

# Diaquabis(*N,N*-diethylnicotinamide- $\kappa$ N<sup>1</sup>)bis[4-(dimethylamino)benzoato- $\kappa$ O]cobalt(II)

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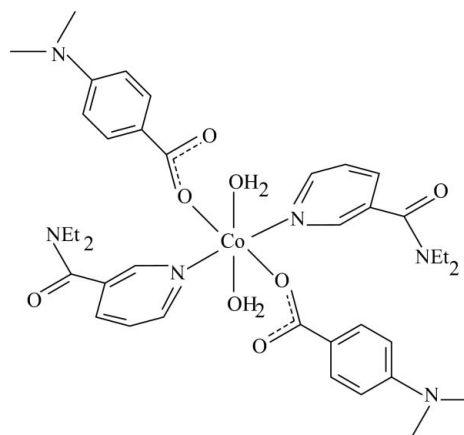
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.031;  $wR$  factor = 0.081; data-to-parameter ratio = 19.2.

The title  $\text{Co}^{\text{II}}$  complex,  $[\text{Co}(\text{C}_9\text{H}_{10}\text{NO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$ , is centrosymmetric. It contains two dimethylamino-benzoate (DMAB) and two diethylnicotinamide (DNA) ligands and two water molecules, all of them being monodentate. The four O atoms in the equatorial plane around the Co atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two pyridine N atoms of DNA ligands with the Co–N distance of 2.1519 (11) Å in the axial positions. The Co atom is displaced out of the least-squares plane of the carboxylate group by  $-0.781$  (1) Å. The dihedral angle between the carboxylate group and the adjacent benzene ring is  $5.05$  (7)°, while the pyridine and benzene rings are oriented at a dihedral angle of  $71.48$  (5)°. In the crystal structure, intermolecular O–H...O and C–H...O hydrogen bonds link the molecules into a three-dimensional network. Two weak C–H... $\pi$  interactions are also present.

## Related literature

For general background, see: Bigoli *et al.* (1972); Krishnamachari (1974). For related structures, see: Hökelek & Necefoğlu (2007); Sertçelik *et al.* (2009).



## Experimental

### Crystal data

$[\text{Co}(\text{C}_9\text{H}_{10}\text{NO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$   
 $M_r = 779.79$   
 Monoclinic,  $P2_1/c$   
 $a = 6.5184$  (1) Å  
 $b = 20.4829$  (3) Å  
 $c = 14.6481$  (2) Å

$\beta = 98.492$  (1)°  
 $V = 1934.31$  (5) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.50$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.42 \times 0.22 \times 0.12$  mm

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2005)  
 $T_{\text{min}} = 0.817$ ,  $T_{\text{max}} = 0.942$

18749 measured reflections  
 4821 independent reflections  
 4137 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.081$   
 $S = 1.05$   
 4821 reflections  
 251 parameters  
 3 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.30$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$         | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|------------------------------|--------------|--------------------|-------------|----------------------|
| O4–H41...O2 <sup>i</sup>     | 0.908 (16)   | 1.777 (15)         | 2.6621 (14) | 164.0 (16)           |
| O4–H42...O2 <sup>ii</sup>    | 0.907 (16)   | 1.898 (15)         | 2.7802 (14) | 163.4 (14)           |
| C9–H9...O3 <sup>iii</sup>    | 0.95         | 2.41               | 3.3447 (17) | 168                  |
| C19–H19A...O3 <sup>iv</sup>  | 0.98         | 2.47               | 3.403 (2)   | 160                  |
| C15–H15A...Cg2 <sup>v</sup>  | 0.98         | 2.86               | 3.734 (2)   | 148                  |
| C18–H18B...Cg1 <sup>vi</sup> | 0.98         | 2.86               | 3.7907 (19) | 158                  |

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x - 1, y, z$ ; (iii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iv)  $x, y, z - 1$ ; (v)  $x + 1, y, z$ ; (vi)  $-x + 1, -y + 1, -z$ . Cg1 and Cg2 are the centroids of the C2–C7 and N1/C8–C12 rings, respectively.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2578).

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**supplementary materials**

*Acta Cryst.* (2009). E65, m1051-m1052 [ doi:10.1107/S1600536809030980 ]

## Diaquabis(*N,N*-diethylnicotinamide- $\kappa N^1$ )bis[4-(dimethylamino)benzoato- $\kappa O$ ]cobalt(II)

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### Comment

As a part of our ongoing investigation on transition metal complexes of nicotinamide (NA), one form of niacin (Krishnamachari, 1974), and/or the nicotinic acid derivative *N,N*-diethylnicotinamide (DENA), an important respiratory stimulant (Bigoli *et al.*, 1972), the title compound was synthesized and its crystal structure is reported herein.

The title compound is a monomeric complex, with Co<sup>II</sup> ion on a centre of symmetry, consisting of two DENA and two dimethylaminobenzoate (DMAB) ligands and two water molecules. The structures of similar DENA and/or NA complexes of Co<sup>II</sup> ion, [Co(C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Sertçelik *et al.*, 2009) and [Co(C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Hökelek & Necefoglu, 2007) have also been determined.

In the title compound, all ligands are monodentate. The four O atoms (O1, O4, and the symmetry-related atoms, O1', O4') in the equatorial plane around the Co atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two pyridine N atoms (N1, N1') of the DENA ligands at 2.1519 (11) Å from the Co atom in the axial positions (Fig. 1). The average Co—O bond length is 2.0955 (10) Å and the Co atom is displaced out of the least-squares plane of the carboxylate group (O1/C1/O2) by -0.781 (1) Å. The dihedral angle between the planar carboxylate group and the benzene ring A (C2—C7) is 5.05 (7)°, while that between rings A and B (N1/C8—C12) is 71.48 (5)°.

In the crystal structure, intermolecular O—H...O and C—H...O hydrogen bonds (Table 1) link the molecules into a three-dimensional network, in which they may be effective in the stabilization of the structure. Two weak C—H... $\pi$  interactions (Table 1) are also found.

### Experimental

The title compound was prepared by the reaction of CoSO<sub>4</sub>·7H<sub>2</sub>O (1.41 g, 5 mmol) in H<sub>2</sub>O (50 ml) and DENA (1.78 g, 10 mmol) in H<sub>2</sub>O (50 ml) with sodium *p*-dimethylaminobenzoate (1.88 g, 10 mmol) in H<sub>2</sub>O (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for one week, giving red single crystals.

### Refinement

Atoms H41 and H42 (for H<sub>2</sub>O) were located in difference Fourier map and refined isotropically, with restrains of O4—H41 = 0.908 (13), O4—H42 = 0.907 (14) Å and H41—O4—H42 = 106.6 (14)°. The remaining H atoms were positioned geometrically with C—H = 0.95, 0.99 and 0.98 Å, for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$ , where  $x = 1.5$  for methyl H and  $x = 1.2$  for all other H atoms.

## Figures

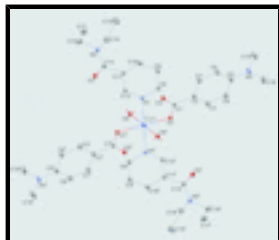


Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are generated by the symmetry operator: (')  $-x, -y, -z$ .

## Diaquabis(*N,N*-diethylnicotinamide- $\kappa N^1$ )bis[4-(dimethylamino)benzoato- $\kappa O$ ]cobalt(II)

### Crystal data

$[\text{Co}(\text{C}_9\text{H}_{10}\text{NO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$

$M_r = 779.79$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 6.5184$  (1) Å

$b = 20.4829$  (3) Å

$c = 14.6481$  (2) Å

$\beta = 98.492$  (1)°

$V = 1934.31$  (5) Å<sup>3</sup>

$Z = 2$

$F_{000} = 826$

$D_x = 1.339$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9065 reflections

$\theta = 2.4\text{--}28.3^\circ$

$\mu = 0.50$  mm<sup>-1</sup>

$T = 100$  K

Block, red

$0.42 \times 0.22 \times 0.12$  mm

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100$  K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.817$ ,  $T_{\max} = 0.942$

18749 measured reflections

4821 independent reflections

4137 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 28.3^\circ$

$\theta_{\min} = 1.7^\circ$

$h = -8 \rightarrow 8$

$k = -26 \rightarrow 27$

$l = -19 \rightarrow 19$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.081$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.7829P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$S = 1.05$   $(\Delta/\sigma)_{\max} < 0.001$   
 4821 reflections  $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$   
 251 parameters  $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$   
 3 restraints Extinction correction: none  
 Primary atom site location: structure-invariant direct methods

*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 ( $\text{\AA}^2$ )*

|     | $x$          | $y$         | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| Co1 | 0.5000       | 0.5000      | 0.5000       | 0.01335 (8)                      |
| O1  | 0.54021 (15) | 0.50614 (5) | 0.36270 (6)  | 0.0169 (2)                       |
| O2  | 0.87853 (15) | 0.52883 (5) | 0.37060 (7)  | 0.0196 (2)                       |
| O3  | 0.76748 (16) | 0.28543 (5) | 0.75280 (7)  | 0.0219 (2)                       |
| O4  | 0.20770 (15) | 0.45517 (5) | 0.45875 (7)  | 0.0182 (2)                       |
| H41 | 0.162 (3)    | 0.4543 (8)  | 0.5144 (10)  | 0.023*                           |
| H42 | 0.114 (3)    | 0.4789 (9)  | 0.4204 (11)  | 0.023*                           |
| N1  | 0.63544 (17) | 0.40399 (6) | 0.51022 (8)  | 0.0155 (2)                       |
| N2  | 1.09307 (19) | 0.27891 (6) | 0.71639 (8)  | 0.0191 (2)                       |
| N3  | 0.6955 (2)   | 0.39432 (7) | -0.02756 (9) | 0.0301 (3)                       |
| C1  | 0.7089 (2)   | 0.50704 (6) | 0.32932 (9)  | 0.0151 (3)                       |
| C2  | 0.7037 (2)   | 0.47929 (7) | 0.23444 (9)  | 0.0163 (3)                       |
| C3  | 0.5191 (2)   | 0.45744 (7) | 0.18361 (10) | 0.0208 (3)                       |
| H3  | 0.3938       | 0.4610      | 0.2092       | 0.025*                           |
| C4  | 0.5143 (2)   | 0.43063 (8) | 0.09649 (10) | 0.0241 (3)                       |
| H4  | 0.3857       | 0.4170      | 0.0628       | 0.029*                           |
| C5  | 0.6975 (2)   | 0.42340 (7) | 0.05741 (10) | 0.0224 (3)                       |
| C6  | 0.8826 (2)   | 0.44567 (8) | 0.10906 (10) | 0.0235 (3)                       |
| H6  | 1.0089       | 0.4418      | 0.0844       | 0.028*                           |
| C7  | 0.8845 (2)   | 0.47324 (7) | 0.19537 (10) | 0.0206 (3)                       |
| H7  | 1.0118       | 0.4883      | 0.2286       | 0.025*                           |
| C8  | 0.6312 (2)   | 0.36554 (7) | 0.43557 (9)  | 0.0172 (3)                       |
| H8  | 0.5692       | 0.3820      | 0.3774       | 0.021*                           |
| C9  | 0.7131 (2)   | 0.30305 (7) | 0.43964 (9)  | 0.0192 (3)                       |
| H9  | 0.7071       | 0.2772      | 0.3855       | 0.023*                           |
| C10 | 0.8040 (2)   | 0.27915 (7) | 0.52449 (10) | 0.0186 (3)                       |

## supplementary materials

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|      |            |              |               |            |
|------|------------|--------------|---------------|------------|
| H10  | 0.8615     | 0.2365       | 0.5295        | 0.022*     |
| C11  | 0.8101 (2) | 0.31852 (7)  | 0.60242 (9)   | 0.0153 (3) |
| C12  | 0.7227 (2) | 0.38028 (7)  | 0.59202 (9)   | 0.0150 (3) |
| H12  | 0.7248     | 0.4069       | 0.6452        | 0.018*     |
| C13  | 0.8903 (2) | 0.29329 (6)  | 0.69730 (9)   | 0.0160 (3) |
| C14  | 1.2464 (2) | 0.29630 (8)  | 0.65634 (11)  | 0.0251 (3) |
| H14A | 1.3649     | 0.3187       | 0.6937        | 0.030*     |
| H14B | 1.1825     | 0.3273       | 0.6086        | 0.030*     |
| C15  | 1.3266 (3) | 0.23750 (10) | 0.60918 (14)  | 0.0388 (4) |
| H15A | 1.4134     | 0.2523       | 0.5640        | 0.058*     |
| H15B | 1.2091     | 0.2124       | 0.5776        | 0.058*     |
| H15C | 1.4089     | 0.2099       | 0.6555        | 0.058*     |
| C16  | 1.1660 (2) | 0.24446 (8)  | 0.80324 (11)  | 0.0248 (3) |
| H16A | 1.1023     | 0.2647       | 0.8537        | 0.030*     |
| H16B | 1.3183     | 0.2495       | 0.8183        | 0.030*     |
| C17  | 1.1129 (3) | 0.17229 (8)  | 0.79793 (12)  | 0.0311 (4) |
| H17A | 1.1568     | 0.1520       | 0.8582        | 0.047*     |
| H17B | 1.1848     | 0.1513       | 0.7515        | 0.047*     |
| H17C | 0.9628     | 0.1670       | 0.7806        | 0.047*     |
| C18  | 0.5005 (3) | 0.37807 (9)  | -0.08350 (11) | 0.0334 (4) |
| H18A | 0.5267     | 0.3611       | -0.1432       | 0.050*     |
| H18B | 0.4139     | 0.4173       | -0.0933       | 0.050*     |
| H18C | 0.4287     | 0.3448       | -0.0519       | 0.050*     |
| C19  | 0.8816 (3) | 0.39299 (9)  | -0.06991 (12) | 0.0361 (4) |
| H19A | 0.8523     | 0.3719       | -0.1305       | 0.054*     |
| H19B | 0.9896     | 0.3685       | -0.0305       | 0.054*     |
| H19C | 0.9295     | 0.4378       | -0.0775       | 0.054*     |

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

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$    | $U^{13}$    | $U^{23}$     |
|-----|--------------|--------------|--------------|-------------|-------------|--------------|
| Co1 | 0.01466 (13) | 0.01570 (13) | 0.00949 (12) | 0.00226 (9) | 0.00115 (9) | -0.00087 (9) |
| O1  | 0.0169 (5)   | 0.0216 (5)   | 0.0122 (4)   | 0.0031 (4)  | 0.0019 (4)  | -0.0006 (4)  |
| O2  | 0.0188 (5)   | 0.0258 (5)   | 0.0138 (5)   | -0.0010 (4) | 0.0015 (4)  | -0.0012 (4)  |
| O3  | 0.0251 (5)   | 0.0259 (5)   | 0.0155 (5)   | 0.0055 (4)  | 0.0056 (4)  | 0.0033 (4)   |
| O4  | 0.0183 (5)   | 0.0221 (5)   | 0.0137 (5)   | 0.0017 (4)  | 0.0008 (4)  | -0.0024 (4)  |
| N1  | 0.0156 (5)   | 0.0179 (6)   | 0.0130 (5)   | 0.0010 (4)  | 0.0020 (4)  | -0.0005 (4)  |
| N2  | 0.0193 (6)   | 0.0192 (6)   | 0.0179 (6)   | 0.0021 (5)  | 0.0001 (5)  | 0.0018 (5)   |
| N3  | 0.0372 (8)   | 0.0363 (8)   | 0.0173 (6)   | 0.0003 (6)  | 0.0056 (6)  | -0.0098 (6)  |
| C1  | 0.0194 (6)   | 0.0140 (6)   | 0.0118 (6)   | 0.0035 (5)  | 0.0016 (5)  | 0.0023 (5)   |
| C2  | 0.0200 (7)   | 0.0168 (6)   | 0.0121 (6)   | 0.0016 (5)  | 0.0028 (5)  | 0.0014 (5)   |
| C3  | 0.0207 (7)   | 0.0245 (7)   | 0.0180 (7)   | -0.0003 (6) | 0.0050 (6)  | -0.0027 (6)  |
| C4  | 0.0243 (8)   | 0.0290 (8)   | 0.0180 (7)   | -0.0020 (6) | 0.0000 (6)  | -0.0041 (6)  |
| C5  | 0.0319 (8)   | 0.0204 (7)   | 0.0153 (7)   | 0.0009 (6)  | 0.0052 (6)  | -0.0018 (5)  |
| C6  | 0.0248 (7)   | 0.0281 (8)   | 0.0193 (7)   | 0.0007 (6)  | 0.0091 (6)  | -0.0032 (6)  |
| C7  | 0.0205 (7)   | 0.0250 (7)   | 0.0164 (7)   | 0.0002 (6)  | 0.0034 (5)  | -0.0010 (6)  |
| C8  | 0.0185 (7)   | 0.0204 (7)   | 0.0126 (6)   | -0.0010 (5) | 0.0017 (5)  | -0.0007 (5)  |
| C9  | 0.0235 (7)   | 0.0194 (7)   | 0.0148 (6)   | -0.0003 (5) | 0.0035 (5)  | -0.0048 (5)  |

|     |             |             |             |             |             |             |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| C10 | 0.0213 (7)  | 0.0162 (6)  | 0.0186 (7)  | 0.0025 (5)  | 0.0038 (5)  | -0.0021 (5) |
| C11 | 0.0150 (6)  | 0.0184 (6)  | 0.0128 (6)  | 0.0001 (5)  | 0.0030 (5)  | 0.0003 (5)  |
| C12 | 0.0153 (6)  | 0.0171 (6)  | 0.0128 (6)  | -0.0001 (5) | 0.0022 (5)  | -0.0019 (5) |
| C13 | 0.0204 (7)  | 0.0121 (6)  | 0.0150 (6)  | 0.0019 (5)  | 0.0008 (5)  | -0.0017 (5) |
| C14 | 0.0182 (7)  | 0.0306 (8)  | 0.0264 (8)  | -0.0030 (6) | 0.0027 (6)  | -0.0001 (6) |
| C15 | 0.0240 (8)  | 0.0493 (11) | 0.0455 (11) | -0.0045 (8) | 0.0126 (8)  | -0.0178 (9) |
| C16 | 0.0257 (8)  | 0.0248 (8)  | 0.0210 (7)  | 0.0051 (6)  | -0.0058 (6) | 0.0027 (6)  |
| C17 | 0.0355 (9)  | 0.0238 (8)  | 0.0331 (9)  | 0.0070 (7)  | 0.0016 (7)  | 0.0064 (7)  |
| C18 | 0.0487 (11) | 0.0339 (9)  | 0.0168 (7)  | -0.0074 (8) | 0.0026 (7)  | -0.0067 (6) |
| C19 | 0.0560 (12) | 0.0315 (9)  | 0.0251 (8)  | -0.0078 (8) | 0.0200 (8)  | -0.0086 (7) |

*Geometric parameters (Å, °)*

|                                      |             |            |             |
|--------------------------------------|-------------|------------|-------------|
| Co1—O1                               | 2.0701 (9)  | C7—H7      | 0.9500      |
| Co1—O1 <sup>i</sup>                  | 2.0701 (9)  | C8—H8      | 0.9500      |
| Co1—O4                               | 2.1209 (10) | C9—C8      | 1.385 (2)   |
| Co1—O4 <sup>i</sup>                  | 2.1209 (10) | C9—C10     | 1.385 (2)   |
| Co1—N1                               | 2.1519 (11) | C9—H9      | 0.9500      |
| Co1—N1 <sup>i</sup>                  | 2.1519 (11) | C10—C11    | 1.3934 (18) |
| O1—C1                                | 1.2676 (16) | C10—H10    | 0.9500      |
| O2—C1                                | 1.2611 (17) | C11—C12    | 1.3863 (19) |
| O3—C13                               | 1.2332 (17) | C12—H12    | 0.9500      |
| O4—H41                               | 0.908 (13)  | C13—C11    | 1.5026 (18) |
| O4—H42                               | 0.907 (14)  | C14—H14A   | 0.9900      |
| N1—C8                                | 1.3445 (17) | C14—H14B   | 0.9900      |
| N1—C12                               | 1.3393 (17) | C15—C14    | 1.519 (2)   |
| N2—C13                               | 1.3423 (18) | C15—H15A   | 0.9800      |
| N2—C14                               | 1.4696 (19) | C15—H15B   | 0.9800      |
| N2—C16                               | 1.4710 (18) | C15—H15C   | 0.9800      |
| N3—C5                                | 1.3782 (18) | C16—H16A   | 0.9900      |
| N3—C18                               | 1.446 (2)   | C16—H16B   | 0.9900      |
| N3—C19                               | 1.442 (2)   | C17—C16    | 1.518 (2)   |
| C2—C1                                | 1.4973 (18) | C17—H17A   | 0.9800      |
| C3—C2                                | 1.392 (2)   | C17—H17B   | 0.9800      |
| C3—H3                                | 0.9500      | C17—H17C   | 0.9800      |
| C4—C3                                | 1.385 (2)   | C18—H18A   | 0.9800      |
| C4—C5                                | 1.406 (2)   | C18—H18B   | 0.9800      |
| C4—H4                                | 0.9500      | C18—H18C   | 0.9800      |
| C6—C7                                | 1.383 (2)   | C19—H19A   | 0.9800      |
| C6—C5                                | 1.403 (2)   | C19—H19B   | 0.9800      |
| C6—H6                                | 0.9500      | C19—H19C   | 0.9800      |
| C7—C2                                | 1.3896 (19) |            |             |
| O1 <sup>i</sup> —Co1—O1              | 180.0       | C8—C9—C10  | 118.46 (13) |
| O1—Co1—O4                            | 89.24 (4)   | C8—C9—H9   | 120.8       |
| O1 <sup>i</sup> —Co1—O4              | 90.76 (4)   | C10—C9—H9  | 120.8       |
| O1—Co1—O4 <sup>i</sup>               | 90.76 (4)   | C9—C10—C11 | 119.15 (13) |
| O1 <sup>i</sup> —Co1—O4 <sup>i</sup> | 89.24 (4)   | C9—C10—H10 | 120.4       |



## supplementary materials

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|                                      |             |               |             |
|--------------------------------------|-------------|---------------|-------------|
| O1—Co1—N1                            | 90.78 (4)   | C11—C10—H10   | 120.4       |
| O1 <sup>i</sup> —Co1—N1              | 89.22 (4)   | C10—C11—C13   | 121.49 (12) |
| O1—Co1—N1 <sup>i</sup>               | 89.22 (4)   | C12—C11—C10   | 118.47 (12) |
| O1 <sup>i</sup> —Co1—N1 <sup>i</sup> | 90.78 (4)   | C12—C11—C13   | 119.79 (12) |
| O4—Co1—O4 <sup>i</sup>               | 180.00 (5)  | N1—C12—C11    | 122.85 (12) |
| O4—Co1—N1                            | 88.07 (4)   | N1—C12—H12    | 118.6       |
| O4 <sup>i</sup> —Co1—N1              | 91.93 (4)   | C11—C12—H12   | 118.6       |
| O4—Co1—N1 <sup>i</sup>               | 91.93 (4)   | O3—C13—N2     | 123.31 (13) |
| O4 <sup>i</sup> —Co1—N1 <sup>i</sup> | 88.07 (4)   | O3—C13—C11    | 118.90 (12) |
| N1—Co1—N1 <sup>i</sup>               | 180.0       | N2—C13—C11    | 117.76 (12) |
| C1—O1—Co1                            | 128.10 (9)  | N2—C14—C15    | 112.96 (14) |
| Co1—O4—H41                           | 98.7 (11)   | N2—C14—H14A   | 109.0       |
| Co1—O4—H42                           | 116.0 (11)  | N2—C14—H14B   | 109.0       |
| H42—O4—H41                           | 106.6 (14)  | C15—C14—H14A  | 109.0       |
| C8—N1—Co1                            | 121.32 (9)  | C15—C14—H14B  | 109.0       |
| C12—N1—Co1                           | 120.62 (9)  | H14A—C14—H14B | 107.8       |
| C12—N1—C8                            | 118.05 (12) | C14—C15—H15A  | 109.5       |
| C13—N2—C14                           | 123.91 (12) | C14—C15—H15B  | 109.5       |
| C13—N2—C16                           | 117.90 (12) | C14—C15—H15C  | 109.5       |
| C14—N2—C16                           | 118.19 (12) | H15A—C15—H15B | 109.5       |
| C5—N3—C18                            | 120.12 (14) | H15A—C15—H15C | 109.5       |
| C5—N3—C19                            | 120.00 (14) | H15B—C15—H15C | 109.5       |
| C19—N3—C18                           | 118.49 (13) | N2—C16—C17    | 112.39 (13) |
| O1—C1—C2                             | 116.77 (12) | N2—C16—H16A   | 109.1       |
| O2—C1—O1                             | 124.70 (12) | N2—C16—H16B   | 109.1       |
| O2—C1—C2                             | 118.53 (12) | C17—C16—H16A  | 109.1       |
| C3—C2—C1                             | 121.19 (12) | C17—C16—H16B  | 109.1       |
| C7—C2—C1                             | 120.78 (13) | H16A—C16—H16B | 107.9       |
| C7—C2—C3                             | 118.01 (13) | C16—C17—H17A  | 109.5       |
| C2—C3—H3                             | 119.3       | C16—C17—H17B  | 109.5       |
| C4—C3—C2                             | 121.36 (14) | C16—C17—H17C  | 109.5       |
| C4—C3—H3                             | 119.3       | H17A—C17—H17B | 109.5       |
| C3—C4—C5                             | 120.77 (14) | H17A—C17—H17C | 109.5       |
| C3—C4—H4                             | 119.6       | H17B—C17—H17C | 109.5       |
| C5—C4—H4                             | 119.6       | N3—C18—H18A   | 109.5       |
| N3—C5—C4                             | 121.18 (14) | N3—C18—H18B   | 109.5       |
| N3—C5—C6                             | 121.37 (14) | N3—C18—H18C   | 109.5       |
| C6—C5—C4                             | 117.44 (13) | H18A—C18—H18B | 109.5       |
| C5—C6—H6                             | 119.5       | H18A—C18—H18C | 109.5       |
| C7—C6—C5                             | 121.10 (14) | H18B—C18—H18C | 109.5       |
| C7—C6—H6                             | 119.5       | N3—C19—H19A   | 109.5       |
| C2—C7—H7                             | 119.3       | N3—C19—H19B   | 109.5       |
| C6—C7—C2                             | 121.30 (14) | N3—C19—H19C   | 109.5       |
| C6—C7—H7                             | 119.4       | H19A—C19—H19B | 109.5       |
| N1—C8—C9                             | 123.02 (13) | H19A—C19—H19C | 109.5       |
| N1—C8—H8                             | 118.5       | H19B—C19—H19C | 109.5       |
| C9—C8—H8                             | 118.5       |               |             |

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

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

| $D-H\cdots A$                       | $D-H$      | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|------------|-------------|-------------|---------------|
| O4—H41 $\cdots$ O2 <sup>i</sup>     | 0.908 (16) | 1.777 (15)  | 2.6621 (14) | 164.0 (16)    |
| O4—H42 $\cdots$ O2 <sup>ii</sup>    | 0.907 (16) | 1.898 (15)  | 2.7802 (14) | 163.4 (14)    |
| C9—H9 $\cdots$ O3 <sup>iii</sup>    | 0.95       | 2.41        | 3.3447 (17) | 168           |
| C19—H19A $\cdots$ O3 <sup>iv</sup>  | 0.98       | 2.47        | 3.403 (2)   | 160           |
| C15—H15A $\cdots$ Cg2 <sup>v</sup>  | 0.98       | 2.86        | 3.734 (2)   | 148           |
| C18—H18B $\cdots$ Cg1 <sup>vi</sup> | 0.98       | 2.86        | 3.7907 (19) | 158           |

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

Fig. 1

