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## Key indicators

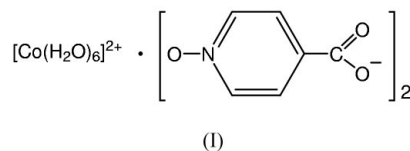
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.036  
 $wR$  factor = 0.082  
Data-to-parameter ratio = 15.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hexaquaacobalt(II) bis(isonicotinate *N*-oxide):  
a redetermination and analysis of the  
hydrogen-bonding interactions

In the crystal structure of the title complex,  $[\text{Co}(\text{H}_2\text{O})_6](L)_2$  ( $L = \text{isonicotinate } N\text{-oxide}, \text{C}_6\text{H}_4\text{NO}_3$ ), the  $\text{Co}^{\text{II}}$  center, on a special position with site symmetry  $2/m$ , is in an elongated octahedral environment composed of six coordinated water molecules. Each water ligand forms two strong  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds with the adjacent isonicotinate *N*-oxide counter-ions, which lie on mirror planes, forming a three-dimensional hydrogen-bonding supramolecular architecture.

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## Comment

Carboxypyridine *N*-oxide compounds contain both *N*-oxide and carboxyl functional groups, and exhibit a variety of coordination modes with metal ions (Mao *et al.*, 1998) and hydrogen-bonding interactions (Du & Zhao, 2003). The crystal structure of the title complex, (I), has been reported previously by Knuuttila (1981) in the monoclinic system and space group  $P2_1/c$  [ $a = 7.747(2)\text{ \AA}$ ,  $b = 9.826(2)\text{ \AA}$ ,  $c = 11.474(2)\text{ \AA}$ ,  $\beta = 91.08(2)^\circ$ ]. Recently, we have redetermined the structure of (I) and two main points will be emphasized in this contribution: (i) the space group of (I) should be  $C2/m$ , which has a higher symmetry, and the bond geometries are significantly more precise than those reported previously, and (ii) the analysis of the interesting hydrogen-bonding interactions.



The crystal structure of (I), illustrated in Fig. 1, consists of a hexaquaacobalt(II) cation and two isonicotinate *N*-oxide anions in its chemical formula unit. Each  $\text{Co}^{\text{II}}$  center, octahedrally coordinated by six water ligands, is located at a special position with site symmetry  $2/m$ . Four crystallographically equivalent water molecules, atoms O3, are in the equatorial plane with  $\text{Co}-\text{O}$  distances of  $2.038(2)\text{ \AA}$ , and two

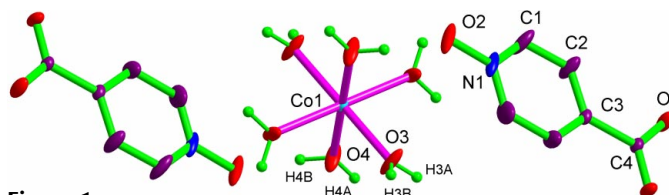
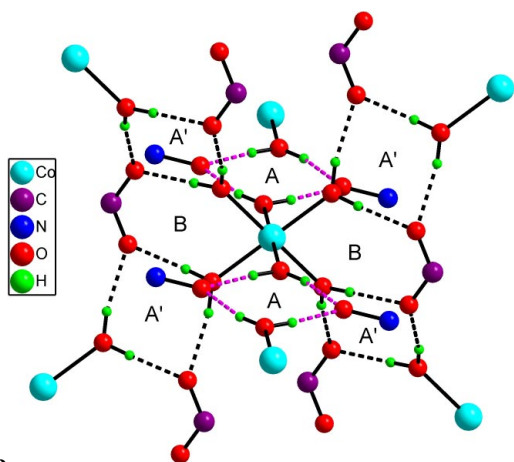
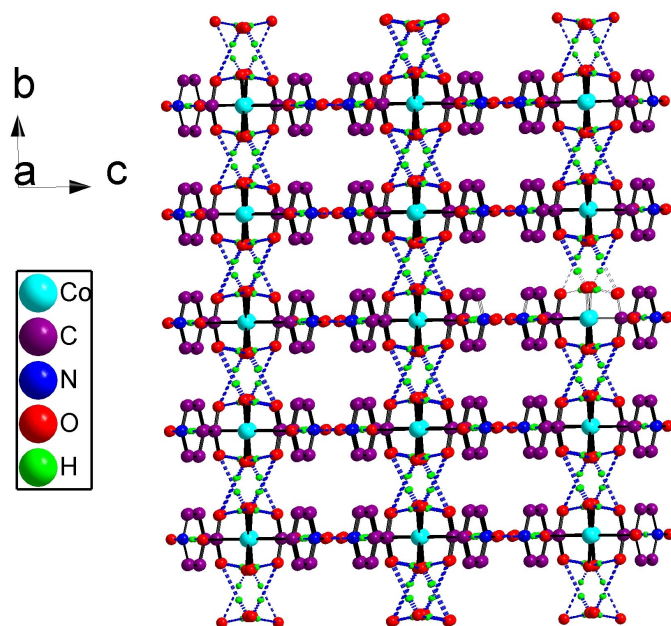


Figure 1

View of the molecular structure of (I), showing the atomic labeling of the asymmetric unit, with displacement ellipsoids drawn at the 30% probability level.



**Figure 2**  
View of the hydrogen bonds (indicated by dashed lines) in the structure of (I).



**Figure 3**  
View of the three-dimensional supramolecular architecture along the [100] direction. Hydrogen-bonding interactions are indicated by blue dashed lines.

water molecules, atoms O4, occupy the axial positions with Co—O lengths of 2.059 (3) Å. Selected bond lengths and angles are listed in Table 1. The coordination environment of Co<sup>II</sup> can be described as a slightly elongated octahedral, with the *cis*-O—Co—O angles in the range 86.05 (13)–93.95 (13)°.

In this structure, the isonicotinate *N*-oxides, which lie on mirror planes, act only as counter-anions to balance the charges, and do not take part in any direct coordination interaction with the metal center. The nearest Co···O1 and Co···O2 distances are 4.113 (2) and 4.032 (3) Å, respectively. The N—O distance is 1.320 (3) Å, which is slightly, but significantly, elongated compared to the average value of 1.304 Å in pyridine *N*-oxides and consistent with the values observed in other carboxypyridine *N*-oxide derivatives (Du & Zhao, 2003).

Analysis of the crystal packing of the title complex reveals the existence of four crystallographically independent intermolecular O—H···O hydrogen bonds, between the coordinated water molecules and the isonicotinate *N*-oxide anions. This results in the formation of a three-dimensional hydrogen-bonding network. As shown in Fig. 2 and Table 2, each O4 water ligand forms two intermolecular hydrogen bonds (indicated by purple dashed lines in Fig. 2), O4—H4A···O2<sup>iv</sup> and O4—H4B···O2<sup>iii</sup> [symmetry codes: (iii) 1 - x, 1 - y, 1 - z; (iv) x, y, z + 1], with the *N*-oxide groups. The resulting motif A, in the formalism of graph-set analysis of hydrogen-bond patterns (Etter, 1990), is characterized as  $N_4 = R_4^2(8)$ . Meanwhile, each carboxylate group serves as hydrogen-bonding acceptors from each O3 aqua ligand (indicated by black dashed lines in Fig. 2), O3—H3A···O1<sup>vii</sup> and O3—H3B···O1<sup>v</sup> [symmetry codes: (v)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ; (vii) 2 - x, 2 - y, 1 - z]. Four similar hydrogen-bonding ring motifs A' [ $N_4 = R_4^2(8)$ ] are observed, together with two new patterns B [ $N_2 = R_2^2(8)$ ]. Thus, the [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations are connected by these O—H···O hydrogen bonds to the anions, forming a three-dimensional supramolecular architecture, as shown in Fig. 3. The relevant hydrogen-bonding geometrical details are listed in Table 2; these values are in the normal range for hydrogen-bonding interactions (Desiraju & Steiner, 1999). Examination of this structure with PLATON (Spek, 2003) indicates that there are no solvent-accessible voids in the crystal structure of (I).

## Experimental

Isonicotinic acid *N*-oxide (0.139 g, 1 mmol) was completely dissolved in methanol (20 ml) with stirring and heating. A solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.119 g, 0.5 mmol) in methanol (10 ml) was added dropwise and the solution turned orange. N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> (2 ml) was then added dropwise to raise the pH to about 7 and the solution turned pink. After filtering the solution, it was left to stand at room temperature. Pink block-like single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent over a period of one week (yield: 60%). Analysis calculated for the title compound: C 32.52, H 4.55, N 6.32%; found: C 32.18, H 4.67, N 6.11%.

## Crystal data

[Co(H<sub>2</sub>O)<sub>6</sub>](C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub>)<sub>2</sub>  
 $M_r = 443.23$   
 Monoclinic,  $C2/m$   
 $a = 11.425$  (4) Å  
 $b = 9.780$  (4) Å  
 $c = 7.726$  (3) Å  
 $\beta = 90.967$  (6)°  
 $V = 863.2$  (6) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.705$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 756 reflections  
 $\theta = 2.7$ – $28.0$ °  
 $\mu = 1.06$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, pink  
 0.28 × 0.20 × 0.12 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.688$ ,  $T_{\max} = 0.880$   
 2775 measured reflections

1086 independent reflections  
 1061 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$   
 $\theta_{\text{max}} = 28.0$ °  
 $h = -8 \rightarrow 13$   
 $k = -11 \rightarrow 9$   
 $l = -9 \rightarrow 9$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 2.5192P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.01$	$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
1086 reflections	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
72 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0032 (9)

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Co1—O3	2.0378 (18)	C4—O1 <sup>i</sup>	1.240 (2)
Co1—O4	2.059 (3)	N1—O2	1.320 (3)
O3—Co1—O3 <sup>i</sup>	86.05 (13)	O3—Co1—O4 <sup>iii</sup>	91.13 (9)
O3—Co1—O3 <sup>ii</sup>	93.95 (13)	O3—Co1—O4	88.87 (9)

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

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4B $\cdots$ N1 <sup>iii</sup>	0.85	2.67	3.495 (4)	163
O4—H4B $\cdots$ O2 <sup>iii</sup>	0.85	1.76	2.603 (4)	172
O4—H4A $\cdots$ O2 <sup>iv</sup>	0.85	1.90	2.715 (4)	161
O3—H3B $\cdots$ O1 <sup>v</sup>	0.84	1.89	2.721 (3)	169
O3—H3A $\cdots$ O1 <sup>vi</sup>	0.85	1.82	2.664 (2)	178

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

Although all the H atoms were visible in difference maps, they were finally placed in geometrically calculated positions, and included in the final refinement in the riding-model approximation; O—H = 0.84–0.85  $\text{\AA}$ , C—H = 0.93  $\text{\AA}$ , and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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