Bis[2-(1H-benzimidazol-2-yl)phenolato]copper(II) dimethylformamide disolvate

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In the crystal structure of the title compound, [Cu(C$_{13}$H$_9$N$_2$O)$_2$]·2C$_3$H$_7$NO, the Cu^{II} ion is coordinated by two N and two O atoms from two deprotonated 2-(1H-benzimidazol-2-yl)phenol ligands to give a four-coordinate distorted tetrahedral geometry. The Cu atom lies on a twofold rotation axis.

Comment

Complexes with imidazole-related and imidazole-containing ligands serve as models for metalloproteins and have been studied extensively (Sundburg & Martin, 1974; Maekawa *et al.*, 1989; Lorosch & Haase, 1985; Benzekri *et al.*, 1991; Crane *et al.*, 1995; McKee *et al.*, 1981). The compound 2-(1H-benzimidazol-2-yl)phenol (Hpbm) is an *N,O*-bidentate ligand that contains two donor groups of relevance to the coordination of metal centers in biological systems, namely phenolate (tyrosine) and imidazole (histidine). In the present paper, we report the synthesis and crystal structure of the dimethylformamide (DMF) disolvate of the Cu^{II} complex with two deprotonated ligands, [Cu(pbm)$_2$]·2DMF, (I).


(I)
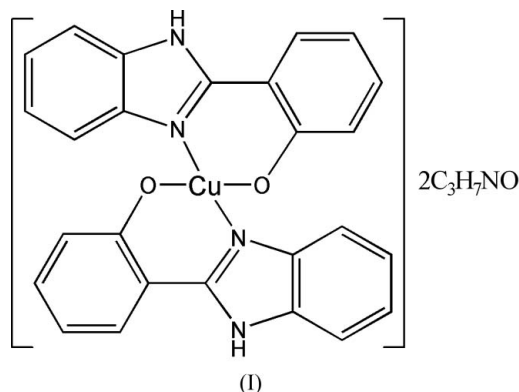
The structure of (I) is shown in Fig. 1 and selected geometric parameters are in Table 1. The Cu atom lies on a twofold rotation axis. The Cu atom adopts a distorted four-coordinate environment, with a dihedral angle of 47.3 (3)° between the two coordinating ligands (as defined by the Cu—N—O planes).

The complex forms an N—H···O hydrogen bond between the N2 proton and the carbonyl O atom of the DMF solvent (Table 2).

Experimental

The ligand 2-(1H-benzimidazol-2-yl)phenol, HL, was synthesized as follows: a solution of salicylaldehyde (2.32 g, 19 mmol) in EtOH (15 ml) was added to a solution of *o*-phenylenediamine (2.05 g, 19 mmol) in EtOH (25 ml) with stirring and heating. The resulting
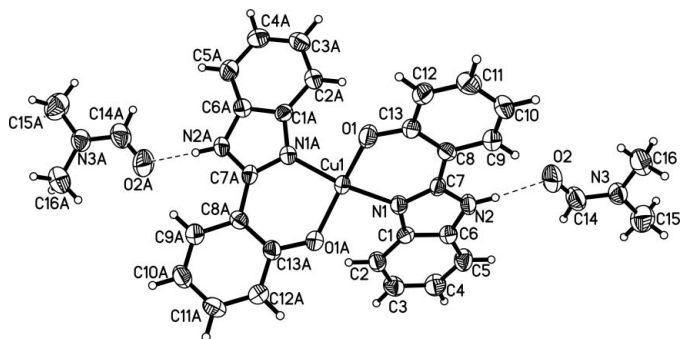
Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are shown as small spheres of arbitrary radii [symmetry code: (A) $-x + 1$, y, $-z + \frac{1}{2}$]. Dashed lines indicate hydrogen bonds.

orange solution was refluxed for 1 h and then cooled to room temperature. After standing in a refrigerator for 12 h, the orange solution was filtered and diethyl ether (15 ml) was added to the solution. Standing in the open air for 2 d yielded orange crystalline needles which were filtered off and air-dried (yield: 60%). The elemental analysis results were completely in agreement with the structural composition of the ligand (m.p. 524–525 K). The title complex was obtained as follows: to a filtered solution of HL (0.420 g, 2 mmol) and KOH (0.112 g, 2 mmol) in methanol (60 ml) at room temperature was added a filtered solution of Cu(OAc)$_2$·H$_2$O (0.200 g, 1 mmol) in methanol (20 ml) with stirring. The product began to crystallize from the solution almost immediately. After 1 h, the brown solid was filtered off, washed with methanol and air-dried. X-ray quality single crystals were grown by the vapour diffusion of diethyl ether into a DMF solution of the solid to yield green crystals of the title complex. Analysis calculated for C$_{32}$H$_{32}$CuN$_6$O$_4$ (%): C 61.18, H 5.13, N 13.38; found (%): C 60.96, H 5.10, N 13.35.

Crystal data

[Cu(C$_{13}$H$_9$N$_2$O)$_2$]·2C$_3$H$_7$NO	Mo $K\alpha$ radiation
$M_r = 628.18$	Cell parameters from 1684
Orthorhombic, $Pbcn$	reflections
$a = 16.1964$ (9) Å	$\theta = 2.5$–$22.3°$
$b = 8.0465$ (4) Å	$\mu = 0.79$ mm^{-1}
$c = 22.5076$ (13) Å	$T = 273$ (2) K
$V = 2933.3$ (3) Å^3	Flake, green
$Z = 4$	$0.32 \times 0.21 \times 0.06$ mm
$D_x = 1.422$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector	3323 independent reflections
diffractometer	2098 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.051$
Absorption correction: multi-scan	$\theta_{max} = 27.4°$
(*ABSCOR*; Higashi, 1995)	$h = -20 \rightarrow 15$
$T_{min} = 0.785$, $T_{max} = 0.954$	$k = -10 \rightarrow 10$
12837 measured reflections	$l = -29 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2)$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.472P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.004$
3323 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
197 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.8904 (17)	Cu1—N1	1.9487 (18)
O1—Cu1—O1^i	146.96 (13)	O1—Cu1—N1^i	96.92 (8)
O1—Cu1—N1	92.76 (8)	N1—Cu1—N1^i	145.50 (12)
O1^i—Cu1—N1	96.92 (8)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O2	0.86	1.93	2.773 (3)	168

C-bound H atoms were treated as riding, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. N-bound H atoms were also riding, with $U_{iso}(H) = 1.2U_{eq}(N)$ and N—H = 0.86 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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