Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

catena-Poly[[tetrakis(μ-2,2-dimethylpropionato-*O*:*O*′)dicopper(**II**)]-μ-dioxane-*O*:*O*′] and *catena*-poly[[tetrakis(μ-3,3-dimethylbutyrato-*O*:*O*′)dicopper(**II**)]-μ-dioxane-*O*,*O*′]

Yoshiyuki Kani,[a] Masanobu Tsuchimoto,[a] Shigeru Ohba[a]* 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

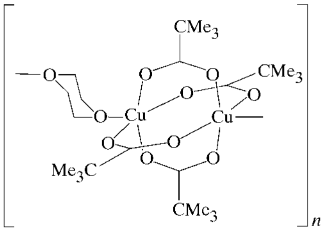
Received 31 January 2000
Accepted 7 February 2000

Data validation number: IUC0000040

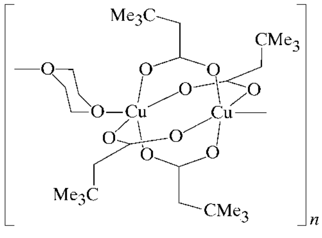
The title two compounds, $[Cu_2(C_5H_9O_2)_4(C_4H_8O_2)]_n$, (I), and $[Cu_2(C_6H_{11}O_2)_4(C_4H_8O_2)]_n$, (II), are isomorphous. The binuclear Cu^{II} units have a cage structure and are linked by the dioxane molecules to form a zigzag chain along the *c* axis. The binuclear copper unit and the dioxane ligand each have a centre of symmetry.

Comment

The magnetic $-2J$ values of the binuclear Cu unit of (I) and (II) were determined to be 387 and 363 cm^{-1}, respectively ($H = -2JS_1.S_2$). The spin-exchange interaction through the dioxane bridge is negligible. The $-2J$ values of $[Cu_2(Me_3CCOO)_4L_2]$ (L = pyridine and 2-methylpyridine) were reported to be 366 and 371 cm^{-1}, respectively (Muto *et al.*, 1986). Structures of dimeric copper(II)–3,3-dimethylbutyrate adducts have been reported recently, the $-2J$ values of $[Cu_2(Me_3CCH_2COO)_4L_2]$ (L = pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine) being in the range 348–363 cm^{-1} (Goto *et al.*, 2000).



(I)



(II)

Experimental

A solution of 2,2-dimethylpropionic acid (613 mg, 6.0 mmol) in 0.25 *M* sodium hydroxide (50 ml) was neutralized with 0.25 *M* nitric acid. An aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (725 mg, 3.0 mmol) was added. After the solution had been stirred for 15 min at room temperature, a green precipitate was collected and dissolved in dioxane. From the solution, blue crystals of (I) were grown by slow evaporation. 3,3–Dimethylbutyric acid (116 mg, 1.0 mmol) and $CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$ (60 mg, 0.25 mmol) were suspended in a mixture of water and methanol (3:1, 20 ml). After the solution had been stirred for 1 h at room temperature, a green precipitate was collected and dissolved in dioxane. From the solution, blue crystals of (II) were grown by slow evaporation.

Compound (I)

Crystal data

$[Cu_2(C_5H_9O_2)_4(C_4H_8O_2)]$
$M_r = 619.70$
Triclinic, $P\overline{1}$
$a = 9.633\ (2)$ Å
$b = 10.665\ (1)$ Å
$c = 9.030\ (2)$ Å
$\alpha = 112.28\ (1)°$
$\beta = 110.19\ (2)°$
$\gamma = 83.72\ (1)°$
$V = 805.4\ (3)$ Å^3

$Z = 1$
$D_x = 1.278$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 1.364$ mm^{-1}
$T = 297$ K
Prism, blue
0.5 × 0.1 × 0.1 mm

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{min} = 0.829$, $T_{max} = 0.886$
4955 measured reflections
4697 independent reflections
2697 reflections with $I > 2\sigma(I)$

$R_{int} = 0.091$
$\theta_{max} = 30°$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 3.9%

Refinement

Refinement on *F*
$R = 0.051$
$wR = 0.070$
$S = 1.08$
2697 reflections
163 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0025|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

$Cu1\cdots Cu1^i$	2.560 (1)	Cu1—O3	1.946 (3)
Cu1—O1	1.959 (3)	$Cu1—O4^i$	1.959 (3)
$Cu1—O2^i$	1.947 (3)	Cu1—O5	2.205 (2)

O1—C1	1.251 (5)	O3—C6	1.253 (5)
O2—C1	1.261 (5)	O4—C6	1.253 (5)
O1—Cu1—O2^{i}	170.0 (1)	O1—C1—O2	124.2 (4)
O3—Cu1—O4^{i}	169.9 (1)	O3—C6—O4	124.5 (4)

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

Compound (II)

Crystal data

$[Cu_2(C_6H_{11}O_2)_4(C_4H_8O_2)]$
$M_r = 675.81$
Triclinic, $P\overline{1}$
$a = 10.080$ (1) Å
$b = 11.308$ (2) Å
$c = 8.952$ (1) Å
$\alpha = 113.30$ (1)°
$\beta = 108.92$ (1)°
$\gamma = 84.64$ (1)°
$V = 885.8$ (2) Å^3

$Z = 1$
$D_x = 1.267$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 1.246$ mm^{-1}
$T = 298$ K
Prism, blue
0.4 × 0.4 × 0.4 mm

Data collection

Rigaku AFC-7R diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\min} = 0.559$, $T_{\max} = 0.665$
5397 measured reflections
5156 independent reflections
3998 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.01$
$\theta_{\max} = 30°$
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 0$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 2.4%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.075$
$S = 1.067$
5155 reflections

181 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0025|F_o|^2]$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1···Cu1^{i}	2.553 (1)	Cu1—O5	2.198 (2)
Cu1—O1	1.964 (2)	O1—C1	1.260 (3)
Cu1—O2^{i}	1.959 (2)	O2—C1	1.266 (3)
Cu1—O3	1.953 (2)	O3—C7	1.257 (3)
Cu1—O4^{i}	1.961 (2)	O4—C7	1.263 (3)
O1—Cu1—O2^{i}	170.7 (1)	O1—C1—O2	124.7 (2)
O3—Cu1—O4^{i}	170.5 (1)	O3—C7—O4	124.6 (3)

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

The positional parameters of all the H atoms were calculated geometrically and fixed with U(H) = 1.2$U_{\rm eq}$(parent atom). The max/min ratio of the atomic displacement parameters are abnormally large for the *tert*-butyl moieties in (I) and (II), which may be due to vibrational and rotational disorder.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *teXsan* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *teXsan*; software used to prepare material for publication: *teXsan*.

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Acta Cryst. (2000). C**56**, e80–e81 Yoshiyuki Kani *et al.* • $[Cu_2(C_5H_9O_2)_4(C_4H_8O_2)]$ and $[Cu_2(C_6H_{11}O_2)_4(C_4H_8O_2)]$ **e81**