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A tetranuclear copper(II) complex constructed from the salen ligand with alkoxo groups

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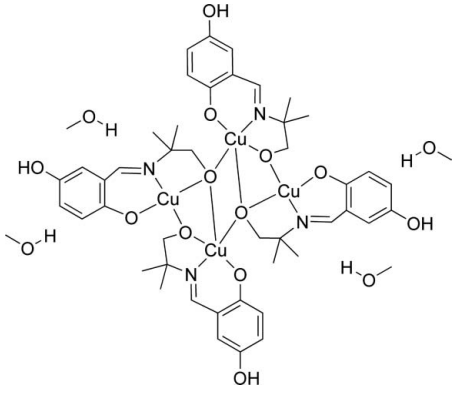
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.036; wR factor = 0.094; data-to-parameter ratio = 16.4.

In the title compound, tetrakis[μ_3-2-(5-hydroxy-2-oxidobenzylideneamino)-2-methylpropanolato]tetracopper(II) methanol tetrasolvate, $[Cu_4(C_{11}H_{13}NO_3)_4]\cdot 4CH_3OH$, two Cu_2 cores are linked by two μ_3-bridging alkoxo O atoms to form a centrosymmetric dimer of dicopper(II) units. Two Cu atoms coordinate to the NO_2 (a phenolic O atom, an alcoholic O atom and an imine N atom) chelator unit of one ligand and an alcohol O atom of the other ligand, forming a distorted planar coordination configure. The remaining Cu atoms coordinate in a pyramidal geometry. The distorted basal plane is also formed by the N_2O unit and the alcohol O atom from the second ligand, while an alcohol O atom from a third ligand occupies the axial position.

Related literature

For related literature, see: Atkins *et al.* (1993); Gatteschi (1994); Kahn (1993, 1995); Liu *et al.* (2005); Xie *et al.* (2007); Paap *et al.* (1981).



Experimental

Crystal data

$[Cu_4(C_{11}H_{13}NO_3)_4]\cdot 4CH_4O$
M_r = 1211.27
Monoclinic, $P2_1/n$
a = 13.2600 (10) Å
b = 15.3170 (11) Å
c = 13.2660 (10) Å
β = 94.9360 (10)°
V = 2684.4 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.63 mm^{-1}
T = 293 (2) K
0.27 × 0.21 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.667, T_{max} = 0.747
15163 measured reflections
5500 independent reflections
4143 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.089
S = 1.01
5500 reflections
335 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AV3116).

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supplementary materials

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A tetranuclear copper(II) complex constructed from the salen ligand with alkoxo groups

M.-S. Zhang, J.-Y. Jin, X. Wu, K.-Z. Shao and Z.-M. Su

Comment

There has been continuous interest in high-nuclearity transition-metal complexes in order to elucidate the fundamentals of magnetic interactions (Kahn O., 1993; Kahn O., 1995; Gatteschi D., 1994). Especially, polynuclear metal complexes including O-bridges arising from O-alkoxo moieties have attracted intense interest (Paap *et al.*, 1981; Atkins *et al.*, 1993). Generally, the flexibility of the coordination sphere around Cu^{II} with varied distortions due to a pseudo-Jahn-Teller effect leads to its tremendous structral diversity. It has been exemplied that contruction of the polynuclear Cu^{II} complexes from the polydentate Schiff-based ligands represents a promising route, because the ligands can function in both bridging and chelating modes (Liu *et al.*, 2005; Xie *et al.*, 2007). Here we report a new tetranuclear Cu^{II} complex constructed from the salen ligand with alkoxo moieties, *N*-(2,5-dihyroxyphenylmethylene)-1-amino-1-methylpropanol.

As shown in Fig. 1, X-ray single-crystal analysis reveals the existance of a tetranulear Cu^{II} molecular skeleton in compound. In an ansymmetry unit, there are two Cu^{II} atoms, two ligands and two solvent methanol molecules. The tetranuclear complex contains two kinds of Cu^{II} center. Two Cu1 atoms each coordinate to the NO2 (a phenolic oxygen atom, an alcoholic oxygen atom and an imine N atom) chelator unit in one ligand and an alcohol oxygen atom from the other ligand, forming a distorted planar coordination sphere. While two Cu2 each coordinate in a pyramidal geometry. Its distorted basal plane is also formed by the N2O unit and the alcohol oxygen atom from the second ligand, and an alcohol oxygen atom from the third ligand occupies the axial position with the Cu—O distance as 2.34 Å. Two of the four alcohol oxygen atoms O3 in the ligands act as one μ_2 bridged atom and the other two O6 act as μ_3 bridge to link to Cu atoms together, resulting in the tetranuclear structure. Such structure can be described as two Cu—Cu cores (separated in 3.05 Å) linked by two μ_3 bridged alcohol oxygen O6 and O6A atoms to form a centrosymmetric dimer of dicopper(II) moieties.

Experimental

1-Amino-1-methylpropanol (0.285 g, 3.20 mmol) was added to the solution of ethyl acetate containing 4-hydroxybenzaldehyde (0.345 g, 2.50 mmol). After keeping stirred at room temperature for 1 h, the precipitated yellow solid was then filtrated. Recrystallization from the mixture solvents (methanol:ethtyl acetate = 1:4) provided a yellow needle as the salen compound. Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.20 (s, 1H), 7.13 (d, J = 7.9 Hz, 1H), 6.12 (d, J = 7.9 Hz, 1H), 6.05 (s, 1H), 4.45 (s, 1H), 3.53 (s, 2H), 3.32 (s, 1H), 1.40 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.27, 166.35, 135.76, 110.06, 106.62, 68.86, 58.14, 22.52. IR (KBr, cm^{-1}): 3061, 2972, 2900, 1636, 1229, 1072. Analysis found: C 63.41, H 7.50, N 6.72%; $C_{11}H_{15}NO_3$ requires: C 63.14, H 7.23, N 6.69%.

The salen ligand (0.230 g, 1.1 mmol) was dissolved in 10 ml me thanol. The other 10 ml of methanol solution containing 0.20 g copper acetate (1.0 mmol) was then slowly added when keeping stirred at room temperature. After two hours, the resulting green solid was filtrated and washed by methanol for 4–6 times. Drying in vacuum provied the tetranuclear Cu^{II}

complex. Crystals suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared. Analysis found: C 47.56, H 5.52, N 4.17%; $C_{48}H_{68}N_4O_{16}Cu_4$ requires: C 47.60, H 5.66, N 4.63%.

Refinement

H atoms were visible in diference maps and were subsequently treated as riding atoms with distances C—H = 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (CH) and O—H = 0.84 Å.

Figures

Fig. 1. *ORTEP* drawing of the tetranuclear Cu^{II} complex, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity. (Symmetry code (A): $-x$, $-y$, $1-z$).

tetrakis[μ3-2-(5-hydroxy-2-oxidobenzylideneamino)-2- methylpropanolato]tetracopper(II) methanol tetrasolvate

Crystal data

$[Cu_4(C_{11}H_{13}N_1O_3)_4]\cdot 4CH_4O$	F_{000} = 1252
M_r = 1211.27	D_x = 1.496 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71069 Å
a = 13.2600 (10) Å	Cell parameters from 198 reflections
b = 15.3170 (11) Å	θ = 2.8–23.6º
c = 13.2660 (10) Å	μ = 1.63 mm^{-1}
β = 94.9360 (10)º	T = 293 (2) K
V = 2684.4 (3) Å^3	Block, green
Z = 2	0.27 × 0.21 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer	5500 independent reflections
Radiation source: fine-focus sealed tube	4143 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.032
T = 293(2) K	θ_{max} = 26.4º
ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	h = −16→16
T_{min} = 0.667, T_{max} = 0.747	k = −16→19
15163 measured reflections	l = −14→16

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.7871P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
5500 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
335 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	−0.03362 (3)	0.14760 (2)	0.40100 (2)	0.03335 (10)
Cu2	0.10141 (2)	−0.02196 (2)	0.43998 (3)	0.03326 (11)
N1	0.23637 (17)	−0.06909 (14)	0.43062 (18)	0.0355 (5)
N2	−0.06058 (17)	0.13685 (14)	0.25524 (17)	0.0343 (5)
O1	0.35289 (19)	0.33567 (14)	0.3623 (2)	0.0738 (8)
H1	0.3034	0.3627	0.3786	0.111*
O2	0.14247 (14)	0.09726 (11)	0.42952 (15)	0.0395 (5)
O3	0.06112 (14)	−0.14255 (11)	0.45695 (14)	0.0336 (4)
O4	−0.1033 (2)	0.55741 (12)	0.27462 (17)	0.0581 (6)
H4	−0.0864	0.5698	0.3338	0.087*
O5	−0.02680 (16)	0.27247 (12)	0.39976 (14)	0.0412 (5)
O6	−0.03814 (13)	0.01988 (11)	0.40057 (14)	0.0329 (4)
O7	−0.08781 (19)	0.65603 (14)	0.44334 (18)	0.0563 (6)
H7A	−0.0479	0.6758	0.4883	0.084*
O8	0.1988 (2)	0.43416 (18)	0.4108 (3)	0.0982 (11)
H8	0.1642	0.4167	0.4550	0.147*
C1	0.3369 (2)	0.2493 (2)	0.3721 (3)	0.0483 (8)
C2	0.2451 (2)	0.21476 (18)	0.3931 (2)	0.0404 (7)

H2	0.1907	0.2523	0.3986	0.048*
C3	0.2311 (2)	0.12554 (17)	0.4062 (2)	0.0342 (6)
C4	0.3151 (2)	0.06916 (18)	0.3953 (2)	0.0368 (6)
C5	0.4071 (2)	0.1072 (2)	0.3714 (3)	0.0511 (8)
H5	0.4618	0.0708	0.3629	0.061*
C6	0.4190 (3)	0.1945 (2)	0.3605 (3)	0.0571 (9)
H6	0.4808	0.2174	0.3454	0.068*
C7	0.3133 (2)	−0.02352 (18)	0.4083 (2)	0.0397 (7)
H7	0.3728	−0.0537	0.3999	0.048*
C8	0.2431 (2)	−0.16499 (17)	0.4481 (2)	0.0411 (7)
C9	0.1356 (2)	−0.19766 (18)	0.4189 (2)	0.0407 (7)
H9A	0.1242	−0.2005	0.3457	0.049*
H9B	0.1285	−0.2562	0.4452	0.049*
C10	0.2748 (3)	−0.1798 (2)	0.5603 (3)	0.0549 (9)
H10A	0.3433	−0.1604	0.5754	0.082*
H10B	0.2702	−0.2408	0.5756	0.082*
H10C	0.2309	−0.1474	0.6003	0.082*
C11	0.3168 (3)	−0.2113 (2)	0.3827 (3)	0.0659 (11)
H11A	0.3052	−0.1916	0.3140	0.099*
H11B	0.3063	−0.2732	0.3854	0.099*
H11C	0.3851	−0.1980	0.4079	0.099*
C12	−0.0571 (2)	0.32373 (17)	0.3224 (2)	0.0341 (6)
C13	−0.0653 (2)	0.41317 (17)	0.3394 (2)	0.0386 (7)
H13	−0.0501	0.4351	0.4043	0.046*
C14	−0.0956 (2)	0.46972 (18)	0.2615 (2)	0.0406 (7)
C15	−0.1183 (3)	0.43913 (19)	0.1646 (2)	0.0475 (8)
H15	−0.1381	0.4776	0.1124	0.057*
C16	−0.1115 (2)	0.35204 (19)	0.1458 (2)	0.0454 (7)
H16	−0.1270	0.3318	0.0802	0.055*
C17	−0.0816 (2)	0.29170 (17)	0.2229 (2)	0.0354 (6)
C18	−0.0791 (2)	0.20114 (18)	0.1946 (2)	0.0373 (6)
H18	−0.0921	0.1881	0.1262	0.045*
C19	−0.0595 (2)	0.04485 (17)	0.2171 (2)	0.0406 (7)
C20	−0.0882 (2)	−0.01003 (18)	0.3081 (2)	0.0422 (7)
H20A	−0.1608	−0.0070	0.3121	0.051*
H20B	−0.0704	−0.0706	0.2977	0.051*
C21	0.0475 (3)	0.0259 (2)	0.1897 (3)	0.0572 (9)
H21A	0.0620	0.0613	0.1330	0.086*
H21B	0.0530	−0.0346	0.1724	0.086*
H21C	0.0949	0.0392	0.2464	0.086*
C22	−0.1361 (3)	0.0277 (2)	0.1279 (3)	0.0657 (10)
H22A	−0.2011	0.0495	0.1427	0.098*
H22B	−0.1407	−0.0340	0.1154	0.098*
H22C	−0.1152	0.0567	0.0690	0.098*
C23	−0.1332 (3)	0.7280 (2)	0.3820 (3)	0.0661 (10)
H23A	−0.1480	0.7756	0.4254	0.099*
H23B	−0.1945	0.7083	0.3454	0.099*
H23C	−0.0866	0.7472	0.3351	0.099*
C24	0.1820 (3)	0.5212 (3)	0.3951 (4)	0.0832 (13)

H24A	0.2104	0.5535	0.4528	0.125*
H24B	0.1105	0.5319	0.3854	0.125*
H24C	0.2134	0.5395	0.3360	0.125*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0420 (2)	0.02276 (17)	0.0347 (2)	0.00045 (14)	−0.00022 (15)	0.00095 (14)
Cu2	0.03172 (18)	0.02416 (18)	0.0440 (2)	0.00098 (13)	0.00402 (15)	0.00292 (14)
N1	0.0353 (13)	0.0261 (12)	0.0450 (14)	0.0032 (10)	0.0037 (11)	−0.0022 (10)
N2	0.0388 (13)	0.0281 (12)	0.0351 (13)	0.0046 (10)	−0.0017 (10)	−0.0032 (10)
O1	0.0655 (17)	0.0387 (14)	0.121 (2)	−0.0166 (11)	0.0278 (17)	0.0148 (14)
O2	0.0327 (10)	0.0263 (10)	0.0598 (13)	−0.0008 (8)	0.0068 (9)	0.0032 (9)
O3	0.0392 (10)	0.0250 (9)	0.0367 (11)	0.0015 (8)	0.0044 (8)	−0.0006 (8)
O4	0.0942 (19)	0.0263 (11)	0.0519 (15)	0.0109 (11)	−0.0045 (14)	0.0002 (9)
O5	0.0641 (13)	0.0240 (10)	0.0337 (11)	−0.0001 (9)	−0.0068 (10)	0.0023 (8)
O6	0.0331 (10)	0.0240 (9)	0.0408 (11)	0.0002 (8)	−0.0017 (8)	0.0014 (8)
O7	0.0670 (16)	0.0447 (13)	0.0548 (15)	−0.0046 (11)	−0.0084 (12)	−0.0100 (11)
O8	0.089 (2)	0.0605 (19)	0.151 (3)	−0.0021 (16)	0.043 (2)	0.0052 (18)
C1	0.0504 (19)	0.0382 (17)	0.058 (2)	−0.0107 (15)	0.0113 (16)	0.0073 (15)
C2	0.0427 (17)	0.0323 (16)	0.0465 (18)	−0.0005 (12)	0.0065 (14)	0.0049 (13)
C3	0.0345 (15)	0.0329 (15)	0.0349 (16)	−0.0060 (12)	0.0014 (12)	0.0000 (12)
C4	0.0350 (15)	0.0362 (16)	0.0400 (16)	−0.0024 (12)	0.0070 (13)	0.0013 (12)
C5	0.0402 (18)	0.052 (2)	0.063 (2)	−0.0013 (15)	0.0153 (16)	0.0037 (16)
C6	0.049 (2)	0.052 (2)	0.073 (3)	−0.0119 (16)	0.0196 (18)	0.0070 (17)
C7	0.0341 (15)	0.0399 (17)	0.0455 (18)	0.0033 (13)	0.0060 (13)	−0.0051 (13)
C8	0.0414 (17)	0.0262 (15)	0.056 (2)	0.0068 (12)	0.0070 (14)	−0.0037 (13)
C9	0.0479 (17)	0.0268 (15)	0.0480 (18)	0.0004 (13)	0.0081 (14)	−0.0084 (13)
C10	0.052 (2)	0.0418 (18)	0.068 (2)	0.0065 (15)	−0.0090 (17)	0.0088 (16)
C11	0.058 (2)	0.0398 (19)	0.103 (3)	0.0079 (16)	0.025 (2)	−0.0133 (19)
C12	0.0356 (15)	0.0281 (14)	0.0388 (16)	0.0028 (11)	0.0044 (12)	0.0043 (12)
C13	0.0509 (18)	0.0282 (15)	0.0360 (16)	0.0023 (13)	0.0010 (13)	−0.0017 (12)
C14	0.0476 (18)	0.0290 (15)	0.0454 (18)	0.0059 (13)	0.0052 (14)	0.0027 (13)
C15	0.069 (2)	0.0336 (17)	0.0382 (18)	0.0074 (15)	−0.0038 (16)	0.0078 (13)
C16	0.061 (2)	0.0393 (17)	0.0344 (17)	0.0060 (15)	−0.0024 (15)	0.0018 (13)
C17	0.0431 (16)	0.0282 (15)	0.0349 (16)	0.0041 (12)	0.0025 (13)	0.0014 (12)
C18	0.0421 (16)	0.0369 (16)	0.0328 (16)	0.0031 (13)	0.0020 (13)	−0.0020 (12)
C19	0.0521 (18)	0.0269 (15)	0.0420 (17)	0.0067 (13)	−0.0013 (14)	−0.0084 (12)
C20	0.0442 (17)	0.0297 (15)	0.0508 (19)	−0.0040 (13)	−0.0064 (14)	−0.0055 (13)
C21	0.071 (2)	0.0448 (19)	0.058 (2)	0.0162 (17)	0.0179 (18)	−0.0056 (16)
C22	0.090 (3)	0.046 (2)	0.056 (2)	0.0023 (19)	−0.023 (2)	−0.0132 (16)
C23	0.076 (3)	0.054 (2)	0.065 (3)	0.0069 (19)	−0.008 (2)	−0.0059 (18)
C24	0.075 (3)	0.069 (3)	0.107 (4)	0.002 (2)	0.018 (3)	0.018 (2)

Geometric parameters (Å, °)

Cu1—O5	1.9150 (18)	C8—C10	1.528 (4)
Cu1—N2	1.943 (2)	C8—C9	1.530 (4)

Cu1—O3^{i}	1.9515 (18)	C8—C11	1.535 (4)
Cu1—O6	1.9572 (17)	C9—H9A	0.9700
Cu1—Cu2^{i}	3.0477 (5)	C9—H9B	0.9700
Cu2—O2	1.9139 (18)	C10—H10A	0.9600
Cu2—O3	1.9414 (17)	C10—H10B	0.9600
Cu2—N1	1.944 (2)	C10—H10C	0.9600
Cu2—O6	1.9853 (17)	C11—H11A	0.9600
Cu2—O6^{i}	2.3419 (18)	C11—H11B	0.9600
Cu2—Cu1^{i}	3.0477 (5)	C11—H11C	0.9600
N1—C7	1.291 (3)	C12—C13	1.394 (4)
N2—C18	1.282 (3)	C13—H13	0.9300
N2—C19	1.498 (3)	C14—C15	1.377 (4)
O1—C1	1.348 (3)	C14—C13	1.382 (4)
O1—H1	0.8200	C15—H15	0.9300
O2—C3	1.314 (3)	C16—C15	1.361 (4)
O3—C9	1.424 (3)	C16—H16	0.9300
O3—Cu1^{i}	1.9515 (18)	C17—C16	1.410 (4)
O4—C14	1.359 (3)	C17—C12	1.420 (4)
O4—H4	0.8200	C17—C18	1.438 (4)
O5—C12	1.327 (3)	C18—H18	0.9300
O6—C20	1.420 (3)	C19—C22	1.515 (4)
O6—Cu2^{i}	2.3419 (18)	C19—C20	1.546 (4)
O7—C23	1.468 (4)	C20—H20A	0.9700
O7—H7A	0.8200	C20—H20B	0.9700
O8—C24	1.365 (4)	C21—C19	1.522 (4)
O8—H8	0.8200	C21—H21A	0.9600
C1—C2	1.378 (4)	C21—H21B	0.9600
C1—C6	1.393 (5)	C21—H21C	0.9600
C2—H2	0.9300	C22—H22A	0.9600
C3—C2	1.392 (4)	C22—H22B	0.9600
C3—C4	1.427 (4)	C22—H22C	0.9600
C4—C5	1.411 (4)	C23—H23A	0.9600
C5—H5	0.9300	C23—H23B	0.9600
C6—C5	1.356 (4)	C23—H23C	0.9600
C6—H6	0.9300	C24—H24A	0.9600
C7—C4	1.430 (4)	C24—H24B	0.9600
C7—H7	0.9300	C24—H24C	0.9600
C8—N1	1.488 (3)		
O5—Cu1—N2	94.64 (8)	C7—N1—C8	122.1 (2)
O5—Cu1—O3^{i}	93.48 (8)	C7—N1—Cu2	124.30 (19)
N2—Cu1—O3^{i}	157.52 (9)	C8—N1—Cu2	113.59 (17)
O5—Cu1—O6	178.80 (8)	O5—C12—C13	118.6 (2)
N2—Cu1—O6	84.80 (8)	O5—C12—C17	123.0 (2)
O3^{i}—Cu1—O6	87.42 (7)	C13—C12—C17	118.4 (2)
O5—Cu1—Cu2^{i}	130.81 (6)	C8—C10—H10A	109.5
N2—Cu1—Cu2^{i}	126.54 (7)	C8—C10—H10B	109.5

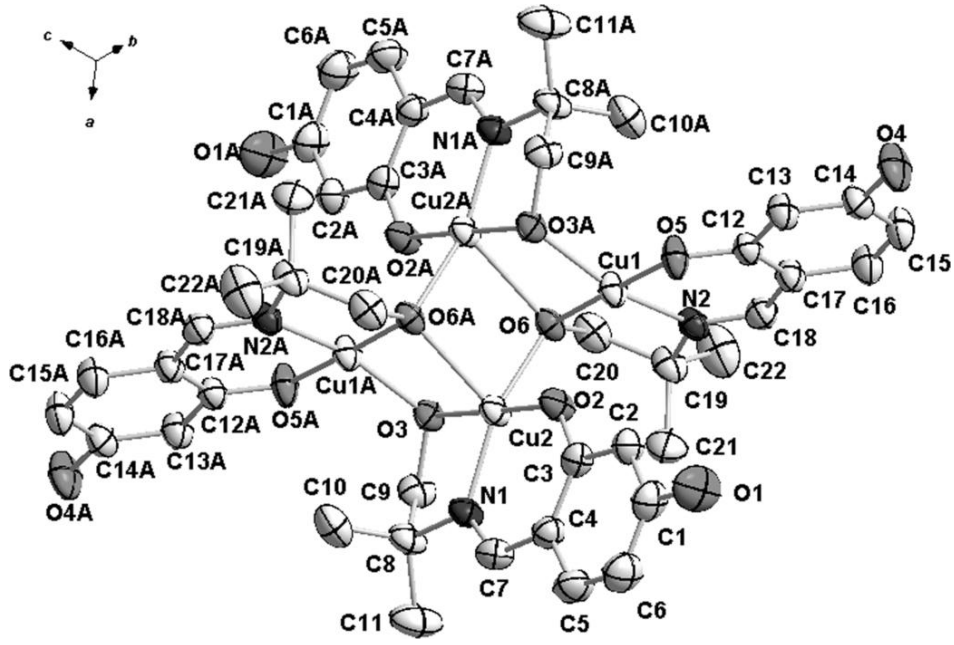
$O3^{i}$—Cu1—$Cu2^{i}$	38.36 (5)	H10A—C10—H10B	109.5
O6—Cu1—$Cu2^{i}$	50.21 (5)	C8—C10—H10C	109.5
O2—Cu2—O3	177.49 (8)	H10A—C10—H10C	109.5
O2—Cu2—N1	94.62 (8)	H10B—C10—H10C	109.5
O3—Cu2—N1	85.30 (8)	O1—C1—C2	123.1 (3)
O2—Cu2—O6	86.42 (8)	O1—C1—C6	116.8 (3)
O3—Cu2—O6	94.48 (7)	C2—C1—C6	120.2 (3)
N1—Cu2—O6	161.01 (9)	N2—C19—C22	113.7 (2)
O2—Cu2—$O6^{i}$	100.30 (7)	N2—C19—C21	107.2 (2)
O3—Cu2—$O6^{i}$	77.56 (7)	C22—C19—C21	110.9 (3)
N1—Cu2—$O6^{i}$	117.78 (8)	N2—C19—C20	103.7 (2)
O6—Cu2—$O6^{i}$	80.52 (7)	C22—C19—C20	108.8 (3)
O2—Cu2—$Cu1^{i}$	139.05 (6)	C21—C19—C20	112.3 (3)
O3—Cu2—$Cu1^{i}$	38.59 (5)	C5—C6—C1	118.9 (3)
N1—Cu2—$Cu1^{i}$	97.91 (7)	C5—C6—H6	120.5
O6—Cu2—$Cu1^{i}$	93.57 (5)	C1—C6—H6	120.5
$O6^{i}$—Cu2—$Cu1^{i}$	39.95 (4)	C16—C15—C14	119.5 (3)
C9—O3—Cu2	108.47 (16)	C16—C15—H15	120.3
C9—O3—$Cu1^{i}$	120.79 (17)	C14—C15—H15	120.3
Cu2—O3—$Cu1^{i}$	103.05 (8)	C14—C13—C12	121.1 (3)
C14—O4—H4	109.5	C14—C13—H13	119.4
C3—O2—Cu2	126.69 (17)	C12—C13—H13	119.4
C20—O6—Cu1	109.69 (15)	O6—C20—C19	111.8 (2)
C20—O6—Cu2	118.65 (16)	O6—C20—H20A	109.3
Cu1—O6—Cu2	107.11 (8)	C19—C20—H20A	109.3
C20—O6—$Cu2^{i}$	127.42 (16)	O6—C20—H20B	109.3
Cu1—O6—$Cu2^{i}$	89.83 (7)	C19—C20—H20B	109.3
Cu2—O6—$Cu2^{i}$	99.48 (7)	H20A—C20—H20B	107.9
C1—O1—H1	109.5	N1—C7—C4	125.9 (3)
C12—O5—Cu1	125.90 (17)	N1—C7—H7	117.0
C18—N2—C19	121.1 (2)	C4—C7—H7	117.0
C18—N2—Cu1	124.65 (19)	C5—C4—C3	118.1 (3)
C19—N2—Cu1	114.20 (17)	C5—C4—C7	117.4 (3)
C16—C17—C12	118.4 (2)	C3—C4—C7	124.5 (2)
C16—C17—C18	117.0 (3)	C1—C2—C3	122.2 (3)
C12—C17—C18	124.6 (2)	C1—C2—H2	118.9
O2—C3—C2	119.0 (2)	C3—C2—H2	118.9
O2—C3—C4	123.1 (2)	C6—C5—C4	122.8 (3)
C2—C3—C4	117.9 (2)	C6—C5—H5	118.6
O4—C14—C15	116.3 (3)	C4—C5—H5	118.6
O4—C14—C13	122.9 (3)	C19—C22—H22A	109.5
C15—C14—C13	120.7 (3)	C19—C22—H22B	109.5
N1—C8—C10	107.8 (2)	H22A—C22—H22B	109.5
N1—C8—C9	104.0 (2)	C19—C22—H22C	109.5
C10—C8—C9	111.7 (3)	H22A—C22—H22C	109.5
N1—C8—C11	113.6 (3)	H22B—C22—H22C	109.5

C10—C8—C11	110.3 (3)	C8—C11—H11A	109.5
C9—C8—C11	109.3 (3)	C8—C11—H11B	109.5
C19—C21—H21A	109.5	H11A—C11—H11B	109.5
C19—C21—H21B	109.5	C8—C11—H11C	109.5
H21A—C21—H21B	109.5	H11A—C11—H11C	109.5
C19—C21—H21C	109.5	H11B—C11—H11C	109.5
H21A—C21—H21C	109.5	C23—O7—H7A	109.5
H21B—C21—H21C	109.5	C24—O8—H8	109.5
N2—C18—C17	125.8 (3)	O7—C23—H23A	109.5
N2—C18—H18	117.1	O7—C23—H23B	109.5
C17—C18—H18	117.1	H23A—C23—H23B	109.5
O3—C9—C8	112.1 (2)	O7—C23—H23C	109.5
O3—C9—H9A	109.2	H23A—C23—H23C	109.5
C8—C9—H9A	109.2	H23B—C23—H23C	109.5
O3—C9—H9B	109.2	O8—C24—H24A	109.5
C8—C9—H9B	109.2	O8—C24—H24B	109.5
H9A—C9—H9B	107.9	H24A—C24—H24B	109.5
C15—C16—C17	121.9 (3)	O8—C24—H24C	109.5
C15—C16—H16	119.1	H24A—C24—H24C	109.5
C17—C16—H16	119.1	H24B—C24—H24C	109.5
O2—Cu2—O3—C9	−108.5 (17)	C11—C8—C9—O3	−164.9 (3)
N1—Cu2—O3—C9	−20.22 (18)	C12—C17—C16—C15	−0.7 (5)
O6—Cu2—O3—C9	140.72 (17)	C18—C17—C16—C15	178.8 (3)
O6^{i}—Cu2—O3—C9	−140.02 (18)	C10—C8—N1—C7	88.9 (3)
Cu1^{i}—Cu2—O3—C9	−129.2 (2)	C9—C8—N1—C7	−152.4 (3)
O2—Cu2—O3—Cu1^{i}	20.7 (18)	C11—C8—N1—C7	−33.6 (4)
N1—Cu2—O3—Cu1^{i}	108.93 (10)	C10—C8—N1—Cu2	−93.2 (2)
O6—Cu2—O3—Cu1^{i}	−90.12 (9)	C9—C8—N1—Cu2	25.5 (3)
O6^{i}—Cu2—O3—Cu1^{i}	−10.87 (7)	C11—C8—N1—Cu2	144.3 (2)
O3—Cu2—O2—C3	97.8 (17)	O2—Cu2—N1—C7	−9.0 (2)
N1—Cu2—O2—C3	9.8 (2)	O3—Cu2—N1—C7	173.5 (2)
O6—Cu2—O2—C3	−151.2 (2)	O6—Cu2—N1—C7	83.4 (3)
O6^{i}—Cu2—O2—C3	129.1 (2)	O6^{i}—Cu2—N1—C7	−113.2 (2)
Cu1^{i}—Cu2—O2—C3	117.5 (2)	Cu1^{i}—Cu2—N1—C7	−150.0 (2)
O5—Cu1—O6—C20	−81 (4)	O2—Cu2—N1—C8	173.09 (19)
N2—Cu1—O6—C20	−18.51 (17)	O3—Cu2—N1—C8	−4.39 (19)
O3^{i}—Cu1—O6—C20	140.38 (17)	O6—Cu2—N1—C8	−94.5 (3)
Cu2^{i}—Cu1—O6—C20	130.12 (18)	O6^{i}—Cu2—N1—C8	68.9 (2)
O5—Cu1—O6—Cu2	49 (4)	Cu1^{i}—Cu2—N1—C8	32.17 (19)
N2—Cu1—O6—Cu2	111.50 (10)	Cu1—O5—C12—C13	167.74 (19)
O3^{i}—Cu1—O6—Cu2	−89.61 (9)	Cu1—O5—C12—C17	−12.3 (4)
Cu2^{i}—Cu1—O6—Cu2	−99.87 (9)	C16—C17—C12—O5	−179.0 (3)
O5—Cu1—O6—Cu2^{i}	149 (4)	C18—C17—C12—O5	1.6 (4)
N2—Cu1—O6—Cu2^{i}	−148.62 (8)	C16—C17—C12—C13	1.0 (4)
O3^{i}—Cu1—O6—Cu2^{i}	10.26 (7)	C18—C17—C12—C13	−178.4 (3)

O2—Cu2—O6—C20	116.44 (18)	C18—N2—C19—C22	−34.7 (4)
O3—Cu2—O6—C20	−65.91 (18)	Cu1—N2—C19—C22	144.6 (2)
N1—Cu2—O6—C20	22.7 (3)	C18—N2—C19—C21	88.3 (3)
O6^{i}—Cu2—O6—C20	−142.5 (2)	Cu1—N2—C19—C21	−92.4 (2)
Cu1^{i}—Cu2—O6—C20	−104.59 (17)	C18—N2—C19—C20	−152.7 (3)
O2—Cu2—O6—Cu1	−8.30 (9)	Cu1—N2—C19—C20	26.6 (3)
O3—Cu2—O6—Cu1	169.35 (9)	O1—C1—C6—C5	178.9 (3)
N1—Cu2—O6—Cu1	−102.1 (2)	C2—C1—C6—C5	−0.9 (5)
O6^{i}—Cu2—O6—Cu1	92.77 (9)	C17—C16—C15—C14	−0.1 (5)
Cu1^{i}—Cu2—O6—Cu1	130.67 (7)	O4—C14—C15—C16	179.6 (3)
O2—Cu2—O6—Cu2^{i}	−101.07 (8)	C13—C14—C15—C16	0.5 (5)
O3—Cu2—O6—Cu2^{i}	76.58 (7)	O4—C14—C13—C12	−179.2 (3)
N1—Cu2—O6—Cu2^{i}	165.1 (2)	C15—C14—C13—C12	−0.2 (5)
O6^{i}—Cu2—O6—Cu2^{i}	0.0	O5—C12—C13—C14	179.4 (3)
Cu1^{i}—Cu2—O6—Cu2^{i}	37.90 (5)	C17—C12—C13—C14	−0.5 (4)
N2—Cu1—O5—C12	13.6 (2)	Cu1—O6—C20—C19	39.3 (3)
O3^{i}—Cu1—O5—C12	−145.4 (2)	Cu2—O6—C20—C19	−84.1 (2)
O6—Cu1—O5—C12	76 (4)	Cu2^{i}—O6—C20—C19	145.01 (18)
Cu2^{i}—Cu1—O5—C12	−135.60 (19)	N2—C19—C20—O6	−42.4 (3)
O5—Cu1—N2—C18	−8.0 (2)	C22—C19—C20—O6	−163.7 (2)
O3^{i}—Cu1—N2—C18	102.8 (3)	C21—C19—C20—O6	73.1 (3)
O6—Cu1—N2—C18	173.0 (2)	C8—N1—C7—C4	−176.7 (3)
Cu2^{i}—Cu1—N2—C18	143.2 (2)	Cu2—N1—C7—C4	5.7 (4)
O5—Cu1—N2—C19	172.70 (19)	O2—C3—C4—C5	−179.2 (3)
O3^{i}—Cu1—N2—C19	−76.5 (3)	C2—C3—C4—C5	−0.3 (4)
O6—Cu1—N2—C19	−6.23 (18)	O2—C3—C4—C7	−0.1 (4)
Cu2^{i}—Cu1—N2—C19	−36.1 (2)	C2—C3—C4—C7	178.8 (3)
Cu2—O2—C3—C2	174.26 (19)	N1—C7—C4—C5	179.7 (3)
Cu2—O2—C3—C4	−6.9 (4)	N1—C7—C4—C3	0.6 (5)
C19—N2—C18—C17	−179.7 (3)	O1—C1—C2—C3	−177.9 (3)
Cu1—N2—C18—C17	1.1 (4)	C6—C1—C2—C3	1.9 (5)
C16—C17—C18—N2	−175.0 (3)	O2—C3—C2—C1	177.7 (3)
C12—C17—C18—N2	4.4 (5)	C4—C3—C2—C1	−1.3 (4)
Cu2—O3—C9—C8	41.2 (3)	C1—C6—C5—C4	−0.7 (5)
Cu1^{i}—O3—C9—C8	−77.2 (3)	C3—C4—C5—C6	1.2 (5)
N1—C8—C9—O3	−43.3 (3)	C7—C4—C5—C6	−177.9 (3)
C10—C8—C9—O3	72.7 (3)		

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

Fig. 1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