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Bis(μ_2-benzoato-κ^2O,O')bis(benzoato-κO)bis(ethanol-κO)bis(μ_3-hydroxido)hexakis(μ-pyrazolato-κ^2N,N')hexacopper(II) ethanol disolvate

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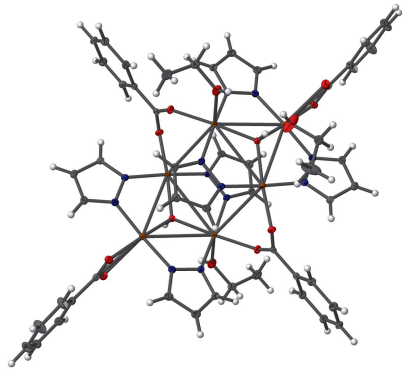
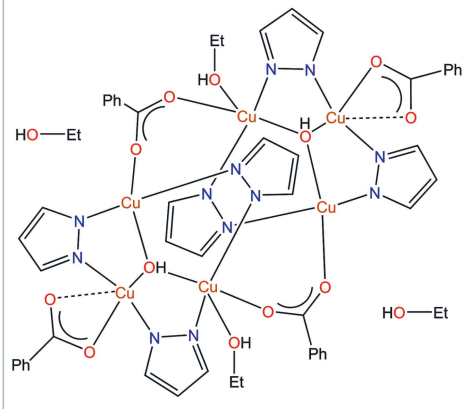
Structural data: full structural data are available from iucrdata.iucr.org

Trinuclear copper–pyrazolate entities are present in various Cu-based enzymes and nanojar supramolecular arrangements. The reaction of copper(II) chloride with pyrazole (pzH) and sodium benzoate (benzNa) assisted by microwave radiation afforded a neutral centrosymmetric hexanuclear copper(II) complex, $[Cu_6(C_7H_5O_2)_4(OH)_2(C_3H_3N_2)_6(C_2H_5OH)_2]\cdot 2C_2H_5OH$. Half a molecule is present in the asymmetric unit that comprises a $[Cu_3(\mu_3\text{-}OH)(pz)_3]^{2+}$ core with the copper(II) atoms arranged in an irregular triangle. The three copper(II) atoms are bridged by an O atom of the central hydroxyl group and by three bridging pyrazolate ligands on each of the sides. The carboxylate groups show a chelating mode to one and a bridging *syn,syn* mode to the other two Cu^{II} atoms. The coordination environment of one Cu^{II} atom is square-planar while it is distorted square-pyramidal for the other two. Two ethanol molecules are present in the asymmetric unit, one binding to one of the Cu^{II} atoms, one as a solvent molecule. In the crystal, stabilization arises from intermolecular O—H···O hydrogen-bonding interactions.

3D view



Chemical scheme



Structure description

Trinuclear copper–pyrazolate complexes find widespread applications as redox mediators in multicopper enzymes (*e.g.* in oxidases, oxygenases, or reductases) and as magnetic units to investigate spin-exchange interactions of metal cations (Kupcewicz *et al.*, 2013; Viciano-Chumillas *et al.*, 2007). Moreover, they make up triangular arrangements of nanojars which consist of structurally diverse supramolecular coordination complexes containing host frameworks that can trap small inorganic anions such as CO_3^{2-}, SO_4^{2-},

Table 1
Selected geometric parameters (Å, °).

Cu1—N6	1.9291 (12)	Cu2—O1	1.9781 (10)
Cu1—N1	1.9392 (12)	Cu2—O7	1.9827 (10)
Cu1—O7	1.9932 (10)	Cu3—N5	1.9550 (12)
Cu1—O3	2.0103 (10)	Cu3—N4	1.9591 (12)
Cu1—O4	2.6155 (10)	Cu3—O7	1.9899 (10)
Cu2—N3	1.9366 (12)	Cu3—O2^{i}	2.0086 (10)
Cu2—N2	1.9471 (12)	Cu3—O5	2.3168 (11)
N6—Cu1—N1	176.43 (5)	O7—Cu3—O5	100.03 (4)
O7—Cu1—O3	170.42 (4)	Cu2—O7—Cu3	117.22 (5)
N3—Cu2—N2	174.97 (5)	Cu2—O7—Cu1	115.10 (5)
O1—Cu2—O7	173.24 (4)	Cu3—O7—Cu1	116.42 (5)
N5—Cu3—N4	170.64 (5)		

Symmetry code: (i) $-x+1, -y+2, -z+1$.

HPO_4^{2-}, and $HAsO_4^{2-}$, as well as NO_3^-, and ClO_4^- (Hartman & Mezei, 2017; Mezei, 2016; Al Isawi *et al.*, 2018). Such supramolecular motifs can also mimic the imidazole metal-binding properties in active sites of metalloenzymes (Kupcewicz *et al.*, 2013; Viciano-Chumillas *et al.*, 2007; Mezei, 2016; Al Isawi *et al.*, 2018).

Coordination compounds can be synthesized under hydro- or solvothermal conditions by *in situ* metal/ligand reactions in the presence of transition-metal ions. In a few cases, unexpected chemical, structural and/or compositional changes in the organic ligands occur during the reaction process. In this context, microwave-assisted synthesis has become a rapidly developing synthetic method of importance since it greatly decreases the reaction time rendering fast reaction rates, along with high yields and high phase purity, so that the procedure is being regarded as an energy-efficient process. Although microwave-assisted methods apply for the preparation of several organic compounds, only a handful of coordination compounds prepared by this procedure have been reported (Delgado *et al.*, 2011). For example, various metal carboxylate clusters of Co_3, Ni_3, Mn_6, Fe_8. Ni_8, Ni_9, Ni_6, and Mn_4, as well Mn_7, and Mn_2Ni_2 have been isolated that could not be prepared by traditional bench-top synthesis (Milios *et al.*, 2006*a*,*b*; Gass *et al.*, 2006; Ledezma-Gairaud *et al.*, 2013, 2015; Pons-Balagué *et al.*, 2011, 2013).

In this work, we report the microwave-assisted synthesis and crystal structure of a carboxylate-bridged Cu^{II} complex. The reaction of copper(II) chloride with pyrazole (pzH) and sodium benzoate (benzNa) in a mixture of ethanol/water (2:1) proceeds under microwave radiation to generate a neutral dimeric trinuclear copper(II) complex of formula $[Cu(\mu_3\text{-}OH)(\mu\text{-pz})_3(\mu_2\text{-benz})(\mu\text{-benz})(EtOH)]_2$ that crystallized as the ethanol disolvate. Although strong bases such as sodium or tetrabutylammonium hydroxide are commonly used for deprotonating pyrazole and as a source of hydroxide ions to self-assembled nanojars, we added instead a weak base like BenzNa to deprotonate the Hpz ligand. The IR spectrum of the title compound shows two similar sets of strong vibrations corresponding to $\upsilon_{as}(COO)$ (1605 and 1572 cm^{-1}) and $\upsilon_s(COO)$ (1403 and 1364 cm^{-1}). The $\Delta\upsilon$ values $[\upsilon_{as}(COO) - \upsilon_s(COO)]$ are in accordance with a nearly symmetric bridging bidentate coordination of carboxylate groups (Deacon & Phillips, 1980; Nakamoto, 1997).

The title compound crystallizes in the triclinic space group $P\overline{1}$ with half a molecule per asymmetric unit, the other half being generated by inversion symmetry. Relevant bond lengths and angles are collated in Table 1. The core of the title compound comprises the trinuclear $[Cu_3(\mu_3\text{-}OH)(pz)_3]^{2+}$ entity (Fig. 1) in which the three Cu^{II} ions are bridged in a μ_3 mode by oxygen atom (O7) of the hydroxyl group. Each of the three pyrazolate ligands, lying at the corners of an irregular Cu···Cu···Cu triangle, bridges two of the Cu^{II} ions of the triangle.

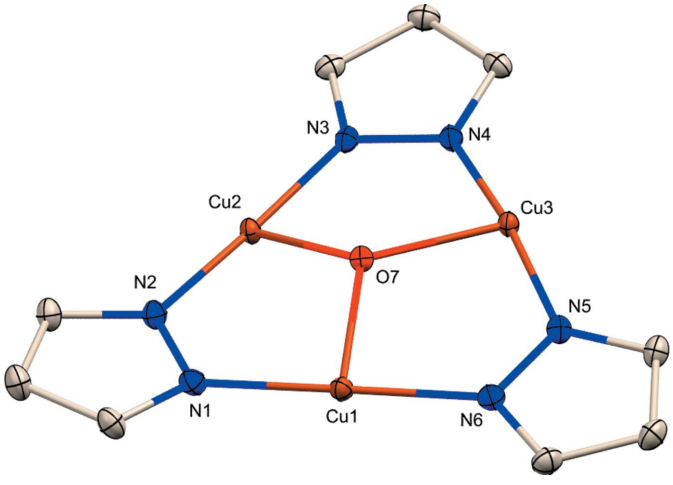


Figure 1
$[Cu_3(\mu_3\text{-}OH)(pyz)_3]^{2+}$ core of the title compound with displacement ellipsoids drawn at the 50% probability level. The H atoms and the solvent molecule are omitted for clarity.

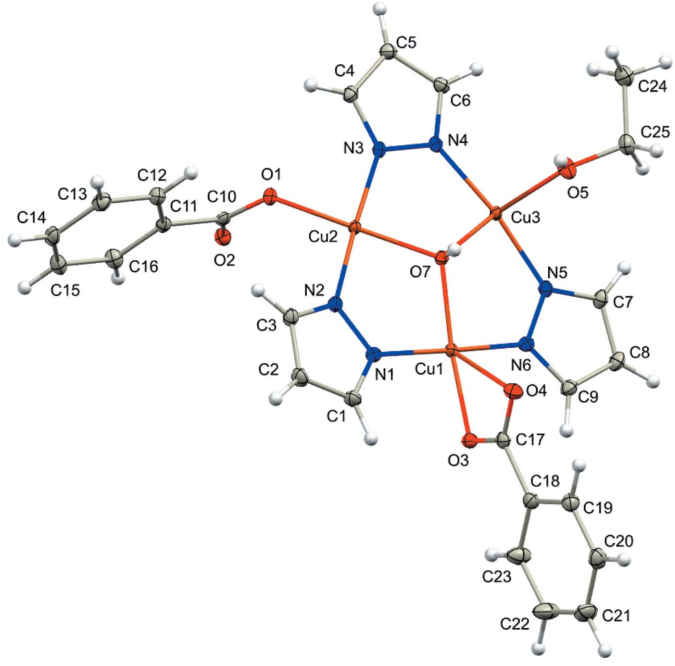


Figure 2
Asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level. The EtOH solvent molecule is omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H10···O4^{ii}	0.73 (3)	2.00 (3)	2.7325 (18)	173 (3)
O7—H11···O8	0.76 (2)	1.87 (2)	2.6175 (17)	168 (2)
O5—H5A···O4^{ii}	0.75	2.0	2.7393 (16)	170

Symmetry code: (ii) $-x+1, -y+1, -z+1$.

The carboxylate groups of the two benzoate anions present in the asymmetric unit bind in different fashions. A chelating mode by carboxylate atoms O3 and O4 is realised to bind to Cu1 whereas a *syn, syn* mode bridging Cu2 and Cu3 of the symmetry-related part is realised for O1 and O2. The latter connectivity is found in various polymeric copper(II) carboxylates (Casarin *et al.*, 2005). A neutral ethanol molecule completes the coordination sphere of Cu3 in the triangle (Fig. 2). From the mean plane through Cu1, Cu2 and Cu3, the bridging O7 atom of the central μ_3-OH ion is displaced by 0.390 (1) Å slightly out of the plane, a feature commonly found for nanojar compounds (Ferrer *et al.*, 2000, 2002; Hulsbergen *et al.*, 1983: Angaroni *et al.*, 1990; Sakai *et al.*, 1996; Casarin *et al.*, 2004,2005). The bond lengths between the three Cu ions and the μ_3-OH ion are very similar; the same applies for the Cu—N distances (Table 1).

The title molecule is located around an inversion center, composed of two symmetry-related trinuclear copper(II) pyrazolate units (Fig. 3) that are connected together by carboxylate ions. The coordination environment of Cu1 is a distorted square pyramid in which the two bond lengths involving the chelating carboxylate group are non-equivalent, Cu1—O3 = 2.010 (1) and Cu1—O4) = 2.616 (1) Å. Cu2 has a square-planar environment formed by two N atoms of two bridging μ-pyrazolate anions and the μ_3-OH group, completed by an oxygen atom from a carboxylate group, Cu2—O1 = 1.978 (1) Å. The Cu3 atom has a distorted square-pyramidal environment with the apical position occupied by the O atom of an ethanol molecule.

In the crystal structure of the title compound, further stabilization arises from intermolecular O—H···O hydrogen bonds. This way, the μ_3-OH group and the oxygen atom O8 of the solvate ethanol molecule, the OH group of the solvate ethanol molecule and the benzoate oxygen atom O4, and the OH group of the coordinating ethanol molecule and the O4 atom of the benzoate ligand are connected (Table 2, Fig. 4).

Synthesis and crystallization

All chemicals and solvents were purchased from commercial sources and used as received; all preparation and manipulations were performed under aerobic conditions, except where otherwise noted. Microwave-assisted reactions were done in a Discover System (CEM Corp.) microwave reactor. FTIR spectra were recorded with a Perkin-Elmer System 2000 FTIR instrument from 4000 to 100 cm^{-1}, KBr solid state.

$CuCl_2{\cdot}2H_2O$ (0.40 g; 2.35 mmol) was added to a solution with sodium benzoate (benzNa) (0.30 g, 2.10 mmol) and pyrazole (pzH) (0.20 g, 2.94 mmol) in EtOH/H_2O (10:5 mL). The reaction mixture was put into a microwave tube in the reactor cavity applying a 150 W microwave pulse for 5 min at 373 K. The obtained jade-green solution was filtered off after cooling for 5 min. The resulting intense blue filtrate was allowed to stand for 4 d at ambient temperature resulting in light-blue block-shaped crystals obtained by slow evaporation of the solvent. The crystalline product was collected by filtration and washed with EtOH (5 × 5 mL). Yield: 0.20 g (11%). Selected FTIR data (KBr, cm^{-1}): 3393 (*br*, *m*); 3215 (*br*, *s*); 3113 (*m*); 2969 (*m*); 1593 (*s*); 1542 (*s*); 1490 (*w*); 1445 (*w*); 1400 (*br*, *s*); 1381 (*w*); 1278 (*m*); 1176 (*s*); 1129 (*m*); 1063(*s*); 967 (*w*); 945 (*w*); 877 (*w*); 848 (*m*); 780 (*s*); 764 (*s*); 720 (*s*); 687 (*m*): 630 (*m*); 599 (*m*); 486 (*br*, *m*).

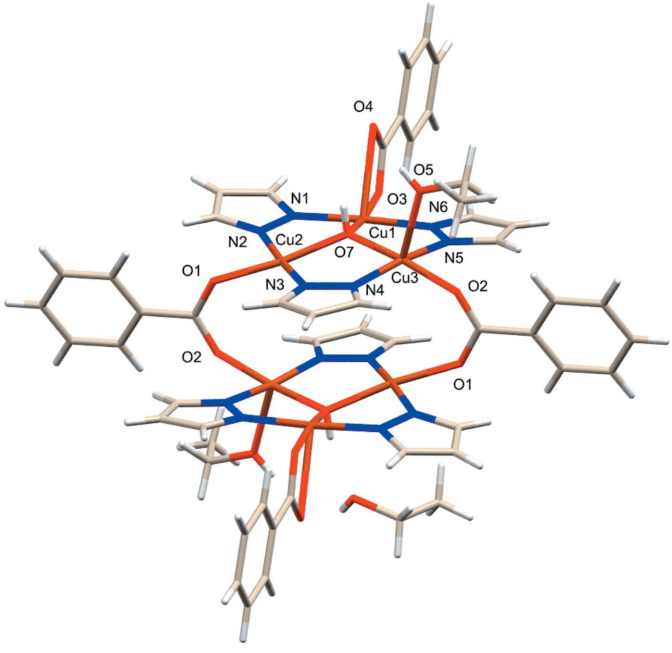


Figure 3
Dimeric-bridged molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

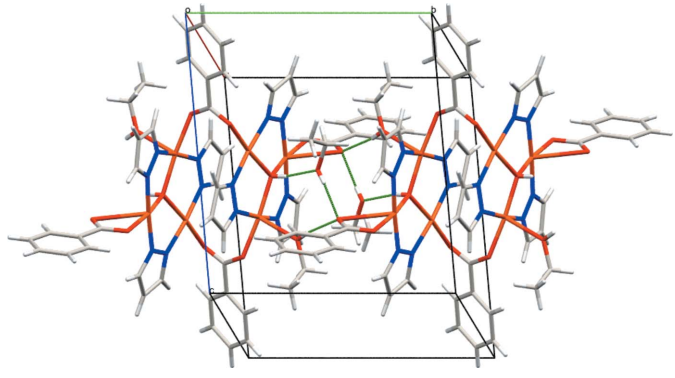


Figure 4
Packing of the molecules of the title compound. O—H···O hydrogen-bonding interactions are shown as green dashed lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu_6(C_7H_5O_2)_4(OH)_2(C_3H_3N_2)_6\text{-}(C_2H_6O)_2]\cdot 2C_2H_6O$
M_r	1486.40
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	10.4608 (5), 11.4064 (5), 13.0357 (6)
α, β, γ (°)	85.061 (1), 72.520 (1), 80.044 (1)
V (Å^3)	1460.29 (12)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.22
Crystal size (mm)	0.35 × 0.25 × 0.15
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.645, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	64647, 6754, 6300
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.653
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.050, 1.04
No. of reflections	6754
No. of parameters	400
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.00, −0.72

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Acknowledgements

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full crystallographic data

IUCrData (2019). **4**, x191190 [https://doi.org/10.1107/S2414314619011908]

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Crystal data

$[Cu_6(C_7H_5O_2)_4(OH)_2(C_3H_3N_2)_6(C_2H_6O)_2]\cdot 2C_2H_6O$
M_r = 1486.40
Triclinic, $P\overline{1}$
a = 10.4608 (5) Å
b = 11.4064 (5) Å
c = 13.0357 (6) Å
α = 85.061 (1)°
β = 72.520 (1)°
γ = 80.044 (1)°
V = 1460.29 (12) Å^3
Z = 1
$F(000)$ = 758
D_x = 1.690 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9612 reflections
θ = 3.0–27.6°
μ = 2.22 mm^{-1}
T = 100 K
Block, clear light blue
0.35 × 0.25 × 0.15 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: Incoatec microsource
Mirrors monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
T_{min} = 0.645, T_{max} = 0.746
64647 measured reflections
6754 independent reflections
6300 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 27.7°, θ_{min} = 2.5°
h = −13→13
k = −14→14
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.050
S = 1.04
6754 reflections
400 parameters
0 restraints
Primary atom site location: inferred from neighbouring sites
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 1.2646P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 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. All hydrogen atoms were placed geometrically and refined using a riding-atom model approximation, with C—H = 0.95–1.00 Å, with U_{iso}(H) = 1.2U_{eq}(C). A rotating model was used for the methyl groups. The H7 atom of the μ_3-OH group was located in the final Fourier difference map and refined freely.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.28967 (2)	0.73986 (2)	0.64822 (2)	0.00957 (4)
Cu2	0.57945 (2)	0.84981 (2)	0.60585 (2)	0.00910 (4)
Cu3	0.44372 (2)	0.84872 (2)	0.40022 (2)	0.00903 (4)
O1	0.71009 (10)	0.89817 (9)	0.67045 (8)	0.0126 (2)
O2	0.58170 (10)	1.06869 (9)	0.73631 (8)	0.0132 (2)
O3	0.13205 (10)	0.66939 (9)	0.74774 (8)	0.0126 (2)
O4	0.27501 (10)	0.51209 (9)	0.67280 (8)	0.0152 (2)
O7	0.45907 (10)	0.78176 (9)	0.54287 (8)	0.00978 (19)
N1	0.37824 (12)	0.72985 (11)	0.76044 (10)	0.0120 (2)
N2	0.49920 (12)	0.76972 (11)	0.74229 (10)	0.0117 (2)
N3	0.66477 (12)	0.91576 (10)	0.46482 (9)	0.0106 (2)
N4	0.60854 (12)	0.91744 (10)	0.38259 (9)	0.0109 (2)
N5	0.26458 (12)	0.80068 (10)	0.43446 (10)	0.0112 (2)
N6	0.20228 (12)	0.76028 (11)	0.53554 (10)	0.0117 (2)
C1	0.35158 (15)	0.67042 (13)	0.85560 (11)	0.0147 (3)
H1	0.2731	0.6339	0.8872	0.018*
C2	0.45569 (16)	0.67008 (13)	0.90129 (12)	0.0159 (3)
H2	0.4632	0.6343	0.9682	0.019*
C3	0.54640 (15)	0.73377 (13)	0.82703 (12)	0.0138 (3)
H3	0.6292	0.7495	0.8349	0.017*
C4	0.78133 (14)	0.96040 (12)	0.42651 (12)	0.0124 (3)
H4	0.8403	0.969	0.4674	0.015*
C5	0.80270 (15)	0.99204 (13)	0.31813 (12)	0.0141 (3)
H5	0.8766	1.0259	0.2709	0.017*
C6	0.69127 (15)	0.96284 (12)	0.29428 (11)	0.0129 (3)
H6	0.6761	0.9735	0.2256	0.015*
C7	0.18136 (15)	0.79900 (13)	0.37370 (12)	0.0134 (3)
H7	0.2006	0.8224	0.2996	0.016*
C8	0.06347 (15)	0.75804 (13)	0.43504 (12)	0.0154 (3)
H8	−0.0123	0.7481	0.4126	0.018*
O8	0.60791 (17)	0.57097 (14)	0.52992 (12)	0.0421 (4)
C9	0.08100 (15)	0.73499 (13)	0.53626 (12)	0.0143 (3)
H9	0.017	0.7057	0.5972	0.017*
C10	0.67100 (14)	0.97951 (12)	0.73796 (11)	0.0112 (3)
H10	0.644 (3)	0.546 (2)	0.477 (2)	0.048 (8)*
C11	0.73560 (14)	0.96907 (12)	0.82770 (11)	0.0114 (3)

H11	0.498 (2)	0.720 (2)	0.5324 (19)	0.033 (6)*
C12	0.85067 (15)	0.88498 (13)	0.82471 (12)	0.0139 (3)
H12	0.8886	0.8338	0.7657	0.017*
C13	0.90977 (15)	0.87607 (14)	0.90811 (12)	0.0165 (3)
H13	0.9883	0.8191	0.906	0.02*
C14	0.85389 (16)	0.95059 (14)	0.99447 (12)	0.0163 (3)
H14	0.894	0.9441	1.0516	0.02*
C15	0.73963 (16)	1.03462 (13)	0.99774 (12)	0.0169 (3)
H15	0.7019	1.0856	1.0568	0.02*
C16	0.68035 (15)	1.04405 (13)	0.91430 (12)	0.0147 (3)
H16	0.6023	1.1016	0.9164	0.018*
C17	0.16176 (14)	0.55833 (13)	0.73175 (11)	0.0124 (3)
C18	0.05533 (15)	0.48198 (13)	0.78522 (11)	0.0136 (3)
C19	0.07998 (16)	0.36048 (13)	0.76582 (12)	0.0157 (3)
H19	0.1649	0.3259	0.72	0.019*
C20	−0.01983 (17)	0.29002 (14)	0.81361 (13)	0.0185 (3)
H20	−0.0025	0.2071	0.8012	0.022*
C21	−0.14445 (18)	0.34064 (15)	0.87923 (14)	0.0236 (3)
H21	−0.213	0.2927	0.9108	0.028*
C22	−0.16933 (18)	0.46163 (16)	0.89891 (15)	0.0273 (4)
H22	−0.2547	0.4961	0.9442	0.033*
C23	−0.06960 (17)	0.53216 (14)	0.85243 (13)	0.0214 (3)
H23	−0.0865	0.6146	0.8664	0.026*
O5	0.54975 (12)	0.68595 (10)	0.29512 (9)	0.0171 (2)
H5A	0.601 (2)	0.6366 (18)	0.3077 (8)	0.026*
C24	0.64511 (17)	0.71837 (16)	0.10209 (13)	0.0223 (3)
H24A	0.6292	0.7106	0.0328	0.033*
H24B	0.734	0.6737	0.1019	0.033*
H24C	0.6429	0.8026	0.1135	0.033*
C25	0.53594 (16)	0.66945 (13)	0.19152 (12)	0.0167 (3)
H25A	0.4458	0.71	0.1876	0.02*
H25B	0.5413	0.5834	0.1818	0.02*
C27	0.67313 (16)	0.52015 (13)	0.60771 (13)	0.0170 (3)
H27A	0.6896	0.4324	0.6031	0.02*
H27B	0.6122	0.5401	0.6804	0.02*
C26	0.8050 (2)	0.56271 (18)	0.5932 (2)	0.0415 (5)
H26A	0.8668	0.5411	0.5222	0.062*
H26B	0.8454	0.5254	0.6491	0.062*
H26C	0.7893	0.6495	0.5988	0.062*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00918 (8)	0.01126 (8)	0.00869 (8)	−0.00253 (6)	−0.00274 (6)	−0.00020 (6)
Cu2	0.01051 (8)	0.00998 (8)	0.00809 (8)	−0.00296 (6)	−0.00396 (6)	0.00012 (6)
Cu3	0.00953 (8)	0.01005 (8)	0.00861 (8)	−0.00248 (6)	−0.00404 (6)	0.00070 (6)
O1	0.0131 (5)	0.0153 (5)	0.0117 (5)	−0.0038 (4)	−0.0056 (4)	−0.0016 (4)
O2	0.0143 (5)	0.0144 (5)	0.0118 (5)	−0.0017 (4)	−0.0061 (4)	0.0021 (4)

O3	0.0113 (5)	0.0131 (5)	0.0127 (5)	−0.0026 (4)	−0.0020 (4)	−0.0008 (4)
O4	0.0127 (5)	0.0166 (5)	0.0141 (5)	−0.0006 (4)	−0.0016 (4)	−0.0009 (4)
O7	0.0106 (5)	0.0099 (5)	0.0094 (5)	−0.0018 (4)	−0.0036 (4)	−0.0001 (4)
N1	0.0122 (6)	0.0129 (6)	0.0110 (6)	−0.0037 (4)	−0.0028 (4)	−0.0004 (4)
N2	0.0128 (6)	0.0121 (5)	0.0114 (6)	−0.0030 (4)	−0.0047 (5)	−0.0005 (4)
N3	0.0109 (5)	0.0111 (5)	0.0108 (5)	−0.0017 (4)	−0.0048 (4)	−0.0006 (4)
N4	0.0118 (6)	0.0124 (5)	0.0094 (5)	−0.0021 (4)	−0.0043 (4)	−0.0002 (4)
N5	0.0128 (6)	0.0108 (5)	0.0110 (5)	−0.0019 (4)	−0.0047 (5)	0.0001 (4)
N6	0.0114 (6)	0.0119 (5)	0.0121 (6)	−0.0028 (4)	−0.0032 (5)	−0.0001 (4)
C1	0.0176 (7)	0.0154 (7)	0.0108 (6)	−0.0053 (5)	−0.0026 (5)	0.0009 (5)
C2	0.0208 (7)	0.0170 (7)	0.0117 (7)	−0.0052 (6)	−0.0066 (6)	0.0018 (5)
C3	0.0166 (7)	0.0142 (7)	0.0128 (7)	−0.0040 (5)	−0.0068 (6)	0.0002 (5)
C4	0.0110 (6)	0.0111 (6)	0.0153 (7)	−0.0014 (5)	−0.0038 (5)	−0.0020 (5)
C5	0.0127 (7)	0.0140 (7)	0.0141 (7)	−0.0029 (5)	−0.0013 (5)	−0.0006 (5)
C6	0.0146 (7)	0.0127 (6)	0.0102 (6)	−0.0024 (5)	−0.0019 (5)	0.0001 (5)
C7	0.0147 (7)	0.0130 (6)	0.0147 (7)	−0.0025 (5)	−0.0077 (5)	0.0005 (5)
C8	0.0124 (7)	0.0165 (7)	0.0193 (7)	−0.0024 (5)	−0.0078 (6)	−0.0006 (6)
O8	0.0558 (10)	0.0408 (8)	0.0249 (7)	0.0325 (7)	−0.0222 (7)	−0.0175 (6)
C9	0.0108 (6)	0.0159 (7)	0.0166 (7)	−0.0030 (5)	−0.0038 (5)	−0.0009 (5)
C10	0.0116 (6)	0.0123 (6)	0.0109 (6)	−0.0063 (5)	−0.0035 (5)	0.0027 (5)
C11	0.0135 (7)	0.0112 (6)	0.0112 (6)	−0.0044 (5)	−0.0051 (5)	0.0020 (5)
C12	0.0139 (7)	0.0149 (7)	0.0137 (7)	−0.0027 (5)	−0.0046 (5)	−0.0009 (5)
C13	0.0136 (7)	0.0188 (7)	0.0181 (7)	−0.0022 (6)	−0.0069 (6)	0.0014 (6)
C14	0.0194 (7)	0.0207 (7)	0.0130 (7)	−0.0081 (6)	−0.0096 (6)	0.0036 (5)
C15	0.0251 (8)	0.0145 (7)	0.0125 (7)	−0.0037 (6)	−0.0069 (6)	−0.0015 (5)
C16	0.0181 (7)	0.0121 (6)	0.0143 (7)	−0.0009 (5)	−0.0064 (6)	0.0009 (5)
C17	0.0125 (6)	0.0156 (7)	0.0102 (6)	−0.0021 (5)	−0.0051 (5)	0.0005 (5)
C18	0.0148 (7)	0.0151 (7)	0.0119 (7)	−0.0038 (5)	−0.0047 (5)	0.0010 (5)
C19	0.0162 (7)	0.0162 (7)	0.0155 (7)	−0.0021 (5)	−0.0054 (6)	−0.0020 (5)
C20	0.0248 (8)	0.0144 (7)	0.0178 (7)	−0.0060 (6)	−0.0069 (6)	−0.0008 (6)
C21	0.0246 (8)	0.0217 (8)	0.0229 (8)	−0.0123 (7)	−0.0001 (7)	0.0010 (6)
C22	0.0214 (8)	0.0217 (8)	0.0296 (9)	−0.0064 (7)	0.0085 (7)	−0.0032 (7)
C23	0.0212 (8)	0.0147 (7)	0.0232 (8)	−0.0040 (6)	0.0019 (6)	−0.0012 (6)
O5	0.0203 (6)	0.0151 (5)	0.0155 (5)	0.0042 (4)	−0.0077 (4)	−0.0029 (4)
C24	0.0227 (8)	0.0292 (9)	0.0161 (7)	−0.0059 (7)	−0.0064 (6)	−0.0009 (6)
C25	0.0205 (7)	0.0152 (7)	0.0161 (7)	−0.0029 (6)	−0.0071 (6)	−0.0026 (5)
C27	0.0198 (7)	0.0130 (7)	0.0181 (7)	−0.0004 (6)	−0.0064 (6)	−0.0011 (5)
C26	0.0208 (9)	0.0276 (10)	0.0754 (16)	−0.0017 (7)	−0.0088 (10)	−0.0209 (10)

Geometric parameters (Å, º)

Cu1—N6	1.9291 (12)	C8—H8	0.95
Cu1—N1	1.9392 (12)	O8—C27	1.417 (2)
Cu1—O7	1.9932 (10)	O8—H10	0.73 (3)
Cu1—O3	2.0103 (10)	C9—H9	0.95
Cu1—O4	2.6155 (10)	C10—C11	1.5041 (19)
Cu2—N3	1.9366 (12)	C11—C16	1.394 (2)
Cu2—N2	1.9471 (12)	C11—C12	1.396 (2)

Cu2—O1	1.9781 (10)	C12—C13	1.392 (2)
Cu2—O7	1.9827 (10)	C12—H12	0.95
Cu3—N5	1.9550 (12)	C13—C14	1.389 (2)
Cu3—N4	1.9591 (12)	C13—H13	0.95
Cu3—O7	1.9899 (10)	C14—C15	1.389 (2)
Cu3—O2^{i}	2.0086 (10)	C14—H14	0.95
Cu3—O5	2.3168 (11)	C15—C16	1.393 (2)
O1—C10	1.2633 (17)	C15—H15	0.95
O2—C10	1.2600 (17)	C16—H16	0.95
O2—Cu3^{i}	2.0086 (10)	C17—C18	1.499 (2)
O3—C17	1.2709 (18)	C18—C23	1.394 (2)
O4—C17	1.2566 (18)	C18—C19	1.396 (2)
O7—H11	0.76 (2)	C19—C20	1.392 (2)
N1—C1	1.3374 (18)	C19—H19	0.95
N1—N2	1.3654 (16)	C20—C21	1.385 (2)
N2—C3	1.3460 (18)	C20—H20	0.95
N3—C4	1.3418 (18)	C21—C22	1.391 (2)
N3—N4	1.3663 (16)	C21—H21	0.95
N4—C6	1.3402 (18)	C22—C23	1.389 (2)
N5—C7	1.3446 (18)	C22—H22	0.95
N5—N6	1.3626 (17)	C23—H23	0.95
N6—C9	1.3461 (18)	O5—C25	1.4320 (18)
C1—C2	1.389 (2)	O5—H5A	0.75 (2)
C1—H1	0.95	C24—C25	1.511 (2)
C2—C3	1.389 (2)	C24—H24A	0.98
C2—H2	0.95	C24—H24B	0.98
C3—H3	0.95	C24—H24C	0.98
C4—C5	1.388 (2)	C25—H25A	0.99
C4—H4	0.95	C25—H25B	0.99
C5—C6	1.391 (2)	C27—C26	1.495 (2)
C5—H5	0.95	C27—H27A	0.99
C6—H6	0.95	C27—H27B	0.99
C7—C8	1.386 (2)	C26—H26A	0.98
C7—H7	0.95	C26—H26B	0.98
C8—C9	1.383 (2)	C26—H26C	0.98

N6—Cu1—N1	176.43 (5)	C27—O8—H10	110 (2)
N6—Cu1—O7	89.83 (5)	N6—C9—C8	109.81 (13)
N1—Cu1—O7	88.66 (5)	N6—C9—H9	125.1
N6—Cu1—O3	90.38 (5)	C8—C9—H9	125.1
N1—Cu1—O3	91.64 (5)	O2—C10—O1	125.14 (13)
O7—Cu1—O3	170.42 (4)	O2—C10—C11	117.31 (12)
N3—Cu2—N2	174.97 (5)	O1—C10—C11	117.55 (12)
N3—Cu2—O1	93.18 (5)	C16—C11—C12	119.80 (13)
N2—Cu2—O1	88.71 (5)	C16—C11—C10	119.76 (13)
N3—Cu2—O7	89.06 (5)	C12—C11—C10	120.44 (13)
N2—Cu2—O7	88.55 (5)	C13—C12—C11	120.01 (14)
O1—Cu2—O7	173.24 (4)	C13—C12—H12	120.0

N5—Cu3—N4	170.64 (5)	C11—C12—H12	120.0
N5—Cu3—O7	89.44 (4)	C14—C13—C12	119.95 (14)
N4—Cu3—O7	87.98 (4)	C14—C13—H13	120.0
N5—Cu3—O2^{i}	90.09 (5)	C12—C13—H13	120.0
N4—Cu3—O2^{i}	91.58 (5)	C13—C14—C15	120.29 (14)
O7—Cu3—O2^{i}	174.28 (4)	C13—C14—H14	119.9
N5—Cu3—O5	93.33 (5)	C15—C14—H14	119.9
N4—Cu3—O5	95.98 (5)	C14—C15—C16	119.95 (14)
O7—Cu3—O5	100.03 (4)	C14—C15—H15	120.0
O2^{i}—Cu3—O5	85.69 (4)	C16—C15—H15	120.0
C10—O1—Cu2	119.78 (9)	C15—C16—C11	120.00 (14)
C10—O2—Cu3^{i}	123.31 (9)	C15—C16—H16	120.0
C17—O3—Cu1	104.76 (9)	C11—C16—H16	120.0
Cu2—O7—Cu3	117.22 (5)	O4—C17—O3	122.41 (13)
Cu2—O7—Cu1	115.10 (5)	O4—C17—C18	119.97 (13)
Cu3—O7—Cu1	116.42 (5)	O3—C17—C18	117.62 (13)
Cu2—O7—H11	99.7 (18)	C23—C18—C19	119.67 (14)
Cu3—O7—H11	105.3 (18)	C23—C18—C17	120.34 (13)
Cu1—O7—H11	98.8 (18)	C19—C18—C17	119.97 (13)
C1—N1—N2	108.23 (12)	C20—C19—C18	120.01 (14)
C1—N1—Cu1	129.67 (10)	C20—C19—H19	120.0
N2—N1—Cu1	121.21 (9)	C18—C19—H19	120.0
C3—N2—N1	107.82 (12)	C21—C20—C19	120.08 (15)
C3—N2—Cu2	131.65 (10)	C21—C20—H20	120.0
N1—N2—Cu2	120.28 (9)	C19—C20—H20	120.0
C4—N3—N4	108.19 (11)	C20—C21—C22	120.08 (15)
C4—N3—Cu2	131.04 (10)	C20—C21—H21	120.0
N4—N3—Cu2	120.71 (9)	C22—C21—H21	120.0
C6—N4—N3	107.81 (11)	C23—C22—C21	120.12 (16)
C6—N4—Cu3	130.08 (10)	C23—C22—H22	119.9
N3—N4—Cu3	121.89 (9)	C21—C22—H22	119.9
C7—N5—N6	107.68 (12)	C22—C23—C18	120.03 (15)
C7—N5—Cu3	131.52 (10)	C22—C23—H23	120.0
N6—N5—Cu3	120.80 (9)	C18—C23—H23	120.0
C9—N6—N5	108.06 (12)	C25—O5—Cu3	124.88 (9)
C9—N6—Cu1	129.94 (10)	C25—O5—H5A	109.5
N5—N6—Cu1	121.93 (9)	Cu3—O5—H5A	125.5
N1—C1—C2	109.86 (13)	C25—C24—H24A	109.5
N1—C1—H1	125.1	C25—C24—H24B	109.5
C2—C1—H1	125.1	H24A—C24—H24B	109.5
C1—C2—C3	104.43 (13)	C25—C24—H24C	109.5
C1—C2—H2	127.8	H24A—C24—H24C	109.5
C3—C2—H2	127.8	H24B—C24—H24C	109.5
N2—C3—C2	109.66 (13)	O5—C25—C24	111.55 (13)
N2—C3—H3	125.2	O5—C25—H25A	109.3
C2—C3—H3	125.2	C24—C25—H25A	109.3
N3—C4—C5	109.74 (13)	O5—C25—H25B	109.3
N3—C4—H4	125.1	C24—C25—H25B	109.3

C5—C4—H4	125.1	H25A—C25—H25B	108.0
C4—C5—C6	104.31 (13)	O8—C27—C26	112.79 (17)
C4—C5—H5	127.8	O8—C27—H27A	109.0
C6—C5—H5	127.8	C26—C27—H27A	109.0
N4—C6—C5	109.95 (13)	O8—C27—H27B	109.0
N4—C6—H6	125.0	C26—C27—H27B	109.0
C5—C6—H6	125.0	H27A—C27—H27B	107.8
N5—C7—C8	110.03 (13)	C27—C26—H26A	109.5
N5—C7—H7	125.0	C27—C26—H26B	109.5
C8—C7—H7	125.0	H26A—C26—H26B	109.5
C9—C8—C7	104.41 (13)	C27—C26—H26C	109.5
C9—C8—H8	127.8	H26A—C26—H26C	109.5
C7—C8—H8	127.8	H26B—C26—H26C	109.5
C1—N1—N2—C3	0.21 (15)	Cu3^{i}—O2—C10—C11	145.05 (10)
Cu1—N1—N2—C3	−169.96 (9)	Cu2—O1—C10—O2	−33.95 (18)
C1—N1—N2—Cu2	175.10 (9)	Cu2—O1—C10—C11	145.80 (10)
Cu1—N1—N2—Cu2	4.94 (14)	O2—C10—C11—C16	11.01 (19)
C4—N3—N4—C6	0.16 (15)	O1—C10—C11—C16	−168.77 (13)
Cu2—N3—N4—C6	−177.39 (9)	O2—C10—C11—C12	−168.85 (13)
C4—N3—N4—Cu3	175.24 (9)	O1—C10—C11—C12	11.38 (19)
Cu2—N3—N4—Cu3	−2.31 (14)	C16—C11—C12—C13	0.1 (2)
C7—N5—N6—C9	−0.45 (15)	C10—C11—C12—C13	179.95 (13)
Cu3—N5—N6—C9	179.42 (9)	C11—C12—C13—C14	0.2 (2)
C7—N5—N6—Cu1	176.74 (9)	C12—C13—C14—C15	−0.4 (2)
Cu3—N5—N6—Cu1	−3.39 (14)	C13—C14—C15—C16	0.2 (2)
N2—N1—C1—C2	−0.25 (16)	C14—C15—C16—C11	0.1 (2)
Cu1—N1—C1—C2	168.82 (10)	C12—C11—C16—C15	−0.3 (2)
N1—C1—C2—C3	0.18 (17)	C10—C11—C16—C15	179.89 (13)
N1—N2—C3—C2	−0.09 (16)	Cu1—O3—C17—O4	6.52 (16)
Cu2—N2—C3—C2	−174.19 (10)	Cu1—O3—C17—C18	−172.80 (10)
C1—C2—C3—N2	−0.05 (17)	O4—C17—C18—C23	178.73 (14)
N4—N3—C4—C5	0.04 (16)	O3—C17—C18—C23	−1.9 (2)
Cu2—N3—C4—C5	177.25 (10)	O4—C17—C18—C19	−2.8 (2)
N3—C4—C5—C6	−0.22 (16)	O3—C17—C18—C19	176.59 (13)
N3—N4—C6—C5	−0.31 (16)	C23—C18—C19—C20	−0.1 (2)
Cu3—N4—C6—C5	−174.84 (10)	C17—C18—C19—C20	−178.63 (13)
C4—C5—C6—N4	0.32 (16)	C18—C19—C20—C21	0.9 (2)
N6—N5—C7—C8	0.35 (16)	C19—C20—C21—C22	−1.1 (3)
Cu3—N5—C7—C8	−179.50 (10)	C20—C21—C22—C23	0.3 (3)
N5—C7—C8—C9	−0.12 (17)	C21—C22—C23—C18	0.5 (3)
N5—N6—C9—C8	0.38 (16)	C19—C18—C23—C22	−0.6 (2)
Cu1—N6—C9—C8	−176.50 (10)	C17—C18—C23—C22	177.90 (16)
C7—C8—C9—N6	−0.16 (17)	Cu3—O5—C25—C24	92.04 (14)
Cu3^{i}—O2—C10—O1	−35.20 (19)		

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H10···O4^{ii}	0.73 (3)	2.00 (3)	2.7325 (18)	173 (3)
O7—H11···O8	0.76 (2)	1.87 (2)	2.6175 (17)	168 (2)
O5—H5*A*···O4^{ii}	0.75	2.0	2.7393 (16)	170
C27—H27*A*···N5^{ii}	0.99	2.68	3.6640 (19)	173

Symmetry code: (ii) −*x*+1, −*y*+1, −*z*+1.