Synthesis and crystal structure of catenapoly[[hexaaqua{μ₃-2-[bis(carboxylatomethyl)-amino]terephthalato}dicobalt(II)] pentahydrate] containing water tapes and pentamers

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The title coordination polymer, [\([\text{Co}_2\{(\text{C}_{12}\text{H}_7\text{NO}_8\text{)}\}\text{(H}_2\text{O})_6\}\cdot5\text{H}_2\text{O}]_n\), was crystallized at room temperature from an aqueous solution of 2-aminodiacetic terephthalic acid (H₄adtp) and cobalt(II) nitrate. The asymmetric unit consists of one adtp⁴⁻ ligand, one and two half CoII ions, six water ligands coordinated to CoII ions and five uncoordinated water molecules. Two of the cobalt cations lie on centres of inversion and are coordinated in octahedral O₂(OH₂)₄ environments, whereas the other adopts a slightly distorted octahedral NO₃(OH₂)₂ environment. The crystal structure contains parallel stacked, one-dimensional zigzag chains, [\([\text{Co}_2\{(\text{C}_{12}\text{H}_7\text{NO}_8\text{)}\}\text{(H}_2\text{O})_6\]\)]ₙ, which assemble into a three-dimensional supramolecular architecture via networks of hydrogen bonds involving the coordinated and free water molecules. One-dimensional ‘water tapes’ are formed, containing alternating six-membered and twelve-membered rings of water molecules, together with water pentamers, in which a central uncoordinated water molecule is hydrogen bonded to two coordinated and two free water molecules in a tetrahedral arrangement.

1. Chemical context

Water clusters, which are aggregations of water molecules assembled via hydrogen bonding, are often observed in organic and organic–inorganic hybrid crystal structures. To date, a number of discrete water clusters of different sizes and conformations have been identified, including tetramers (Thakur et al., 2021; Ahmed et al., 2018), pentamers (Ghosh & Bharadwaj, 2006), hexamers (Zhao et al., 2015; Li et al., 2020), heptamers (He et al., 2012; Hedayetullah Mir & Vittal, 2008), octamers (Hao et al., 2013; Wei et al., 2009; Ghosh & Bharadwaj, 2006), decamers (Mukhopadhyay & Bernal, 2006), and other higher member clusters (Liu et al., 2018; Chen et al., 2020). In addition, examples of infinite water clusters consisting of one-dimensional water chains or ‘tapes’ (Gacki et al., 2020; Zhao et al., 2019; Saraei et al., 2019; Han et al., 2019; Liu et al., 2020; Saraei et al., 2018), two-dimensional water layers (Mei et al., 2016) and three-dimensional water frameworks (Huang et al., 2007, 2019; Wu et al., 2013) have also been reported recently. Water clusters are often held in the cavities of the host structures as guest molecules, which can enhance the stability of the structure. Water clusters, when hydrogen bonded to the host structures, play a vital role in assembling organic and organic–inorganic complex molecules into three-dimensional architectures (Thakur et al., 2021; Zia et al., 2020;
Huang et al., 2019; Liu et al., 2018). Our work focuses on the construction of metal complexes using semi-rigid multicarboxylic acids containing aminodiacetate moieties, and analysing the affects of weak hydrogen-bonding interactions on their supramolecular assemblies (Ma et al., 2015a). We have previously reported the synthesis of two CuII complexes based on 2-(carboxyphenyl)-aminodiacetic acid (H2cpida) and 1,10-phenanthroline (phen), and discussed the influence of hydrogen bonding on the resulting structures (Ma et al., 2015b). Herein we report the synthesis and structural characterization of a CoII coordination polymer, [Co2(C12H7-NO8)(H2O)6] (I), based on 2-aminodiacetic terephthalic acid (H4adtp). The hydrogen-bonding interactions in (I), which result in the formation of one-dimensional water tapes and isolated water pentamers, are discussed in detail.

2. Structural commentary

Compound (I) crystallizes in the triclinic space group P1. The asymmetric unit comprises three crystallographically distinct CoII ions, one adtp4− ligand, six coordinated water ligands and five free water molecules. Regarding the adtp4− ligand, the carboxylic groups of the aminodiacetate moiety and that in the meta-position adopt monodentate coordination modes on bonding to cobalt, whereas the carboxylic group in the ortho-position coordinates in a syn-anti bidentate bridging fashion (see Scheme). As shown in Fig. 1, Co2 is located in a distorted octahedral N6O5 environment. The adip4− ion chelates to Co2 via the amino nitrogen atom (N1), two acetate oxygen atoms (O2, O2i for Co1; O3, O3ii for Co3). The remaining two cis-related sites around Co2 are ligated by oxygen atoms (O9 and O14) of terminal water molecules. Co1 and Co3 both lie on inversion centres and are located in octahedral O6 environments. In each case, a pair of trans-related coordination sites are bonded to equivalent carboxylate oxygen atoms (O2, O2′ for Co1; O3, O3′ for Co3). The remaining trans-related sites of Co1 and Co3 are ligated by two pairs of equivalent oxygen atoms from terminal water molecules (O12, O12′ and O13, O13′ for Co1; O10, O10′ and O11, O11′ for Co3, respectively). The length of the Co2—N1 bond is 2.1712 (18) Å and the Co—O distances lie in the range 2.0128 (15)−2.1330 (15) Å, all of which are reasonable values. The adtp4− ligand links the Co1 and Co3 atoms via the ortho- and meta-position carboxylate groups and a zigzag chain is formed by inversion operations with the closest Co1...Co3 and Co2...Co3 distances being 10.657 (1) and 5.194 (1) Å, respectively (Fig. 2).

3. Supramolecular features

The zigzag chains are arranged parallel to each other and intermolecular hydrogen bonds (Table 1) between adjacent

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O14—H14A...O1i | 0.87 | 1.87 | 2.723 (2) | 166 |
| O14—H14B...O19i | 0.87 | 1.92 | 2.743 (2) | 158 |
| O9—H9A...O15ii | 0.87 | 1.84 | 2.702 (2) | 168 |
| O9—H9B...O6iii | 0.87 | 1.87 | 2.742 (2) | 175 |
| O13—H13A...O5iv | 0.87 | 1.88 | 2.727 (2) | 162 |
| O13—H13B...O1ii | 0.87 | 1.98 | 2.759 (2) | 148 |
| O18—H18A...O5iv | 0.87 | 1.93 | 2.752 (2) | 158 |
| O18—H18B...O7i | 0.87 | 1.88 | 2.750 (2) | 177 |
| O15—H15A...O19 | 0.87 | 1.87 | 2.738 (2) | 177 |
| O15—H15B...O16 | 0.87 | 1.85 | 2.692 (3) | 162 |
| O15—H15B...O16A | 0.87 | 2.02 | 2.833 (7) | 156 |
| O11—H11C...O13vi | 0.87 | 1.82 | 2.686 (2) | 172 |
| O11—H11D...O1vi | 0.87 | 1.95 | 2.786 (2) | 161 |
| O10—H10A...O17iii | 0.87 | 1.88 | 2.705 (2) | 158 |
| O10—H10B...O4 | 0.87 | 2.11 | 2.740 (2) | 129 |
| O12—H12A...O8ii | 0.87 | 1.92 | 2.773 (2) | 166 |
| O12—H12B...O6ii | 0.87 | 1.98 | 2.846 (2) | 172 |
| O19—H19A...O18 | 0.87 | 1.85 | 2.719 (2) | 175 |
| O19—H19B...O11ii | 0.87 | 1.94 | 2.786 (2) | 165 |
| O17—H17A...O7vii | 0.87 | 1.88 | 2.702 (2) | 157 |
| O17—H17B...O18 | 0.87 | 1.95 | 2.804 (2) | 166 |
| O16A—H16C...O17vi | 0.87 | 2.11 | 2.861 (8) | 144 |
| O16H—H16A...O17iv | 0.87 | 2.10 | 2.921 (4) | 156 |

Symmetry codes: (i) x, y, z; (ii) −x, −y, −z; (iii) −x, −y, −z; (iv) −x, y, z; (v) x, −y, −z; (vi) x, −y, z; (vii) x, y, 1−z; (viii) −x, −y, 1−z; (ix) x, y, 1−z; (x) x, y, z.

The crystallographic structure of CoII ions in (I) with displacement ellipsoids shown at the 50% probability level. H atoms have been omitted for clarity. Please label C atoms.
Chains play a significant role in assembling the three-dimensional supramolecular architecture. As shown in Fig. 3, one zigzag chain, highlighted in yellow, associates directly via hydrogen bonds with three pairs of nearby chains, which are highlighted in green, red and blue. The intermolecular hydrogen bonds between two adjacent chains can be classified into three groups: (I) intermolecular hydrogen bonds involving $O_{11} - H_{11} D_i/C1/C1/O_{11}$, $O_{12}^i - H_{12} B_{ii}/C1/C1/O_{6}$ and $O_{13}^{ii} - H_{13} A_{ii}/C1/C1/O_{5}$ (Fig. 4a); (II) intermolecular hydrogen bonds involving $O_9 - H_{9} B_{i}/C1/C1/O_6$ and equivalent $O_9^i - H_{9} B_{ii}/C1/C1/O_6$ (Fig. 5a) and (III) intermolecular hydrogen bonds involving $O_{12} - H_{12} A_{i}/C1/C1/O_8$ and $O_{14} - H_{14} A_{i}/C1/C1/O_{1i}$ (Fig. 6a). The yellow zigzag chain connects with two neighbouring green chains via the group I intermolecular hydrogen bonds, resulting in a two-dimensional supramolecular layer (Fig. 4b). The yellow chain also connects with the red and blue chains, assembling into two-dimensional supramolecular layers via the intermolecular hydrogen bonds of groups II (Fig. 5b) and III (Fig. 6b), respectively.

In addition, there are a number of other hydrogen-bonding interactions within the structure. The free water molecule $H_2O_{19}$ forms four hydrogen bonds, two with coordinated water molecules $H_2O_{11}$ and $H_2O_{14}$, and two with free water.
molecules H$_2$O$_{15}$ and H$_2$O$_{18}$ (Fig. 7a), generating a tetrahedral water pentamer. Similar pentamers have been observed previously (Saraei et al., 2018; Liu et al., 2020). In addition, the five free water molecules H$_2$O$_{15}$, H$_2$O$_{16}$ (which is disordered over two positions, H$_2$O$_{16}$A and H$_2$O$_{16}$B), H$_2$O$_{17}$, H$_2$O$_{18}$ and H$_2$O$_{19}$ are linked into a one-dimensional water chain via hydrogen bonds (Fig. 7b). The water chains are then further connected into a hydrogen-bonded supramolecular layer via the coordinated water molecule, H$_2$O$_{11}$, and the carboxylate oxygen atom, O$_7$ (Fig. 7c). The resulting water layer contains alternating six- and twelve-membered oxygen rings and can be viewed as a one-dimensional T$_6$ (3)12 (3) water tape. Similar water tapes have been reported previously (Han et al., 2019; Liu et al., 2012; Zhao et al., 2019, Hao et al., 2013).

4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.42, May 2021 update; Groom et al., 2016) reveals 19 structures containing H$_4$adtp, three of which are Co$^{II}$ complexes,
including one two-dimensional coordination polymer (refcode CUFDIS; Ma et al., 2021) and two discrete coordination complexes (RAXJUX and RAXKEI; Liu et al., 2012b). No structures containing H4adtp with similar cell parameters to those of the title compound have been reported.

5. Synthesis and crystallization

H4adtp was synthesized using a method based on that described in the literature (Xu et al., 2006). The other chemicals were purchased from commercial sources and used without further purification. A mixture of Co(NO3)2·6H2O (0.2910 g, 1 mmol), H4adtp (0.0594 g, 0.2 mmol) and hexamethylenetetramine (0.0701 g, 0.5 mmol) was dissolved in 6 mL of water. The solvent was allowed to evaporate slowly at room temperature. Crystals in the form of light-pink blocks were grown after one week, collected by filtration and dried in air. A 62% yield based on H4adtp was obtained. Analysis of the title compound was performed by element analysis (Elementar Vario EL III). Anal. Calc. for C15H29N1O19Co2: C 54.10, H 6.40, N 5.21; Found: C 54.05, H 6.30, N 5.25.

The phase purity of (I) was demonstrated by powder X-ray diffraction analysis (PXRD; Fig. S1 in the supporting information). The peak positions of the experimental PXRD pattern match well with those simulated from the single-crystal X-ray data, indicating that the pure phase was synthesized.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. During the refinement of (I), O16 was found to be disordered over two sites (O16 and O16A) with occupancies of 0.704 (5) and 0.296 (5). The hydrogen atoms of the water molecules were found in electron-density maps and refined as riding, with Uiso(H) = 1.5 Ueq(O). Other hydrogen atoms were placed at geometrically calculated positions and treated as riding, with Cap1—H = 0.93 Å, Cap2—H = 0.97 Å and Uiso(H) = 1.2 Ueq(C).

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Synthesis and crystal structure of catena-poly[[hexaaqua{μ₃-2-[bis(carboxylatomethyl)amino]terephthalato}dicobalt(II)] pentahydrate] containing water tapes and pentamers

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Computing details

Data collection: CrystalClear (Rigaku, 2008); cell refinement: CrystalClear (Rigaku, 2008); data reduction: CrystalClear (Rigaku, 2008); program(s) used to solve structure: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

catena-Poly[[hexaaqua{μ₃-2-[bis(carboxylatomethyl)amino]terephthalato}dicobalt(II)] pentahydrate]

Crystal data

[Co₂(C₁₂H₇NO₈)(H₂O)₆]·5H₂O  Z = 2
Mᵣ = 609.22  F(000) = 628
Triclinic, P T
a = 9.7653 (15) Å  Dᵣ = 1.751 Mg m⁻³
b = 11.725 (2) Å  Mo Kα radiation, λ = 0.71073 Å
(c = 11.8191 (15) Å  Cell parameters from 3650 reflections
α = 64.882 (5)°  θ = 2.0–27.5°
β = 71.276 (7)°  μ = 1.53 mm⁻¹
γ = 86.692 (8)°  T = 293 K
V = 1155.6 (3) Å³  Block, clear light red
0.2 × 0.2 × 0.2 mm

Data collection

Rigaku Saturn724+ (2x2 bin mode)  10193 measured reflections
diffractometer  4052 independent reflections
Radiation source: Sealed Tube, Rotating Anode  3498 reflections with I > 2σ(I)
Graphite monochromator  Rint = 0.029
Detector resolution: 28.5714 pixels mm⁻¹  θmax = 25.0°, θmin = 2.1°
CCD_Profile_fitting scans  h = −11→11
Absorption correction: multi-scan  k = −13→13
(CrystalClear; Rigaku, 2008)  l = −14→14
Tmin = 0.844, Tmax = 1.000

Refinement

Refinement on F²  348 parameters
Least-squares matrix: full  2 restraints
R[F² > 2σ(F²)] = 0.027  Primary atom site location: structure-invariant
wR(F²) = 0.069  direct methods
S = 1.02  Hydrogen site location: mixed
4052 reflections  H-atom parameters constrained
supporting information

\[ w = \frac{1}{[\sigma^2(F_o^2) + (0.0373P)^2]} \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

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

\[ \Delta \rho_{\text{max}} = 0.97 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.45 \text{ e Å}^{-3} \]

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x   | y   | z   | U_{iso}*/U_{eq} | Occ. (<1) |
|----|-----|-----|-----|-----------------|-----------|
| Co1| 0.500000 | 0.000000 | 1.000000 | 0.01013 (11) |           |
| O1 | 0.71506 (15) | 0.16282 (13) | 0.67122 (14) | 0.0116 (3) |           |
| C1 | 0.6534 (2) | 0.36754 (19) | 0.6586 (2) | 0.0097 (4) |           |
| Co2| 0.92914 (3) | 0.81788 (3) | 0.25427 (3) | 0.00926 (9) |           |
| O2 | 0.53599 (15) | 0.17746 (13) | 0.83918 (14) | 0.0128 (3) |           |
| C2 | 0.7374 (2) | 0.43193 (19) | 0.5263 (2) | 0.0097 (4) |           |
| H2 | 0.787693 | 0.385882 | 0.481028 | 0.012* |           |
| Co3| 0.500000 | 1.000000 | 0.500000 | 0.00977 (11) |           |
| O3 | 0.53886 (16) | 0.81035 (13) | 0.52932 (14) | 0.0142 (3) |           |
| O14| 0.99581 (16) | 0.76339 (14) | 0.42109 (14) | 0.0152 (3) |           |
| H14A| 1.084005 | 0.796585 | 0.396511 | 0.023* |           |
| H14B| 0.943474 | 0.796773 | 0.472202 | 0.023* |           |
| C3 | 0.7484 (2) | 0.56273 (19) | 0.4598 (2) | 0.0090 (4) |           |
| O4 | 0.72895 (16) | 0.84545 (13) | 0.35178 (15) | 0.0158 (3) |           |
| O9 | 1.00200 (19) | 1.00342 (14) | 0.17472 (15) | 0.0207 (4) |           |
| H9A| 0.971354 | 1.053917 | 0.212391 | 0.031* |           |
| H9B| 1.039011 | 1.053478 | 0.090961 | 0.031* |           |
| C4 | 0.6636 (2) | 0.63255 (19) | 0.5254 (2) | 0.0098 (4) |           |
| O5 | 0.78350 (17) | 0.73838 (14) | 0.00522 (15) | 0.0163 (3) |           |
| C5 | 0.5863 (2) | 0.5667 (2) | 0.6599 (2) | 0.0113 (5) |           |
| H5 | 0.535647 | 0.611872 | 0.706117 | 0.014* |           |
| O6 | 0.86627 (16) | 0.84612 (13) | 0.08939 (14) | 0.0128 (3) |           |
| C6 | 0.5822 (2) | 0.43705 (19) | 0.7268 (2) | 0.0111 (5) |           |
| H6 | 0.532011 | 0.396404 | 0.817033 | 0.013* |           |
| O7 | 1.19306 (16) | 0.59855 (14) | 0.11284 (15) | 0.0188 (4) |           |
| O13| 0.36628 (16) | 0.07573 (13) | 1.12298 (15) | 0.0137 (3) |           |
| H13A| 0.305886 | 0.121648 | 1.085472 | 0.021* |           |
| H13B| 0.310559 | 0.014679 | 1.194882 | 0.021* |           |
| C7 | 0.6342 (2) | 0.22445 (19) | 0.7282 (2) | 0.0102 (5) |           |
| O18| 0.69274 (18) | 0.62405 (15) | 0.87758 (17) | 0.0216 (4) |           |
| H18A| 0.722316 | 0.639556 | 0.932159 | 0.032* |           |
| H18B| 0.730870 | 0.554995 | 0.878060 | 0.032* |           |
| O8 | 1.11592 (15) | 0.75971 (13) | 0.16099 (14) | 0.0126 (3) |           |
| C8 | 0.6440 (2) | 0.77274 (19) | 0.4638 (2) | 0.0099 (5) |           |
| C9 | 0.9740 (2) | 0.55842 (19) | 0.2918 (2) | 0.0123 (5) |           |
| H9C| 0.950428 | 0.492589 | 0.270057 | 0.015* |           |
Atomic displacement parameters (Å²)

|     | U¹¹ | U²² | U³³ | U¹² | U¹³ | U²³ |
|-----|-----|-----|-----|-----|-----|-----|
| Co1 | 0.0094 (2) | 0.0072 (2) | 0.0088 (2) | −0.00013 (16) | 0.00000 (18) | −0.00093 (17) |
| O1  | 0.0127 (8) | 0.0080 (7) | 0.0114 (8) | 0.0007 (6) | −0.0014 (7) | −0.0037 (6) |
| C1  | 0.0082 (11) | 0.0080 (11) | 0.0119 (11) | 0.0000 (8) | −0.00045 (9) | −0.0024 (9) |
| Co2 | 0.00941 (17) | 0.00736 (16) | 0.00848 (16) | −0.00012 (12) | −0.00072 (13) | −0.00260 (12) |
| O2  | 0.0119 (8) | 0.0074 (8) | 0.0098 (8) | −0.0006 (6) | 0.0021 (7) | 0.0008 (6) |
| C2  | 0.0097 (11) | 0.0101 (11) | 0.0098 (11) | 0.0021 (9) | −0.0027 (9) | −0.0054 (9) |
| Co3 | 0.0105 (2) | 0.0074 (2) | 0.0096 (2) | 0.00172 (16) | −0.00197 (18) | −0.00311 (17) |
| O3  | 0.0135 (8) | 0.0097 (8) | 0.0136 (8) | 0.0030 (6) | 0.0013 (7) | −0.0043 (7) |
| O14 | 0.0111 (8) | 0.0197 (8) | 0.0139 (8) | −0.0006 (7) | −0.0018 (7) | −0.0079 (7) |
| C3  | 0.0073 (11) | 0.0099 (11) | 0.0080 (11) | −0.0009 (8) | −0.0019 (9) | −0.0024 (9) |
| O4  | 0.0135 (8) | 0.0086 (8) | 0.0137 (8) | 0.0024 (6) | 0.0030 (7) | 0.0000 (7) |
| O9  | 0.0336 (10) | 0.0086 (8) | 0.0113 (8) | −0.0064 (7) | 0.0039 (8) | −0.0036 (7) |
| C4  | 0.0090 (11) | 0.0085 (11) | 0.0113 (11) | −0.0008 (8) | −0.0038 (9) | −0.0032 (9) |
### Geometric parameters (Å, °)

| Bond/Distance | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 |
|---------------|---------|---------|---------|---------|---------|---------|
| Co1—O2i      | 2.0890 (14) | O5—C12 | 1.240 (3) |         |         |         |
| Co1—O2       | 2.0890 (14) | C5—H5  | 0.9300   |         |         |         |
| Co1—O3i      | 2.0856 (15) | C5—C6  | 1.380 (3) |         |         |         |
| Co1—O3       | 2.0856 (15) | O6—C12 | 1.279 (3) |         |         |         |
| Co1—O12i     | 2.1231 (15) | C6—H6  | 0.9300   |         |         |         |
| Co1—O12      | 2.1231 (15) | O7—C10 | 1.239 (3) |         |         |         |
| O1—C7        | 1.267 (3)   | O13—H13A | 0.8734 |         |         |         |
| C1—C2        | 1.391 (3)   | O13—H13B | 0.8731 |         |         |         |
| C1—C6        | 1.389 (3)   | O18—H18A | 0.8706 |         |         |         |
| C1—C7        | 1.514 (3)   | O18—H18B | 0.8700 |         |         |         |
| Co2—O14      | 2.1039 (15) | O8—C10 | 1.270 (3) |         |         |         |
| Co2—O4       | 2.0128 (15) | C9—H9C  | 0.9700   |         |         |         |
| Co2—O9       | 2.0336 (15) | C9—H9D  | 0.9700   |         |         |         |
| Co2—O6       | 2.1168 (15) | C9—C10  | 1.534 (3) |         |         |         |
| Co2—O8       | 2.0521 (15) | C9—N1   | 1.492 (3) |         |         |         |
| Co2—N1       | 2.1712 (18) | O15—H15A | 0.8738 |         |         |         |
| O2—C7        | 1.259 (2)   | O15—H15B | 0.8699 |         |         |         |
| C2—H2        | 0.9300      | C11—H11A | 0.9700 |         |         |         |
| C2—C3        | 1.387 (3)   | C11—H11B | 0.9700 |         |         |         |
| Co3—O3       | 2.1311 (14) | C11—C12 | 1.516 (3) |         |         |         |
| Co3—O3i      | 2.1311 (14) | C11—N1  | 1.486 (3) |         |         |         |
| Co3—O11      | 2.1330 (14) | O11—H11C | 0.8700 |         |         |         |
Co₃—O₁₁\textsuperscript{ii} 2.1330 (15) O₁₁—H₁₁D 0.8692
Co₃—O₁₀\textsuperscript{ii} 2.0234 (15) O₁₀—H₁₀A 0.8702
Co₃—O₁₀ 2.0235 (15) O₁₀—H₁₀B 0.8699
O₃—C₈ 1.255 (3) O₁₂—H₁₂A 0.8720
O₁₄—H₁₄A 0.8716 O₁₂—H₁₂B 0.8707
O₁₄—H₁₄B 0.8710 O₁₉—H₁₉A 0.8703
C₃—C₄ 1.416 (3) O₁₉—H₁₉B 0.8698
C₃—N₁ 1.472 (3) O₁₇—H₁₇A 0.8702
O₄—C₈ 1.260 (2) O₁₇—H₁₇B 0.8697
O₉—H₉A 0.8696 O₁₆—H₁₆A 0.8710
O₉—H₉B 0.8699 O₁₆—H₁₆B 0.8700
C₄—C₅ 1.395 (3) O₁₆A—H₁₆C 0.8695
C₄—C₈ 1.518 (3) O₁₆A—H₁₆D 0.8699

O₂—Co₁—O₂ 180.0 Co₂—O₉—H₉B 126.4
O₂—Co₁—O₁₂\textsuperscript{i} 89.84 (6) H₉Α—O₉—H₉B 104.6
O₂—Co₁—O₁₂\textsuperscript{i} 90.16 (6) C₃—C₄—C₈ 126.71 (19)
O₂—Co₁—O₁₂ 89.84 (6) C₅—C₄—C₃ 117.58 (18)
O₂—Co₁—O₁₂ 90.16 (6) C₅—C₄—C₈ 115.68 (18)
O₁₃—Co₁—O₂ 89.80 (6) C₄—C₅—H₅ 118.8
O₁₃—Co₁—O₂ 89.80 (6) C₆—C₅—C₄ 122.4 (2)
O₁₃—Co₁—O₂\textsuperscript{i} 90.20 (6) C₆—C₅—H₅ 118.8
O₁₃—Co₁—O₂\textsuperscript{i} 90.20 (6) C₁₂—O₆—Co₂ 114.05 (13)
O₁₃—Co₁—O₁₃ 180.0 C₁—C₆—H₆ 120.2
O₁₃—Co₁—O₁₂\textsuperscript{i} 89.48 (6) C₅—C₆—C₁ 119.66 (19)
O₁₃—Co₁—O₁₂\textsuperscript{i} 90.52 (6) C₅—C₆—H₆ 120.2
O₁₃—Co₁—O₁₂ 89.48 (6) Co₁—O₁₃—H₁₃A 109.5
O₁₃—Co₁—O₁₂ 90.52 (6) Co₁—O₁₃—H₁₃B 109.4
O₁₂—Co₁—O₁₂\textsuperscript{i} 180.0 H₁₃A—O₁₃—H₁₃B 104.3
C₂—C₁—C₇ 121.71 (19) O₁—C₇—C₁ 118.59 (18)
C₆—C₁—C₂ 118.73 (19) O₁—C₇—O₁ 125.81 (19)
C₆—C₁—C₇ 119.54 (19) O₁—C₇—C₁ 115.60 (18)
O₁₄—Co₂—O₆ 171.86 (6) H₁₈A—O₁₈—H₁₈B 104.5
O₁₄—Co₂—N₁ 91.18 (6) C₁₀—O₈—Co₂ 114.07 (13)
O₄—Co₂—O₁₄ 92.18 (6) C₃—C₈—O₄ 122.76 (19)
O₄—Co₂—O₉ 93.01 (7) C₃—C₈—C₄ 116.55 (18)
O₄—Co₂—O₆ 91.31 (6) C₄—C₈—C₄ 120.68 (18)
O₄—Co₂—O₈ 169.72 (6) H₉C—C₉—H₉D 107.7
O₄—Co₂—N₁ 86.41 (6) C₁₀—C₉—H₉C 108.9
O₉—Co₂—O₁₄ 95.30 (6) C₁₀—C₉—H₉D 108.9
O₉—Co₂—O₆ 91.86 (6) N₁—C₉—H₉C 108.9
O₉—Co₂—O₈ 96.83 (6) N₁—C₉—H₉D 108.9
O₉—Co₂—N₁ 173.51 (7) N₁—C₉—C₁₀ 113.37 (16)
O₆—Co₂—N₁ 81.70 (6) O₇—C₁₀—O₈ 124.6 (2)
O₈—Co₂—O₁₄ 89.88 (6) O₇—C₁₀—C₉ 117.42 (18)
O₈—Co₂—O₆ 85.42 (6) O₈—C₁₀—C₉ 117.84 (18)
O₈—Co₂—N₁ 83.48 (6) H₁₅A—O₁₅—H₁₅B 103.9
C₇—O₂—Co₁ 132.21 (13) H₁₁A—C₁₁—H₁₁B 107.6
| Bond          | Angle (°)       | Bond          | Angle (°)       |
|---------------|-----------------|---------------|-----------------|
| C1—C2—H2     | 119.0           | C12—C11—H11A | 108.7           |
| C3—C2—C1     | 121.99 (19)     | C12—C11—H11B | 108.7           |
| C3—C2—H2     | 119.0           | N1—C11—H11A  | 108.7           |
| O3—Co3—O3ii  | 180.0           | N1—C11—C12   | 114.38 (17)     |
| O3—Co3—O111i | 90.75 (6)       | O5—C12—O6    | 123.83 (19)     |
| O3—Co3—O111i | 89.25 (6)       | O5—C12—C11   | 118.53 (19)     |
| O3—Co3—O111  | 90.75 (6)       | O6—C12—C11   | 117.50 (18)     |
| O11—Co3—O111i| 180.00 (8)      | Co3—O11—H11C | 109.3           |
| O10—Co3—O3   | 93.04 (6)       | Co3—O11—H11D | 109.3           |
| O10—Co3—O3ii | 86.96 (6)       | H11C—O11—H11D| 104.5           |
| O10—Co3—O3ii | 93.04 (6)       | Co3—O10—H10A | 127.0           |
| O10—Co3—O3   | 86.96 (6)       | Co3—O10—H10B | 122.3           |
| O10—Co3—O11  | 90.32 (6)       | H10A—O10—H10B| 104.5           |
| O10—Co3—O11i | 89.68 (6)       | C3—N1—Co2    | 115.69 (12)     |
| O10—Co3—O111 | 89.68 (6)       | C3—N1—C9     | 112.36 (16)     |
| O10—Co3—O11i | 90.32 (6)       | C3—N1—C11    | 109.16 (16)     |
| O10—Co3—O10  | 180.0           | C9—N1—Co2    | 103.66 (12)     |
| C8—O3—Co3    | 127.99 (13)     | C11—N1—Co2   | 105.14 (12)     |
| Co2—O14—H14A | 109.5           | C11—N1—C9    | 110.49 (16)     |
| Co2—O14—H14B | 109.4           | Co1—O12—H12A | 109.4           |
| H14A—O14—H14B| 104.4           | Co1—O12—H12B | 109.4           |
| C2—C3—C4     | 119.14 (19)     | H12A—O12—H12B| 104.5           |
| C2—C3—N1     | 119.40 (18)     | H19A—O19—H19B| 104.5           |
| C4—C3—N1     | 121.39 (18)     | H17A—O17—H17B| 104.5           |
| C8—O4—Co2    | 128.55 (13)     | H16A—O16—H16B| 104.4           |
| Co2—O9—H9A   | 124.8           | H16C—O16A—H16D| 104.6           |
| Co1—O2—C7—O1 | 21.8 (3)        | C4—C3—N1—C9  | 148.70 (19)     |
| Co1—O2—C7—C1 | −158.96 (13)    | C4—C3—N1—C11 | −88.4 (2)       |
| C1—C2—C3—C4  | −4.6 (3)        | C4—C5—C6—C1  | −2.0 (3)        |
| C1—C2—C3—N1  | 178.43 (18)     | C5—C4—C8—O3  | −15.1 (3)       |
| Co2—O4—C8—O3 | 161.71 (15)     | C5—C4—C8—O4  | 165.91 (19)     |
| Co2—O4—C8—C4 | −19.4 (3)       | C6—C1—C2—C3  | −2.0 (3)        |
| Co2—O6—C12—O5| −168.82 (16)    | C6—C1—C7—O1  | −170.27 (19)    |
| Co2—O6—C12—C11| 15.5 (2)       | C6—C1—C7—O2  | 10.5 (3)        |
| Co2—O8—C10—O7| 166.73 (17)     | C7—C1—C2—C3  | 176.06 (19)     |
| Co2—O8—C10—C9| −17.3 (2)       | C7—C1—C6—C5  | −172.81 (18)    |
| C2—C1—C6—C5  | 5.3 (3)         | C8—C4—C5—C6  | 173.80 (19)     |
| C2—C1—C7—O1  | 11.7 (3)        | C10—C9—N1—Co2| −26.61 (19)     |
| C2—C1—C7—O2  | −167.56 (19)    | C10—C9—N1—C3 | −152.23 (17)    |
| C2—C3—C4—C5  | 7.8 (3)         | C10—C9—N1—C11| 85.6 (2)        |
| C2—C3—C4—C8  | −170.45 (19)    | C12—C11—N1—Co2| 27.1 (2)       |
| C2—C3—N1—Co2 | −153.20 (15)    | C12—C11—N1—C3| 151.78 (17)     |
| C2—C3—N1—C9  | −34.4 (3)       | C12—C11—N1—C9| −84.2 (2)       |
| C2—C3—N1—C11 | 88.5 (2)        | N1—C3—C4—C5  | −175.36 (18)    |
| Co3—O3—C8—O4 | −15.4 (3)       | N1—C3—C4—C8  | 6.4 (3)         |
| Co3—O3—C8—C4 | 165.66 (13)     | N1—C9—C10—O7 | −152.01 (19)    |
C3—C4—C5—C6  -4.6 (3)  N1—C9—C10—O8  31.7 (3)
C3—C4—C8—O3  163.1 (2)  N1—C11—C12—O5  153.61 (19)
C3—C4—C8—O4  -15.9 (3)  N1—C11—C12—O6  -30.4 (3)
C4—C3—N1—Co2  29.9 (2)

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

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O14—H14A···O1iii | 0.87 | 1.87 | 2.723 (2) | 166 |
| O14—H14B···O19 | 0.87 | 1.92 | 2.743 (2) | 158 |
| O9—H9B···O15iv | 0.87 | 1.84 | 2.702 (2) | 168 |
| O9—H9B···O6v | 0.87 | 1.87 | 2.742 (2) | 175 |
| O13—H13A···O5vi | 0.87 | 1.88 | 2.727 (2) | 162 |
| O13—H13B···O1i | 0.87 | 1.98 | 2.759 (2) | 148 |
| O18—H18A···O5vii | 0.87 | 1.93 | 2.752 (2) | 158 |
| O18—H18B···O7iii | 0.87 | 1.88 | 2.750 (2) | 177 |
| O15—H15A···O19 | 0.87 | 1.87 | 2.738 (2) | 177 |
| O15—H15B···O16 | 0.87 | 1.85 | 2.692 (3) | 162 |
| O15—H15B···O164 | 0.87 | 2.02 | 2.833 (7) | 156 |
| O11—H11C···O15viii | 0.87 | 1.82 | 2.686 (2) | 172 |
| O11—H11D···O1iv | 0.87 | 1.95 | 2.786 (2) | 161 |
| O10—H10A···O17xi | 0.87 | 1.88 | 2.705 (2) | 158 |
| O10—H10B···O4 | 0.87 | 2.11 | 2.740 (2) | 129 |
| O12—H12A···O8iii | 0.87 | 1.92 | 2.773 (2) | 166 |
| O12—H12B···O6ix | 0.87 | 1.98 | 2.846 (2) | 172 |
| O19—H19A···O18 | 0.87 | 1.85 | 2.719 (2) | 175 |
| O19—H19B···O11ii | 0.87 | 1.94 | 2.786 (2) | 165 |
| O17—H17A···O7x | 0.87 | 1.88 | 2.702 (2) | 157 |
| O17—H17B···O18 | 0.87 | 1.95 | 2.804 (2) | 166 |
| O16—H16C···O17xi | 0.87 | 2.11 | 2.861 (8) | 144 |
| O16—H16D···O17ii | 0.87 | 2.10 | 2.921 (4) | 156 |

Symmetry codes: (i) -x+1, -y, -z+2; (ii) -x+1, -y+2, -z+1; (iii) -x+2, -y+1, -z+1; (iv) -x+2, -y+2, -z+1; (v) -x+2, -y+2, -z; (vi) -x+1, -y+1, -z+1; (vii) x, y, z+1; (viii) x+1, y, z; (ix) x, y+1, z+1; (x) x-1, y, z+1; (xi) x+1, y, z.