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Bis[bis(2-pyridyl)methanediol-$\kappa^3 N,N',O$]-copper(II) bis(adamantane-1-carboxylate)

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Key indicators

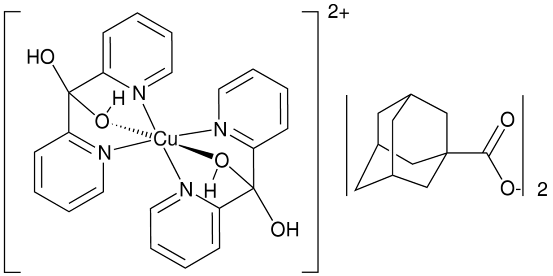
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 15.3

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

Di-2-pyridyl ketone reacts with copper(II) nitrate and sodium adamantane-1-carboxylate in acetonitrile–water to form bis[bis(2-pyridyl)methanediol]copper(II) bis(adamantane-1-carboxylate), $[Cu(C_{11}H_{10}N_2O_2)_2](C_{11}H_{15}O_2)_2$. The Cu atom in this dicationic complex occupies a special position at an inversion centre and has a tetragonally distorted octahedral coordination, formed by four 'normal' Cu—N [2.0114 (16) and 2.0155 (16) Å] and two 'long' Cu—O bonds [2.3690 (14) Å]. The methanediol hydroxyl groups are hydrogen-bonded to the adamantane-1-carboxylate anions.

Comment

Di-2-pyridyl ketone, $(C_5H_4N)_2CO$ (dpk), and its hydrolyzed derivative $(C_5H_4N)_2C(OH)_2$ (dpd), are good chelating ligands, and a few polynuclear complexes of the monoanion or dianion of the *gem*-diol form of di-2-pyridyl ketone (dpd-H and dpd-2H) obtained from metal carboxylates and dpk have been isolated and structurally characterized (Tangoulis *et al.*, 1997; Serna *et al.*, 2000; Tong *et al.*, 1998, 1999, 2000, 2002). The title complex, (I), was obtained in an attempt to prepare a polynuclear copper–dpk complex.



(I)

The crystal structure of (I) is built up of bis[bis(2-pyridyl)methanediol]copper(II) dications and adamantane-1-carboxylate anions. The Cu^{II} atom, which occupies a special position at an inversion centre, is chelated by two pyridyl N atoms and one of the hydroxyl O atoms of the two ligands, and has a tetragonally distorted octahedral coordination, formed by four 'normal' Cu—N and two 'long' Cu—O bonds (Fig. 1). The Cu1—N1 and Cu1—N2 bond lengths [2.0155 (16) and 2.0114 (16) Å, respectively] are similar to those found in bis[bis(2-pyridyl)methanediol]copper(II) diperchlorate [1.994 (5)–2.098 (5) Å; Tong *et al.*, 1998]. The Cu1—O1 bond [2.3690 (14) Å], however, is noticeably shorter than analogous bonds found in the latter structure [2.454 (2) Å]. The angular distortions of the coordination octahedron are determined by the chelate formation and result in substantial deviations of the chelate bite angles N1—Cu1—N2, O1—Cu1—N1 and

O1—Cu1—N2 [87.49 (7), 74.70 (6) and 75.91 (6)°, respectively] from 90°.

Both hydroxyl groups in (I) act as hydrogen-bond donors, with the O atoms of the adamantane-1-carboxylate anion serving as the acceptors [O1···O3 2.545 (2) Å and O1—H1···O3 176 (3)°, and O2···O4 2.604 (2) and O2—H2···O4 173 (3)°].

Experimental

Di-2-pyridyl ketone (0.092 g, 0.5 mmol) was dissolved in water (2 ml) and mixed with an acetonitrile–water solution (4:1 *v*/*v*) containing sodium adamantane-1-carboxylate (0.101 g, 0.5 mmol) and copper(II) nitrate (0.120 g, 0.5 mmol). The mixture was then heated at 323 K for 20 min. Deep-blue crystals of (I), with a complex polyhedral shape, separated from the solution in about 75% yield after several days.

Crystal data

$[Cu(C_{11}H_{10}N_2O_2)_2](C_{11}H_{15}O_2)_2$
$M_r = 826.42$
Monoclinic, $C2/c$
$a = 24.947\ (5)$ Å
$b = 11.5988\ (17)$ Å
$c = 15.284\ (3)$ Å
$\beta = 118.576\ (3)°$
$V = 3883.8\ (11)$ Å^3
$Z = 4$

$D_x = 1.413$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9994 reflections
$\theta = 3.0$–$27.0°$
$\mu = 0.62$ mm^{-1}
$T = 293\ (2)$ K
Block, blue
0.38 × 0.32 × 0.30 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
$T_{min} = 0.789$, $T_{max} = 0.829$
9994 measured reflections

4078 independent reflections
3389 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.0°$
$h = -26 \rightarrow 29$
$k = -14 \rightarrow 11$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.112$
$S = 1.05$
4078 reflections
267 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3	0.845 (10)	1.702 (10)	2.545 (2)	176 (3)
O2—H2···O4	0.848 (10)	1.760 (11)	2.604 (2)	173 (3)

The pyridyl and adamantane-1-carboxylate H atoms were included in geometrically calculated positions and constrained to ride, with $U_{iso}(H) = 1.2U_{eq}(C)$, at distances of 0.93 (pyridyl) and 0.97 Å (adamantane) from their parent C atoms. The hydroxyl H atoms were located in difference Fourier maps and refined subject to a restraint of O—H = 0.85 (1) Å, with isotropic atomic displacement parameters.

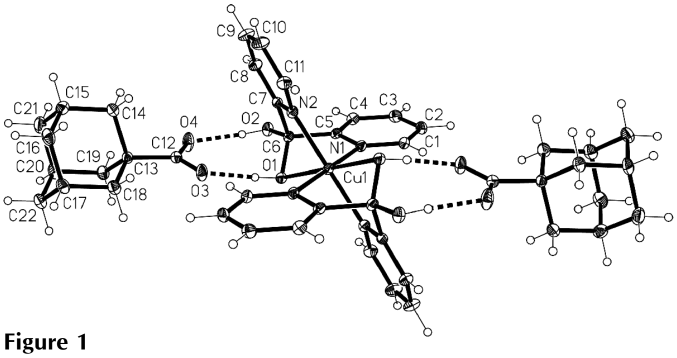


Figure 1
A view of a fragment of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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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