Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Bis(imidazolium) diaquabis(pyridine-2,5-dicarboxylato-$\kappa^2 N,O$)cobaltate(II) tetrahydrate

**Qian-Jun Deng,[a,b] Zhuang-Tian Liu[a] and Ming-Hua Zeng[a]***

[a]Department of Chemistry, Guangxi Normal University, Guilin 541000, Guangxi, People's Republic of China, and [b]School of Science, Foshan University, Foshan 528000, Guangdong, People's Republic of China

Correspondence e-mail: zmhzsu@163.com

Received 2 June 2005
Accepted 5 July 2005
Online 9 July 2005

**Key indicators**

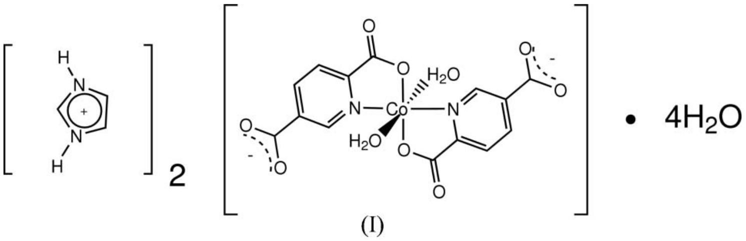
Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.053
$wR$ factor = 0.149
Data-to-parameter ratio = 14.4

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

The title complex, $(C_3H_5N_2)_2[Co(C_7H_3NO_4)_2(H_2O)_2]\cdot 4H_2O$, was prepared by a hydrothermal reaction. Each Co$^{II}$ atom is located on a crystallographic inversion centre and displays a distorted octahedral coordination geometry. The face-to-face distance of 3.529 (7) Å between partially overlapped parallel pyridine rings reflects a $\pi$–$\pi$ stacking interaction between neighbouring Co$^{II}$ complex molecules. A network of O—H$\cdots$O and O—H$\cdots$N hydrogen bonds helps to stabilize the crystal packing.

## Comment

The unique strength and direction of hydrogen bonding play a dominant role in the generation of a variety of molecular architectures and molecular recognition in chemical and biological sciences (Lehn *et al.*, 1996; Steiner, 2002). The ligand pyridine-2,5-dicarboxylic acid, known both as a multiple proton donor and acceptor (MacDonald *et al.*, 2000), can use its carboxylate O and pyridine N atoms, to form both monodentate and/or multidentate $M$—O and $M$—N metal–ligand bonds (Zeng *et al.*, 2004). Protonated imidazole (Him) readily takes part in forming hydrogen-bonded networks (MacDonald et al., 2000). We report here the hydrothermal synthesis and crystal structure of the title complex, (I).



(I)

In (I), each Co$^{II}$ atom is coordinated by two N atoms and two O atoms from two chelating pyridine-2,5-dicarboxylate (pdc) ligands, and two O atoms from two aqua ligands to furnish a distorted octahedral geometry. The aqua ligands are located at the axial positions (Table 1 and Fig. 1).

The face-to-face distance of 3.529 (7) Å between partially overlapped parallel pyridine rings reflects a $\pi$–$\pi$ stacking interaction between neighbouring Co$^{II}$ complex anions. In addition, neighbouring Co$^{II}$ complex anions are linked to each other by O—H$\cdots$O hydrogen bonds. With the help of $\pi$–$\pi$ stacking interactions and hydrogen bonds, these complex anions form one-dimensional linear chains running along the $a$ axis. Protonated imidazoles link to the chains by O—H$\cdots$N hydrogen bonds (Fig. 2 and Table 2). These chains are linked into a complex network by O—H$\cdots$O (uncoordinated water and carboxylate, aqua ligands and uncoordinated water) and

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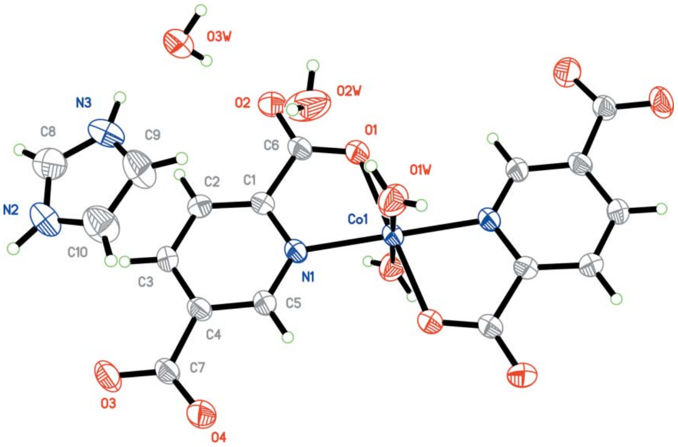

**Figure 1**
The molecular structure of (I), shown with 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry operator ($-x, 2-y, -z$).

N—H···O (protonated imidazoles and uncoordinated water) hydrogen bonds (Fig. 3).

## Experimental

Pyridine-2,5-dicarboxylic acid (0.5 mmol), imidazole (0.5 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol) and water (8 ml) were stirred for 15 min in air, then transferred and sealed in a 23 ml Teflon reactor, which was heated at 413 K for 2 d and then cooled to room temperature at a rate of 5 K h$^{-1}$. Red block-shaped crystals were obtained, and were washed with deionized water and absolute ethanol (yield > 20%, based on Co).

*Crystal data*

$(C_3H_5N_2)_2[Co(C_7H_3NO_4)_2(H_2O)_2] \cdot 4H_2O$
$M_r = 635.41$
Triclinic, $P\overline{1}$
$a = 8.844\ (5)$ Å
$b = 9.062\ (4)$ Å
$c = 9.635\ (4)$ Å
$\alpha = 97.70\ (3)^\circ$
$\beta = 116.80\ (3)^\circ$
$\gamma = 93.26\ (3)^\circ$
$V = 677.0\ (6)$ Å$^3$

$Z = 1$
$D_x = 1.559$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2$–$7^\circ$
$\mu = 0.71$ mm$^{-1}$
$T = 293\ (2)$ K
Block, red
0.49 × 0.38 × 0.29 mm

*Data collection*

Siemens *R3m* diffractometer
$\omega$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.721$, $T_{max} = 0.820$
3153 measured reflections
2959 independent reflections
2532 reflections with $I > 2\sigma(I)$

$R_{int} = 0.042$
$\theta_{max} = 27.0^\circ$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 10$
2 standard reflections every 200 reflections intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.149$
$S = 1.05$
2959 reflections
205 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0964P)^2 + 0.3143P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å$^{-3}$
$\Delta\rho_{min} = -0.51$ e Å$^{-3}$

**Figure 2**
Perspective view of the chain along the *a* axis. Hydrogen bonds and $\pi$–$\pi$ stacking interactions are shown as dashed lines.

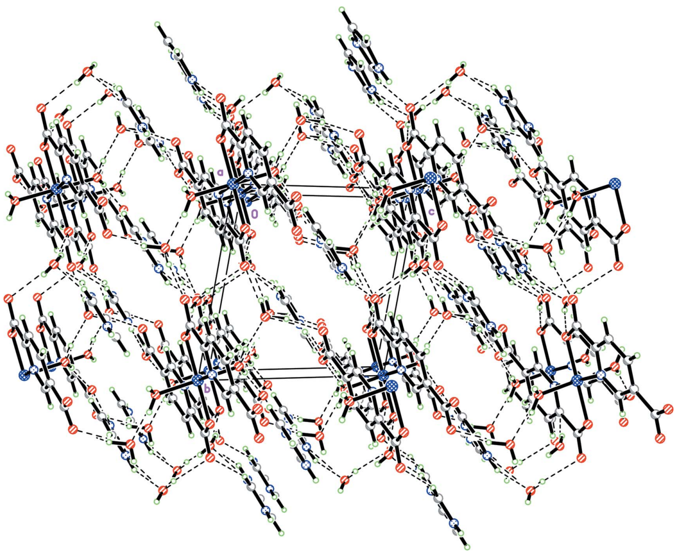

**Figure 3**
Packing diagram of (I). Dashed lines indicate hydrogen bonds.

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Co1—O1*W* | 2.085 (2) | Co1—N1 | 2.124 (2) |
| Co1—O1 | 2.098 (2) | | |
| O1*W*—Co1—O1$^i$ | 89.90 (9) | O1*W*—Co1—N1$^i$ | 91.07 (10) |
| O1*W*—Co1—O1 | 90.10 (9) | O1$^i$—Co1—N1 | 101.77 (9) |
| O1*W*$^i$—Co1—N1 | 91.08 (10) | O1—Co1—N1 | 78.23 (9) |
| O1*W*—Co1—N1 | 88.92 (10) | | |

Symmetry code: (i) $-x, -y+2, -z$.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*A*···O3$^{ii}$ | 0.70 (5) | 2.01 (5) | 2.703 (3) | 169 (5) |
| O1*W*—H1*B*···O2*W* | 0.86 (5) | 1.85 (5) | 2.688 (4) | 166 (4) |
| O2*W*—H2*C*···O4$^{iii}$ | 0.97 (6) | 1.78 (7) | 2.731 (4) | 165 (5) |
| O2*W*—H2*D*···O2$^{iv}$ | 0.82 (7) | 1.96 (7) | 2.777 (4) | 169 (6) |
| O3*W*—H3*C*···O1$^{iv}$ | 0.93 (6) | 1.94 (6) | 2.855 (4) | 167 (5) |
| O3*W*—H3*D*···O2 | 0.75 (6) | 2.14 (6) | 2.882 (4) | 168 (6) |
| N2—H2*B*···O3$^{v}$ | 0.86 | 1.92 | 2.726 (4) | 157 |
| N3—H3*A*···O3*W* | 0.86 | 1.99 | 2.797 (4) | 156 |

Symmetry codes: (ii) $x-1, y, z$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x, -y+1, -z$; (v) $-x+2, -y+2, -z+1$.

*Acta Cryst.* (2005). E**61**, m1514–m1516 Deng *et al.* • $(C_3H_5N_2)_2[Co(C_7H_3NO_4)_2(H_2O)_2] \cdot 4H_2O$ **m1515**

H atoms attached to C or N atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.86 Å) and refined as riding on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C or N). O-bound H atoms were located in difference Fourier maps and refined with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

Data collection: *R3m Software* (Siemens, 1990); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank the Guangxi Normal University and the Guangxi Science Fund for Distinguished Young Scholars (0447019) for supporting this study.

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**m1516** Deng *et al.* • $(C_3H_5N_2)_2[Co(C_7H_3NO_4)_2(H_2O)_2]\cdot4H_2O$ *Acta Cryst.* (2005). E**61**, m1514–m1516