

Di- μ_2 -acetato-1:2 κ^2 O:O';2:3 κ^2 O:O'-bis $\{\mu_2$ -4,4'-dichloro-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}-1:2 κ^6 O,N,N',O':-O,O';2:3 κ^6 O,O':O,N,N',O'-tricopper(II)

Koji Kubono,* Keita Tani and Kunihiko Yokoi

Division of Natural Sciences, Osaka Kyoiku University, Kashiwara, Osaka 582-8582, Japan

Correspondence e-mail: kubono@cc.osaka-kyoiku.ac.jp

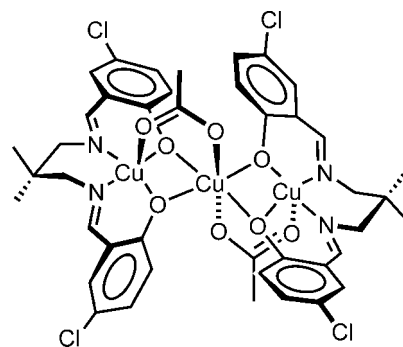
Received 16 October 2012; accepted 25 October 2012

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.035; wR factor = 0.105; data-to-parameter ratio = 17.9.

The title compound, $[\text{Cu}_3(\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2)_2(\text{CH}_3\text{CO}_2)_2]$, is a linear homo-trinuclear Cu^{II} complex. The central Cu^{II} atom is located on a centre of inversion and has a distorted octahedral coordination environment formed by six O atoms from two tetradentate Schiff base ligands and two bridging acetate ligands. The coordination geometry of the terminal Cu^{II} atom is square-pyramidal with a tetradentate ligand in the basal plane. The apical site is occupied by one O atom from an acetate ligand. The acetate-bridged $\text{Cu}\cdots\text{Cu}$ distance is 3.0910 (5) Å. An intramolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond forms an $S(6)$ ring motif. The crystal of the trinuclear complex is stabilized by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the supramolecular chemistry of related complexes, see: Chen *et al.* (2010); von Richthofen *et al.* (2009); Gianneschi *et al.* (2003). For related structures, see: Atakol *et al.* (1999); Feng *et al.* (2007); Ray *et al.* (2009); Yang *et al.* (2004). For background to this work, see: Fukuhara *et al.* (1990); Kargar *et al.* (2012); Kubono *et al.* (2009, 2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For analysis of ring conformations, see: Cremer & Pople (1975).



Experimental

Crystal data

$[\text{Cu}_3(\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_2]$
 $M_r = 1063.25$
 Orthorhombic, $Pbca$
 $a = 19.0732$ (18) Å
 $b = 11.6191$ (11) Å
 $c = 19.693$ (3) Å

$V = 4364.2$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.75$ mm⁻¹
 $T = 298$ K
 $0.23 \times 0.20 \times 0.16$ mm

Data collection

Rigaku AFC7R diffractometer
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.675$, $T_{\text{max}} = 0.756$
 7325 measured reflections
 5006 independent reflections

2796 reflections with $F^2 > 2.0\sigma(F^2)$
 $R_{\text{int}} = 0.024$
 3 standard reflections every 150 reflections
 intensity decay: 0.5%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.105$
 $S = 1.00$
 5006 reflections

280 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C}2-\text{H}2\cdots\text{O}4^i$	0.93	2.58	3.115 (4)	117
$\text{C}15-\text{H}15\cdots\text{O}3^{ii}$	0.93	2.59	3.289 (4)	133

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$.

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2010); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *CrystalStructure*.

This study was supported financially in part by Grants-in-Aid for Scientific Research (grant Nos. 20550075 and 23550094) from the Japan Society for the Promotion of Science.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MW2092).

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Atakol, O., Arıcı, C., Ercan, F. & Ülkü, D. (1999). *Acta Cryst.* **C55**, 511–513.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed.* **34**, 1555–1573.
- Chen, B., Xiang, S. & Qian, G. (2010). *Acc. Chem. Res.* **43**, 1115–1124.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Feng, Y.-F., Wu, H.-Y., Zhu, B.-L., Wang, S.-R. & Huang, W.-P. (2007). *Acta Cryst.* **E63**, m1107–m1108.
- Fukuhara, C., Tsuneyoshi, K., Matsumoto, N., Kida, S., Mikuriya, M. & Mori, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3473–3479.
- Gianneschi, N. C., Bertin, P. A., Nguyen, S. T., Mirkin, C. A., Zakharov, L. N. & Rheingold, L. (2003). *J. Am. Chem. Soc.* **125**, 10508–10509.
- Kargar, H., Kia, R., Ganji, F. & Mirkhani, V. (2012). *Acta Cryst.* **E68**, m1135.
- Kubono, K., Noshita, C., Tani, K. & Yokoi, K. (2009). *Acta Cryst.* **E65**, m1685–m1686.
- Kubono, K., Tsuno, Y., Tani, K. & Yokoi, K. (2010). *Acta Cryst.* **E66**, m1397–m1398.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Ray, A., Sadhukhan, D., Rosair, G. M., Gómez-García, C. J. & Mitra, S. (2009). *Polyhedron*, **28**, 3542–3550.
- Richthofen, C.-G. F. von, Stammler, A., Bögge, H., DeGroot, M. W., Long, J. R. & Glaser, T. (2009). *Inorg. Chem.* **48**, 10165–10176.
- Rigaku (2006). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2010). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Yang, S.-P., Hong, Y., Chen, H.-M., Zhang, F., Chen, Q.-Q. & Yu, X.-B. (2004). *Acta Cryst.* **E60**, m582–m584.

supporting information

Acta Cryst. (2012). E68, m1430–m1431 [doi:10.1107/S1600536812044315]

Di- μ_2 -acetato-1:2 κ^2 O:O';2:3 κ^2 O:O'-bis{ μ_2 -4,4'-dichloro-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}-1:2 κ^6 O,N,N',O':O,O';2:3 κ^6 O,O':O,N,N',O'-tricopper(II)

Koji Kubono, Keita Tani and Kunihiko Yokoi

S1. Comment

Supramolecular complexes, formed by hydrogen bonds or coordination linkages have received much attention, because of their interesting and functional properties such as molecular recognition, magnetism and catalysis (Chen *et al.*, 2010; von Richthofen *et al.*, 2009; Gianneschi *et al.*, 2003). We have previously studied the structures of supramolecular Cu^{II} complexes with planar tetradentate piperazine ligands containing fluoro or chloro groups (Kubono *et al.*, 2010; Kubono *et al.*, 2009). These Cu^{II} complexes form either a dimer, or a dinuclear structure through C—H \cdots F, or C—H \cdots Cl hydrogen bonds. Complexes with the tetradentate Schiff base ligand, bis(salicylidene)propane-1,3-diamine can form trinuclear complexes with coordinating anions or solvents to generate supramolecular architectures (Atakol *et al.*, 1999; Fukuhara *et al.*, 1990; Ray *et al.*, 2009). However no structures of trinuclear complexes with bis-halogenosalicylidene and anionic ligands have been reported. We have attempted to assemble such a species from the mononuclear Cu^{II} complex {4,4'-dichloro-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}copper(II) (Kargar *et al.*, 2012) and copper(II) acetate as the building blocks. Herein, the structure of the title trinuclear complex is reported.

The central Cu^{II} atom is located on a centre of inversion and has a distorted octahedral coordination environment formed by four O atoms from two tetradentate Schiff base ligands in the equatorial plane and an O atom from each of the two bridging acetate ligands in the axial positions. The coordination geometry of the terminal Cu^{II} atom is square-pyramidal with the basal plane comprised of two phenolate O and two imine N atoms from a tetradentate ligand. The apical site is occupied by one O atom from a bridging acetate ligand. The terminal Cu^{II} atom is located 0.2370 (4) Å from the mean basal plane (N1/N2/O1/O2). The six-membered Cu1/N1/C8/C9/C10/N2 ring adopts a chair conformation with puckering parameters (Cremer & Pople, 1975): Q = 0.549 (4) Å, θ = 16.4 (3)° and φ = 141.7 (13)°. Bond lengths and angles involving Cu^{II} are comparable to those observed in related structures (Atakol *et al.*, 1999). The dihedral angle between the benzene rings (C1–C6 and C14–C19) is 68.73 (12)°. The acetate-bridged Cu \cdots Cu distance is 3.0910 (5) Å, similar to those of related linear homo-trinuclear Cu^{II} complexes (Atakol *et al.*, 1999; Feng *et al.*, 2007; Yang *et al.*, 2004). There is an intramolecular C2—H2 \cdots O4ⁱ hydrogen bond [symmetry code: (i) $-x + 1, -y, -z + 1$; Table 1], forming a S(6) ring motif (Bernstein *et al.*, 1995). The molecular conformation of the trinuclear complex is stabilized by the intramolecular hydrogen bonds. In the crystal, the trinuclear complex molecules are linked through intermolecular C—H \cdots O hydrogen bonds into a two-dimensional supramolecular network, parallel to the *ab* plane (Table 1 and Fig. 2).

S2. Experimental

The ligand (0.40 mmol) was dissolved in 20 mL of hot methanol. Then 20 mL of a methanol solution of copper acetate monohydrate (0.60 mmol) were added to this solution. The mixture was stirred for 20 min at 340 K. After a few days at

room temperature, green crystals of title complex were obtained. Yield 52%. Analysis calculated for $C_{42}H_{42}Cl_4Cu_3N_4O_8$: C 47.44, H 3.98, N 5.27%; found: C 47.48, H 3.92, N 5.21%.

S3. Refinement

All H atoms bound to carbon were placed in idealized positions and refined using a riding model, with $C-H = 0.93-0.97$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

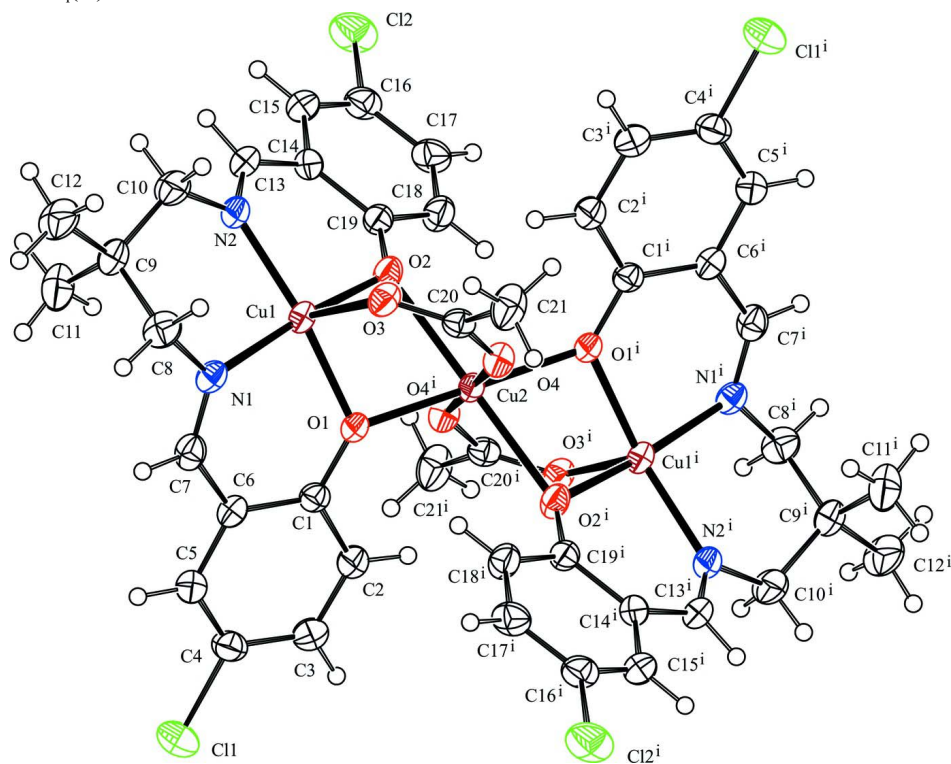


Figure 1

The molecule of the title complex showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are represented by circles of arbitrary size. [symmetry code: (i) $-x + 1, -y, -z + 1$.]

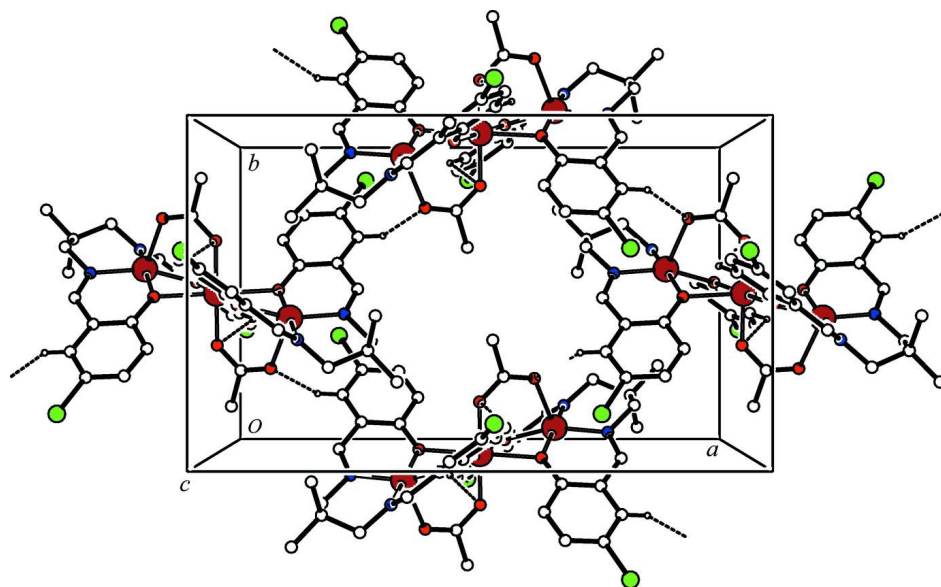


Figure 2

Packing diagram of the title complex, viewed down the c axis. The intramolecular and intermolecular C—H...O hydrogen bonds are shown as dashed lines.

Di- μ_2 -acetato-1:2 κ^2 O:O';2:3 κ^2 O:O'-bis[μ_2 -4,4'-dichloro-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}-1:2 κ^6 O,N,N',O':O,O'; 2:3 κ^6 O,O':O,N,N',O'-tricopper(II)

Crystal data

[Cu₃(C₁₉H₁₈Cl₂N₂O₂)₂(C₂H₃O₂)₂]

$M_r = 1063.25$

Orthorhombic, $Pbca$

Hall symbol: -P 2ac 2ab

$a = 19.0732$ (18) Å

$b = 11.6191$ (11) Å

$c = 19.693$ (3) Å

$V = 4364.2$ (9) Å³

$Z = 4$

$F(000) = 2164.00$

$D_x = 1.618$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 25 reflections

$\theta = 15.0$ – 17.4°

$\mu = 1.75$ mm⁻¹

$T = 298$ K

Prismatic, green

$0.23 \times 0.20 \times 0.16$ mm

Data collection

Rigaku AFC7R
diffractometer

ω - 2θ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.675$, $T_{\max} = 0.756$

7325 measured reflections

5006 independent reflections

2796 reflections with $F^2 > 2.0\sigma(F^2)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.5^\circ$

$h = -13 \rightarrow 24$

$k = -8 \rightarrow 15$

$l = -25 \rightarrow 0$

3 standard reflections every 150 reflections

intensity decay: 0.5%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.105$

$S = 1.00$

5006 reflections

280 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.7391P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

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 was performed using all reflections. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.64313 (2)	0.07637 (3)	0.44178 (2)	0.03103 (12)
Cu2	0.5000	0.0000	0.5000	0.02727 (14)
Cl1	0.47496 (6)	-0.12235 (10)	0.13509 (5)	0.0602 (3)
Cl2	0.77615 (6)	-0.36381 (9)	0.66639 (5)	0.0635 (3)
O1	0.54772 (11)	0.0350 (2)	0.40871 (11)	0.0336 (5)
O2	0.61636 (11)	-0.01062 (19)	0.52089 (11)	0.0359 (6)
O3	0.60366 (11)	0.23406 (18)	0.48839 (11)	0.0363 (6)
O4	0.49941 (11)	0.16268 (18)	0.52142 (11)	0.0341 (5)
N1	0.66389 (14)	0.1401 (2)	0.35159 (14)	0.0326 (6)
N2	0.74426 (14)	0.0639 (2)	0.46700 (14)	0.0349 (7)
C1	0.53159 (17)	0.0020 (3)	0.34682 (16)	0.0302 (7)
C2	0.47113 (18)	-0.0639 (3)	0.33434 (18)	0.0384 (8)
H2	0.4416	-0.0830	0.3702	0.046*
C3	0.45508 (19)	-0.1003 (3)	0.27000 (18)	0.0418 (9)
H3	0.4152	-0.1447	0.2628	0.050*
C4	0.49741 (19)	-0.0718 (3)	0.21590 (18)	0.0405 (9)
C5	0.55477 (18)	-0.0033 (3)	0.22513 (18)	0.0385 (8)
H5	0.5816	0.0188	0.1879	0.046*
C6	0.57347 (17)	0.0342 (3)	0.29035 (17)	0.0320 (8)
C7	0.63314 (18)	0.1099 (3)	0.29713 (19)	0.0374 (8)
H7	0.6511	0.1401	0.2570	0.045*
C8	0.72103 (18)	0.2234 (3)	0.34661 (19)	0.0433 (9)
H8A	0.7110	0.2877	0.3765	0.052*
H8B	0.7229	0.2527	0.3005	0.052*
C9	0.79266 (17)	0.1737 (3)	0.36505 (18)	0.0390 (9)
C10	0.79631 (19)	0.1469 (3)	0.44084 (18)	0.0465 (10)
H10A	0.8428	0.1175	0.4509	0.056*
H10B	0.7908	0.2185	0.4656	0.056*
C11	0.8086 (2)	0.0676 (4)	0.3228 (2)	0.0584 (11)
H11A	0.7764	0.0072	0.3345	0.088*
H11B	0.8557	0.0426	0.3316	0.088*

H11C	0.8038	0.0859	0.2755	0.088*
C12	0.8473 (2)	0.2683 (4)	0.3510 (2)	0.0592 (12)
H12A	0.8928	0.2418	0.3646	0.089*
H12B	0.8353	0.3362	0.3763	0.089*
H12C	0.8477	0.2859	0.3034	0.089*
C13	0.76749 (18)	-0.0137 (3)	0.50710 (17)	0.0407 (9)
H13	0.8160	-0.0181	0.5115	0.049*
C14	0.72733 (18)	-0.0952 (3)	0.54648 (16)	0.0345 (8)
C15	0.76437 (19)	-0.1790 (3)	0.58283 (18)	0.0426 (9)
H15	0.8130	-0.1824	0.5795	0.051*
C16	0.72974 (19)	-0.2558 (3)	0.62314 (18)	0.0416 (9)
C17	0.65761 (19)	-0.2510 (3)	0.63013 (18)	0.0434 (9)
H17	0.6346	-0.3027	0.6585	0.052*
C18	0.62008 (19)	-0.1695 (3)	0.59500 (17)	0.0408 (9)
H18	0.5715	-0.1677	0.5993	0.049*
C19	0.65340 (17)	-0.0887 (3)	0.55256 (16)	0.0312 (7)
C20	0.54487 (18)	0.2416 (3)	0.51585 (16)	0.0312 (7)
C21	0.5241 (2)	0.3555 (3)	0.5462 (2)	0.0532 (11)
H21A	0.5584	0.4126	0.5345	0.080*
H21B	0.5214	0.3484	0.5947	0.080*
H21C	0.4792	0.3781	0.5287	0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0229 (2)	0.0343 (2)	0.0359 (2)	-0.00107 (18)	0.00405 (18)	0.00024 (19)
Cu2	0.0223 (3)	0.0305 (3)	0.0290 (3)	-0.0010 (2)	0.0029 (2)	-0.0011 (2)
Cl1	0.0663 (7)	0.0744 (7)	0.0398 (5)	-0.0041 (6)	-0.0070 (5)	-0.0176 (5)
Cl2	0.0759 (8)	0.0619 (7)	0.0526 (6)	0.0295 (6)	-0.0149 (6)	0.0059 (5)
O1	0.0232 (12)	0.0450 (13)	0.0324 (13)	-0.0047 (11)	0.0016 (10)	-0.0044 (11)
O2	0.0274 (12)	0.0403 (14)	0.0400 (13)	0.0061 (11)	0.0050 (10)	0.0114 (12)
O3	0.0290 (12)	0.0341 (13)	0.0459 (15)	-0.0015 (11)	0.0017 (11)	-0.0057 (11)
O4	0.0318 (13)	0.0287 (12)	0.0419 (14)	-0.0008 (11)	0.0038 (11)	-0.0014 (10)
N1	0.0263 (15)	0.0311 (15)	0.0404 (17)	-0.0023 (12)	0.0009 (13)	0.0044 (13)
N2	0.0267 (15)	0.0431 (18)	0.0348 (15)	-0.0058 (13)	0.0037 (13)	-0.0025 (14)
C1	0.0291 (18)	0.0295 (18)	0.0320 (18)	0.0061 (15)	-0.0024 (15)	0.0003 (15)
C2	0.0329 (19)	0.045 (2)	0.0372 (19)	-0.0049 (16)	0.0018 (16)	-0.0017 (17)
C3	0.036 (2)	0.046 (2)	0.044 (2)	-0.0065 (18)	-0.0038 (18)	-0.0029 (18)
C4	0.042 (2)	0.046 (2)	0.034 (2)	0.0053 (19)	-0.0068 (16)	-0.0066 (17)
C5	0.034 (2)	0.046 (2)	0.0355 (19)	0.0010 (18)	0.0019 (16)	0.0012 (17)
C6	0.0263 (18)	0.0307 (18)	0.0390 (19)	0.0015 (14)	0.0011 (15)	0.0007 (15)
C7	0.035 (2)	0.0363 (19)	0.041 (2)	0.0015 (16)	0.0056 (16)	0.0098 (17)
C8	0.041 (2)	0.036 (2)	0.053 (2)	-0.0105 (17)	-0.0012 (18)	0.0059 (18)
C9	0.029 (2)	0.042 (2)	0.046 (2)	-0.0053 (16)	0.0060 (17)	0.0026 (17)
C10	0.035 (2)	0.056 (2)	0.048 (2)	-0.0185 (18)	-0.0001 (18)	0.0040 (19)
C11	0.048 (3)	0.062 (3)	0.065 (3)	0.000 (2)	0.020 (2)	-0.009 (2)
C12	0.042 (2)	0.068 (3)	0.067 (3)	-0.024 (2)	0.002 (2)	0.018 (2)
C13	0.0235 (18)	0.059 (3)	0.039 (2)	-0.0007 (17)	0.0005 (15)	-0.0009 (19)

C14	0.0304 (19)	0.043 (2)	0.0300 (18)	0.0035 (16)	0.0013 (14)	-0.0050 (16)
C15	0.031 (2)	0.056 (2)	0.040 (2)	0.0092 (18)	-0.0029 (16)	-0.0001 (19)
C16	0.045 (2)	0.042 (2)	0.037 (2)	0.0148 (19)	-0.0076 (17)	-0.0029 (17)
C17	0.050 (2)	0.043 (2)	0.038 (2)	0.0009 (19)	-0.0065 (18)	0.0115 (17)
C18	0.032 (2)	0.047 (2)	0.043 (2)	0.0013 (17)	0.0041 (17)	0.0103 (18)
C19	0.0289 (18)	0.0321 (18)	0.0325 (18)	-0.0001 (15)	0.0003 (14)	-0.0026 (15)
C20	0.0343 (18)	0.0285 (18)	0.0309 (19)	0.0034 (15)	-0.0048 (15)	0.0007 (14)
C21	0.046 (2)	0.039 (2)	0.075 (3)	0.0012 (19)	0.014 (2)	-0.019 (2)

Geometric parameters (Å, °)

Cu1—O2	1.926 (2)	C7—H7	0.9300
Cu1—N1	1.965 (3)	C8—C9	1.527 (5)
Cu1—O1	1.992 (2)	C8—H8A	0.9700
Cu1—N2	1.997 (3)	C8—H8B	0.9700
Cu1—O3	2.183 (2)	C9—C11	1.518 (5)
Cu2—O4 ⁱ	1.937 (2)	C9—C10	1.526 (5)
Cu2—O4	1.937 (2)	C9—C12	1.540 (5)
Cu2—O1	2.056 (2)	C10—H10A	0.9700
Cu2—O1 ⁱ	2.056 (2)	C10—H10B	0.9700
Cu2—O2 ⁱ	2.260 (2)	C11—H11A	0.9600
Cu2—O2	2.260 (2)	C11—H11B	0.9600
Cl1—C4	1.750 (4)	C11—H11C	0.9600
Cl2—C16	1.756 (4)	C12—H12A	0.9600
O1—C1	1.314 (4)	C12—H12B	0.9600
O2—C19	1.308 (4)	C12—H12C	0.9600
O3—C20	1.248 (4)	C13—C14	1.444 (5)
O4—C20	1.267 (4)	C13—H13	0.9300
N1—C7	1.272 (4)	C14—C15	1.400 (5)
N1—C8	1.461 (4)	C14—C19	1.417 (4)
N2—C13	1.277 (4)	C15—C16	1.364 (5)
N2—C10	1.477 (4)	C15—H15	0.9300
C1—C2	1.406 (5)	C16—C17	1.384 (5)
C1—C6	1.419 (4)	C17—C18	1.374 (4)
C2—C3	1.371 (5)	C17—H17	0.9300
C2—H2	0.9300	C18—C19	1.408 (4)
C3—C4	1.377 (5)	C18—H18	0.9300
C3—H3	0.9300	C20—C21	1.504 (5)
C4—C5	1.365 (5)	C21—H21A	0.9600
C5—C6	1.402 (4)	C21—H21B	0.9600
C5—H5	0.9300	C21—H21C	0.9600
C6—C7	1.445 (5)		
O2—Cu1—N1	169.27 (11)	N1—C8—C9	113.6 (3)
O2—Cu1—O1	84.00 (9)	N1—C8—H8A	108.8
N1—Cu1—O1	88.83 (10)	C9—C8—H8A	108.8
O2—Cu1—N2	90.96 (11)	N1—C8—H8B	108.8
N1—Cu1—N2	93.31 (11)	C9—C8—H8B	108.8

O1—Cu1—N2	161.12 (11)	H8A—C8—H8B	107.7
O2—Cu1—O3	90.51 (9)	C11—C9—C10	111.2 (3)
N1—Cu1—O3	97.66 (10)	C11—C9—C8	110.8 (3)
O1—Cu1—O3	91.44 (9)	C10—C9—C8	110.5 (3)
N2—Cu1—O3	106.83 (10)	C11—C9—C12	110.2 (3)
O4 ⁱ —Cu2—O4	180.00 (13)	C10—C9—C12	106.9 (3)
O4 ⁱ —Cu2—O1	89.99 (9)	C8—C9—C12	107.0 (3)
O4—Cu2—O1	90.01 (9)	N2—C10—C9	116.3 (3)
O4 ⁱ —Cu2—O1 ⁱ	90.01 (9)	N2—C10—H10A	108.2
O4—Cu2—O1 ⁱ	89.99 (9)	C9—C10—H10A	108.2
O1—Cu2—O1 ⁱ	180.00 (10)	N2—C10—H10B	108.2
O4 ⁱ —Cu2—O2 ⁱ	91.11 (8)	C9—C10—H10B	108.2
O4—Cu2—O2 ⁱ	88.89 (8)	H10A—C10—H10B	107.4
O1—Cu2—O2 ⁱ	105.35 (8)	C9—C11—H11A	109.5
O1 ⁱ —Cu2—O2 ⁱ	74.65 (8)	C9—C11—H11B	109.5
O4 ⁱ —Cu2—O2	88.89 (8)	H11A—C11—H11B	109.5
O4—Cu2—O2	91.11 (8)	C9—C11—H11C	109.5
O1—Cu2—O2	74.65 (8)	H11A—C11—H11C	109.5
O1 ⁱ —Cu2—O2	105.35 (8)	H11B—C11—H11C	109.5
O2 ⁱ —Cu2—O2	180.0	C9—C12—H12A	109.5
C1—O1—Cu1	126.0 (2)	C9—C12—H12B	109.5
C1—O1—Cu2	130.5 (2)	H12A—C12—H12B	109.5
Cu1—O1—Cu2	99.58 (9)	C9—C12—H12C	109.5
C19—O2—Cu1	127.3 (2)	H12A—C12—H12C	109.5
C19—O2—Cu2	130.9 (2)	H12B—C12—H12C	109.5
Cu1—O2—Cu2	94.85 (9)	N2—C13—C14	127.6 (3)
C20—O3—Cu1	123.5 (2)	N2—C13—H13	116.2
C20—O4—Cu2	133.1 (2)	C14—C13—H13	116.2
C7—N1—C8	118.1 (3)	C15—C14—C19	119.7 (3)
C7—N1—Cu1	124.4 (2)	C15—C14—C13	117.6 (3)
C8—N1—Cu1	117.4 (2)	C19—C14—C13	122.6 (3)
C13—N2—C10	116.3 (3)	C16—C15—C14	120.5 (3)
C13—N2—Cu1	122.7 (2)	C16—C15—H15	119.7
C10—N2—Cu1	121.0 (2)	C14—C15—H15	119.7
O1—C1—C2	120.9 (3)	C15—C16—C17	120.9 (3)
O1—C1—C6	121.2 (3)	C15—C16—C12	120.3 (3)
C2—C1—C6	117.9 (3)	C17—C16—C12	118.8 (3)
C3—C2—C1	120.9 (3)	C18—C17—C16	119.7 (3)
C3—C2—H2	119.6	C18—C17—H17	120.1
C1—C2—H2	119.6	C16—C17—H17	120.1
C2—C3—C4	120.7 (3)	C17—C18—C19	121.5 (3)
C2—C3—H3	119.7	C17—C18—H18	119.2
C4—C3—H3	119.7	C19—C18—H18	119.2
C5—C4—C3	120.5 (3)	O2—C19—C18	120.1 (3)
C5—C4—C11	120.9 (3)	O2—C19—C14	122.3 (3)
C3—C4—C11	118.7 (3)	C18—C19—C14	117.6 (3)
C4—C5—C6	120.4 (3)	O3—C20—O4	127.0 (3)
C4—C5—H5	119.8	O3—C20—C21	118.1 (3)

C6—C5—H5	119.8	O4—C20—C21	115.0 (3)
C5—C6—C1	119.5 (3)	C20—C21—H21A	109.5
C5—C6—C7	118.3 (3)	C20—C21—H21B	109.5
C1—C6—C7	122.1 (3)	H21A—C21—H21B	109.5
N1—C7—C6	127.5 (3)	C20—C21—H21C	109.5
N1—C7—H7	116.2	H21A—C21—H21C	109.5
C6—C7—H7	116.2	H21B—C21—H21C	109.5
O2—Cu1—O1—C1	-137.9 (3)	Cu1—O1—C1—C2	156.4 (2)
N1—Cu1—O1—C1	34.1 (3)	Cu2—O1—C1—C2	3.4 (5)
N2—Cu1—O1—C1	-62.7 (4)	Cu1—O1—C1—C6	-25.2 (4)
O3—Cu1—O1—C1	131.8 (2)	Cu2—O1—C1—C6	-178.2 (2)
O2—Cu1—O1—Cu2	21.70 (10)	O1—C1—C2—C3	-178.6 (3)
N1—Cu1—O1—Cu2	-166.30 (11)	C6—C1—C2—C3	3.0 (5)
N2—Cu1—O1—Cu2	96.9 (3)	C1—C2—C3—C4	-0.9 (6)
O3—Cu1—O1—Cu2	-68.66 (10)	C2—C3—C4—C5	-2.3 (6)
O4 ⁱ —Cu2—O1—C1	50.4 (3)	C2—C3—C4—C11	179.1 (3)
O4—Cu2—O1—C1	-129.6 (3)	C3—C4—C5—C6	3.3 (5)
O2 ⁱ —Cu2—O1—C1	-40.8 (3)	C11—C4—C5—C6	-178.2 (3)
O2—Cu2—O1—C1	139.2 (3)	C4—C5—C6—C1	-1.1 (5)
O4 ⁱ —Cu2—O1—Cu1	-107.81 (10)	C4—C5—C6—C7	-177.8 (3)
O4—Cu2—O1—Cu1	72.19 (10)	O1—C1—C6—C5	179.6 (3)
O2 ⁱ —Cu2—O1—Cu1	161.04 (9)	C2—C1—C6—C5	-2.0 (5)
O2—Cu2—O1—Cu1	-18.96 (9)	O1—C1—C6—C7	-3.8 (5)
N1—Cu1—O2—C19	85.3 (6)	C2—C1—C6—C7	174.6 (3)
O1—Cu1—O2—C19	133.6 (3)	C8—N1—C7—C6	-176.5 (3)
N2—Cu1—O2—C19	-28.2 (3)	Cu1—N1—C7—C6	6.9 (5)
O3—Cu1—O2—C19	-135.0 (3)	C5—C6—C7—N1	-169.5 (3)
N1—Cu1—O2—Cu2	-67.7 (5)	C1—C6—C7—N1	13.9 (5)
O1—Cu1—O2—Cu2	-19.43 (9)	C7—N1—C8—C9	-113.3 (4)
N2—Cu1—O2—Cu2	178.80 (10)	Cu1—N1—C8—C9	63.6 (4)
O3—Cu1—O2—Cu2	71.96 (9)	N1—C8—C9—C11	54.7 (4)
O4 ⁱ —Cu2—O2—C19	-41.8 (3)	N1—C8—C9—C10	-69.0 (4)
O4—Cu2—O2—C19	138.2 (3)	N1—C8—C9—C12	174.9 (3)
O1—Cu2—O2—C19	-132.1 (3)	C13—N2—C10—C9	134.9 (3)
O1 ⁱ —Cu2—O2—C19	47.9 (3)	Cu1—N2—C10—C9	-46.4 (4)
O4 ⁱ —Cu2—O2—Cu1	109.72 (10)	C11—C9—C10—N2	-64.1 (4)
O4—Cu2—O2—Cu1	-70.28 (10)	C8—C9—C10—N2	59.5 (4)
O1—Cu2—O2—Cu1	19.42 (9)	C12—C9—C10—N2	175.6 (3)
O1 ⁱ —Cu2—O2—Cu1	-160.58 (9)	C10—N2—C13—C14	171.2 (3)
O2—Cu1—O3—C20	-48.2 (2)	Cu1—N2—C13—C14	-7.4 (5)
N1—Cu1—O3—C20	124.9 (2)	N2—C13—C14—C15	174.8 (3)
O1—Cu1—O3—C20	35.9 (2)	N2—C13—C14—C19	-9.1 (6)
N2—Cu1—O3—C20	-139.3 (2)	C19—C14—C15—C16	1.2 (5)
O1—Cu2—O4—C20	-44.3 (3)	C13—C14—C15—C16	177.4 (3)
O1 ⁱ —Cu2—O4—C20	135.7 (3)	C14—C15—C16—C17	-1.4 (6)
O2 ⁱ —Cu2—O4—C20	-149.7 (3)	C14—C15—C16—C12	177.8 (3)
O2—Cu2—O4—C20	30.3 (3)	C15—C16—C17—C18	1.4 (6)

O2—Cu1—N1—C7	23.8 (7)	C12—C16—C17—C18	-177.9 (3)
O1—Cu1—N1—C7	-24.2 (3)	C16—C17—C18—C19	-1.1 (5)
N2—Cu1—N1—C7	137.0 (3)	Cu1—O2—C19—C18	-159.7 (2)
O3—Cu1—N1—C7	-115.5 (3)	Cu2—O2—C19—C18	-16.4 (4)
O2—Cu1—N1—C8	-152.9 (5)	Cu1—O2—C19—C14	20.9 (4)
O1—Cu1—N1—C8	159.1 (2)	Cu2—O2—C19—C14	164.2 (2)
N2—Cu1—N1—C8	-39.6 (2)	C17—C18—C19—O2	-178.6 (3)
O3—Cu1—N1—C8	67.8 (2)	C17—C18—C19—C14	0.9 (5)
O2—Cu1—N2—C13	20.7 (3)	C15—C14—C19—O2	178.5 (3)
N1—Cu1—N2—C13	-149.5 (3)	C13—C14—C19—O2	2.5 (5)
O1—Cu1—N2—C13	-53.4 (5)	C15—C14—C19—C18	-0.9 (5)
O3—Cu1—N2—C13	111.5 (3)	C13—C14—C19—C18	-176.9 (3)
O2—Cu1—N2—C10	-157.9 (2)	Cu1—O3—C20—O4	0.0 (5)
N1—Cu1—N2—C10	31.9 (3)	Cu1—O3—C20—C21	179.9 (2)
O1—Cu1—N2—C10	128.0 (3)	Cu2—O4—C20—O3	6.2 (5)
O3—Cu1—N2—C10	-67.1 (3)	Cu2—O4—C20—C21	-173.7 (2)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C2—H2 \cdots O4 ⁱ	0.93	2.58	3.115 (4)	117
C15—H15 \cdots O3 ⁱⁱ	0.93	2.59	3.289 (4)	133

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