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A two-dimensional coordination polymer containing linear trinuclear copper(II) clusters

Ji-Jiang Wang, Bo Zhang, Hui-Ming Shu, Chuan-Qin Du and Huai-Ming Hu*

Department of Chemistry, Northwest University, Xi'an 710069, People's Republic of China
Correspondence e-mail: chemhu1@nwu.edu.cn

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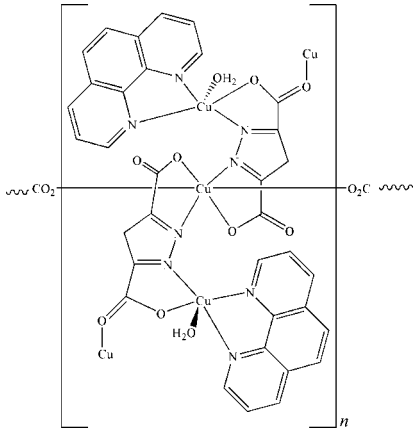
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.075; data-to-parameter ratio = 14.9.

The title coordination polymer, poly[diaqua(1,10-phenanthroline)(μ_3-pyrazole-3,5-dicarboxylato)tricopper(II)], $[Cu_3(C_5HN_2O_4)_2(C_{12}H_8N_2)_2(H_2O)_2]_n$, was hydrothermally synthesized and structurally characterized. It consists of linear trinuclear copper(II) clusters of $[Cu_3(pdc)_2(phen)_2(H_2O)_2]$ units (H_3pdc = pyrazole-3,5-dicarboxylic acid and phen = 1,10-phenanthroline), in which two pdc^{3-} ligands chelate three Cu^{II} ions with the central Cu^{II} ion on an inversion center. An infinite two-dimensional sheet structure is constructed by connecting adjacent linear trinuclear copper(II) units through coordination bonds between the central Cu^{II} atom and an O atom of the carboxylate group coordinated to the terminal Cu^{II} atom from the pdc^{3-} ligand.

Related literature

For related literature, see: Gutierrez *et al.* (2000, 2002); Kahn (2000); Mrozinski (2005); Pan, Huang & Li (2000); Pan, Huang, Li *et al.* (2000); Song *et al.* (2003, 2005); Vigato & Tamburini (2004).



Experimental

Crystal data

$[Cu_3(C_5HN_2O_4)_2(C_{12}H_8N_2)_2(H_2O)_2]$
M_r = 893.22
Monoclinic, $P2_1/c$
a = 12.6709 (13) Å
b = 15.7250 (16) Å
c = 7.9628 (8) Å
β = 97.620 (1)°
V = 1572.6 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.09 mm^{-1}
T = 296 (2) K
0.18 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.705, T_{max} = 0.788
9788 measured reflections
3817 independent reflections
3022 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.04
3817 reflections
256 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O3^{i}	0.836 (10)	1.932 (13)	2.754 (2)	168 (4)
O5—H5A···O1^{ii}	0.836 (10)	1.953 (10)	2.789 (2)	178 (4)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1995); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HJ3043).

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supplementary materials

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A two-dimensional coordination polymer containing linear trinuclear copper(II) clusters

J.-J. Wang, B. Zhang, H.-M. Shu, C.-Q. Du and H.-M. Hu

Comment

Polynuclear copper(II) complexes are attracting attention because of their interesting magnetic properties and their relevance to the active centers of a number of metalloproteins (Kahn, 2000; Vigato & Tamburini, 2004; Mrozinski, 2005). Although the greatest effort and success have been in the study of dinuclear copper(II) complexes, there has been little work on copper(II) complexes with more than two copper ions, particularly on linear trinuclear compounds (Gutierrez, *et al.*, 2000; Song, *et al.*, 2005). In this work, we have chosen a multifunctional ligand pyrazole-3,5-dicarboxylic acid (H_3pdc), since it has potential coordination sites involving both nitrogen atoms of the pyrazole ring and oxygen atoms of the carboxylate groups. Therefore, it can coordinate with metal ions in multidentate ways to form a series of complexes with novel structures and interesting properties (Pan, *et al.*, 2000). With the hydrothermal method, H_3pdc ligand reacted with copper(II) ions and employed phen as an auxiliary ligand to tune the final structure. Here we report the synthesis and crystal structure of a novel two-dimensional coordination polymer $[Cu_3(pdc)_2(phen)_2(H_2O)_2]_n$, (I).

Single crystal X-ray diffraction analysis reveals that complex (I) consists of trinuclear copper(II) unit, $[Cu_3(pdc)_2(phen)_2(H_2O)_2]$ (Figure 1). The planar trinuclear unit contains a six-coordinate and two five-coordinate Cu^{II} ions chelated by two pdc^{3-} ligands, in which the three copper(II) ions are arranged in a strict linear fashion [Cu1—Cu2—Cu1A= 180 °] with Cu2 on the inversion center and the Cu1···Cu2 distance is 4.318 (1) Å. The terminal copper(II) ions (Cu1 and Cu1A) have a distorted square pyramidal geometry coordinated by one N atom [Cu1—N1=1.9422 (17) Å] and one O atom [Cu1—O1=1.9939 (16) Å] of pdc^{3-} ligand, two N atoms [Cu1—N3=1.9870 (17) Å and Cu1—N4=2.0396 (18) Å] of a phen molecule and one O atom [Cu1—O5=2.2354 (18) Å] of a water molecule. The N—Cu1—N and N—Cu1—O bond angles fall in the ranges 81.77 (7)–174.61 (7) ° and 82.22 (7)–144.28 (7) °, respectively. The center Cu2 ion presents a distorted octahedral geometry formed from the O3 [Cu2—O3=1.9554 (14) Å], O3A [Cu2—O3A = 1.9554 (14) Å], N2 [Cu2—N2 = 1.9690 (17) Å], N2A [Cu2—N2A = 1.9690 (17) Å], O2B [Cu2—O2B = 2.781 (17) Å] and O2C [Cu2—O2C = 2.781 (17) Å] of pdc^{3-} ligands. The very long axial Cu—O bonds from the semi-coordinated pdc^{3-} ligands (O2B and O2C) indicate center Cu2 ion have a distorted octahedral environment due to Jahn-Teller effect. Therefore, the equatorial coordination plane is an N2O2 donor set [for Cu2: N2, N2A, O3, O3A]. The Cu—O bond lengths of the central Cu2 atom [1.9554 (14) Å] are shorter than those of the equatorial Cu—O bonds of the terminal Cu1 atoms [1.9939 (16) and 2.2354 (18) Å], which is attributed to the two different coordination geometries (octahedral and square pyramidal, respectively). As can be seen from Figure 1, the pdc^{3-} ligand bite angle at the two different Cu^{II} ions (Cu1 and Cu2) is similar, 82.22 (7) ° and 83.07 °, respectively. This implies that H_3pdc is a fairly rigid ligand and retains its integrity on metal chelation. However, the carboxylate groups are twisted out of the plane of the pyrazole ring as a results of the coordination of O1 and O3 to their respective Cu^{II} ions. In complex (I), all the Cu—O and Cu—N bond lengths are similar to those found in the previously linear trinuclear copper(II) complexes (Gutierrez, *et al.*, 2002; Song, *et al.*, 2003). As shown in Figure 2, an infinite two-dimensional sheet structure is constructed by connecting adjacent linear triunclear copper(II) units through coordination bonds between the

central copper(II) atom (Cu2) and the oxygen atom (O2) of carboxylate group coordinated to the terminal copper(II) atom (Cu1) from the pdc^{3-} ligand.

Experimental

H_3pdc was purchased from Aldrich and was used without further purification. Complex (I) was synthesized under hydrothermal conditions. A mixture of $CuCO_3{\cdot}Cu(OH)_2$ (0.0066 g, 0.03 mmol), phen (0.0040 g, 0.02 mmol), H_3pdc (0.0174 g, 0.10 mmol) and water (10 ml) was stirred for 30 min in air, then sealed in a 25 ml Telfon-lined stainless steel constainer, which was heated to 433 K for 72 h. After cooling to to room temperature at a rate of 1 K every 10 min. Blue crystals of (I) were obtained in *ca* 45% yield. The complex is insoluble in common organic solvents and water. Elmental analysis for $C_{34}H_{22}Cu_3N_8O_{10}$ calculated: C 45.72, H 2.48, N 12.54%; found: C 45.70, H 2.59, N12.68%.

Refinement

The water H atoms were located in a difference Fourier map and refined with restrained O—H bond lengths [0.85 (1) Å] and fixed isotropic displacement parameters (0.080 $Å^2$). The H atoms were placed at calculated positions (C—H = 0.93–0.96 Å, N—H = 0.89–0.90 Å) and refined as riding with $U_{iso}(H) = 1.2\ U_{eq}$(carrier).

Figures

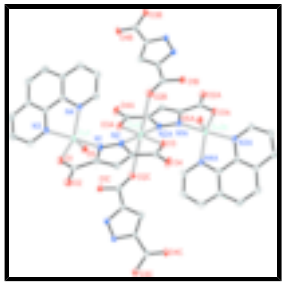

Fig. 1. The linear trinuclear copper(II) unit of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Atoms labelled with the suffixes A—C are at the symmetry positions (−*x* + 1, −*y*, −*z* + 1), (*x*, −*y* + 1/2, *z* + 1/2) and (−*x* + 1, *y* − 1/2, −*z* + 1/2), respectively.

Fig. 2. View of a two-dimensional sheets constructed by linear trinuclear copper(II) clusters units in (I). Hydrogen atoms and carbon atoms of phen have been omitted for clarity.

poly[diaqua(1,10-phenanthroline)(μ3-pyrazole-3,5- dicarboxylato)tricopper(II)],

Crystal data

$[Cu_3(C_5HN_2O_4)_2(C_{12}H_8N_2)_2(H_2O)_2]$	F_{000} = 898
M_r = 893.22	D_x = 1.886 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *K*α radiation λ = 0.71073 Å
a = 12.6709 (13) Å	Cell parameters from 3518 reflections
b = 15.7250 (16) Å	θ = 2.6–27.4°
c = 7.9628 (8) Å	μ = 2.09 mm^{-1}

β = 97.6200 (10)º	T = 296 (2) K
V = 1572.6 (3) Å^3	Block, blue
Z = 2	0.18 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3817 independent reflections
Radiation source: fine-focus sealed tube	3022 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.022
T = 296(2) K	θ_{max} = 28.2º
φ and ω scans	θ_{min} = 1.6º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -16 \rightarrow 10$
T_{min} = 0.705, T_{max} = 0.788	$k = -19 \rightarrow 20$
9788 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.029	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.075	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.6259P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
3817 reflections	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
256 parameters	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
2 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.28454 (2)	0.168599 (16)	0.19425 (3)	0.02894 (9)
Cu2	0.5000	0.0000	0.5000	0.03363 (11)
N1	0.42958 (14)	0.16741 (11)	0.3095 (2)	0.0273 (4)
N2	0.50013 (13)	0.11089 (11)	0.3852 (2)	0.0271 (4)
N3	0.13893 (14)	0.18077 (11)	0.0690 (2)	0.0290 (4)
N4	0.28236 (14)	0.06081 (11)	0.0514 (2)	0.0276 (4)
O1	0.31016 (12)	0.29372 (10)	0.1950 (2)	0.0359 (4)
O2	0.44176 (14)	0.38926 (10)	0.2441 (2)	0.0410 (4)
O3	0.65009 (12)	0.02691 (10)	0.5697 (2)	0.0348 (4)
O4	0.76794 (13)	0.13185 (11)	0.5688 (2)	0.0444 (4)
O5	0.21785 (13)	0.11277 (11)	0.4160 (2)	0.0354 (4)
C1	0.40786 (18)	0.31623 (13)	0.2446 (3)	0.0301 (5)
C2	0.47807 (17)	0.24388 (13)	0.3089 (3)	0.0269 (4)
C3	0.58241 (17)	0.23682 (13)	0.3844 (3)	0.0298 (5)
H3	0.6341	0.2791	0.3990	0.036*
C4	0.59219 (16)	0.15300 (13)	0.4328 (3)	0.0258 (4)
C5	0.67875 (17)	0.10245 (14)	0.5313 (3)	0.0299 (5)
C6	0.06794 (18)	0.24134 (15)	0.0850 (3)	0.0367 (5)
H6	0.0883	0.2876	0.1546	0.044*
C7	−0.03601 (19)	0.23830 (17)	0.0018 (3)	0.0405 (6)
H7	−0.0840	0.2814	0.0177	0.049*
C8	−0.06678 (18)	0.17152 (16)	−0.1034 (3)	0.0377 (6)
H8	−0.1358	0.1690	−0.1598	0.045*
C9	0.00700 (17)	0.10639 (14)	−0.1259 (3)	0.0310 (5)
C10	−0.0152 (2)	0.03495 (16)	−0.2368 (3)	0.0407 (6)
H10	−0.0820	0.0296	−0.3002	0.049*
C11	0.0596 (2)	−0.02445 (16)	−0.2502 (3)	0.0412 (6)
H11	0.0433	−0.0701	−0.3232	0.049*
C12	0.16378 (19)	−0.01951 (14)	−0.1555 (3)	0.0330 (5)
C13	0.2453 (2)	−0.07966 (15)	−0.1605 (3)	0.0383 (5)
H13	0.2335	−0.1276	−0.2288	0.046*
C14	0.3416 (2)	−0.06765 (15)	−0.0652 (3)	0.0374 (5)
H14	0.3965	−0.1064	−0.0710	0.045*
C15	0.35758 (18)	0.00311 (14)	0.0413 (3)	0.0331 (5)
H15	0.4232	0.0100	0.1074	0.040*
C16	0.18722 (16)	0.04984 (13)	−0.0473 (3)	0.0271 (4)
C17	0.10915 (17)	0.11403 (13)	−0.0348 (3)	0.0270 (4)
H5A	0.247 (3)	0.1404 (19)	0.499 (3)	0.080*
H5B	0.251 (2)	0.0664 (12)	0.426 (4)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02010 (14)	0.02947 (15)	0.03436 (15)	0.00124 (10)	−0.00714 (10)	−0.00091 (11)
Cu2	0.01976 (19)	0.0324 (2)	0.0448 (2)	−0.00645 (15)	−0.01020 (16)	0.01441 (17)
N1	0.0206 (8)	0.0277 (9)	0.0312 (9)	0.0006 (7)	−0.0050 (7)	0.0040 (7)
N2	0.0184 (8)	0.0277 (9)	0.0327 (9)	−0.0031 (7)	−0.0059 (7)	0.0040 (7)
N3	0.0213 (9)	0.0332 (10)	0.0312 (9)	0.0045 (7)	−0.0021 (7)	−0.0010 (8)

N4	0.0231 (9)	0.0310 (9)	0.0274 (9)	0.0028 (7)	−0.0013 (7)	0.0007 (7)
O1	0.0312 (8)	0.0303 (8)	0.0426 (9)	0.0029 (7)	−0.0092 (7)	0.0026 (7)
O2	0.0467 (10)	0.0260 (8)	0.0480 (10)	−0.0029 (7)	−0.0028 (8)	0.0027 (7)
O3	0.0215 (8)	0.0331 (8)	0.0462 (9)	−0.0034 (6)	−0.0090 (7)	0.0091 (7)
O4	0.0252 (8)	0.0458 (10)	0.0568 (11)	−0.0117 (7)	−0.0149 (8)	0.0106 (8)
O5	0.0299 (9)	0.0385 (9)	0.0360 (9)	−0.0016 (7)	−0.0020 (7)	−0.0001 (7)
C1	0.0311 (12)	0.0293 (11)	0.0283 (11)	0.0023 (9)	−0.0013 (9)	−0.0002 (9)
C2	0.0256 (11)	0.0258 (10)	0.0281 (10)	−0.0027 (8)	−0.0013 (9)	−0.0003 (8)
C3	0.0240 (11)	0.0276 (11)	0.0360 (12)	−0.0059 (9)	−0.0019 (9)	−0.0018 (9)
C4	0.0195 (10)	0.0292 (10)	0.0271 (10)	−0.0036 (8)	−0.0022 (8)	−0.0026 (8)
C5	0.0224 (10)	0.0344 (11)	0.0310 (11)	−0.0024 (9)	−0.0035 (9)	0.0004 (9)
C6	0.0297 (12)	0.0401 (13)	0.0385 (13)	0.0073 (10)	−0.0019 (10)	−0.0055 (10)
C7	0.0277 (12)	0.0503 (15)	0.0424 (14)	0.0148 (11)	0.0010 (10)	0.0020 (11)
C8	0.0223 (11)	0.0526 (15)	0.0361 (12)	0.0040 (10)	−0.0036 (9)	0.0092 (11)
C9	0.0243 (11)	0.0390 (12)	0.0278 (11)	−0.0037 (9)	−0.0035 (9)	0.0057 (9)
C10	0.0340 (13)	0.0473 (14)	0.0370 (13)	−0.0093 (11)	−0.0096 (10)	0.0015 (11)
C11	0.0446 (15)	0.0394 (13)	0.0366 (13)	−0.0091 (11)	−0.0061 (11)	−0.0059 (10)
C12	0.0359 (13)	0.0322 (11)	0.0299 (11)	−0.0042 (10)	0.0007 (10)	−0.0004 (9)
C13	0.0474 (15)	0.0316 (12)	0.0370 (13)	−0.0010 (11)	0.0100 (11)	−0.0063 (10)
C14	0.0376 (13)	0.0328 (12)	0.0437 (14)	0.0068 (10)	0.0125 (11)	0.0035 (10)
C15	0.0262 (11)	0.0370 (12)	0.0355 (12)	0.0054 (9)	0.0019 (9)	0.0042 (10)
C16	0.0239 (10)	0.0296 (11)	0.0269 (10)	−0.0004 (9)	0.0006 (8)	0.0034 (8)
C17	0.0236 (10)	0.0317 (11)	0.0245 (10)	−0.0001 (9)	−0.0016 (8)	0.0021 (8)

Geometric parameters (Å, °)

Cu1—N1	1.9422 (17)	C3—C4	1.374 (3)
Cu1—N3	1.9870 (17)	C3—H3	0.9300
Cu1—O1	1.9939 (16)	C4—C5	1.491 (3)
Cu1—N4	2.0396 (18)	C6—C7	1.395 (3)
Cu1—O5	2.2354 (18)	C6—H6	0.9300
Cu2—O3^{i}	1.9554 (14)	C7—C8	1.367 (3)
Cu2—O3	1.9554 (14)	C7—H7	0.9300
Cu2—N2^{i}	1.9690 (17)	C8—C9	1.414 (3)
Cu2—N2	1.9690 (17)	C8—H8	0.9300
N1—N2	1.345 (2)	C9—C17	1.402 (3)
N1—C2	1.351 (3)	C9—C10	1.434 (3)
N2—C4	1.351 (2)	C10—C11	1.345 (4)
N3—C6	1.328 (3)	C10—H10	0.9300
N3—C17	1.358 (3)	C11—C12	1.432 (3)
N4—C15	1.326 (3)	C11—H11	0.9300
N4—C16	1.360 (3)	C12—C16	1.397 (3)
O1—C1	1.298 (3)	C12—C13	1.405 (3)
O2—C1	1.226 (3)	C13—C14	1.362 (3)
O3—C5	1.290 (3)	C13—H13	0.9300
O4—C5	1.221 (3)	C14—C15	1.398 (3)
O5—H5A	0.836 (10)	C14—H14	0.9300
O5—H5B	0.836 (10)	C15—H15	0.9300
C1—C2	1.492 (3)	C16—C17	1.426 (3)

C2—C3	1.382 (3)		
N1—Cu1—N3	174.61 (7)	N2—C4—C3	110.42 (18)
N1—Cu1—O1	82.22 (7)	N2—C4—C5	115.72 (18)
N3—Cu1—O1	92.66 (7)	C3—C4—C5	133.78 (19)
N1—Cu1—N4	101.39 (7)	O4—C5—O3	124.8 (2)
N3—Cu1—N4	81.77 (7)	O4—C5—C4	121.3 (2)
O1—Cu1—N4	144.28 (7)	O3—C5—C4	113.88 (18)
N1—Cu1—O5	93.23 (7)	N3—C6—C7	122.6 (2)
N3—Cu1—O5	90.65 (7)	N3—C6—H6	118.7
O1—Cu1—O5	117.62 (7)	C7—C6—H6	118.7
N4—Cu1—O5	97.79 (7)	C8—C7—C6	119.5 (2)
$O3^{i}$—Cu2—O3	180.00 (10)	C8—C7—H7	120.3
$O3^{i}$—Cu2—$N2^{i}$	83.07 (6)	C6—C7—H7	120.3
O3—Cu2—$N2^{i}$	96.93 (6)	C7—C8—C9	119.6 (2)
$O3^{i}$—Cu2—N2	96.93 (6)	C7—C8—H8	120.2
O3—Cu2—N2	83.07 (6)	C9—C8—H8	120.2
$N2^{i}$—Cu2—N2	180.00 (5)	C17—C9—C8	116.9 (2)
N2—N1—C2	108.30 (16)	C17—C9—C10	118.6 (2)
N2—N1—Cu1	138.51 (14)	C8—C9—C10	124.5 (2)
C2—N1—Cu1	113.09 (13)	C11—C10—C9	120.7 (2)
N1—N2—C4	107.44 (16)	C11—C10—H10	119.7
N1—N2—Cu2	138.74 (14)	C9—C10—H10	119.7
C4—N2—Cu2	110.95 (13)	C10—C11—C12	122.0 (2)
C6—N3—C17	118.42 (19)	C10—C11—H11	119.0
C6—N3—Cu1	128.05 (15)	C12—C11—H11	119.0
C17—N3—Cu1	113.32 (14)	C16—C12—C13	116.5 (2)
C15—N4—C16	117.87 (19)	C16—C12—C11	118.2 (2)
C15—N4—Cu1	130.22 (15)	C13—C12—C11	125.3 (2)
C16—N4—Cu1	111.91 (14)	C14—C13—C12	119.9 (2)
C1—O1—Cu1	114.73 (13)	C14—C13—H13	120.1
C5—O3—Cu2	115.19 (13)	C12—C13—H13	120.1
Cu1—O5—H5A	104 (2)	C13—C14—C15	119.7 (2)
Cu1—O5—H5B	101 (2)	C13—C14—H14	120.1
H5A—O5—H5B	102 (3)	C15—C14—H14	120.1
O2—C1—O1	125.1 (2)	N4—C15—C14	122.3 (2)
O2—C1—C2	121.5 (2)	N4—C15—H15	118.9
O1—C1—C2	113.43 (18)	C14—C15—H15	118.9
N1—C2—C3	109.65 (18)	N4—C16—C12	123.7 (2)
N1—C2—C1	115.41 (18)	N4—C16—C17	116.11 (18)
C3—C2—C1	134.65 (19)	C12—C16—C17	120.18 (19)
C4—C3—C2	104.16 (18)	N3—C17—C9	123.0 (2)
C4—C3—H3	127.9	N3—C17—C16	116.74 (18)
C2—C3—H3	127.9	C9—C17—C16	120.30 (19)
N3—Cu1—N1—N2	−166.8 (7)	N1—C2—C3—C4	−1.4 (3)
O1—Cu1—N1—N2	174.8 (2)	C1—C2—C3—C4	172.0 (2)
N4—Cu1—N1—N2	−41.3 (2)	N1—N2—C4—C3	−1.4 (2)
O5—Cu1—N1—N2	57.3 (2)	Cu2—N2—C4—C3	−166.02 (15)

N3—Cu1—N1—C2	9.1 (9)	N1—N2—C4—C5	175.59 (18)
O1—Cu1—N1—C2	−9.32 (15)	Cu2—N2—C4—C5	11.0 (2)
N4—Cu1—N1—C2	134.61 (16)	C2—C3—C4—N2	1.7 (3)
O5—Cu1—N1—C2	−126.77 (16)	C2—C3—C4—C5	−174.6 (2)
C2—N1—N2—C4	0.5 (2)	Cu2—O3—C5—O4	177.53 (19)
Cu1—N1—N2—C4	176.58 (17)	Cu2—O3—C5—C4	−3.0 (2)
C2—N1—N2—Cu2	158.44 (18)	N2—C4—C5—O4	173.9 (2)
Cu1—N1—N2—Cu2	−25.5 (4)	C3—C4—C5—O4	−10.0 (4)
O3^{i}—Cu2—N2—N1	12.8 (2)	N2—C4—C5—O3	−5.6 (3)
O3—Cu2—N2—N1	−167.2 (2)	C3—C4—C5—O3	170.6 (2)
N2^{i}—Cu2—N2—N1	152 (79)	C17—N3—C6—C7	1.0 (4)
O3^{i}—Cu2—N2—C4	170.19 (15)	Cu1—N3—C6—C7	−173.30 (18)
O3—Cu2—N2—C4	−9.81 (15)	N3—C6—C7—C8	−1.2 (4)
N2^{i}—Cu2—N2—C4	−51 (80)	C6—C7—C8—C9	0.2 (4)
N1—Cu1—N3—C6	−55.7 (9)	C7—C8—C9—C17	0.9 (3)
O1—Cu1—N3—C6	−37.4 (2)	C7—C8—C9—C10	−177.9 (2)
N4—Cu1—N3—C6	178.0 (2)	C17—C9—C10—C11	1.5 (4)
O5—Cu1—N3—C6	80.3 (2)	C8—C9—C10—C11	−179.7 (2)
N1—Cu1—N3—C17	129.7 (8)	C9—C10—C11—C12	0.1 (4)
O1—Cu1—N3—C17	148.01 (16)	C10—C11—C12—C16	−0.4 (4)
N4—Cu1—N3—C17	3.48 (15)	C10—C11—C12—C13	178.9 (2)
O5—Cu1—N3—C17	−94.30 (16)	C16—C12—C13—C14	−1.2 (3)
N1—Cu1—N4—C15	1.8 (2)	C11—C12—C13—C14	179.5 (2)
N3—Cu1—N4—C15	177.3 (2)	C12—C13—C14—C15	2.1 (4)
O1—Cu1—N4—C15	94.3 (2)	C16—N4—C15—C14	−0.5 (3)
O5—Cu1—N4—C15	−93.2 (2)	Cu1—N4—C15—C14	−179.99 (17)
N1—Cu1—N4—C16	−177.79 (14)	C13—C14—C15—N4	−1.3 (4)
N3—Cu1—N4—C16	−2.23 (14)	C15—N4—C16—C12	1.4 (3)
O1—Cu1—N4—C16	−85.29 (18)	Cu1—N4—C16—C12	−179.00 (17)
O5—Cu1—N4—C16	87.30 (14)	C15—N4—C16—C17	−178.96 (19)
N1—Cu1—O1—C1	8.85 (16)	Cu1—N4—C16—C17	0.7 (2)
N3—Cu1—O1—C1	−169.44 (16)	C13—C12—C16—N4	−0.6 (3)
N4—Cu1—O1—C1	−89.86 (18)	C11—C12—C16—N4	178.8 (2)
O5—Cu1—O1—C1	98.43 (16)	C13—C12—C16—C17	179.8 (2)
O3^{i}—Cu2—O3—C5	−20 (100)	C11—C12—C16—C17	−0.9 (3)
N2^{i}—Cu2—O3—C5	−172.82 (16)	C6—N3—C17—C9	0.2 (3)
N2—Cu2—O3—C5	7.18 (16)	Cu1—N3—C17—C9	175.31 (17)
Cu1—O1—C1—O2	175.08 (19)	C6—N3—C17—C16	−179.3 (2)
Cu1—O1—C1—C2	−6.4 (2)	Cu1—N3—C17—C16	−4.2 (2)
N2—N1—C2—C3	0.5 (3)	C8—C9—C17—N3	−1.1 (3)
Cu1—N1—C2—C3	−176.61 (15)	C10—C9—C17—N3	177.8 (2)
N2—N1—C2—C1	−174.19 (18)	C8—C9—C17—C16	178.4 (2)
Cu1—N1—C2—C1	8.6 (2)	C10—C9—C17—C16	−2.8 (3)
O2—C1—C2—N1	177.1 (2)	N4—C16—C17—N3	2.3 (3)
O1—C1—C2—N1	−1.4 (3)	C12—C16—C17—N3	−178.0 (2)
O2—C1—C2—C3	4.1 (4)	N4—C16—C17—C9	−177.17 (19)
O1—C1—C2—C3	−174.5 (2)	C12—C16—C17—C9	2.5 (3)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5B···O3^{i}	0.836 (10)	1.932 (13)	2.754 (2)	168 (4)
O5—H5A···O1^{ii}	0.836 (10)	1.953 (10)	2.789 (2)	178 (4)

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

Fig. 1

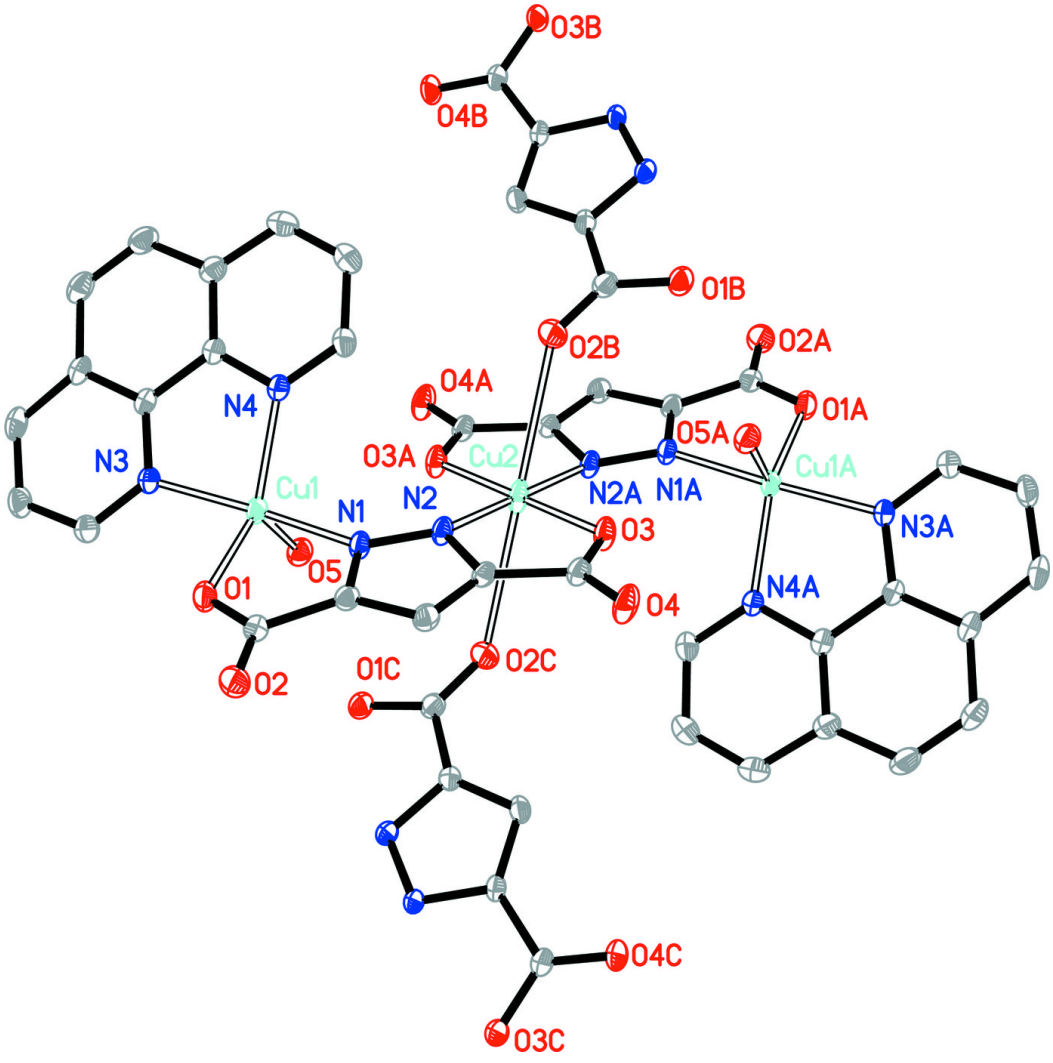
O3B
O4B
O1B
O2B
O2A
O4A
O1A
O5A
O3A
Cu2
Cu1A
N4
N3
Cu1
N1
N2
N2A
N1A
N3A
O3
O5
O1
O4
N4A
O2
O1C
O2C
O4C
O3C

Fig. 2