

# Bis(1*H*-imidazole- $\kappa$ N<sup>3</sup>)bis(2-oxido-pyridinium-3-carboxylato- $\kappa^2$ O<sup>2</sup>,O<sup>3</sup>)-cobalt(II)

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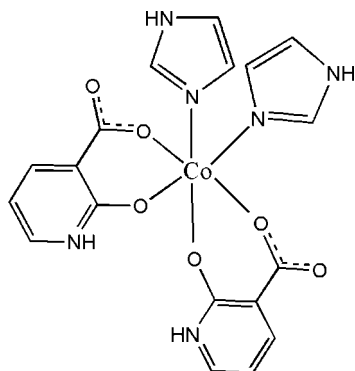
Received 18 July 2009; accepted 20 July 2009

Key indicators: single-crystal X-ray study;  $T = 294$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.028;  $wR$  factor = 0.065; data-to-parameter ratio = 12.9.

In the molecule of the title Co<sup>II</sup> complex, [Co(C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>], the Co<sup>II</sup> atom is located on a twofold rotation axis and chelated by two oxidopyridiniumcarboxylate anions and further *cis*-coordinated by two imidazole ligands in a distorted octahedral geometry. The shorter C—O bond distance of 1.260 (2) Å suggests electron delocalization between the oxido group and the pyridinium ring. The uncoordinated carboxylate O atom links with the imidazole and pyridinium rings of adjacent molecules *via* N—H...O hydrogen bonding. Weak C—H...O hydrogen bonding is also present in the crystal structure.

## Related literature

For the isostructural Ni<sup>II</sup> complex, see: Zhang *et al.* (2009). For the shorter C—O bond distance between the pyridine ring and the hydroxy-O atom in 2-oxido-pyridinium-3-carboxylate complexes and in 2-hydroxypyridinecarboxylate complexes, see: Yao *et al.* (2004); Yan & Hu (2007*a,b*); Wen & Liu (2007); Quintal *et al.* (2002). For the corresponding C—O bond distances in 2-hydroxybenzencarboxylic acid and in metal complexes of 2-hydroxybenzencarboxylate, see: Munshi & Guru Row (2006); Su & Xu (2005); Li *et al.* (2005).



## Experimental

### Crystal data

[Co(C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]  
 $M_r = 471.30$   
 Monoclinic,  $C2/c$   
 $a = 16.594$  (2) Å  
 $b = 10.0524$  (12) Å  
 $c = 12.8271$  (15) Å  
 $\beta = 111.407$  (4)°

$V = 1992.1$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.91$  mm<sup>-1</sup>  
 $T = 294$  K  
 $0.40 \times 0.30 \times 0.26$  mm

### Data collection

Rigaku R-Axis RAPID IP diffractometer  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.665$ ,  $T_{\max} = 0.790$

10627 measured reflections  
 1824 independent reflections  
 1527 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.065$   
 $S = 1.07$   
 1824 reflections

141 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.22$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Co—O1	2.0684 (13)	Co—N2	2.1107 (16)
Co—O3	2.1402 (13)		

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>
N1—H1...O2 <sup>i</sup>	0.86	1.93	2.789 (2)	177
N3—H3...O2 <sup>ii</sup>	0.86	2.04	2.806 (2)	148
C3—H3A...O3 <sup>iii</sup>	0.93	2.43	3.341 (3)	168

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The project was supported by the ZIJIN project of Zhejiang University, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2743).

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**supplementary materials**

*Acta Cryst.* (2009). E65, m987-m988 [ doi:10.1107/S1600536809028694 ]

## Bis(1*H*-imidazole- $\kappa N^3$ )bis(2-oxidopyridinium-3-carboxylato- $\kappa^2 O^2, O^3$ )cobalt(II)

B.-Y. Zhang, J.-J. Nie and D.-J. Xu

### Comment

The title Co<sup>II</sup> complex is isostructural with the Ni<sup>II</sup> complex (Zhang *et al.* 2009).

In the title molecule, the Co atom is located on a twofold axis and is coordinated by two imidazole molecules in *cis*-configuration, two oxidopyridinium-carboxylate anions further chelate to the Co atom with carboxyl-O and deprotonated hydroxy-O atoms to complete the distorted octahedral coordination geometry (Fig. 1 and Table 1). The benzene ring is twisted with respect to the carboxyl group and O1/O3/Co coordination plane with dihedral angles of 21.52 (13)° and 41.05 (7)°, respectively. The shorter C1—O3 [1.260 (2) Å] bond agrees with those found in the isostructural Ni complex (Zhang *et al.* 2009) and in the other transition metal complexes of oxidopyridinium-carboxylate (Yao *et al.*, 2004; Yan & Hu, 2007a, b; Wen & Liu, 2007), it is also consistent with that found in hydroxy-pyridinecarboxylate complexes (Quintal *et al.* 2002). This finding suggests the electron delocalization between pyridine ring and hydroxy group. But this shorter C1—O3 bond is much different from the C—O bond distance of *ca* 1.35 Å between benzene ring and hydroxy-O atom found in hydroxybenzenecarboxylic acid (Munshi & Row, 2006) and metal complexes of hydroxybenzenecarboxylate (Su & Xu, 2005; Li *et al.*, 2005).

The uncoordinated carboxyl O atom simultaneously links with the imidazole and pyridinium rings *via* N—H $\cdots$ O hydrogen bonding of adjacent molecules (Table 2). Weak C—H $\cdots$ O hydrogen bonding is also present in the crystal structure.

### Experimental

2-Hydroxy-pyridine-3-carboxylic acid (0.13 g, 1 mmol), NaOH (0.04 g, 1 mmol), imidazole (0.14 g, 2 mmol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (0.24 g, 1 mmol) were dissolved in water (15 ml). The solution was refluxed for 4.5 h, after cooling to room temperature the solution was filtered. The single crystals of the title complex were obtained from the filtrate after one week.

### Refinement

H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

### Figures

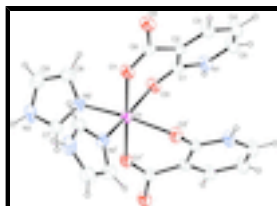


Fig. 1. The molecular structure of the title complex with 40% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (i) 1 - *x*, *y*, 1/2 - *z*].

## Bis(1*H*-imidazole- $\kappa$ N<sup>3</sup>)bis(2-oxidopyridinium-3-carboxylato- $\kappa^2$ O<sup>2</sup>,O<sup>3</sup>)cobalt(II)

### Crystal data

[Co(C <sub>6</sub> H <sub>4</sub> NO <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> ]	$F_{000} = 964$
$M_r = 471.30$	$D_x = 1.571 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C\ 2yc$	Cell parameters from 4226 reflections
$a = 16.594 (2) \text{ \AA}$	$\theta = 2.5\text{--}25.2^\circ$
$b = 10.0524 (12) \text{ \AA}$	$\mu = 0.91 \text{ mm}^{-1}$
$c = 12.8271 (15) \text{ \AA}$	$T = 294 \text{ K}$
$\beta = 111.407 (4)^\circ$	Block, pink
$V = 1992.1 (4) \text{ \AA}^3$	$0.40 \times 0.30 \times 0.26 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku R-Axis RAPID IP diffractometer	1824 independent reflections
Radiation source: fine-focus sealed tube	1527 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.034$
Detector resolution: $10.00 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 25.4^\circ$
$T = 294 \text{ K}$	$\theta_{\text{min}} = 2.4^\circ$
$\omega$ scans	$h = -20 \rightarrow 20$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -12 \rightarrow 12$
$T_{\text{min}} = 0.665$ , $T_{\text{max}} = 0.790$	$l = -14 \rightarrow 15$
10627 measured reflections	

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 1.9358P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1824 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
141 parameters	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
	Extinction correction: none

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co	0.5000	0.24771 (3)	0.2500	0.02958 (13)
N1	0.61270 (11)	-0.12644 (16)	0.30331 (13)	0.0369 (4)
H1	0.6138	-0.1391	0.2376	0.044*
N2	0.58362 (11)	0.39282 (16)	0.22623 (13)	0.0348 (4)
N3	0.62322 (13)	0.56271 (17)	0.14899 (16)	0.0468 (5)
H3	0.6198	0.6308	0.1070	0.056*
O1	0.56130 (10)	0.24739 (13)	0.42230 (11)	0.0392 (4)
O2	0.62213 (10)	0.16732 (14)	0.59300 (10)	0.0410 (4)
O3	0.58952 (9)	0.09062 (13)	0.25972 (10)	0.0352 (3)
C1	0.59989 (12)	0.00073 (18)	0.33196 (15)	0.0293 (4)
C2	0.60117 (12)	0.01700 (18)	0.44393 (15)	0.0288 (4)
C3	0.61152 (14)	-0.0923 (2)	0.51100 (17)	0.0375 (5)
H3A	0.6115	-0.0814	0.5830	0.045*
C4	0.62211 (16)	-0.2203 (2)	0.47472 (18)	0.0454 (6)
H4	0.6278	-0.2938	0.5209	0.055*
C5	0.62375 (16)	-0.2340 (2)	0.37099 (19)	0.0449 (6)
H5	0.6325	-0.3175	0.3457	0.054*
C6	0.59387 (12)	0.15307 (19)	0.48875 (15)	0.0299 (4)
C7	0.55679 (15)	0.4904 (2)	0.15344 (18)	0.0396 (5)
H7	0.4990	0.5071	0.1105	0.048*
C8	0.67219 (15)	0.4046 (2)	0.27010 (19)	0.0458 (6)
H8	0.7094	0.3488	0.3242	0.055*
C9	0.69703 (16)	0.5089 (2)	0.2231 (2)	0.0510 (6)
H9	0.7533	0.5381	0.2383	0.061*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co	0.0402 (2)	0.02722 (19)	0.0222 (2)	0.000	0.01241 (16)	0.000
N1	0.0554 (12)	0.0342 (9)	0.0257 (9)	0.0042 (8)	0.0204 (8)	-0.0020 (7)
N2	0.0400 (11)	0.0327 (9)	0.0318 (9)	0.0006 (8)	0.0132 (8)	0.0052 (7)
N3	0.0641 (14)	0.0341 (10)	0.0528 (12)	-0.0039 (9)	0.0340 (11)	0.0065 (9)

## supplementary materials

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O1	0.0589 (10)	0.0309 (7)	0.0245 (7)	0.0071 (7)	0.0115 (7)	-0.0005 (6)
O2	0.0612 (10)	0.0410 (8)	0.0201 (7)	0.0046 (7)	0.0142 (7)	-0.0032 (6)
O3	0.0529 (9)	0.0334 (7)	0.0254 (7)	0.0071 (6)	0.0214 (7)	0.0040 (6)
C1	0.0330 (11)	0.0313 (10)	0.0254 (10)	0.0008 (8)	0.0129 (8)	-0.0023 (8)
C2	0.0332 (11)	0.0319 (10)	0.0227 (10)	0.0011 (8)	0.0118 (8)	-0.0005 (8)
C3	0.0507 (14)	0.0394 (11)	0.0271 (10)	0.0019 (10)	0.0196 (10)	0.0012 (9)
C4	0.0715 (17)	0.0337 (11)	0.0357 (12)	0.0057 (11)	0.0250 (12)	0.0072 (9)
C5	0.0686 (16)	0.0295 (11)	0.0415 (13)	0.0051 (10)	0.0259 (12)	0.0002 (9)
C6	0.0332 (11)	0.0354 (10)	0.0243 (10)	-0.0003 (9)	0.0142 (8)	-0.0014 (8)
C7	0.0446 (13)	0.0367 (11)	0.0375 (12)	0.0002 (10)	0.0149 (10)	0.0041 (9)
C8	0.0411 (14)	0.0475 (13)	0.0471 (14)	0.0035 (10)	0.0141 (11)	0.0018 (10)
C9	0.0435 (15)	0.0493 (14)	0.0666 (17)	-0.0068 (11)	0.0278 (13)	-0.0092 (12)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Co—O1 <sup>i</sup>	2.0684 (13)	O2—C6	1.253 (2)
Co—O1	2.0684 (13)	O3—C1	1.260 (2)
Co—O3 <sup>i</sup>	2.1402 (13)	C1—C2	1.438 (3)
Co—O3	2.1402 (13)	C2—C3	1.367 (3)
Co—N2	2.1107 (16)	C2—C6	1.506 (3)
Co—N2 <sup>i</sup>	2.1107 (16)	C3—C4	1.401 (3)
N1—C5	1.357 (3)	C3—H3A	0.9300
N1—C1	1.368 (2)	C4—C5	1.348 (3)
N1—H1	0.8600	C4—H4	0.9300
N2—C7	1.315 (2)	C5—H5	0.9300
N2—C8	1.374 (3)	C7—H7	0.9300
N3—C7	1.339 (3)	C8—C9	1.347 (3)
N3—C9	1.359 (3)	C8—H8	0.9300
N3—H3	0.8600	C9—H9	0.9300
O1—C6	1.258 (2)		
O1 <sup>i</sup> —Co—O1	179.82 (7)	O3—C1—C2	126.95 (17)
O1 <sup>i</sup> —Co—N2	86.54 (6)	N1—C1—C2	115.31 (16)
O1—Co—N2	93.59 (6)	C3—C2—C1	119.33 (17)
O1 <sup>i</sup> —Co—N2 <sup>i</sup>	93.59 (6)	C3—C2—C6	119.94 (16)
O1—Co—N2 <sup>i</sup>	86.54 (6)	C1—C2—C6	120.71 (16)
N2—Co—N2 <sup>i</sup>	92.57 (9)	C2—C3—C4	122.10 (18)
O1 <sup>i</sup> —Co—O3 <sup>i</sup>	82.90 (5)	C2—C3—H3A	119.0
O1—Co—O3 <sup>i</sup>	96.97 (5)	C4—C3—H3A	119.0
N2—Co—O3 <sup>i</sup>	168.64 (5)	C5—C4—C3	118.14 (19)
N2 <sup>i</sup> —Co—O3 <sup>i</sup>	92.26 (6)	C5—C4—H4	120.9
O1 <sup>i</sup> —Co—O3	96.97 (5)	C3—C4—H4	120.9
O1—Co—O3	82.90 (5)	C4—C5—N1	120.26 (19)
N2—Co—O3	92.26 (6)	C4—C5—H5	119.9
N2 <sup>i</sup> —Co—O3	168.64 (5)	N1—C5—H5	119.9
O3 <sup>i</sup> —Co—O3	84.91 (8)	O2—C6—O1	122.54 (17)
C5—N1—C1	124.81 (17)	O2—C6—C2	117.41 (17)

C5—N1—H1	117.6	O1—C6—C2	120.05 (16)
C1—N1—H1	117.6	N2—C7—N3	111.4 (2)
C7—N2—C8	105.13 (18)	N2—C7—H7	124.3
C7—N2—Co	123.24 (15)	N3—C7—H7	124.3
C8—N2—Co	131.44 (14)	C9—C8—N2	109.9 (2)
C7—N3—C9	107.46 (18)	C9—C8—H8	125.1
C7—N3—H3	126.3	N2—C8—H8	125.1
C9—N3—H3	126.3	C8—C9—N3	106.1 (2)
C6—O1—Co	130.35 (12)	C8—C9—H9	126.9
C1—O3—Co	118.52 (12)	N3—C9—H9	126.9
O3—C1—N1	117.74 (16)		

Symmetry codes: (i)  $-x+1, y, -z+1/2$ .

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O2 <sup>ii</sup>	0.86	1.93	2.789 (2)	177
N3—H3 $\cdots$ O2 <sup>iii</sup>	0.86	2.04	2.806 (2)	148
C3—H3A $\cdots$ O3 <sup>iv</sup>	0.93	2.43	3.341 (3)	168

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



Fig. 1

