Tetranuclear copper(II) complex of 2-hydroxy-N,N'-bis[1-(2-hydroxyphenyl)ethyldiene]propane-1,3-diamine

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The title molecular structure, namely, \((\mu_2\text{-acetato})(\mu_2\text{-acetato})\text{bis}(\mu_3\text{-1,3-bis[1-}\text{(2-oxidophenyl)ethyldiene} ]\text{amino} \text{propan-2-olato})\text{tetracopper(II)} \text{ monohydrate,} \ [\text{Cu}_4(\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3)\text{2(CH}_3\text{CO}_2)]\text{-H}_2\text{O,} \) corresponds to a non-symmetric tetranuclear copper complex. The complex exhibits one ligand molecule that connects two copper CuII 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 \(\eta^2:\eta^2\)-\(\mu_3\)-mode. A chair-like Cu3O3 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 CuO3N 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 CuO4N units and the CuO3N unit to another CuO3N unit, which is out of the chair-like structure. Each of the two pentacoordinated CuII cations has a distorted NO4 square-pyramidal environment. The geometry of each of the two CuNO3 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). Tetracoordinated (Asadi et al., 2018; Manna et al., 2019), pentacoordinated (Hari et al., 2019; Ghosh, Cléram et al., 2013) hexacoordinated (Shit et al., 2013; Kébé et al., 2021) and heptacoordinated (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., 2018a,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 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

\[ N,N'-\text{Bis[1-(2-hydroxyphenylethylidene)]-2-hydroxypropene-1, 3-diamine} \] (H\(_2\)L) was synthesized via a condensation reaction between 1,3-diaminopropan-2-ol and 1-(2-hydroxyphenylethane) in a 1:2 ratio in ethanol. Mixing H\(_2\)L and hydrated copper acetate yielded a tetranuclear complex formulated as \([\text{Cu}_4\text{L}_2\text{(CH}_3\text{CO}_2)_2\text{]}\cdot\text{H}_2\text{O}\) 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 (1-O\(_{\text{phenolate}}\), 2-N\(_{\text{imino}}, 3-O\(_{\text{enolato}}, 4-N\(_{\text{imino}}, 5-O\(_{\text{enolato}}, 6-N_{\text{imino}}\)) and heptadentate (1-O\(_{\text{phenolate}}, 2-N_{\text{imino}}, 3-O_{\text{enolato}}, 4-N_{\text{imino}}, 5-O_{\text{phenolate}}, 6-N_{\text{imino}}, 7-O_{\text{phenolate}}\)) fashions. Four five-membered CuOCN rings and four six-membered CuOCCCN rings are formed upon the coordination of the ligand molecules. In the tetranuclear complex, two discrete CuO\(_2\)N and CuO\(_2\)N 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) |
| Cu2–O3 | 1.877 (3) |
| Cu2–O11 | 1.940 (3) |
| Cu2–O8 | 2.703 (4) |
| Cu2–N2 | 1.961 (4) |
| Cu1–O5 | 2.749 (3) |
| Cu1–O2 | 1.916 (3) |
| Cu1–O10 | 1.982 (3) |
| Cu1–O1 | 1.876 (3) |
| O3–Cu2–O2 | 173.00 (15) |
| O11–Cu2–N2 | 161.66 (15) |
| O1—Cu1—O2 | 176.33 (14) |

Figure 1

A view of the title compound, showing the atom-numbering scheme.
square-pyramidal. The Addison τ parameter (Addison et al., 1984) calculated from the largest angles (Table 1; τ = 0 for perfect square-pyramidal and τ = 1 for perfect trigonal-bipyramidal geometries, respectively) around the metal ion are τ = 0.1103 for Cu1 and τ = 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 \( \eta^1\eta^1\mu_3 \) 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 \([\text{Cu1}–\text{N}_{\text{ligand}} = 1.966 (4) \, \text Å, \text{Cu1}–\text{O}_{\text{ligand}} = 1.878 (3) \, \text Å and \text{Cu1}–\text{O}_{\text{acetate}} = 1.982 (3) \, \text Å]\), as expected for a Jahn–Teller distortion (Monfared et al., 2009). The cisoid and transoid angles are in the ranges 85.01 (14)–95.10 (14)° and 161.66 (15)–173.00 (15)°, 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 \([\text{Cu2}–\text{N}_{\text{ligand}} = 1.961 (4) \, \text Å, \text{Cu2}–\text{O}_{\text{ligand}} = 1.877 (3) \, \text Å and \text{Cu2}–\text{O}_{\text{acetate}} = 1.940 (3) \, \text Å]\). 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: \text{Cu1}–\text{O2} = 1.916 (3) Å and \text{Cu2}–\text{O2} = 1.920 (3) Å. The distances between the \( \mu_2 \)-bridging ethanolato oxygen

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

| D–H—A | D–H | H···A | D···A | D–H···A |
|-------|-----|------|------|--------|
| O9—H9C···O4 | 0.85 | 2.08 | 2.894 (5) | 159 |
| O9—H9C···O8 | 0.85 | 2.56 | 3.158 (5) | 128 |
| O9—H9D···O3 | 1.97 | 2.58 | 3.437 (6) | 146 |
| C28–H28A···O1 | 0.98 | 2.60 | 3.424 (5) | 142 |
| C10–H10–O6\( ^\wedge \) | 0.98 | 2.51 | 3.351 (6) | 144 |
| C8–H8A···O9\( ^\wedge \) | 0.96 | 2.44 | 3.372 (6) | 163 |
| C9–H9B···O6 | 0.97 | 2.65 | 3.521 (6) | 150 |
| C32–H32A···O9\( ^\wedge \) | 0.96 | 2.38 | 3.304 (6) | 162 |
| C42–H42A···O1\( ^\wedge \) | 0.96 | 2.66 | 3.256 (7) | 121 |

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

The copper cations are very different: \text{Cu1}–O5 = 2.749 (3) Å, \text{Cu3}–O5 = 1.907 (3) Å and \text{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 \( \eta^1\eta^1\mu_2 \) acetate group (O8 for Cu3 and O7 for Cu4).

The \text{Cu3}–O4 [1.873 (3) Å], \text{Cu3}–O5 [1.907 (3) Å], \text{Cu3}–N3 [1.947 (4) Å], \text{Cu3}–O8 [1.957 (3) Å], \text{Cu4}–O6 [1.869 (3) Å], \text{Cu4}–O5 [1.921 (3) Å], \text{Cu4}–N4 [1.962 (4) Å] and \text{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 described as distorted square planar with r.m.s. deviations of 0.0787 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°, the tetragonality parameter (Singh et al., 2017) \( \tau_g \) 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.

3. Supramolecular features

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

![Figure 2](image2.png)

**Figure 2**

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

![Figure 3](image3.png)

**Figure 3**

Sheets parallel to the ac plane.
an oxygen atom of acetate group and C—H···Ophenoxo 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···Ophenoxo, C—H···Owater, C—H···Oacetate; 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)ethyldiene)]-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 NiII cations (KARPOK and KARPUQ (Liu et al., 2012); OMOFUS (Banerjee et al., 2011)). Four entries are complexes of CuII cations (KUKTAM (Basak et al., 2009); NADDIJ and NADDOF (Osypiuk et al., 2020), OVOWAA (Kébé et al., 2021)). In addition, two CoII complexes (OMOFOM and OMOGAZ; Banerjee et al., 2011), one FeIII (RIDHUJ; Biswas et al., 2013) and one VV 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, NADDOF 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)ethyldiene)]-2-hydroxypropane-1,3-diamine (HL2) 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 H2L. 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, ν, cm−1): 3538 (OH), 3268 (OH), 1605 (C=O), 1538 (C=C), 1528 (C=C), 1445 (C=C), 1247 (C=O), 1043, 760. Analysis calculated for C13H22N2O3: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.90; H, 6.76; N, 8.56%.

A solution of Cu(CH3CO2)2·(H2O) (0.1996 g, 1 mmol) in 5 mL of ethanol was added to a solution of H2L (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 [Cu4(C19H19N2O3)2(C2H3O2)2]·H2O.

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, CH2, CH3 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 $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for CH$_3$ and OH groups.

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References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Aly, M. M. (1999). *J. Coord. Chem.*

Asadi, Z., Golchin, M., Eigner, V., Dusek, M. & Amirghofran, Z. (2018). *J. Photochem. Photobiol. Chem.* **361**, 93–104.

Banerjee, A. & Chattopadhyay, S. (2019). *Acta Cryst.* **E**.

Biswas, R., Diaz, C., Bauza, A., Frontera, A. & Ghosh, A. (2013). *Dalton Trans.* **42**, 12274–12283.

Bruker (2016). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Das, A., Goswami, S. & Ghosh, A. (2018). *New J. Chem.* **42**, 19377–19389.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Ferguson, A., Parkin, A. & Murrie, M. (2006). *Dalton Trans.* pp. 3627–3628.

Fernandes, C., Neves, A., Vencato, I., Bortoluzzi, A. J., Drago, V., Weyhermüller, T. & Rentschler, E. (2000). *Chem. Lett.* **29**, 540–541.

Gheorghe, R., Ionita, G. A., Maxim, C., Caneschi, A., Sorace, L. & Andruh, M. (2019). *Polyhedron.* **171**, 269–278.

Ghosh, A. K., Bauza, A., Bertolasi, V., Frontera, A. & Ray, D. (2013). *Polyhedron.* **53**, 32–39.

Ghosh, A. K., Clérac, R., Mathonière, C. & Ray, D. (2013). *Polyhedron.* **54**, 196–200.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

Haldar, S., Patra, A., Vijaykumar, G., Carrella, L. & Bera, M. (2016). *Polyhedron.* **117**, 542–551.

Hari, N., Ghosh, S. & Mohanta, S. (2019). *Inorg. Chim. Acta.* **491**, 34–41.

Kébé, M., Thiam, I. E., Sow, M. M., Diouf, O., Barry, A. H., Sall, A. S., Retailleau, P. & Gaye, M. (2021). *Acta Cryst.* **E77**, 708–713.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Liu, S., Wang, S., Cao, F., Fu, H., Li, D. & Dou, J. (2012). *RSC Adv.* **2**, 1310–1313.

Lukov, V. V., Shcherbakov, I. N., Levchenkov, S. I., Popov, L. D. & Pankov, I. V. (2017). *Russ. J. Coord. Chem.* **43**, 1–20.

Mamour, S., Mayoro, D., Elhadj Ibrahim, T., Mohamed, G., Aliou Hamady, B. & Ellena, J. (2018). *Acta Cryst.* **E74**, 642–645.

Manna, S., Zangrando, E., Puschmann, H. & Manna, S. C. (2019). *Polyhedron.* **162**, 285–292.

Maurya, M. R., Bish, M., Chaudhary, N., Aveccilla, F., Kumar, U. & Hsu, H.-F. (2013). *Polyhedron.* **54**, 180–188.

Mitra, M., Maji, A. K., Ghosh, B. K., Raghavaiah, P., Ribas, J. & Ghosh, R. (2014). *Polyhedron.* **67**, 19–26.

Monfared, H. H., Sanchez, J., Kalantari, Z. & Jania, C. (2009). *Inorg. Chim. Acta.* **362**, 3791–3795.

Nesterova, O. V., Bondarenko, O. E., Ponomario, A. J. L. & Nesterov, D. S. (2020). *Dalton Trans.* **49**, 4710–4724.

Ospiuik, D., Cristovão, B. & Bartysz, A. (2020). *Crystals.* **10**, 1004.

Patra, A., Haldar, S., Kumar, G. V., Carrella, L., Ghosh, A. K. & Bera, M. (2015). *Inorg. Chim. Acta.* **436**, 195–204.

Popov, L. D., Levchenkov, S. I., Shcherbakov, I. N., Lukov, V. V., Suponitsky, K. Y. & Kogan, V. A. (2012). *Inorg. Chem. Commun.* **17**, 1–4.

Sall, O., Tamboura, F. B., Sy, A., Barry, A. H., Thiam, E. I., Gaye, M. & Ellena, J. (2019). *Acta Cryst.* **E75**, 1069–1075.

Sanyal, R., Ketkov, S., Purkait, S., Maurer, F. N., Xhigulin, G. & Das, D. (2017). *New J. Chem.* **41**, 8586–8597.

Sarr, M., Diop, M., Thiam, I. E., Gaye, M., Barry, A. H., Alvarez, N. & Ellena, J. (2018a). *Eur. J. Chem.* **9**, 67–73.

Sarr, M., Diop, M., Thiam, I. E., Gaye, M., Barry, A. H., Orton, J. B. & Coles, S. J. (2018b). *Acta Cryst.* **E74**, 1862–1866.

Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

Shit, S., Nandy, M., Rosair, G., Fadilah, M. S. E., Ribas, J., Garrubba, E. & Mitra, S. (2013). *Polyhedron.* **52**, 963–969.

Silviu, G. S. & Murthy, N. N. (2009). *Polyhedron.* **28**, 2149–2156.

Singh, Y. P., Patel, R. N., Singh, Y., Choquesillo-Lazarte, D. & Butcher, R. J. (2017). *Dalton Trans.* **46**, 2803–2820.

Song, Y., Gamez, P., Roubeau, O., Lutz, M., Spek, A. L. & Reedijk, J. (2003). *Eur. J. Inorg. Chem.* pp. 2924–2928.

Xie, Q.-W., Chen, X., Hu, K.-Q., Wang, Y.-T., Cui, A.-L. & Kou, H.-Z. (2012). *Polyhedron.* **38**, 213–217.
**Tetranuclear copper(II) complex of 2-hydroxy-\(N,N'\)-bis[1-(2-hydroxyphenyl)ethylidene]propane-1,3-diamine**

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**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).

\[
(\mu_3\text {-Acetato})(\mu_2\text {-acetato})\text {bis(\mu}_3\text {,1,3-bis[[1-(2-oxidophenyl)ethylidene]amino]propan-2-olato})\text {tetracopper(II)}
\]

**Crystal data**

\[
[Cu_4(C_19H_{19}N_2O_3)_{2}(C_2H_3O_2)_2]\cdot H_2O
\]

\[
M_r = 1037.02
\]

Monoclinic, \(P_2_1/n\)

\[
a = 6.9688\ (1)\ \text{Å}
\]

\[
b = 25.8066\ (4)\ \text{Å}
\]

\[
c = 22.8290\ (4)\ \text{Å}
\]

\[
\beta = 95.418\ (2)^\circ
\]

\[
V = 4087.25\ (11)\ \text{Å}^3
\]

\[
Z = 4
\]

**Data collection**

Nonius KappaCCD diffractometer

CCD scans

Absorption correction: multi-scan

(SADABS; Krause *et al*., 2015)

\[
T_{\text{min}} = 0.967,\ T_{\text{max}} = 1.000
\]

12039 measured reflections

12039 independent reflections

10024 reflections with \(I > 2\sigma(I)\)

\[
R_{\text{int}} = 0.008
\]

\[
\theta_{\text{max}} = 27.6^\circ,\ \theta_{\text{min}} = 1.8^\circ
\]

\[
h = -9\rightarrow9
\]

\[
k = -33\rightarrow33
\]

\[
l = -29\rightarrow28
\]

**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

\[
w = 1/[\sigma(F_c^2) + (0.038P)^2 + 21.6332P]
\]

\[
\Delta F_{\text{max}} = 1.69\ \text{e Å}^{-3}
\]

\[
\Delta F_{\text{min}} = -0.88\ \text{e Å}^{-3}
\]
**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)**

| Atom | x       | y       | z       | Uiso/* | Ueq   |
|------|---------|---------|---------|--------|-------|
| 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     | −0.09428     | 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)   |       |
| Atomic  | x     | y     | z     | Ueq  | Ueq  |
|---------|-------|-------|-------|------|------|
| C17     | 0.7117 (7) | 0.12003 (18) | 0.4666 (2) | 0.0174 (10) | 0.021* |
| H17     | 0.710667 | 0.084111 | 0.469778 | 0.0121 (9) |      |
| C28     | 0.8313 (6) | 0.37427 (16) | 0.09623 (19) | 0.014* |      |
| 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) | 0.015* |
| H29     | 1.088626 | 0.380870 | 0.148407 | 0.015* |      |
| C11     | 0.6906 (6) | 0.36775 (17) | 0.40348 (19) | 0.0126 (9) | 0.015* |
| H11A    | 0.822806 | 0.379269 | 0.402534 | 0.015* |      |
| H11B    | 0.640320 | 0.382256 | 0.438117 | 0.015* | 0.0129 (9) |
| C10     | 0.5701 (6) | 0.38526 (17) | 0.3486 (2) | 0.0149 (9) |      |
| H10     | 0.433277 | 0.380043 | 0.353554 | 0.149 (9) | 0.015* |
| C6      | 0.4719 (6) | 0.50930 (18) | 0.1912 (2) | 0.0123 (9) |      |
| C7      | 0.5306 (6) | 0.49832 (17) | 0.2530 (2) | 0.0149 (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) | 0.0150 (9) |
| C15     | 0.7586 (7) | 0.20325 (18) | 0.5103 (2) | 0.015* |      |
| 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 | 0.343604 | 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) |      |
### Supporting Information

Atomic displacement parameters ($\AA^2$)

|        | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|--------|-----------|-----------|-----------|----------|----------|----------|
| 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) |

*Estimated standard deviations in parentheses.
### Geometric parameters (Å, °)

|                  | Cu2—O2 | Cu2—O3 | Cu2—O11 | Cu2—O8 | Cu2—N2 | Cu1—O5 | Cu1—O2 |
|------------------|--------|--------|---------|--------|--------|--------|--------|
| C17—C18          | 1.920 (3) | 1.877 (3) | 1.940 (3) | 2.703 (4) | 1.961 (4) | 2.749 (3) | 1.916 (3) |
| C17—C18          |        |        |         |        |        |        |        |

**sup-5**

*Acta Cryst.* (2022), E78, 349-353
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
| Bond          | Distance  |
|---------------|-----------|
| C27—H27C     | 0.9600    |
| C14—C12      | 1.466 (6) |
| C14—C15      | 1.412 (6) |
| C25—C24      | 1.409 (6) |
| C17—H17      | 0.9300    |
| O2—Cu2—O11   | 96.89 (14) |
| O2—Cu2—O8    | 84.89 (12) |
| O2—Cu2—N2    | 115.93 (13)|
| O2—Cu1—O5    | 80.48 (12) |
| O2—Cu1—O10   | 95.10 (14) |
| O2—Cu1—N1    | 85.01 (14) |
| O10—Cu1—O5   | 83.75 (13) |
| O1—Cu1—O5    | 97.68 (12) |
| O1—Cu1—O2    | 176.33 (14)|
| O1—Cu1—O10   | 87.83 (14) |
| O1—Cu1—N1    | 92.51 (15) |
| N1—Cu1—O5    | 106.38 (13)|
| N1—Cu1—O10   | 169.71 (16)|
| O5—Cu3—O8    | 92.44 (14) |
| O5—Cu3—N3    | 86.17 (14) |
| O4—Cu3—O5    | 177.07 (15)|
| O4—Cu3—O8    | 88.43 (14) |
| O4—Cu3—N3    | 93.29 (15) |
| N3—Cu3—O8    | 173.28 (15)|
| O5—Cu4—O7    | 96.93 (14) |
| O5—Cu4—N4    | 84.04 (14) |
| O7—Cu4—N4    | 164.11 (15)|
| O6—Cu4—O5    | 170.48 (14)|
| O6—Cu4—O7    | 87.96 (14) |
| O6—Cu4—N4    | 93.50 (15) |
| Cu3—O5—Cu1   | 98.74 (12) |
| Cu3—O5—Cu4   | 129.24 (17)|
| Cu4—O5—Cu1   | 95.83 (12) |
| C29—O5—Cu1   | 116.7 (2)  |
| C29—O5—Cu3   | 108.9 (3)  |
| C29—O5—Cu4   | 107.0 (2)  |
| Cu1—O2—Cu2   | 129.60 (17)|
| C10—O2—Cu2   | 105.8 (3)  |
| C10—O2—Cu1   | 108.9 (3)  |
| C39—O10—Cu1  | 132.3 (3)  |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| 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)    |
| Cu4—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        |
| Bond Combination               | Angle (°) | Bond Combination               | Angle (°) | Bond Combination               | Angle (°) |
|-------------------------------|----------|-------------------------------|----------|-------------------------------|----------|
| 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    | C36—C35—H36                  | 119.9    |                             |          |
| C29—C28—H28B                 | 110.4    | C37—C36—H36                  | 120.2 (5)|                             |          |
| O5—C29—C28                   | 108.0 (3)| C37—C36—H36                  | 119.9    |                             |          |
| O5—C29—C29                   | 109.3    | C38—C37—H37                  | 119.1    |                             |          |
| O5—C29—C30                   | 108.4 (4)| C36—C37—C38                  | 121.8 (5)|                             |          |
| C28—C29—C29                  | 109.3    | C36—C37—H37                  | 119.1    |                             |          |
| 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—C25               | 177.3 (4)|                             |          |
| Cu1—O1—C1—C2                 | 174.4 (3)| C28—C29—C30—N4               | 160.4 (4)|                             |          |
| Cu1—N1—C7—C6                 | 8.2 (6)  | C11—N2—C12—C13               | 0.8 (6)  |                             |          |
| Cu1—N1—C7—C8                 | −171.3 (3)| C11—N2—C12—C14              | −179.7 (4)|                             |          |
| 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) |                             |          |
### Hydrogen-bond geometry (Å, °)

| D       | H  | A      | D···A   | D—H···A |
|---------|----|--------|---------|---------|
| O9—H9C| 0.85 | 2.08   | 2.894 (5) | 159     |
| O9—H9C | 0.85 | 2.56   | 3.158 (5) | 128     |
| O9—H9D | 0.85 | 2.08   | 2.928 (5) | 175     |

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**Acta Cryst. (2022), E78, 349-353**

sup-10
C28—H28\(\cdots\)O1  
C29—H29\(\cdots\)O1\(\text{ii}\)  
C10—H10\(\cdots\)O6\(\text{ii}\)  
C8—H8\(\cdots\)O9\(\text{iii}\)  
C9—H9\(\cdots\)O6  
C32—H32\(\cdots\)O9\(\text{iii}\)  
C42—H42\(\cdots\)O11\(\text{i}\)

| Bond          | r (Å) | d (Å)  | E (kcal mol\(^{-1}\)) | Angle (°) |
|---------------|-------|--------|------------------------|-----------|
| C28—H28\(\cdots\)O1 | 0.97  | 2.58   | 3.427 (6)              | 146       |
| C29—H29\(\cdots\)O1\(\text{ii}\) | 0.98  | 2.60   | 3.424 (5)              | 142       |
| C10—H10\(\cdots\)O6\(\text{ii}\) | 0.98  | 2.51   | 3.351 (6)              | 144       |
| C8—H8\(\cdots\)O9\(\text{iii}\) | 0.96  | 2.44   | 3.372 (6)              | 163       |
| C9—H9\(\cdots\)O6       | 0.97  | 2.65   | 3.521 (6)              | 150       |
| C32—H32\(\cdots\)O9\(\text{iii}\) | 0.96  | 2.38   | 3.304 (6)              | 162       |
| C42—H42\(\cdots\)O11\(\text{i}\) | 0.96  | 2.66   | 3.256 (7)              | 121       |

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