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catena-Poly[[tetrakis(μ-3,3-dimethylbutyrato-*O*:*O*′)dicopper(**II**)]-μ-3,3-dimethylbutyrato-*O*:*O*′-[bis(2,6-dimethylpyridine-*N*)copper(**II**)]-μ-3,3-dimethylbutyrato-*O*:*O*′] and tetrakis(μ-2,2-dimethylpropanoato-*O*:*O*′)bis[(2,6-dimethylpyridine-*N*)copper(**II**)]

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The two title compounds, $[Cu_3(C_6H_{11}O_2)_6(C_7H_9N)_2]_n$, (I), and $[Cu_2(C_5H_9O_2)_4(C_7H_9N)_2]$, (II), have chain and finite-molecular structures, respectively. In (I), binuclear cage units and mononuclear 2,6-dimethylpyridine complexes, both of which have inversion centres, are arranged alternately and are linked by the carboxylate ions to form one-dimensional chains along the *a* axis. In (II), the binuclear cage unit has an inversion centre and the coordination geometry around the Cu atom is typical square pyramidal, with 2,6-dimethylpyridine at the apical position.

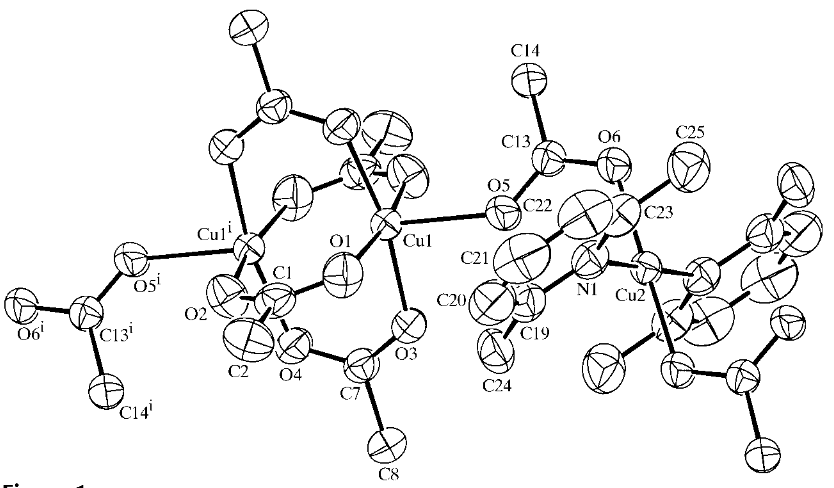
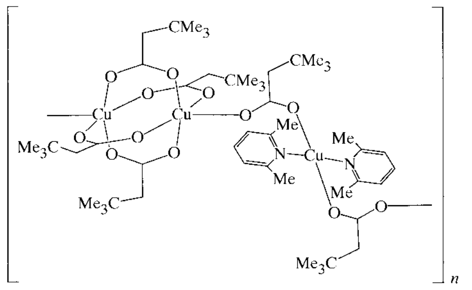


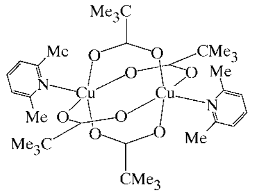
Figure 1
The linear chain structure of (I) with displacement ellipsoids at the 50% probability level. H atoms and the *tert*-butyl groups of the dimethylbutyrate ligands have been omitted for clarity (symmetry code as in Table 1).

Comment

Copper(II) carboxylates usually have a cage structure with square-pyramidal coordination geometry and a monodentate ligand bonded at the axial position. 2,6-Dimethylpyridine (2,6-Me_2py) is a bulky ligand which may cause a deformation of this cage structure, as observed in the crystal structure of $[Cu_2(PhMe_2CCOO)_2(2,6\text{-}Me_2py)_2]$, where the geometry about the Cu^{II} is deformed from square-pyramidal toward trigonal bipyramidal (TBP). Alternatively, only a mononuclear complex, $[Cu(RCOO)_2(2,6\text{-}Me_2py)_2]$, will be produced, as for R = Ph_3C or Ph_2MeC (Fujita *et al.*, 1993). In this context, the crystal structures of the title compounds, (I) and (II), are presented here.



(I)



(II)

In (I), a novel polymeric structure was observed. The mononuclear moiety $[Cu(RCOO)_2(2,6\text{-}Me_2py)_2]$ acts as the axial ligand to the binuclear unit. The carboxylate bridge between the mononuclear and binuclear units has a *syn–anti* conformation. An analysis of the temperature dependence of the magnetic susceptibility indicated that the spin-exchange interaction between the mononuclear and binuclear units is negligible. The Cu$\cdots$Cu distance in the binuclear unit is 2.652 (1) Å, which is similar to that of the 3,3-dimethylbutyric acid adduct [2.599 (1) Å; Goto *et al.*, 2000].

In (II), the binuclear cage structure of the copper pivalate does not have a TBP distortion, which is consistent with the high magnetic $-2J$ value of 379 cm^{-1} ($H = -2JS_1{\cdot}S_2$; Muto *et al.*, 1986). The acridine adduct of copper(II) pivalate also has a cage structure with square-pyramidal coordination, the Cu$\cdots$Cu and Cu—N distances being 2.702 (1) and 2.371 (5) Å, respectively (Kirillova *et al.*, 1980). Copper pivalate remains a discrete dimeric structure even after the removal of the axial solvent ligands (Muto *et al.*, 1986; Kato & Muto, 1988). In polymeric copper(II) pivalate, prepared by

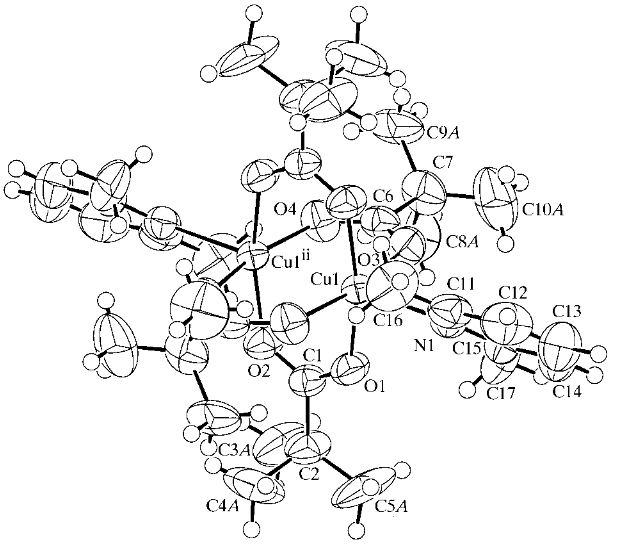


Figure 2
The molecular structure of (II). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Only one orientation of the *tert*-butyl groups is shown, indicated by the suffix *A* (symmetry code as in Table 2).

sublimation, the dinuclear cage is deformed and the coordination geometry around the Cu atom has a TBP distortion (Il'ina *et al.*, 1992).

Experimental

For (I), 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, the green precipitate was collected and dissolved in acetonitrile and 2,6-dimethylpyridine (54 mg, 0.5 mmol) was added. Blue crystals of (I) were grown from the solution by slow evaporation. For (II), 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 and 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, the green precipitate was collected and dissolved in acetonitrile and 2,6-dimethylpyridine (321 mg, 3.0 mmol) was added. Green crystals of (II) were grown from the solution by slow evaporation.

Compound (I)

Crystal data

$[Cu_3(C_6H_{11}O_2)_6(C_7H_9N)_2]$
$M_r = 1095.86$
Triclinic, $P\bar{1}$
$a = 12.525$ (2) Å
$b = 12.736$ (2) Å
$c = 10.033$ (2) Å
$\alpha = 94.64$ (1)°
$\beta = 102.51$ (1)°
$\gamma = 109.32$ (1)°
$V = 1454.1$ (5) Å^3
$Z = 1$
$D_x = 1.251$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 1.141$ mm^{-1}
$T = 298$ K
Prism, blue
0.4 × 0.1 × 0.1 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{min} = 0.472$, $T_{max} = 0.753$
6956 measured reflections
6651 independent reflections
4193 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 16$
$k = -17 \rightarrow 17$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.115$
$S = 1.08$
6651 reflections
304 parameters
H-atom parameters constrained
$w = 1/\{\sigma^2F_o^2 + [0.05(F_o^2 + 2F_c^2)/3]^2\}$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-3}

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

Cu1—Cu1^{i}	2.652 (1)	Cu1—O5	2.185 (2)
Cu1—O1	1.972 (3)	Cu2—O5	2.923 (2)
Cu1—O2^{i}	1.965 (2)	Cu2—O6	1.938 (2)
Cu1—O3	1.967 (2)	Cu2—N1	2.050 (3)
Cu1—O4^{i}	1.967 (2)		
O1—Cu1—O2^{i}	167.7 (1)	O1—C1—O2	125.9 (3)
O3—Cu1—O4^{i}	167.7 (1)	O3—C7—O4	125.3 (3)
O6—Cu2—N1	92.2 (1)	O5—C13—O6	121.9 (3)
Cu1—O5—C13	134.1 (2)		
Cu1—O5—C13—O6	173.8 (2)	Cu2—O6—C13—O5	7.7 (4)

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

Compound (II)

Crystal data

$[Cu_2(C_5H_9O_2)_4(C_7H_9N)_2]$
$M_r = 745.90$
Triclinic, $P\bar{1}$
$a = 10.986$ (4) Å
$b = 11.195$ (5) Å
$c = 9.564$ (4) Å
$\alpha = 107.66$ (4)°
$\beta = 97.15$ (4)°
$\gamma = 61.82$ (3)°
$V = 987.7$ (8) Å^3
$Z = 1$
$D_x = 1.254$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 1.122$ mm^{-1}
$T = 298$ K
Prism, green
0.25 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{min} = 0.803$, $T_{max} = 0.844$
4761 measured reflections
4524 independent reflections
3449 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 3$
3 standard reflections every 150 reflections intensity decay: 4.1%

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

Cu1—Cu1^{ii}	2.722 (1)	Cu1—O3	1.964 (2)
Cu1—O1	1.964 (2)	Cu1—O4^{ii}	1.962 (3)
Cu1—O2^{ii}	1.973 (2)	Cu1—N1	2.360 (3)
O1—Cu1—O2^{ii}	165.5 (1)	O1—C1—O2	125.2 (3)
O3—Cu1—O4^{ii}	165.3 (1)	O3—C6—O4	125.1 (3)

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

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.152$
$S = 1.05$
4524 reflections
226 parameters
H-atom parameters constrained
$w = 1/\{\sigma^2F_o^2 + [0.1(F_o^2 + 2F_c^2)/3]^2\}$
$(\Delta/\sigma)_{\max} = 0.027$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Initially, both of the structures were refined as usual. The anisotropy in the atomic displacement parameters became abnormally large for the methyl C atoms of the *tert*-butyl groups, suggesting libration and/or rotational disorder. Therefore, a split-site model was investigated for the *tert*-butyl groups in both compounds; it was found to be applicable for (II), but not for (I). For (II), the six methyl-C atoms were initially refined isotropically. Two sets of half-occupancy methyl groups, offset from one another by *ca* 30°, could be modelled for both *tert*-butyl groups based on the difference synthesis. Their anisotropic displacement parameters were then refined with their positional parameters fixed to avoid unreasonable geometry. Compared with the unsplit model, $R(F)$ slightly decreased from 0.050 to 0.048 on increasing the number of parameters from 208 to 226. The magnitude of the displacement ellipsoids of the methyl C atoms apparently decreased, but the abnormal anisotropy of the displacement parameters did not disappear. In this manuscript, the split-site model is reported for (II). The positional parameters of all the H atoms were calculated geometrically and fixed with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}$(parent atom).

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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1098). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

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

Fujita, T., Ohba, S., Nagamatsu, M., Tokii, T., Jury, C. F., Steward, O. W. & Kato, M. (1993). *Acta Cryst.* C**49**, 2095–2100.

Goto, M., Kani, Y., Tsuchimoto, M., Ohba, S., Matsushima, H. & Tokii, T. (2000). *Acta Cryst.* C**56**, 7–11.

Il'ina, E. G., Troyanov, S. I. & Dunaeva, K. M. (1992). *Koord. Khim.* **18**, 882–890.

Kato, M. & Muto, Y. (1988). *Coord. Chem. Rev.* **92**, 45–83.

Kirillova, N. I., Struchkov, Y. T., Porai-Koshits, M. A., Pasynskii, A. A., Antsyshkina, A. S., Minacheva, L. K., Sadikov, G. G., Idrisov, T. C. & Kalinnikov, V. T. (1980). *Inorg. Chim. Acta*, **40**, 115–119.

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

Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.

Muto, Y., Hirashima, N., Tokii, T., Kato, M. & Suzuki, I. (1986). *Bull. Chem. Soc. Jpn*, **59**, 3672–3674.