# Poly[[(μ-aqua)[μ4-4-(carboxylatomethyl)benzoato]cobalt(II)] hemi[1,4-bis(pyridin-4-ylmethyl)piperazine] hemihydrate]

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In the title compound, $\{[Co(C_9H_6O_4)(H_2O)]\cdot 0.5C_{16}H_{20}N_4\cdot 0.5H_2O\}_n$, two-dimensional coordination polymer slabs are held together in the three-dimensional crystal structure by means of O—H···N hydrogen bonding between bound water molecules and pyridyl N atoms of cocrystallized 1,4-bis(pyridin-4-ylmethyl)piperazine molecules.

### 3D view



### Chemical scheme
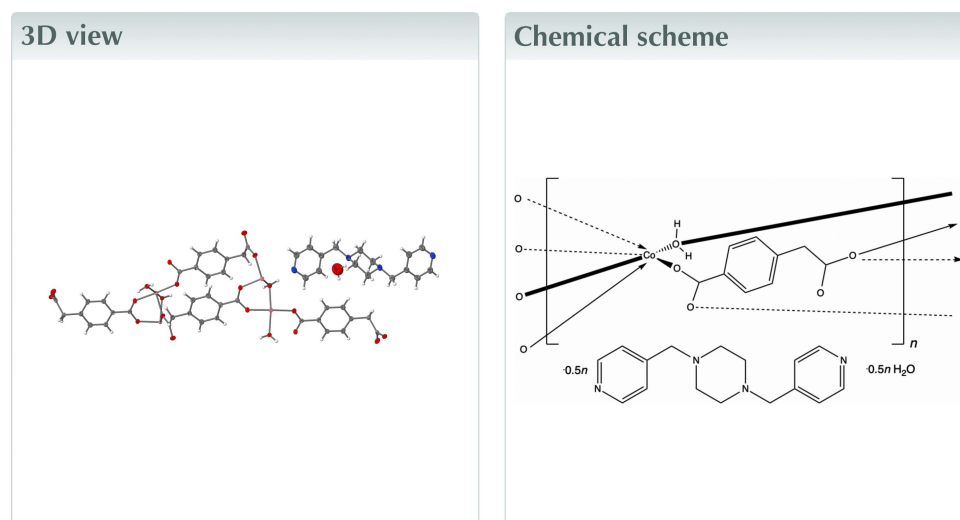


## Structure description

Our group has demonstrated the utility of 1,4-bis(pyridin-4-ylmethyl)piperazine (bpmp) for the construction of divalent metal coordination polymers with a striking variety of interesting topologies (Robinson *et al.*, 2015). For instance, the cobalt oxalate (ox) bpmp phase $\{[Co(H_2O)_4(bpmp)](ox)\}_n$ displays cationic one-dimensional chain motifs with unligated ox moieties. A higher temperature polymorph, $\{[Co(ox)(bpmp)]\cdot 3H_2O\}_n$, manifests a threefold interpenetrated three-dimensional **dia** topology. Use of isophthalate (iph) as the dicarboxylate ligand afforded $\{[Co(iph)(bpmp)]\cdot H_2O\}_n$, which exhibits a dimer-based two-dimensional layered structure (Martin *et al.*, 2007). The title compound was isolated during an attempt to prepare a divalent cobalt coordination polymer containing both bpmp and 4-(carboxylatomethyl)benzoate (cmb) ligands.

The asymmetric unit of the title compound contains a divalent Co atom, a fully deprotonated cmb ligand, a bound water molecule, a cocrystallized water molecule best refined at half-occupancy, and half of an unligated bpmp molecule whose central piperazine ring is sited on a crystallographic inversion center. The Co atom is coordinated in a $\{CoO_6\}$ distorted octahedral fashion (Fig. 1) with carboxylate O-atom donors from four cmb ligands in the nominal equatorial plane. The two nominally axial positions are taken up by bound water molecules. Pertinent bond distances and angles for the coordination sphere are listed in Table 1.

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Co1—O1 | 2.011 (2) | Co1—O4$^{iii}$ | 2.140 (2) |
| Co1—O2$^{i}$ | 2.029 (2) | Co1—O5 | 2.139 (2) |
| Co1—O4$^{ii}$ | 2.094 (2) | Co1—O5$^{i}$ | 2.169 (2) |
| | | | |
| O1—Co1—O2$^{i}$ | 177.55 (9) | O2$^{i}$—Co1—O5$^{i}$ | 87.29 (9) |
| O1—Co1—O4$^{iii}$ | 92.37 (9) | O4$^{ii}$—Co1—O4$^{iii}$ | 170.65 (6) |
| O1—Co1—O4$^{ii}$ | 95.23 (9) | O4$^{iii}$—Co1—O5$^{i}$ | 93.25 (8) |
| O1—Co1—O5$^{i}$ | 93.31 (9) | O4$^{ii}$—Co1—O5$^{i}$ | 80.90 (9) |
| O1—Co1—O5 | 92.67 (9) | O4$^{ii}$—Co1—O5 | 104.48 (9) |
| O2$^{i}$—Co1—O4$^{iii}$ | 85.22 (9) | O5—Co1—O4$^{iii}$ | 80.55 (9) |
| O2$^{i}$—Co1—O4$^{ii}$ | 87.21 (9) | O5—Co1—O5$^{i}$ | 171.56 (4) |
| O2$^{i}$—Co1—O5 | 86.49 (9) | | |

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

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C11—H11$\cdots$N2 | 0.95 | 2.53 | 2.860 (5) | 101 |
| O1W—H1WA$\cdots$N2 | 0.87 | 2.16 | 2.847 (10) | 136 |
| O5—H5A$\cdots$O3$^{i}$ | 0.85 (2) | 1.79 (2) | 2.619 (3) | 164 (4) |
| O5—H5B$\cdots$N1 | 0.86 (2) | 1.82 (2) | 2.672 (4) | 175 (5) |

Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$.

in a chelating *syn–syn* fashion, while the other carboxylate group donates a single O atom to two adjacent Co atoms. One carboxylate O atom (O3) of each cmb ligand remains unligated. The chain motifs are connected into [Co$_2$($\mu$-H$_2$O)$_2$(cmb)]$_n$ two-dimensional slabs by the exo-tetradentate

The bound water molecules bridge adjacent Co atoms to construct [Co($\mu$-H$_2$O)]$_n$ one-dimensional chain submotifs arranged parallel to the *b* crystal axis, in which the Co$\cdots$Co internuclear distance measures 3.170 (1) Å. Carboxylate groups from cmb ligands and single carboxylate O atoms from other cmb ligands also bridge the same Co$\cdots$Co internuclear distance, thereby affording [Co(OCO)($\mu$-H$_2$O)($\mu$-O)]$_n$ chain motifs oriented along the *b* crystal direction (Fig. 2). One carboxylate terminus of the cmb ligands bridges two Co atoms



**Figure 3**
A [Co($\mu$-H$_2$O)(cmb)]$_n$ coordination polymer slab in the title compound.
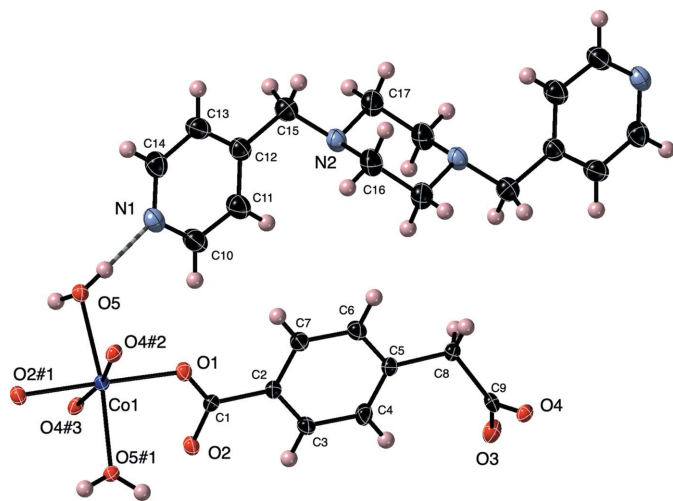


**Figure 1**
The cobalt coordination environment in the title compound with a full cmb ligand and cocrystallized species. Displacement ellipsoids are drawn at the 50% probability level. Water molecule O1W has been omitted. Color code: Co dark blue, O red, N light blue, C black, and H pink. The symmetry codes are as listed in Table 1.
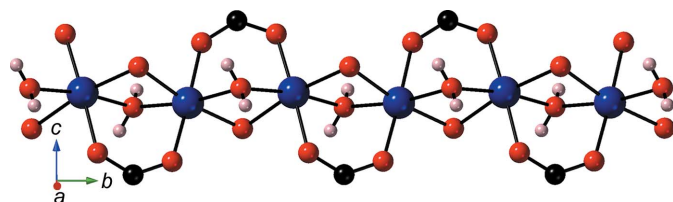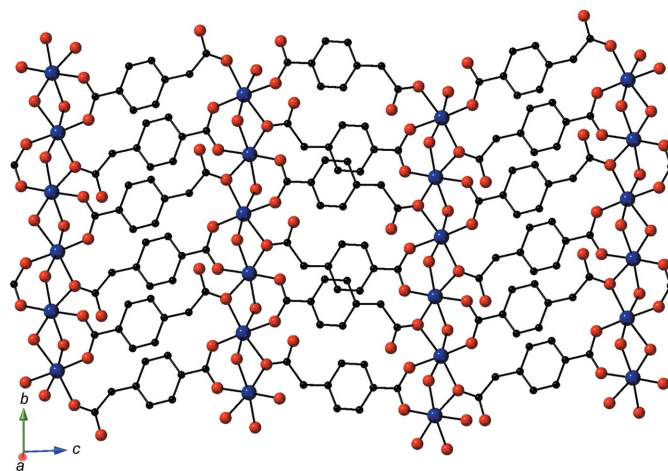


**Figure 2**
The [Co(OCO)($\mu$-H$_2$O)($\mu$-O)]$_n$ coordination polymer chain in the title compound.



**Figure 4**
The supramolecular three-dimensional structure formed by O—H$\cdots$N hydrogen bonding (hatched bonds) between [Co(cmb)($\mu$-H$_2$O)]$_n$ slabs and cocrystallized bpmp molecules.

## Table 3
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | [Co(C$_9$H$_6$O$_4$)(H$_2$O)]·0.5C$_{16}$H$_{20}$N$_4$·0.5H$_2$O |
| $M_r$ | 796.54 |
| Crystal system, space group | Monoclinic, $C2/c$ |
| Temperature (K) | 173 |
| $a$, $b$, $c$ (Å) | 27.036 (6), 6.3093 (13), 20.653 (5) |
| $\beta$ (°) | 105.536 (6) |
| $V$ (Å$^3$) | 3394.2 (13) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.05 |
| Crystal size (mm) | 0.27 × 0.14 × 0.09 |
| | |
| **Data collection** | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2014) |
| $T_{min}$, $T_{max}$ | 0.669, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8691, 3089, 2334 |
| $R_{int}$ | 0.044 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.604 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.041, 0.113, 1.06 |
| No. of reflections | 3089 |
| No. of parameters | 243 |
| No. of restraints | 3 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.65, −0.66 |

Computer programs: *COSMO* (Bruker, 2009), *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2008), and *OLEX2* (Dolomanov *et al.*, 2009).

cmb ligands; these slabs are oriented parallel to the *bc* crystal planes (Fig. 3).

[Co($\mu$-H$_2$O)(cmb)]$_n$ layers are connected into the three-dimensional crystal structure by hydrogen bonding mediated by the unligated bpmp molecules in the interlamellar regions. The pyridyl termini of the cocrystallized bpmp molecules accept hydrogen bonds from the bridging water molecules in two adjacent layer motifs (Fig. 4). Cocrystallized water molecules are held in the crystal by donating hydrogen bonds to the bpmp piperazine N atoms. Details regarding the hydrogen-bonding patterns in the title compound are listed in Table 2.

## Synthesis and crystallization

Co(NO$_3$)$_2$·6H$_2$O (108 mg, 0.37 mmol), 4-(carboxymethyl)-benzoic acid (cmbH$_2$) (67 mg, 0.37 mmol), 1,4-bis(pyridin-4-ylmethyl)piperazine (bpmp) (99 mg, 0.37 mmol), and 0.75 ml of a 1.0 *M* NaOH solution were placed in 10 ml distilled H$_2$O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 393 K for 48 h and then cooled slowly to 273 K. Pink crystals of the title complex were obtained in 68% yield.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms attached to C atoms were placed in calculated positions and refined with a riding model. The H atoms bound to the water O5 atom were found *via* a difference map and were refined freely with a restraint of 0.85 Å for the O—H distances, but those bound to atom O1*W* were positioned geometrically and refined using a riding model.

## References

Bruker (2009). *COSMO*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2014). *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Martin, D. P., Braverman, M. A. & LaDuca, R. L. (2007). *Cryst. Growth Des.* **7**, 2609–2619.

Robinson, M. E., Mizzi, J. E., Staples, R. J. & LaDuca, R. L. (2015). *Cryst. Growth Des.* **15**, 2260–2271.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.

# full crystallographic data

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**Poly[[(μ-aqua)[μ4-4-(carboxylatomethyl)benzoato]cobalt(II)] hemi[1,4-bis(pyridin-4-ylmethyl)piperazine] hemihydrate]**

*Crystal data*

| | |
|---|---|
| $[Co(C_9H_6O_4)(H_2O)] \cdot 0.5C_{16}H_{20}N_4 \cdot 0.5H_2O$ | $F(000) = 1648$ |
| $M_r = 796.54$ | $D_x = 1.559$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 27.036$ (6) Å | Cell parameters from 3416 reflections |
| $b = 6.3093$ (13) Å | $\theta = 2.1$–25.4° |
| $c = 20.653$ (5) Å | $\mu = 1.05$ mm$^{-1}$ |
| $\beta = 105.536$ (6)° | $T = 173$ K |
| $V = 3394.2$ (13) Å$^3$ | Block, pink |
| $Z = 4$ | $0.27 \times 0.14 \times 0.09$ mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 8691 measured reflections |
| Radiation source: sealed tube | 3089 independent reflections |
| Graphite monochromator | 2334 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 8.36 pixels mm$^{-1}$ | $R_{int} = 0.044$ |
| $\omega$ scans | $\theta_{max} = 25.4°$, $\theta_{min} = 2.1°$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2014) | $h = -31 \rightarrow 32$ |
| | $k = -7 \rightarrow 7$ |
| $T_{min} = 0.669$, $T_{max} = 0.745$ | $l = -24 \rightarrow 24$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: mixed |
| Least-squares matrix: full | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | |
| $wR(F^2) = 0.113$ | $w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 5.8489P]$ |
| $S = 1.06$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 3089 reflections | $(\Delta/\sigma)_{max} = 0.002$ |
| 243 parameters | $\Delta\rho_{max} = 0.65$ e Å$^{-3}$ |
| 3 restraints | $\Delta\rho_{min} = -0.66$ e Å$^{-3}$ |
| Primary atom site location: dual | |

*Special details*

**Experimental**. Data was collected using a BRUKER CCD (charge coupled device) based diffractometer equipped with an Oxford low-temperature apparatus operating at 173 K. A suitable crystal was chosen and mounted on a nylon loop using Paratone oil. Data were measured using omega scans of 0.5° per frame for 30 s. The total number of images were based on results from the program COSMO where redundancy was expected to be 4 and completeness to 0.83Å to 100%. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections.Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS6 multi-scan technique, supplied by George Sheldrick. The structure was solved by the direct method using the SHELXT program and refined by least squares method on F2, SHELXL, incorporated in OLEX2.

**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**. The structure was refined by Least Squares using version 2018/3 of XL (Sheldrick, 2015) incorporated in Olex2 (Dolomanov *et al.*, 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the Hydrogen atom on the nitrogen atom which was found by difference Fourier methods and refined isotropically.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

|      | $x$ | $y$ | $z$ | $U_{iso}$\*/$U_{eq}$ | Occ. (<1) |
| --- | --- | --- | --- | --- | --- |
| Co1 | 0.74834 (2) | 0.12245 (6) | 0.74217 (2) | 0.01613 (16) | |
| O1 | 0.77518 (9) | 0.2010 (3) | 0.66350 (10) | 0.0218 (5) | |
| O2 | 0.77731 (9) | 0.5545 (3) | 0.67641 (10) | 0.0214 (5) | |
| O3 | 0.84413 (9) | 0.8638 (3) | 0.37647 (11) | 0.0251 (6) | |
| O4 | 0.79387 (8) | 0.6398 (3) | 0.30472 (10) | 0.0177 (5) | |
| O5 | 0.69426 (9) | 0.3776 (3) | 0.72357 (11) | 0.0176 (5) | |
| N1 | 0.61639 (12) | 0.3261 (5) | 0.77903 (15) | 0.0320 (7) | |
| N2 | 0.50168 (11) | 0.4195 (5) | 0.93570 (14) | 0.0300 (7) | |
| C1 | 0.78312 (12) | 0.3868 (5) | 0.64604 (14) | 0.0174 (7) | |
| C2 | 0.80076 (12) | 0.4150 (5) | 0.58368 (15) | 0.0200 (7) | |
| C3 | 0.80611 (13) | 0.6162 (5) | 0.56001 (16) | 0.0222 (7) | |
| H3 | 0.799069 | 0.736233 | 0.583858 | 0.027\* | |
| C4 | 0.82169 (14) | 0.6449 (5) | 0.50162 (16) | 0.0272 (8) | |
| H4 | 0.824641 | 0.784229 | 0.485601 | 0.033\* | |
| C5 | 0.83291 (12) | 0.4727 (5) | 0.46672 (14) | 0.0185 (7) | |
| C6 | 0.82768 (13) | 0.2713 (5) | 0.49056 (16) | 0.0255 (8) | |
| H6 | 0.835191 | 0.151654 | 0.466903 | 0.031\* | |
| C7 | 0.81175 (13) | 0.2408 (5) | 0.54812 (16) | 0.0251 (8) | |
| H7 | 0.808268 | 0.101157 | 0.563545 | 0.030\* | |
| C8 | 0.85144 (13) | 0.4970 (5) | 0.40366 (14) | 0.0202 (7) | |
| H8A | 0.889229 | 0.513829 | 0.417283 | 0.024\* | |
| H8B | 0.843514 | 0.364930 | 0.377015 | 0.024\* | |
| C9 | 0.82837 (13) | 0.6809 (5) | 0.35940 (15) | 0.0195 (7) | |
| C10 | 0.60190 (15) | 0.4890 (7) | 0.81086 (19) | 0.0395 (10) | |
| H10 | 0.617359 | 0.623322 | 0.809065 | 0.047\* | |
| C11 | 0.56540 (16) | 0.4711 (6) | 0.8464 (2) | 0.0419 (10) | |
| H11 | 0.556036 | 0.591621 | 0.867983 | 0.050\* | |
| C12 | 0.54265 (14) | 0.2779 (6) | 0.85029 (17) | 0.0304 (8) | |

| C13 | 0.55802 (15) | 0.1093 (6) | 0.81812 (19) | 0.0355 (9) | |
| H13 | 0.543538 | −0.027144 | 0.819787 | 0.043* | |
| C14 | 0.59459 (15) | 0.1393 (6) | 0.78341 (19) | 0.0354 (9) | |
| H14 | 0.604698 | 0.020841 | 0.761580 | 0.043* | |
| C15 | 0.50169 (15) | 0.2492 (7) | 0.88805 (19) | 0.0373 (10) | |
| H15A | 0.467525 | 0.242547 | 0.855163 | 0.045* | |
| H15B | 0.507536 | 0.112621 | 0.912525 | 0.045* | |
| C16 | 0.54563 (14) | 0.4017 (6) | 0.99510 (18) | 0.0345 (9) | |
| H16A | 0.577929 | 0.403010 | 0.981173 | 0.041* | |
| H16B | 0.543748 | 0.265931 | 1.018344 | 0.041* | |
| C17 | 0.45449 (14) | 0.4153 (7) | 0.95746 (19) | 0.0371 (10) | |
| H17A | 0.452101 | 0.279572 | 0.980461 | 0.045* | |
| H17B | 0.424369 | 0.426346 | 0.917854 | 0.045* | |
| O1W | 0.4535 (4) | 0.7370 (16) | 0.8420 (5) | 0.131 (4) | 0.5 |
| H1WA | 0.455906 | 0.672793 | 0.879981 | 0.196* | 0.5 |
| H1WB | 0.468736 | 0.858073 | 0.853331 | 0.196* | 0.5 |
| H5A | 0.6813 (14) | 0.440 (6) | 0.6864 (13) | 0.044 (12)* | |
| H5B | 0.6705 (14) | 0.359 (7) | 0.743 (2) | 0.072 (17)* | |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.0225 (3) | 0.0114 (2) | 0.0161 (2) | −0.00011 (18) | 0.00797 (18) | 0.00042 (16) |
| O1 | 0.0344 (15) | 0.0149 (12) | 0.0194 (11) | 0.0002 (10) | 0.0130 (10) | 0.0009 (9) |
| O2 | 0.0313 (14) | 0.0169 (12) | 0.0196 (11) | −0.0004 (10) | 0.0132 (10) | 0.0000 (9) |
| O3 | 0.0346 (15) | 0.0200 (13) | 0.0178 (11) | −0.0065 (11) | 0.0019 (10) | 0.0005 (9) |
| O4 | 0.0228 (13) | 0.0150 (12) | 0.0127 (10) | −0.0003 (9) | 0.0003 (9) | −0.0008 (8) |
| O5 | 0.0221 (13) | 0.0143 (12) | 0.0168 (11) | 0.0021 (10) | 0.0061 (10) | 0.0019 (9) |
| N1 | 0.0281 (19) | 0.0404 (19) | 0.0293 (16) | 0.0012 (15) | 0.0109 (14) | 0.0035 (14) |
| N2 | 0.0225 (17) | 0.0423 (19) | 0.0271 (15) | −0.0019 (14) | 0.0101 (13) | −0.0023 (13) |
| C1 | 0.0181 (18) | 0.0184 (17) | 0.0152 (15) | 0.0010 (14) | 0.0037 (13) | 0.0017 (13) |
| C2 | 0.0214 (19) | 0.0233 (18) | 0.0160 (15) | 0.0024 (14) | 0.0059 (13) | 0.0013 (13) |
| C3 | 0.034 (2) | 0.0137 (16) | 0.0223 (16) | 0.0006 (15) | 0.0127 (15) | −0.0021 (13) |
| C4 | 0.045 (2) | 0.0169 (18) | 0.0232 (17) | −0.0018 (16) | 0.0160 (16) | 0.0033 (14) |
| C5 | 0.0194 (18) | 0.0206 (17) | 0.0148 (14) | −0.0006 (14) | 0.0034 (13) | −0.0001 (13) |
| C6 | 0.036 (2) | 0.0184 (18) | 0.0257 (17) | 0.0017 (16) | 0.0138 (16) | −0.0015 (14) |
| C7 | 0.037 (2) | 0.0154 (17) | 0.0270 (17) | 0.0014 (16) | 0.0160 (16) | 0.0031 (14) |
| C8 | 0.0246 (19) | 0.0197 (17) | 0.0171 (15) | 0.0014 (15) | 0.0069 (14) | 0.0028 (13) |
| C9 | 0.0214 (19) | 0.0230 (18) | 0.0172 (15) | −0.0015 (14) | 0.0104 (14) | −0.0021 (13) |
| C10 | 0.046 (3) | 0.035 (2) | 0.043 (2) | −0.004 (2) | 0.022 (2) | 0.0025 (19) |
| C11 | 0.053 (3) | 0.034 (2) | 0.050 (2) | −0.002 (2) | 0.032 (2) | −0.006 (2) |
| C12 | 0.028 (2) | 0.035 (2) | 0.0288 (18) | −0.0014 (18) | 0.0088 (16) | 0.0007 (16) |
| C13 | 0.038 (2) | 0.030 (2) | 0.042 (2) | −0.0035 (18) | 0.0172 (18) | 0.0008 (17) |
| C14 | 0.040 (2) | 0.034 (2) | 0.036 (2) | 0.0052 (19) | 0.0168 (18) | −0.0008 (17) |
| C15 | 0.036 (2) | 0.043 (2) | 0.037 (2) | −0.005 (2) | 0.0162 (18) | −0.0036 (18) |
| C16 | 0.022 (2) | 0.050 (3) | 0.033 (2) | 0.0060 (18) | 0.0099 (16) | −0.0004 (18) |
| C17 | 0.020 (2) | 0.061 (3) | 0.0313 (19) | −0.0041 (19) | 0.0076 (16) | −0.0082 (18) |
| O1W | 0.165 (10) | 0.120 (8) | 0.115 (8) | −0.008 (8) | 0.052 (7) | 0.013 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—O1 | 2.011 (2) | C5—C8 | 1.523 (4) |
| Co1—O2i | 2.029 (2) | C6—H6 | 0.9500 |
| Co1—O4ii | 2.094 (2) | C6—C7 | 1.382 (4) |
| Co1—O4iii | 2.140 (2) | C7—H7 | 0.9500 |
| Co1—O5 | 2.139 (2) | C8—H8A | 0.9900 |
| Co1—O5i | 2.169 (2) | C8—H8B | 0.9900 |
| O1—C1 | 1.262 (4) | C8—C9 | 1.505 (4) |
| O2—C1 | 1.261 (4) | C10—H10 | 0.9500 |
| O3—C9 | 1.248 (4) | C10—C11 | 1.383 (5) |
| O4—C9 | 1.284 (4) | C11—H11 | 0.9500 |
| O5—H5A | 0.851 (19) | C11—C12 | 1.377 (5) |
| O5—H5B | 0.855 (19) | C12—C13 | 1.376 (5) |
| N1—C10 | 1.334 (5) | C12—C15 | 1.526 (5) |
| N1—C14 | 1.332 (5) | C13—H13 | 0.9500 |
| N2—C15 | 1.457 (5) | C13—C14 | 1.381 (5) |
| N2—C16 | 1.466 (5) | C14—H14 | 0.9500 |
| N2—C17 | 1.462 (4) | C15—H15A | 0.9900 |
| C1—C2 | 1.499 (4) | C15—H15B | 0.9900 |
| C2—C3 | 1.382 (4) | C16—H16A | 0.9900 |
| C2—C7 | 1.397 (4) | C16—H16B | 0.9900 |
| C3—H3 | 0.9500 | C16—C17iv | 1.515 (5) |
| C3—C4 | 1.392 (4) | C17—H17A | 0.9900 |
| C4—H4 | 0.9500 | C17—H17B | 0.9900 |
| C4—C5 | 1.382 (4) | O1W—H1WA | 0.8698 |
| C5—C6 | 1.384 (5) | O1W—H1WB | 0.8699 |
| | | | |
| O1—Co1—O2i | 177.55 (9) | C7—C6—H6 | 119.4 |
| O1—Co1—O4iii | 92.37 (9) | C2—C7—H7 | 119.9 |
| O1—Co1—O4ii | 95.23 (9) | C6—C7—C2 | 120.1 (3) |
| O1—Co1—O5i | 93.31 (9) | C6—C7—H7 | 119.9 |
| O1—Co1—O5 | 92.67 (9) | C5—C8—H8A | 108.6 |
| O2i—Co1—O4iii | 85.22 (9) | C5—C8—H8B | 108.6 |
| O2i—Co1—O4ii | 87.21 (9) | H8A—C8—H8B | 107.5 |
| O2i—Co1—O5 | 86.49 (9) | C9—C8—C5 | 114.8 (3) |
| O2i—Co1—O5i | 87.29 (9) | C9—C8—H8A | 108.6 |
| O4ii—Co1—O4iii | 170.65 (6) | C9—C8—H8B | 108.6 |
| O4iii—Co1—O5i | 93.25 (8) | O3—C9—O4 | 123.2 (3) |
| O4ii—Co1—O5i | 80.90 (9) | O3—C9—C8 | 119.1 (3) |
| O4ii—Co1—O5 | 104.48 (9) | O4—C9—C8 | 117.7 (3) |
| O5—Co1—O4iii | 80.55 (9) | N1—C10—H10 | 118.5 |
| O5—Co1—O5i | 171.56 (4) | N1—C10—C11 | 122.9 (4) |
| C1—O1—Co1 | 125.86 (19) | C11—C10—H10 | 118.5 |
| C1—O2—Co1v | 134.8 (2) | C10—C11—H11 | 120.1 |
| Co1ii—O4—Co1vi | 96.93 (8) | C12—C11—C10 | 119.8 (4) |
| C9—O4—Co1ii | 138.0 (2) | C12—C11—H11 | 120.1 |
| C9—O4—Co1vi | 123.7 (2) | C11—C12—C15 | 122.1 (3) |

| | | | |
|---|---|---|---|
| Co1—O5—Co1[v] | 94.73 (9) | C13—C12—C11 | 117.3 (3) |
| Co1—O5—H5A | 127 (3) | C13—C12—C15 | 120.6 (3) |
| Co1[v]—O5—H5A | 93 (3) | C12—C13—H13 | 120.2 |
| Co1[v]—O5—H5B | 120 (3) | C12—C13—C14 | 119.7 (4) |
| Co1—O5—H5B | 112 (3) | C14—C13—H13 | 120.2 |
| H5A—O5—H5B | 108 (4) | N1—C14—C13 | 123.2 (4) |
| C14—N1—C10 | 117.0 (3) | N1—C14—H14 | 118.4 |
| C15—N2—C16 | 111.2 (3) | C13—C14—H14 | 118.4 |
| C15—N2—C17 | 110.6 (3) | N2—C15—C12 | 112.9 (3) |
| C17—N2—C16 | 108.7 (3) | N2—C15—H15A | 109.0 |
| O1—C1—C2 | 118.3 (3) | N2—C15—H15B | 109.0 |
| O2—C1—O1 | 125.7 (3) | C12—C15—H15A | 109.0 |
| O2—C1—C2 | 116.0 (3) | C12—C15—H15B | 109.0 |
| C3—C2—C1 | 120.0 (3) | H15A—C15—H15B | 107.8 |
| C3—C2—C7 | 118.7 (3) | N2—C16—H16A | 109.7 |
| C7—C2—C1 | 121.3 (3) | N2—C16—H16B | 109.7 |
| C2—C3—H3 | 119.6 | N2—C16—C17[iv] | 110.0 (3) |
| C2—C3—C4 | 120.7 (3) | H16A—C16—H16B | 108.2 |
| C4—C3—H3 | 119.6 | C17[iv]—C16—H16A | 109.7 |
| C3—C4—H4 | 119.7 | C17[iv]—C16—H16B | 109.7 |
| C5—C4—C3 | 120.6 (3) | N2—C17—C16[iv] | 109.8 (3) |
| C5—C4—H4 | 119.7 | N2—C17—H17A | 109.7 |
| C4—C5—C6 | 118.6 (3) | N2—C17—H17B | 109.7 |
| C4—C5—C8 | 122.4 (3) | C16[iv]—C17—H17A | 109.7 |
| C6—C5—C8 | 119.0 (3) | C16[iv]—C17—H17B | 109.7 |
| C5—C6—H6 | 119.4 | H17A—C17—H17B | 108.2 |
| C7—C6—C5 | 121.3 (3) | H1WA—O1W—H1WB | 104.5 |
| | | | |
| Co1—O1—C1—O2 | 2.7 (5) | C5—C6—C7—C2 | −0.3 (5) |
| Co1—O1—C1—C2 | −176.9 (2) | C5—C8—C9—O3 | 76.4 (4) |
| Co1[v]—O2—C1—O1 | −3.5 (5) | C5—C8—C9—O4 | −105.1 (3) |
| Co1[v]—O2—C1—C2 | 176.2 (2) | C6—C5—C8—C9 | 145.6 (3) |
| Co1[vi]—O4—C9—O3 | −11.0 (4) | C7—C2—C3—C4 | 0.6 (5) |
| Co1[ii]—O4—C9—O3 | −174.2 (2) | C8—C5—C6—C7 | 179.0 (3) |
| Co1[vi]—O4—C9—C8 | 170.56 (19) | C10—N1—C14—C13 | 0.8 (6) |
| Co1[ii]—O4—C9—C8 | 7.3 (4) | C10—C11—C12—C13 | 0.3 (6) |
| O1—C1—C2—C3 | 175.1 (3) | C10—C11—C12—C15 | −179.3 (4) |
| O1—C1—C2—C7 | −4.5 (5) | C11—C12—C13—C14 | −0.5 (6) |
| O2—C1—C2—C3 | −4.6 (5) | C11—C12—C15—N2 | −18.8 (5) |
| O2—C1—C2—C7 | 175.8 (3) | C12—C13—C14—N1 | −0.1 (6) |
| N1—C10—C11—C12 | 0.5 (6) | C13—C12—C15—N2 | 161.7 (3) |
| C1—C2—C3—C4 | −179.0 (3) | C14—N1—C10—C11 | −1.0 (6) |
| C1—C2—C7—C6 | 179.6 (3) | C15—N2—C16—C17[iv] | 178.2 (3) |
| C2—C3—C4—C5 | −1.0 (5) | C15—N2—C17—C16[iv] | −177.9 (3) |
| C3—C2—C7—C6 | 0.1 (5) | C15—C12—C13—C14 | 179.1 (4) |
| C3—C4—C5—C6 | 0.8 (5) | C16—N2—C15—C12 | −73.7 (4) |
| C3—C4—C5—C8 | −178.3 (3) | C16—N2—C17—C16[iv] | 59.7 (4) |

| | | | |
|---|---|---|---|
| C4—C5—C6—C7 | −0.2 (5) | C17—N2—C15—C12 | 165.4 (3) |
| C4—C5—C8—C9 | −35.2 (5) | C17—N2—C16—C17$^{iv}$ | −59.8 (4) |

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

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C11—H11···N2 | 0.95 | 2.53 | 2.860 (5) | 101 |
| O1$W$—H1$WA$···N2 | 0.87 | 2.16 | 2.847 (10) | 136 |
| O5—H5$A$···O3$^{vii}$ | 0.85 (2) | 1.79 (2) | 2.619 (3) | 164 (4) |
| O5—H5$B$···N1 | 0.86 (2) | 1.82 (2) | 2.672 (4) | 175 (5) |

Symmetry code: (vii) −$x$+3/2, −$y$+3/2, −$z$+1.