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## Structure Reports

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***fac*-Tris(pyridine-2-carboxylato- $\kappa^2$ N,O)-cobalt(III)**Irina A. Golenia,<sup>a</sup> Alexander N. Boyko,<sup>a</sup> Natalia V. Kotova,<sup>a</sup> Matti Haukka<sup>b</sup> and Valentina A. Kalibabchuk<sup>c\*</sup>

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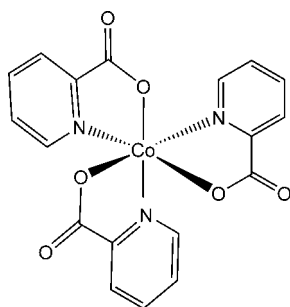
Received 11 October 2011; accepted 19 October 2011

Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{C}-\text{C}) = 0.017$  Å;  $R$  factor = 0.068;  $wR$  factor = 0.197; data-to-parameter ratio = 11.4.

In the title compound,  $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_3]$ , the  $\text{Co}^{\text{III}}$  ion lies on a threefold rotation axis and is in a distorted octahedral environment defined by three N and three O donor atoms from three *fac*-disposed pyridine-2-carboxylate ligands. The ligands are coordinated in a chelate fashion, forming three five-membered rings. In the crystal, translationally related complex molecules are organized into columns along  $[001]$  via  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the use of hydroxamate ligands in the synthesis of polynuclear compounds, see: Dobosz *et al.* (1999); Fritsky *et al.* (1998); Sachse *et al.* (2008). For hydrolytic destruction of hydroxamate ligands upon complex formation, see: Świątek-Kozłowska *et al.* (2000). For related structures, see: Fritsky *et al.* (2001); Fu & Wang (2005); Kovbasyuk *et al.* (2004); Krämer & Fritsky (2000); Mokhir *et al.* (2002); Moroz *et al.* (2010); Pelizzi & Pelizzi (1981); Sliva *et al.* (1997); Wörl, Fritsky *et al.* (2005); Wörl, Pritzkow *et al.* (2005). For the synthesis of pyridine-2-hydroxamic acid, see: Hynes (1970).



## Experimental

## Crystal data

$[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_3]$   
 $M_r = 425.24$   
 Hexagonal,  $P6$   
 $a = 12.8617$  (12) Å  
 $c = 6.2122$  (9) Å  
 $V = 890.0$  (2) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.01$  mm<sup>-1</sup>  
 $T = 120$  K  
 $0.23 \times 0.08 \times 0.03$  mm

## Data collection

Nonius KappaCCD diffractometer  
 Absorption correction: multi-scan  
 (DENZO/SCALEPACK;  
 Otwinowski & Minor, 1997)  
 $T_{\text{min}} = 0.800$ ,  $T_{\text{max}} = 0.970$

5635 measured reflections  
 978 independent reflections  
 893 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.043$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$   
 $wR(F^2) = 0.197$   
 $S = 1.16$   
 978 reflections  
 86 parameters  
 1 restraint

H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.05$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.59$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 400 Friedel pairs  
 Flack parameter:  $-0.02$  (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C3}-\text{H3}\cdots\text{O2}^i$	0.95	2.60	3.212 (14)	123

Symmetry code: (i)  $x - y + 1, x, z - 1$ .

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK; program(s) used to solve structure: SIR2004 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2479).

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## supporting information

*Acta Cryst.* (2011). E67, m1596–m1597 [doi:10.1107/S1600536811043303]

***fac*-Tris(pyridine-2-carboxylato- $\kappa^2$ N,O)cobalt(III)**

**Irina A. Golenia, Alexander N. Boyko, Natalia V. Kotova, Matti Haukka and Valentina A. Kalibabchuk**

**S1. Comment**

Hydroxamic groups and their derivatives are often used in syntheses of polynuclear metal complexes (Dobosz *et al.*, 1999; Fritsky *et al.*, 1998; Sachse *et al.*, 2008). However, functionalized hydroxamate ligands having additional donor functions often undergo hydrolytic destruction when complex formation with 3d-metal ions takes place (Dobosz *et al.*, 1999; Świątek-Kozłowska *et al.*, 2000). As a result, a carboxylic group is formed. The title compound was obtained as a result of hydrolytic decomposition of pyridine-2-hydroxamic acid during the reaction of complex formation with cobalt(II) perchlorate.

In the title compound, the Co<sup>III</sup> ion lies on a threefold rotation axis and is in a distorted octahedral environment of three N and three O donor atoms from three pyridine-2-carboxylate ligands (Fig. 1). Unlike in the case of earlier reported tris-(pyridine-2-carboxylato)cobalt(III) monohydrate, in which the realization of *mer*-isomer is observed, in the title complex three pyridine-2-carboxylate ligands are disposed in a *fac*-fashion (Fu & Wang, 2005; Pelizzi & Pelizzi, 1981). The ligands are coordinated in a chelate mode, forming three five-membered rings. The Co—N and Co—O bond lengths are consistent with the values typically quoted for the octahedral cobalt(III) complexes with N,O-mixed donor ligands (Mokhir *et al.*, 2002; Sliva *et al.*, 1997). The C—O bond lengths in the deprotonated carboxylate groups of the ligands differ significantly [1.232 (14) and 1.339 (15) Å], which is typical for monodentately coordinated carboxylates (Wörl, Fritsky *et al.*, 2005; Wörl, Pritzkow *et al.*, 2005). The C—C and C—N bond lengths in the pyridine rings are normal for 2-substituted pyridine derivatives (Fritsky *et al.*, 2001; Kovbasyuk *et al.*, 2004; Krämer & Fritsky, 2000; Moroz *et al.*, 2010).

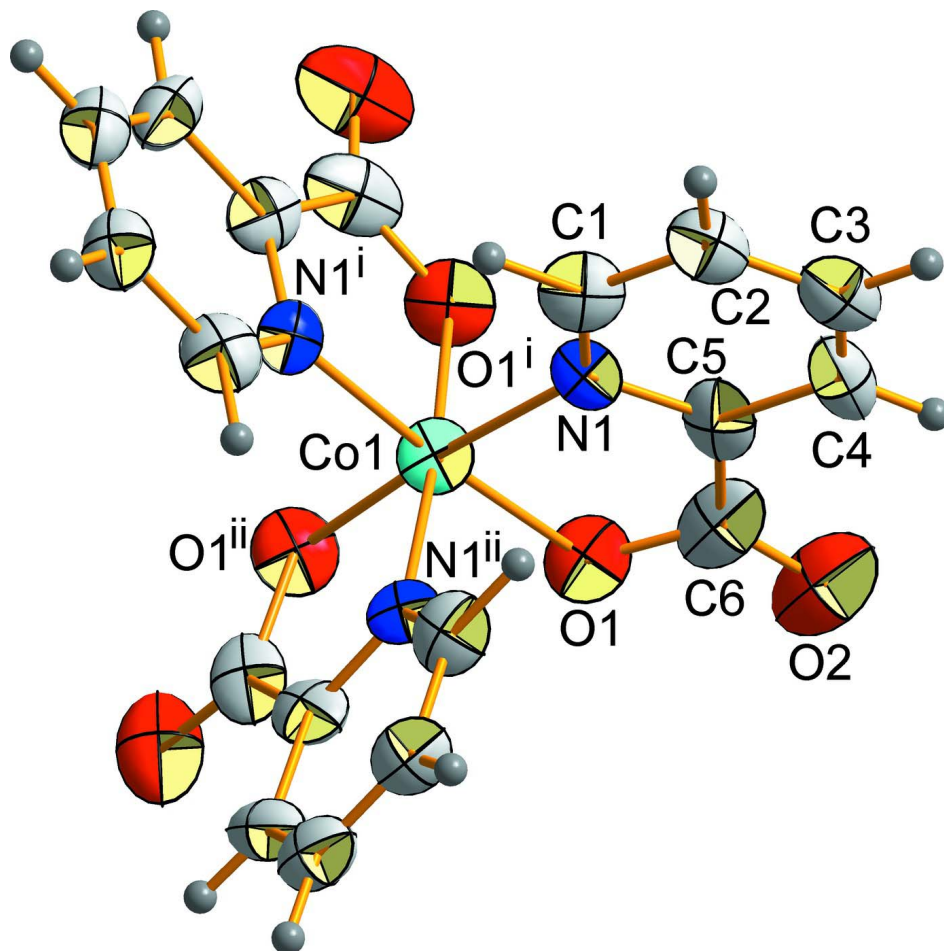
In the crystal, the translational complex molecules are organized into columns along the *c* axis (Fig. 2). The neighboring molecules are united by C—H $\cdots$ O hydrogen bonds (Table 1).

**S2. Experimental**

Cobalt(II) perchlorate hexahydrate (0.0365 g, 0.1 mmol) was dissolved in water (3 ml) and mixed with a solution of pyridine-2-hydroxamic acid (0.0414 g, 0.3 mmol) (Hynes, 1970) in methanol (3 ml). The resulting clear red solution was set aside for crystallization by slow diffusion of diethyl ether into the formed solution. The pink crystals formed in 5–7 days were filtered off, washed with diethyl ether and air-dried (yield: 83%).

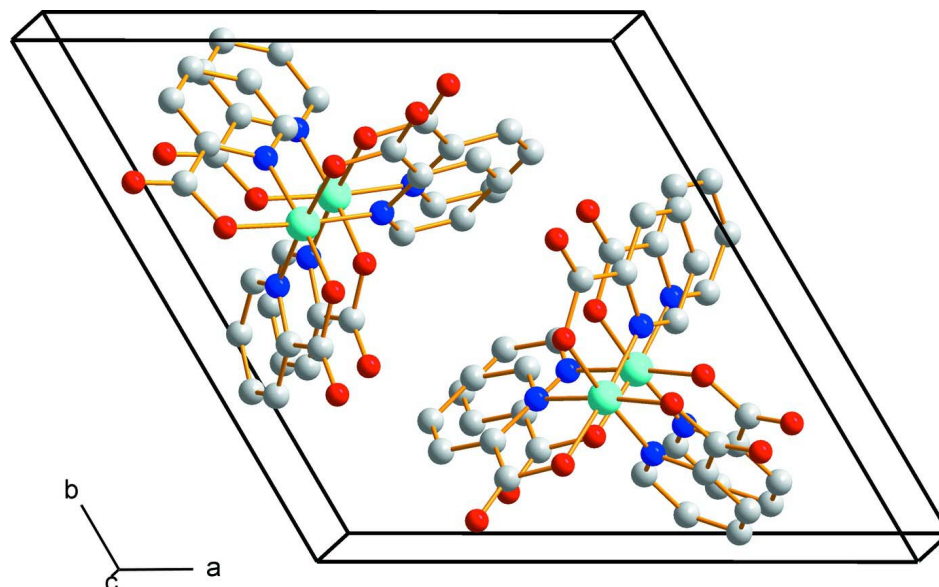
**S3. Refinement**

The final structure refinement was performed by using a twin law (-1 -1 0 0 1 0 0 0 -1) with the final BASF parameter refining to 0.80178. H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.95 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level.

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

**Figure 2**

A packing diagram of the title compound. H atoms have been omitted for clarity.

### *fac*-Tris(pyridine-2-carboxylato- $\kappa^2N,O$ )cobalt(III)

#### Crystal data

[Co(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>3</sub>]

$M_r = 425.24$

Hexagonal, *P6*

Hall symbol: *P 6*

$a = 12.8617(12) \text{ \AA}$

$c = 6.2122(9) \text{ \AA}$

$V = 890.0(2) \text{ \AA}^3$

$Z = 2$

$F(000) = 432$

$D_x = 1.587 \text{ Mg m}^{-3}$

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

Cell parameters from 713 reflections

$\theta = 3.2\text{--}24.5^\circ$

$\mu = 1.01 \text{ mm}^{-1}$

$T = 120 \text{ K}$

Block, pink

$0.23 \times 0.08 \times 0.03 \text{ mm}$

#### Data collection

Nonius KappaCCD  
diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal  
monochromator

Detector resolution:  $9 \text{ pixels mm}^{-1}$

$\varphi$  and  $\omega$  scans with  $\kappa$  offset

Absorption correction: multi-scan

(*DENZO/SCALEPACK*; Otwinowski & Minor,  
1997)

$T_{\min} = 0.800$ ,  $T_{\max} = 0.970$

5635 measured reflections

978 independent reflections

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

$R_{\text{int}} = 0.043$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 3.2^\circ$

$h = -15 \rightarrow 15$

$k = -15 \rightarrow 15$

$l = -7 \rightarrow 7$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.068$

$wR(F^2) = 0.197$

$S = 1.16$

978 reflections

86 parameters

1 restraint

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  
 $w = 1/[\sigma^2(F_o^2) + (0.1316P)^2 + 0.9442P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.05 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983), 400 Friedel  
 pairs  
 Absolute structure parameter:  $-0.02 (7)$

*Special details*

**Experimental.** The final structural refinement was performed by using the twin law -1 -1 0 0 1 0 0 0 -1 with the final BASF parameter refining to 0.80178.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.3333	0.6667	0.3408 (2)	0.0379 (5)
O1	0.4550 (7)	0.7860 (7)	0.5147 (11)	0.0514 (18)
O2	0.6490 (9)	0.8907 (8)	0.5627 (16)	0.083 (3)
N1	0.4619 (6)	0.6785 (6)	0.1705 (12)	0.0332 (15)
C1	0.4622 (10)	0.6303 (9)	-0.0009 (17)	0.051 (2)
H1	0.3875	0.5756	-0.0656	0.061*
C2	0.5687 (9)	0.6533 (9)	-0.1037 (17)	0.050 (2)
H2	0.5659	0.6145	-0.2355	0.061*
C3	0.6747 (10)	0.7308 (9)	-0.0138 (18)	0.052 (2)
H3	0.7483	0.7480	-0.0795	0.062*
C4	0.6729 (9)	0.7796 (9)	0.159 (2)	0.052 (3)
H4	0.7469	0.8358	0.2241	0.062*
C5	0.5690 (8)	0.7548 (9)	0.2577 (18)	0.048 (2)
C6	0.5660 (11)	0.8159 (9)	0.4512 (18)	0.057 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0513 (7)	0.0513 (7)	0.0111 (8)	0.0256 (3)	0.000	0.000
O1	0.067 (4)	0.066 (4)	0.018 (4)	0.031 (4)	-0.007 (3)	-0.008 (3)
O2	0.105 (7)	0.067 (5)	0.054 (6)	0.027 (4)	-0.036 (5)	0.004 (4)
N1	0.045 (4)	0.047 (4)	0.014 (3)	0.028 (3)	-0.001 (3)	0.007 (3)
C1	0.065 (5)	0.056 (5)	0.034 (5)	0.031 (4)	0.006 (4)	0.008 (4)
C2	0.061 (5)	0.058 (5)	0.041 (6)	0.036 (5)	0.010 (4)	0.006 (4)
C3	0.060 (6)	0.059 (6)	0.046 (6)	0.038 (5)	0.014 (5)	0.016 (5)
C4	0.042 (5)	0.067 (6)	0.055 (7)	0.033 (4)	0.012 (5)	0.023 (6)
C5	0.048 (5)	0.057 (5)	0.042 (6)	0.029 (4)	-0.005 (4)	0.021 (5)
C6	0.071 (7)	0.052 (6)	0.036 (6)	0.021 (5)	-0.027 (6)	0.010 (5)

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

Co1—O1 <sup>i</sup>	1.889 (7)	C1—C2	1.402 (14)
Co1—O1	1.889 (7)	C1—H1	0.9500
Co1—O1 <sup>ii</sup>	1.889 (7)	C2—C3	1.344 (16)
Co1—N1 <sup>i</sup>	1.904 (7)	C2—H2	0.9500
Co1—N1 <sup>ii</sup>	1.904 (7)	C3—C4	1.251 (15)

Co1—N1	1.904 (7)	C3—H3	0.9500
O1—C6	1.339 (15)	C4—C5	1.354 (14)
O2—C6	1.232 (14)	C4—H4	0.9500
N1—C1	1.233 (14)	C5—C6	1.447 (15)
N1—C5	1.343 (12)		
O1 <sup>i</sup> —Co1—O1	90.6 (3)	N1—C1—C2	122.4 (10)
O1 <sup>i</sup> —Co1—O1 <sup>ii</sup>	90.6 (3)	N1—C1—H1	118.8
O1—Co1—O1 <sup>ii</sup>	90.6 (3)	C2—C1—H1	118.8
O1 <sup>i</sup> —Co1—N1 <sup>i</sup>	85.4 (3)	C3—C2—C1	119.3 (10)
O1—Co1—N1 <sup>i</sup>	92.1 (2)	C3—C2—H2	120.4
O1 <sup>ii</sup> —Co1—N1 <sup>i</sup>	175.1 (3)	C1—C2—H2	120.4
O1 <sup>i</sup> —Co1—N1 <sup>ii</sup>	92.1 (2)	C4—C3—C2	117.6 (10)
O1—Co1—N1 <sup>ii</sup>	175.1 (3)	C4—C3—H3	121.2
O1 <sup>ii</sup> —Co1—N1 <sup>ii</sup>	85.4 (3)	C2—C3—H3	121.2
N1 <sup>i</sup> —Co1—N1 <sup>ii</sup>	92.1 (3)	C3—C4—C5	122.2 (11)
O1 <sup>i</sup> —Co1—N1	175.1 (3)	C3—C4—H4	118.9
O1—Co1—N1	85.4 (3)	C5—C4—H4	118.9
O1 <sup>ii</sup> —Co1—N1	92.1 (2)	N1—C5—C4	121.4 (11)
N1 <sup>i</sup> —Co1—N1	92.1 (3)	N1—C5—C6	115.8 (10)
N1 <sup>ii</sup> —Co1—N1	92.1 (3)	C4—C5—C6	122.5 (11)
C6—O1—Co1	113.3 (7)	O2—C6—O1	116.2 (13)
C1—N1—C5	117.1 (9)	O2—C6—C5	130.0 (13)
C1—N1—Co1	131.3 (7)	O1—C6—C5	113.8 (10)
C5—N1—Co1	111.5 (7)		
O1 <sup>i</sup> —Co1—O1—C6	179.0 (6)	C1—C2—C3—C4	-0.2 (14)
O1 <sup>ii</sup> —Co1—O1—C6	88.4 (8)	C2—C3—C4—C5	1.2 (15)
N1—Co1—O1—C6	-3.7 (7)	C1—N1—C5—C4	1.3 (13)
O1—Co1—N1—C1	-175.4 (8)	Co1—N1—C5—C4	-177.9 (7)
O1 <sup>ii</sup> —Co1—N1—C1	94.2 (9)	C1—N1—C5—C6	176.1 (7)
N1 <sup>i</sup> —Co1—N1—C1	-83.4 (7)	Co1—N1—C5—C6	-3.1 (8)
N1 <sup>ii</sup> —Co1—N1—C1	8.8 (8)	C3—C4—C5—N1	-1.8 (14)
O1—Co1—N1—C5	3.7 (6)	C3—C4—C5—C6	-176.3 (8)
O1 <sup>ii</sup> —Co1—N1—C5	-86.7 (6)	Co1—O1—C6—O2	-177.8 (7)
N1 <sup>i</sup> —Co1—N1—C5	95.7 (7)	Co1—O1—C6—C5	2.9 (9)
N1 <sup>ii</sup> —Co1—N1—C5	-172.1 (6)	N1—C5—C6—O2	-179.0 (10)
C5—N1—C1—C2	-0.3 (13)	C4—C5—C6—O2	-4.2 (13)
Co1—N1—C1—C2	178.7 (6)	N1—C5—C6—O1	0.2 (9)
N1—C1—C2—C3	-0.2 (14)	C4—C5—C6—O1	174.9 (9)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 $\cdots$ O2 <sup>iii</sup>	0.95	2.60	3.212 (14)	123

Symmetry code: (iii)  $x-y+1, x, z-1$ .