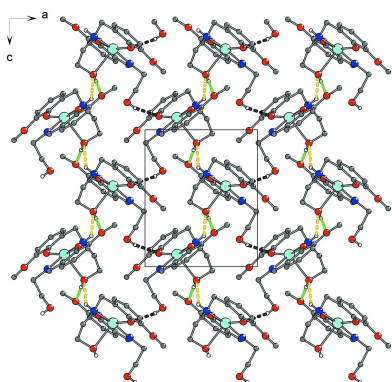
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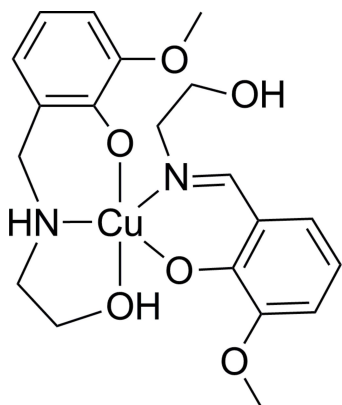
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The molecular bis-chelate complex (2-[(2-hydroxyethyl)- $\kappa O$ ]amino- $\kappa N$ ]methyl]-6-methoxyphenolato- $\kappa O$ )(2-[(2-hydroxyethyl)imino- $\kappa N$ ]methyl]-6-methoxyphenolato- $\kappa O$ )copper(II), [Cu(C<sub>10</sub>H<sub>14</sub>NO<sub>3</sub>)(C<sub>10</sub>H<sub>12</sub>NO<sub>3</sub>)] or [Cu(HL<sup>im</sup>)(HL<sup>am</sup>)]; HL<sup>im</sup> = C<sub>10</sub>H<sub>14</sub>NO<sub>3</sub>; HL<sup>am</sup> = C<sub>10</sub>H<sub>12</sub>NO<sub>3</sub>, represents the first compound containing a salicylidene-2-ethanolamine type ligand in both imino HL<sup>im</sup> (Schiff base) and amino HL<sup>am</sup> (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<sup>II</sup> ion in an (*N,O*<sub>phen</sub>)-bidentate and an (*N,O*<sub>phen</sub>,*O*<sub>alc</sub>)-tridentate fashion in the case of the imino and amino forms, respectively. The shape of the CuN<sub>2</sub>O<sub>3</sub> coordination polyhedron is a distorted square-pyramid (geometry index  $\tau_5 = 0.26$ ). 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 (Kozozay *et al.*, 2018), we have investigated the following system: zinc (powder) – copper (powder) – H<sub>2</sub>L – ammonium thiocyanate – methanol, to prepare heterometallic Cu/Zn complexes with the Schiff base H<sub>2</sub>L<sup>im</sup>, which is formed *in situ* upon condensation of *o*-vanillin and 2-aminoethanol. The complex [Cu(HL<sup>im</sup>)(HL<sup>am</sup>)] (where H<sub>2</sub>L<sup>im</sup> = 2-[(2-hydroxyethyl)iminomethyl]-6-methoxyphenol; H<sub>2</sub>L<sup>am</sup> = 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.

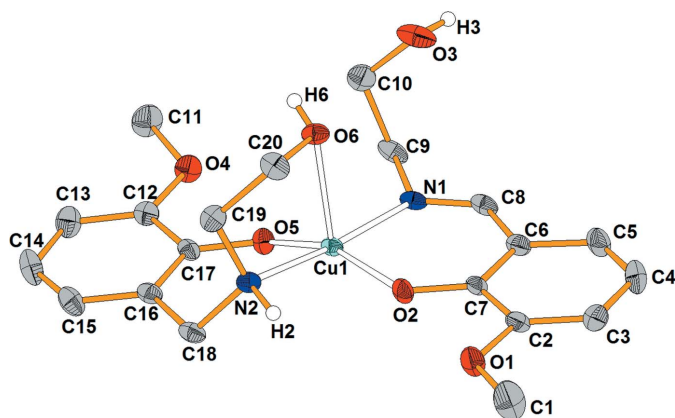




Herein, we report the crystal structure of the title compound,  $[\text{Cu}(\text{HL}^{\text{im}})(\text{HL}^{\text{am}})]$  (I), which represents the first example of a mixed (SB/RSB) complex derived from salicylidene-2-aminoethanol type ligands.

## 2. Structural commentary

The asymmetric unit of (I) comprises one neutral molecular complex  $[\text{Cu}(\text{HL}^{\text{im}})(\text{HL}^{\text{am}})]$  (Fig. 1). The copper(II) ion has an  $\text{O}_3\text{N}_2$  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,  $[\text{Cu}(\text{SB})_2]$  complexes are square-planar and  $[\text{Cu}(\text{RSB})_2]$  complexes are octahedral. For the corresponding imine complexes, see: Li *et al.* (2005); Zabierowski *et al.* (2013, 2014); Xin *et al.* (2019); for amine complexes, see: Xie *et al.* (2000). It is worth noting that such a dependence was not found for similar  $\text{Ni}^{\text{II}}$  complexes, which have an octahedral shape *via* both tridentate imino and amino ligands. For  $[\text{Ni}(\text{SB})_2]$ , see: Floyd *et al.* (2005); Wang *et al.* (2011a,b); for



**Figure 1**  
Molecular structure of (I), with the numbering scheme and displacement ellipsoids drawn at the 50% probability level (carbon-bound H atoms are omitted for clarity).

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

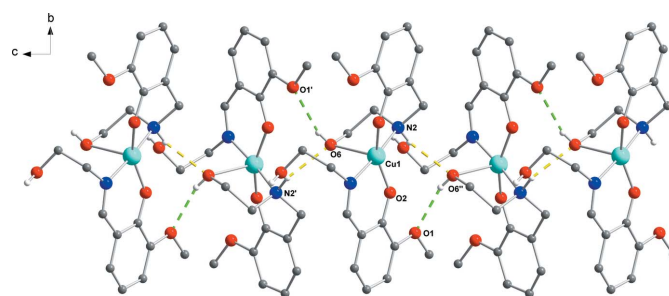
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3}\cdots\text{O5}^{\text{i}}$	0.82	1.98	2.766 (3)	161
$\text{O6}-\text{H6}\cdots\text{O1}^{\text{ii}}$	0.75 (5)	2.19 (5)	2.916 (4)	163 (5)
$\text{N2}-\text{H2}\cdots\text{O6}^{\text{iii}}$	0.98	2.27	3.107 (4)	142

Symmetry codes: (i)  $-x+2, -y+1, z+\frac{1}{2}$ ; (ii)  $-x+1, -y+1, z+\frac{1}{2}$ ; (iii)  $-x+1, -y+1, z-\frac{1}{2}$ .

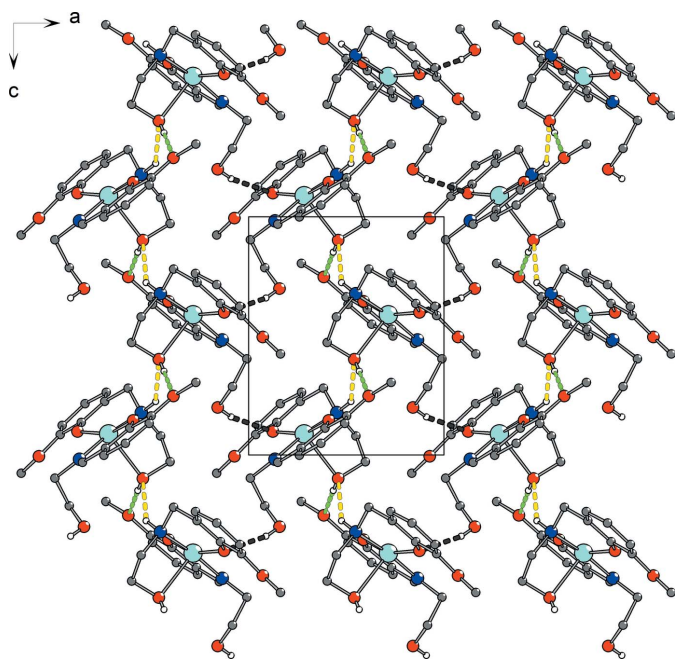
$[\text{Ni}(\text{RSB})_2]$ , see: Zhang *et al.* (2007). The shape of the coordination polyhedron of the  $\text{Cu}^{\text{II}}$  ion in (I) can be described as distorted  $[4+1]$  square-pyramidal. The equatorial  $\text{Cu}-\text{O}(\text{N})$  bond lengths vary from 1.923 (2) to 2.030 (3)  $\text{\AA}$  and are in accordance with those found in related complexes (Stetsiuk *et al.*, 2018; Xie *et al.*, 2000; Zabierowski *et al.*, 2013). The length of the long apical  $\text{Cu}-\text{O}$  bond of 2.432 (3)  $\text{\AA}$  lies within the range of  $\text{Cu}^{\text{II}}-\text{O}$  bond lengths extending up to *ca* 2.70  $\text{\AA}$  (Alvarez, 2013). The deviations in *cis* and *trans*  $[\text{O}-\text{Cu}-\text{O}(\text{N})]$  angles  $[80.08(10)-108.36(10)^\circ$  and  $157.96(12)-173.44(11)^\circ$ , respectively] are caused by the steric hindrances that are typical for chelate rings. According to the  $\tau$  criterion for five-coordinate complexes (Addison *et al.*, 1984; O'Sullivan *et al.*, 1999), the distortion of the  $\text{CuN}_2\text{O}_3$  coordination polyhedron is about 26% along the pathway from regular square-pyramidal to regular trigonal-bipyramidal. The bond-valence sums calculated for  $\text{Cu}^{\text{II}}$  with  $\text{CN} = 4$  (1.86 valence units) and  $\text{CN} = 5$  (1.99 valence units) (Allmann, 1975; Shields *et al.*, 2000) can serve as an additional argument in favor of the coordination number of 5 for  $\text{Cu}^{\text{II}}$  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  $\text{O6}-\text{H6}\cdots\text{O1}^{\text{ii}}$  and  $\text{iii}\text{O6}\cdots\text{H2}-\text{N2}$  (Table 1, Fig. 2) are formed along  $[001]$ . These



**Figure 2**  
Fragment of the crystal packing of (I), showing intermolecular  $\text{O6}-\text{H6}\cdots\text{O1}$  (green) and  $\text{N2}-\text{H2}\cdots\text{O6}$  (yellow) hydrogen bonds forming chains along  $[001]$ . [Symmetry codes: (')  $1-x, 1-y, \frac{1}{2}+z$ ; (')'  $1-x, 1-y, -\frac{1}{2}+z$ ].


**Figure 3**

The hydrogen-bonded sheet extending parallel to (010) in the crystal structure of (I). N—H...O (yellow) and O—H...O hydrogen bonds through participation of coordinating (green) and free (black) hydroxyethyl groups are shown.

chains are linked by O3—H3...O5<sup>i</sup> 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

*o*-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 NH<sub>4</sub>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

**Table 2**

Experimental details.

Crystal data	[Cu(C <sub>10</sub> H <sub>14</sub> NO <sub>3</sub> )(C <sub>10</sub> H <sub>12</sub> NO <sub>3</sub> )]
Chemical formula	453.97
<i>M<sub>r</sub></i>	Orthorhombic, <i>Pna</i> <sub>21</sub>
Crystal system, space group	150
Temperature (K)	8.3068 (9), 24.3280 (19), 10.1370 (9)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )
	2048.6 (3)
	<i>Z</i>
	4
	Radiation type
	Mo <i>K</i> α
	<i>μ</i> (mm <sup>-1</sup> )
	1.11
	Crystal size (mm)
	0.31 × 0.15 × 0.05
Data collection	
Diffractometer	New Gemini, Dual, Cu at zero, Atlas
Absorption correction	Analytical ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.509, 0.855
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	10546, 3777, 3539
<i>R<sub>int</sub></i>	0.036
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.679
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	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
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.31, −0.38
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter	−0.011 (15)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *pubCIF* (Westrip, 2010).

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.

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## supporting information

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

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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-(2-Hydroxyethyl- $\kappa$ O)amino- $\kappa$ N]methyl]-6-methoxyphenolato- $\kappa$ O)(2-[[2-(2-hydroxyethyl)imino- $\kappa$ N]methyl]-6-methoxyphenolato- $\kappa$ O)copper(II)

### Crystal data

[Cu(C<sub>10</sub>H<sub>14</sub>NO<sub>3</sub>)(C<sub>10</sub>H<sub>12</sub>NO<sub>3</sub>)]

$M_r = 453.97$

Orthorhombic, *Pna*2<sub>1</sub>

$a = 8.3068$  (9) Å

$b = 24.3280$  (19) Å

$c = 10.1370$  (9) Å

$V = 2048.6$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 948$

$D_x = 1.472$  Mg m<sup>-3</sup>

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

Cell parameters from 4616 reflections

$\theta = 4.1$ – $28.6^\circ$

$\mu = 1.11$  mm<sup>-1</sup>

$T = 150$  K

Plate, green

$0.31 \times 0.15 \times 0.05$  mm

### Data collection

New Gemini, Dual, Cu at zero, Atlas diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 10.6426 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.509$ ,  $T_{\max} = 0.855$

10546 measured reflections

3777 independent reflections

3539 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 28.8^\circ$ ,  $\theta_{\min} = 3.5^\circ$

$h = -10 \rightarrow 9$

$k = -31 \rightarrow 31$

$l = -13 \rightarrow 12$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.079$

$S = 1.06$

3777 reflections

268 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement



$$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.2171P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

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

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

Absolute structure: Classical Flack method

preferred over Parsons because s.u. lower

Absolute structure parameter:  $-0.011(15)$

### 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 Uiso 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 ( $\text{Å}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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	0.5898 (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	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*

H9B	1.066860	0.460018	0.627594	0.025*
C10	0.9173 (5)	0.51648 (16)	0.7138 (4)	0.0246 (8)
H10A	1.000746	0.536379	0.760726	0.029*
H10B	0.838544	0.542958	0.682967	0.029*
C11	1.1634 (5)	0.67643 (17)	0.5768 (4)	0.0309 (9)
H11A	1.234707	0.695184	0.517408	0.046*
H11B	1.225148	0.658469	0.644258	0.046*
H11C	1.091562	0.702508	0.616645	0.046*
C12	0.9635 (3)	0.65617 (12)	0.4146 (4)	0.0180 (6)
C13	0.9540 (4)	0.71095 (14)	0.3758 (4)	0.0247 (8)
H13	1.025083	0.736751	0.410207	0.030*
C14	0.8373 (5)	0.72677 (16)	0.2852 (4)	0.0294 (9)
H14	0.832475	0.763044	0.256536	0.035*
C15	0.7285 (5)	0.68872 (16)	0.2376 (4)	0.0249 (8)
H15	0.648537	0.699987	0.179372	0.030*
C16	0.7364 (4)	0.63357 (14)	0.2756 (3)	0.0172 (7)
C17	0.8560 (4)	0.61619 (13)	0.3639 (3)	0.0156 (7)
C18	0.6167 (4)	0.59254 (15)	0.2197 (3)	0.0191 (7)
H18A	0.529395	0.612378	0.177709	0.023*
H18B	0.669693	0.570550	0.152753	0.023*
C19	0.4499 (4)	0.58501 (13)	0.4204 (4)	0.0201 (7)
H19A	0.354505	0.599835	0.378298	0.024*
H19B	0.510825	0.615315	0.457572	0.024*
C20	0.4019 (4)	0.54520 (15)	0.5289 (4)	0.0220 (8)
H20A	0.329361	0.563357	0.589924	0.026*
H20B	0.345529	0.514124	0.490604	0.026*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.01244 (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)	0.0563 (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)	0.0013 (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)

C10	0.024 (2)	0.0272 (19)	0.0228 (18)	0.0012 (17)	-0.0099 (17)	-0.0019 (16)
C11	0.029 (2)	0.029 (2)	0.035 (2)	-0.0051 (17)	-0.0109 (18)	-0.0042 (18)
C12	0.0134 (14)	0.0215 (14)	0.0191 (14)	0.0022 (11)	0.0007 (17)	0.000 (2)
C13	0.0205 (18)	0.0205 (15)	0.033 (2)	-0.0040 (13)	0.0023 (15)	0.0013 (15)
C14	0.027 (2)	0.0220 (18)	0.039 (2)	0.0011 (16)	0.0012 (18)	0.0126 (17)
C15	0.0217 (19)	0.027 (2)	0.025 (2)	0.0035 (15)	-0.0027 (15)	0.0091 (17)
C16	0.0152 (17)	0.0231 (17)	0.0132 (16)	0.0018 (13)	0.0022 (13)	0.0021 (15)
C17	0.0144 (16)	0.0184 (15)	0.0139 (14)	0.0030 (13)	0.0054 (12)	0.0038 (13)
C18	0.0179 (18)	0.0265 (18)	0.0129 (15)	0.0031 (14)	-0.0018 (13)	0.0026 (15)
C19	0.0137 (15)	0.0221 (14)	0.0245 (17)	0.0014 (11)	0.0019 (16)	-0.0019 (19)
C20	0.0126 (18)	0.0302 (19)	0.0232 (18)	0.0016 (14)	0.0009 (14)	0.0037 (16)

*Geometric parameters (Å, °)*

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		
O2—Cu1—O6	93.16 (10)	N1—C9—H9A	109.5
O2—Cu1—N1	92.92 (11)	N1—C9—H9B	109.5
O2—Cu1—N2	87.35 (11)	N1—C9—C10	110.5 (3)



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—H15	119.4
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

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)	C11—O4—C12—C13	9.3 (5)
O1—C2—C3—C4	179.1 (3)	C11—O4—C12—C17	-169.1 (3)
O1—C2—C7—O2	1.8 (4)	C12—C13—C14—C15	2.2 (6)
O1—C2—C7—C6	-178.6 (3)	C13—C12—C17—O5	177.7 (3)
O4—C12—C13—C14	-178.6 (3)	C13—C12—C17—C16	-1.6 (5)
O4—C12—C17—O5	-3.9 (5)	C13—C14—C15—C16	-2.2 (6)
O4—C12—C17—C16	176.9 (3)	C14—C15—C16—C17	0.3 (6)
N1—C9—C10—O3	63.7 (4)	C14—C15—C16—C18	-179.0 (3)
N2—C19—C20—O6	63.9 (4)	C15—C16—C17—O5	-177.6 (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 ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 $\cdots$ O5 <sup>i</sup>	0.82	1.98	2.766 (3)	161
O6—H6 $\cdots$ O1 <sup>ii</sup>	0.75 (5)	2.19 (5)	2.916 (4)	163 (5)
N2—H2 $\cdots$ O6 <sup>iii</sup>	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)  $-x+1, -y+1, z-1/2$ .