References

Aston, K. W., Henke, S. L., Modak, A. S., Riley, D. P., Sample, K. R., Weiss, R. H. & Neumann, W. L. (1994). *Tetrahedron Lett.* **35**, 3687–3690.

Bencini, A., Bianchi, A., G.-Espana, E., Giusti, M., Mangani, S., Micheloni, M., Orioli, P. & Paoletti, P. (1987). *Inorg. Chem.* **26**, 1243–1247.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF94 Program System.* Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Hancock, R. D. (1989). *Prog. Inorg. Chem.* **37**, 187–291.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kim, J., Suh, M. P. & Shin, W. (1991). *Acta Cryst.* C**47**, 745–747.

Mitewa, M. & Bontchev, P. R. (1994). *Coord. Chem. Rev.* **135**, 129–163.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Rigaku Corporation (1988). *Rigaku/AFC Diffractometer Control Software.* Rigaku Corporation, Tokyo, Japan.

Sakurai, T., Kobayashi, K., Hasegawa, A., Tsuboyama, S. & Tsuboyama, K. (1982). *Acta Cryst.* B**38**, 107–111.

Seki, Y., Miyake, H., Kojima, Y., Doi, M. & Yano, S. (1996). *Mol. Cryst. Liq. Cryst.* **276**, 79–84.

Yoshiki, N., Seki, Y., Miyake, H., Kojima, Y., Doi, M. & Yano, S. (1996). *Mol. Cryst. Liq. Cryst.* **276**, 85–90.

Bis(methyl 3-pyridyl-κN¹-carbamate)bis-(propionato-κO)copper(II)–Water (4/1)

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Abstract

The Cu^{II} centre in the title compound, [Cu(C$_3$H$_5$O$_2$)$_2$(C$_7$H$_8$N$_2$O$_2$)$_2$].0.25H$_2$O, is situated on an inversion centre and has tetragonally distorted coordination. It is bonded in a *trans*-square-planar arrangement to the pyridyl N atoms of two methyl 3-pyridylcarbamate molecules [Cu—N1 2.025 (2) Å] and one carboxylate O atom from each of two propionate anions [Cu—O1 1.955 (2) Å]. The axial positions are occupied by

the other propionate O atoms [Cu···O2 2.653 (2) Å]. The propionate groups exhibit very small O1—Cu···O2 chelate angles of 54.23 (8)°.

Comment

While dimeric Cu$_2$(propionate)$_4$(substituted pyridine)$_2$ species have been reported previously (Borel & Leclaire, 1976a,b, 1978; Borel et al., 1976, 1981; Smolander et al., 1992; Melník et al., 1998), the monomeric analogues have not. We report here such a monomer, namely, bis(methyl 3-pyridylcarbamate)bis-(propionato)copper(II) 0.25-hydrate, (I).

(I)
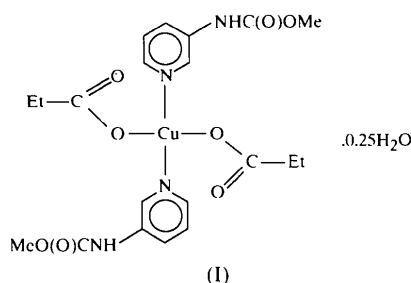
The structure (Fig. 1) consists of discrete complex cations and H$_2$O molecules linked by hydrogen bonds [O4^i···H8 2.520 Å and O2^{ii}···H2 1.975 Å; symmetry codes: (i) y, $\frac{1}{2} - x$, $\frac{1}{2} - z$; (ii) x, y, $1 + z$] and van der Waals forces. The stereochemistry around the Cu^{II} centre may be described as axially elongated octahedral. Molecules of the cation lie on a crystallographic inversion centre, with the Cu^{II} atom coordinated by the pyridyl N atoms of two different methyl 3-pyridylcarbamate molecules and by an O atom from each of the two propionate anions to give a square-planar arrangement, with Cu—N1 and Cu—O1 bond lengths of 2.025 (2) and 1.955 (2) Å, respectively. The remaining carboxylate O atoms in each propionate anion participates in much longer axial bonding [Cu—O2
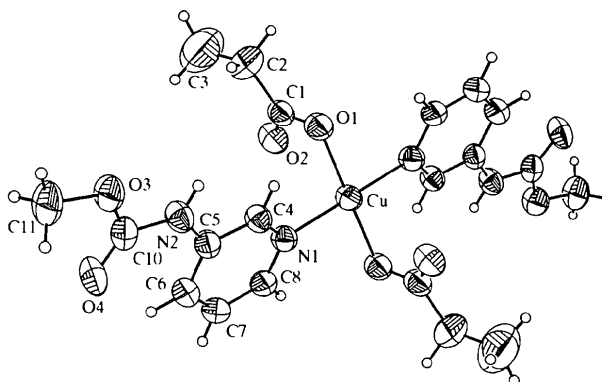

Fig. 1. A view of the title compound, without the hydrate molecule, showing displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.
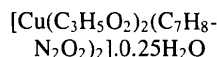
2.653 (2) Å] to complete a distorted octahedral environment around Cu^{II}. The C1—O1 and C1—O2 distances [1.268 (4) and 1.227 (4) Å, respectively] are significantly different.

The propionate chelate angle O1—Cu—O2 is very acute at 54.23 (8)°. When propionate is coordinated as a chelate, the mean Cu—O bond distance of 2.30 Å is about 0.33 Å longer than when coordinated in a syn–syn arrangement (Melník, 1982).

Experimental

The title compound was prepared by treating methyl 3-pyridyl-carbamate (3.043 g, 0.02 mol) with copper(II) propionate (2.097 g, 0.01 mol) in hot methanol solution (50 ml). The crude product was recrystallized from methanol to give single crystals.

Crystal data

[Cu(C3H5O2)2(C7H8-N2O2)2].0.25H2O	Cu $K\alpha$ radiation
$M_r = 518.5$	$\lambda = 1.54180$ Å
Tetragonal	Cell parameters from 25
$P4_2/n$	reflections
$a = 20.674 (3)$ Å	$\theta = 4.5–12.9°$
$c = 5.8040 (10)$ Å	$\mu = 1.648$ mm^{-1}
$V = 2480.7 (7)$ Å^3	$T = 293 (2)$ K
$Z = 4$	Square prism
$D_x = 1.388$ Mg m^{-3}	$0.45 \times 0.32 \times 0.25$ mm
$D_m = 1.40$ Mg m^{-3}	Violet
D_m measured by flotation in C6H6/CHBr3	

Data collection

Syntex $P2_1$ diffractometer	$\theta_{max} = 80.30°$
θ–2θ scans	$h = -19 \rightarrow 26$
Absorption correction: none	$k = 0 \rightarrow 26$
2996 measured reflections	$l = 0 \rightarrow 7$
2640 independent reflections	2 standard reflections
1508 reflections with	every 100 reflections
$I > 2\sigma(I)$	intensity decay: 15%
$R_{int} = 0.079$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{max} = 0.46$ e Å^{-3}
$wR(F^2) = 0.165$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
$S = 0.789$	Extinction correction:
2590 reflections	SHELXL93
158 parameters	Extinction coefficient:
H atoms: riding model	0.0013 (2)
$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 2.2069P]$	Scattering factors from International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—O1	1.955 (2)	O3—C11	1.439 (4)
Cu—N1	2.025 (2)	N1—C4	1.330 (3)
O1—C1	1.268 (4)	N1—C8	1.342 (3)
O2—C1	1.227 (4)	N2—C10	1.355 (3)
O3—C10	1.337 (4)	N2—C5	1.395 (4)

O1—Cu—N1^i	90.61 (8)	C10—O3—C11	115.7 (3)
O1—Cu—N1	89.39 (8)	C4—N1—Cu	121.0 (2)
C1—O1—Cu	107.2 (2)	C8—N1—Cu	119.4 (2)

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

The instability of the crystal at room temperature precluded the application of an absorption correction.

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: XP21 (Pavelčík, 1993). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEP (Johnson, 1965). Software used to prepare material for publication: SHELXL93.

References

Borel, M. M., Busnot, F., Busnot, A., Leclaire, A. & Bernard, M. A. (1981). Rev. Chim. Miner. 18, 235–240.
Borel, M. M., Busnot, A. & Leclaire, A. (1976). J. Inorg. Nucl. Chem. 38, 1557–59.
Borel, M. M. & Leclaire, A. (1976a). Acta Cryst. B32, 1273–1275.
Borel, M. M. & Leclaire, A. (1976b). Acta Cryst. B32, 3333–3337.
Borel, M. M. & Leclaire, A. (1978). Acta Cryst. B34, 99–102.
Johnson, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Melník, M. (1982). Coord. Chem. Rev. 42, 259–293.
Melník, M., Koman, M., Macašková, L., Glowiak, T., Grobelny, R. & Mrozinski, J. (1998). Polyhedron. In the press.
Pavelčík, F. (1993). XP21. Pharmaceutical Faculty, Comenius University, Bratislava, Slovakia.
Sheldrick, G. M. (1990). Acta Cryst. A46, 467–473.
Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
Smolander, M., Macko, M., Valko, M. & Melník, M. (1992). Acta Chem. Scand. 46, 29–33.

Dichlorobis(quinoline-N)zinc(II)

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Abstract

In the structure of the title complex, [ZnCl2(C9H7N)2], the Zn atom is coordinated by two chloride ligands and by two N atoms from two quinoline ligands. The geometry around the Zn atom is distorted tetrahedral,