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Aquanitritobis(picolinato-κ^2*N*,*O*)cobalt(III)

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Key indicators

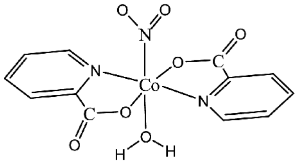
Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.002 Å
R factor = 0.030
wR factor = 0.086
Data-to-parameter ratio = 13.8

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

The title compound, $[Co(C_6H_4NO_2)_2(NO_2)(H_2O)]$, displays O—H···O hydrogen bonds, leading to the formation of a two-dimensional network structure. Interestingly, the oxidation and decomposition of α-pyridoin and the auto-redox reaction of cobalt nitrate occurred during the reaction process.

Comment

Pyridine-2-carboxylic acid and its analogs have been used increasingly in the synthesis of high-nuclearity transition metallacrowns with high spin values, which could be used as single-molecule magnets (Sessoli *et al.*, 1993; Thomas *et al.*, 1996; Aubin *et al.*, 1996; Gatteschi *et al.*, 2000; Winpenny, 1999; Liu *et al.*, 2001). As a tetradentate ligand, α-pyridoin attracted our attention for the process of constructing metallacrowns. However, an unexpected mononuclear compound was obtained as a result of the oxidation and decomposition of the ligand α-pyridoin to form pyridine-2-carboxylic acid. We report here the synthesis and crystal structure of the title compound, $[Co(III)(pca)_2(NO_2)(H_2O)]$ (Hpca is pyridine-2-carboxylic acid), (I).



(I)

Compound (I) was prepared from the reaction of α-pyridoin and $Co(NO_3)_2{\cdot}6H_2O$. As shown in Fig. 1, the cobalt ion has a slightly distorted octahedral geometry, coordinated by two N atoms and two O atoms from chelating pca ligands arranged pseudo-centrosymmetrically in the equatorial plane, and an N atom and an O atom from a nitrite group and a water molecule, respectively, occupying the apical sites. The N3—Co1—O7 bond angle is 178.29 (5)°, and the N1—Co1—N2 and O4—Co1—O2 angles are 178.24 (5) and 178.95 (4)°, respectively. The Co1—N3 bond length is 1.9078 (15) Å, which is consistent with a cobalt(III) complex (Jensen *et al.*, 1997).

The crystal structure involves O—H···O hydrogen bonds, leading to the formation of a two-dimensional network structure, as shown in Fig. 2.

The intriguing factor in this work is the redox reaction that leads to the formation of the title compound. The oxidation and decomposition of α-pyridoin produce pyridine-2-carboxylic acid. The nitrite group existing in (I) should come from the reduction of nitrate. According to charge-balance requirements, the oxidation state of Co is assigned as +3,

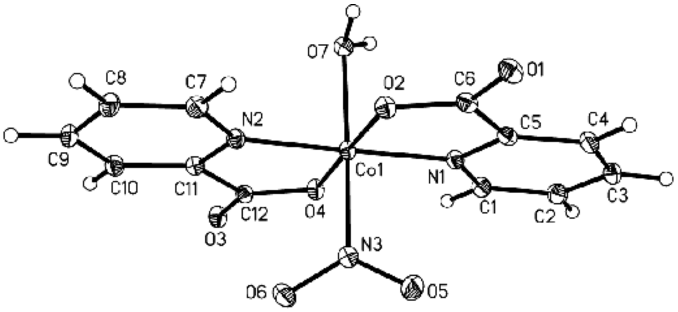


Figure 1
Perspective view of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

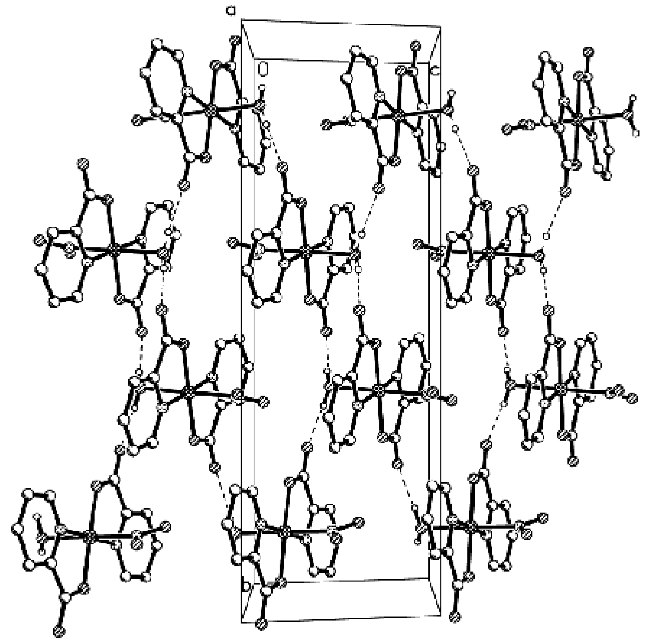


Figure 2
The two-dimensional packing structure of the title complex, viewed along the *a* axis. H atoms not involved in hydrogen bonding have been omitted and hydrogen bonds are shown as dashed lines.

attributed to the auto-oxidation reaction of cobalt nitrate (Chen, 2002).

Experimental

The α-pyridoin (0.043 g, 0.2 mmol) ligand was added to a stirred solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.029 g, 0.1 mmol) in acetonitrile (20 ml). The resulting dark-red–brown precipitate was filtered off and the dark-red–brown filtrate was left to evaporate slowly at room temperature. After several days, dark-red crystals suitable for X-ray diffraction studies were obtained.

Crystal data

$[Co(C_6H_4NO_2)_2(NO_2)(H_2O)]$
$M_r = 367.16$
Monoclinic, $P2_1/c$
$a = 9.065\ (2)$ Å
$b = 20.736\ (5)$ Å
$c = 7.1111\ (18)$ Å
$\beta = 102.166\ (2)°$
$V = 1306.8\ (6)$ Å^3
$Z = 4$
$D_x = 1.866$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4323 reflections
$\theta = 2.0–27.5°$
$\mu = 1.36$ mm^{-1}
$T = 130\ (2)$ K
Prism, red
$0.60 \times 0.40 \times 0.25$ mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.510$, $T_{max} = 0.710$
9662 measured reflections
2958 independent reflections
2785 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -25 \rightarrow 26$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.086$
$S = 1.04$
2958 reflections
214 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.5096P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O4	1.8844 (12)	Co1—N3	1.9107 (15)
Co1—O2	1.8948 (12)	Co1—N2	1.9135 (13)
Co1—N1	1.9071 (13)	Co1—O7	1.9700 (12)
O4—Co1—O2	178.96 (5)	N1—Co1—N2	178.17 (5)
O4—Co1—N1	94.00 (5)	N3—Co1—N2	91.26 (6)
O2—Co1—N1	85.22 (5)	O4—Co1—O7	89.38 (5)
O4—Co1—N3	89.73 (5)	O2—Co1—O7	91.32 (5)
O2—Co1—N3	89.59 (5)	N1—Co1—O7	91.26 (5)
N1—Co1—N3	90.26 (6)	N3—Co1—O7	178.29 (5)
O4—Co1—N2	84.99 (5)	N2—Co1—O7	87.20 (5)
O2—Co1—N2	95.81 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$A\cdots$O3^{i}	0.839 (15)	1.908 (16)	2.7405 (17)	171 (2)
O7—H7$B\cdots$O1^{ii}	0.892 (15)	1.830 (16)	2.7124 (17)	170 (2)

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

H7*A* and H7*B* were located in difference Fourier maps and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(parent atom). All other H atoms were positioned geometrically (C—H = 0.95 Å) and allowed to ride on their respective parent atoms, $[U_{iso}(H) = U_{eq}(C,O)]$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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