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## Key indicators

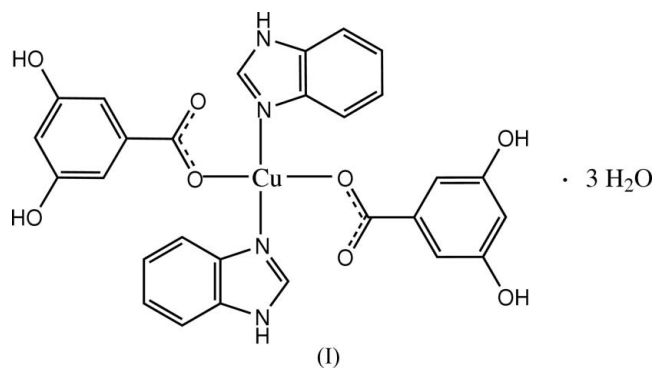
Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.043  
 $wR$  factor = 0.105  
Data-to-parameter ratio = 16.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis(benzimidazole- $\kappa N$ )bis(3,5-dihydroxy-  
benzoato- $\kappa O$ )copper(II) trihydrate

In the crystal structure of the title compound,  $[\text{Cu}(\text{C}_7\text{H}_5\text{O}_4)_2(\text{C}_7\text{H}_6\text{N}_2)_2] \cdot 3\text{H}_2\text{O}$ , the  $\text{Cu}^{\text{II}}$  ion is coordinated by two benzimidazole (bzim) molecules and two 3,5-dihydroxybenzoate (dhba) anions in a tetrahedrally distorted square-planar geometry. Aromatic  $\pi$ - $\pi$  stacking is observed between parallel bzim ligands and between roughly parallel bzim and dhba units. An extensive  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen-bonding network helps to consolidate the crystal structure.

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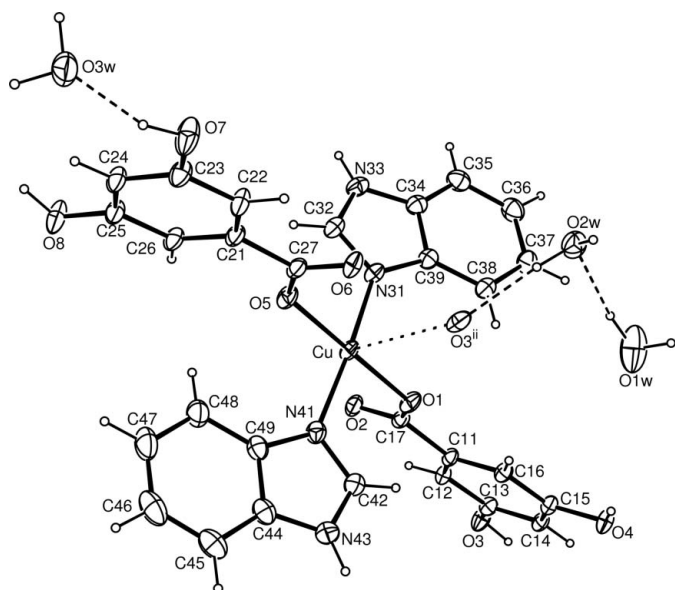
## Comment

$\pi$ - $\pi$  Stacking between aromatic rings is an important non-covalent interaction and is correlated with electron-transfer processes in some biological systems (Deisenhofer & Michel, 1989). As part of our ongoing investigations on the nature of  $\pi$ - $\pi$  stacking (Chen *et al.*, 2003; Li *et al.*, 2005), the title  $\text{Cu}^{\text{II}}$  complex, (I) (Fig. 1), has been prepared and its crystal structure is reported here.

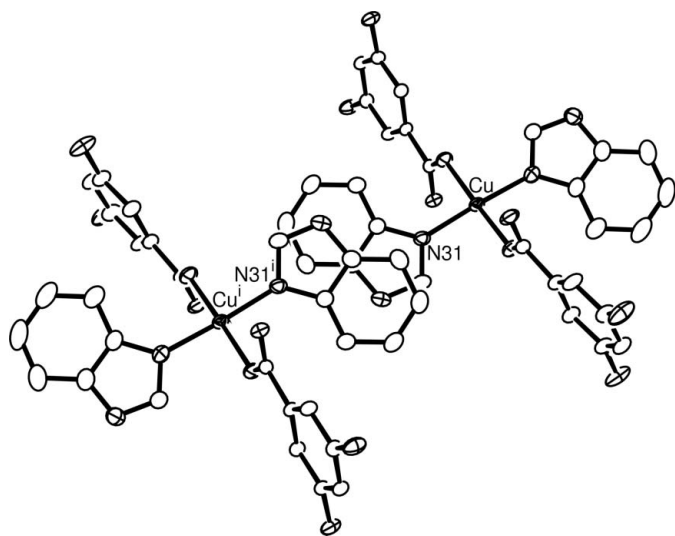


The  $\text{Cu}^{\text{II}}$  ion in (I) is coordinated by two benzimidazole (bzim) molecules and two 3,5-dihydroxybenzoate (dhba) anions in a tetrahedrally distorted *trans*- $\text{CuN}_2\text{O}_2$  square-planar geometry (Table 1), the dihedral angle between the O1/Cu/N31 plane and the O5/Cu/N41 plane being  $6.3(2)^\circ$ . A hydroxy O3<sup>ii</sup> atom [symmetry code: (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ] of a neighboring complex occupies a possible apical site for the  $\text{Cu}^{\text{II}}$  ion, but the very long  $\text{Cu} \cdots \text{O3}^{\text{ii}}$  separation of  $2.813(2)$  Å, indicates negligible bonding between these atoms. There is little difference between the C—O— bond lengths of the C17/O1/O2 and C27/O5/O6 carboxylate groups (Table 1), implying electronic delocalization.

A partially overlapped arrangement between parallel N31-containing bzim and N31<sup>i</sup>-bzim ligands is observed (Fig. 2) [symmetry code: (i)  $1 - x, -y, 1 - z$ ]. The face-to-face separation of  $3.338(9)$  Å clearly implies the existence of  $\pi$ - $\pi$



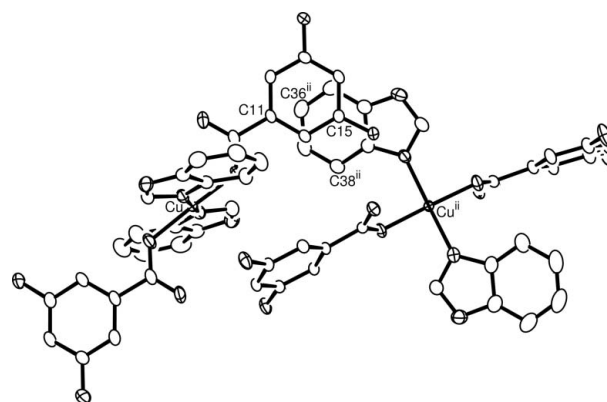
**Figure 1**  
The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate hydrogen-bonding interactions. [Symmetry code: (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ .]



**Figure 2**  
 $\pi$ - $\pi$  Stacking between parallel bzim ligands in (I) [symmetry code: (i)  $1 - x, -y, 1 - z$ ]. H atoms have been omitted.

stacking between these bzim ligands. In addition, the C11-benzene ring is roughly parallel to [dihedral angle =  $18.3(2)^\circ$ ] and partially overlapped with the C36<sup>ii</sup>-bzim ligand (Fig. 3) [symmetry code: (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ]. The separation of C15 and the C36<sup>ii</sup>-benzene plane is  $3.276(3) \text{ \AA}$ , and the distance of the C36<sup>ii</sup> atom from the C11-benzene plane is  $3.383(3) \text{ \AA}$ . These findings suggest the existence of  $\pi$ - $\pi$  stacking between bzim and dhba ligands. A Cambridge Structural Database (Version 5.27; Allen, 2002) search indicates this is the first report of  $\pi$ - $\pi$  stacking involving the dhba anion.

An extensive O—H...O and N—H...O hydrogen-bonding network occurs in (I) (Table 2), which helps to consolidate the crystal structure.



**Figure 3**  
 $\pi$ - $\pi$  Stacking between roughly parallel bzim and dhba ligands in (I) [symmetry code: (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ]. H atoms have been omitted.

## Experimental

A water/ethanol solution (20 ml, 9:1) containing  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1 mmol),  $\text{Na}_2\text{CO}_3$  (1 mmol), benzimidazole (2 mmol) and 3,5-dihydroxybenzoic acid (2 mmol) was stirred for 1 h at 333 K and then filtered. Blue single crystals of (I) were obtained from the filtrate after 12 d.

### Crystal data

$[\text{Cu}(\text{C}_7\text{H}_5\text{O}_4)_2(\text{C}_7\text{H}_6\text{N}_2)_2] \cdot 3\text{H}_2\text{O}$   
 $M_r = 660.08$   
 Monoclinic,  $P2_1/n$   
 $a = 16.313(5) \text{ \AA}$   
 $b = 9.740(2) \text{ \AA}$   
 $c = 17.838(5) \text{ \AA}$   
 $\beta = 97.605(12)^\circ$   
 $V = 2809.4(13) \text{ \AA}^3$

$Z = 4$   
 $D_x = 1.561 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.85 \text{ mm}^{-1}$   
 $T = 295(2) \text{ K}$   
 Prism, blue  
 $0.33 \times 0.23 \times 0.10 \text{ mm}$

### Data collection

Rigaku R-Axis RAPID  
 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.735, T_{\max} = 0.920$

26824 measured reflections  
 6430 independent reflections  
 4732 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$   
 $\theta_{\max} = 27.5^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.105$   
 $S = 1.04$   
 6430 reflections  
 397 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 1.3478P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.51 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{ \AA}$ ,  $^\circ$ ).

Cu—O1	1.9365 (17)	C17—O1	1.274 (3)
Cu—O5	1.9449 (17)	C17—O2	1.249 (3)
Cu—N31	1.990 (2)	C27—O5	1.268 (3)
Cu—N41	2.001 (2)	C27—O6	1.249 (3)
O1—Cu—O5	177.50 (7)	O1—Cu—N41	87.78 (8)
O1—Cu—N31	92.29 (7)	O5—Cu—N41	91.19 (8)
O5—Cu—N31	88.96 (8)	N31—Cu—N41	174.07 (8)

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N33—H33···O2W <sup>i</sup>	0.86	2.03	2.845 (3)	158
N43—H43···O1W <sup>ii</sup>	0.86	2.03	2.875 (4)	167
O3—H3···O6 <sup>iii</sup>	0.88	1.75	2.610 (2)	165
O4—H4···O2 <sup>ii</sup>	0.98	1.70	2.681 (3)	174
O7—H7···O3W	0.89	1.79	2.639 (3)	160
O8—H8···O4 <sup>iv</sup>	0.89	1.97	2.832 (3)	165
O1W—H1A···O7 <sup>v</sup>	0.89	2.03	2.907 (4)	168
O1W—H1B···O2W	0.95	2.26	3.160 (4)	160
O2W—H2A···O6 <sup>v</sup>	0.92	1.96	2.882 (3)	175
O2W—H2B···O3 <sup>ii</sup>	0.92	1.96	2.878 (3)	175
O3W—H3A···O7 <sup>vi</sup>	0.97	2.03	2.951 (3)	158
O3W—H3B···O2 <sup>vii</sup>	0.96	1.79	2.753 (3)	173

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

Hydroxy H atoms and water H atoms were located in a difference map and refined as riding in their as-found relative positions, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . Other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and refined in riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/

MSC, 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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## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.  
 Chen, Z., Xu, D.-J., Li, Z.-Y., Wu, J.-Y. & Chiang, M. Y. (2003). *J. Coord. Chem.* **56**, 253–259.  
 Deisenhofer, J. & Michel, H. (1989). *EMBO J.* **8**, 2149–2170.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.  
 Li, H., Yin, K.-L. & Xu, D.-J. (2005). *Acta Cryst.* **C61**, m19–m21.  
 Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.  
 Rigaku/MS (2002). *CrystalStructure*. Version 3.00. Rigaku/MS, The Woodlands, Texas, USA.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.