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Tetrakis(μ_2-2,2-dimethylpropanoato-κ^2O,O')-bis[(pyridine-κN)copper(II)]

Gavin Blewett, Catharine Esterhuysen, Martin W. Bredenkamp and Klaus R. Koch*

Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

Correspondence e-mail: krk@sun.ac.za

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Key indicators

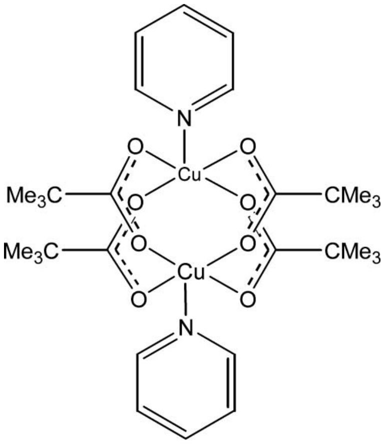
Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.006 Å
R factor = 0.045
wR factor = 0.103
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Cu_2(C_5H_9O_2)_4(C_5H_5N)_2]$, consists of centrosymmetric binuclear cage units with four dimethylpropanoate bridges linking the two Cu centres [Cu···Cu = 2.6229 (9) Å]. The square-pyramidal Cu coordination is completed by a pyridine N atom at the apical site. A π–π stacking interaction helps to consolidate the crystal packing.

Comment

As part of a systematic investigation into a new class of N-acyl-N',N'-dialkylurea ligands and their coordination chemistry with a variety of transition metals, the title compound, (I), arose as an unexpected product from the bi-phase reaction of copper(II) perchlorate hexahydrate with N-pivaloyl-N',N'-dimethylurea in the presence of pyridine during an attempt to isolate crystals of Cu(L-O,O)$_2$ (HL = N-pivaloyl-N',N'-dimethylurea). Presumably, this 'lantern-type' dimeric copper complex results from the hydrolysis of N-pivaloyl-N',N'-dimethylurea under these reaction conditions (see *Experimental*).



(I)

The first copper(II) carboxylate-bridged dimer was reported as early as 1953 (van Niekerk & Schoening, 1953), and numerous related compounds have been synthesized and structurally characterized since [Cambridge Structural Database (CSD), Version 5.26; Allen, 2002]. Centrosymmetric compound (I) (Fig. 1, Table 1) complements this family.

Of interest is the close proximity of the Cu atoms [Cu1···Cu1^{i} = 2.6229 (9) Å; symmetry code: (i) $1 - x$, $1 - y$, $1 - z$]. In comparable 'lantern-type' dimeric copper complexes in which axial ligands are absent, such as $[Cu_2(PhN_3Ph)_4]$, a Cu···Cu bond of 2.44 Å was observed (Harris *et al.*, 1959; Kirillova *et al.*, 1980). Nevertheless, the

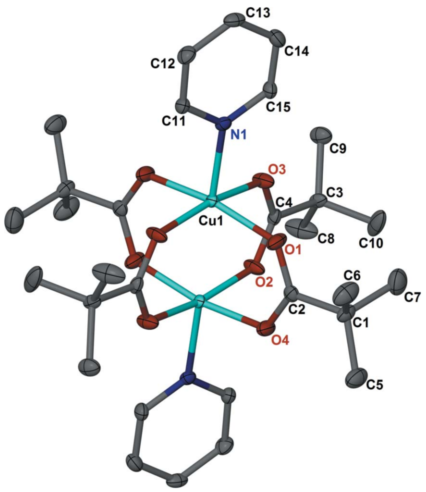


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Unlabelled atoms are related to labelled atoms by the symmetry operator ($1 - x, 1 - y, 1 - z$).

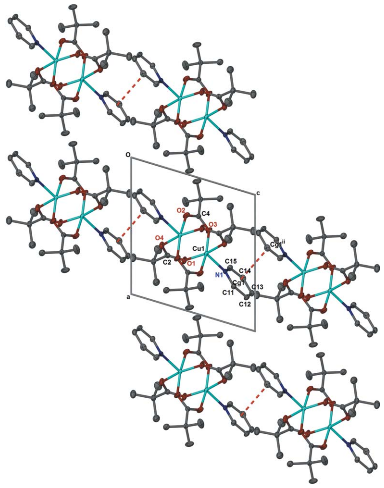


Figure 2
A packing diagram for (I), viewed along [010]. The pyridine π–π interactions are indicated as dashed lines. *Cg* is the centroid of the pyridine ring. [Symmetry code: (ii) $1 - x, 1 - y, 2 - z$.]

longer Cu1$\cdots$Cu1^{i} distance observed in compound (I) is similar to the average of 2.660 (5) Å for the reported interatomic Cu$\cdots$Cu distances of the 447 structures of dimeric copper(II) centres bridged by carboxylate ligands listed in the CSD.

The Cu^{II} atoms in (I) are each displaced towards their bound pyridine N atom from the basal O1/O2/O3/O4 plane by 0.200 (1) Å. It has previously been reported that the degree of displacement of the Cu atoms from the basal plane and the resulting interatomic Cu$\cdots$Cu distances are related to the degree of steric hindrance of both the apical substituents and the *R* groups on the carboxylate bridges (Kani *et al.*, 2000; Mikuriya *et al.*, 1999).

The Cu—N bond length in (I) [2.153 (3) Å] is significantly shorter than the comparable Cu—N bond length of 2.360 (3) Å reported for the structurally analogous tetrakis(μ_2-2,2-dimethylpropanoato-*O*,*O*′)-bis(2,6-dimethylpyridine-*N*)dicopper(II) (Kani *et al.*, 2000). Kirillova *et al.* (1980) proposed that, in general, an increase in electron density on the Cu atoms, due to the electron-releasing property of the *tert*-butyl groups on the carboxylate bridges, would most likely weaken the pyridine–Cu donor–acceptor interaction. This hypothesis is supported by the Cu—N bond lengths in [C_9H_7N-Cu(OOC*R*)$_2$]$_2$, which decreased from 2.224 to 2.107 Å on replacing *R* = CH_3 with CF_3 (Kirillova *et al.*, 1980). Interestingly in (I), the Cu—N bond length remains relatively short, despite the presence of the *tert*-butyl groups on the carboxylate bridges.

The chelation rings of the bridging carboxylate groups are almost planar, with atom Cu1 deviating from the C2/O1/O4 least-squares plane by −0.022 (2) Å and from the C4/O3/O2 least-squares plane by 0.0362 (2) Å. In turn, the planar axial pyridine substituents are twisted away from these planes, with the N1/C11–C15 least-squares plane of the pyridine ring intersecting the C2/O1/O4 and C4/O3/O2 least-squares planes at 66.1 (2) and 23.5 (2)°, respectively. The overall symmetry of the complex results in the Cu1–N1 bond being almost collinear with the Cu1$\cdots$Cu1^{i} axis [N1—Cu1$\cdots$Cu1^{i} = 172.75 (8)°].

No inter- or intramolecular hydrogen bonds or interactions are observed between molecules of (I) in the unit cell. However, a π–π stacking interaction between the pyridine rings of adjacent molecules is observed [$Cg\cdots Cg^{ii}$ = 3.628 Å, where *Cg* is the centroid of the pyridine ring; symmetry code: (ii) $1 - x, 1 - y, 2 - z$]. This π–π interaction allows the molecules of (I) to extend as one-dimensional molecular chains along [001], as indicated in Fig. 2.

Experimental

Pyridine (0.55 mmol) was added dropwise with stirring to a solution of *N*-pivaloyl-*N*′,*N*′-dimethylurea (0.005 mmol) dissolved in chloroform (20 ml). The reaction mixture was stirred at room temperature for 10 min. Copper perchlorate hexahydrate (0.25 mmol) dissolved in water (20 ml) was added and the reaction mixture was stirred at room temperature overnight. The two phases were separated and the aqueous phase was repeatedly extracted with small volumes of chloroform and diethyl ether (10 ml). The organic fractions were combined and the crude product was recovered as an amorphous blue solid under reduced pressure and dried under high vacuum. The crude product was further purified by crystallization from a solution in chloroform. Hexane was added to a concentrated chloroform solution of the crude product until the solution became turbid. Upon standing at room temperature for a couple of weeks, crystals of (I) suitable for single-crystal X-ray diffraction were obtained and isolated manually under a microscope (yield 71%, based on Cu).

Crystal data

[$Cu_2(C_5H_9O_2)_4(C_5H_5N)_2$]
M_r = 689.77
Triclinic, $P\overline{1}$
a = 9.7378 (19) Å
b = 10.0428 (19) Å
c = 10.435 (2) Å
α = 61.520 (3)°
β = 72.495 (3)°
γ = 84.200 (3)°
V = 854.3 (3) Å^3

Z = 1
D_x = 1.341 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 3879 reflections
θ = 2.2–28.3°
μ = 1.29 mm^{-1}
T = 273 (2) K
Rectangular slab, blue–green
0.20 × 0.17 × 0.10 mm

Acta Cryst. (2006). E**62**, m420–m422 Blewett *et al.* • [$Cu_2(C_5H_9O_2)_4(C_5H_5N)_2$] **m421**

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3317 independent reflections
ω scans	2568 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 2002)	$R_{\rm int} = 0.065$
$T_{\rm min} = 0.782$, $T_{\rm max} = 0.882$	$\theta_{\rm max} = 26.0°$
7897 measured reflections	$h = -12 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{\rm max} < 0.001$
$S = 0.98$	$\Delta\rho_{\rm max} = 1.31$ e Å^{-3}
3317 reflections	$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
197 parameters	

Table 1
Selected bond lengths (Å).

Cu1—O1	1.963 (2)	Cu1—O4	1.977 (2)
Cu1—O3	1.968 (2)	Cu1—N1	2.153 (3)
Cu1—O2	1.968 (2)		

All H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier) or 1.5$U_{\rm eq}$(methyl carrier). A residual electron-density peak of 1.31 e Å^{-3} was observed 1.58 Å from atom H151 but it could not be assigned.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001; Atwood & Barbour, 2003); software used to prepare material for publication: *X-SEED*.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Atwood, J. L. & Barbour, L. J. (2003). *Cryst. Growth Des.* **3**, 3–8.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2001). *SMART*. Version 5.625. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2002). *SAINT*. Version 6.36a. Bruker AXS Inc. Madison, Wisconsin, USA.
Harris, C. M., Hoskins, B. F. & Martin, R. L. (1959). *J. Chem. Soc.* pp. 3728–3736.
Kani, Y., Tsuchimoto, M., Ohba, S., Matsushima, H. & Tokii, T. (2000). *Acta Cryst.* C**56**, 923–925.
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*, **42**, 115–119.
Mikuriya, M., Azuma, H., Nukada, R. & Handa, M. (1999). *Chem. Lett.* **1**, 57–58.
Niekerk, J. N. van & Schoening, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. Version 2.05. University of Göttingen, Germany.

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