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## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
Disorder in solvent or counterion  
 $R$  factor = 0.042  
 $wR$  factor = 0.115  
Data-to-parameter ratio = 13.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis(benzimidazole)bis(4-hydroxybenzoato)cobalt(II)  
0.25-hydrate

In the title compound,  $[\text{Co}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_7\text{H}_6\text{N}_2)_2] \cdot 0.25\text{H}_2\text{O}$ , the  $\text{Co}^{\text{II}}$  atom is coordinated by two 4-hydroxybenzoate (hbz) anions and two benzimidazole (bzim) ligands in a distorted trigonal-bipyramidal geometry. The carboxylate group of one of the hbz anions chelates to the Co atom with a normal Co—O bond [1.993 (2) Å] and a longer Co—O bond [2.561 (3) Å]. Aromatic  $\pi$ – $\pi$  stacking is observed between neighbouring bzim ligands but not between hbz ligands.

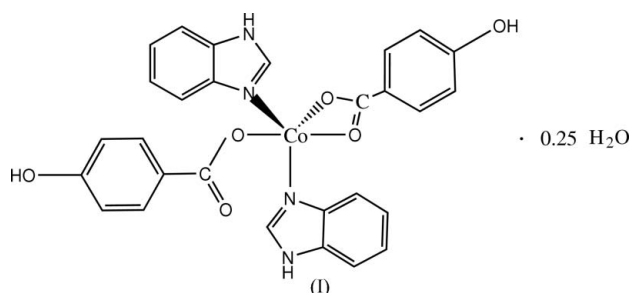
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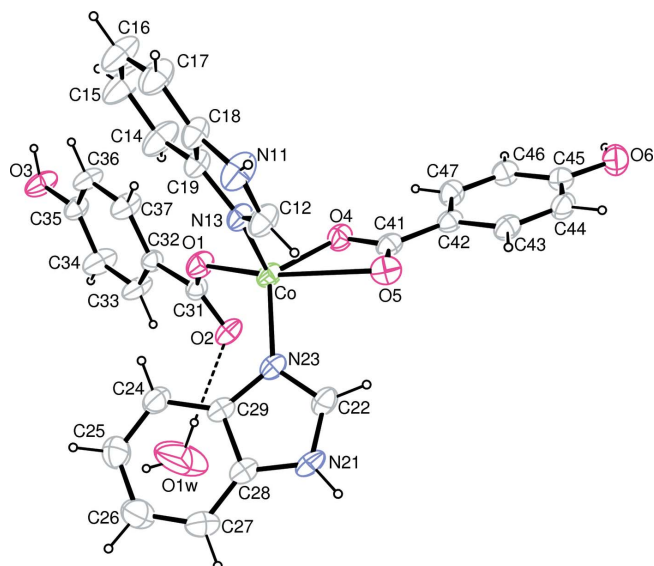
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## Comment

Aromatic  $\pi$ – $\pi$  stacking is an important intermolecular interaction which is correlated with electron transfer in some biosystems (Deisenhofer & Michel, 1989). In order to investigate further the nature of  $\pi$ – $\pi$  stacking, a series of metal complexes incorporating aromatic ligands such as quinoline (Pan & Xu, 2004), phenanthroline (Su *et al.*, 2005) and benzimidazole (bzim) (Li *et al.*, 2005) has been prepared in our laboratory. As part of this ongoing research, we present here the structure of the title  $\text{Co}^{\text{II}}$  complex, (I), with aromatic bzim and 4-hydroxybenzoate (hbz) ligands (Fig. 1).



The Co atom in (I) is coordinated by two bzim ligands and two hbz anions. The Co···O5 distance is much longer than the normal Co—O1 and Co—O4 bond distances (Table 1). At the same time, the Co—O4—C41 bond angle [103.5 (2)°] appears to be compressed in order to allow Co and O5 to approach each other. This implies the existence of a weak but genuine bonding interaction between Co and O5, *i.e.* the C41-carboxylate group coordinates to the Co atom in a chelating mode. This observation agrees with the situations found in a  $\text{Co}^{\text{II}}$  complex with phthalate (Pan & Xu, 2005), in a  $\text{Mn}^{\text{II}}$  complex with adipate (Liu *et al.*, 2005) and in a  $\text{Cu}^{\text{II}}$  complex with salicylate (Li *et al.*, 2005). The other hbz ligand has a larger Co—O1—C31 angle of 127.7 (2)° and a much longer Co···O2 distance of 3.227 (3) Å, which suggest no bonding between the Co and O2 atoms. Thus, the coordination geometry around the Co atom can be described as distorted trigonal bipyramidal, with atoms O1 and O5 in the axial sites.



**Figure 1**

The molecular structure of (I), with 30% probability displacement ellipsoids and arbitrary spheres for H atoms. Dashed lines show the hydrogen bonding. Only one orientation of the disordered water molecule is shown.

A partially overlapped arrangement of neighbouring parallel N23-imidazole and N23<sup>iv</sup>-imidazole rings [symmetry code: (iv)  $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$ ] is observed in the structure of (I) (Fig. 2). The shorter face-to-face separation of 3.28 (5) Å clearly indicates the existence of  $\pi$ - $\pi$  stacking between the bzim ligands. Conversely, the distances from the C atoms of the hbz C32-benzene ring to the nearby C32<sup>v</sup>-benzene mean plane [symmetry code: (v)  $1 - x, y, \frac{1}{2} - z$ ] range from 3.702 (7) (C33) to 3.750 (5) Å (C35) [average distance = 3.724 (6) Å]. These are identical to the van der Waals thickness of the benzene ring and suggest there is little, if any, significant  $\pi$ - $\pi$  stacking interaction between the nearly parallel hbz ligands [dihedral angle 0.9 (2)°], although these two benzene rings are well overlapped with respect to each other (Fig. 3).

As an acceptor, the uncoordinated carboxylate atom O2 is involved in three hydrogen bonds (Table 2).

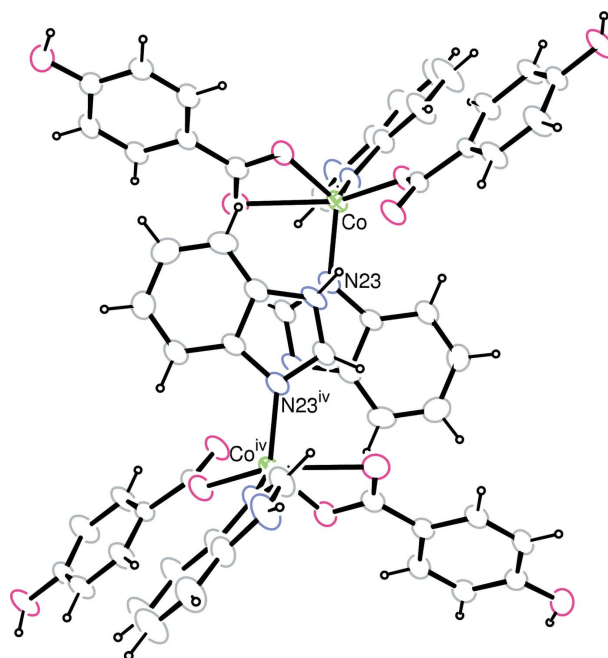
## Experimental

Cobalt acetate tetrahydrate (1 mmol, 0.25 g), 4-hydroxybenzoic acid (2 mmol, 0.27 g), benzimidazole (2 mmol, 0.24 g) and Na<sub>2</sub>CO<sub>3</sub> (1 mmol, 0.11 g) were dissolved in a water (15 ml)-ethanol (5 ml) solution. The mixture was refluxed for 5 h and filtered after cooling to room temperature. Red single crystals of (I) were obtained from the filtrate after 5 d.

### Crystal data

[Co(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>)<sub>2</sub>].0.25H<sub>2</sub>O  
*M<sub>r</sub>* = 573.93  
 Monoclinic, C2/c  
*a* = 12.952 (5) Å  
*b* = 27.564 (11) Å  
*c* = 15.147 (6) Å  
 $\beta$  = 104.499 (6)°  
*V* = 5235 (4) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.456 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 11022 reflections  
 $\theta$  = 2.0–24.0°  
 $\mu$  = 0.71 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Prism, red  
 0.32 × 0.30 × 0.22 mm



**Figure 2**

Detail of (I), showing the  $\pi$ - $\pi$  stacking between bzim ligands of neighbouring complexes [symmetry code: (iv)  $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$ ].

### Data collection

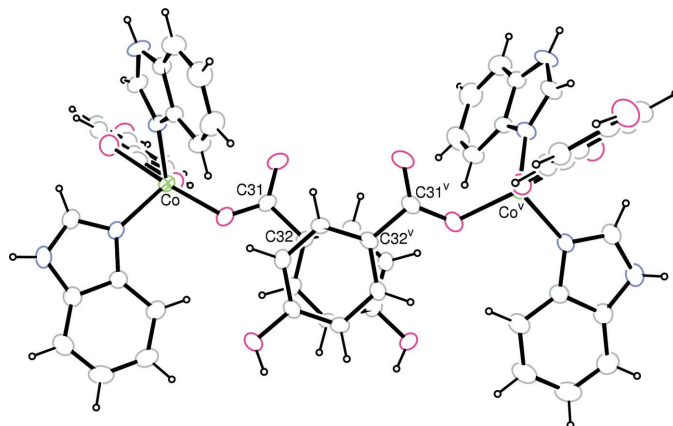
Rigaku R-Axis RAPID  
 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.782, T_{\max} = 0.862$   
 13970 measured reflections

4745 independent reflections  
 2922 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$   
 $\theta_{\max} = 25.2^\circ$   
 $h = -15 \rightarrow 15$   
 $k = -28 \rightarrow 33$   
 $l = -14 \rightarrow 18$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.115$   
 $S = 1.00$   
 4745 reflections  
 361 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 6.148P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$



**Figure 3**

A diagram showing the overlapped arrangement of 4-hydroxybenzoate ligands in (I) [symmetry code: (v)  $1 - x, y, \frac{1}{2} - z$ ].

**Table 1**

Selected geometric parameters (Å, °).

Co—O1	1.970 (2)	Co—N13	2.026 (3)
Co—O4	1.993 (2)	Co—N23	2.013 (3)
Co—O5	2.561 (3)		
O1—Co—O4	101.13 (10)	O4—Co—N13	112.23 (11)
O1—Co—O5	157.27 (10)	O4—Co—N23	121.29 (11)
O1—Co—N13	101.91 (11)	O5—Co—N13	89.90 (9)
O1—Co—N23	110.53 (11)	O5—Co—N23	83.52 (10)
O4—Co—O5	56.20 (9)	N13—Co—N23	107.89 (12)

**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>
O1 <i>W</i> —H1 <i>A</i> ...O2	0.98	2.36	3.339 (19)	177
O3—H3 <i>A</i> ...O4 <sup>i</sup>	0.86	1.89	2.730 (4)	164
O6—H6 <i>A</i> ...O2 <sup>ii</sup>	0.92	1.81	2.724 (4)	170
N11—H11...O3 <sup>iii</sup>	0.86	2.06	2.913 (4)	174
N21—H21...O2 <sup>iv</sup>	0.86	1.95	2.806 (4)	172

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

The solvent water molecule (O1*W*), situated adjacent to a twofold axis, was located in a difference map and is disordered. The site occupancy factor for O1*W* was refined and converged to 0.243 (11), and it was then fixed at 0.25 in the final cycles of refinement. The H atoms attached to O1*W* were located in their theoretical positions (Nardelli, 1999). H atoms on hydroxy groups were located in a difference Fourier map. H atoms bonded to O atoms were 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 were included in the final cycles of refinement in riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

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