Crystal structure, Hirshfeld surface analysis and DFT studies of tetrakis(μ-3-nitrobenzoato-κ2O1:O1′)bis[(N,N-dimethylformamide-κO)-copper(II)] dimethylformamide disolvate

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The title compound, [Cu2(C7H4NO4)2(C3H7NO)2](C3H7NO), is a binuclear copper(II) complex located on an inversion center midway between the two copper(II) cations. The asymmetric unit consists of one CuII cation, two 3-nitrobenzoato ligands, and two dimethylformamide (DMF) molecules, one of which coordinates to the CuII cation and one is a solvate molecule. The carboxylate groups of the ligands bridge two CuII cations with a Cu—Cu distance of 2.6554 (6) Å, completing a distorted octahedral O6Cu coordination environment. The dihedral angles between the carboxylate and the aromatic ring planes of the two independent ligands are different from one another, viz. 5.2 (3) and 23.9 (3)°. The three-dimensional structure is consolidated by weak C—H···O interactions and stabilized by π-π stacking interactions between the aromatic rings. The complex and the free ligand were further characterized by Fourier-transform infrared spectroscopy (FT–IR), and the energies of the frontier molecular orbitals of the complex were determined by DFT calculations at the B3LYP/def2-TZVP level of theory.

1. Chemical context

Copper complexes have been explored extensively due to the fact that copper is a bio-essential element responsible for numerous bioactivities in living organisms (Tapiero & Tew, 2003). Moreover, it is well known that CuII complexation plays an important role in the pharmacological profile of antimicrobial activities (Haiduca & Silvestru, 1989; Linder & Goode, 1991). The first syn–syn bridged binuclear structure of a large number of copper(II) carboxylates with general formula [Cu(RCOO)2(L)]2 (L = co-ligand), was reported for simple copper(II) acetate monohydrate (Van Niekerk & Schoening, 1953). This classical structure consists of a binuclear [Cu2O4] unit in which each copper(II) atom is surrounded by four oxygen atoms of carboxylate groups in an almost square-planar coordination. An additional ligand, here the O atom of a water molecule, is attached in an apical position at longer Cu—O distances. The Cu—Cu contact completes a distorted octahedral coordination sphere around each copper(II) atom. This motif is also observed in polymeric copper(II) carboxylates, where the apical ligand has two coordination centers and links dimeric units (Rao et al., 1983; Zhu et al., 2003). In the situation where the apical ligand is absent, a zigzag polymeric structure is formed with direct
bonding between [Cu₂O₈] units via the metal and one of the basal oxygen atoms of the neighbouring unit (Drozdowski et al., 2004).

Copper(II) carboxylates, including copper(II) benzoates, have been studied extensively from different points of view, because the carboxylato ligands exhibit different binding modes that are related to their properties, e.g. the basicity of the anion or the position of substituents on the aromatic ring. A bulky benzene ring substituent in an ortho position to the carboxylate group is believed to prefer the dimeric copper(II) benzoate structure (Harrison et al., 1972; Ueyama et al., 1996). In general, copper(II) carboxylates exhibit a dimeric paddle-wheel cage structure. More than 500 crystal structures containing the Cu₂(OOCR)₄ core have been determined on the basis of X-ray data and can be found in the Cambridge Structural Database (Groom et al., 2016), of which more than 250 are of the type [Cu₂(OOCR)₄(L)₂], where L is an apical ligand with an oxygen, a nitrogen, a chlorine or a phosphorus donor atom. We report here on the molecular and crystal structure of a similar binuclear copper(II) complex, [Cu₂(C₇H₄NO₄)(C₃H₇NO)₂]·(C₃H₇NO)₂, further characterized by infrared spectroscopy and DFT calculations.

2. Structural commentary

[Cu₂(C₇H₄NO₄)₂(C₃H₇NO)₂]·(C₃H₇NO)₂ crystallizes as a dimethylformamide disolvate (Fig. 1). The neutral [Cu₂(C₇H₄NO₄)(C₃H₇NO)₂] complex is centrosymmetric, with the inversion center located midway between the two CuII cations. The asymmetric unit comprises one CuII cation, two 3-nitrobenzoato ligands and two dimethylformamide molecules, one ligating and one as a solvent. The complex displays a paddle-wheel-shaped binuclear structure. Each CuII cation is coordinated by four carboxylate oxygen atoms, forming the base of a slightly distorted square pyramid supplemented by a fifth oxygen atom of the dimethylformamide molecule at the apical position (Fig. 1). The overall distorted octahedral coordination environment is completed by the neighbouring CuII cation with a Cu—Cu distance of 2.6554 (6) Å. This distance is close to that reported for similar binuclear complexes (Wang et al., 2018).

In the binuclear complex, the carboxylate groups of the 3-nitrobenzoato ligands link the two CuII cations with short Cu—O distances [from 1.9620 (17) to 1.9751 (16) Å; Table 1] whereas the distance to the O atom of the dimethylformamide ligand is elongated [2.1453 (17) Å]. The carboxylate groups of the 3-nitrobenzoato ligands adopt a bidentate syn–syn bridging mode (Su et al., 2015; Wang et al., 2018), with dihedral angles between the carboxylate planes and the aromatic rings of 5.2 (3) and 23.9 (3)°, respectively.

3. Supramolecular features

The binuclear complex molecules are allocated with their central parts parallel to (001). The crystal packing shows slipped π–π stacking interactions between the aromatic rings of symmetry-related 3-nitrobenzoato ligands [Cg1···Cg1(−x + 2, −y + 1, −z + 1) = 4.117 (2) Å where Cg1 is the centroid of the C9–C14 phenyl ring; slippage 2.202 Å]. The nitro group of the second 3-nitrobenzoato ligand weakly interacts by O···C contacts [O7···C17(−x + 1, y + 1/2, −z + 3/2) = 3.087 (3) Å] with the coordinating dimethylformamide molecule, forming zigzag chains parallel to [01T]. Through these interactions, the complex molecules form a channel-like

| Table 1 | Selected bond lengths (Å) |
|---------|--------------------------|
| Cu1−O1  | 1.9620 (17)              |
| Cu1−O3  | 1.9650 (16)              |
| Cu1−O2  | 1.9719 (18)              |
| Cu1−O4  | 1.9751 (16)              |
| Cu1−O5  | 2.1453 (17)              |
| Cu1−Cu1 | 2.6554 (6)               |

Symmetry code: (i) −x + 1, −y + 1, −z + 1.
structure with the channels, in which the dimethylformamide solvate molecules are located, extending parallel to [010]. They interact via weak amide-π interactions [N4···Cg1 = 3.597 (3) Å] and weak C—H···O(nitro group) hydrogen bonds (Fig. 2, Table 2). The latter interactions cause a greater rotation [23.9 (3)°] of the aromatic ring relative to the carboxylate group in the second 3-nitrobenzoato ligand.

4. Hirshfeld surface analysis

Intramolecular and intermolecular interactions of \([\text{Cu}_2(C_7H_4NO_4)_4(C_3H_7NO)_2]\) were quantified by Hirshfeld surface analysis using Crystal Explorer 17.5 (Turner et al., 2017). The presence of strong interactions on the Hirshfeld surface is indicated by red spots, while the blue areas indicate weak interactions, as shown in Fig. 3. Two-dimensional fingerprint plots with all interactions and delineated into individual contacts with relative contributions are displayed in Fig. 4. The most important intermolecular interactions are O···H/H···O (38.9%), followed by H···H (33.3%), C···H/H···C (12.7%) and O···C/C···O (5.9%). Other interactions contribute less than 5% to the overall Hirshfeld surface.

5. DFT calculations

Theoretical calculations were carried out by the hybrid density functional theory (DFT) at the B3LYP level of theory (Becke, 1988; Lee et al., 1988) using Aldrich’s def2-TZVP basis set, which has been successfully tested in one of our previous

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|-------|
| C4···H4···O4 | 0.93 | 2.47 | 3.360 (4) | 161 |
| C15···H15···O1 | 0.93 | 2.50 | 3.100 (4) | 123 |
| C16···H16···O5 | 0.96 | 2.40 | 2.770 (4) | 102 |
| C19···H19···O10 | 0.96 | 2.35 | 2.753 (8) | 104 |
| C20···H20···O10 | 0.96 | 2.59 | 3.503 (7) | 160 |

Symmetry codes: (ii) −x + 1, y − ½, −z + ½; (iii) −x + 2, y + ½, −z + ½.
studies (Ibragimov et al., 2021). Input files for the DFT calculations using the ORCA 4.2.0 program package (Neese, 2012) were generated by Avogadro (Hanwell et al., 2012) using the CIF of the title compound. Results of these calculations were analyzed with the aid of Avogadro and Multiwfn (Lu & Chen, 2012).

Homonuclear CuII complexes form a closed system in which [Ar]d9 electrons of two neighbouring CuII cations are paired with each other. Such a system is usually characterized by a singlet ground state. However, triplet and quintet electronic states are also possible, depending on the nature of the ligand molecules. The bond lengths and angles of the complex were therefore fully optimized in the singlet, triplet and quintet electronic spin states with the result that the singlet electronic state was found to be the energetically optimal structure. Calculated and experimentally determined bond lengths and angles are compared in Tables S1 and S2 in the supporting information, and mean absolute errors (MAE), largest errors (LE) and the correlation coefficients $R^2$ were determined. The very low values of MAE and LE, and also the high $R^2$ coefficient of 0.997 reveal the suitability of the applied method for calculation of the electronic structure parameters of the complex.

Calculations of electron densities on atoms in the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals (MO), as well as the energies of the frontier MOs (FMO) were carried out. The charge distributions on atoms and on the FMOs, as well as the energy of FMOs are one of the main parameters of the electronic structure of chemical compounds (Karelson et al., 1996; Rauk, 2001; Miar et al., 2021). The energy of the HOMO is related to the electron-donating ability of a molecule and the energy of the LUMO is related to the electron-accepting ability of a molecule. The parameter for chemical hardness (η) is calculated based on the HOMO–LUMO energy gap ($\eta = \Delta E/2$). The shape of the FMOs and the HOMO–LUMO energy gap of the complex are displayed in Fig. 5. The contribution of both CuII d orbitals in the HOMO and LUMO are 58.14% and 52.72%, respectively. The contribution of the p orbitals of the eight oxygen atoms of the 3-nitrobenzoate ligands in the HOMO and LUMO are 37.15% and 38.06%, respectively. A higher contribution of CuII d electrons (56.74%) was observed in the case of second occupied MO ($E_{\text{HOMO-1}} = -7.0 \text{ eV}$), and the next unoccupied MO ($E_{\text{LUMO+1}} = -2.74 \text{ eV}$) consists of the antibonding p orbitals of the 3-nitrobenzoate fragment.

The complex has a very low HOMO–LUMO energy gap, which can be seen from Fig. 5 and also from the total density of state diagram (TDOS, Fig. S1) of the complex. The low energy gap is caused by a significant decreasing of the energy level of the LUMO of the complex. In other words, the electron accepting ability of the complex is very high and thus the molecule becomes more susceptible to nucleophile attack which makes this complex interesting in chemistry and physics due to its electrical properties and light absorption at a low energy level.

Atomic charge analysis (Fig. S2) shows that the largest negative charges and the largest positive charges are located on oxygen atoms and carbon atoms of the carboxylic group, respectively.

6. FT–IR analysis

The FT–IR (ATR) spectrum of dimethylformamide (see Fig. S1) comprises the following absorption bands (cm$^{-1}$): 2926, 2856 (–CH, NCH$_3$), 2780 (C–H, CHO), 1662 (C=O), 1384 (CH, NCH$_3$), 1089 (C–N). The FTIR (ATR) spectrum of 3-nitrobenzoic acid (Fig. 6) comprises the following absorption bands (cm$^{-1}$): 3095 (C–H, Ar), 2500–3000 (OH, dimeric form), 1689 (C=O), 1614, 1583 (Ar), 1525, 1350 (–NO$_2$), 1288 (C–O, COOH). The FTIR (ATR) spectrum of the
Table 3
Experimental details.

| Crystal data | Chemical formula | [Cu₂(C₇H₄NO₄)₄(C₃H₇NO)₂]·2C₇H₄NO |
|--------------|------------------|------------------------------------|
| M₀           | 1083.91          |                                    |
| Crystal system, space group | Monoclinic, P2₁/c | |
| Temperature (K) | 293             |                                    |
| a, b, c (Å) | 11.5657 (4), 10.4851 (3), 19.7258 (5) | |
| β (°)       | 91.581 (3)       |                                    |
| V (Å³)      | 2391.19 (12)     |                                    |
| Z           | 2                |                                    |
| Radiation type | Cu K             |                                    |
| μ (mm⁻¹)    | 1.84             |                                    |
| Crystal size (mm) | 0.20 × 0.15 × 0.10 | |

Data collection

| Diffractometer | Xcalibur, Ruby |
|----------------|----------------|
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2018) |
| T_max, T_min | 0.386, 1.000 |
| No. of measured, independent and observed | 17186, 4940, 4016 |
| R_wp | 0.041 |
| (sin θ/λ)max (Å⁻¹) | 0.630 |

Refinement

| R(F² > 2σ(F²)), wR(F²), S | 0.043, 0.120, 1.05 |
| No. of reflections | 4940 |
| No. of parameters | 320 |
| H-atom treatment | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.38, -0.66 |

Computer programs: CrysAlis PRO (Rigaku OD, 2018), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and pubCIF (Westrip, 2010).

8. Synthesis and crystallization

The crystals were grown from low-cost standard materials. 3-Nitrobenzoic acid (20.0 mg, 0.12 mmol) and CuSO₄·5H₂O (20 mg, 0.056 mmol) were mixed and stirred at room temperature for 1 h. Then, in a gradual way, dimethylformamide (DMF; 0.78 mmol) was added dropwise to the stirred mixture throughout 60 min at 303 K, immediately after which the solution was cooled down and kept for several hours. Darkish blue single crystals suitable for X-ray analysis were grown by slow evaporation at ambient temperature for one week and collected by filtration. They were finally washed with pure DMF. Yield: 70%.

9. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms bonded to carbon atoms were placed in calculated positions and refined to ride on their parent atoms with C—H = 0.93 Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogen atoms, and with C—H = 0.96 Å and Uiso(H) = 1.5Ueq(C) for methyl hydrogen atoms.

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Crystal structure, Hirshfeld surface analysis and DFT studies of tetrakis(μ-3-nitrobenzoato-κ²O¹:O¹′)bis[(N,N-dimethylformamide-κO)copper(II)] dimethylformamide disolvate

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2018); cell refinement: CrysAlis PRO (Rigaku OD, 2018); data reduction: CrysAlis PRO (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: publCIF (Westrip, 2010).

Tetrakis(μ-3-nitrobenzoato-κ²O¹:O¹′)bis[(N,N-dimethylformamide-κO)copper(II)] dimethylformamide disolvate

Crystal data

[Cu₂(C₇H₄NO₄)₂(C₃H₇NO)₂]·2C₃H₇NO

Mr = 1083.91

Monoclinic, P2₁/c

a = 11.5657 (4) Å
b = 10.4851 (3) Å
c = 19.7258 (5) Å
β = 91.581 (3)°

V = 2391.19 (12) Å³

Z = 2

F(000) = 1116

Dₐ = 1.505 Mg m⁻³

Cu Kα radiation, λ = 1.54184 Å

Cell parameters from 5941 reflections

θ = 4.2–75.5°

µ = 1.84 mm⁻¹

T = 293 K

Plate, blue

0.20 × 0.15 × 0.10 mm

Data collection

Xcalibur, Ruby diffractometer

Radiation source: Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 10.2576 pixels mm⁻¹

wσcans Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)

Tmin = 0.366, Tmax = 1.000

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.043

wR(F²) = 0.120

S = 1.05

4940 reflections

320 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
**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.

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

|    | x     | y     | z     | Uiso*/Ueq |
|----|-------|-------|-------|-----------|
| Cu1| 0.52536 (3) | 0.37834 (3) | 0.48912 (2) | 0.03259 (12) |
| O1 | 0.67889 (15) | 0.43281 (17) | 0.52255 (9)  | 0.0438 (4)   |
| O2 | 0.63778 (15) | 0.63846 (16) | 0.54126 (9)  | 0.0442 (4)   |
| O3 | 0.48321 (16) | 0.35248 (16) | 0.58396 (8)  | 0.0447 (4)   |
| O4 | 0.43655 (16) | 0.55704 (16) | 0.60163 (8)  | 0.0438 (4)   |
| O5 | 0.57752 (17) | 0.18687 (16) | 0.46685 (9)  | 0.0474 (4)   |
| O6 | 0.2420 (2)   | 0.6543 (3)   | 0.81319 (13) | 0.0853 (8)   |
| O7 | 0.2426 (3)   | 0.5167 (3)   | 0.89371 (12) | 0.0977 (10)  |
| O8 | 1.1930 (2)   | 0.3843 (3)   | 0.60860 (15) | 0.0927 (9)   |
| O9 | 1.0475 (2)   | 0.2614 (3)   | 0.59089 (17) | 0.1004 (10)  |
| N1 | 0.7192 (2)   | 0.0413 (2)   | 0.45278 (11) | 0.0533 (6)   |
| N2 | 0.2717 (2)   | 0.5527 (3)   | 0.83778 (12) | 0.0612 (7)   |
| N3 | 1.0906 (2)   | 0.3660 (3)   | 0.59792 (14) | 0.0659 (8)   |
| C1 | 0.4512 (2)   | 0.4433 (2)   | 0.62026 (11) | 0.0376 (5)   |
| C2 | 0.4313 (2)   | 0.4157 (2)   | 0.69403 (11) | 0.0376 (5)   |
| C3 | 0.4849 (3)   | 0.3128 (3)   | 0.72534 (13) | 0.0509 (7)   |
| H3 | 0.5305       | 0.2581       | 0.7004       | 0.061*       |
| C4 | 0.4709 (3)   | 0.2912 (3)   | 0.79400 (15) | 0.0614 (8)   |
| H4 | 0.5092       | 0.2233       | 0.8150       | 0.074*       |
| C5 | 0.4012 (3)   | 0.3685 (3)   | 0.83118 (13) | 0.0543 (7)   |
| H5 | 0.3909       | 0.3534       | 0.8771       | 0.065*       |
| C6 | 0.3469 (2)   | 0.4689 (3)   | 0.79880 (12) | 0.0445 (6)   |
| C7 | 0.3616 (2)   | 0.4953 (2)   | 0.73090 (12) | 0.0411 (6)   |
| H7 | 0.3253       | 0.5651       | 0.7105       | 0.049*       |
| C8 | 0.7049 (2)   | 0.5442 (2)   | 0.54082 (11) | 0.0373 (5)   |
| C9 | 0.8275 (2)   | 0.5637 (2)   | 0.56579 (12) | 0.0398 (5)   |
| C10| 0.8687 (3)   | 0.6832 (3)   | 0.58268 (15) | 0.0547 (7)   |
| H10| 0.8197       | 0.7534       | 0.5794       | 0.066*       |
| C11| 0.9830 (3)   | 0.6997 (3)   | 0.60457 (18) | 0.0701 (9)   |
| H11| 1.0098       | 0.7807       | 0.6161       | 0.084*       |
| C12| 1.0562 (3)   | 0.5977 (3)   | 0.60927 (17) | 0.0654 (9)   |
| H12| 1.1332       | 0.6084       | 0.6231       | 0.078*       |
| C13| 1.0132 (2)   | 0.4784 (3)   | 0.59303 (14) | 0.0504 (7)   |
| C14| 0.9006 (2)   | 0.4592 (3)   | 0.57205 (12) | 0.0449 (6)   |
| H14| 0.8736       | 0.3776       | 0.5622       | 0.054*       |
| C15| 0.6799 (3)   | 0.1556 (3)   | 0.46790 (13) | 0.0482 (6)   |
### Atomic displacement parameters (Å²)

|   | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| Cu1 | 0.0397 (2) | 0.02672 (19) | 0.03118 (18) | 0.00108 (14) | −0.00230 (14) | −0.00010 (12) |
| O1 | 0.0408 (10) | 0.0382 (9) | 0.0517 (10) | 0.0001 (8) | −0.0074 (8) | −0.0067 (8) |
| O2 | 0.0428 (10) | 0.0384 (10) | 0.0511 (10) | 0.0009 (8) | −0.0070 (8) | −0.0056 (8) |
| O3 | 0.0604 (12) | 0.0393 (10) | 0.0346 (8) | 0.0024 (8) | 0.0043 (8) | 0.0023 (7) |
| O4 | 0.0626 (12) | 0.0360 (9) | 0.0328 (8) | −0.0022 (8) | 0.0026 (8) | 0.0038 (7) |
| O5 | 0.0572 (12) | 0.0315 (9) | 0.0533 (10) | 0.0070 (8) | 0.0008 (9) | −0.0047 (8) |
| O6 | 0.108 (2) | 0.0639 (15) | 0.0859 (17) | 0.0257 (15) | 0.0341 (15) | 0.0078 (13) |
| O7 | 0.125 (2) | 0.122 (2) | 0.0477 (13) | 0.0305 (19) | 0.0330 (14) | 0.0112 (14) |
| O8 | 0.0399 (13) | 0.133 (3) | 0.105 (2) | 0.0118 (14) | −0.0095 (13) | 0.0151 (17) |
| O9 | 0.0694 (17) | 0.0748 (18) | 0.156 (3) | 0.0204 (15) | −0.0189 (17) | −0.0202 (19) |
| N1 | 0.0728 (17) | 0.0353 (12) | 0.0528 (13) | 0.0130 (11) | 0.0181 (12) | 0.0010 (10) |
| N2 | 0.0669 (17) | 0.0692 (18) | 0.0480 (13) | 0.0005 (14) | 0.0093 (12) | −0.0031 (13) |
| N3 | 0.0449 (16) | 0.089 (2) | 0.0635 (16) | 0.0140 (15) | −0.0027 (12) | 0.0034 (15) |
| C1 | 0.0405 (13) | 0.0390 (13) | 0.0330 (11) | −0.0051 (11) | −0.0030 (9) | 0.0045 (10) |
| C2 | 0.0425 (14) | 0.0361 (12) | 0.0339 (11) | −0.0029 (11) | −0.0014 (10) | 0.0042 (9) |
| C3 | 0.0568 (17) | 0.0503 (16) | 0.0456 (14) | 0.0095 (14) | 0.0034 (12) | 0.0074 (12) |
| C4 | 0.074 (2) | 0.062 (2) | 0.0476 (15) | 0.0153 (17) | −0.0003 (14) | 0.0188 (14) |
| C5 | 0.0636 (19) | 0.0632 (19) | 0.0359 (13) | 0.0016 (15) | 0.0001 (12) | 0.0138 (12) |
| C6 | 0.0498 (15) | 0.0479 (15) | 0.0361 (12) | −0.0027 (12) | 0.0035 (11) | 0.0015 (11) |
| C7 | 0.0435 (14) | 0.0391 (14) | 0.0404 (12) | −0.0016 (11) | −0.0025 (10) | 0.0076 (10) |
| C8 | 0.0409 (13) | 0.0399 (13) | 0.0310 (11) | −0.0013 (11) | −0.0013 (9) | 0.0010 (9) |
| C9 | 0.0402 (14) | 0.0434 (14) | 0.0357 (11) | −0.0029 (11) | −0.0014 (10) | −0.0003 (10) |
| C10 | 0.0547 (17) | 0.0478 (16) | 0.0610 (17) | −0.0100 (14) | −0.0097 (14) | 0.0025 (13) |
supporting information

Geometric parameters (Å, °)

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| Cu1—O1           | 1.9620   | C6—C7            | 1.383    |
| Cu1—O3           | 1.9650   | C7—H7            | 0.930    |
| Cu1—O2i          | 1.9719   | C8—C9            | 1.502    |
| Cu1—O4i          | 1.9751   | C9—C10           | 1.378    |
| Cu1—O5           | 2.1453   | C9—C14           | 1.387    |
| Cu1—Cu1i         | 2.6554   | C10—C11          | 1.390    |
| O1—C8            | 1.257    | C10—H10          | 0.930    |
| O2—C8            | 1.257    | C11—C12          | 1.365    |
| O2—Cu1i          | 1.9718   | C11—H11          | 0.930    |
| O3—C1            | 1.254    | C12—C13          | 1.381    |
| O4—C1            | 1.258    | C12—H12          | 0.930    |
| O4—Cu1i          | 1.9751   | C13—C14          | 1.371    |
| O5—C15           | 1.229    | C14—H14          | 0.930    |
| O6—N2            | 1.216    | C15—H15          | 0.930    |
| O7—N2            | 1.222    | C16—H16A         | 0.960    |
| O8—N3            | 1.213    | C16—H16B         | 0.960    |
| O9—N3            | 1.211    | C16—H16C         | 0.960    |
| N1—C15           | 1.318    | C17—H17A         | 0.960    |
| N1—C16           | 1.432    | C17—H17B         | 0.960    |
| N1—C17           | 1.467    | C17—H17C         | 0.960    |
| N2—C6            | 1.469    | O10—C18          | 1.209    |
| N3—C13           | 1.481    | N4—C18           | 1.339    |
| C1—C2            | 1.508    | N4—C19           | 1.407    |
| C2—C3            | 1.381    | N4—C20           | 1.441    |
| C2—C7            | 1.381    | C18—H18          | 0.930    |
| C3—C4            | 1.387    | C19—H19A         | 0.960    |
| C3—H3            | 0.930    | C19—H19B         | 0.960    |
| C4—C5            | 1.370    | C19—H19C         | 0.960    |
| C4—H4            | 0.930    | C20—H20A         | 0.960    |
| C5—C6            | 1.374    | C20—H20B         | 0.960    |
| C5—H5            | 0.9300   | C20—H20C         | 0.960    |
| O1—Cu1—O3        | 88.06    | O1—C8—C9         | 115.9    |

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sup-4
| Bond  | Angle (°) (E77) | Bond  | Angle (°) (E77) |
|-------|----------------|-------|----------------|
| O1—Cu1—O2 | 167.89 (7) | C10—C9—C14 | 119.4 (2) |
| O3—Cu1—O2 | 90.95 (8) | C10—C9—C8 | 121.3 (2) |
| O1—Cu1—O4 | 88.98 (8) | C14—C9—C8 | 119.3 (2) |
| O3—Cu1—O4 | 167.85 (7) | C9—C10—C11 | 120.5 (3) |
| O2—Cu1—O4 | 89.47 (8) | C9—C10—H10 | 119.7 |
| O3—Cu1—O5 | 94.83 (7) | C11—C10—H10 | 119.7 |
| O3—Cu1—O5 | 98.30 (7) | C12—C11—C10 | 120.4 (3) |
| O2—Cu1—O5 | 97.26 (7) | C12—C11—H11 | 119.8 |
| O4—Cu1—O5 | 93.69 (7) | C10—C11—H11 | 119.8 |
| O1—Cu1—Cu1 | 82.41 (5) | C11—C12—C13 | 118.4 (3) |
| O3—Cu1—Cu1 | 85.24 (5) | C11—C12—H12 | 120.8 |
| O2—Cu1—Cu1 | 85.48 (5) | C13—C12—H12 | 120.8 |
| O4—Cu1—Cu1 | 82.68 (5) | C14—C13—C12 | 122.4 (3) |
| O5—Cu1—Cu1 | 175.46 (6) | C14—C13—N3 | 118.0 (3) |
| C8—O1—Cu1 | 125.04 (17) | C12—C13—N3 | 119.5 (3) |
| C8—O2—Cu1 | 120.92 (16) | C13—C14—C9 | 118.9 (3) |
| C1—O3—Cu1 | 121.59 (15) | C13—C14—H14 | 120.6 |
| C1—O4—Cu1 | 123.95 (16) | C9—C14—H14 | 120.6 |
| C15—O5—Cu1 | 121.53 (18) | O5—C15—N1 | 125.2 (3) |
| C15—N1—C16 | 120.8 (3) | O5—C15—H15 | 117.4 |
| C15—N1—C17 | 120.4 (3) | N1—C15—H15 | 117.4 |
| C16—N1—C17 | 118.5 (3) | N1—C16—H16A | 109.5 |
| O6—N2—O7 | 123.3 (3) | N1—C16—H16B | 109.5 |
| O6—N2—C6 | 118.7 (2) | H16A—C16—H16B | 109.5 |
| O7—N2—C6 | 118.0 (3) | N1—C16—H16C | 109.5 |
| O9—N3—O8 | 124.1 (3) | H16A—C16—H16C | 109.5 |
| O9—N3—C13 | 117.9 (3) | H16B—C16—H16C | 109.5 |
| O8—N3—C13 | 118.1 (3) | N1—C17—H17A | 109.5 |
| O3—C1—O4 | 126.4 (2) | N1—C17—H17B | 109.5 |
| O3—C1—C2 | 117.4 (2) | H17A—C17—H17B | 109.5 |
| O4—C1—C2 | 116.2 (2) | N1—C17—H17C | 109.5 |
| C3—C2—C7 | 119.8 (2) | H17A—C17—H17C | 109.5 |
| C3—C2—C1 | 120.2 (2) | H17B—C17—H17C | 109.5 |
| C7—C2—C1 | 119.9 (2) | C18—N4—C19 | 119.9 (4) |
| C2—C3—C4 | 120.1 (3) | C18—N4—C20 | 119.8 (4) |
| C2—C3—H3 | 120.0 | C19—N4—C20 | 120.3 (4) |
| C4—C3—H3 | 120.0 | O10—C18—N4 | 125.5 (5) |
| C5—C4—C3 | 120.8 (3) | O10—C18—H18 | 117.3 |
| C5—C4—H4 | 119.6 | N4—C18—H18 | 117.3 |
| C3—C4—H4 | 119.6 | N4—C19—H19A | 109.5 |
| C4—C5—C6 | 118.2 (2) | N4—C19—H19B | 109.5 |
| C4—C5—H5 | 120.9 | H19A—C19—H19B | 109.5 |
| C6—C5—H5 | 120.9 | N4—C19—H19C | 109.5 |
| C5—C6—C7 | 122.5 (3) | H19A—C19—H19C | 109.5 |
| C5—C6—N2 | 119.0 (2) | H19B—C19—H19C | 109.5 |
| C7—C6—N2 | 118.5 (2) | N4—C20—H20A | 109.5 |
| C2—C7—C6 | 118.6 (2) | N4—C20—H20B | 109.5 |
| C2—C7—H7 | 120.7 | H20A—C20—H20B | 109.5 |
C6—C7—H7 120.7  N4—C20—H20C 109.5  
O2—C8—O1 126.1 (2)  H20A—C20—H20C 109.5  
O2—C8—C9 118.0 (2)  H20B—C20—H20C 109.5  
Cu1—O3—C1—O4 3.6 (4)  Cu1—O1—C8—C9 179.02 (15)  
Cu1—O3—C1—C2 −174.57 (15)  O2—C8—C9—C10 −6.0 (4)  
Cu1′—O4—C1—O3 −5.6 (4)  O1—C8—C9—C10 175.3 (2)  
Cu1′—O4—C1—C2 172.56 (15)  O2—C8—C9—C14 173.9 (2)  
O3—C1—C2—C3 23.2 (4)  O1—C8—C9—C14 −4.8 (3)  
O4—C1—C2—C3 −155.2 (3)  C14—C9—C10—C11 1.2 (4)  
O4—C1—C2—C7 −158.5 (2)  C8—C9—C10—C11 −178.9 (3)  
O4—C1—C2—C7 23.1 (3)  C9—C10—C11—C12 0.4 (5)  
C7—C2—C3—C4 −1.4 (4)  C10—C11—C12—C13 −1.2 (5)  
C1—C2—C3—C4 176.9 (3)  C11—C12—C13—C14 0.5 (5)  
C2—C3—C4—C5 2.0 (5)  C11—C12—C13—N3 −179.8 (3)  
C3—C4—C5—C6 −0.8 (5)  O9—N3—C13—C14 −8.5 (4)  
C4—C5—C6—C7 −1.0 (4)  O8—N3—C13—C14 171.4 (3)  
C4—C5—C6—N2 179.9 (3)  O9—N3—C13—C12 −8.4 (3)  
C6—C2—C7—C6 1.6 (4)  O8—N3—C13—C12 171.8 (3)  
C7—C2—C3—C4 −178.7 (2)  C8—C9—C10—C11 −178.2 (2)  
C1—C2—C7—C6 −178.7 (2)  Cu1—O5—C15—N1 −177.7 (2)  
C5—C6—C7—C2 1.6 (4)  C16—N1—C15—O5 −3.6 (4)  
N2—C6—C7—C2 −179.3 (2)  C17—N1—C15—O5 −176.6 (3)  
Cu1′—O2—C8—O1 −0.5 (3)  C19—N4—C18—O10 2.5 (7)  
Cu1′—O2—C8—C9 −178.98 (15)  C20—N4—C18—O10 −178.0 (4)  
Cu1—O1—C8—O2 0.5 (4)  

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

\[ \begin{array}{cccccc} 
D—H···A & D—H & H···A & D···A & D—H···A \\
\hline 
C4—H4···O4\textsuperscript{a} & 0.93 & 2.47 & 3.360 (4) & 161 
C15—H15···O1 & 0.93 & 2.50 & 3.100 (4) & 123 
C16—H16C···O5 & 0.96 & 2.40 & 2.770 (4) & 102 
C19—H19A···O10 & 0.96 & 2.35 & 2.753 (8) & 104 
C20—H20C···O10\textsuperscript{ii} & 0.96 & 2.59 & 3.503 (7) & 160 
\end{array} \]

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