



# Crystal structure of diaquabis(*N,N*-diethylnicotinamide- $\kappa N^1$ )bis(2,4,6-trimethylbenzoato- $\kappa O^1$ )cobalt(II)

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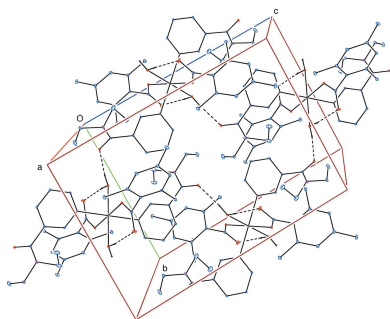
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The centrosymmetric molecule in the monomeric title cobalt complex,  $[\text{Co}(\text{C}_{10}\text{H}_{11}\text{O}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$ , contains two water molecules, two 2,4,6-trimethylbenzoate (TMB) ligands and two diethylnicotinamide (DENA) ligands. All ligands coordinate to the  $\text{Co}^{\text{II}}$  atom in a monodentate fashion. The four O atoms around the  $\text{Co}^{\text{II}}$  atom form a slightly distorted square-planar arrangement, with the distorted octahedral coordination sphere completed by two pyridine N atoms of the DENA ligands. The dihedral angle between the planar carboxylate group and the adjacent benzene ring is  $84.2(4)^\circ$ , while the benzene and pyridine rings are oriented at a dihedral angle of  $38.87(10)^\circ$ . The water molecules exhibit both intramolecular (to the non-coordinating carboxylate O atom) and intermolecular (to the amide carbonyl O atom)  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. The latter lead to the formation of layers parallel to (100), enclosing  $R_4^4(32)$  ring motifs. These layers are further linked *via* weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, resulting in a three-dimensional network. One of the two ethyl groups of the DENA ligand is disordered over two sets of sites with an occupancy ratio of 0.490 (13):0.510 (13).

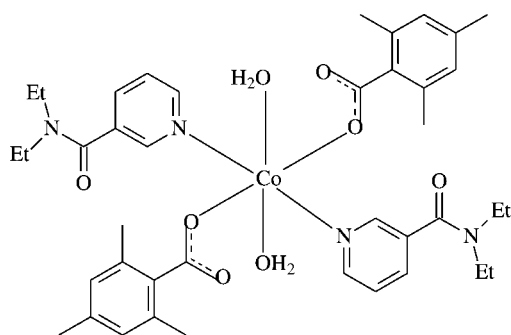
## 1. Chemical context

*N,N*-Diethylnicotinamide (DENA), a nicotinic acid derivative, is an important respiratory stimulant (Bigoli *et al.*, 1972). The crystal structure of the complex  $[\text{Co}(\text{CH}_3\text{CO}_2)_2(\text{DENA})_2(\text{H}_2\text{O})_2]$  [(II); Mikelashvili, 1982] is isostructural with the analogous Ni, Mn, Zn and Cd complexes (Sergienko *et al.*, 1980). The structures of some complexes obtained from the reactions of transition metal(II) ions with DENA as ligand, *e.g.*  $[\text{Cu}_2(\text{DENA})_2(\text{C}_6\text{H}_5\text{COO})_4]$  [(III); Hökelek *et al.*, 1995],  $[\text{Zn}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{DENA})_2]\cdot 2\text{H}_2\text{O}$  [(IV); Hökelek & Necefoğlu, 1996],  $[\text{Mn}(\text{DENA})_2(\text{NCS})_2]$  [(V); Bigoli *et al.*, 1973a],  $[\text{Zn}(\text{DENA})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$  [(VI); Bigoli *et al.*, 1973b] and  $[\text{Cd}(\text{DENA})(\text{SCN})_2]$  [(VII); Bigoli *et al.*, 1972], have been determined previously. In complex (V), DENA is a bidentate ligand, while in complexes (III), (IV), (VI) and (VII), DENA is a monodentate ligand. In complex (III), the benzoate ion acts as a bidentate ligand, whereas in complex (IV), two of the benzoate ions act as monodentate ligands, while the other two are bidentate, bridging the two  $\text{Zn}^{\text{II}}$  atoms.

The structure–function–coordination relationships of aryl-carboxylate ions in  $\text{Co}^{\text{II}}$  complexes of benzoic acid derivatives may change depending on the nature and position of the



substituted groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the pH conditions and temperature of synthesis (Shnulin *et al.*, 1981; Nadzhafov *et al.*, 1981; Antsyshkina *et al.*, 1980; Adiwidjaja *et al.*, 1978). When pyridine or its derivatives are used instead of water molecules, the resulting structure is completely different (Catterick *et al.*, 1974). In this context, we synthesized a Co<sup>II</sup>-containing compound with 2,4,6-trimethylbenzoate (TMB) and DENA ligands, namely diaquabis(*N,N*-diethylnicotinamide- $\kappa N^1$ )bis(2,4,6-trimethylbenzoato- $\kappa O^1$ )-cobalt(II), [Co(DENA)<sub>2</sub>(TMB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and report herein its crystal structure.



## 2. Structural commentary

The asymmetric unit of the mononuclear title complex contains one Co<sup>II</sup> atom located on an inversion centre, one TMB ligand, one DENA ligand and one water molecule, with all ligands coordinating to the metal ion in a monodentate fashion (Fig. 1).

The two carboxylate O atoms (O2 and O2<sup>i</sup>) of the two symmetry-related TMB anions and the two symmetry-related

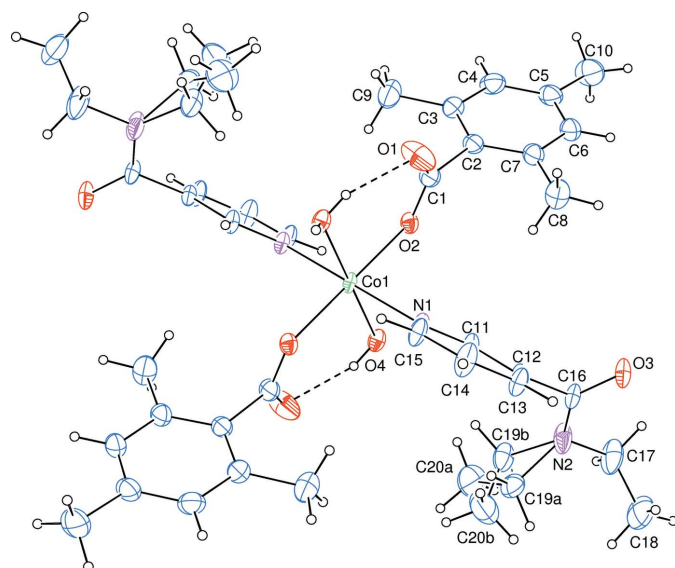


Figure 1

The molecular structure of the title complex with the atom-numbering scheme for the asymmetric unit. Unlabelled atoms are generated by symmetry code (1 - *x*, 1 - *y*, -*z*). Displacement ellipsoids are drawn at the 40% probability level. Intramolecular O—H...O hydrogen bonds are shown as dashed lines.

Table 1  
Selected bond lengths (Å).

Co1—O2	2.0336 (18)	Co1—N1	2.1913 (19)
Co1—O4	2.1561 (18)		

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>
O4—H1W...O1 <sup>i</sup>	0.80 (6)	1.87 (6)	2.634 (3)	160 (7)
O4—H2W...O3 <sup>ii</sup>	0.76 (7)	2.10 (7)	2.850 (3)	170 (7)
C10—H10A...O1 <sup>iii</sup>	0.96	2.43	3.365 (6)	165
C15—H15...O3 <sup>iv</sup>	0.93	2.50	3.420 (4)	172

Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

water O atoms (O4 and O4<sup>i</sup>) form a slightly distorted square-planar arrangement around the Co1 atom. The slightly distorted octahedral coordination sphere is completed by the two pyridine N atoms (N1 and N1<sup>i</sup>) of the two symmetry-related DENA ligands in axial positions [symmetry code: (i) 1 - *x*, 1 - *y*, -*z*] (Fig. 1). The Co—O bond lengths for water oxygens atoms are by *ca* 0.1 Å longer than those involving the benzoate oxygen atoms. The Co—N bond length is the longest in the CoO<sub>4</sub>N<sub>2</sub> octahedron (Table 1). The deviation of the O—Co—O and O—Co—N bond angles from ideal values is minute [range 87.66 (7) to 92.34 (7)° for *cis* angles; all *trans* angles are 180° due to symmetry]. The near equalities of the C1—O1 [1.245 (4) Å] and C1—O2 [1.254 (4) Å] bonds in the carboxylate group indicate delocalized bonding arrangements, rather than localized single and double bonds. The dihedral angle between the planar carboxylate group (O1/O2/C1) and the adjacent benzene ring *A* (C2—C7) is 84.2 (4)°, while the benzene (*A*) and pyridine rings (*B*) (N1/C11—C15) are inclined by a dihedral angle of 38.87 (10)°.

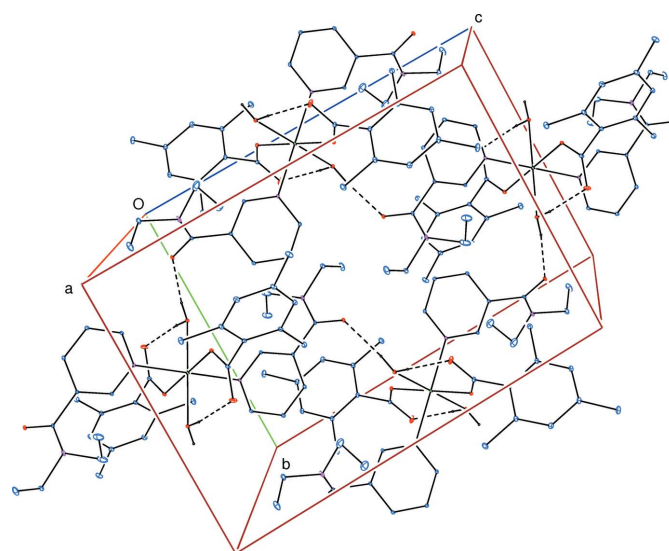


Figure 2

Part of the crystal structure viewed approximately down [100]. Intra- and intermolecular O—H...O hydrogen bonds, shown as dashed lines, enclose *R*<sub>4</sub><sup>4</sup>(32) ring motifs. Only one part of the disordered group and only H atoms involved in hydrogen bonding have been included for clarity.

### 3. Supramolecular features

Intramolecular O—H<sub>w</sub>···O<sub>c</sub> (w = water, c = non-coordinating carboxylate O atom) hydrogen bonds (Table 2) link the water ligands to the TMB anions (Fig. 1). The other water H atom is involved in intermolecular O—H<sub>w</sub>···O<sub>DENA</sub> (O<sub>DENA</sub> = carbonyl O atom of *N,N*-diethylnicotinamide) hydrogen bonds (Table 2), leading to the formation of layers parallel to (100) enclosing *R*<sub>4</sub><sup>4</sup>(32) ring motifs (Fig. 2). The layers are further linked into a three-dimensional network structure *via* weak C—H<sub>TMB</sub>···O<sub>c</sub> (TMB = 2,4,6-trimethylbenzoate) and C—H<sub>DENA</sub>···O<sub>DENA</sub> hydrogen bonds (Table 2), enclosing *R*<sub>2</sub><sup>2</sup>(7) ring motifs (Fig. 3).

### 4. Synthesis and crystallization

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 (100 ml) and *N,N*-diethylnicotinamide (1.78 g, 10 mmol) in H<sub>2</sub>O (10 ml) with sodium 2,4,6-trimethylbenzoate (1.86 g, 10 mmol) in H<sub>2</sub>O (150 ml). The mixture was filtered and set aside to crystallize at ambient temperature for three weeks, giving pink single crystals.

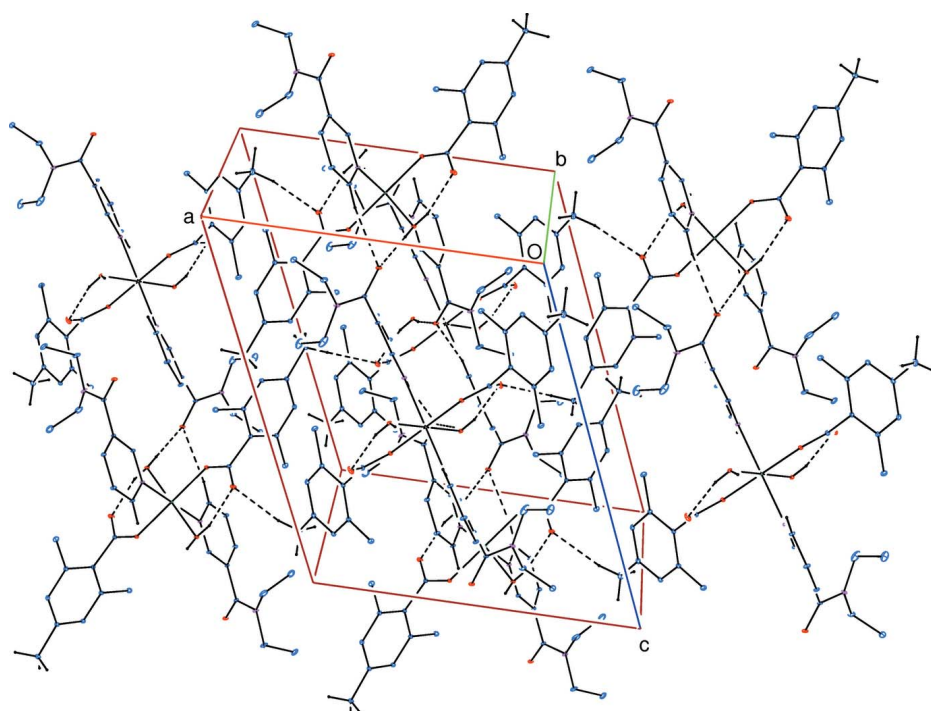
### 5. Refinement

Experimental details including crystal data, data collection and refinement are summarized in Table 3. Atoms H1W and H2W (of the water molecule) were located in a difference Fourier map. Their coordinates were refined freely, with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). C-bound H atoms were positioned

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[Co(C <sub>10</sub> H <sub>11</sub> O <sub>2</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> ]
<i>M</i> <sub>r</sub>	777.80
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.9646 (4), 10.8636 (3), 15.6297 (5)
$\beta$ (°)	111.596 (3)
<i>V</i> (Å <sup>3</sup> )	2046.79 (12)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.47
Crystal size (mm)	0.45 × 0.40 × 0.33
Data collection	
Diffractometer	Bruker SMART BREEZE CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2012)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.754, 0.861
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	42492, 5124, 3701
<i>R</i> <sub>int</sub>	0.041
(sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.670
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.063, 0.155, 1.07
No. of reflections	5124
No. of parameters	270
No. of restraints	42
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.63, -0.39

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).



**Figure 3**

A partial view of the crystal packing of the title compound. The O—H<sub>w</sub>···O<sub>c</sub>, O—H<sub>w</sub>···O<sub>DENA</sub>, C—H<sub>TMB</sub>···O<sub>c</sub> and C—H<sub>DENA</sub>···O<sub>DENA</sub> (w = water, c = carboxylate, DENA = *N,N*-diethylnicotinamide and TMB = 2,4,6-trimethylbenzoate) hydrogen bonds, enclosing *R*<sub>2</sub><sup>2</sup>(7) and *R*<sub>4</sub><sup>4</sup>(32) ring motifs, are shown as dashed lines (see Table 2). Only one part of the disordered group and only H atoms involved in hydrogen bonding have been included for clarity.

geometrically, with C—H = 0.93, 0.96 and 0.97 Å for aromatic, methyl and methylene H atoms, respectively, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$ , where  $k = 1.5$  for methyl H atoms and  $k = 1.2$  for other H atoms. The disordered ethyl group (C19, C20) was refined over two sets of sites with distance restraints and SIMU and DELU restraints (Sheldrick, 2008). The refined occupancy ratio of the two orientations is 0.490 (13):0.510 (13).

### Acknowledgements

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## supporting information

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## Crystal structure of diaquabis(*N,N*-diethylnicotinamide- $\kappa N^1$ )bis(2,4,6-trimethylbenzoato- $\kappa O^1$ )cobalt(II)

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### Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

### Diaquabis(*N,N*-diethylnicotinamide- $\kappa N^1$ )bis(2,4,6-trimethylbenzoato- $\kappa O^1$ )cobalt(II)

#### Crystal data

[Co(C<sub>10</sub>H<sub>11</sub>O<sub>2</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>]

$M_r = 777.80$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.9646$  (4) Å

$b = 10.8636$  (3) Å

$c = 15.6297$  (5) Å

$\beta = 111.596$  (3)°

$V = 2046.79$  (12) Å<sup>3</sup>

$Z = 2$

$F(000) = 826$

$D_x = 1.262$  Mg m<sup>-3</sup>

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

Cell parameters from 9990 reflections

$\theta = 2.3$ – $28.4$ °

$\mu = 0.47$  mm<sup>-1</sup>

$T = 100$  K

Block, translucent light pink

$0.45 \times 0.40 \times 0.33$  mm

#### Data collection

Bruker SMART BREEZE CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2012)

$T_{\min} = 0.754$ ,  $T_{\max} = 0.861$

42492 measured reflections

5124 independent reflections

3701 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 28.5$ °,  $\theta_{\min} = 1.7$ °

$h = -17 \rightarrow 16$

$k = -14 \rightarrow 14$

$l = -20 \rightarrow 20$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.063$

$wR(F^2) = 0.155$

$S = 1.07$

5124 reflections

270 parameters

42 restraints

Primary atom site location: structure-invariant  
direct methods

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

$$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 1.2728P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.63 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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  $F^2 > 2\sigma(F^2)$  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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.5000	0.5000	0.0000	0.03723 (16)	
O1	0.7500 (2)	0.6149 (3)	0.1133 (2)	0.1140 (12)	
O2	0.64234 (15)	0.45260 (17)	0.10503 (11)	0.0476 (4)	
O3	0.47496 (19)	0.62630 (18)	0.39053 (11)	0.0613 (5)	
O4	0.41728 (17)	0.35512 (17)	0.04417 (13)	0.0495 (5)	
H1W	0.358 (6)	0.358 (7)	0.004 (5)	0.201*	
H2W	0.440 (6)	0.290 (6)	0.057 (5)	0.201*	
N1	0.45672 (18)	0.62382 (18)	0.09231 (13)	0.0434 (5)	
N2	0.3331 (3)	0.5092 (3)	0.30486 (19)	0.0929 (12)	
C1	0.7318 (3)	0.5109 (3)	0.1382 (2)	0.0589 (8)	
C2	0.8208 (2)	0.4486 (3)	0.21743 (19)	0.0546 (7)	
C3	0.8883 (3)	0.3599 (3)	0.2011 (2)	0.0684 (9)	
C4	0.9635 (3)	0.2965 (4)	0.2757 (3)	0.0784 (10)	
H4	1.0091	0.2369	0.2654	0.094*	
C5	0.9713 (3)	0.3208 (4)	0.3649 (2)	0.0761 (10)	
C6	0.9055 (3)	0.4105 (4)	0.3785 (2)	0.0713 (9)	
H6	0.9109	0.4279	0.4383	0.086*	
C7	0.8310 (3)	0.4766 (3)	0.3068 (2)	0.0621 (8)	
C8	0.7606 (4)	0.5758 (4)	0.3247 (3)	0.0895 (12)	
H8A	0.7634	0.5690	0.3867	0.134*	
H8B	0.6853	0.5668	0.2827	0.134*	
H8C	0.7882	0.6550	0.3161	0.134*	
C9	0.8814 (4)	0.3334 (5)	0.1040 (3)	0.1066 (15)	
H9A	0.9321	0.2684	0.1052	0.160*	
H9B	0.9005	0.4062	0.0783	0.160*	
H9C	0.8072	0.3087	0.0670	0.160*	
C10	1.0488 (4)	0.2448 (5)	0.4441 (3)	0.1131 (16)	
H10A	1.1133	0.2225	0.4313	0.170*	
H10B	1.0112	0.1717	0.4513	0.170*	
H10C	1.0709	0.2923	0.4998	0.170*	
C11	0.4479 (2)	0.5794 (2)	0.16908 (15)	0.0457 (6)	
H11	0.4627	0.4964	0.1823	0.055*	

C12	0.4181 (2)	0.6499 (2)	0.22983 (15)	0.0425 (6)	
C13	0.4001 (3)	0.7736 (3)	0.21270 (19)	0.0602 (8)	
H13	0.3822	0.8244	0.2531	0.072*	
C14	0.4095 (3)	0.8204 (3)	0.1337 (2)	0.0735 (10)	
H14	0.3980	0.9038	0.1201	0.088*	
C15	0.4357 (3)	0.7430 (3)	0.07530 (18)	0.0574 (7)	
H15	0.4390	0.7755	0.0213	0.069*	
C16	0.4100 (3)	0.5942 (2)	0.31519 (16)	0.0501 (7)	
C17	0.3272 (4)	0.4478 (4)	0.3879 (3)	0.1070 (16)	
H17A	0.3127	0.3608	0.3753	0.128*	
H17B	0.3983	0.4558	0.4381	0.128*	
C18	0.2407 (5)	0.5002 (6)	0.4159 (4)	0.154 (3)	
H18A	0.2431	0.4618	0.4719	0.231*	
H18B	0.1695	0.4862	0.3685	0.231*	
H18C	0.2528	0.5871	0.4258	0.231*	
C19A	0.2227 (8)	0.5259 (10)	0.2181 (7)	0.080 (3)	0.490 (13)
H19A	0.1601	0.5419	0.2364	0.096*	0.490 (13)
H19B	0.2294	0.5928	0.1794	0.096*	0.490 (13)
C19B	0.2696 (8)	0.4402 (8)	0.2180 (5)	0.077 (3)	0.510 (13)
H19C	0.2477	0.3595	0.2318	0.093*	0.510 (13)
H19D	0.3135	0.4307	0.1798	0.093*	0.510 (13)
C20A	0.2102 (12)	0.4038 (11)	0.1694 (9)	0.128 (5)	0.490 (13)
H20A	0.1443	0.4049	0.1148	0.192*	0.490 (13)
H20B	0.2047	0.3392	0.2094	0.192*	0.490 (13)
H20C	0.2736	0.3896	0.1529	0.192*	0.490 (13)
C20B	0.1696 (11)	0.5203 (13)	0.1714 (9)	0.134 (5)	0.510 (13)
H20D	0.1236	0.4828	0.1146	0.201*	0.510 (13)
H20E	0.1933	0.5999	0.1592	0.201*	0.510 (13)
H20F	0.1281	0.5292	0.2109	0.201*	0.510 (13)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0546 (3)	0.0354 (2)	0.0260 (2)	-0.0004 (2)	0.0197 (2)	0.00073 (17)
O1	0.0881 (19)	0.100 (2)	0.115 (2)	-0.0333 (16)	-0.0081 (16)	0.0591 (18)
O2	0.0552 (11)	0.0477 (10)	0.0375 (9)	-0.0020 (9)	0.0143 (8)	0.0047 (8)
O3	0.1013 (16)	0.0519 (11)	0.0305 (9)	-0.0127 (11)	0.0240 (10)	-0.0057 (8)
O4	0.0709 (13)	0.0412 (10)	0.0428 (10)	-0.0004 (9)	0.0287 (9)	0.0037 (8)
N1	0.0644 (14)	0.0388 (11)	0.0315 (10)	0.0001 (10)	0.0231 (10)	0.0017 (8)
N2	0.121 (3)	0.122 (3)	0.0444 (14)	-0.066 (2)	0.0413 (17)	-0.0121 (15)
C1	0.0588 (18)	0.0664 (19)	0.0506 (16)	-0.0066 (15)	0.0188 (14)	0.0134 (14)
C2	0.0478 (16)	0.0628 (17)	0.0507 (15)	-0.0064 (14)	0.0154 (13)	0.0107 (13)
C3	0.0615 (19)	0.085 (2)	0.0600 (18)	-0.0051 (18)	0.0241 (16)	0.0060 (17)
C4	0.059 (2)	0.093 (3)	0.086 (2)	0.0135 (19)	0.0313 (19)	0.016 (2)
C5	0.0547 (19)	0.100 (3)	0.067 (2)	0.0009 (18)	0.0144 (16)	0.0269 (19)
C6	0.063 (2)	0.095 (3)	0.0503 (17)	-0.0042 (19)	0.0149 (15)	0.0123 (17)
C7	0.0588 (18)	0.072 (2)	0.0528 (17)	-0.0072 (15)	0.0173 (14)	0.0084 (14)
C8	0.108 (3)	0.088 (3)	0.074 (2)	0.013 (2)	0.036 (2)	0.002 (2)

C9	0.112 (3)	0.142 (4)	0.076 (3)	0.014 (3)	0.046 (3)	-0.005 (3)
C10	0.087 (3)	0.147 (4)	0.095 (3)	0.028 (3)	0.021 (2)	0.054 (3)
C11	0.0712 (18)	0.0384 (13)	0.0309 (11)	-0.0009 (12)	0.0229 (12)	0.0006 (9)
C12	0.0573 (15)	0.0439 (13)	0.0293 (11)	-0.0054 (11)	0.0193 (11)	-0.0032 (9)
C13	0.095 (2)	0.0503 (16)	0.0467 (14)	0.0119 (15)	0.0400 (16)	-0.0028 (12)
C14	0.136 (3)	0.0410 (15)	0.0594 (17)	0.0231 (17)	0.054 (2)	0.0102 (13)
C15	0.095 (2)	0.0469 (15)	0.0424 (13)	0.0085 (15)	0.0403 (15)	0.0102 (12)
C16	0.0799 (19)	0.0448 (14)	0.0334 (12)	-0.0066 (14)	0.0300 (13)	-0.0068 (10)
C17	0.167 (5)	0.104 (3)	0.069 (2)	-0.057 (3)	0.065 (3)	-0.003 (2)
C18	0.151 (5)	0.246 (8)	0.095 (4)	-0.066 (5)	0.080 (4)	-0.016 (4)
C19A	0.077 (7)	0.100 (7)	0.077 (6)	-0.026 (6)	0.043 (5)	-0.015 (5)
C19B	0.110 (6)	0.068 (5)	0.064 (5)	-0.040 (5)	0.043 (4)	-0.023 (4)
C20A	0.129 (10)	0.123 (9)	0.129 (9)	-0.050 (8)	0.045 (8)	-0.064 (8)
C20B	0.110 (9)	0.165 (13)	0.097 (9)	-0.019 (7)	0.004 (7)	-0.011 (8)

*Geometric parameters (Å, °)*

Co1—O2	2.0336 (18)	C9—H9C	0.9600
Co1—O2 <sup>i</sup>	2.0336 (18)	C10—H10A	0.9600
Co1—O4	2.1561 (18)	C10—H10B	0.9600
Co1—O4 <sup>i</sup>	2.1561 (19)	C10—H10C	0.9600
Co1—N1	2.1913 (19)	C11—H11	0.9300
Co1—N1 <sup>i</sup>	2.1913 (19)	C12—C11	1.381 (3)
O2—C1	1.254 (4)	C12—C16	1.503 (3)
O4—H1W	0.80 (7)	C13—C12	1.374 (4)
O4—H2W	0.76 (7)	C13—C14	1.382 (4)
N1—C11	1.336 (3)	C13—H13	0.9300
N1—C15	1.330 (3)	C14—C15	1.372 (4)
N2—C17	1.486 (4)	C14—H14	0.9300
N2—C19A	1.579 (11)	C15—H15	0.9300
N2—C19B	1.503 (8)	C16—N2	1.325 (4)
C1—O1	1.245 (4)	C17—H17A	0.9700
C1—C2	1.508 (4)	C17—H17B	0.9700
C2—C7	1.387 (4)	C18—C17	1.462 (7)
C3—C2	1.387 (5)	C18—H18A	0.9600
C3—C4	1.396 (5)	C18—H18B	0.9600
C3—C9	1.514 (5)	C18—H18C	0.9600
C4—H4	0.9300	C19A—C20A	1.508 (13)
C5—C4	1.385 (5)	C19A—H19A	0.9700
C5—C10	1.519 (5)	C19A—H19B	0.9700
C6—C5	1.363 (5)	C19B—C20B	1.508 (14)
C6—H6	0.9300	C19B—H19C	0.9700
C7—C6	1.381 (4)	C19B—H19D	0.9700
C7—C8	1.504 (5)	C20A—H20A	0.9600
C8—H8A	0.9600	C20A—H20B	0.9600
C8—H8B	0.9600	C20A—H20C	0.9600
C8—H8C	0.9600	C20B—H20D	0.9600
C9—H9A	0.9600	C20B—H20E	0.9600



C9—H9B	0.9600	C20B—H20F	0.9600
O2 <sup>i</sup> —Co1—O2	180.00 (13)	C5—C10—H10A	109.5
O2—Co1—O4	88.12 (7)	C5—C10—H10B	109.5
O2 <sup>i</sup> —Co1—O4	91.88 (7)	C5—C10—H10C	109.5
O2—Co1—O4 <sup>i</sup>	91.88 (7)	H10A—C10—H10B	109.5
O2 <sup>i</sup> —Co1—O4 <sup>i</sup>	88.12 (7)	H10A—C10—H10C	109.5
O2—Co1—N1	90.01 (8)	H10B—C10—H10C	109.5
O2 <sup>i</sup> —Co1—N1	89.99 (8)	N1—C11—C12	123.7 (2)
O2—Co1—N1 <sup>i</sup>	89.99 (8)	N1—C11—H11	118.1
O2 <sup>i</sup> —Co1—N1 <sup>i</sup>	90.01 (8)	C12—C11—H11	118.1
O4—Co1—O4 <sup>i</sup>	180.00 (9)	C11—C12—C16	121.1 (2)
O4—Co1—N1	87.66 (7)	C13—C12—C11	118.6 (2)
O4 <sup>i</sup> —Co1—N1	92.34 (7)	C13—C12—C16	120.3 (2)
O4—Co1—N1 <sup>i</sup>	92.34 (7)	C12—C13—C14	118.0 (2)
O4 <sup>i</sup> —Co1—N1 <sup>i</sup>	87.66 (7)	C12—C13—H13	121.0
N1—Co1—N1 <sup>i</sup>	180.00 (7)	C13—C14—H14	120.2
C1—O2—Co1	129.21 (18)	C14—C13—H13	121.0
Co1—O4—H1W	99 (5)	C15—C14—C13	119.6 (3)
Co1—O4—H2W	125 (5)	C15—C14—H14	120.2
H1W—O4—H2W	115 (6)	N1—C15—C14	123.1 (2)
C11—N1—Co1	119.79 (16)	N1—C15—H15	118.5
C15—N1—Co1	123.32 (16)	C14—C15—H15	118.5
C15—N1—C11	116.9 (2)	O3—C16—N2	122.6 (2)
C16—N2—C17	119.0 (3)	O3—C16—C12	119.6 (2)
C16—N2—C19A	115.4 (4)	N2—C16—C12	117.9 (2)
C16—N2—C19B	126.5 (3)	N2—C17—H17A	109.1
C17—N2—C19A	118.7 (4)	N2—C17—H17B	109.1
C17—N2—C19B	112.2 (4)	C18—C17—N2	112.3 (5)
O1—C1—O2	125.6 (3)	C18—C17—H17A	109.1
O1—C1—C2	119.2 (3)	C18—C17—H17B	109.1
O2—C1—C2	115.1 (2)	H17A—C17—H17B	107.9
C3—C2—C1	120.3 (3)	C17—C18—H18A	109.5
C3—C2—C7	120.4 (3)	C17—C18—H18B	109.5
C7—C2—C1	119.3 (3)	C17—C18—H18C	109.5
C2—C3—C4	118.8 (3)	H18A—C18—H18B	109.5
C2—C3—C9	120.6 (3)	H18A—C18—H18C	109.5
C4—C3—C9	120.6 (4)	H18B—C18—H18C	109.5
C3—C4—H4	119.4	N2—C19A—H19A	111.1
C5—C4—C3	121.1 (3)	N2—C19A—H19B	111.1
C5—C4—H4	119.4	C20A—C19A—N2	103.1 (10)
C4—C5—C10	119.9 (4)	C20A—C19A—H19A	111.1
C6—C5—C4	118.4 (3)	C20A—C19A—H19B	111.1
C6—C5—C10	121.7 (4)	H19A—C19A—H19B	109.1
C5—C6—C7	122.4 (3)	N2—C19B—C20B	103.7 (9)
C5—C6—H6	118.8	N2—C19B—H19C	111.0
C7—C6—H6	118.8	N2—C19B—H19D	111.0
C2—C7—C8	120.4 (3)	C20B—C19B—H19C	111.0

C6—C7—C2	118.8 (3)	C20B—C19B—H19D	111.0
C6—C7—C8	120.8 (3)	H19C—C19B—H19D	109.0
C7—C8—H8A	109.5	C19A—C20A—H20A	109.5
C7—C8—H8B	109.5	C19A—C20A—H20B	109.5
C7—C8—H8C	109.5	C19A—C20A—H20C	109.5
H8A—C8—H8B	109.5	H20A—C20A—H20B	109.5
H8A—C8—H8C	109.5	H20A—C20A—H20C	109.5
H8B—C8—H8C	109.5	H20B—C20A—H20C	109.5
C3—C9—H9A	109.5	C19B—C20B—H20D	109.5
C3—C9—H9B	109.5	C19B—C20B—H20E	109.5
C3—C9—H9C	109.5	C19B—C20B—H20F	109.5
H9A—C9—H9B	109.5	H20D—C20B—H20E	109.5
H9A—C9—H9C	109.5	H20D—C20B—H20F	109.5
H9B—C9—H9C	109.5	H20E—C20B—H20F	109.5
O4—Co1—O2—C1	-165.8 (2)	C1—C2—C7—C8	-5.2 (5)
O4 <sup>i</sup> —Co1—O2—C1	14.2 (2)	C3—C2—C7—C6	-3.2 (5)
N1—Co1—O2—C1	-78.1 (2)	C3—C2—C7—C8	177.8 (3)
N1 <sup>i</sup> —Co1—O2—C1	101.9 (2)	C4—C3—C2—C1	-174.6 (3)
O2—Co1—N1—C11	-57.7 (2)	C4—C3—C2—C7	2.4 (5)
O2 <sup>i</sup> —Co1—N1—C11	122.3 (2)	C9—C3—C2—C1	6.1 (5)
O2—Co1—N1—C15	123.9 (2)	C9—C3—C2—C7	-177.0 (3)
O2 <sup>i</sup> —Co1—N1—C15	-56.1 (2)	C2—C3—C4—C5	0.0 (5)
O4—Co1—N1—C11	30.5 (2)	C9—C3—C4—C5	179.4 (4)
O4 <sup>i</sup> —Co1—N1—C11	-149.5 (2)	C6—C5—C4—C3	-1.5 (6)
O4—Co1—N1—C15	-148.0 (2)	C10—C5—C4—C3	176.2 (4)
O4 <sup>i</sup> —Co1—N1—C15	32.0 (2)	C7—C6—C5—C4	0.7 (5)
Co1—O2—C1—O1	2.1 (5)	C7—C6—C5—C10	-177.0 (4)
Co1—O2—C1—C2	179.24 (18)	C2—C7—C6—C5	1.6 (5)
Co1—N1—C11—C12	-178.2 (2)	C8—C7—C6—C5	-179.4 (3)
C15—N1—C11—C12	0.4 (4)	C13—C12—C11—N1	-2.4 (4)
Co1—N1—C15—C14	-179.5 (3)	C16—C12—C11—N1	-179.8 (3)
C11—N1—C15—C14	2.0 (5)	C11—C12—C16—O3	113.7 (3)
C16—N2—C17—C18	99.5 (5)	C11—C12—C16—N2	-64.8 (4)
C19A—N2—C17—C18	-49.9 (7)	C13—C12—C16—O3	-63.7 (4)
C19B—N2—C17—C18	-96.4 (6)	C13—C12—C16—N2	117.9 (4)
C16—N2—C19A—C20A	125.7 (6)	C14—C13—C12—C11	2.0 (5)
C17—N2—C19A—C20A	-83.8 (7)	C14—C13—C12—C16	179.5 (3)
C19B—N2—C19A—C20A	8.4 (7)	C12—C13—C14—C15	0.2 (5)
C16—N2—C19B—C20B	-89.3 (8)	C13—C14—C15—N1	-2.3 (6)
C17—N2—C19B—C20B	108.1 (8)	O3—C16—N2—C17	-1.6 (6)
C19A—N2—C19B—C20B	-0.6 (9)	O3—C16—N2—C19A	148.8 (5)
O1—C1—C2—C3	-99.3 (4)	O3—C16—N2—C19B	-163.2 (6)
O1—C1—C2—C7	83.8 (4)	C12—C16—N2—C17	176.8 (3)
O2—C1—C2—C3	83.4 (4)	C12—C16—N2—C19A	-32.8 (5)

O2—C1—C2—C7	-93.6 (4)	C12—C16—N2—C19B	15.2 (7)
C1—C2—C7—C6	173.8 (3)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O4—H1W...O1 <sup>i</sup>	0.80 (6)	1.87 (6)	2.634 (3)	160 (7)
O4—H2W...O3 <sup>ii</sup>	0.76 (7)	2.10 (7)	2.850 (3)	170 (7)
C10—H10A...O1 <sup>iii</sup>	0.96	2.43	3.365 (6)	165
C15—H15...O3 <sup>iv</sup>	0.93	2.50	3.420 (4)	172

Symmetry codes: (i)  $-x+1, -y+1, -z$ ; (ii)  $-x+1, y-1/2, -z+1/2$ ; (iii)  $-x+2, y-1/2, -z+1/2$ ; (iv)  $x, -y+3/2, z-1/2$ .