

***trans*-Diaquabis(5-carboxy-1*H*-imidazole-4-carboxylato- $\kappa^2N^3,O^4$ )cobalt(II) 4,4'-bipyridine solvate**

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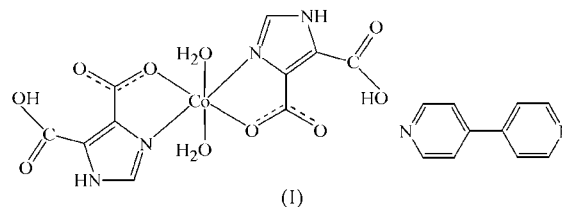
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In the title compound,  $[\text{Co}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot \text{C}_{10}\text{H}_8\text{N}_2$ , the Co atom is *trans*-coordinated by two pairs of N and O atoms from two monoanionic 4,5-dicarboxyimidazole ligands, and by two O atoms from two coordinated water molecules, in a distorted octahedral geometry. The 4,4'-bipyridine solvent molecule is not involved in coordination but is linked by an  $\text{N} \cdots \text{H} \cdots \text{N}$  hydrogen bond to the neutral  $[\text{Co}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  molecule. Both molecules are located on inversion centers. The crystal packing is stabilized by  $\text{N} \cdots \text{H} \cdots \text{N}$  and  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds, which produce a three-dimensional hydrogen-bonded network. Offset  $\pi$ - $\pi$  stacking interactions between the pyridine rings of adjacent 4,4'-bipyridine molecules were observed, with a face-to-face distance of 3.345 (1) Å.

**Comment**

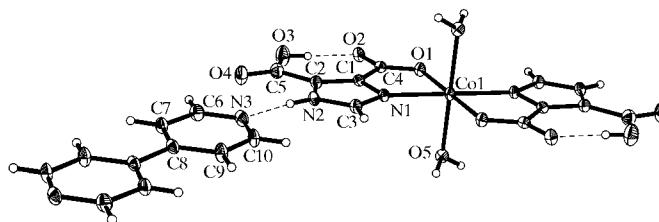
The chemistry of  $\alpha$ -*N*-carboxyheterocyclic ligands, such as 2-carboxypyridine, 2-carboxypyrazine, 4,5-dicarboxyimidazole and 2,3-dicarboxypyrazine, is attracting increasing attention because they possess efficient N- and O-atom donors in diverse coordination environments (Chatterjee *et al.*, 1998; Elliot & Shepherd, 1987; Dougherty *et al.*, 1984). Numerous metal complexes containing  $\alpha$ -*N*-carboxyheterocyclic ligands have been reported in recent years (Lannon *et al.*, 1984; Chatterjee *et al.*, 1997), but metal complexes of the 4,5-dicarboxyimidazole ligand ( $\text{H}_3\text{dcbi}$ ) are relatively rare. In this field, five manganese complexes of the  $\text{H}_3\text{dcbi}$  ligand have been reported for the simulation of relevant manganese enzymes (Caudle *et al.*, 1997; Rajendiran *et al.*, 2003; Ma *et al.*, 2003; Huang *et al.*, 2001; Zhang *et al.*, 2004). In addition, five other metal  $\text{H}_3\text{dcbi}$  complexes have been reported to date (Net *et al.*, 1989; Sengupta *et al.*, 2001; Bayon *et al.*, 1987; Smith *et al.*, 2000; Wang *et al.*, 2004). Among these, there is only one example of a cobalt complex containing  $\text{H}_3\text{dcbi}$  ligands (Wang *et al.*, 2004). We report here the crystal structure of a novel

example of a cobalt complex with 4,5-dicarboxyimidazole ligands, which act as *N,O*-bidentate donors.

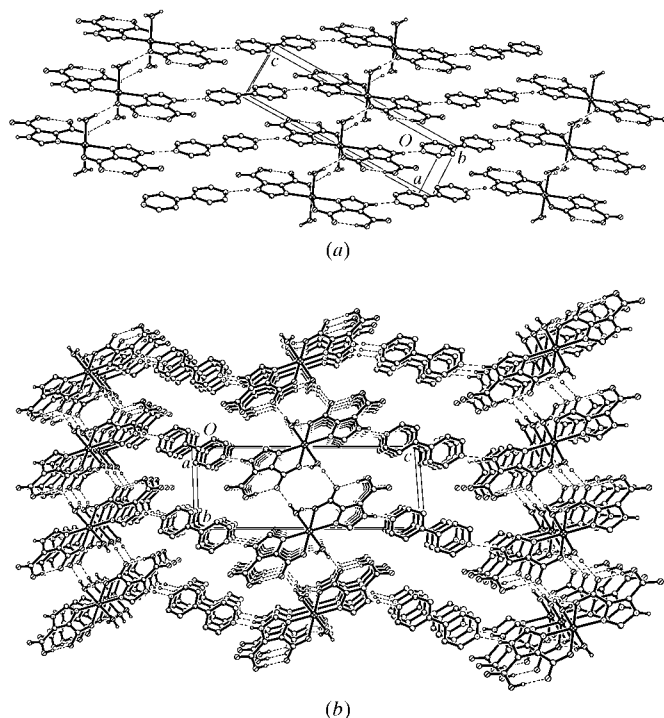


The structure of the title compound, (I), consists of two independent molecules (Fig. 1), namely a neutral mononuclear  $[\text{Co}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  molecule and a 4,4'-bipyridine (4,4'-bipy) molecule, both located on inversion centers. The asymmetric unit of (I) contains one-half of the complex molecule. The other half of the complex molecule is related by a center of symmetry at the Co atom. The Co atom is six-coordinated by two pairs of N and O atoms from two symmetry-related  $\text{H}_2\text{dcbi}^-$  ligands, and by two O atoms from two symmetry-related coordinated water molecules. The  $\text{CoN}_2\text{O}_4$  group adopts a distorted octahedral configuration. The  $\text{Co1/N1/C1/C4/O1}$  basal plane exhibits a mean deviation of 0.0027 Å.

The two  $\text{H}_2\text{dcbi}^-$  ligands are situated *trans* with respect to one another. Each  $\text{H}_2\text{dcbi}^-$  ligand behaves as an *N,O*-bidentate ligand, and the uncoordinated carboxy group of the ligand is protonated [ $\text{C5}-\text{O3} = 1.325$  (3) Å and  $\text{C5}-\text{O4} = 1.214$  (3) Å]; the structure of (I) thus differs from those of the related compounds  $\text{Na}_2[\text{Co}_4(\text{dcbi})_4(2,2'\text{-bipy})_4]$  (Wang *et al.*, 2004) and  $[\text{Mn}(\text{salen})_2(\text{H}_2\text{dcbi})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  (salen is *N,N'*-disalicylideneethylenediamine; Huang *et al.*, 2001). The  $\text{H}_2\text{dcbi}^-$  ligands in (I) are planar (the mean deviation is 0.0069 Å), the maximum deviation, of 0.021 (4) Å for O2, being the result of hydrogen bonds involving atoms O2 and O3. The two coordinated water molecules occupy the apical sites. The linear  $\text{O5/Co/O5}^i$  group is nearly perpendicular to the  $\text{N1/O1/N1}^i/\text{O1}^i$  basal plane, as indicated by the basal angles subtended at atom Co1 [Table 1; symmetry code: (i)  $-x + 2, -y, -z + 1$ ]. The  $\text{Co1}-\text{N1}$  and  $\text{Co1}-\text{O1}$  distances [2.108 (2) and 2.116 (1) Å, respectively] are comparable to those reported in related cobalt complexes (Cheng *et al.*, 2002; Kumagai *et al.*, 2002). The  $\text{Co1}-\text{O5}$  distance is identical to the  $\text{Co1}-\text{N1}$  distance. The similar cobalt-ligand bond lengths and highly octahedral ligand arrangement are indicative of there being no Jahn-Teller effect in the  $\text{Co}^{2+}$  ( $d^7$ ) ion.

**Figure 1**

A view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
Packing diagrams of (I), showing (a) part of the two-dimensional hydrogen-bonded network and (b) the hydrogen-bonded three-dimensional supramolecular framework.

The 4,4'-bipyridine molecule is not coordinated to the Co atom but acts as an independent molecule. The two independent fragments are linked by an N2—H2···N3 hydrogen bond (Table 2). The non-H atoms in the 4,4'-bipyridine molecule are nearly coplanar, with a mean deviation of 0.0048 Å. Interestingly, the 4,4'-bipyridine ring is nearly coplanar with the H<sub>2</sub>dcbi<sup>−</sup> ligand, with a dihedral angle of 2.4 (2)°. There are strong face-to-face  $\pi$ – $\pi$  interactions, involving the offset pyridine rings of adjacent 4,4'-bipyridine ligands, with a face-to-face stacking distance of 3.3451 (1) Å.

In the asymmetric unit, atom O2 of the carboxylate group links atom O3 of the carboxy group of the H<sub>2</sub>dcbi<sup>−</sup> ligand through an O3—H3···O2 hydrogen bond (Table 2). The molecules in the crystal structure are linked by N2—H2···N3 and O5—H5B···O1<sup>iii</sup> hydrogen bonds (see Table 2 for symmetry codes), which produce a two-dimensional network in the (112) crystallographic plane (Fig. 2a). In the two-dimensional network, the molecules are further linked to one another via O5—H5A···O2<sup>iii</sup> hydrogen bonds (see Table 2 for symmetry codes), which produce a three-dimensional supramolecular framework (Fig. 2b).

## Experimental

The title compound was synthesized by a hydrothermal method under autogenous pressure. A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (291 mg, 1 mmol), imidazole-4,5-dicarboxylic acid (312 mg, 2 mmol), 4,4'-bipyridine (156 mg, 1 mmol) and distilled water (15 ml) was stirred under ambient conditions, and then triethylamine (0.25 ml) was added slowly to the suspension. The mixture was sealed in a 25 ml

Teflon-lined stainless steel autoclave, heated at 358 K for 3 d and then cooled to room temperature. The resulting prism-shaped crystals were recovered by filtration, washed with distilled water and dried in air (yield 59%). Analysis calculated for C<sub>20</sub>H<sub>18</sub>CoN<sub>6</sub>O<sub>10</sub>: C 42.78, H 3.21, N 14.97%; found: C 42.72, H 3.11, N 14.92%.

### Crystal data

[Co(C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	Z = 1
<i>M<sub>r</sub></i> = 561.33	<i>D<sub>x</sub></i> = 1.741 Mg m <sup>−3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 4.971 (2) Å	Cell parameters from 1479 reflections
<i>b</i> = 6.558 (3) Å	$\theta$ = 3.3–27.5°
<i>c</i> = 17.274 (8) Å	$\mu$ = 0.88 mm <sup>−1</sup>
$\alpha$ = 86.009 (9)°	<i>T</i> = 293 (2) K
$\beta$ = 86.729 (8)°	Prism, red
$\gamma$ = 72.526 (8)°	0.48 × 0.20 × 0.04 mm
<i>V</i> = 535.5 (4) Å <sup>3</sup>	

### Data collection

Siemens SMART CCD area-detector diffractometer	2417 independent reflections
$\varphi$ and $\omega$ scans	2299 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> <sub>int</sub> = 0.022
<i>T</i> <sub>min</sub> = 0.816, <i>T</i> <sub>max</sub> = 0.966	$\theta$ <sub>max</sub> = 27.5°
4137 measured reflections	<i>h</i> = −6 → 6
	<i>k</i> = −6 → 8
	<i>l</i> = −21 → 22

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.7039P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
<i>S</i> = 1.01	$\Delta\rho$ <sub>max</sub> = 0.42 e Å <sup>−3</sup>
2417 reflections	$\Delta\rho$ <sub>min</sub> = −0.47 e Å <sup>−3</sup>
176 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

Co1—O5	2.108 (2)	O2—C4	1.259 (2)
Co1—N1	2.108 (2)	O3—C5	1.325 (3)
Co1—O1	2.116 (1)	O4—C5	1.214 (3)
O1—C4	1.264 (2)		
O5—Co1—N1	88.39 (6)	N1—Co1—O1	79.38 (6)
O5—Co1—O1	89.74 (6)		

**Table 2**

Hydrogen-bonding 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>
O3—H3···O2	0.82	1.72	2.537 (2)	178
N2—H2···N3	0.86	1.92	2.767 (2)	170
O5—H5A···O2 <sup>iii</sup>	0.82 (2)	1.88 (2)	2.691 (2)	169 (2)
O5—H5B···O1 <sup>ii</sup>	0.82 (2)	1.93 (2)	2.711 (2)	160 (2)

Symmetry codes: (ii) 3 − *x*, −*y*, 1 − *z*; (iii) *x*, *y* − 1, *z*.

Aromatic H atoms and carboxylic acid H atoms were placed in calculated positions and treated using a riding-model approximation (C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å). Water H atoms were visible in difference maps and were included in the refinement with an O—H distance restraint of 0.82 (1) Å.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve

structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1204). Services for accessing these data are described at the back of the journal.

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