

# Crystal structure of *catena*-poly[[[tetraaquacobalt(II)]- $\mu_2$ -1,5-dihydroxynaphthalene-2,6-dicarboxylato] dimethylformamide disolvate]

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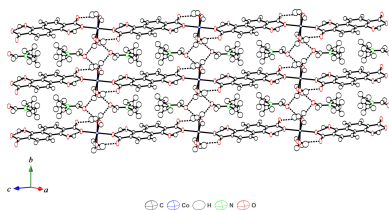
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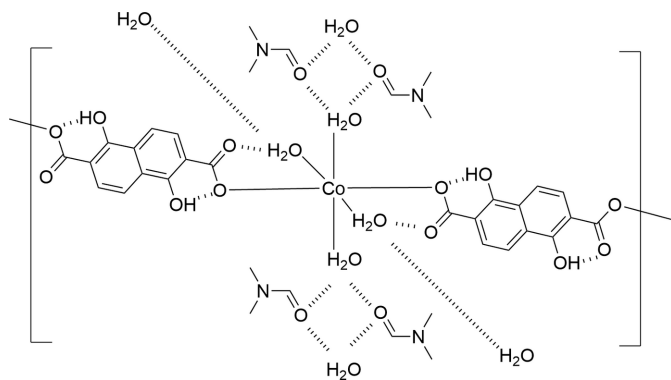
The asymmetric unit of the title compound,  $\{[\text{Co}(\text{C}_{12}\text{H}_6\text{O}_6)(\text{H}_2\text{O})_4]\cdot 2\text{C}_3\text{H}_7\text{NO}\}_n$  or  $\{[\text{Co}(\text{H}_2\text{dondc})(\text{H}_2\text{O})_4]\cdot 2\text{DMF}\}_n$ , comprises half of a  $\text{Co}^{\text{II}}$  ion, half of a 1,5-dihydroxynaphthalene-2,6-dicarboxylate dianion ( $\text{H}_2\text{dondc}^{2-}$ ), two water molecules and a dimethylformamide (DMF) molecule. The  $\text{Co}^{\text{II}}$  ion, which is located on a crystallographic inversion center, exhibits a distorted six-coordinated octahedral geometry with two oxygen atoms of the  $\text{H}_2\text{dondc}^{2-}$  ligand and four oxygen atoms of the water molecules. The carboxylate group is almost coplanar with the naphthalene moiety and shows monodentate coordination to the  $\text{Co}^{\text{II}}$  ion. The  $\text{Co}^{\text{II}}$  ions are bridged by the  $\text{H}_2\text{dondc}^{2-}$  ligand to form a one-dimensional chain. The hydroxy groups of the ligand have intra-chain hydrogen bonding interactions with coordinated water molecules. The coordinated water molecules exhibit not only intra-chain hydrogen bonding interactions, but also inter-chain hydrogen-bonding interactions. The chains are connected by inter-chain hydrogen-bonding interactions and are arranged in parallel to form a two-dimensional network. The chains are further connected by inter-chain hydrogen-bonding interactions *via* the DMF molecules and C—H... $\pi$  interactions to give a three-dimensional network.

## 1. Chemical context

Metal–organic frameworks (MOFs) or coordination polymers (CPs) are being actively investigated due to their applications in gas adsorption, separation and catalysis (Cheetham *et al.*, 1999; Eddaoudi *et al.*, 2002; Kitagawa *et al.*, 2004). Polycarboxylate ligands such as benzenedicarboxylate ( $\text{bdc}^{2-}$  dianion), also known as a terephthalate dianion, are well-known linkers that yield functional materials (Furukawa *et al.*, 2010; Kurmoo, 2009). We have not only prepared electrode materials using the terephthalate dianion and its derivatives (Ogihara *et al.*, 2014, 2021, 2023; Yasuda & Ogihara, 2014), but also magnetic materials that involve polycarboxylates in which the number of carboxylate groups and the distances between carboxylate groups vary systematically (Kumagai *et al.*, 2001, 2002; Kurmoo *et al.*, 2001, 2003). The functionalization of an organic ligand provides further coordination capabilities, reaction centers, and interaction sites for specific functions. The 2,5-dihydroxy-1,4-benzenedicarboxylic acid (2,5- $\text{H}_4\text{dobdc}$ ) ligand is a 1,4-benzenedicarboxylic acid derivative with two hydroxy groups introduced as functional groups and functional MOFs with this ligand have been reported (Caskey *et al.*, 2008; Cozzolino *et al.*, 2014; Geier *et al.*, 2013; Maurice *et al.*, 2013; Queen *et al.*, 2014). 1,5-Dihydroxynaphthalene-2,6-dicarboxylate ( $\text{H}_4\text{dondc}$ ) is an analogue of 2,5- $\text{H}_4\text{dobdc}$ . The  $\text{H}_4\text{dondc}$  ligand can be deprotonated to give four available

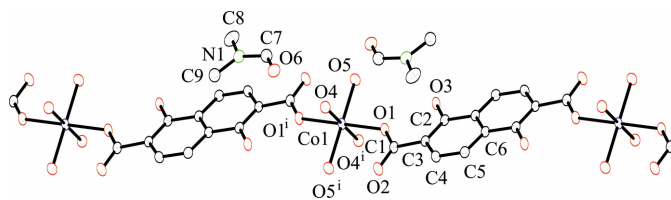


charges (1- to 4-); however, only metal complexes of the 4-anion have been reported (Dietzel *et al.*, 2020; Yeon *et al.*, 2015). In this contribution, we have focused on the use of 1,5-dihydroxynaphthalene-2,6-dicarboxylate ( $\text{H}_2\text{dondc}^{2-}$ ) in the synthesis of a  $\text{Co}^{\text{II}}-\text{H}_2\text{dondc}^{2-}$  dianion system and report on the single-crystal structure of  $[\text{Co}(\text{H}_2\text{dondc})(\text{H}_2\text{O})_4]\cdot 2\text{DMF}$  in which the ligand is a 2- anion. This is a new structure of the metal complex synthesized from  $\text{H}_4\text{dondc}$ .



## 2. Structural commentary

The title compound,  $[\text{Co}(\text{H}_2\text{dondc})(\text{H}_2\text{O})_4]\cdot 2\text{DMF}$ , consists of a  $\text{Co}^{\text{II}}$  ion, a 1,5-dihydroxynaphthalene-2,6-dicarboxylate dianion ( $\text{H}_2\text{dondc}^{2-}$ ), four water molecules and two DMF molecules. The  $\text{Co}^{\text{II}}$  ion lies on a crystallographic inversion center and its asymmetric unit consists of half of a  $\text{Co}^{\text{II}}$  ion, half of a  $\text{H}_2\text{dondc}^{2-}$  ligand, two water molecules and a DMF molecule. The key feature of the structure is a three-dimensional (3D) hydrogen-bonding network that consists of one-dimensional (1D) coordination chains built up by  $\text{CoO}_6$  octahedra bridged by  $\text{H}_2\text{dondc}^{2-}$  ligands and interchain  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions. Fig. 1 shows the 1D chain structure of  $[\text{Co}(\text{H}_2\text{dondc})(\text{H}_2\text{O})_4]$  and DMF molecules with the numbering scheme. The  $\text{Co}^{\text{II}}$  ion occupies a crystallographic inversion center; therefore, each pair of  $\text{H}_2\text{dondc}^{2-}$  ligands and water molecules coordinate *trans* to each other to form a linear chain. The  $\text{Co}-\text{O}1$  (carboxylate) bond length [2.0750 (9) Å] in the title compound is shorter than the  $\text{Co}-\text{O}$  ( $\text{H}_2\text{O}$ ) bond lengths [2.0931 (10) and 2.1023 (10) Å], which is indicative of the compressed octahedral geometry of the  $\text{Co}^{\text{II}}$  ion. The  $\text{Co}\cdots\text{Co}$  separation defined by  $\text{Co}-\text{H}_2\text{dondc}^{2-}-\text{Co}$  connectivity within the chain is 13.27 Å. We have reported CPs that consist of tetrahalogenated terephthalate dianions as



**Figure 1**  
One-dimensional chain structure of the title compound with the atom-labeling scheme and 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

**Table 1**  
Hydrogen-bond geometry (Å, °).

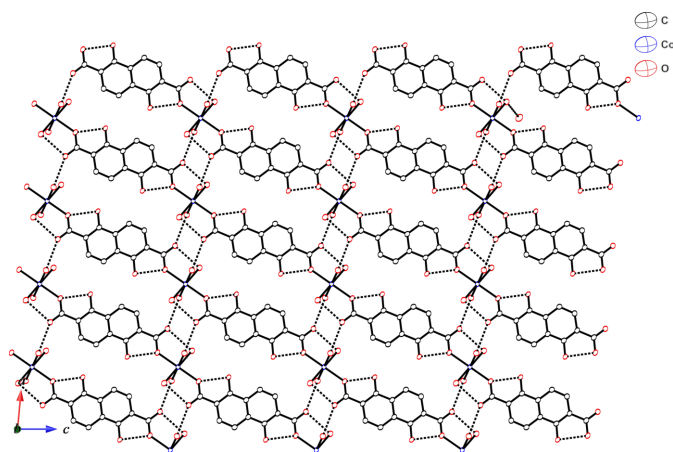
$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}3-\text{H}3\cdots\text{O}1$	0.78 (2)	1.81 (2)	2.5168 (13)	149.1 (19)
$\text{O}4-\text{H}1\cdots\text{O}6$	0.76 (2)	1.99 (2)	2.7449 (16)	178 (2)
$\text{O}4-\text{H}2\cdots\text{O}2^{\text{i}}$	0.78 (2)	1.96 (2)	2.7284 (15)	168 (2)
$\text{O}5-\text{H}6\cdots\text{O}2^{\text{ii}}$	0.79 (3)	2.00 (3)	2.7182 (14)	151 (2)
$\text{O}5-\text{H}10\cdots\text{O}6^{\text{iii}}$	0.85 (2)	1.95 (2)	2.7836 (15)	166 (2)
$\text{C}8-\text{H}8\text{C}\cdots\text{C}3^{\text{ii}}$	0.98	2.85	3.497 (2)	124

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

bridging ligands in which the carboxylate groups exhibited monodentate coordination similar to the title compound. The  $\text{Co}\cdots\text{Co}$  separation distance (*ca.* 11 Å) is shorter than that observed in the title compound (Kumagai *et al.*, 2021), which is due to the long naphthalene backbone. The carboxylate group exhibits monodentate coordination, and the dihedral angle between the carboxylate group and the naphthalene ring system is slightly tilted with an  $\text{O}1-\text{C}1-\text{C}3-\text{C}4$  torsion angle of 171.94 (11)°. Non-coordinated oxygen atoms of the carboxylate groups show intra-chain hydrogen-bonding interactions with coordinated water molecules. The non-coordinated oxygen atoms of the carboxylate groups act as hydrogen-bond acceptors and coordinated water molecules act as hydrogen-bond donors. The  $\text{H}_2\text{dondc}^{2-}$  ligand binds to the  $\text{Co}^{\text{II}}$  ion solely through its carboxylate oxygen atoms and the phenolic hydroxyl groups show no coordination bonding to  $\text{Co}^{\text{II}}$  ions. The hydroxyl groups act as hydrogen-bond donors and undergo hydrogen bonding with the coordinated carboxylate oxygen atoms as hydrogen-bond acceptors. The  $\text{H}_4\text{dondc}$  ligand can be deprotonated to give four available charges (1- to 4-), although only metal complexes of the 4-anion have been reported so far. Both the hydroxy and carboxylic acid groups of the ligand are deprotonated to give a 4- anion and the resultant oxido and carboxylate groups are coordinated by metal ions to give the  $M_2(\text{dondc})$  composition ( $M = \text{Mn}, \text{Mg}, \text{Ni}, \text{Co}$ ) and a honeycomb-like structure (Dietzel *et al.*, 2020; Yeon *et al.*, 2015).

## 3. Supramolecular features

The coordinated water molecules in the crystal structure act as hydrogen-bonding donors and the oxygen atoms of the DMF molecules act as hydrogen-bonding acceptors (Table 1). The coordinated water molecule (O4) shows two types of hydrogen-bonding interactions. One is an inter-chain hydrogen-bonding interaction between the non-coordinated oxygen atom of the adjacent chain to give a two-dimensional hydrogen-bonding network in which the chains are arranged in parallel when viewed along the *b*-axis direction (Fig. 2). The other is an inter-molecular hydrogen-bonding interaction between the DMF and water molecules. The coordinated water molecule (O5) exhibits not only inter-chain hydrogen-bonding interactions with the oxygen atom of a DMF molecule but also intra-chain hydrogen-bonding interactions with an oxygen atom (O2) of the carboxylate group not bound to

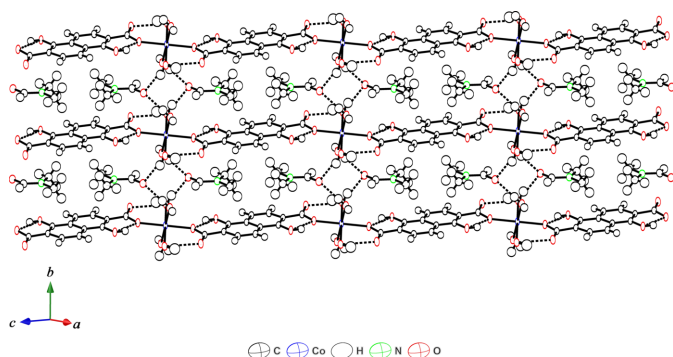


**Figure 2**  
View of the two-dimensional hydrogen-bonding network with inter- and intra-chain hydrogen-bonding interactions. Dashed lines represent hydrogen bonds.

the  $\text{Co}^{\text{II}}$  ions. The DMF molecule acts as a hydrogen-bond acceptor for both O4 and O5 in different chains to yield a hydrogen-bonding network (Fig. 3). The  $\text{C3}\cdots\text{C8}$  distance of 3.497 (2) Å between the carbon atoms of DMF molecules and the naphthalene ring system, and the  $\text{C8}\cdots$ centroid distance of 3.53 Å are indicative of some degree of  $\text{C}-\text{H}\cdots\pi$  interaction (Nishio, 2011; Nishio *et al.*, 2009). Therefore, the DMF molecules are held in between the one-dimensional chains by hydrogen-bonding interactions and  $\text{C}-\text{H}\cdots\pi$  interactions (Fig. S1 in the supporting information). The presence of DMF molecules between the chains prevents  $\pi-\pi$  stacking interactions between the planar naphthalene moieties and the two naphthalene moieties are 6.96 Å apart.

#### 4. Database survey

Although a search of the Sci Finder database for structures with a  $\text{H}_2\text{donc}^{2-}$  and  $\text{Co}^{\text{II}}$  ion resulted in no complete matches, partially matched structures were found. They are metal complexes composed of a  $\text{Mn}^{\text{II}}$  ion and a  $\text{donc}^{4-}$  ligand that form a three-dimensional network consisting of hexagonal channels (CADYOZ and CADYUF; Dietzel *et al.*,



**Figure 3**  
Inter-chain hydrogen-bonding interactions *via* DMF molecules. Dashed lines represent inter-chain hydrogen bonds.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$[\text{Co}(\text{C}_{12}\text{H}_6\text{O}_6)(\text{H}_2\text{O})_4]\cdot 2\text{C}_3\text{H}_7\text{NO}$
$M_r$	523.35
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	110
$a, b, c$ (Å)	6.886 (1), 6.945 (1), 12.0366 (15)
$\alpha, \beta, \gamma$ (°)	85.543 (5), 84.371 (5), 83.981 (5)
$V$ (Å <sup>3</sup> )	568.37 (14)
$Z$	1
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.82
Crystal size (mm)	0.25 × 0.25 × 0.10
Data collection	
Diffractometer	Rigaku R-Axis RAPID
Absorption correction	Multi-scan (ABSCOR; Rigaku, 1995)
$T_{\text{min}}, T_{\text{max}}$	0.760, 0.922
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	9228, 2595, 2413
$R_{\text{int}}$	0.027
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.074, 1.11
No. of reflections	2595
No. of parameters	173
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.62, -0.24

Computer programs: RAPID-AUTO (Rigaku, 2002), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and Yadokari-XG (Wakita, 2001).

2020). A search of the Web of Science database for the keywords 2,6-naphthalenedicarboxylic acid and 1,5-dihydroxy- led to lanthanide-based compounds [DUDXOS (La) and DUDXUY (Ce); Mahmoud *et al.*, 2020] and an  $\text{Mg}^{\text{II}}$  compound (Yeon *et al.*, 2015). The structure of the  $\text{Mg}^{\text{II}}$  compound is similar to that of the  $\text{Mn}^{\text{II}}$  compound.

#### 5. Synthesis and crystallization

Cobalt(II) nitrate hexahydrate (0.12 g, 0.4 mmol) and  $\text{H}_2\text{donc}$  were dissolved in an ethanol (10 mL)–*N,N*-dimethylformamide (20 mL) mixture. The mixture was placed in the Teflon liner of an autoclave, sealed, and heated at 353 K for two days. The mixture was then cooled to room temperature. Pink crystals were obtained and one of these crystals was used for single-crystal X-ray crystallography analysis.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to oxygen atoms of the ligand and water molecules were extracted from difference-Fourier maps. Other hydrogen atoms were placed in idealized positions ( $\text{C}-\text{H} = 0.95-0.98$  Å) and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

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## supporting information

*Acta Cryst.* (2025). E81 [https://doi.org/10.1107/S2056989025000982]

## Crystal structure of *catena*-poly[[[tetraaquacobalt(II)]- $\mu_2$ -1,5-dihydroxy-naphthalene-2,6-dicarboxylato] dimethylformamide disolvate]

Hitoshi Kumagai, Satoshi Kawata and Nobuhiro Ogihara

### Computing details

*catena*-Poly[[[tetraaquacobalt(II)]- $\mu_2$ -1,5-dihydroxynaphthalene-2,6-dicarboxylato] dimethylformamide disolvate]

#### Crystal data

[Co(C<sub>12</sub>H<sub>6</sub>O<sub>6</sub>)(H<sub>2</sub>O)<sub>4</sub>] $\cdot$ 2C<sub>3</sub>H<sub>7</sub>NO

$M_r = 523.35$

Triclinic,  $P\bar{1}$

$a = 6.886$  (1) Å

$b = 6.945$  (1) Å

$c = 12.0366$  (15) Å

$\alpha = 85.543$  (5)°

$\beta = 84.371$  (5)°

$\gamma = 83.981$  (5)°

$V = 568.37$  (14) Å<sup>3</sup>

$Z = 1$

$F(000) = 273$

$D_x = 1.529$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 7544 reflections

$\theta = 3.3$ – $27.5$ °

$\mu = 0.82$  mm<sup>-1</sup>

$T = 110$  K

Block, orange

$0.25 \times 0.25 \times 0.10$  mm

#### Data collection

Rigaku R-AXIS RAPID

diffractometer

$\omega$  scans

Absorption correction: multi-scan

(ABSCOR; Rigaku, 1995)

$T_{\min} = 0.760$ ,  $T_{\max} = 0.922$

9228 measured reflections

2595 independent reflections

2413 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.3$ °

$h = -8 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -15 \rightarrow 14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.074$

$S = 1.11$

2595 reflections

173 parameters

0 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

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.1029P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.62$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.24$  e Å<sup>-3</sup>

*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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.500000	0.500000	0.500000	0.01471 (10)
O1	0.67306 (14)	0.46799 (15)	0.35020 (7)	0.0190 (2)
O2	0.96008 (13)	0.33348 (15)	0.40363 (8)	0.0210 (2)
O3	0.62385 (13)	0.54304 (15)	0.14635 (8)	0.0179 (2)
H3	0.597 (3)	0.535 (3)	0.2110 (17)	0.030 (5)*
O4	0.66579 (15)	0.72005 (16)	0.53529 (8)	0.0191 (2)
O5	0.30573 (15)	0.69999 (16)	0.41516 (8)	0.0199 (2)
O6	0.50238 (16)	0.98724 (16)	0.68258 (9)	0.0271 (2)
N1	0.22328 (19)	1.01767 (18)	0.80010 (10)	0.0243 (3)
C1	0.85613 (19)	0.41209 (19)	0.33048 (10)	0.0156 (3)
C2	0.81861 (18)	0.50097 (18)	0.12707 (10)	0.0142 (2)
C3	0.94074 (18)	0.44228 (18)	0.21177 (10)	0.0141 (2)
C4	1.14541 (18)	0.40885 (19)	0.18353 (10)	0.0161 (3)
H4	1.229079	0.371976	0.241383	0.019*
C5	1.22599 (18)	0.42820 (19)	0.07517 (11)	0.0160 (3)
H5	1.363922	0.406279	0.058549	0.019*
C6	1.10219 (17)	0.48131 (18)	−0.01250 (10)	0.0138 (2)
C7	0.3219 (2)	1.0217 (2)	0.70011 (12)	0.0250 (3)
H7	0.249193	1.053293	0.636960	0.030*
C8	0.0115 (2)	1.0587 (2)	0.81476 (16)	0.0349 (4)
H8A	−0.039095	1.089840	0.741516	0.042*
H8B	−0.022584	1.169262	0.861194	0.042*
H8C	−0.046646	0.944645	0.851466	0.042*
C9	0.3257 (3)	0.9726 (2)	0.90075 (13)	0.0345 (4)
H9A	0.299710	1.081591	0.948870	0.041*
H9B	0.466950	0.950019	0.879845	0.041*
H9C	0.279186	0.855710	0.941191	0.041*
H1	0.619 (3)	0.795 (3)	0.5747 (18)	0.034 (6)*
H2	0.769 (3)	0.690 (3)	0.5561 (16)	0.028 (5)*
H6	0.214 (4)	0.728 (4)	0.458 (2)	0.057 (7)*
H10	0.351 (3)	0.806 (3)	0.3928 (17)	0.037 (5)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.01037 (14)	0.02391 (15)	0.00905 (13)	−0.00095 (9)	0.00171 (8)	−0.00044 (9)
O1	0.0131 (4)	0.0315 (5)	0.0112 (4)	0.0002 (4)	0.0027 (3)	−0.0011 (4)
O2	0.0125 (4)	0.0359 (6)	0.0131 (4)	−0.0005 (4)	0.0008 (3)	0.0026 (4)
O3	0.0106 (4)	0.0320 (5)	0.0102 (4)	−0.0008 (4)	0.0025 (3)	−0.0015 (4)

O4	0.0128 (5)	0.0269 (5)	0.0175 (5)	-0.0001 (4)	-0.0010 (4)	-0.0032 (4)
O5	0.0142 (5)	0.0277 (5)	0.0161 (5)	-0.0004 (4)	0.0018 (4)	0.0024 (4)
O6	0.0247 (5)	0.0275 (5)	0.0273 (6)	-0.0020 (4)	0.0060 (4)	-0.0019 (4)
N1	0.0268 (7)	0.0218 (6)	0.0231 (6)	-0.0044 (5)	0.0058 (5)	-0.0024 (5)
C1	0.0133 (6)	0.0206 (6)	0.0131 (6)	-0.0046 (5)	0.0018 (4)	-0.0028 (5)
C2	0.0112 (6)	0.0176 (6)	0.0139 (6)	-0.0034 (4)	0.0025 (4)	-0.0036 (5)
C3	0.0129 (6)	0.0172 (6)	0.0121 (6)	-0.0023 (5)	0.0023 (4)	-0.0027 (4)
C4	0.0133 (6)	0.0215 (6)	0.0134 (6)	-0.0024 (5)	-0.0008 (4)	-0.0009 (5)
C5	0.0110 (6)	0.0217 (6)	0.0152 (6)	-0.0017 (5)	0.0009 (4)	-0.0027 (5)
C6	0.0122 (6)	0.0165 (6)	0.0128 (6)	-0.0028 (5)	0.0016 (4)	-0.0029 (5)
C7	0.0272 (8)	0.0252 (7)	0.0222 (7)	-0.0049 (6)	0.0021 (6)	-0.0009 (6)
C8	0.0272 (8)	0.0304 (8)	0.0463 (10)	-0.0085 (7)	0.0131 (7)	-0.0098 (7)
C9	0.0504 (11)	0.0291 (8)	0.0220 (8)	0.0001 (7)	0.0024 (7)	-0.0014 (6)

*Geometric parameters (Å, °)*

Co1—O1 <sup>i</sup>	2.0750 (9)	N1—C9	1.458 (2)
Co1—O1	2.0750 (9)	C1—C3	1.4969 (17)
Co1—O4 <sup>i</sup>	2.0931 (10)	C2—C3	1.3945 (18)
Co1—O4	2.0931 (10)	C2—C6 <sup>ii</sup>	1.4334 (17)
Co1—O5	2.1023 (10)	C3—C4	1.4161 (17)
Co1—O5 <sup>i</sup>	2.1023 (10)	C4—C5	1.3687 (17)
O1—C1	1.2842 (16)	C4—H4	0.9500
O2—C1	1.2460 (17)	C5—C6	1.4235 (18)
O3—C2	1.3436 (15)	C5—H5	0.9500
O3—H3	0.78 (2)	C6—C6 <sup>ii</sup>	1.411 (2)
O4—H1	0.76 (2)	C7—H7	0.9500
O4—H2	0.78 (2)	C8—H8A	0.9800
O5—H6	0.79 (3)	C8—H8B	0.9800
O5—H10	0.85 (2)	C8—H8C	0.9800
O6—C7	1.2409 (19)	C9—H9A	0.9800
N1—C7	1.3226 (19)	C9—H9B	0.9800
N1—C8	1.452 (2)	C9—H9C	0.9800
O1 <sup>i</sup> —Co1—O1	180.0	O3—C2—C6 <sup>ii</sup>	116.24 (11)
O1 <sup>i</sup> —Co1—O4 <sup>i</sup>	89.40 (4)	C3—C2—C6 <sup>ii</sup>	120.54 (11)
O1—Co1—O4 <sup>i</sup>	90.60 (4)	C2—C3—C4	119.02 (11)
O1 <sup>i</sup> —Co1—O4	90.60 (4)	C2—C3—C1	120.40 (11)
O1—Co1—O4	89.40 (4)	C4—C3—C1	120.57 (11)
O4 <sup>i</sup> —Co1—O4	180.0	C5—C4—C3	121.81 (12)
O1 <sup>i</sup> —Co1—O5	91.09 (4)	C5—C4—H4	119.1
O1—Co1—O5	88.91 (4)	C3—C4—H4	119.1
O4 <sup>i</sup> —Co1—O5	88.28 (4)	C4—C5—C6	119.71 (12)
O4—Co1—O5	91.72 (4)	C4—C5—H5	120.1
O1 <sup>i</sup> —Co1—O5 <sup>i</sup>	88.91 (4)	C6—C5—H5	120.1
O1—Co1—O5 <sup>i</sup>	91.09 (4)	C6 <sup>ii</sup> —C6—C5	120.13 (14)
O4 <sup>i</sup> —Co1—O5 <sup>i</sup>	91.72 (4)	C6 <sup>ii</sup> —C6—C2 <sup>ii</sup>	118.74 (14)
O4—Co1—O5 <sup>i</sup>	88.28 (4)	C5—C6—C2 <sup>ii</sup>	121.14 (11)

O5—Co1—O5 <sup>i</sup>	180.00 (8)	O6—C7—N1	124.91 (14)
C1—O1—Co1	130.95 (8)	O6—C7—H7	117.5
C2—O3—H3	107.8 (14)	N1—C7—H7	117.5
Co1—O4—H1	118.7 (16)	N1—C8—H8A	109.5
Co1—O4—H2	117.9 (14)	N1—C8—H8B	109.5
H1—O4—H2	104 (2)	H8A—C8—H8B	109.5
Co1—O5—H6	107.4 (18)	N1—C8—H8C	109.5
Co1—O5—H10	114.6 (14)	H8A—C8—H8C	109.5
H6—O5—H10	105 (2)	H8B—C8—H8C	109.5
C7—N1—C8	122.13 (14)	N1—C9—H9A	109.5
C7—N1—C9	120.50 (14)	N1—C9—H9B	109.5
C8—N1—C9	117.37 (13)	H9A—C9—H9B	109.5
O2—C1—O1	123.35 (11)	N1—C9—H9C	109.5
O2—C1—C3	120.55 (12)	H9A—C9—H9C	109.5
O1—C1—C3	116.08 (11)	H9B—C9—H9C	109.5
O3—C2—C3	123.22 (11)		
Co1—O1—C1—O2	12.6 (2)	O1—C1—C3—C4	171.94 (11)
Co1—O1—C1—C3	-168.77 (8)	C2—C3—C4—C5	-1.54 (19)
O3—C2—C3—C4	-177.43 (11)	C1—C3—C4—C5	177.49 (12)
C6 <sup>ii</sup> —C2—C3—C4	2.82 (19)	C3—C4—C5—C6	-0.7 (2)
O3—C2—C3—C1	3.5 (2)	C4—C5—C6—C6 <sup>ii</sup>	1.6 (2)
C6 <sup>ii</sup> —C2—C3—C1	-176.22 (11)	C4—C5—C6—C2 <sup>ii</sup>	-178.74 (12)
O2—C1—C3—C2	169.63 (12)	C8—N1—C7—O6	-179.71 (14)
O1—C1—C3—C2	-9.05 (18)	C9—N1—C7—O6	0.7 (2)
O2—C1—C3—C4	-9.39 (19)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 $\cdots$ O1	0.78 (2)	1.81 (2)	2.5168 (13)	149.1 (19)
C7—H7 $\cdots$ O4 <sup>iii</sup>	0.95	2.56	3.2322 (18)	128
O4—H1 $\cdots$ O6	0.76 (2)	1.99 (2)	2.7449 (16)	178 (2)
O4—H2 $\cdots$ O2 <sup>iv</sup>	0.78 (2)	1.96 (2)	2.7284 (15)	168 (2)
O5—H6 $\cdots$ O2 <sup>i</sup>	0.79 (3)	2.00 (3)	2.7182 (14)	151 (2)
O5—H10 $\cdots$ O6 <sup>iii</sup>	0.85 (2)	1.95 (2)	2.7836 (15)	166 (2)
C8—H8C $\cdots$ C3 <sup>i</sup>	0.98	2.85	3.497 (2)	124

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