

Bis(1*H*-imidazole- κ N³)bis(2-oxido-pyridinium-3-carboxylato- κ^2 O²,O³)-cobalt(II)

Bing-Yu Zhang, Jing-Jing Nie and Duan-Jun Xu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

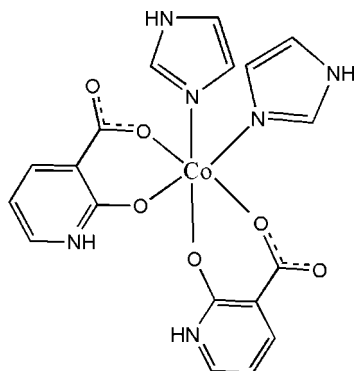
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 Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.028; wR factor = 0.065; data-to-parameter ratio = 12.9.

In the molecule of the title Co^{II} complex, $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_3)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$, the Co^{II} 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^{II} 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

$[\text{Co}(\text{C}_6\text{H}_4\text{NO}_3)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$
 $M_r = 471.30$
 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) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.91$ mm⁻¹
 $T = 294$ 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)
 $T_{\text{min}} = 0.665$, $T_{\text{max}} = 0.790$

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
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

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 ⁱ	0.86	1.93	2.789 (2)	177
N3—H3...O2 ⁱⁱ	0.86	2.04	2.806 (2)	148
C3—H3A...O3 ⁱⁱⁱ	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).

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

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supporting information

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

Bis(1*H*-imidazole- κN^3)bis(2-oxidopyridinium-3-carboxylato- $\kappa^2 O^2, O^3$)cobalt(II)**Bing-Yu Zhang, Jing-Jing Nie and Duan-Jun Xu****S1. Comment**

The title Co^{II} complex is isostructural with the Ni^{II} 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, 2007*a, 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).

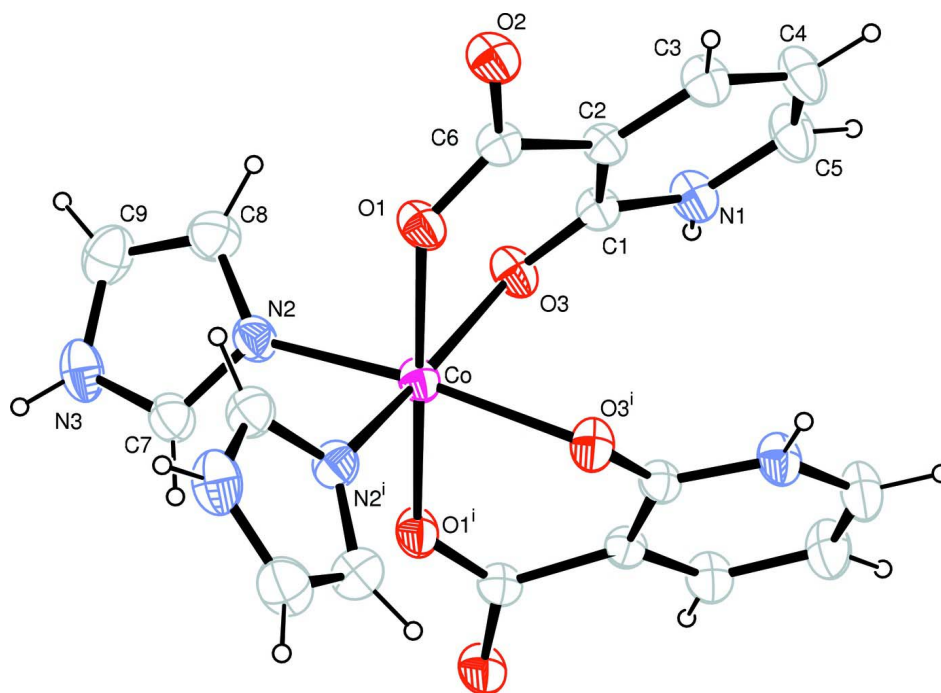
The uncoordinated carboxyl O atom simultaneously links with the imidazole and pyridinium rings *via* N—H \cdots O hydrogen bonding of adjacent molecules (Table 2). Weak C—H \cdots O hydrogen bonding is also present in the crystal structure.

S2. 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 CoCl₂·6H₂O (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.

S3. 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

**Figure 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- κ -N³)bis(2-oxido-3-carboxylato- κ^2 O²,O³)cobalt(II)

Crystal data

[Co(C₆H₄NO₃)₂(C₃H₄N₂)₂]

$M_r = 471.30$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 16.594\ (2)\ \text{\AA}$

$b = 10.0524\ (12)\ \text{\AA}$

$c = 12.8271\ (15)\ \text{\AA}$

$\beta = 111.407\ (4)^\circ$

$V = 1992.1\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 964$

$D_x = 1.571\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4226 reflections

$\theta = 2.5\text{--}25.2^\circ$

$\mu = 0.91\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Block, pink

$0.40 \times 0.30 \times 0.26\ \text{mm}$

Data collection

Rigaku R-AXIS RAPID IP

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $10.00\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.665$, $T_{\max} = 0.790$

10627 measured reflections

1824 independent reflections

1527 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -20 \rightarrow 20$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.065$
 $S = 1.07$
 1824 reflections
 141 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 1.9358P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{Å}^{-3}$

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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\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)
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 (\AA , $^\circ$)

Co—O1 ⁱ	2.0684 (13)	O2—C6	1.253 (2)
Co—O1	2.0684 (13)	O3—C1	1.260 (2)
Co—O3 ⁱ	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 ⁱ	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 ⁱ —Co—O1	179.82 (7)	O3—C1—C2	126.95 (17)
O1 ⁱ —Co—N2	86.54 (6)	N1—C1—C2	115.31 (16)
O1—Co—N2	93.59 (6)	C3—C2—C1	119.33 (17)
O1 ⁱ —Co—N2 ⁱ	93.59 (6)	C3—C2—C6	119.94 (16)
O1—Co—N2 ⁱ	86.54 (6)	C1—C2—C6	120.71 (16)
N2—Co—N2 ⁱ	92.57 (9)	C2—C3—C4	122.10 (18)
O1 ⁱ —Co—O3 ⁱ	82.90 (5)	C2—C3—H3A	119.0
O1—Co—O3 ⁱ	96.97 (5)	C4—C3—H3A	119.0
N2—Co—O3 ⁱ	168.64 (5)	C5—C4—C3	118.14 (19)
N2 ⁱ —Co—O3 ⁱ	92.26 (6)	C5—C4—H4	120.9

O1 ⁱ —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 ⁱ —Co—O3	168.64 (5)	N1—C5—H5	119.9
O3 ⁱ —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 code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<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 ⁱⁱ	0.86	1.93	2.789 (2)	177
N3—H3 \cdots O2 ⁱⁱⁱ	0.86	2.04	2.806 (2)	148
C3—H3A \cdots O3 ^{iv}	0.93	2.43	3.341 (3)	168

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