

Tetra- μ -2-methylbenzoato- $\kappa^8O:O'$ -bis-[(ethanol- κO)copper(II)]

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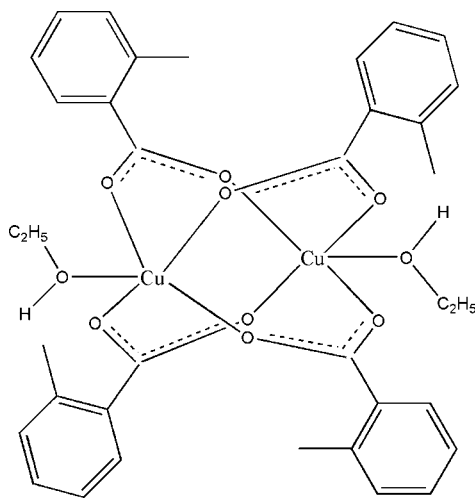
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.050; wR factor = 0.166; data-to-parameter ratio = 18.3.

In the title dinuclear complex, $[\text{Cu}_2(\text{C}_8\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_5\text{OH})_2]$, four 2-methylbenzoato anions form a cage around two Cu^{II} ions in a *syn-anti* configuration. Two ethanol molecules coordinate the Cu atoms in apical positions, giving an overall square-pyramidal coordination geometry. The $\text{Cu}\cdots\text{Cu}$ separation is 2.600 (1) Å. In the crystal, molecules are assembled into chains extending in [001] through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the crystal structures of related complexes, see: Melnik *et al.* (1984); Sunil *et al.* (2008); Danish *et al.* (2010).



Experimental

Crystal data

$[\text{Cu}_2(\text{C}_8\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_5\text{O})_2]$	$\gamma = 85.46$ (3)°
$M_r = 759.76$	$V = 1758.4$ (7) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 10.989$ (2) Å	Mo $K\alpha$ radiation
$b = 12.369$ (3) Å	$\mu = 1.27$ mm ⁻¹
$c = 14.143$ (3) Å	$T = 298$ K
$\alpha = 66.58$ (3)°	$0.28 \times 0.12 \times 0.10$ mm
$\beta = 87.79$ (3)°	

Data collection

Rigaku R-Axis RAPID CCD diffractometer	17320 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	7931 independent reflections
$T_{\text{min}} = 0.831$, $T_{\text{max}} = 0.886$	4219 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	433 parameters
$wR(F^2) = 0.166$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\text{max}} = 1.54$ e Å ⁻³
7931 reflections	$\Delta\rho_{\text{min}} = -1.64$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O9}-\text{H91}\cdots\text{O5}^{\text{i}}$	0.85	2.04	2.841 (6)	156
$\text{O10}-\text{H101}\cdots\text{O4}^{\text{ii}}$	0.86	2.00	2.831 (6)	162

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: CV5148).

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supplementary materials

Acta Cryst. (2011). E67, m1565 [doi:10.1107/S1600536811042322]

Tetra- μ -2-methylbenzoato- $\kappa^8 O:O'$ -bis[(ethanol- κO)copper(II)]

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Comment

Recently, a number of crystal structures of dinuclear Cu complexes with 2-methylbenzoic acid were published, for example, tetrakis(μ -2-methylbenzoato- $\kappa^2 O:O'$)-bis [(methanol- κO)copper(II)] (II) (Danish *et al.*, 2010) and tetrakis(μ -2-methylbenzoato- $\kappa^2 O:O'$)-bis [(2-methylbenzoic acid- κO)copper(II)] (III) (Sunil *et al.*, 2008) are among others [see (Melnik *et al.*, 1984)]. Herewith we present the crystal of the title compound (I), a new dinuclear Cu complex with 2-methylbenzoic acid.

In (I) (Fig. 1), four 2-methylbenzoate ligands form a cage around two Cu atoms in a *syn-anti* configuration. The Cu1...Cu2 separation is 2.600 (1) Å, the Cu—O bond lengths of the cage carboxylates vary in 1.928 (4) – 2.017 (4) Å. The ethanol coordinating bond lengths [Cu1—O9 of 2.149 (4) Å and Cu2—O10 of 2.161 (4) Å] are normal, though slightly different from those observed in (II), where Cu centers are coordinated by methanol.

In the crystal structure, the molecules are assembled into one-dimensional chains extending in [001] through O—H...O hydrogen bonds.

Experimental

Freshly prepared CuCO₃ was essential for an optimal synthesis. At first, 1.0 cm³ (1 M) aqueous Na₂CO₃ was dropwise added to a stirred aqueous solution of (0.2490 g, 1.0 mmol) CuSO₄·5H₂O in 4 cm³ of H₂O, the produced a blue precipitate, Cu(OH)_{2-2x}(CO₃)_x·yH₂O, which was centrifuged and washed with doubly distilled water until no SO₄²⁻ anions were detected in the supernatant. The freshly blue precipitate was subsequently added to a stirred solution of 2-methyl benzoic acid (0.5450 g, 4.0 mmol) in 20 cm³ C₂H₅OH–H₂O (1:1, v/v). The mixture was stirred for 1 h and filtered. Insoluble solid was then filtered out, the resulting blue filtrate (pH = 4.80) was allowed to stand at room temperature, and green block crystals were obtained by slow evaporation for some days (yield:42%).

Refinement

All H-atoms bonded to C were positioned geometrically and refined using a riding model, with d(C–H) = 0.93–0.96 Å and $U_{iso}(H) = 1.2$ – $1.5 U_{eq}(C)$. H atoms attached to O atoms were found in a difference Fourier map and were refined using a riding model, with the O–H distances fixed as initially found and with $U_{iso}(H)$ values set at $1.2 U_{eq}(O)$.

Figures

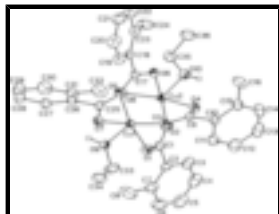


Fig. 1. ORTEP view of the title compound with atomic numbering. The displacement ellipsoids are drawn at 45% probability level. C-bound H atoms omitted for clarity.

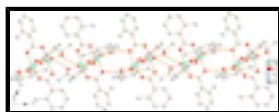


Fig. 2. A portion of the crystal packing showing hydrogen-bonded (dashed lines) chain. C-bound H atoms omitted for clarity.

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Crystal data

[Cu₂(C₈H₇O₂)₄(C₂H₆O)₂]

$M_r = 759.76$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 10.989$ (2) Å

$b = 12.369$ (3) Å

$c = 14.143$ (3) Å

$\alpha = 66.58$ (3)°

$\beta = 87.79$ (3)°

$\gamma = 85.46$ (3)°

$V = 1758.4$ (7) Å³

$Z = 2$

$F(000) = 788$

$D_x = 1.435$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 3.1$ – 27.5 °

$\mu = 1.27$ mm⁻¹

$T = 298$ K

Block, green

$0.28 \times 0.12 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.831$, $T_{\max} = 0.886$

17320 measured reflections

7931 independent reflections

4219 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.1$ °

$h = -14 \rightarrow 14$

$k = -14 \rightarrow 16$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

$$wR(F^2) = 0.166$$

$$S = 1.15$$

7931 reflections

433 parameters

0 restraints

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 5.9014P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 1.54 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.64 \text{ e } \text{\AA}^{-3}$$

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 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.58348 (6)	0.50009 (6)	0.33035 (5)	0.03815 (19)
Cu2	0.46734 (6)	0.46678 (6)	0.18848 (5)	0.0400 (2)
O1	0.7225 (4)	0.4244 (4)	0.2814 (3)	0.0526 (10)
O2	0.6104 (4)	0.3689 (4)	0.1814 (3)	0.0488 (10)
O3	0.6149 (4)	0.6533 (3)	0.2222 (3)	0.0456 (10)
O4	0.5480 (4)	0.6110 (3)	0.0932 (3)	0.0468 (10)
O5	0.4181 (4)	0.5712 (3)	0.3508 (3)	0.0456 (9)
O6	0.3379 (4)	0.5751 (4)	0.2062 (3)	0.0472 (10)
O7	0.5379 (4)	0.3471 (3)	0.4254 (3)	0.0475 (10)
O8	0.4080 (4)	0.3342 (3)	0.3120 (3)	0.0471 (10)
O9	0.6783 (3)	0.5316 (3)	0.4460 (3)	0.0439 (9)
H91	0.6299	0.5026	0.4969	0.053*
O10	0.3609 (4)	0.4337 (4)	0.0787 (3)	0.0568 (11)
H101	0.3857	0.4044	0.0352	0.068*
C1	0.7095 (6)	0.3671 (5)	0.2257 (4)	0.0469 (14)
C2	0.8146 (6)	0.2912 (5)	0.2094 (5)	0.0459 (14)
C3	0.8103 (7)	0.2638 (6)	0.1239 (5)	0.0596 (17)
H6A	0.7450	0.2945	0.0788	0.072*
C4	0.9016 (8)	0.1910 (6)	0.1042 (6)	0.076 (2)
H1A	0.8980	0.1734	0.0463	0.091*
C5	0.9964 (8)	0.1459 (7)	0.1708 (7)	0.085 (3)
H16A	1.0579	0.0969	0.1585	0.102*
C6	1.0021 (7)	0.1721 (7)	0.2555 (7)	0.080 (2)
H2A	1.0673	0.1395	0.3004	0.095*
C7	0.9123 (6)	0.2467 (6)	0.2769 (5)	0.0592 (17)

supplementary materials

C8	0.9261 (8)	0.2716 (8)	0.3714 (6)	0.096 (3)
H86A	1.0008	0.2327	0.4054	0.144*
H86B	0.8584	0.2429	0.4174	0.144*
H86C	0.9278	0.3552	0.3519	0.144*
C9	0.5966 (5)	0.6777 (5)	0.1277 (4)	0.0398 (13)
C10	0.6395 (5)	0.7941 (5)	0.0541 (4)	0.0418 (13)
C11	0.7440 (6)	0.8295 (6)	0.0808 (5)	0.0555 (16)
H12A	0.7828	0.7819	0.1423	0.067*
C12	0.7921 (7)	0.9338 (6)	0.0185 (6)	0.073 (2)
H83A	0.8637	0.9561	0.0366	0.088*
C13	0.7326 (8)	1.0048 (6)	-0.0712 (6)	0.076 (2)
H15A	0.7642	1.0755	-0.1144	0.091*
C14	0.6286 (8)	0.9723 (6)	-0.0965 (5)	0.067 (2)
H29A	0.5886	1.0225	-0.1564	0.080*
C15	0.5788 (6)	0.8655 (5)	-0.0357 (4)	0.0508 (15)
C16	0.4611 (7)	0.8351 (7)	-0.0678 (6)	0.078 (2)
H21A	0.4396	0.7593	-0.0188	0.117*
H21B	0.4716	0.8329	-0.1347	0.117*
H21C	0.3974	0.8939	-0.0702	0.117*
C17	0.3361 (5)	0.6038 (5)	0.2817 (4)	0.0415 (13)
C18	0.2326 (5)	0.6838 (5)	0.2932 (4)	0.0410 (13)
C19	0.2546 (6)	0.7553 (5)	0.3447 (5)	0.0556 (16)
H18A	0.3320	0.7509	0.3709	0.067*
C20	0.1648 (7)	0.8324 (6)	0.3579 (6)	0.067 (2)
H4A	0.1816	0.8801	0.3920	0.081*
C21	0.0502 (7)	0.8382 (6)	0.3201 (6)	0.070 (2)
H7A	-0.0115	0.8893	0.3291	0.084*
C22	0.0272 (6)	0.7685 (6)	0.2692 (5)	0.0657 (19)
H41A	-0.0509	0.7734	0.2441	0.079*
C23	0.1162 (6)	0.6902 (6)	0.2532 (5)	0.0543 (16)
C24	0.0820 (7)	0.6149 (8)	0.1987 (6)	0.083 (2)
H68A	0.1524	0.5665	0.1931	0.124*
H68B	0.0528	0.6647	0.1311	0.124*
H68C	0.0191	0.5655	0.2371	0.124*
C25	0.4550 (5)	0.2973 (5)	0.4010 (4)	0.0442 (14)
C26	0.4049 (5)	0.1916 (5)	0.4846 (4)	0.0437 (13)
C27	0.4027 (6)	0.1904 (5)	0.5840 (4)	0.0524 (16)
H20A	0.4376	0.2499	0.5958	0.063*
C28	0.3494 (7)	0.1019 (7)	0.6645 (5)	0.070 (2)
H65A	0.3445	0.1034	0.7298	0.084*
C29	0.3034 (8)	0.0113 (7)	0.6471 (6)	0.091 (3)
H61A	0.2679	-0.0493	0.7011	0.109*
C30	0.3095 (8)	0.0097 (6)	0.5504 (6)	0.081 (2)
H66A	0.2790	-0.0531	0.5405	0.098*
C31	0.3604 (6)	0.0998 (6)	0.4662 (5)	0.0580 (17)
C32	0.3659 (8)	0.0916 (6)	0.3629 (6)	0.079 (2)
H70A	0.4027	0.1594	0.3134	0.119*
H70B	0.2847	0.0891	0.3414	0.119*
H70C	0.4137	0.0212	0.3679	0.119*

C33	0.8056 (6)	0.5374 (8)	0.4439 (6)	0.073 (2)
H24A	0.8317	0.5775	0.3729	0.088*
H24B	0.8434	0.4576	0.4692	0.088*
C34	0.8510 (6)	0.5986 (6)	0.5052 (5)	0.068 (2)
H71A	0.9383	0.5985	0.4996	0.102*
H71B	0.8279	0.5584	0.5761	0.102*
H71C	0.8162	0.6785	0.4797	0.102*
C35	0.2514 (6)	0.3709 (6)	0.1090 (5)	0.0588 (17)
H10A	0.2210	0.3734	0.1734	0.071*
H10B	0.2706	0.2888	0.1203	0.071*
C36	0.1552 (7)	0.4221 (7)	0.0298 (6)	0.078 (2)
H64A	0.0840	0.3780	0.0524	0.117*
H64B	0.1846	0.4187	-0.0338	0.117*
H64C	0.1346	0.5029	0.0195	0.117*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0415 (4)	0.0413 (4)	0.0305 (3)	-0.0075 (3)	-0.0003 (3)	-0.0122 (3)
Cu2	0.0427 (4)	0.0457 (4)	0.0323 (3)	-0.0081 (3)	0.0004 (3)	-0.0153 (3)
O1	0.051 (3)	0.055 (3)	0.058 (3)	-0.006 (2)	0.000 (2)	-0.029 (2)
O2	0.051 (3)	0.054 (2)	0.055 (2)	-0.005 (2)	0.002 (2)	-0.036 (2)
O3	0.059 (3)	0.042 (2)	0.0348 (19)	-0.0204 (19)	0.0013 (18)	-0.0114 (17)
O4	0.061 (3)	0.048 (2)	0.0336 (19)	-0.018 (2)	-0.0009 (18)	-0.0157 (18)
O5	0.047 (2)	0.055 (2)	0.037 (2)	0.0012 (19)	-0.0004 (18)	-0.0210 (18)
O6	0.049 (2)	0.062 (3)	0.0323 (19)	-0.002 (2)	0.0009 (18)	-0.0216 (19)
O7	0.051 (2)	0.045 (2)	0.042 (2)	-0.0176 (19)	-0.0063 (19)	-0.0103 (18)
O8	0.053 (3)	0.046 (2)	0.040 (2)	-0.0239 (19)	0.0015 (19)	-0.0119 (18)
O9	0.047 (2)	0.052 (2)	0.0370 (19)	-0.0150 (19)	0.0031 (18)	-0.0194 (18)
O10	0.053 (3)	0.084 (3)	0.050 (2)	-0.022 (2)	0.007 (2)	-0.042 (2)
C1	0.051 (4)	0.039 (3)	0.043 (3)	-0.012 (3)	0.001 (3)	-0.006 (3)
C2	0.046 (4)	0.036 (3)	0.053 (3)	-0.008 (3)	0.014 (3)	-0.015 (3)
C3	0.071 (5)	0.052 (4)	0.061 (4)	-0.009 (3)	0.020 (3)	-0.028 (3)
C4	0.094 (6)	0.058 (4)	0.079 (5)	-0.009 (4)	0.026 (5)	-0.033 (4)
C5	0.089 (7)	0.061 (5)	0.095 (6)	0.011 (4)	0.034 (5)	-0.027 (5)
C6	0.063 (5)	0.060 (5)	0.097 (6)	0.014 (4)	0.003 (5)	-0.016 (5)
C7	0.054 (4)	0.050 (4)	0.067 (4)	-0.003 (3)	0.006 (3)	-0.017 (3)
C8	0.094 (7)	0.110 (7)	0.088 (6)	0.026 (5)	-0.037 (5)	-0.046 (6)
C9	0.039 (3)	0.044 (3)	0.032 (3)	0.000 (3)	0.004 (2)	-0.012 (2)
C10	0.049 (3)	0.038 (3)	0.035 (3)	-0.006 (3)	0.001 (3)	-0.010 (2)
C11	0.061 (4)	0.049 (4)	0.052 (4)	-0.019 (3)	0.001 (3)	-0.013 (3)
C12	0.079 (5)	0.066 (5)	0.071 (5)	-0.030 (4)	0.011 (4)	-0.021 (4)
C13	0.106 (7)	0.050 (4)	0.063 (5)	-0.027 (4)	0.024 (5)	-0.011 (4)
C14	0.097 (6)	0.046 (4)	0.046 (4)	-0.005 (4)	0.004 (4)	-0.007 (3)
C15	0.065 (4)	0.043 (3)	0.043 (3)	0.001 (3)	0.002 (3)	-0.017 (3)
C16	0.082 (6)	0.072 (5)	0.070 (5)	0.004 (4)	-0.026 (4)	-0.017 (4)
C17	0.042 (3)	0.042 (3)	0.031 (3)	-0.008 (3)	0.001 (2)	-0.004 (2)
C18	0.043 (3)	0.037 (3)	0.037 (3)	-0.008 (3)	0.003 (3)	-0.007 (2)

supplementary materials

C19	0.063 (4)	0.049 (4)	0.059 (4)	-0.006 (3)	0.006 (3)	-0.025 (3)
C20	0.086 (6)	0.047 (4)	0.076 (5)	-0.003 (4)	0.011 (4)	-0.031 (4)
C21	0.062 (5)	0.060 (4)	0.078 (5)	0.011 (4)	0.009 (4)	-0.020 (4)
C22	0.047 (4)	0.074 (5)	0.070 (5)	0.007 (4)	-0.009 (3)	-0.023 (4)
C23	0.051 (4)	0.059 (4)	0.048 (3)	-0.002 (3)	-0.002 (3)	-0.016 (3)
C24	0.057 (5)	0.116 (7)	0.091 (6)	0.004 (5)	-0.022 (4)	-0.057 (5)
C25	0.048 (4)	0.046 (3)	0.034 (3)	0.001 (3)	0.007 (3)	-0.012 (3)
C26	0.043 (3)	0.033 (3)	0.047 (3)	-0.005 (2)	0.001 (3)	-0.007 (3)
C27	0.061 (4)	0.045 (3)	0.041 (3)	-0.003 (3)	0.003 (3)	-0.008 (3)
C28	0.073 (5)	0.067 (5)	0.049 (4)	-0.007 (4)	0.012 (4)	-0.002 (3)
C29	0.097 (7)	0.068 (5)	0.072 (5)	-0.031 (5)	0.008 (5)	0.014 (4)
C30	0.094 (6)	0.055 (4)	0.084 (6)	-0.038 (4)	-0.007 (5)	-0.009 (4)
C31	0.057 (4)	0.047 (4)	0.059 (4)	-0.014 (3)	-0.008 (3)	-0.008 (3)
C32	0.099 (6)	0.056 (4)	0.083 (5)	-0.016 (4)	-0.017 (5)	-0.025 (4)
C33	0.042 (4)	0.117 (7)	0.086 (5)	-0.023 (4)	0.008 (4)	-0.065 (5)
C34	0.057 (4)	0.075 (5)	0.075 (5)	-0.017 (4)	-0.012 (4)	-0.029 (4)
C35	0.059 (4)	0.066 (4)	0.053 (4)	-0.008 (3)	-0.004 (3)	-0.024 (3)
C36	0.058 (5)	0.078 (5)	0.084 (5)	-0.014 (4)	-0.013 (4)	-0.017 (4)

Geometric parameters (\AA , $^\circ$)

Cu1—O7	1.928 (4)	C14—H29A	0.9300
Cu1—O3	1.952 (4)	C15—C16	1.509 (9)
Cu1—O1	1.975 (4)	C16—H21A	0.9600
Cu1—O5	2.017 (4)	C16—H21B	0.9600
Cu1—O9	2.149 (4)	C16—H21C	0.9600
Cu1—Cu2	2.6005 (11)	C17—C18	1.495 (8)
Cu2—O2	1.931 (4)	C18—C19	1.389 (8)
Cu2—O6	1.954 (4)	C18—C23	1.402 (8)
Cu2—O8	1.993 (4)	C19—C20	1.378 (9)
Cu2—O4	2.008 (4)	C19—H18A	0.9300
Cu2—O10	2.161 (4)	C20—C21	1.372 (10)
O1—C1	1.269 (7)	C20—H4A	0.9300
O2—C1	1.271 (7)	C21—C22	1.367 (10)
O3—C9	1.269 (6)	C21—H7A	0.9300
O4—C9	1.270 (6)	C22—C23	1.397 (9)
O5—C17	1.275 (6)	C22—H41A	0.9300
O6—C17	1.252 (6)	C23—C24	1.500 (9)
O7—C25	1.268 (7)	C24—H68A	0.9600
O8—C25	1.271 (6)	C24—H68B	0.9600
O9—C33	1.405 (7)	C24—H68C	0.9600
O9—H91	0.8523	C25—C26	1.498 (7)
O10—C35	1.442 (7)	C26—C31	1.389 (8)
O10—H101	0.8558	C26—C27	1.399 (8)
C1—C2	1.500 (8)	C27—C28	1.378 (8)
C2—C3	1.382 (8)	C27—H20A	0.9300
C2—C7	1.391 (9)	C28—C29	1.374 (11)
C3—C4	1.389 (9)	C28—H65A	0.9300
C3—H6A	0.9300	C29—C30	1.376 (11)

C4—C5	1.361 (11)	C29—H61A	0.9300
C4—H1A	0.9300	C30—C31	1.401 (9)
C5—C6	1.363 (11)	C30—H66A	0.9300
C5—H16A	0.9300	C31—C32	1.503 (10)
C6—C7	1.405 (10)	C32—H70A	0.9600
C6—H2A	0.9300	C32—H70B	0.9600
C7—C8	1.501 (10)	C32—H70C	0.9600
C8—H86A	0.9600	C33—C34	1.479 (9)
C8—H86B	0.9600	C33—H24A	0.9700
C8—H86C	0.9600	C33—H24B	0.9700
C9—C10	1.502 (7)	C34—H71A	0.9600
C10—C11	1.378 (8)	C34—H71B	0.9600
C10—C15	1.385 (8)	C34—H71C	0.9600
C11—C12	1.375 (9)	C35—C36	1.482 (9)
C11—H12A	0.9300	C35—H10A	0.9700
C12—C13	1.377 (10)	C35—H10B	0.9700
C12—H83A	0.9300	C36—H64A	0.9600
C13—C14	1.347 (10)	C36—H64B	0.9600
C13—H15A	0.9300	C36—H64C	0.9600
C14—C15	1.400 (9)		
O7—Cu1—O3	172.78 (16)	C15—C14—H29A	118.9
O7—Cu1—O1	90.04 (18)	C10—C15—C14	117.3 (6)
O3—Cu1—O1	90.54 (18)	C10—C15—C16	123.1 (6)
O7—Cu1—O5	89.64 (17)	C14—C15—C16	119.5 (6)
O3—Cu1—O5	87.92 (17)	C15—C16—H21A	109.5
O1—Cu1—O5	164.85 (16)	C15—C16—H21B	109.5
O7—Cu1—O9	93.24 (15)	H21A—C16—H21B	109.5
O3—Cu1—O9	93.82 (15)	C15—C16—H21C	109.5
O1—Cu1—O9	97.89 (16)	H21A—C16—H21C	109.5
O5—Cu1—O9	97.25 (15)	H21B—C16—H21C	109.5
O7—Cu1—Cu2	87.80 (12)	O6—C17—O5	124.8 (5)
O3—Cu1—Cu2	85.12 (11)	O6—C17—C18	119.1 (5)
O1—Cu1—Cu2	82.78 (12)	O5—C17—C18	116.1 (5)
O5—Cu1—Cu2	82.07 (11)	C19—C18—C23	119.4 (6)
O9—Cu1—Cu2	178.76 (11)	C19—C18—C17	117.8 (5)
O2—Cu2—O6	171.58 (17)	C23—C18—C17	122.8 (6)
O2—Cu2—O8	90.35 (18)	C20—C19—C18	121.7 (7)
O6—Cu2—O8	90.75 (17)	C20—C19—H18A	119.1
O2—Cu2—O4	90.02 (18)	C18—C19—H18A	119.1
O6—Cu2—O4	86.69 (17)	C21—C20—C19	119.3 (7)
O8—Cu2—O4	164.46 (15)	C21—C20—H4A	120.4
O2—Cu2—O10	96.24 (17)	C19—C20—H4A	120.4
O6—Cu2—O10	91.96 (17)	C22—C21—C20	119.7 (7)
O8—Cu2—O10	95.56 (16)	C22—C21—H7A	120.2
O4—Cu2—O10	99.84 (16)	C20—C21—H7A	120.2
O2—Cu2—Cu1	85.76 (12)	C21—C22—C23	122.8 (7)
O6—Cu2—Cu1	86.17 (11)	C21—C22—H41A	118.6
O8—Cu2—Cu1	80.87 (11)	C23—C22—H41A	118.6
O4—Cu2—Cu1	83.67 (11)	C22—C23—C18	117.2 (6)

supplementary materials

O10—Cu2—Cu1	175.93 (12)	C22—C23—C24	119.1 (6)
C1—O1—Cu1	122.8 (4)	C18—C23—C24	123.6 (6)
C1—O2—Cu2	122.0 (4)	C23—C24—H68A	109.5
C9—O3—Cu1	122.4 (4)	C23—C24—H68B	109.5
C9—O4—Cu2	121.0 (3)	H68A—C24—H68B	109.5
C17—O5—Cu1	121.7 (4)	C23—C24—H68C	109.5
C17—O6—Cu2	121.4 (4)	H68A—C24—H68C	109.5
C25—O7—Cu1	119.6 (3)	H68B—C24—H68C	109.5
C25—O8—Cu2	124.4 (4)	O7—C25—O8	124.5 (5)
C33—O9—Cu1	122.3 (4)	O7—C25—C26	117.4 (5)
C33—O9—H91	130.1	O8—C25—C26	118.0 (5)
Cu1—O9—H91	99.7	C31—C26—C27	120.7 (5)
C35—O10—Cu2	121.6 (3)	C31—C26—C25	123.0 (5)
C35—O10—H101	96.1	C27—C26—C25	116.3 (5)
Cu2—O10—H101	128.2	C28—C27—C26	120.7 (6)
O1—C1—O2	124.0 (6)	C28—C27—H20A	119.7
O1—C1—C2	120.0 (6)	C26—C27—H20A	119.7
O2—C1—C2	116.0 (6)	C29—C28—C27	119.1 (7)
C3—C2—C7	120.0 (6)	C29—C28—H65A	120.4
C3—C2—C1	117.1 (6)	C27—C28—H65A	120.4
C7—C2—C1	122.9 (6)	C28—C29—C30	120.4 (7)
C2—C3—C4	121.2 (7)	C28—C29—H61A	119.8
C2—C3—H6A	119.4	C30—C29—H61A	119.8
C4—C3—H6A	119.4	C29—C30—C31	121.9 (7)
C5—C4—C3	119.0 (8)	C29—C30—H66A	119.0
C5—C4—H1A	120.5	C31—C30—H66A	119.0
C3—C4—H1A	120.5	C26—C31—C30	117.1 (7)
C4—C5—C6	120.6 (8)	C26—C31—C32	123.7 (6)
C4—C5—H16A	119.7	C30—C31—C32	119.2 (6)
C6—C5—H16A	119.7	C31—C32—H70A	109.5
C5—C6—C7	121.9 (8)	C31—C32—H70B	109.5
C5—C6—H2A	119.0	H70A—C32—H70B	109.5
C7—C6—H2A	119.0	C31—C32—H70C	109.5
C2—C7—C6	117.3 (7)	H70A—C32—H70C	109.5
C2—C7—C8	124.2 (6)	H70B—C32—H70C	109.5
C6—C7—C8	118.5 (7)	O9—C33—C34	114.9 (6)
C7—C8—H86A	109.5	O9—C33—H24A	108.6
C7—C8—H86B	109.5	C34—C33—H24A	108.6
H86A—C8—H86B	109.5	O9—C33—H24B	108.6
C7—C8—H86C	109.5	C34—C33—H24B	108.6
H86A—C8—H86C	109.5	H24A—C33—H24B	107.5
H86B—C8—H86C	109.5	C33—C34—H71A	109.5
O3—C9—O4	124.9 (5)	C33—C34—H71B	109.5
O3—C9—C10	115.2 (5)	H71A—C34—H71B	109.5
O4—C9—C10	119.8 (5)	C33—C34—H71C	109.5
C11—C10—C15	120.1 (5)	H71A—C34—H71C	109.5
C11—C10—C9	116.5 (5)	H71B—C34—H71C	109.5
C15—C10—C9	123.5 (5)	O10—C35—C36	111.8 (5)
C12—C11—C10	121.3 (6)	O10—C35—H10A	109.3

C12—C11—H12A	119.3	C36—C35—H10A	109.3
C10—C11—H12A	119.3	O10—C35—H10B	109.3
C11—C12—C13	118.9 (7)	C36—C35—H10B	109.3
C11—C12—H83A	120.6	H10A—C35—H10B	107.9
C13—C12—H83A	120.6	C35—C36—H64A	109.5
C14—C13—C12	120.2 (7)	C35—C36—H64B	109.5
C14—C13—H15A	119.9	H64A—C36—H64B	109.5
C12—C13—H15A	119.9	C35—C36—H64C	109.5
C13—C14—C15	122.3 (7)	H64A—C36—H64C	109.5
C13—C14—H29A	118.9	H64B—C36—H64C	109.5

Hydrogen-bond geometry (\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>
O9—H91 \cdots O5 ⁱ	0.85	2.04	2.841 (6)	156
O10—H101 \cdots O4 ⁱⁱ	0.86	2.00	2.831 (6)	162

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

Fig. 1

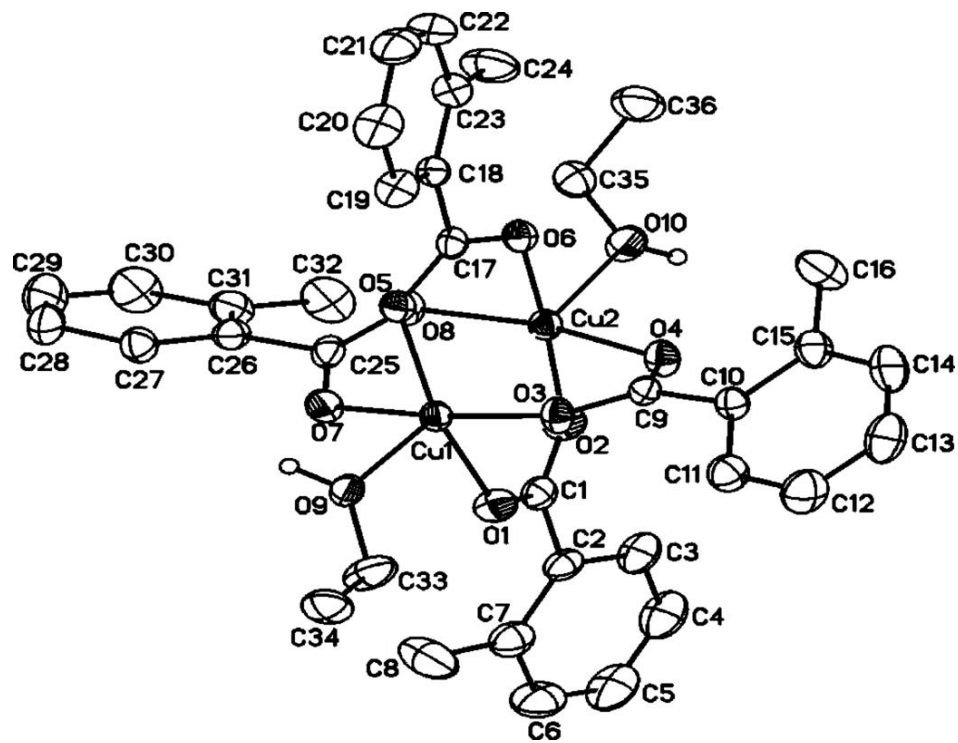


Fig. 2

