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## Key indicators

Single-crystal X-ray study

T = 295 K

Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$ 

R factor = 0.058

wR factor = 0.164

Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tris[2,5-bis(1*H*-benzimidazol-2-yl)pyridinato- $\kappa^2\text{N}^1, \text{N}^2$ ]cobalt(III) dihydrate

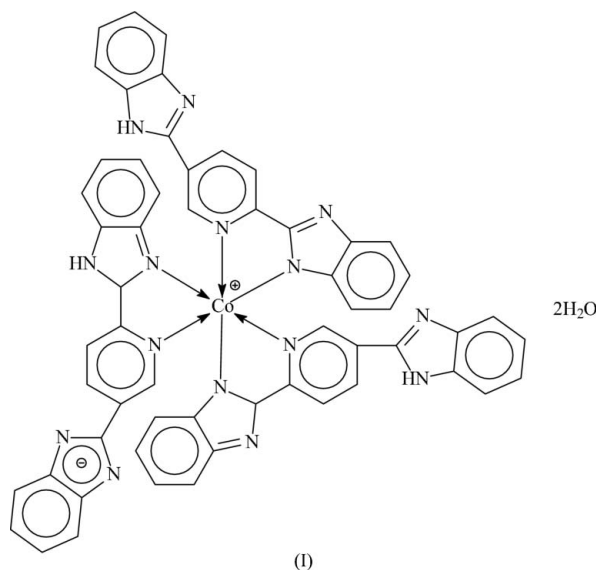
In the title compound,  $[\text{Co}(\text{C}_{19}\text{H}_{12}\text{N}_5)_3] \cdot 2\text{H}_2\text{O}$ , three mono-deprotonated 2,5-bis(benzimidazolyl)pyridine heterocycles chelate to cobalt(III) through the N atom of one benzimidazolyl arm of the heterocycle as well as through the pyridyl N atom to form a fairly regular six-coordinate, octahedral geometry geometry for cobalt. A network of  $\text{N}-\text{H} \cdots \text{N}$ ,  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds involving the non-coordinated water molecules results in a layered structure.

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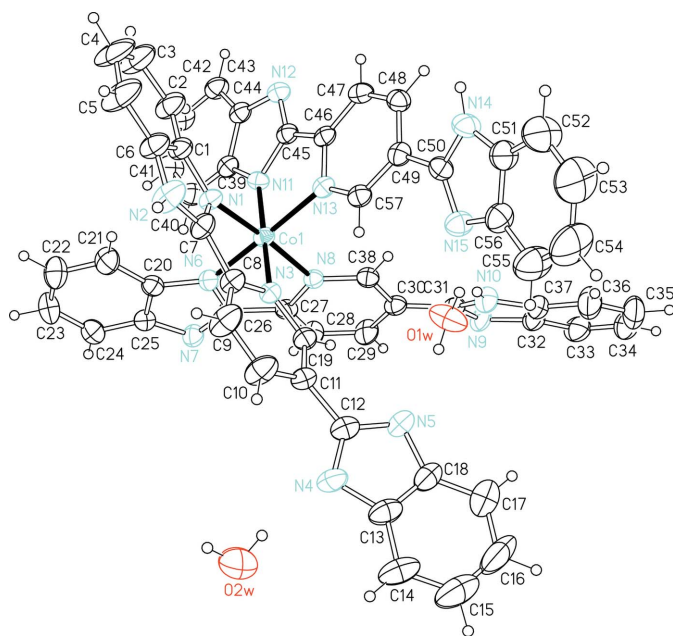
Accepted 27 February 2006

## Comment

2,5-Bis(benzimidazolyl)pyridine (Hbbp), an *N*-heterocycle having several Lewis basic sites, was first claimed in a patent (Chimetron S.a.r.l., 1967). No complexes with metals have been reported, unlike the more symmetrical 2,6-bis(benzimidazolyl)pyridine isomer which affords a large number of metal complexes, as noted from a survey of the Cambridge Structural Database (Version 5.27 of December 2005; Allen, 2002).



In the title cobalt(III) derivative, (I) (Fig. 1), three mono-deprotonated  $\text{bbp}^-$  anions chelate to the metal atom. However, the nature of the anion is different for one of them. For the N6- and N11-containing anions, the Co atom is chelated through the N atom of one benzimidazolyl arm of the heterocycle as well as through the pyridyl N atom. The N1-containing anion formally has its negative charge in the five-membered imidazolyl ring as the two N atoms are both two-coordinate; the molecule of (I) thus formally exists as a zwitterion. Various hydrogen bonds link the complex molecule



**Figure 1**  
View of (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

with the two non-coordinated water molecules (Table 2) to give a layer motif.

The oxidation of the cobalt(II) starting material to cobalt(III) may have occurred by reaction with dissolved  $O_2$  at elevated temperature and pressure (Gajda *et al.*, 1997).

## Experimental

Cobalt(II) chloride hexahydrate (0.0595 g, 0.25 mmol) and 2,5-bis(1*H*-benzimidazolyl)pyridine (0.0384 g, 0.125 mmol) were dissolved in a mixture of ethanol (3 ml) and water (15 ml). The solution was placed in a 23-ml Teflon-lined stainless steel Parr bomb. The bomb was heated at 433 K for 120 h. The cooled mixture yielded red block-shaped crystals of (I) in about 30% yield. The crystals were washed with water and then dried in air.

### Crystal data

$[Co(C_{19}H_{12}N_5)_3] \cdot 2H_2O$	$Z = 2$
$M_r = 1025.97$	$D_x = 1.334 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.1623 (8) \text{ \AA}$	Cell parameters from 3578 reflections
$b = 13.2460 (8) \text{ \AA}$	$\theta = 2.3\text{--}24.5^\circ$
$c = 17.485 (1) \text{ \AA}$	$\mu = 0.40 \text{ mm}^{-1}$
$\alpha = 111.712 (1)^\circ$	$T = 295 (2) \text{ K}$
$\beta = 100.538 (1)^\circ$	Block, red
$\gamma = 92.334 (1)^\circ$	$0.28 \times 0.18 \times 0.08 \text{ mm}$
$V = 2554.7 (3) \text{ \AA}^3$	

### Data collection

Bruker SMART CCD diffractometer	10874 independent reflections
$\varphi$ and $\omega$ scans	6132 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.040$
$T_{min} = 0.897$ , $T_{max} = 0.969$	$\theta_{max} = 27.1^\circ$
17019 measured reflections	$h = -15 \rightarrow 15$
	$k = -14 \rightarrow 16$
	$l = -22 \rightarrow 22$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.164$   
 $S = 0.99$   
 10874 reflections  
 688 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0796P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.60 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.76 \text{ e \AA}^{-3}$

**Table 1**  
Selected bond lengths ( $\text{\AA}$ ).

Co1—N1	1.911 (3)	Co1—N8	1.975 (3)
Co1—N3	1.993 (3)	Co1—N11	1.911 (3)
Co1—N6	1.897 (3)	Co1—N13	1.966 (3)

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1w—H1w1 $\cdots$ N5	0.84 (1)	1.97 (1)	2.785 (4)	165 (4)
O1w—H1w2 $\cdots$ N15	0.84 (1)	2.14 (2)	2.949 (4)	162 (4)
O2w—H2w1 $\cdots$ N4	0.85 (1)	2.00 (2)	2.819 (5)	163 (6)
N2—H2n $\cdots$ N9 <sup>i</sup>	0.85	2.20	2.888 (4)	138
N10—H10n $\cdots$ O1w	0.85	2.12	2.885 (4)	150
N14—H14n $\cdots$ O2w <sup>ii</sup>	0.85	1.97	2.818 (5)	176

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x, y - 1, z$ .

The carbon and nitrogen-bound H atoms were placed in idealized locations ( $C-H = 0.93 \text{ \AA}$  and  $N-H = 0.85 \text{ \AA}$ ) and refined as riding. The water H atoms were located in a difference map and were refined with distance restraints of  $O-H = 0.85 (1) \text{ \AA}$  and  $H \cdots H = 1.39 (1) \text{ \AA}$ . The constraint  $U_{iso}(H) = 1.2U_{eq}(\text{carrier})$  was applied in all cases. A consideration of the hydrogen-bonding interactions leads to a formulation having two 2,5-bis(1*H*-benzimidazolyl)pyridine anions whose negative charge formally resides on the N atom of one deprotonated benzimidazolyl arm, and a 2,5-bis(1*H*-benzimidazolyl)pyridine anion whose negative charge is formally delocalized over the imidazolyl ring. Neither of the N atoms of this ring is involved in coordination to cobalt (see scheme), but both are involved in hydrogen bonding as acceptors. The O1w water molecule forms two hydrogen bonds, whereas the O2w water molecule forms only one hydrogen bond. However, the O2w water molecule is not a hydroxide anion, as this would raise the oxidation state of Co to 4+.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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