metal-organic papers

A C-centered monoclinic modification of bis(di-2-pyridylmethanediol-$\kappa^3 N,O,N'$)-copper(II) diacetate tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.119
Data-to-parameter ratio = 18.1

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

Di-2-pyridyl ketone undergoes hydrolysis when reacted with copper(II) acetate to form the title compound, [Cu($C_{11}H_{10}N_2O_2$)$_2$]($C_2H_3O_2$)$_2$·4H$_2$O. The crystal structure consists of octahedral cations that are linked to the anions and to the uncoordinated water molecules, giving rise to a three-dimensional network structure. This C-centered monoclinic modification is less compact than the primitive monoclinic modification reported by Reinoso et al. [(2003). Acta Cryst. E**59**, m548–m550]. The Cu atom is located at a center of inversion.

Comment

A previous synthesis of the di-2-pyridylmethanediol derivative of nickel dilactate in an organic aqueous medium gave the complex as the anhydrous dilactate (Li et al., 2005). A similar synthesis with copper acetate has afforded the expected compound, which crystallizes as a tetrahydrate, (I) (Fig. 1).
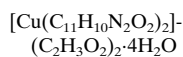

(I)
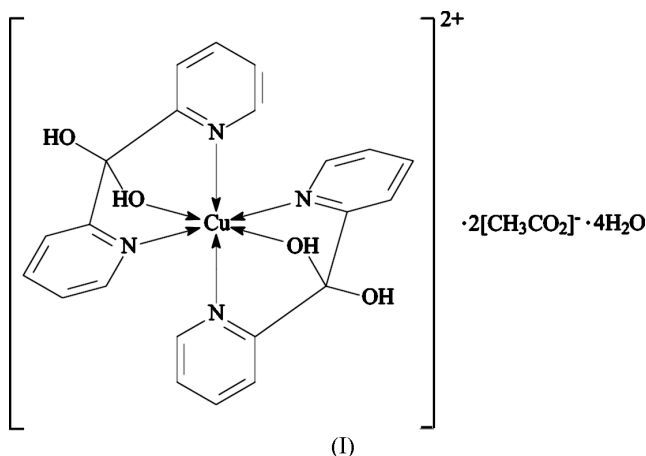
The crystal structure consists of bis(di-2-pyridyl-methanediol)copper(II) cations, acetate anions and uncoordinated water molecules. The Cu atom, which is located at a center of inversion, is chelated by two pyridyl N atoms and a hydroxyl O atom of the ligand in an octahedral environment. The bond dimensions involving the Cu atom are not significantly different from those found in the primitive monoclinic modification (Reinoso et al., 2003); however, the C-centered modification is much less compact, as noted from the lower density (1.366 Mg m^{-3} compared with 1.408 Mg m^{-3} for the primitive modification). The structure is consolidated by hydrogen bonds that link the cations, anions and water molecules into an intricate network motif. Both water molecules furnish only one such bond each (Table 2).

Experimental

Di-2-pyridyl ketone (0.091 g, 0.5 mmol) suspended in water (5 ml) was added to an acetonitrile/water solution (4:1 v/v) of copper(II) acetate monohydrate (0.100 g, 0.5 mmol). The mixture was heated to dissolve the reagents. Purple prismatic crystals separated from the solution in about 50% yield after several days.

Crystal data

$[Cu(C_{11}H_{10}N_2O_2)_2]\cdot$	$D_x = 1.366$ Mg m^{-3}
$(C_2H_3O_2)_2\cdot 4H_2O$	Mo $K\alpha$ radiation
$M_r = 658.11$	Cell parameters from 9126
Monoclinic, $C2/c$	reflections
$a = 23.557$ (2) Å	$\theta = 2.5-27.0°$
$b = 8.5744$ (6) Å	$\mu = 0.75$ mm^{-1}
$c = 15.848$ (1) Å	$T = 293$ (2) K
$\beta = 91.983$ (1)°	Prism, purple
$V = 3199.2$ (4) Å^3	$0.36 \times 0.34 \times 0.28$ mm
$Z = 4$	

Data collection

Rigaku Mercury CCD	3587 independent reflections
diffractometer	3064 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*CrystalClear*; Rigaku/MSC,	$h = -30 \rightarrow 29$
2002)	$k = -10 \rightarrow 7$
$T_{min} = 0.772$, $T_{max} = 0.811$	$l = -19 \rightarrow 20$
9126 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0725P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 1.3743P]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
3587 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
198 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.394 (1)	Cu1—N2	2.002 (2)
Cu1—N1	2.021 (2)		
O1—Cu1—O1^i	180	N1—Cu1—N1^i	180
O1—Cu1—N1	73.81 (5)	N1—Cu1—N2	87.84 (6)
O1—Cu1—N1^i	106.19 (6)	N1—Cu1—N2^i	92.16 (6)
O1—Cu1—N2	75.68 (5)	N2—Cu1—N2^i	180
O1—Cu1—N2^i	104.32 (5)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$o\cdots$O3	0.82	2.19	2.564 (2)	108
O2—H2$o\cdots$O4	0.82	1.83	2.643 (2)	171
O1w—H1$w1\cdots$O3	0.82	1.93	2.738 (3)	171
O2w—H2$w1\cdots$O4^{ii}	0.83	2.05	2.790 (3)	149

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

The methyl group was rotated to fit the electron density [C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$], as was the free hydroxyl group [O—H = 0.82 Å and $U_{iso}(H) = 1.2U_{eq}(O)$]. The H atom of the coordinated
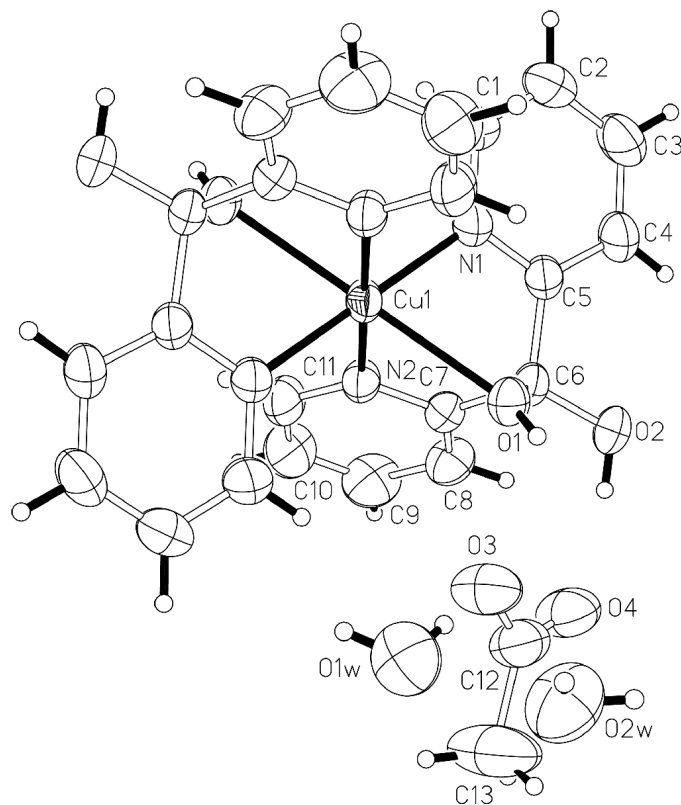

Figure 1
*ORTEP*II (Johnson, 1976) plot, showing the numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The symmetry code for unlabeled atoms is as in Table 1.

hydroxyl group was placed at a calculated position assuming sp^3 hybridization [O—H = 0.82 Å and $U_{iso}(H) = 1.2U_{eq}(O)$]. The aromatic H atoms were generated geometrically [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. These H atoms were included in the refinements in the riding-model approximation. Those on the water molecules were placed at chemically sensible positions; their displacement parameters were tied to those of the O atoms by a factor of 1.2. Atoms H1$w2$ and H2w do not have acceptors, and they are probably disordered. Atom H1o is a little more than 2 Å from the H atom of an adjacent molecule.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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metal-organic papers

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