metal-organic papers

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Key indicators

Single-crystal X-ray study T = 295 KMean $\sigma(\text{C}-\text{C}) = 0.005 \text{ Å}$ Disorder in main residue R factor = 0.038 wR factor = 0.106 Data-to-parameter ratio = 13.5

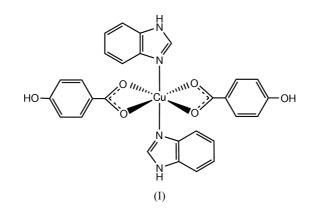
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Bis(1*H*-benzimidazole- κN^3)bis(4-hydroxybenzoato- $\kappa^2 O_r O'$)copper(II)

In the title complex, $[Cu(C_7H_5O_3)_2(C_7H_6N_2)_2]$, (I), the Cu^{II} atom, located on an inversion center, is surrounded by two 4-hydroxybenzoate anions and two benzimidazole molecules in an elongated octahedral geometry, the longer Cu–O distance being 2.618 (2) Å in the axial direction. The partially overlapped arrangement and the short face-to-face distance of 3.405 (6) Å suggest π - π stacking between benzimidazole ligands of neighboring molecules.

Comment

 π - π stacking is an important intermolecular non-covalent interaction and is correlated with electron transfer in some biological systems (Deisenhofer & Michel, 1989). As part of an ongoing investigation into π - π stacking in metal complexes (Pan & Xu, 2004; Liu *et al.*, 2004), we have prepared the title Cu^{II} complex, (I), and present its crystal structure here.



The molecular structure of (I) is illustrated in Fig. 1. The Cu^{II} atom is located on an inversion center and assumes an elongated octahedral coordination geometry. Two N atoms of benzimidazole (bzim) ligands and two O atoms (O1) of 4hydroxybenzoate anions form the equatorial plane, with normal bond distances (Table 1). The other carboxyl O atoms (O2) coordinate axially, with a longer Cu-O2 distance, 2.618 (2) Å; the bond distances in the axial direction are usually longer than those in the equatorial plane by about 0.2-0.6 Å. The difference of 0.656 (3) Å in Cu–O distances found in (I) is greater than those found in most Cu^{II} complexes, but the Cu-O1-C1 bond angle, $106.11(15)^\circ$, which is much smaller than the 120° expected for an O atom with normal sp^2 hybridization, suggests the existence of a genuine bonding interaction between atoms Cu and O2 (Li et al., 2005). Thus the coordination geometry in (I) is best described as elongated octahedral rather than as square planar.

A partially overlapped arrangement is observed between parallel N13-bzim and N13^{iv}-bzim rings [symmetry code: (iv)

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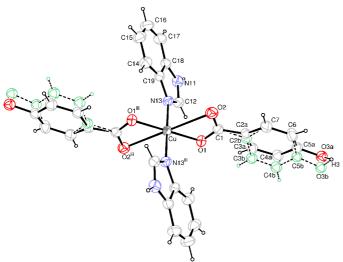
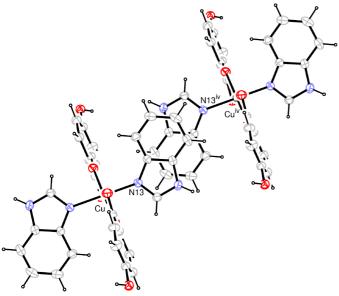


Figure 1

The molecular structure of (I), with 30% probability displacement ellipsoids. Dashed lines show the minor disordered component. [Symmetry code: (iii) 1 - x, 1 - y, 1 - z.]





The π - π stacking between bzim rings of neighboring complex molecules; one disordered component has been omitted for clarity. [Symmetry code: (iv) 1 - x, -y, 1 - z.]

1 - x, -y, 1 - z; Fig. 2]. The face-to-face distance of 3.405 (6) Å suggests the existence of π - π stacking between bzim ligands of neighboring complex molecules in (I). The corresponding centroid-to-centroid distance between the benzene rings of the neighboring benzimidazole ligands is 3.6629 (17) Å.

The 4-hydroxybenzoate anion is disordered in (I) (Fig. 1). Both disordered hydroxy O atoms share the same H atom, H3. Neighboring complex molecules are linked to one another *via* $O3A - H3 \cdots O2^i$ and $O3B - H3 \cdots O2^i$ hydrogen bonds [symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$], to form a supramolecular structure (Fig. 3). Intermolecular hydrogen bonding also occurs between the disordered hydroxy groups and the bzim ligands (Table 2).

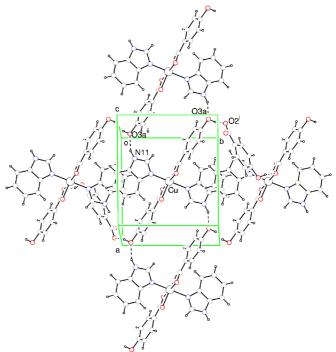


Figure 3

A packing diagram showing intermolecular hydrogen bonding; one of the disordered components has been omitted for clarity. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) -x, 1 - y, 1 - z.]

Experimental

Each reagent was commercially available and of analytical grade. $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol), 4-hydroxybenzoic acid (0.14 g, 1 mmol), bzim (0.24 g, 2 mmol) and NaOH (0.08 g, 2 mmol) were dissolved in water (20 ml). The mixture was refluxed for 5 h, and then cooled to room temperature and filtered. Blue single crystals were obtained from the filtrate after 2 d.

Crystal data

$[Cu(C_7H_5O_3)_2(C_7H_6N_2)_2]$	$D_x = 1.453 \text{ Mg m}^{-3}$		
$M_r = 574.05$	Mo $K\alpha$ radiation		
Monoclinic, $P2_1/n$	Cell parameters from 8947		
a = 11.2017 (10) Å	reflections		
b = 9.7789 (6) Å	$\theta = 2.8-24.0^{\circ}$		
c = 13.2237 (14) Å	$\mu = 0.88 \text{ mm}^{-1}$		
$\beta = 115.035 \ (9)^{\circ}$	T = 295 (2) K		
$\beta = 115.035 \ (9)^{\circ}$ V = 1312.4 (2) Å ³	Platelet, blue		
Z = 2	$0.41 \times 0.30 \times 0.10 \text{ mm}$		

Data collection

Rigaku R-AXIS RAPID
diffractometer2370 independent reflections
2063 reflections with $I > 2\sigma(I)$ ω scans $R_{int} = 0.040$ Absorption correction: multi-scan
(ABSCOR; Higashi, 1995) $\theta_{max} = 25.2^{\circ}$
 $h = -13 \rightarrow 13$
 $T_{min} = 0.739, T_{max} = 0.917$ $k = -11 \rightarrow 11$ 9589 measured reflections $l = -15 \rightarrow 15$

Refinement

 $\begin{array}{ll} \mbox{Refinement on } F^2 & w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 \\ R[F^2 > 2\sigma(F^2)] = 0.038 & w \mbox{ere} \ P = (F_o^2 + 2F_c^2)/3 \\ w \mbox{Ref} \ P = (F_o^2 + 2F_c^2)/3 \\ S = 1.06 & (\Delta/\sigma)_{\rm max} < 0.001 \\ 2370 \ {\rm reflections} & \Delta\rho_{\rm max} = 0.45 \ {\rm e} \ {\rm \AA}^{-3} \\ 175 \ {\rm parameters} & \Delta\rho_{\rm min} = -0.31 \ {\rm e} \ {\rm \AA}^{-3} \\ \mbox{H-atom parameters constrained} \\ \end{array}$

Table 1	
Selected geometric parameters (Å, $^{\circ}$).	

Cu–O1 Cu–O2	1.9619 (17) 2.618 (2)	Cu-N13	1.989 (2)
O1-Cu-O2	55.43 (7)	O2-Cu-N13	86.63 (7)
O1-Cu-N13	89.09 (8)	C1-O1-Cu	106.11 (15)

Table 2 Hydrogen-bond geometry $(\mathring{A},\,{}^\circ)$.

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$O3A - H3 \cdots O2^i$	0.90	1.77	2.639 (4)	160
$O3B - H3 \cdot \cdot \cdot O2^{i}$	0.87	1.77	2.589 (5)	154
N11 $-$ H11 $\cdot \cdot \cdot$ O3 A^{ii}	0.86	2.03	2.767 (5)	144
$N11 - H11 \cdots O3B^{ii}$	0.86	2.09	2.910 (5)	160

Symmetry codes: (i) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$; (ii) -x, -y + 1, -z + 1.

Two 4-hydroxyphenyl rings with different spatial orientations and the same coordinates for atoms C6 and C7 were found in a difference Fourier map. These were refined isotropically and the occupancies converged to 0.488 (4) and 0.512 (4), respectively. They were each fixed at 0.5 in the final cycles of refinement. The common H atom of the disordered hydroxy groups was located in a difference Fourier map and included in the structure factor calculations with fixed positional parameters and isotropic displacement parameter $U_{\rm iso}(H)$ = 0.05 Å². H atoms on the aromatic rings were placed in calculated positions, with C-H = 0.93 Å and N-H = 0.86 Å and were included in the final cycles of refinement in riding mode, with $U_{iso}(H)$ values of $1.2U_{eq}$ of the carrier atoms.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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