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# Tetranuclear copper(II) complex of 2-hydroxy-*N*,*N*′-bis[1-(2-hydroxyphenyl)ethylidene]propane-1,3-diamine

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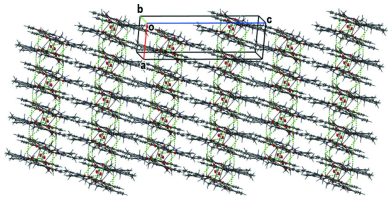
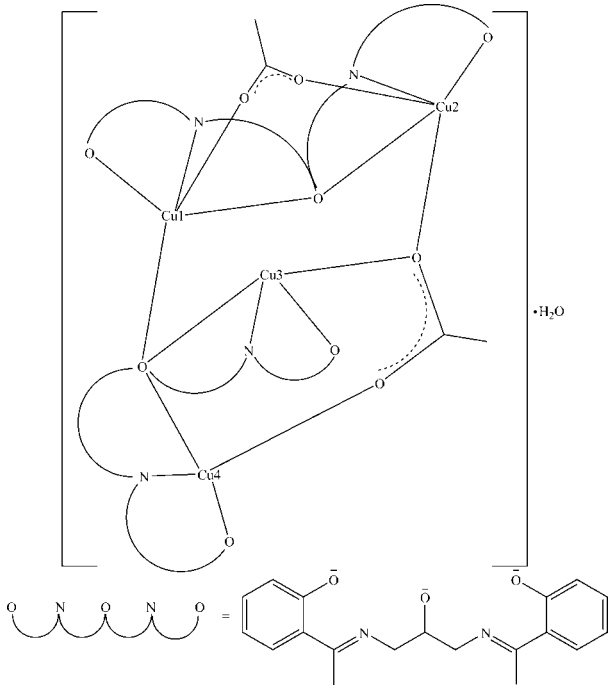
The title molecular structure, namely, ($\mu_3$-acetato)($\mu_2$-acetato)bis($\mu_3$-1,3-bis{[1-(2-oxidophenyl)ethylidene]amino}propan-2-olato)tetracopper(II) monohydrate, $[Cu_4(C_{19}H_{19}N_2O_3)_2(CH_3CO_2)_2]\cdot H_2O$, corresponds to a non-symmetric tetranuclear copper complex. The complex exhibits one ligand molecule that connects two copper $Cu^{II}$ metal centres *via* its ethanolato oxygen anion acting in a $\mu_2$-mode and one ligand molecule that connects three copper $Cu^{II}$ metal centres *via* its ethanolato oxygen anion acting in a $\mu_3$-mode. One bridging acetate group acting in an $\eta^1$:$\eta^1$-$\mu_2$-mode connects two copper(II) ions while another bridging acetate group connects three copper(II) ions in an $\eta^1$:-$\eta^2$-$\mu_3$-mode. A chair-like $Cu_3O_3$ structure is generated in which the two $CuO_4N$ units are connected by one $\mu_2$-O ethanolate oxygen atom. These two units are connected respectively to the $CuO_3N$ unit *via* one $\mu_3$-O ethanolate oxygen atom and one $\mu_2$-O atom from an acetate group. The $\mu_3$-O atom also connects one of the $CuO_4N$ units and the $CuO_3N$ unit to another $CuO_3N$ unit, which is out of the chair-like structure. Each of the two pentacoordinated $Cu^{II}$ cations has a distorted $NO_4$ square-pyramidal environment. The geometry of each of the two $CuNO_3$ units is best described as a slightly square-planar environment. A series of intramolecular O—H···O hydrogen bonds is observed. In the crystal, the units are connected by intermolecular C—H···O and O—H···O hydrogen bonds, thus forming sheets parallel to the *ac* plane

## 1. Chemical context

The controlled design of new coordination complexes of transition metals from polydentate ligands is of great interest for research, because of the potential applications that these functional materials can have and for their interesting structural diversity (Popov *et al.*, 2012; Mitra *et al.*, 2014). In this context, important research is being devoted to the chemistry of transition-metal complexes with different oxidation states incorporating polydentate ligands with N and O donor sites (Xie *et al.*, 2012; Banerjee & Chattopadhyay, 2019; Ferguson *et al.*, 2006). These ligands can act in a versatile manner and generate compounds with very different structures, depending on the metal–ligand ratio and the nature of the metal cation (Fernandes *et al.*, 2000). In this context, pentadentate Schiff bases have made it possible to synthesize several complexes with various transition-metal cations, resulting in an unusual coordination environment with interesting stereochemistry (Banerjee *et al.*, 2011). Depending on the size of the cation and



its external electronic configuration and the flexibility of the ligand, novel structures with high nuclearity have been obtained (Aly, 1999). These compounds are very attractive for the above reasons, and they have been widely used in several studies. Many multinuclear transition-metal complexes with various structures have been generated, depending on the disposition of the metal ions and donor sites (N or O). Tetranuclear (Asadi *et al.*, 2018; Manna *et al.*, 2019), pentanuclear (Hari *et al.*, 2019; Ghosh, Clérac *et al.*, 2013) hexanuclear (Shit *et al.*, 2013; Kébé *et al.*, 2021) and heptanuclear (Gheorghe *et al.*, 2019; Ghosh, Bauzá *et al.*, 2013) forms have reported with potential applications in the fields of magnetism (Gheorghe *et al.*, 2019), catalysis (Nesterova *et al.*, 2020; Das *et al.*, 2018) or biomimetic synthesis (Nesterova *et al.*, 2020; Sanyal *et al.*, 2017). Our research group has already enabled us to prepare several multidentate Schiff base complexes (Mamour *et al.*, 2018; Sarr *et al.*, 2018*a*,*b*; Sall *et al.*, 2019). We then explored the possibility of preparing complexes with several metal cations from a pentadentate Schiff base obtained by condensation of 1,3-diaminopropan-2-ol and 1-(2-hydroxyphenyl)ethanone, which is rich in hydroxyl groups. From this Schiff base we prepared a hexanuclear complex with an open-cube structure (Kébé *et al.*, 2021). In a continuation of our work with this Schiff base, we obtained the title tetranuclear copper complex (Fig. 1) whose structure is presented herein.




## 2. Structural commentary

*N*,*N*′-Bis{[1-(2-hydroxyphenyl)ethylidene)]}-2-hydroxypropane-1, 3-diamine ($H_3L$ was synthesized *via* a condensation reaction between 1,3-diaminopropan-2-ol and 1-(2-hydroxyphenyl)ethanone in a 1:2 ratio in ethanol. Mixing $H_3L$ and hydrated copper acetate yielded a tetranuclear complex formulated as $[Cu_4L_2(CH_3CO_2)_2]\cdot H_2O$ in which the ligand acts in its tri-deprotonated $L^{-3}$ form. In the tetranuclear complex, one of the $L^{-3}$ anions acts in $\mu_2$-mode, connecting the two pentacoordinated $Cu^{II}$ cations. The second $L^{-3}$ anion acts in $\mu_3$ mode, connecting the two tetracoordinated $Cu^{II}$ cations and one of the pentacoordinated $Cu^{II}$ cations. The second pentacoordinated $Cu^{II}$ cation is connected to the two tetracoordinated $Cu^{II}$ cations *via* an acetate group acting in $\eta^1{:}\eta^2{-}\mu_3$ mode. Additionally, the two pentacoordinated $Cu^{II}$ cations are connected by an acetate group acting in $\eta^1{:}\eta^1{-}\mu_2$ mode. For each ligand, the azomethine nitrogen atom and the phenolate oxygen atom of one arm are both linked to one $Cu^{II}$ cation while the corresponding atoms of the other arm are bonded to another $Cu^{II}$ cation. No phenolate oxygen atom acts in bridging mode. In one ligand the ethanolate oxygen atom bridges the two pentacoordinated $Cu^{II}$ cations, and in the second ligand the ethanolate oxygen atom bridges the two tetracoordinated $Cu^{II}$ cations and one pentacoordinated $Cu^{II}$ cation. The two $L^{-3}$ ligands are coordinated differently in hexadentate ($-\eta^1$-$O_{phenolate}$, $-\eta^1$-$N_{imino}$, $-\mu_2$-$O_{enolato}$, $-\eta^1$-$N_{imino}$, $-\eta^1$-$O_{phenolato}$) and heptadentate ($-\eta^1$-$O_{phenolate}$, $-\eta^1$-$N_{imino}$, $-\mu_3$-$O_{enolato}$, $-\eta^1$-$N_{imino}$, $-\eta^1$-$O_{phenolato}$) fashions. Four five-membered CuOCCN rings and four six-membered CuOCCCN rings are formed upon the coordination of the ligand molecules. In the tetranuclear complex, two discrete $CuO_4N$ and $CuO_3N$ units are observed.

Atoms Cu1 and Cu2 are pentacoordinated and their environments can be best described as slightly distorted

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu2—O2 | 1.920 (3) | Cu1—N1 | 1.966 (4) |
| Cu2—O3 | 1.877 (3) | Cu3—O5 | 1.907 (3) |
| Cu2—O11 | 1.940 (3) | Cu3—O4 | 1.873 (3) |
| Cu2—O8 | 2.703 (4) | Cu3—O8 | 1.957 (3) |
| Cu2—N2 | 1.961 (4) | Cu3—N3 | 1.947 (4) |
| Cu1—O5 | 2.749 (3) | Cu4—O5 | 1.921 (3) |
| Cu1—O2 | 1.916 (3) | Cu4—O7 | 1.955 (3) |
| Cu1—O10 | 1.982 (3) | Cu4—O6 | 1.869 (3) |
| Cu1—O1 | 1.878 (3) | Cu4—N4 | 1.962 (4) |
| | | | |
| O3—Cu2—O2 | 173.00 (15) | O4—Cu3—O5 | 177.07 (15) |
| O11—Cu2—N2 | 161.66 (15) | N3—Cu3—O8 | 173.28 (15) |
| O1—Cu1—O2 | 176.33 (14) | O7—Cu4—N4 | 164.11 (15) |
| N1—Cu1—O10 | 169.71 (16) | | |

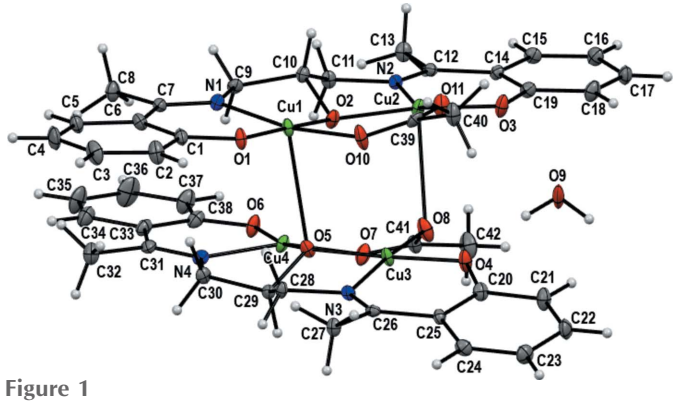



**Figure 1**
A view of the title compound, showing the atom-numbering scheme.

square-pyramidal. The Addison $\tau$ parameter (Addison *et al.*, 1984) calculated from the largest angles (Table 1; $\tau$ = 0 for perfect square-pyramidal and $\tau$ = 1 for perfect trigonal–bipyramidal geometries, respectively) around the metal ion are $\tau$ = 0.1103 for Cu1 and $\tau$ = 0.1887 for Cu2. For Cu1 and Cu2, the basal planes are occupied by one phenolate oxygen anion, one azomethine nitrogen atom, one ethanolate oxygen atom and one oxygen atom from the $\eta^1$:$\eta^1$-$\mu_2$ acetate group, the apical position being occupied by an ethanolate oxygen atom from a second ligand molecule for Cu1 and an oxygen atom from the $\eta^1$:$\eta^2$-$\mu_3$ acetate group for Cu2. The atoms forming the basal plane for Cu1 (N1, O1, O2, O10) are almost coplanar (r.m.s. deviation = 0.1088 Å) and the Cu1 atom is displaced toward the O5 atom, which occupies the apical position, by 0.0545 (2) Å. The Cu1—O5 distance of 2.749 (3) Å is longer than the distances between Cu1 and the atoms in the basal plane [Cu1—$N_{ligand}$ = 1.966 (4) Å, Cu1—$O_{ligand}$ = 1.878 (3) and 1.916 (3) Å and Cu1—$O_{acetate}$ = 1.982 (3) Å)], as expected for a Jahn–Teller distortion (Monfared *et al.*, 2009), typical of a $Cu^{II}$ $d^9$ configuration (Monfared *et al.*, 2009). These values are in accordance with those in similar copper(II) complexes (Haldar *et al.*, 2016; Siluvai & Murthy, 2009). The *cisoid* and *transoid* angles are in the ranges 85.01 (14)–95.10 (14)° and 169.71 (16)–176.33 (14)°, respectively. The atoms forming the basal plane for Cu2 (N2, O2, O11, O3) are less coplanar than those around Cu1 (r.m.s. deviation = 0.2086 Å) and the Cu2 atom is displaced toward the O8 atom, which occupies the apical position, by 0.0808 (1) Å. The from Cu2—O8 distance of 2.703 (4) Å is longer than those to atoms in the equatorial plane [Cu2—$N_{ligand}$ = 1.961 (4) Å, Cu2—$O_{ligand}$ = 1.877 (3) and 1.920 (3) Å and Cu2—$O_{acetate}$ = 1.940 (3) Å]. As observed for Cu1, Jahn–Teller distortion (Monfared *et al.*, 2009) is responsible of the elongation of the distance between Cu2 and the apical atom O8. The *cisoid* and *transoid* angles are in the ranges 85.74 (15)–96.89 (14)° and 161.66 (15)–173.00 (15)°, respectively. The bond lengths involving the $\mu_2$-bridging ethanolato oxygen atom and the copper cations are asymmetrical: Cu1—O2 = 1.916 (3) Å and Cu2—O2 = 1.920 (3) Å. The distances between the $\mu_3$-bridging ethanolato oxygen atom and the copper cations are very different: Cu1—O5 = 2.749 (3) Å, Cu3—O5 = 1.907 (3) Å and Cu4—O5 = 1.921 (3) Å. The copper cations Cu3 and Cu4 are coordinated by one ethanolato oxygen anion, one phenoxo oxygen anion, one azomethine nitrogen atom of the ligand and one oxygen atom of a $\eta^1$:$\eta^2$-$\mu_3$ acetate group (O8 for Cu3 and O7 for Cu4). The Cu3—O4 [1.873 (3) Å], Cu3—O5 [1.907 (3) Å], Cu3—N3 [1.947 (4) Å], Cu3—O8 [1.957 (3) Å], Cu4—O6 [1.869 (3) Å], Cu4—O5 [1.921 (3) Å], Cu4—N4 [1.962 (4) Å] and Cu4—O7 [1.955 (3) Å] distances are in close proximity to values reported for copper(II) complexes with analogous Schiff base ligands (Patra *et al.*, 2015; Lukov *et al.*, 2017). For the Cu3 and Cu4 centres, the coordination environment can be best described as distorted square planar with r.m.s. deviations of 0.7870 Å for N3/O4/O8/O5/Cu3 and 0.7921 Å for O5/O7/O6/N4/Cu4. These planes, which share one vertex (O5), form a dihedral angle of 65.67 (1)°. The tetragonality parameter (Singh *et al.*, 2017) $\tau_4$ values of 0.0993 (Cu3) and 0.1801 (Cu4) suggested distorted square-planar geometries. For the two copper cations the *cisoid* angles are in the ranges 86.17 (14)–93.29 (15)° for Cu3 and 84.04 (14)–96.93 (14)° for Cu4 and the *transoid* angles are O4—Cu3—O5 = 177.07 (15)°, O8—Cu3—N3 = 173.28 (15)°, O6—Cu4—O5 = 170.48 (14)° and O7—Cu3—N4 = 164.11 (15)°. The C—N bonds are in the range 1.291 (6)–1.300 (6) Å, indicative of double-bond character and the presence of the imino groups in the two ligands.

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O9—H9*C*···O4 | 0.85 | 2.08 | 2.894 (5) | 159 |
| O9—H9*C*···O8 | 0.85 | 2.56 | 3.158 (5) | 128 |
| O9—H9*D*···O3 | 0.85 | 2.08 | 2.928 (5) | 175 |
| C28—H28*A*···O1 | 0.97 | 2.58 | 3.427 (6) | 146 |
| C29—H29···O1$^{i}$ | 0.98 | 2.60 | 3.424 (5) | 142 |
| C10—H10···O6$^{ii}$ | 0.98 | 2.51 | 3.351 (6) | 144 |
| C8—H8*A*···O9$^{iii}$ | 0.96 | 2.44 | 3.372 (6) | 163 |
| C9—H9*B*···O6 | 0.97 | 2.65 | 3.521 (6) | 150 |
| C32—H32*A*···O9$^{iii}$ | 0.96 | 2.38 | 3.304 (6) | 162 |
| C42—H42*A*···O11$^{i}$ | 0.96 | 2.66 | 3.256 (7) | 121 |

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

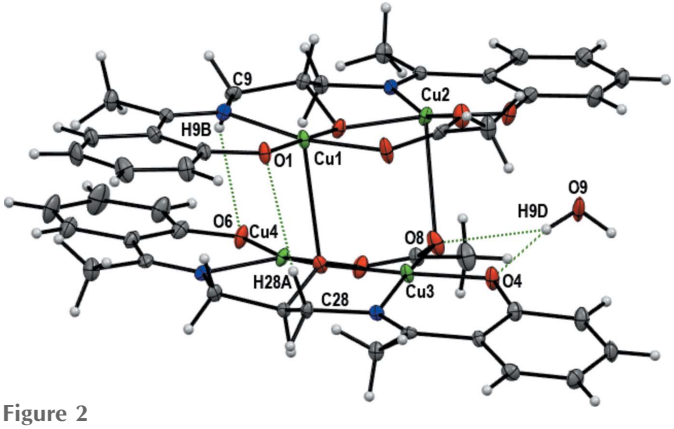



**Figure 2**
Detail of the structure of the complex showing the O—H···O and C—H···O hydrogen bonds.

## 3. Supramolecular features

Intramolecular O—H···O hydrogen bonds involving the uncoordinated water molecule, a phenoxo oxygen atom and

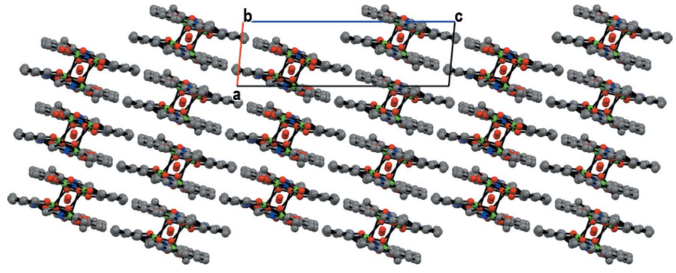



**Figure 3**
Sheets parallel to the *ac* plane.

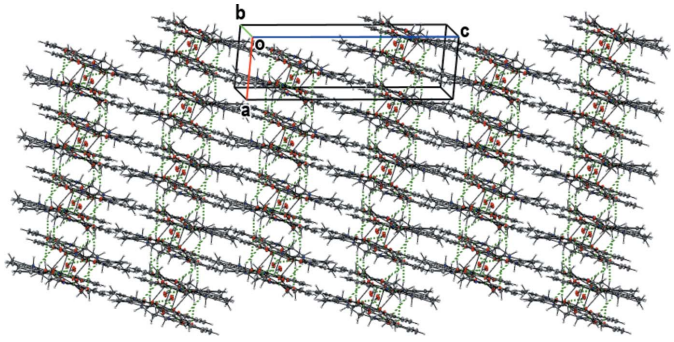



**Figure 4**
View of the two-dimensional sheets parallel to the *ac* plane.

an oxygen atom of acetate group and C—H···$O_{phenoxo}$ are observed (Fig. 2, Table 2). The uncoordinated water molecule is situated into the void of the tetranuclear complex and has O···O contacts of 2.894 (5) and 3.158 (5) Å suggesting medium-strength hydrogen bonds. In the crystal, the complex molecules are arranged in sheets parallel to the *ac* plane (Fig. 3). The sheets are connected by C—H···O bonds (C—H···$O_{phenoxo}$, C—H···$O_{water}$, C—H···$O_{acetate}$; Table 2). The series of intermolecular and intramolecular hydrogen bonds stabilize and link the components into two-dimensional sheets parallel to the *ac* plane (Fig. 4).

## 4. Database survey

*N*,*N*′–Bis[(1-(2-hydroxyphenyl)ethylidene)]-2-hydroxypropane-1,3-diamine is widely used in coordination chemistry. The current release of the CSD (Version 5.42, November 2021 update; Groom *et al.*, 2016) gave eleven hits. Three are complexes of the ligand with $Ni^{II}$ cations [KARPOK and KARPUQ (Liu *et al.*, 2012); OMOFUS (Banerjee *et al.*, 2011)]. Four entries are complexes of $Cu^{II}$ cations [KUKTAM (Basak *et al.*, 2009), NADDIJ and NADDOP (Osypiuk *et al.*, 2020), OVOWAA (Kébé *et al.*, 2021)]. In addition, two $Co^{II}$ complexes (OMOFOM and OMOGAZ; Banerjee *et al.*, 2011), one $Fe^{II}$ (RIDHUJ; Biswas *et al.*, 2013) and one $V^{V}$ complex (KEWGUQ; Maurya *et al.*, 2013) have been reported. In all eleven cases, the ligand acts in a pentadentate mode through the two soft azomethine nitrogen atoms, the two hard phenolate oxygen anions and the one hard enolate oxygen anion. In seven cases (KARPOK, KARPUQ, OMOFUS, KUKTAM, NADDIJ, NADDOP and OMOGAZ), the complexes are tetranuclear while two dinuclear (OMOFOM and RIDHUJ), one mononuclear (KEWGUQ) and one hexanuclear (OVOWAA) complex have been reported.

## 5. Synthesis and crystallization

The ligand *N*,*N*′-bis[(1-(2-hydroxyphenyl)ethylidene)]-2-hydroxypropane-1,3-diamine ($HL_3$) was prepared from 1-(2-hydroxyphenyl)ethanone and 2-hydroxypropane-1,3-diamine in a 2:1 ratio in ethanol according to a slight modification of a literature method (Song *et al.*, 2003). To a solution of 1,3-diaminopropane-2-ol (0.900 g, 10 mmol) in 25 mL of ethanol was added dropwise (2-hydroxyphenyl)ethanone (2.720 g, 20 mmol). The resulting orange mixture was refluxed for 3 h, affording the organic ligand $H_3L$. On cooling, the yellow precipitate that appeared was recovered by filtration and dried in air. Yield 75%. m.p. 479–480 K. FT–IR (KBr, $\nu$, $cm^{-1}$): 3538 (OH), 3268 (OH), 1605 (C═N), 1538 (C═C), 1528 (C═C), 1455 (C═C), 1247 (C—O), 1043, 760. Analysis calculated for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.90; H, 6.76; N, 8.56%.

A solution of $Cu(CH_3CO_2)_2\cdot(H_2O)$ (0.1996 g, 1 mmol) in 5 mL of ethanol was added to a solution of $H_3L$ (0.163 g, 0.5 mmol) in 10 mL of ethanol at room temperature. The initial yellow solution immediately turned deep green and was stirred for 30 min before being filtered. The filtrate was kept at 298 K. After one week, light-green crystals suitable for X-ray diffraction were collected and formulated as $[Cu_4L_2(CH_3CO_2)_2]\cdot H_2O$. FT–IR (KBr, $\nu$, $cm^{-1}$): 3404, 1601, 1532, 1332, 1299, 895, 760. Analysis calculated for $C_{42}H_{46}Cu_4N_4O_{11}$: C, 48.64; H, 4.47; N, 5.40. Found: C, 48.60; H, 4.49; N, 5.44%.

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Cu_4(C_{19}H_{19}N_2O_3)_2(C_2H_3O_2)_2]\cdot H_2O$ |
| $M_r$ | 1037.02 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 293 |
| $a$, $b$, $c$ (Å) | 6.9688 (1), 25.8066 (4), 22.8290 (4) |
| $\beta$ (°) | 95.418 (2) |
| $V$ (Å$^3$) | 4087.25 (11) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ ($mm^{-1}$) | 2.12 |
| Crystal size (mm) | 0.25 × 0.2 × 0.1 |
| | |
| Data collection | |
| Diffractometer | Nonius KappaCCD |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{min}$, $T_{max}$ | 0.967, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12039, 12039, 10024 |
| $R_{int}$ | 0.008 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.651 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.056, 0.131, 1.13 |
| No. of reflections | 12039 |
| No. of parameters | 560 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.69, −0.88 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to the hydroxyl group and water molecules were located in a difference-Fourier map and freely refined. Other H atoms (CH, $CH_2$, $CH_3$ groups and hydroxyl of ethanol molecules) were geometrically optimized (O—H = 0.85 Å, C—H = 0.93–

0.97 Å) and refined using a riding model (AFIX instructions) with $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(C) for $CH_3$ and OH groups.

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Authors' contributions are as follows: Conceptualization, MD, MG, MGN, ASD and IET; investigation, ASD and IET; writing (original draft), MG; writing (review and editing of the manuscript), MG, IET, MNG and MD; formal analysis, IET, JO and SC; resources, MG and MD; supervision, MG and IET.

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# supporting information

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## Tetranuclear copper(II) complex of 2-hydroxy-*N*,*N*′-bis[1-(2-hydroxyphenyl)-ethylidene]propane-1,3-diamine

**Alassane Saïdou Diallo, Ibrahima Elhadji Thiam, Mbossé Gueye-Ndiaye, Moussa Dieng, James Orton, Coles Simon and Mohamed Gaye**

### Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### ($\mu_3$-Acetato)($\mu_2$-acetato)bis($\mu_3$-1,3-bis{[1-(2-oxidophenyl)ethylidene]amino}propan-2-olato)tetracopper(II) monohydrate

*Crystal data*

$[Cu_4(C_{19}H_{19}N_2O_3)_2(C_2H_3O_2)_2]\cdot H_2O$
$M_r$ = 1037.02
Monoclinic, $P2_1/n$
$a$ = 6.9688 (1) Å
$b$ = 25.8066 (4) Å
$c$ = 22.8290 (4) Å
$\beta$ = 95.418 (2)°
$V$ = 4087.25 (11) Å$^3$
$Z$ = 4
$F(000)$ = 2120
$D_x$ = 1.685 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71075 Å
Cell parameters from 5800 reflections
$\theta$ = 2.4–28.7°
$\mu$ = 2.12 mm$^{-1}$
$T$ = 293 K
Prismatic, light-green
0.25 × 0.2 × 0.1 mm

*Data collection*

Nonius KappaCCD diffractometer
CCD scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min}$ = 0.967, $T_{max}$ = 1.000
12039 measured reflections
12039 independent reflections
10024 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.008
$\theta_{max}$ = 27.6°, $\theta_{min}$ = 1.8°
$h$ = −9→9
$k$ = −33→33
$l$ = −29→28

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.131
$S$ = 1.13
12039 reflections
560 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 21.6332P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.69 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.88 e Å$^{-3}$

*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**. Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu2 | 0.60863 (8) | 0.28366 (2) | 0.32611 (2) | 0.01219 (13) |
| Cu1 | 0.52144 (8) | 0.38573 (2) | 0.22819 (2) | 0.01203 (13) |
| Cu3 | 0.84495 (8) | 0.29191 (2) | 0.17735 (2) | 0.01246 (13) |
| Cu4 | 1.01850 (8) | 0.39019 (2) | 0.27079 (2) | 0.01232 (13) |
| O5 | 0.8865 (4) | 0.36243 (12) | 0.20000 (13) | 0.0132 (6) |
| O2 | 0.6231 (5) | 0.35435 (12) | 0.30062 (14) | 0.0140 (6) |
| O10 | 0.4526 (5) | 0.31935 (13) | 0.18788 (15) | 0.0222 (8) |
| O7 | 1.1025 (5) | 0.32394 (12) | 0.30599 (15) | 0.0181 (7) |
| O3 | 0.6275 (5) | 0.21453 (12) | 0.35156 (15) | 0.0185 (7) |
| O4 | 0.7906 (5) | 0.22334 (12) | 0.15452 (14) | 0.0181 (7) |
| O1 | 0.4344 (5) | 0.41970 (12) | 0.15789 (14) | 0.0152 (7) |
| O6 | 1.1072 (5) | 0.42189 (12) | 0.34184 (15) | 0.0180 (7) |
| O11 | 0.4548 (5) | 0.25787 (13) | 0.25696 (15) | 0.0202 (7) |
| O8 | 0.9004 (5) | 0.26730 (13) | 0.25825 (15) | 0.0208 (7) |
| N1 | 0.5427 (5) | 0.45103 (14) | 0.27266 (17) | 0.0126 (8) |
| C41 | 1.0334 (7) | 0.27956 (17) | 0.2974 (2) | 0.0137 (9) |
| N3 | 0.8224 (5) | 0.31721 (14) | 0.09664 (16) | 0.0111 (7) |
| O9 | 0.7291 (6) | 0.15395 (13) | 0.25055 (17) | 0.0264 (8) |
| H9C | 0.770732 | 0.177114 | 0.228491 | 0.040* |
| H9D | 0.703080 | 0.170249 | 0.281168 | 0.040* |
| N2 | 0.6827 (5) | 0.31062 (14) | 0.40532 (16) | 0.0114 (7) |
| N4 | 1.0044 (5) | 0.45572 (14) | 0.22705 (16) | 0.0121 (7) |
| C39 | 0.4116 (6) | 0.27589 (17) | 0.2067 (2) | 0.0143 (9) |
| C19 | 0.6706 (6) | 0.19719 (18) | 0.4053 (2) | 0.0135 (9) |
| C26 | 0.7822 (6) | 0.29142 (17) | 0.04858 (19) | 0.0110 (8) |
| C16 | 0.7556 (7) | 0.15045 (19) | 0.5168 (2) | 0.0180 (10) |
| H16 | 0.781948 | 0.135243 | 0.553591 | 0.022* |
| C20 | 0.7860 (6) | 0.20455 (18) | 0.1007 (2) | 0.0145 (9) |
| C13 | 0.7848 (7) | 0.31399 (18) | 0.5103 (2) | 0.0156 (9) |
| H13A | 0.823194 | 0.348621 | 0.501483 | 0.023* |
| H13B | 0.890648 | 0.296314 | 0.531695 | 0.023* |
| H13C | 0.677661 | 0.315238 | 0.533833 | 0.023* |
| C27 | 0.7355 (6) | 0.31943 (17) | −0.00920 (19) | 0.0138 (9) |
| H27A | 0.688273 | 0.353526 | −0.001780 | 0.021* |
| H27B | 0.638722 | 0.300470 | −0.033070 | 0.021* |
| H27C | 0.849757 | 0.322077 | −0.029428 | 0.021* |
| C14 | 0.7197 (6) | 0.22864 (17) | 0.45570 (19) | 0.0113 (8) |
| C25 | 0.7812 (6) | 0.23439 (17) | 0.0480 (2) | 0.0117 (8) |

| | | | | |
|---|---|---|---|---|
| C17 | 0.7117 (7) | 0.12003 (18) | 0.4666 (2) | 0.0174 (10) |
| H17 | 0.710667 | 0.084111 | 0.469778 | 0.021* |
| C28 | 0.8313 (6) | 0.37427 (16) | 0.09623 (19) | 0.0121 (9) |
| H28A | 0.702933 | 0.388882 | 0.095759 | 0.014* |
| H28B | 0.889213 | 0.386413 | 0.061739 | 0.014* |
| C29 | 0.9539 (6) | 0.39016 (17) | 0.1520 (2) | 0.0122 (9) |
| H29 | 1.088626 | 0.380870 | 0.148407 | 0.015* |
| C11 | 0.6906 (6) | 0.36775 (17) | 0.40348 (19) | 0.0126 (9) |
| H11A | 0.822806 | 0.379269 | 0.402534 | 0.015* |
| H11B | 0.640320 | 0.382256 | 0.438117 | 0.015* |
| C10 | 0.5701 (6) | 0.38526 (17) | 0.3486 (2) | 0.0129 (9) |
| H10 | 0.433277 | 0.380043 | 0.353554 | 0.015* |
| C6 | 0.4719 (6) | 0.50930 (18) | 0.1912 (2) | 0.0149 (9) |
| C7 | 0.5306 (6) | 0.49832 (17) | 0.2530 (2) | 0.0123 (9) |
| C1 | 0.4262 (6) | 0.47000 (17) | 0.1482 (2) | 0.0149 (9) |
| C12 | 0.7266 (6) | 0.28539 (17) | 0.45387 (19) | 0.0113 (8) |
| C15 | 0.7586 (7) | 0.20325 (18) | 0.5103 (2) | 0.0150 (9) |
| H15 | 0.787888 | 0.223430 | 0.543726 | 0.018* |
| C30 | 0.9411 (7) | 0.44745 (17) | 0.1646 (2) | 0.0132 (9) |
| H30A | 1.022816 | 0.466698 | 0.140256 | 0.016* |
| H30B | 0.809436 | 0.459367 | 0.155977 | 0.016* |
| C8 | 0.5798 (7) | 0.54254 (18) | 0.2947 (2) | 0.0182 (10) |
| H8A | 0.633216 | 0.570576 | 0.273896 | 0.027* |
| H8B | 0.672434 | 0.531122 | 0.325863 | 0.027* |
| H8C | 0.465288 | 0.554100 | 0.311060 | 0.027* |
| C31 | 1.0235 (6) | 0.50243 (18) | 0.2480 (2) | 0.0150 (9) |
| C22 | 0.7727 (7) | 0.12579 (18) | 0.0412 (2) | 0.0197 (10) |
| H22 | 0.769101 | 0.089808 | 0.039118 | 0.024* |
| C23 | 0.7695 (7) | 0.15510 (19) | −0.0106 (2) | 0.0190 (10) |
| H23 | 0.764424 | 0.138974 | −0.047193 | 0.023* |
| C24 | 0.7741 (7) | 0.20798 (18) | −0.0062 (2) | 0.0158 (9) |
| H24 | 0.772348 | 0.227402 | −0.040560 | 0.019* |
| C9 | 0.6056 (7) | 0.44167 (17) | 0.33513 (19) | 0.0136 (9) |
| H9A | 0.533894 | 0.463677 | 0.359735 | 0.016* |
| H9B | 0.741610 | 0.449663 | 0.343064 | 0.016* |
| C38 | 1.1219 (7) | 0.47204 (18) | 0.3522 (2) | 0.0171 (10) |
| C33 | 1.0824 (6) | 0.51236 (18) | 0.3101 (2) | 0.0156 (9) |
| C5 | 0.4589 (7) | 0.56179 (18) | 0.1719 (2) | 0.0189 (10) |
| H5 | 0.490277 | 0.587974 | 0.199175 | 0.023* |
| C40 | 0.2961 (8) | 0.23976 (18) | 0.1642 (2) | 0.0206 (10) |
| H40A | 0.208940 | 0.259722 | 0.138055 | 0.031* |
| H40B | 0.224171 | 0.215968 | 0.185905 | 0.031* |
| H40C | 0.382332 | 0.220786 | 0.141722 | 0.031* |
| C32 | 0.9831 (7) | 0.54776 (18) | 0.2068 (2) | 0.0202 (10) |
| H32A | 0.930339 | 0.575865 | 0.227686 | 0.030* |
| H32B | 0.892338 | 0.537490 | 0.174626 | 0.030* |
| H32C | 1.100792 | 0.558715 | 0.191900 | 0.030* |
| C34 | 1.1021 (7) | 0.56421 (19) | 0.3302 (2) | 0.0227 (11) |

| | | | | |
|---|---|---|---|---|
| H34 | 1.074325 | 0.590881 | 0.303313 | 0.027* |
| C4 | 0.4018 (8) | 0.57527 (19) | 0.1147 (2) | 0.0243 (11) |
| H4 | 0.392435 | 0.609970 | 0.103828 | 0.029* |
| C18 | 0.6705 (7) | 0.14284 (19) | 0.4130 (2) | 0.0196 (10) |
| H18 | 0.641327 | 0.121833 | 0.380232 | 0.023* |
| C2 | 0.3711 (7) | 0.48541 (19) | 0.0895 (2) | 0.0211 (10) |
| H2 | 0.342570 | 0.460076 | 0.061062 | 0.025* |
| C3 | 0.3585 (8) | 0.5367 (2) | 0.0733 (2) | 0.0236 (11) |
| H3 | 0.320682 | 0.545600 | 0.034466 | 0.028* |
| C21 | 0.7810 (7) | 0.14995 (18) | 0.0949 (2) | 0.0194 (10) |
| H21 | 0.783417 | 0.129738 | 0.128740 | 0.023* |
| C42 | 1.1047 (8) | 0.2371 (2) | 0.3389 (2) | 0.0256 (11) |
| H42A | 1.242630 | 0.238701 | 0.345497 | 0.038* |
| H42B | 1.067072 | 0.204078 | 0.322069 | 0.038* |
| H42C | 1.049827 | 0.241244 | 0.375637 | 0.038* |
| C35 | 1.1599 (9) | 0.5768 (2) | 0.3872 (3) | 0.0300 (13) |
| H35 | 1.173262 | 0.611278 | 0.398564 | 0.036* |
| C36 | 1.1985 (9) | 0.5374 (2) | 0.4282 (3) | 0.0339 (14) |
| H36 | 1.236433 | 0.545609 | 0.467253 | 0.041* |
| C37 | 1.1808 (8) | 0.4863 (2) | 0.4112 (2) | 0.0249 (11) |
| H37 | 1.208207 | 0.460476 | 0.439069 | 0.030* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu2 | 0.0193 (3) | 0.0094 (3) | 0.0074 (3) | 0.0025 (2) | −0.0014 (2) | −0.0003 (2) |
| Cu1 | 0.0176 (3) | 0.0091 (3) | 0.0087 (3) | −0.0023 (2) | −0.0022 (2) | 0.0013 (2) |
| Cu3 | 0.0198 (3) | 0.0098 (3) | 0.0073 (3) | −0.0045 (2) | −0.0008 (2) | 0.0007 (2) |
| Cu4 | 0.0161 (3) | 0.0101 (3) | 0.0100 (3) | 0.0023 (2) | −0.0029 (2) | −0.0027 (2) |
| O5 | 0.0194 (16) | 0.0129 (16) | 0.0070 (15) | −0.0049 (13) | 0.0006 (12) | −0.0013 (12) |
| O2 | 0.0222 (17) | 0.0105 (15) | 0.0091 (15) | 0.0017 (12) | −0.0001 (12) | −0.0017 (12) |
| O10 | 0.040 (2) | 0.0114 (17) | 0.0146 (17) | −0.0102 (15) | 0.0000 (15) | 0.0005 (13) |
| O7 | 0.0219 (17) | 0.0133 (17) | 0.0176 (18) | 0.0033 (13) | −0.0062 (13) | −0.0013 (13) |
| O3 | 0.0324 (19) | 0.0102 (16) | 0.0123 (16) | 0.0036 (14) | −0.0016 (14) | −0.0016 (13) |
| O4 | 0.0315 (19) | 0.0108 (16) | 0.0113 (16) | −0.0033 (13) | −0.0014 (14) | 0.0001 (13) |
| O1 | 0.0227 (17) | 0.0093 (15) | 0.0125 (17) | −0.0023 (12) | −0.0040 (13) | 0.0029 (12) |
| O6 | 0.0260 (18) | 0.0109 (16) | 0.0158 (18) | 0.0015 (13) | −0.0054 (14) | −0.0052 (13) |
| O11 | 0.0298 (19) | 0.0160 (17) | 0.0137 (17) | −0.0020 (14) | −0.0034 (14) | 0.0002 (13) |
| O8 | 0.0314 (19) | 0.0184 (18) | 0.0114 (17) | −0.0083 (14) | −0.0038 (14) | 0.0047 (13) |
| N1 | 0.0165 (18) | 0.0117 (19) | 0.0093 (19) | 0.0018 (14) | −0.0001 (15) | 0.0004 (14) |
| C41 | 0.020 (2) | 0.012 (2) | 0.008 (2) | −0.0020 (17) | 0.0000 (17) | 0.0008 (17) |
| N3 | 0.0141 (18) | 0.0114 (18) | 0.0076 (18) | −0.0008 (14) | 0.0005 (14) | 0.0007 (14) |
| O9 | 0.053 (2) | 0.0092 (16) | 0.0194 (19) | −0.0017 (16) | 0.0144 (17) | −0.0007 (14) |
| N2 | 0.0147 (18) | 0.0110 (18) | 0.0086 (18) | −0.0016 (14) | 0.0015 (14) | −0.0024 (14) |
| N4 | 0.0136 (18) | 0.0144 (19) | 0.0080 (18) | 0.0009 (14) | −0.0006 (14) | −0.0019 (14) |
| C39 | 0.017 (2) | 0.014 (2) | 0.012 (2) | 0.0041 (17) | 0.0022 (17) | −0.0051 (18) |
| C19 | 0.016 (2) | 0.015 (2) | 0.009 (2) | 0.0034 (17) | 0.0010 (17) | 0.0008 (17) |
| C26 | 0.0094 (19) | 0.014 (2) | 0.009 (2) | 0.0010 (16) | 0.0019 (16) | 0.0022 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 0.023 (2) | 0.018 (2) | 0.013 (2) | 0.0036 (19) | 0.0018 (19) | 0.0033 (18) |
| C20 | 0.016 (2) | 0.014 (2) | 0.013 (2) | −0.0024 (17) | −0.0026 (17) | −0.0024 (17) |
| C13 | 0.021 (2) | 0.015 (2) | 0.010 (2) | −0.0007 (18) | −0.0033 (18) | −0.0007 (17) |
| C27 | 0.019 (2) | 0.012 (2) | 0.010 (2) | −0.0004 (17) | −0.0016 (17) | 0.0010 (17) |
| C14 | 0.013 (2) | 0.011 (2) | 0.010 (2) | 0.0027 (16) | 0.0008 (16) | 0.0011 (16) |
| C25 | 0.011 (2) | 0.010 (2) | 0.013 (2) | −0.0013 (16) | −0.0007 (16) | 0.0006 (17) |
| C17 | 0.026 (2) | 0.011 (2) | 0.016 (2) | 0.0021 (18) | 0.0032 (19) | 0.0027 (18) |
| C28 | 0.018 (2) | 0.009 (2) | 0.009 (2) | 0.0009 (16) | 0.0009 (17) | 0.0005 (16) |
| C29 | 0.013 (2) | 0.010 (2) | 0.013 (2) | 0.0006 (16) | 0.0026 (17) | 0.0008 (17) |
| C11 | 0.019 (2) | 0.012 (2) | 0.006 (2) | −0.0015 (17) | −0.0012 (17) | −0.0015 (16) |
| C10 | 0.015 (2) | 0.011 (2) | 0.013 (2) | 0.0004 (16) | 0.0002 (17) | −0.0010 (17) |
| C6 | 0.016 (2) | 0.013 (2) | 0.015 (2) | −0.0029 (17) | 0.0019 (18) | 0.0025 (18) |
| C7 | 0.011 (2) | 0.011 (2) | 0.015 (2) | −0.0008 (16) | 0.0027 (17) | −0.0006 (17) |
| C1 | 0.015 (2) | 0.011 (2) | 0.019 (2) | −0.0008 (17) | 0.0009 (18) | 0.0035 (18) |
| C12 | 0.0106 (19) | 0.012 (2) | 0.011 (2) | −0.0005 (16) | 0.0024 (16) | −0.0007 (17) |
| C15 | 0.018 (2) | 0.017 (2) | 0.009 (2) | 0.0005 (17) | 0.0011 (17) | 0.0002 (18) |
| C30 | 0.018 (2) | 0.013 (2) | 0.009 (2) | −0.0024 (17) | 0.0006 (17) | −0.0027 (17) |
| C8 | 0.024 (2) | 0.012 (2) | 0.017 (2) | −0.0014 (18) | −0.0004 (19) | −0.0027 (19) |
| C31 | 0.011 (2) | 0.013 (2) | 0.021 (3) | 0.0017 (17) | 0.0033 (17) | −0.0001 (18) |
| C22 | 0.027 (3) | 0.010 (2) | 0.022 (3) | −0.0043 (18) | 0.004 (2) | −0.0017 (19) |
| C23 | 0.024 (2) | 0.018 (2) | 0.016 (2) | −0.0026 (19) | 0.0020 (19) | −0.0049 (19) |
| C24 | 0.018 (2) | 0.018 (2) | 0.011 (2) | −0.0009 (18) | 0.0012 (17) | 0.0015 (18) |
| C9 | 0.018 (2) | 0.014 (2) | 0.009 (2) | 0.0018 (17) | 0.0029 (17) | 0.0004 (17) |
| C38 | 0.016 (2) | 0.016 (2) | 0.019 (2) | 0.0026 (17) | −0.0010 (18) | −0.0039 (19) |
| C33 | 0.016 (2) | 0.013 (2) | 0.018 (2) | 0.0001 (17) | 0.0012 (18) | −0.0063 (18) |
| C5 | 0.024 (2) | 0.012 (2) | 0.021 (3) | −0.0036 (18) | 0.004 (2) | 0.0026 (19) |
| C40 | 0.032 (3) | 0.013 (2) | 0.016 (2) | −0.003 (2) | −0.002 (2) | 0.0004 (19) |
| C32 | 0.026 (3) | 0.013 (2) | 0.021 (3) | −0.0004 (19) | −0.001 (2) | 0.0007 (19) |
| C34 | 0.025 (3) | 0.016 (2) | 0.026 (3) | 0.003 (2) | 0.002 (2) | −0.005 (2) |
| C4 | 0.036 (3) | 0.012 (2) | 0.024 (3) | −0.001 (2) | 0.004 (2) | 0.008 (2) |
| C18 | 0.027 (3) | 0.016 (2) | 0.015 (2) | 0.0018 (19) | 0.0003 (19) | −0.0048 (19) |
| C2 | 0.029 (3) | 0.015 (2) | 0.019 (3) | −0.004 (2) | −0.004 (2) | 0.0023 (19) |
| C3 | 0.029 (3) | 0.021 (3) | 0.019 (3) | −0.001 (2) | −0.005 (2) | 0.011 (2) |
| C21 | 0.028 (3) | 0.013 (2) | 0.016 (2) | −0.0007 (19) | −0.003 (2) | 0.0024 (18) |
| C42 | 0.033 (3) | 0.021 (3) | 0.021 (3) | −0.002 (2) | −0.008 (2) | 0.008 (2) |
| C35 | 0.044 (3) | 0.017 (3) | 0.028 (3) | 0.003 (2) | −0.003 (2) | −0.013 (2) |
| C36 | 0.052 (4) | 0.028 (3) | 0.019 (3) | 0.002 (3) | −0.007 (3) | −0.015 (2) |
| C37 | 0.035 (3) | 0.020 (3) | 0.018 (3) | 0.003 (2) | −0.004 (2) | −0.006 (2) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| Cu2—O2 | 1.920 (3) | C17—C18 | 1.364 (7) |
| Cu2—O3 | 1.877 (3) | C28—H28A | 0.9700 |
| Cu2—O11 | 1.940 (3) | C28—H28B | 0.9700 |
| Cu2—O8 | 2.703 (4) | C28—C29 | 1.522 (6) |
| Cu2—N2 | 1.961 (4) | C29—H29 | 0.9800 |
| Cu1—O5 | 2.749 (3) | C29—C30 | 1.510 (6) |
| Cu1—O2 | 1.916 (3) | C11—H11A | 0.9700 |

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|---|---|---|---|
| Cu1—O10 | 1.982 (3) | C11—H11B | 0.9700 |
| Cu1—O1 | 1.878 (3) | C11—C10 | 1.509 (6) |
| Cu1—N1 | 1.966 (4) | C10—H10 | 0.9800 |
| Cu3—O5 | 1.907 (3) | C10—C9 | 1.513 (6) |
| Cu3—O4 | 1.873 (3) | C6—C7 | 1.458 (6) |
| Cu3—O8 | 1.957 (3) | C6—C1 | 1.427 (7) |
| Cu3—N3 | 1.947 (4) | C6—C5 | 1.424 (6) |
| Cu4—O5 | 1.921 (3) | C7—C8 | 1.506 (6) |
| Cu4—O7 | 1.955 (3) | C1—C2 | 1.415 (7) |
| Cu4—O6 | 1.869 (3) | C15—H15 | 0.9300 |
| Cu4—N4 | 1.962 (4) | C30—H30A | 0.9700 |
| O5—C29 | 1.424 (5) | C30—H30B | 0.9700 |
| O2—C10 | 1.432 (5) | C8—H8A | 0.9600 |
| O10—C39 | 1.244 (6) | C8—H8B | 0.9600 |
| O7—C41 | 1.251 (5) | C8—H8C | 0.9600 |
| O3—C19 | 1.313 (5) | C31—C33 | 1.461 (7) |
| O4—C20 | 1.319 (5) | C31—C32 | 1.511 (7) |
| O1—C1 | 1.317 (5) | C22—H22 | 0.9300 |
| O6—C38 | 1.318 (6) | C22—C23 | 1.403 (7) |
| O11—C39 | 1.248 (6) | C22—C21 | 1.373 (7) |
| O8—C41 | 1.266 (6) | C23—H23 | 0.9300 |
| N1—C7 | 1.300 (6) | C23—C24 | 1.369 (7) |
| N1—C9 | 1.472 (6) | C24—H24 | 0.9300 |
| C41—C42 | 1.503 (6) | C9—H9A | 0.9700 |
| N3—C26 | 1.291 (6) | C9—H9B | 0.9700 |
| N3—C28 | 1.474 (5) | C38—C33 | 1.426 (7) |
| O9—H9C | 0.8499 | C38—C37 | 1.418 (7) |
| O9—H9D | 0.8500 | C33—C34 | 1.417 (6) |
| N2—C11 | 1.476 (6) | C5—H5 | 0.9300 |
| N2—C12 | 1.297 (6) | C5—C4 | 1.374 (7) |
| N4—C30 | 1.467 (5) | C40—H40A | 0.9600 |
| N4—C31 | 1.299 (6) | C40—H40B | 0.9600 |
| C39—C40 | 1.520 (6) | C40—H40C | 0.9600 |
| C19—C14 | 1.424 (6) | C32—H32A | 0.9600 |
| C19—C18 | 1.414 (7) | C32—H32B | 0.9600 |
| C26—C27 | 1.512 (6) | C32—H32C | 0.9600 |
| C26—C25 | 1.472 (6) | C34—H34 | 0.9300 |
| C16—H16 | 0.9300 | C34—C35 | 1.366 (7) |
| C16—C17 | 1.399 (7) | C4—H4 | 0.9300 |
| C16—C15 | 1.371 (7) | C4—C3 | 1.385 (8) |
| C20—C25 | 1.427 (6) | C18—H18 | 0.9300 |
| C20—C21 | 1.415 (6) | C2—H2 | 0.9300 |
| C13—H13A | 0.9600 | C2—C3 | 1.376 (7) |
| C13—H13B | 0.9600 | C3—H3 | 0.9300 |
| C13—H13C | 0.9600 | C21—H21 | 0.9300 |
| C13—C12 | 1.508 (6) | C42—H42A | 0.9600 |
| C27—H27A | 0.9600 | C42—H42B | 0.9600 |
| C27—H27B | 0.9600 | C42—H42C | 0.9600 |

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|---|---|---|---|
| C27—H27C | 0.9600 | C35—H35 | 0.9300 |
| C14—C12 | 1.466 (6) | C35—C36 | 1.389 (8) |
| C14—C15 | 1.412 (6) | C36—H36 | 0.9300 |
| C25—C24 | 1.409 (6) | C36—C37 | 1.377 (7) |
| C17—H17 | 0.9300 | C37—H37 | 0.9300 |
| | | | |
| O2—Cu2—O11 | 96.89 (14) | C30—C29—C28 | 112.6 (4) |
| O2—Cu2—O8 | 84.89 (12) | C30—C29—H29 | 109.3 |
| O2—Cu2—N2 | 85.74 (14) | N2—C11—H11A | 110.2 |
| O3—Cu2—O2 | 173.00 (15) | N2—C11—H11B | 110.2 |
| O3—Cu2—O11 | 86.73 (14) | N2—C11—C10 | 107.7 (3) |
| O3—Cu2—O8 | 89.68 (13) | H11A—C11—H11B | 108.5 |
| O3—Cu2—N2 | 92.70 (15) | C10—C11—H11A | 110.2 |
| O11—Cu2—O8 | 82.40 (13) | C10—C11—H11B | 110.2 |
| O11—Cu2—N2 | 161.66 (15) | O2—C10—C11 | 107.7 (4) |
| N2—Cu2—O8 | 115.93 (13) | O2—C10—H10 | 109.6 |
| O2—Cu1—O5 | 80.48 (12) | O2—C10—C9 | 108.7 (4) |
| O2—Cu1—O10 | 95.10 (14) | C11—C10—H10 | 109.6 |
| O2—Cu1—N1 | 85.01 (14) | C11—C10—C9 | 111.6 (4) |
| O10—Cu1—O5 | 83.75 (13) | C9—C10—H10 | 109.6 |
| O1—Cu1—O5 | 97.68 (12) | C1—C6—C7 | 123.5 (4) |
| O1—Cu1—O2 | 176.33 (14) | C5—C6—C7 | 119.2 (4) |
| O1—Cu1—O10 | 87.83 (14) | C5—C6—C1 | 117.4 (4) |
| O1—Cu1—N1 | 92.51 (15) | N1—C7—C6 | 121.3 (4) |
| N1—Cu1—O5 | 106.38 (13) | N1—C7—C8 | 119.3 (4) |
| N1—Cu1—O10 | 169.71 (16) | C6—C7—C8 | 119.4 (4) |
| O5—Cu3—O8 | 92.44 (14) | O1—C1—C6 | 125.6 (4) |
| O5—Cu3—N3 | 86.17 (14) | O1—C1—C2 | 116.1 (4) |
| O4—Cu3—O5 | 177.07 (15) | C2—C1—C6 | 118.3 (4) |
| O4—Cu3—O8 | 88.43 (14) | N2—C12—C13 | 120.5 (4) |
| O4—Cu3—N3 | 93.29 (15) | N2—C12—C14 | 121.3 (4) |
| N3—Cu3—O8 | 173.28 (15) | C14—C12—C13 | 118.1 (4) |
| O5—Cu4—O7 | 96.93 (14) | C16—C15—C14 | 123.5 (4) |
| O5—Cu4—N4 | 84.04 (14) | C16—C15—H15 | 118.2 |
| O7—Cu4—N4 | 164.11 (15) | C14—C15—H15 | 118.2 |
| O6—Cu4—O5 | 170.48 (14) | N4—C30—C29 | 108.0 (4) |
| O6—Cu4—O7 | 87.96 (14) | N4—C30—H30A | 110.1 |
| O6—Cu4—N4 | 93.50 (15) | N4—C30—H30B | 110.1 |
| Cu3—O5—Cu1 | 98.74 (12) | C29—C30—H30A | 110.1 |
| Cu3—O5—Cu4 | 129.24 (17) | C29—C30—H30B | 110.1 |
| Cu4—O5—Cu1 | 95.83 (12) | H30A—C30—H30B | 108.4 |
| C29—O5—Cu1 | 116.7 (2) | C7—C8—H8A | 109.5 |
| C29—O5—Cu3 | 108.9 (3) | C7—C8—H8B | 109.5 |
| C29—O5—Cu4 | 107.0 (2) | C7—C8—H8C | 109.5 |
| Cu1—O2—Cu2 | 129.60 (17) | H8A—C8—H8B | 109.5 |
| C10—O2—Cu2 | 105.8 (3) | H8A—C8—H8C | 109.5 |
| C10—O2—Cu1 | 108.9 (3) | H8B—C8—H8C | 109.5 |
| C39—O10—Cu1 | 132.3 (3) | N4—C31—C33 | 122.0 (4) |

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| C41—O7—Cu4 | 129.8 (3) | N4—C31—C32 | 118.8 (4) |
| C19—O3—Cu2 | 128.0 (3) | C33—C31—C32 | 119.2 (4) |
| C20—O4—Cu3 | 126.4 (3) | C23—C22—H22 | 119.8 |
| C1—O1—Cu1 | 127.5 (3) | C21—C22—H22 | 119.8 |
| C38—O6—Cu4 | 126.8 (3) | C21—C22—C23 | 120.3 (4) |
| C39—O11—Cu2 | 133.4 (3) | C22—C23—H23 | 120.8 |
| Cu3—O8—Cu2 | 113.47 (15) | C24—C23—C22 | 118.5 (5) |
| C41—O8—Cu2 | 95.5 (3) | C24—C23—H23 | 120.8 |
| C41—O8—Cu3 | 130.7 (3) | C25—C24—H24 | 118.4 |
| C7—N1—Cu1 | 128.8 (3) | C23—C24—C25 | 123.1 (4) |
| C7—N1—C9 | 119.5 (4) | C23—C24—H24 | 118.4 |
| C9—N1—Cu1 | 111.1 (3) | N1—C9—C10 | 108.4 (4) |
| O7—C41—O8 | 125.8 (4) | N1—C9—H9A | 110.0 |
| O7—C41—C42 | 118.0 (4) | N1—C9—H9B | 110.0 |
| O8—C41—C42 | 116.1 (4) | C10—C9—H9A | 110.0 |
| C26—N3—Cu3 | 128.5 (3) | C10—C9—H9B | 110.0 |
| C26—N3—C28 | 121.0 (4) | H9A—C9—H9B | 108.4 |
| C28—N3—Cu3 | 110.0 (3) | O6—C38—C33 | 126.0 (4) |
| H9C—O9—H9D | 104.5 | O6—C38—C37 | 115.9 (4) |
| C11—N2—Cu2 | 109.6 (3) | C37—C38—C33 | 118.1 (4) |
| C12—N2—Cu2 | 129.1 (3) | C38—C33—C31 | 123.0 (4) |
| C12—N2—C11 | 121.3 (4) | C34—C33—C31 | 119.3 (4) |
| C30—N4—Cu4 | 111.4 (3) | C34—C33—C38 | 117.6 (5) |
| C31—N4—Cu4 | 127.9 (3) | C6—C5—H5 | 118.7 |
| C31—N4—C30 | 120.3 (4) | C4—C5—C6 | 122.6 (5) |
| O10—C39—O11 | 127.6 (4) | C4—C5—H5 | 118.7 |
| O10—C39—C40 | 117.2 (4) | C39—C40—H40A | 109.5 |
| O11—C39—C40 | 115.2 (4) | C39—C40—H40B | 109.5 |
| O3—C19—C14 | 125.2 (4) | C39—C40—H40C | 109.5 |
| O3—C19—C18 | 116.8 (4) | H40A—C40—H40B | 109.5 |
| C18—C19—C14 | 117.9 (4) | H40A—C40—H40C | 109.5 |
| N3—C26—C27 | 120.4 (4) | H40B—C40—H40C | 109.5 |
| N3—C26—C25 | 121.6 (4) | C31—C32—H32A | 109.5 |
| C25—C26—C27 | 118.0 (4) | C31—C32—H32B | 109.5 |
| C17—C16—H16 | 120.8 | C31—C32—H32C | 109.5 |
| C15—C16—H16 | 120.8 | H32A—C32—H32B | 109.5 |
| C15—C16—C17 | 118.3 (4) | H32A—C32—H32C | 109.5 |
| O4—C20—C25 | 125.8 (4) | H32B—C32—H32C | 109.5 |
| O4—C20—C21 | 116.8 (4) | C33—C34—H34 | 118.5 |
| C21—C20—C25 | 117.4 (4) | C35—C34—C33 | 122.9 (5) |
| H13A—C13—H13B | 109.5 | C35—C34—H34 | 118.5 |
| H13A—C13—H13C | 109.5 | C5—C4—H4 | 120.3 |
| H13B—C13—H13C | 109.5 | C5—C4—C3 | 119.5 (5) |
| C12—C13—H13A | 109.5 | C3—C4—H4 | 120.3 |
| C12—C13—H13B | 109.5 | C19—C18—H18 | 118.8 |
| C12—C13—H13C | 109.5 | C17—C18—C19 | 122.5 (4) |
| C26—C27—H27A | 109.5 | C17—C18—H18 | 118.8 |
| C26—C27—H27B | 109.5 | C1—C2—H2 | 119.0 |

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| C26—C27—H27C | 109.5 | C3—C2—C1 | 122.0 (5) |
| H27A—C27—H27B | 109.5 | C3—C2—H2 | 119.0 |
| H27A—C27—H27C | 109.5 | C4—C3—H3 | 119.9 |
| H27B—C27—H27C | 109.5 | C2—C3—C4 | 120.2 (5) |
| C19—C14—C12 | 123.5 (4) | C2—C3—H3 | 119.9 |
| C15—C14—C19 | 117.5 (4) | C20—C21—H21 | 118.9 |
| C15—C14—C12 | 119.0 (4) | C22—C21—C20 | 122.2 (5) |
| C20—C25—C26 | 122.2 (4) | C22—C21—H21 | 118.9 |
| C24—C25—C26 | 119.4 (4) | C41—C42—H42A | 109.5 |
| C24—C25—C20 | 118.4 (4) | C41—C42—H42B | 109.5 |
| C16—C17—H17 | 119.9 | C41—C42—H42C | 109.5 |
| C18—C17—C16 | 120.3 (4) | H42A—C42—H42B | 109.5 |
| C18—C17—H17 | 119.9 | H42A—C42—H42C | 109.5 |
| N3—C28—H28A | 110.4 | H42B—C42—H42C | 109.5 |
| N3—C28—H28B | 110.4 | C34—C35—H35 | 120.3 |
| N3—C28—C29 | 106.5 (3) | C34—C35—C36 | 119.3 (5) |
| H28A—C28—H28B | 108.6 | C36—C35—H35 | 120.3 |
| C29—C28—H28A | 110.4 | C35—C36—H36 | 119.9 |
| C29—C28—H28B | 110.4 | C37—C36—C35 | 120.2 (5) |
| O5—C29—C28 | 108.0 (3) | C37—C36—H36 | 119.9 |
| O5—C29—H29 | 109.3 | C38—C37—H37 | 119.1 |
| O5—C29—C30 | 108.4 (4) | C36—C37—C38 | 121.8 (5) |
| C28—C29—H29 | 109.3 | C36—C37—H37 | 119.1 |

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| Cu2—O2—C10—C11 | 50.9 (4) | N2—C11—C10—O2 | −47.4 (5) |
| Cu2—O2—C10—C9 | 172.0 (3) | N2—C11—C10—C9 | −166.7 (4) |
| Cu2—O3—C19—C14 | −2.5 (7) | N4—Cu4—O6—C38 | 7.3 (4) |
| Cu2—O3—C19—C18 | 178.5 (3) | N4—C31—C33—C38 | −0.5 (7) |
| Cu2—O11—C39—O10 | −4.0 (8) | N4—C31—C33—C34 | 179.5 (4) |
| Cu2—O11—C39—C40 | 175.8 (3) | C19—C14—C12—N2 | 1.8 (7) |
| Cu2—O8—C41—O7 | −90.7 (5) | C19—C14—C12—C13 | −178.8 (4) |
| Cu2—O8—C41—C42 | 85.7 (4) | C19—C14—C15—C16 | 1.5 (7) |
| Cu2—N2—C11—C10 | 21.0 (4) | C26—N3—C28—C29 | −158.3 (4) |
| Cu2—N2—C12—C13 | 178.5 (3) | C26—C25—C24—C23 | −178.9 (4) |
| Cu2—N2—C12—C14 | −2.0 (6) | C16—C17—C18—C19 | 0.2 (8) |
| Cu1—O5—C29—C28 | −66.2 (4) | C20—C25—C24—C23 | 0.7 (7) |
| Cu1—O5—C29—C30 | 56.0 (4) | C27—C26—C25—C20 | −167.5 (4) |
| Cu1—O2—C10—C11 | −166.2 (3) | C27—C26—C25—C24 | 12.0 (6) |
| Cu1—O2—C10—C9 | −45.1 (4) | C14—C19—C18—C17 | 1.3 (7) |
| Cu1—O10—C39—O11 | −22.5 (8) | C25—C20—C21—C22 | 0.3 (7) |
| Cu1—O10—C39—C40 | 157.7 (4) | C17—C16—C15—C14 | 0.1 (7) |
| Cu1—O1—C1—C6 | −4.2 (7) | C28—N3—C26—C27 | −2.4 (6) |
| Cu1—O1—C1—C2 | 174.4 (3) | C28—N3—C26—C25 | 177.3 (4) |
| Cu1—N1—C7—C6 | 8.2 (6) | C28—C29—C30—N4 | 160.4 (4) |
| Cu1—N1—C7—C8 | −171.3 (3) | C11—N2—C12—C13 | 0.8 (6) |
| Cu1—N1—C9—C10 | −18.5 (4) | C11—N2—C12—C14 | −179.7 (4) |
| Cu3—O5—C29—C28 | 44.4 (4) | C11—C10—C9—N1 | 159.8 (4) |
| Cu3—O5—C29—C30 | 166.7 (3) | C6—C1—C2—C3 | −0.8 (7) |

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| Cu3—O4—C20—C25 | −14.1 (7) | C6—C5—C4—C3 | −1.3 (8) |
| Cu3—O4—C20—C21 | 167.4 (3) | C7—N1—C9—C10 | 169.2 (4) |
| Cu3—O8—C41—O7 | 36.9 (7) | C7—C6—C1—O1 | −1.4 (7) |
| Cu3—O8—C41—C42 | −146.7 (4) | C7—C6—C1—C2 | −179.9 (4) |
| Cu3—N3—C26—C27 | 168.8 (3) | C7—C6—C5—C4 | −179.0 (5) |
| Cu3—N3—C26—C25 | −11.5 (6) | C1—C6—C7—N1 | −0.8 (7) |
| Cu3—N3—C28—C29 | 29.0 (4) | C1—C6—C7—C8 | 178.7 (4) |
| Cu4—O5—C29—C28 | −172.1 (3) | C1—C6—C5—C4 | 1.1 (7) |
| Cu4—O5—C29—C30 | −49.8 (4) | C1—C2—C3—C4 | 0.6 (8) |
| Cu4—O7—C41—O8 | 7.7 (7) | C12—N2—C11—C10 | −160.9 (4) |
| Cu4—O7—C41—C42 | −168.7 (3) | C12—C14—C15—C16 | 179.9 (4) |
| Cu4—O6—C38—C33 | −3.7 (7) | C15—C16—C17—C18 | −1.0 (7) |
| Cu4—O6—C38—C37 | 175.7 (3) | C15—C14—C12—N2 | −176.6 (4) |
| Cu4—N4—C30—C29 | −13.5 (4) | C15—C14—C12—C13 | 2.9 (6) |
| Cu4—N4—C31—C33 | 7.3 (6) | C30—N4—C31—C33 | 178.8 (4) |
| Cu4—N4—C31—C32 | −172.6 (3) | C30—N4—C31—C32 | −1.1 (6) |
| O5—Cu1—O1—C1 | −98.9 (4) | C31—N4—C30—C29 | 173.8 (4) |
| O5—C29—C30—N4 | 41.0 (5) | C31—C33—C34—C35 | −178.8 (5) |
| O2—C10—C9—N1 | 41.1 (5) | C22—C23—C24—C25 | −0.2 (7) |
| O10—Cu1—O1—C1 | 177.7 (4) | C23—C22—C21—C20 | 0.2 (8) |
| O7—Cu4—O6—C38 | 171.5 (4) | C9—N1—C7—C6 | 179.0 (4) |
| O3—C19—C14—C12 | 0.6 (7) | C9—N1—C7—C8 | −0.5 (6) |
| O3—C19—C14—C15 | 178.9 (4) | C38—C33—C34—C35 | 1.3 (8) |
| O3—C19—C18—C17 | −179.6 (4) | C33—C38—C37—C36 | 0.6 (8) |
| O4—C20—C25—C26 | 0.4 (7) | C33—C34—C35—C36 | −1.2 (9) |
| O4—C20—C25—C24 | −179.2 (4) | C5—C6—C7—N1 | 179.4 (4) |
| O4—C20—C21—C22 | 178.9 (4) | C5—C6—C7—C8 | −1.2 (6) |
| O1—C1—C2—C3 | −179.4 (5) | C5—C6—C1—O1 | 178.5 (4) |
| O6—C38—C33—C31 | −1.5 (7) | C5—C6—C1—C2 | 0.0 (7) |
| O6—C38—C33—C34 | 178.4 (4) | C5—C4—C3—C2 | 0.5 (8) |
| O6—C38—C37—C36 | −178.8 (5) | C32—C31—C33—C38 | 179.4 (4) |
| O11—Cu2—O3—C19 | −159.8 (4) | C32—C31—C33—C34 | −0.5 (7) |
| O8—Cu2—O3—C19 | 117.8 (4) | C34—C35—C36—C37 | 0.8 (9) |
| O8—Cu3—O4—C20 | −161.1 (4) | C18—C19—C14—C12 | 179.6 (4) |
| N1—Cu1—O1—C1 | 8.0 (4) | C18—C19—C14—C15 | −2.1 (6) |
| N3—Cu3—O4—C20 | 12.3 (4) | C21—C20—C25—C26 | 178.9 (4) |
| N3—C26—C25—C20 | 12.8 (6) | C21—C20—C25—C24 | −0.7 (6) |
| N3—C26—C25—C24 | −167.7 (4) | C21—C22—C23—C24 | −0.3 (7) |
| N3—C28—C29—O5 | −47.9 (4) | C35—C36—C37—C38 | −0.5 (9) |
| N3—C28—C29—C30 | −167.5 (4) | C37—C38—C33—C31 | 179.1 (4) |
| N2—Cu2—O3—C19 | 1.9 (4) | C37—C38—C33—C34 | −0.9 (7) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O9—H9*C*···O4 | 0.85 | 2.08 | 2.894 (5) | 159 |
| O9—H9*C*···O8 | 0.85 | 2.56 | 3.158 (5) | 128 |
| O9—H9*D*···O3 | 0.85 | 2.08 | 2.928 (5) | 175 |

| | | | | |
|---|---|---|---|---|
| C28—H28*A*···O1 | 0.97 | 2.58 | 3.427 (6) | 146 |
| C29—H29···O1$^{i}$ | 0.98 | 2.60 | 3.424 (5) | 142 |
| C10—H10···O6$^{ii}$ | 0.98 | 2.51 | 3.351 (6) | 144 |
| C8—H8*A*···O9$^{iii}$ | 0.96 | 2.44 | 3.372 (6) | 163 |
| C9—H9*B*···O6 | 0.97 | 2.65 | 3.521 (6) | 150 |
| C32—H32*A*···O9$^{iii}$ | 0.96 | 2.38 | 3.304 (6) | 162 |
| C42—H42*A*···O11$^{i}$ | 0.96 | 2.66 | 3.256 (7) | 121 |

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $-x+3/2, y+1/2, -z+1/2$.