Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dimeric copper(II) 3,3-dimethylbutyrate adducts with ethanol, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine and 3,3-dimethylbutyric acid

Masato Goto,[a] Yoshiyuki Kani,[a] Masanobu Tsuchimoto,[a] Shigeru Ohba,[a]* Hideaki Matsushima[b] and Tadashi Tokii[b]

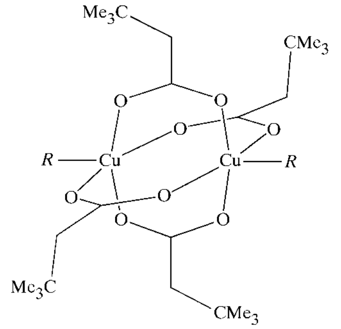
[a]Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan, and [b]Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840-8502, Japan
Correspondence e-mail: ohba@chem.keio.ac.jp

Received 8 June 1999
Accepted 22 September 1999

In the crystals of the five title compounds, tetrakis(*μ*-3,3-dimethylbutyrato-*O*:*O*′)bis(ethanol-*O*)dicopper(II)–ethanol (1/2), $[Cu_2(C_6H_{11}O_2)_4(C_2H_6O)_2]\cdot 2C_2H_6O$, (I), tetrakis(*μ*-3,3-dimethylbutyrato-*O*:*O*′)bis(2-methylpyridine-*N*)dicopper(II), $[Cu_2(C_6H_{11}O_2)_4(C_6H_7N)_2]$, (II), tetrakis(*μ*-3,3-dimethylbutyrato-*O*:*O*′)bis(3-methylpyridine-*N*)dicopper(II), $[Cu_2(C_6H_{11}O_2)_4(C_6H_7N)_2]$, (III), tetrakis(*μ*-3,3-dimethylbutyrato-*O*:*O*′)bis(4-methylpyridine-*N*)dicopper(II), $[Cu_2(C_6H_{11}O_2)_4(C_6H_7N)_2]$, (IV), and tetrakis(*μ*-3,3-dimethylbutyrato-*O*:*O*′)bis(3,3-dimethylbutyric acid-*O*)dicopper(II), $[Cu_2(C_6H_{11}O_2)_4(C_6H_{12}O_2)_2]$, (V), the dinuclear Cu^{II} complexes all have centrosymmetric cage structures and (IV) has two independent molecules. The Cu···Cu separations are: (I) 2.602 (3) Å, (II) 2.666 (3) Å, (III) 2.640 (2) Å, (IV) 2.638 (4) Å and (V) 2.599 (1) Å.

Comment

The structures and magnetic properties of dimeric copper(II) carboxylates have been investigated revealing that the electronic structure of the OCO bridge reflects the strength of the antiferromagnetic interaction (Yamanaka *et al.*, 1991; Harada *et al.*, 1997). The organosilane group directly bonded to the OCO bridge greatly enhances the antiferromagnetic interaction due to the *σ*-electron donation character. For example, the complex $[Cu_2(PhMe_2SiCOO)_4(H_2O)_2]$ has a $-2J$ value of 1000 ± 150 cm^{-1} (Steward *et al.*, 1986). Recently, the $-2J$ values of the trimethylsilylacetate copper(II) complexes $[Cu_2(Me_3SiCH_2COO)_4L_2]$ (L = pyridine, 2-methylpyridine, 3-methylpyridine and quinoline) were determined to be 328 cm^{-1} on average (Nakagawa *et al.*, 2000). In this paper, the corresponding carbon carboxylate copper(II) complexes $[Cu_2(Me_3CCH_2COO)_4L_2]$ [L = 2-methylpyridine, (II), 3-methylpyridine, (III), and 4-methylpyridine, (IV)] were examined. The magnetic $-2J$ value of the pyridine adduct, $[Cu_2(Me_3CCH_2COO)_4(py)_2]$, was determined to be 348 cm^{-1}, and those of 2-, 3-, and 4-methylpyridine adducts were determined to be 363, 355 and 354 cm^{-1} ($H = -2JS_1{\cdot}S_2$), respectively. This indicates that the Si atom bonded to the *α*-carbon of the carboxylato bridge slightly reduces the antiferromagnetic interaction.



(I) $R = C_2H_6O$, diethanol solvate
(II) R = *o*-Me-C_5H_4N
(III) R = *m*-Me-C_5H_4N
(IV) R = f-Me-C_5H_4N
(V) $R = MeC(Me)_2CH_2CO_2H$, *O*-coordinated

The $-2J$ value of the non-adduct, $[Cu_2(Me_3CCH_2COO)_4]$, obtained from (V) by removing the axial acid ligands in a vacuum is 364 cm^{-1}, which is almost in the range 348–363 cm^{-1} for the pyridine and methylpyridine adducts. This suggests that the non-adduct created from (V) has a discrete

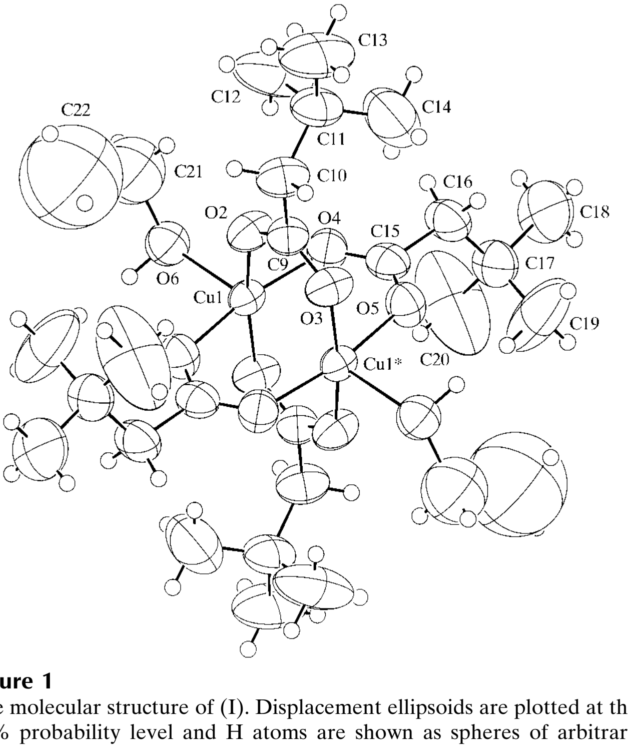


Figure 1
The molecular structure of (I). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

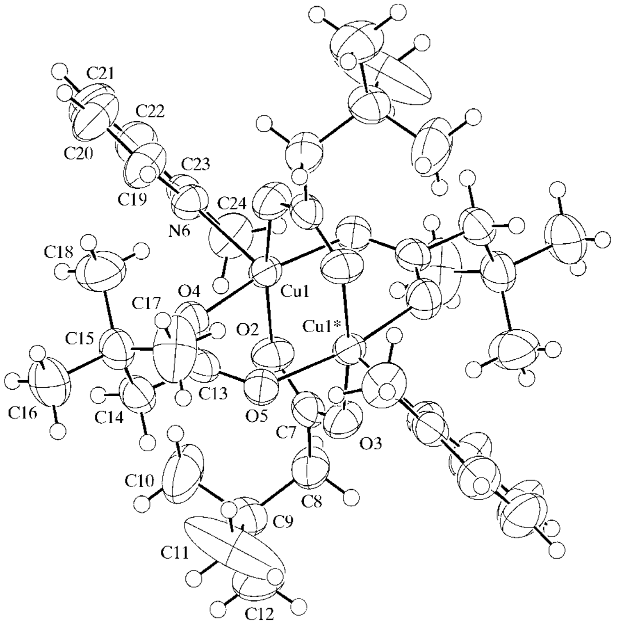


Figure 2
The molecular structure of (II). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

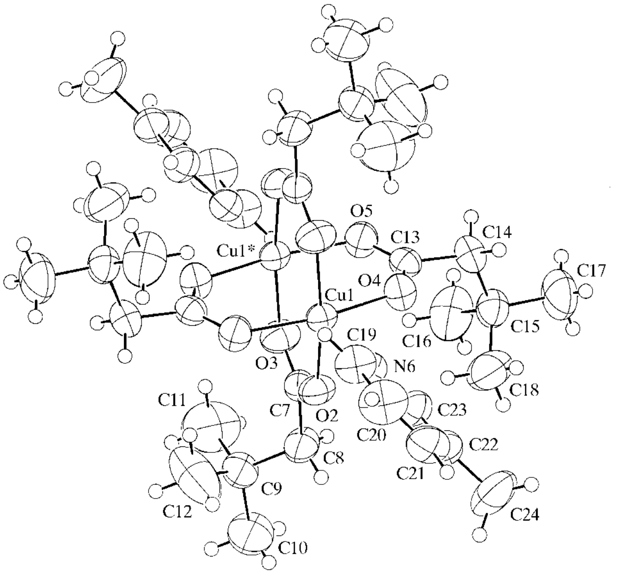


Figure 3
The molecular structure of (III). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

dimer structure, with the apical position free from coordination.

The binuclear copper complexes (I)–(V) have a centre of symmetry, and the geometry around the Cu atoms is a typical square-pyramidal coordination. The Cu···Cu distances are 2.602 (3) in (I) and 2.599 (1) Å in (V) for O-donor axial ligands, and 2.638 (4)–2.666 (3) Å in (II)–(IV) for N-donor axial ligands. This is the result of a larger deviation of the Cu atom from the O_4 basal plane to the N atom than that to the O atom at the apical position. In (V), the Cu1—O2 bond length of 2.005 (4) Å is 0.05 Å longer than those of the other Cu—O bonds in the cage due to the intramolecular O7—H7···O2 hydrogen bond.

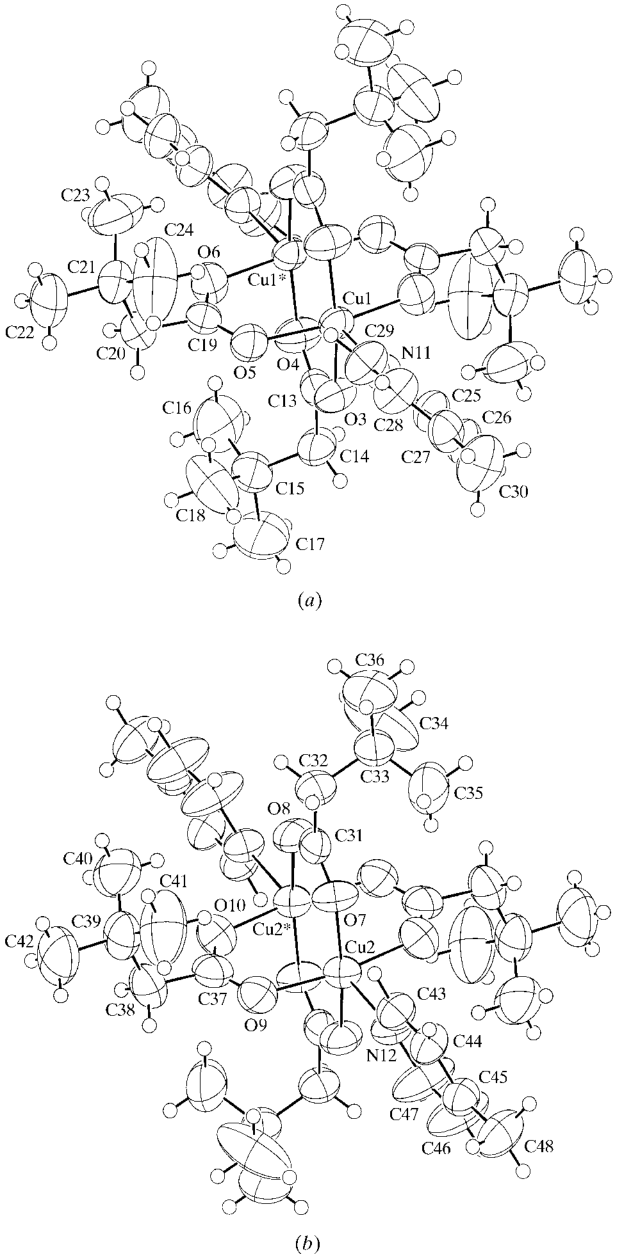


Figure 4
The molecular structure of (IV); (a) and (b) show the two independent molecules. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

3,3-Dimethylbutyric acid (116 mg, 1.0 mmol) and $CuCO_3$·$Cu(OH)_2$·H_2O (60 mg, 0.25 mmol) were suspended in a mixture of water and methanol (3:1, 20 ml). After the solution was stirred for 1 h at room temperature, a green precipitate was collected and dissolved in ethanol. From the solution, green crystals of (I) were grown by

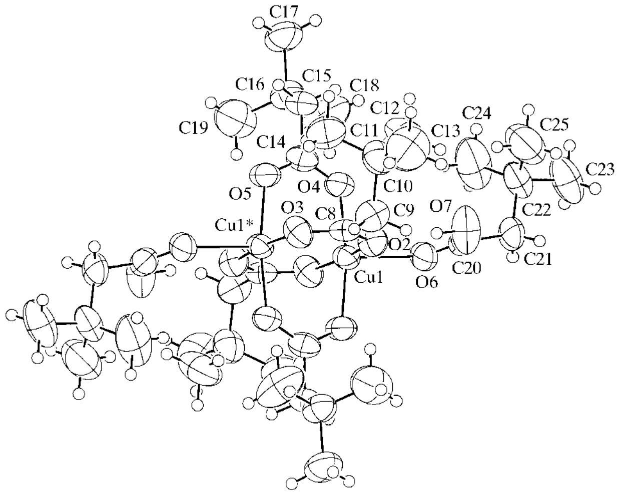


Figure 5
The molecular structure of (V). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

slow evaporation. When 2-, 3-, or 4-methylpyridine (46.5 mg, 0.50 mmol) was added to the solution, the colour changed from green to blue, and green crystals of (II), (III) or (IV) were obtained.

Crystals of the pyridine adduct were prepared in a similar way: $[Cu_2(C_6H_{11}O_2)_4(C_5H_5N)_2]$, monoclinic, $P2_1/c$, a = 9.956 (2), b = 18.445 (2), c = 21.703 (2) Å, β = 98.11 (1)°, V = 3946 (1) Å^3, Z = 4, Cu···Cu = 2.634 (3) Å, $-2J$ = 348 cm^{-1}. Crystals of the acid adduct, (V), were grown from an acetonitrile solution of (I) with the addition of 3,3-dimethylbutyric acid (58 mg, 0.50 mmol). The crystal specimen of (I) was sealed in a capillary with mother liquor, and that of (II) was coated with adhesive to avoid efflorescence.

Compound (I)

Crystal data

$[Cu_2(C_6H_{11}O_2)_4(C_2H_6O)_2]\cdot 2C_2H_6O$
M_r = 771.98
Triclinic, $P\overline{1}$
a = 10.765 (2) Å
b = 10.923 (2) Å
c = 9.820 (1) Å
α = 105.43 (1)°
β = 106.50 (1)°
γ = 88.43 (1)°
V = 1065.8 (3) Å^3

Z = 1
D_x = 1.203 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.047 mm^{-1}
T = 299 K
Prism, green
0.5 × 0.4 × 0.3 mm

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
T_{min} = 0.569, T_{max} = 0.822
5151 measured reflections
4888 independent reflections
3646 reflections with $|F_o| > 3\sigma(|F_o|)$

R_{int} = 0.012
θ_{max} = 27.5°
$h = 0 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
R = 0.076
wR = 0.077
S = 1.44
3646 reflections
182 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 1.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cu1^i	2.602 (3)	Cu1—O6	2.164 (3)
Cu1—O2	1.971 (3)	O2—C9	1.250 (4)
Cu1—O3^i	1.968 (3)	O3—C9	1.268 (5)
Cu1—O4	1.952 (3)	O4—C15	1.243 (5)
Cu1—O5^i	1.958 (3)	O5—C15	1.250 (5)
O2—Cu1—O3^i	168.9 (1)	O2—C9—O3	123.9 (4)
O4—Cu1—O5^i	168.8 (2)	O4—C15—O5	126.2 (4)

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

Compound (II)

Crystal data

$[Cu_2(C_6H_{11}O_2)_4(C_6H_7N)_2]$
M_r = 773.96
Monoclinic, $P2_1/a$
a = 10.040 (2) Å
b = 18.468 (1) Å
c = 11.649 (1) Å
β = 109.16 (1)°
V = 2040.3 (4) Å^3
Z = 2

D_x = 1.260 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.089 mm^{-1}
T = 299 K
Prism, green
0.5 × 0.2 × 0.2 mm

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
T_{min} = 0.794, T_{max} = 0.830
5080 measured reflections
4678 independent reflections
3226 reflections with $|F_o| > 3\sigma(|F_o|)$

R_{int} = 0.014
θ_{max} = 27.5°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 24$
$l = -15 \rightarrow 15$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
R = 0.050
wR = 0.044
S = 1.24
3226 reflections
217 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 2
Selected geometric parameters (Å, °).

Cu1—Cu1^i	2.666 (3)	Cu1—N6	2.238 (3)
Cu1—O2	1.969 (2)	O2—C7	1.251 (4)
Cu1—O3^i	1.982 (2)	O3—C7	1.249 (4)
Cu1—O4	1.969 (2)	O4—C13	1.258 (4)
Cu1—O5^i	1.967 (2)	O5—C13	1.254 (4)
O2—Cu1—O3^i	167.2 (1)	O2—C7—O3	125.7 (3)
O4—Cu1—O5^i	167.3 (1)	O4—C13—O5	125.2 (3)

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

Compound (III)

Crystal data

$[Cu_2(C_6H_{11}O_2)_4(C_6H_7N)_2]$
M_r = 773.96
Triclinic, $P\overline{1}$
a = 10.603 (2) Å
b = 11.216 (2) Å
c = 10.289 (1) Å
α = 105.80 (1)°
β = 101.01 (1)°
γ = 63.11 (1)°
V = 1046.7 (3) Å^3

Z = 1
D_x = 1.228 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.061 mm^{-1}
T = 299 K
Prism, green
0.6 × 0.4 × 0.4 mm

Acta Cryst. (2000). C56, 7–11 Masato Goto et al. • Five $[Cu_2(C_6H_{11}O_2)_4]$ adducts 9

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\rm min} = 0.965$, $T_{\rm max} = 0.973$
5071 measured reflections
4810 independent reflections
4058 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.046$
$wR = 0.048$
$S = 1.19$
4058 reflections
217 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.72$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °).

Cu1—Cu1^{i}	2.640 (2)	Cu1—N6	2.163 (2)
Cu1—O2	1.975 (2)	O2—C7	1.260 (2)
Cu1—O3^{i}	1.968 (2)	O3—C7	1.257 (2)
Cu1—O4	1.976 (2)	O4—C13	1.245 (2)
Cu1—O5^{i}	1.973 (2)	O5—C13	1.251 (2)
O2—Cu1—O3^{i}	168.1 (1)	O2—C7—O3	125.6 (2)
O4—Cu1—O5^{i}	167.7 (1)	O4—C13—O5	125.3 (2)

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

Compound (IV)

Crystal data

$[Cu_2(C_6H_{11}O_2)_4(C_6H_7N)_2]$
$M_r = 773.96$
Triclinic, $P\overline{1}$
$a = 11.346$ (2) Å
$b = 18.584$ (3) Å
$c = 10.606$ (2) Å
$\alpha = 90.44$ (1)°
$\beta = 101.40$ (1)°
$\gamma = 74.80$ (1)°
$V = 2113.2$ (6) Å^3

$Z = 2$
$D_x = 1.216$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 1.051$ mm^{-1}
$T = 297$ K
Prism, green
0.5 × 0.4 × 0.2 mm

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\rm min} = 0.967$, $T_{\rm max} = 0.984$
10 177 measured reflections
9683 independent reflections
5211 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 15$
$k = -24 \rightarrow 24$
$l = -14 \rightarrow 14$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.067$
$wR = 0.052$
$S = 1.32$
5211 reflections
433 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.66$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.66$ e Å^{-3}

Table 4
Selected geometric parameters (Å, °).

Cu1—Cu1^{i}	2.638 (4)	Cu2—O10^{ii}	1.960 (4)
Cu1—O3	1.967 (3)	Cu2—N12	2.167 (4)
Cu1—O4^{i}	1.966 (3)	O3—C13	1.258 (6)
Cu1—O5	1.960 (4)	O4—C13	1.266 (6)
Cu1—O6^{i}	1.961 (4)	O5—C19	1.272 (6)
Cu1—N11	2.175 (4)	O6—C19	1.240 (6)
Cu2—Cu2^{ii}	2.641 (4)	O7—C31	1.228 (7)
Cu2—O7	1.967 (3)	O8—C31	1.278 (6)
Cu2—O8^{ii}	1.985 (4)	O9—C37	1.259 (7)
Cu2—O9	1.974 (4)	O10—C37	1.249 (7)
O3—Cu1—O4^{i}	168.1 (2)	O3—C13—O4	124.7 (5)
O5—Cu1—O6^{i}	168.0 (2)	O5—C19—O6	124.9 (5)
O7—Cu2—O8^{ii}	168.1 (2)	O7—C31—O8	125.7 (5)
O9—Cu2—O10^{ii}	168.0 (2)	O9—C37—O10	125.5 (5)

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

Compound (V)

Crystal data

$[Cu_2(C_6H_{11}O_2)_4(C_6H_{12}O_2)_2]$
$M_r = 820.02$
Monoclinic, $P2_1/c$
$a = 10.890$ (2) Å
$b = 18.211$ (2) Å
$c = 11.787$ (1) Å
$\beta = 103.98$ (1)°
$V = 2268.2$ (5) Å^3
$Z = 2$

$D_x = 1.201$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.988$ mm^{-1}
$T = 297$ K
Prism, green
0.3 × 0.3 × 0.25 mm

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\rm min} = 0.792$, $T_{\rm max} = 0.793$
5475 measured reflections
5214 independent reflections
2610 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = -15 \rightarrow 15$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.070$
$wR = 0.054$
$S = 1.33$
2610 reflections
226 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\rm max} = 0.008$
$\Delta\rho_{\rm max} = 0.93$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.74$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °).

Cu1—Cu1^{i}	2.599 (1)	Cu1—O6	2.186 (5)
Cu1—O2	2.005 (4)	O2—C8	1.285 (8)
Cu1—O3^{i}	1.955 (4)	O3—C8	1.243 (8)
Cu1—O4	1.950 (4)	O4—C14	1.255 (8)
Cu1—O5^{i}	1.946 (4)	O5—C14	1.262 (8)
O2—Cu1—O3^{i}	169.3 (2)	O2—C8—O3	123.6 (6)
O4—Cu1—O5^{i}	169.0 (2)	O4—C14—O5	124.4 (6)

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

Table 6
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$\cdots$O2	0.96	1.72	2.617 (5)	154

In (I), there is a positional disorder of the O atom in the ethanol of crystallization. The O and C atoms of the disordered ethanol were refined isotropically and the occupation factors of the ethanol O7 and O8 positions were assumed to be 30 and 70%, respectively, based on the displacement parameters. There are hydrogen bonds involving these O atoms: O6—H6$\cdots$O8(x−1, y, z−1), O6$\cdots$O8 = 2.718 (5) Å; O3—H$\cdots$O7(1−x, −y, 1−z), O3$\cdots$O7 = 3.040 (10) Å; O3—H$\cdots$O8(x−1, y, z), O3$\cdots$O8 = 2.884 (5) Å. Non-H atoms of the ligating ethanol in (I) were also refined isotropically to avoid unusual displacement parameters.

The max/min ratio of the atom displacement parameters are abnormally large for the methyl-C atoms of the *tert*-butyl groups, which may be due to vibrational and rotational disorder. The positions of all the H atoms were calculated geometrically except for those of the ethanol of crystallization in (I) and a riding model was used in their refinement [C—H 0.96 Å, $U_{\rm iso}$ (H) = 0.3 Å^2 for (I), 0.2 Å^2 for (I)–(IV)].

The magnetic susceptibilities over the temperature range 80–300 K were determined by the Faraday method at Saga University. The procedure for determining the $-2J$ value from cryomagnetic data based on the Bleaney–Bowers equation is described elsewhere (Harada *et al.*, 1997).

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: local programs; program(s) used to solve structure: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structure: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1094). Services for accessing these data are described at the back of the journal.

References

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1996). *CRYSTAN-GM. Program for the Solution and Refinement of Crystal Structures.* Version 6.3. MacScience Co. Ltd, Yokohama, Japan.

Harada, A., Tsuchimoto, M., Ohba, S., Iwasawa, K. & Tokii, T. (1997). *Acta Cryst.* B**53**, 654–661.

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nakagawa, H., Kani, Y., Tsuchimoto, M., Ohba, S., Matsushima, H. & Tokii, T. (2000). *Acta Cryst.* C**56**, 12–16.

Steward, O. W., McAfee, R. C., Chang, S. C., Piskor, S. R., Schreiber, W. J., Jury, C. F., Taylor, C. E., Pletcher, J. F. & Chen, C. S. (1986). *Inorg. Chem.* **25**, 771–777.

Yamanaka, M., Uekusa, H., Ohba, S., Saito, Y., Iwata, S., Kato, M., Tokii, T., Muto, Y. & Steward, O. W. (1991). *Acta Cryst.* B**47**, 344–355.