

Synthesis, crystal structure and magnetic properties of poly[[diaqua{ μ_6 -2-[bis(carboxylatomethyl)-amino]terephthalato}dicobalt(II)] 1.6-hydrate]

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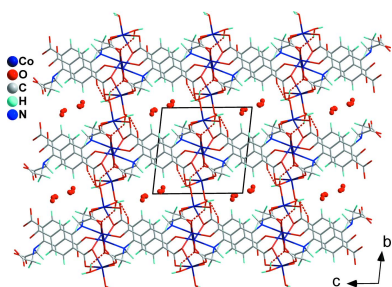
Edited by M. Weil, Vienna University of
Technology, Austria**Keywords:** crystal structure; 2-aminodiacetic
terephthalic acid; tetranuclear Co^{II} units; layered
structure.**CCDC reference:** 2063394**Supporting information:** this article has
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The asymmetric unit of the polymeric title compound $\{[\text{Co}_2(\text{C}_{12}\text{H}_7\text{NO}_8)(\text{H}_2\text{O})_2] \cdot 1.6\text{H}_2\text{O}\}_n$ comprises two Co^{II} ions, which are coordinated by fully deprotonated 2-aminodiacetic terephthalic acid (adtp^{4-}) and terminal water molecules in distorted octahedral N_1O_5 and O_6 coordination environments. The title compound features tetranuclear Co^{II} units bridged by $\kappa^3\text{O}:\text{O}:\text{O}'$ - and $\kappa^3\text{O}:\text{O}:\text{O}'$ -carboxylate groups, which are joined into ribbons *via syn-anti* carboxylate bridges. The parallel adtp^{4-} ligands with an alternately reversed arrangement further link adjacent Co^{II} ribbons into (010) layers, which are assembled into a three-dimensional supramolecular network *via* intermolecular hydrogen bonds. The disordered water solvent molecules are situated in channels parallel to [100]. Magnetic measurements and analyses reveal that the title compound displays antiferromagnetic behaviour. The purity of the title compound was characterized by X-ray powder diffraction.

1. Chemical context

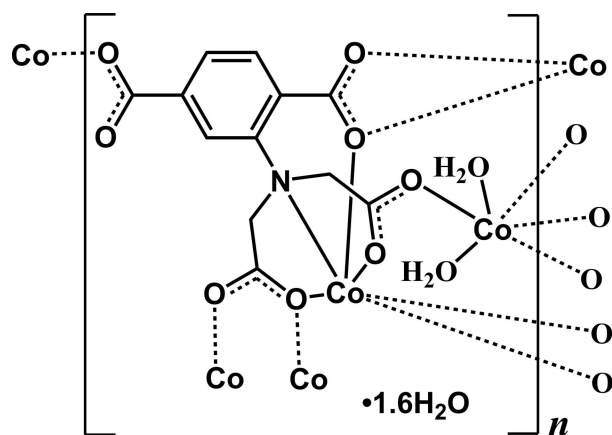
Over the last two decades, coordination polymers (CPs) have become one of the most attractive fields in chemistry because of their fascinating structures and promising applications in adsorption and separation (Gan *et al.*, 2020; Yang *et al.*, 2020; Qian *et al.*, 2020; Islamoglu *et al.*, 2020), catalysis (Bavykina *et al.*, 2020), sensing (Allendorf *et al.*, 2020), luminescence (Rice *et al.*, 2020) and magnetism (Thorarinsdottir & Harris, 2020; Wang *et al.*, 2019b). Multicarboxylic acids have been employed to synthesize compounds comprising of various dimensional structures such as chains, layers and three-dimensional frameworks. Immense efforts have been devoted to the construction of CPs for successful predictions and the rational design of definite structures; many significant advances in the construction of CPs have occurred by employing well-defined rigid multicarboxylic acids (Padial *et al.*, 2020; Li *et al.*, 2020b; Wang *et al.*, 2019a; Shen *et al.*, 2017; Pang *et al.*, 2017). However, using semi-rigid or flexible ligands, predictions are still tricky and confusing owing to the diversity of ligand configurations, the formation of various polynuclear metal units and the influence of weak interatomic interactions.

Our previous studies have focused on the construction of CPs based on semi-rigid multicarboxylic acids with the aminodiacetate moiety such as 2-aminodiacetic terephthalic acid (H_4adtp) (Liu *et al.*, 2009). The *ortho*-carboxylate group of H_4adtp can be regarded as three carboxylic arms attached to one amino nitrogen atom. The three arms can chelate and/



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or bridge metal ions through their carboxylate groups into polynuclear metal units or chains. The residual phenyl carboxylate group can cross-link the polynuclear metal units or chains into layers or three-dimensional frameworks. In previous work, we have reported the supramolecular hydrogen-bonded pillar-layered structure of $[\text{Mn}(\text{H}_2\text{adtp})(\text{H}_2\text{O})]_n$ where the three arms connect Mn^{II} ions into layers with Mn^{II} chains and H_2adtp ligands joined by hydrogen bonding act as pillars (Ma *et al.*, 2015). Herein we report the layer structure of the title compound, $[\text{Co}_2(\text{C}_{12}\text{H}_7\text{NO}_8)(\text{H}_2\text{O})_2] \cdot 1.6\text{H}_2\text{O}]_n$ (**I**), based on fully deprotonated H_4adtp as one of the ligands. The crystal structure, power X-ray diffraction pattern and magnetism of (**I**) were also studied in detail.



2. Structural commentary

The asymmetric unit of (**I**) comprises two Co^{II} ions, one adtp^{4-} ligand, two terminal water ligands and 1.6 disordered solvent water molecules. Regarding the adtp^{4-} ligand, one carboxylate group (C12, O7, O8) of the aminodiacetate moiety adopts a $\kappa^3\text{-O:O:O'}$ coordination mode and the other one (C10, O5, O6) employs a *syn-anti* bidentate bridging fashion, whereas the carboxylate group in the *ortho*-position (C1, O1, O2) coordinates in a $\kappa^3\text{-O:O:O'}$ mode and that in the *meta*-position (C8, O3, O4) binds to one Co^{II} ion in monodentate fashion

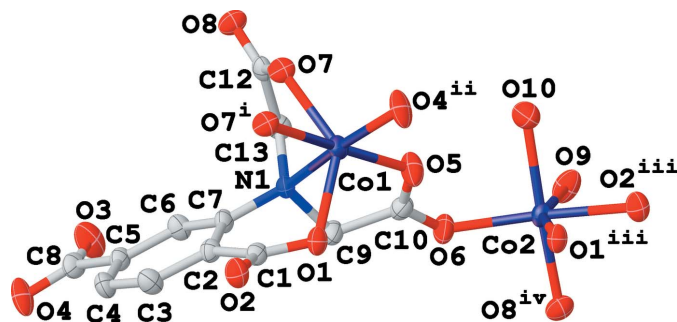


Figure 1
Coordination environments of the Co^{II} ions in (**I**) with displacement ellipsoids drawn at the 50% probability level; H atoms and the disordered lattice water molecules have been omitted for clarity. Symmetry codes refer to Table 1.

Table 1
Selected bond lengths (\AA).

Co1—O5	2.049 (3)	Co2—O2 ⁱⁱⁱ	2.161 (2)
Co1—O7	2.033 (3)	Co2—O9	2.057 (3)
Co1—O7 ⁱ	2.362 (3)	Co2—O8 ^{iv}	2.065 (3)
Co1—O4 ⁱⁱ	1.992 (3)	Co2—O6	2.038 (3)
Co1—O1	2.083 (3)	Co2—O1 ⁱⁱⁱ	2.212 (2)
Co1—N1	2.241 (3)	Co2—O10	2.126 (3)

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

(see Scheme). As shown in Fig. 1, Co1 and Co2 are both six-coordinated and located in distorted octahedral environments with an N_1O_5 coordination set for Co1 and an O_6 set for Co2. The adtp^{4-} ligand chelates Co1 with the amino nitrogen atom (N1) and carboxylate oxygen atoms (O1, O5 and O7) from the aminodiacetate moiety and its *ortho*-positioned carboxylate group. The residual *cis*-related sites are occupied by one *meta*-positioned carboxylate oxygen atom (O4ⁱⁱ) and one aminodiacetate oxygen atom (O7ⁱ) from two other adtp^{4-} ligands (for symmetry codes refer to Table 1). The *ortho*-positioned carboxylate group (O1ⁱⁱⁱ and O2ⁱⁱⁱ) from another adtp^{4-} ligand chelates Co2, two *cis*-related positions of which are occupied by two aminodiacetate oxygen atoms (O8^{iv} and O6) from two different adtp^{4-} ligands. The remaining two *cis*-related sites of Co2 are occupied by two terminal water ligands (O9 and O10). The length of the Co—N bond is 2.241 (3) \AA and the Co—O distances are between 1.992 (3) and 2.362 (3) \AA , which are all in the expected ranges. As shown in Fig. 2, two inversion-related adtp^{4-} ligands bridge two pairs of Co^{II} ions (Co1, Co1ⁱⁱ, Co2ⁱ and Co2ⁱⁱⁱ) into a tetranuclear unit with their $\kappa^3\text{O:O:O'}$ -carboxylate groups from the aminodiacetate moieties and *ortho*-positioned $\kappa^3\text{O:O:O'}$ -carboxylate groups (Li *et al.*, 2020a; Zhang *et al.*, 2019a,b; Liu *et al.*, 2018), wherein two equivalent μ_2 -oxygen atoms (O7 and O7ⁱ) from $\kappa^3\text{O:O:O'}$ -carboxylate groups doubly bridge Co1 and Co1ⁱⁱ into a dinuclear unit. The dinuclear unit is further joined with two equivalent Co2ⁱ and Co2ⁱⁱⁱ atoms *via* $\kappa^3\text{O:O:O'}$ -carboxylate groups and μ_2 -oxygen bridges (O1 and O1ⁱ) from $\kappa^3\text{O:O:O'}$ -carboxylate groups. Adjacent tetranuclear units are linked

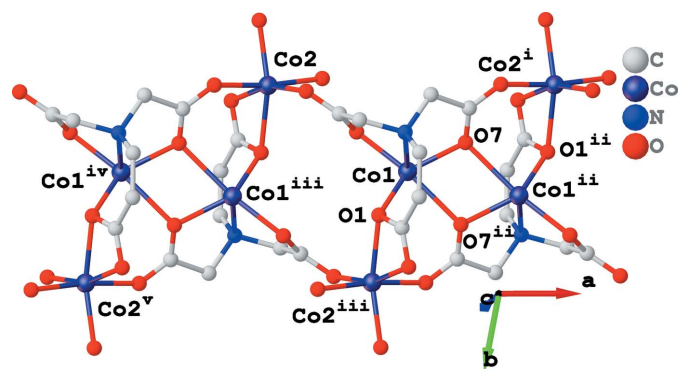


Figure 2
Tetranuclear Co^{II} units and a Co^{II} ribbon in (**I**). Phenyl and *meta*-positioned carboxylate groups and the disordered lattice water molecules have been omitted for clarity. [Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$; (iv) $-1 + x, y, z$; (v) $-1 - x, 1 - y, 1 - z$.]

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9–H9A \cdots O3 ^v	0.87	1.93	2.701 (4)	146
O9–H9B \cdots O2 ^{vi}	0.87	2.00	2.809 (4)	153
O10–H10A \cdots O12	0.89	1.98	2.849 (10)	164
O10–H10B \cdots O5	0.92	2.02	2.798 (4)	141

Symmetry codes: (v) $-x, -y, -z$; (vi) $x-1, y-1, z$.

into a ribbon *via* double *syn-anti* bridging carboxylate groups from the aminodiacetate moieties. The closest Co1 \cdots Co2 and Co1 \cdots Co1 distances in the ribbon are 3.7074 (8) and 3.5762 (8) Å, respectively. Parallel-aligned adtp⁴⁻ ligands with an alternately reversed arrangement bind adjacent Co^{II} ribbons into a layer extending parallel to (010) (Fig. 3).

3. Supramolecular features

The (010) layers of **(I)** are assembled into a three-dimensional supramolecular network *via* intermolecular hydrogen bonds O9–H9A \cdots O3^v and O9–H9B \cdots O2^{vi} (Table 2, Fig. 4). The positionally and occupationally disordered solvent water molecules (O11–O14) are situated in channels extending parallel to [100].

4. Magnetic properties

The variable-temperature magnetic susceptibilities (χ_M) of **(I)** were measured in the range 2–300 K under 1000 Oe. The χ_M , χ_M^{-1} and $\chi_M T$ versus T plots are shown in Fig. 5. The value of $\chi_M T$ at 300 K is 5.43 cm³ K mol⁻¹, which is much larger than

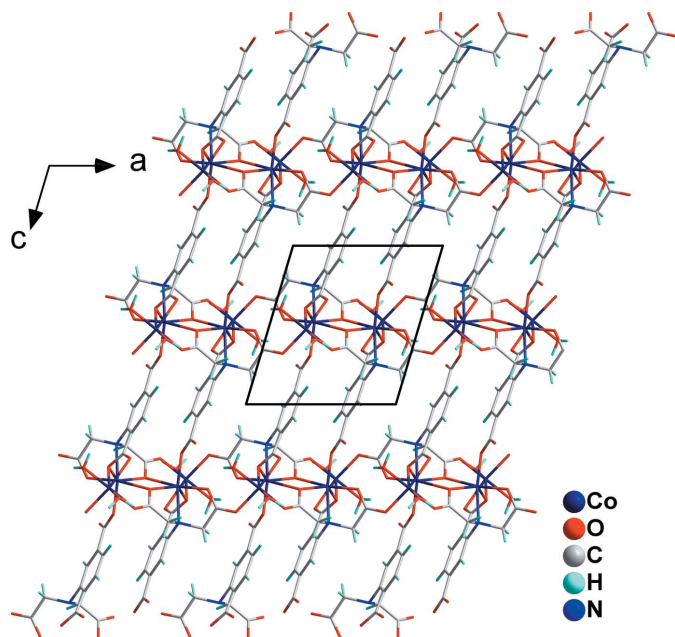


Figure 3
A view along [010], emphasizing the layered arrangement in the crystal structure of **(I)**.

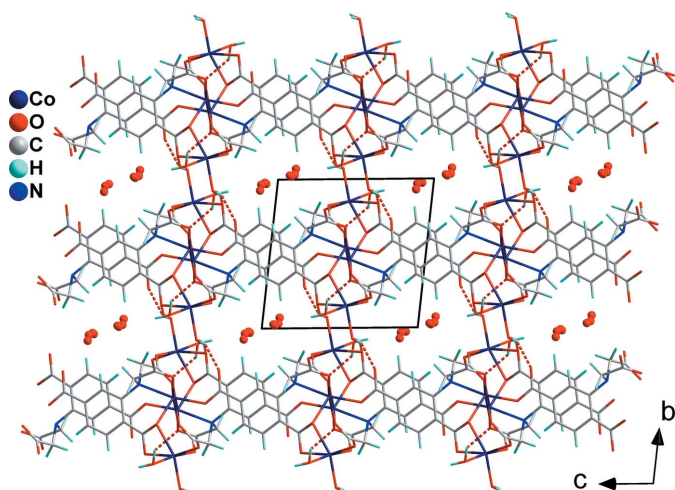


Figure 4
The three-dimensional supramolecular network of **(I)** constructed *via* intermolecular hydrogen bonds. The disordered water solvent molecules are located in channels parallel to [100].

the expected spin-only value (3.75 cm³ K mol⁻¹) of two isolated Co^{II} ions with $g = 2.0$, $S = 3/2$, which may be due to the contribution of the incompletely quenched orbital magnetic moment. As the temperature decreases, the $\chi_M T$ value decreases slowly between 300 and 50 K and then it descends more steeply to the minimum value of 0.51 cm³ K mol⁻¹ at 2 K. The curve clearly indicates that the dominant anti-ferromagnetic coupling is operating. The temperature dependence of χ_M^{-1} follows the Curie–Weiss law, and the linear fit by the equation $1/\chi_M = (T - \theta)/C$ gives $C = 5.76$ cm³ K mol⁻¹ and $\theta = -21.99$ K, which is consistent with an anti-ferromagnetic behaviour.

5. Database survey

A search of the Cambridge Structural Database (CSD version 5.42, May 2021 update; Groom *et al.*, 2016) for complexes with 2-aminodiacetic terephthalic acid gave 19 hits, of which three are Co^{II} complexes including the title compound (Refcode:

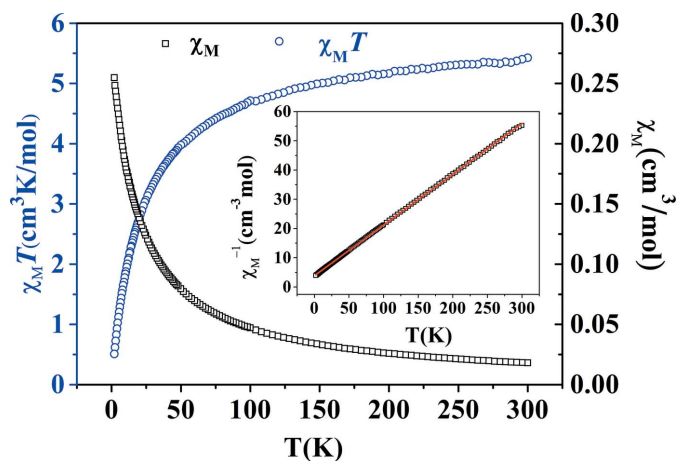


Figure 5
 χ_M and $\chi_M T$ versus T curves for compound **(I)**. Inset: χ_M^{-1} versus T plot. The red solid line represents the best-fit curve.

CUFDIS). The other two Co^{II} complexes are discrete coordination molecules (Liu *et al.*, 2012). Three other complexes with layer structures based on 2-aminodiacetic terephthalic acid without another organic ligand have also been reported, *viz.* MUMBON, an Mn^{II} complex (Ma *et al.*, 2015), NEVJII, a Cd^{II} complex (Ma *et al.*, 2013), and NEVJUV, a Zn^{II} complex (Ma *et al.*, 2013). NEVJUV has similar cell parameters to the title compound, but similar tetranuclear metal units are not found in NEVJUV because the Zn^{II} atoms have lower coordination numbers and the carboxylate oxygen atoms do not bridge the Zn^{II} atoms as in the title compound. To the best of our knowledge, similar tetranuclear metal units have not been reported so far. Besides, one Co^{II} coordination polymer (CCDC reference: 2063370; Ma *et al.*, 2021), {[Co₂(adtp)-(H₂O)₆]·5H₂O}_n, has been synthesized, which consists of parallel stacked zigzag chains in which Co^{II} cations are linked together through μ₃-adtp⁴⁻ anions.

6. Synthesis and crystallization

H₄adtp was prepared using a similar protocol to that reported in the literature (Xu *et al.*, 2006). The other chemicals were purchased from commercial sources and used without further purification. A solution of 0.2 mmol (0.0594 g) H₄adtp in 5.0 ml of H₂O was adjusted to a pH of 6.1 by adding a 1.0 M KHCO₃ solution drop by drop. The above solution was mixed with 0.5 mmol (0.1455 g) of Co(NO₃)₂·6H₂O and 5.0 ml of CH₃CN, then transferred into a 25.0 ml Teflon-lined stainless steel autoclave. The autoclave was sealed, heated to 393 K and held at that temperature for 72 h. The autoclave was allowed to cool to 303 K within 24 h. Plate-like pink crystals of (**I**) were collected in 66% yield based on H₄adtp. Analysis calculated (%) for C₁₂Co₂N₁O_{11.6}H_{14.2} (*M_r* = 475.90): C 30.29, H 3.01, N, 2.94; found: C 30.18, H 3.15, N 3.06. Selected IR data (KBr pellet, cm⁻¹): 3389 (*s*), 1631 (*s*), 1570 (*m*), 1405 (*s*), 1373 (*s*), 1319 (*b*), 1111 (*b*), 780 (*b*), 712 (*b*).

The phase purity of compound (**I**) was confirmed by powder X-ray diffraction analysis (PXRD; Fig. S1 in the supporting information). The peak positions of the experimental PXRD patterns are in good agreement with those simulated on basis of the present single-crystal X-ray data, indicating that a pure phase was obtained.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The solvent water molecules (O11, O12, O13 and O14) were found to be disordered and were refined isotropically with site occupancies of 0.5, 0.5, 0.35 and 0.25, respectively. The hydrogen atoms of the non-disordered water molecules (O9, O10) were found in an difference density map and refined as riding, with *U*_{iso}(H) = 1.5 *U*_{eq}(O). Other hydrogen atoms were placed at geometrically calculated positions and treated as riding, with *Csp*²-H = 0.93 Å, *Csp*³-H = 0.97 Å and *U*_{iso}(H) = 1.2 *U*_{eq}(C). H atoms of O11, O12, O13 and O14 are not included in the model but were taken into account in the overall formula.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Co ₂ (C ₁₂ H ₇ NO ₈)(H ₂ O) ₂].1.6H ₂ O
<i>M_r</i>	475.90
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.0064 (9), 9.2340 (8), 9.8426 (9)
α , β , γ (°)	93.859 (3), 105.571 (4), 99.483 (5)
<i>V</i> (Å ³)	772.37 (13)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.22
Crystal size (mm)	0.30 × 0.25 × 0.05
Data collection	
Diffractometer	Rigaku Saturn70 (4x4 bin mode)
Absorption correction	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2008)
<i>T</i> _{min} , <i>T</i> _{max}	0.908, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5012, 2619, 2245
<i>R</i> _{int}	0.022
(sin θ/λ) _{max} (Å ⁻¹)	0.595
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.084, 1.04
No. of reflections	2619
No. of parameters	244
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.80, -0.41

Computer programs: *CrystalClear* (Rigaku, 2008), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *pubCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2021). E77, 939-943 [https://doi.org/10.1107/S2056989021008355]

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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: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[[diaqua $\{\mu_6$ -2-[bis(carboxylatomethyl)amino]terephthalato}dicobalt(II)] 1.6-hydrate]

Crystal data

$[\text{Co}_2(\text{C}_{12}\text{H}_7\text{NO}_8)(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_{1.6}$

$M_r = 475.90$

Triclinic, $P\bar{1}$

$a = 9.0064$ (9) Å

$b = 9.2340$ (8) Å

$c = 9.8426$ (9) Å

$\alpha = 93.859$ (3)°

$\beta = 105.571$ (4)°

$\gamma = 99.483$ (5)°

$V = 772.37$ (13) Å³

$Z = 2$

$F(000) = 480$

$D_x = 2.046$ Mg m⁻³

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

Cell parameters from 1889 reflections

$\theta = 2.3$ – 27.5 °

$\mu = 2.22$ mm⁻¹

$T = 293$ K

Plate, clear light red

$0.30 \times 0.25 \times 0.05$ mm

Data collection

Rigaku Saturn70 (4x4 bin mode)
diffractometer

Radiation source: fine-focus sealed tube

Graphite Monochromator monochromator

Detector resolution: 28.5714 pixels mm⁻¹

CCD_Profile_fitting scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2008)

$T_{\min} = 0.908$, $T_{\max} = 1.000$

5012 measured reflections

2619 independent reflections

2245 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 3.0$ °

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.084$

$S = 1.04$

2619 reflections

244 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 1.7231P]$

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

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

$$\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.29415 (6)	0.45959 (5)	0.48240 (5)	0.01675 (15)	
O5	0.0863 (3)	0.3198 (3)	0.4645 (3)	0.0269 (6)	
C1	0.2786 (4)	0.7012 (4)	0.3125 (4)	0.0166 (8)	
O7	0.4739 (3)	0.3593 (3)	0.4646 (3)	0.0194 (6)	
C2	0.2925 (4)	0.6185 (4)	0.1820 (4)	0.0163 (8)	
Co2	-0.25268 (6)	0.14862 (5)	0.47212 (5)	0.01611 (15)	
O2	0.3336 (3)	0.8376 (3)	0.3404 (3)	0.0213 (6)	
C3	0.3371 (5)	0.7042 (4)	0.0822 (4)	0.0209 (8)	
H3	0.362867	0.806555	0.103109	0.025*	
C4	0.3438 (5)	0.6402 (4)	-0.0464 (4)	0.0208 (8)	
H4	0.376198	0.698823	-0.110146	0.025*	
C5	0.3021 (4)	0.4882 (4)	-0.0798 (4)	0.0170 (8)	
C6	0.2603 (4)	0.4025 (4)	0.0199 (4)	0.0185 (8)	
H6	0.232662	0.300415	-0.002608	0.022*	
O9	-0.3388 (3)	-0.0735 (3)	0.4106 (3)	0.0273 (6)	
H9A	-0.294396	-0.105535	0.348644	0.041*	
H9B	-0.438376	-0.087425	0.364194	0.041*	
C7	0.2586 (4)	0.4641 (4)	0.1514 (4)	0.0166 (8)	
C8	0.2993 (4)	0.4154 (4)	-0.2221 (4)	0.0203 (8)	
O8	0.5342 (3)	0.1757 (3)	0.3424 (3)	0.0214 (6)	
C9	0.0396 (4)	0.3315 (4)	0.2165 (4)	0.0203 (8)	
H9C	-0.000542	0.253614	0.137501	0.024*	
H9D	-0.004209	0.417680	0.188115	0.024*	
C10	-0.0098 (4)	0.2809 (4)	0.3444 (4)	0.0194 (8)	
O4	0.3328 (3)	0.5005 (3)	-0.3085 (3)	0.0283 (7)	
C13	0.2808 (4)	0.2309 (4)	0.2585 (4)	0.0195 (8)	
H13A	0.285691	0.196842	0.164707	0.023*	
H13B	0.212473	0.154326	0.287781	0.023*	
C12	0.4434 (4)	0.2572 (4)	0.3616 (4)	0.0177 (8)	
O3	0.2624 (4)	0.2777 (3)	-0.2452 (3)	0.0328 (7)	
O6	-0.1453 (3)	0.2040 (3)	0.3200 (3)	0.0242 (6)	
O1	0.2057 (3)	0.6374 (3)	0.3941 (3)	0.0194 (6)	
O10	-0.0424 (3)	0.0957 (3)	0.6003 (3)	0.0286 (6)	
H10A	-0.052816	0.076051	0.685363	0.043*	
H10B	0.017174	0.187022	0.599944	0.043*	
N1	0.2142 (3)	0.3688 (3)	0.2523 (3)	0.0153 (6)	
O11	0.3252 (12)	0.0275 (10)	0.9277 (10)	0.069 (2)*	0.5

O12	-0.0171 (11)	0.0705 (10)	0.8922 (10)	0.074 (2)*	0.5
O13	0.2365 (15)	0.0205 (11)	0.9190 (11)	0.047 (3)*	0.35
O14	0.100 (3)	0.029 (3)	0.899 (3)	0.104 (7)*	0.25

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0195 (3)	0.0195 (3)	0.0122 (3)	0.0038 (2)	0.0062 (2)	0.00157 (19)
O5	0.0250 (16)	0.0349 (16)	0.0172 (14)	-0.0055 (13)	0.0071 (12)	0.0012 (12)
C1	0.0154 (19)	0.0204 (19)	0.0136 (18)	0.0037 (15)	0.0040 (15)	0.0008 (14)
O7	0.0190 (14)	0.0198 (13)	0.0172 (13)	0.0035 (11)	0.0026 (11)	-0.0023 (10)
C2	0.016 (2)	0.0189 (18)	0.0141 (18)	0.0026 (15)	0.0051 (15)	0.0004 (14)
Co2	0.0175 (3)	0.0160 (3)	0.0165 (3)	0.0032 (2)	0.0082 (2)	0.00012 (19)
O2	0.0288 (16)	0.0168 (13)	0.0201 (14)	0.0024 (12)	0.0116 (12)	-0.0006 (10)
C3	0.027 (2)	0.0183 (18)	0.0181 (19)	0.0059 (16)	0.0073 (16)	0.0019 (15)
C4	0.024 (2)	0.025 (2)	0.0160 (19)	0.0061 (17)	0.0090 (16)	0.0060 (15)
C5	0.0161 (19)	0.0233 (19)	0.0116 (17)	0.0038 (16)	0.0043 (14)	0.0008 (14)
C6	0.023 (2)	0.0162 (17)	0.0161 (18)	0.0024 (15)	0.0063 (15)	0.0007 (14)
O9	0.0234 (16)	0.0212 (14)	0.0379 (17)	0.0016 (12)	0.0137 (13)	-0.0051 (12)
C7	0.016 (2)	0.0223 (19)	0.0122 (18)	0.0034 (16)	0.0061 (15)	0.0028 (14)
C8	0.021 (2)	0.028 (2)	0.0118 (18)	0.0054 (17)	0.0047 (15)	-0.0001 (15)
O8	0.0198 (14)	0.0211 (13)	0.0235 (14)	0.0074 (12)	0.0054 (11)	-0.0018 (11)
C9	0.014 (2)	0.029 (2)	0.0182 (19)	0.0028 (16)	0.0050 (15)	0.0048 (16)
C10	0.016 (2)	0.0204 (19)	0.023 (2)	0.0044 (16)	0.0073 (16)	0.0028 (15)
O4	0.0367 (18)	0.0335 (16)	0.0126 (13)	-0.0052 (13)	0.0117 (12)	-0.0010 (11)
C13	0.023 (2)	0.0166 (18)	0.0173 (19)	0.0030 (16)	0.0046 (16)	0.0001 (14)
C12	0.021 (2)	0.0157 (18)	0.0188 (19)	0.0019 (16)	0.0095 (16)	0.0052 (15)
O3	0.055 (2)	0.0272 (16)	0.0197 (15)	0.0098 (14)	0.0167 (14)	-0.0012 (12)
O6	0.0177 (15)	0.0345 (15)	0.0207 (14)	0.0010 (12)	0.0085 (11)	0.0043 (12)
O1	0.0217 (14)	0.0209 (13)	0.0174 (13)	0.0021 (11)	0.0107 (11)	-0.0001 (10)
O10	0.0263 (16)	0.0333 (16)	0.0275 (15)	0.0067 (13)	0.0076 (12)	0.0101 (12)
N1	0.0157 (16)	0.0177 (15)	0.0141 (15)	0.0030 (13)	0.0063 (12)	0.0037 (12)

Geometric parameters (Å, °)

Co1—O5	2.049 (3)	C5—C8	1.504 (5)
Co1—O7	2.033 (3)	C6—H6	0.9300
Co1—O7 ⁱ	2.362 (3)	C6—C7	1.383 (5)
Co1—O4 ⁱⁱ	1.992 (3)	O9—H9A	0.8744
Co1—O1	2.083 (3)	O9—H9B	0.8742
Co1—N1	2.241 (3)	C7—N1	1.461 (4)
O5—C10	1.252 (5)	C8—O4	1.258 (5)
C1—C2	1.495 (5)	C8—O3	1.249 (5)
C1—O2	1.258 (4)	O8—C12	1.240 (4)
C1—O1	1.281 (4)	C9—H9C	0.9700
O7—C12	1.276 (4)	C9—H9D	0.9700
C2—C3	1.401 (5)	C9—C10	1.521 (5)
C2—C7	1.403 (5)	C9—N1	1.491 (5)

Co2—O2 ⁱⁱⁱ	2.161 (2)	C10—O6	1.259 (5)
Co2—O9	2.057 (3)	C13—H13A	0.9700
Co2—O8 ^{iv}	2.065 (3)	C13—H13B	0.9700
Co2—O6	2.038 (3)	C13—C12	1.512 (5)
Co2—O1 ⁱⁱⁱ	2.212 (2)	C13—N1	1.492 (5)
Co2—O10	2.126 (3)	O10—H10A	0.8942
C3—H3	0.9300	O10—H10B	0.9225
C3—C4	1.381 (5)	O11—O13	0.771 (12)
C4—H4	0.9300	O12—O14	1.17 (3)
C4—C5	1.384 (5)	O13—O14	1.21 (3)
C5—C6	1.391 (5)		
O5—Co1—O7 ⁱ	170.67 (10)	C6—C5—C8	119.9 (3)
O5—Co1—O1	99.02 (11)	C5—C6—H6	118.9
O5—Co1—N1	76.91 (11)	C7—C6—C5	122.2 (3)
O7—Co1—O5	115.34 (11)	C7—C6—H6	118.9
O7—Co1—O7 ⁱ	71.31 (11)	Co2—O9—H9A	109.7
O7—Co1—O1	133.46 (10)	Co2—O9—H9B	109.8
O7—Co1—N1	78.36 (10)	H9A—O9—H9B	104.3
O4 ⁱⁱ —Co1—O5	91.10 (11)	C2—C7—N1	121.3 (3)
O4 ⁱⁱ —Co1—O7 ⁱ	80.73 (10)	C6—C7—C2	118.7 (3)
O4 ⁱⁱ —Co1—O7	103.42 (11)	C6—C7—N1	119.9 (3)
O4 ⁱⁱ —Co1—O1	106.43 (11)	O4—C8—C5	116.2 (3)
O4 ⁱⁱ —Co1—N1	167.23 (11)	O3—C8—C5	118.0 (3)
O1—Co1—O7 ⁱ	79.19 (9)	O3—C8—O4	125.8 (3)
O1—Co1—N1	80.14 (10)	C12—O8—Co2 ^v	130.6 (2)
N1—Co1—O7 ⁱ	111.56 (10)	H9C—C9—H9D	108.2
C10—O5—Co1	119.4 (2)	C10—C9—H9C	109.6
O2—C1—C2	119.7 (3)	C10—C9—H9D	109.6
O2—C1—O1	118.9 (3)	N1—C9—H9C	109.6
O1—C1—C2	121.4 (3)	N1—C9—H9D	109.6
Co1—O7—Co1 ⁱ	108.69 (10)	N1—C9—C10	110.1 (3)
C12—O7—Co1 ⁱ	120.4 (2)	O5—C10—C9	117.6 (3)
C12—O7—Co1	116.8 (2)	O5—C10—O6	125.6 (3)
C3—C2—C1	116.4 (3)	O6—C10—C9	116.8 (3)
C3—C2—C7	118.8 (3)	C8—O4—Co1 ^{vi}	129.3 (2)
C7—C2—C1	124.8 (3)	H13A—C13—H13B	108.0
O2 ⁱⁱⁱ —Co2—O1 ⁱⁱⁱ	59.97 (9)	C12—C13—H13A	109.4
O9—Co2—O2 ⁱⁱⁱ	96.68 (10)	C12—C13—H13B	109.4
O9—Co2—O8 ^{iv}	84.76 (11)	N1—C13—H13A	109.4
O9—Co2—O1 ⁱⁱⁱ	156.66 (10)	N1—C13—H13B	109.4
O9—Co2—O10	89.06 (11)	N1—C13—C12	111.1 (3)
O8 ^{iv} —Co2—O2 ⁱⁱⁱ	92.24 (10)	O7—C12—C13	116.7 (3)
O8 ^{iv} —Co2—O1 ⁱⁱⁱ	95.29 (10)	O8—C12—O7	125.3 (3)
O8 ^{iv} —Co2—O10	173.82 (11)	O8—C12—C13	117.9 (3)
O6—Co2—O2 ⁱⁱⁱ	161.71 (11)	C10—O6—Co2	124.7 (2)
O6—Co2—O9	101.55 (11)	Co1—O1—Co2 ⁱⁱⁱ	119.35 (12)
O6—Co2—O8 ^{iv}	90.90 (11)	C1—O1—Co1	115.4 (2)

O6—Co2—O1 ⁱⁱⁱ	101.79 (10)	C1—O1—Co2 ⁱⁱⁱ	89.1 (2)
O6—Co2—O10	90.63 (11)	Co2—O10—H10A	110.5
O10—Co2—O2 ⁱⁱⁱ	88.17 (11)	Co2—O10—H10B	93.8
O10—Co2—O1 ⁱⁱⁱ	90.26 (10)	H10A—O10—H10B	114.8
C1—O2—Co2 ⁱⁱⁱ	92.0 (2)	C7—N1—Co1	117.5 (2)
C2—C3—H3	119.3	C7—N1—C9	109.1 (3)
C4—C3—C2	121.5 (3)	C7—N1—C13	113.8 (3)
C4—C3—H3	119.3	C9—N1—Co1	105.0 (2)
C3—C4—H4	120.2	C9—N1—C13	110.2 (3)
C3—C4—C5	119.7 (3)	C13—N1—Co1	100.6 (2)
C5—C4—H4	120.2	O11—O13—O14	171 (2)
C4—C5—C6	119.0 (3)	O12—O14—O13	164 (2)
C4—C5—C8	121.1 (3)		
Co1—O5—C10—C9	4.5 (4)	C4—C5—C8—O4	-1.8 (5)
Co1—O5—C10—O6	-174.9 (3)	C4—C5—C8—O3	179.1 (4)
Co1 ⁱ —O7—C12—O8	51.6 (4)	C5—C6—C7—C2	3.3 (6)
Co1—O7—C12—O8	-173.0 (3)	C5—C6—C7—N1	-179.8 (3)
Co1—O7—C12—C13	4.5 (4)	C5—C8—O4—Co1 ^{vi}	-163.4 (2)
Co1 ⁱ —O7—C12—C13	-130.8 (3)	C6—C5—C8—O4	177.4 (4)
O5—C10—O6—Co2	9.2 (5)	C6—C5—C8—O3	-1.7 (5)
C1—C2—C3—C4	-175.7 (3)	C6—C7—N1—Co1	158.5 (3)
C1—C2—C7—C6	173.2 (3)	C6—C7—N1—C9	-82.2 (4)
C1—C2—C7—N1	-3.7 (6)	C6—C7—N1—C13	41.4 (5)
C2—C1—O2—Co2 ⁱⁱⁱ	178.1 (3)	C7—C2—C3—C4	1.9 (6)
C2—C1—O1—Co1	59.6 (4)	C8—C5—C6—C7	-179.0 (3)
C2—C1—O1—Co2 ⁱⁱⁱ	-178.0 (3)	C9—C10—O6—Co2	-170.2 (2)
C2—C3—C4—C5	1.6 (6)	C10—C9—N1—Co1	-33.2 (3)
C2—C7—N1—Co1	-24.7 (4)	C10—C9—N1—C7	-160.1 (3)
C2—C7—N1—C9	94.7 (4)	C10—C9—N1—C13	74.3 (4)
C2—C7—N1—C13	-141.8 (3)	C12—C13—N1—Co1	-40.3 (3)
Co2 ^v —O8—C12—O7	9.3 (5)	C12—C13—N1—C7	86.3 (4)
Co2 ^v —O8—C12—C13	-168.3 (2)	C12—C13—N1—C9	-150.7 (3)
O2—C1—C2—C3	-13.0 (5)	O3—C8—O4—Co1 ^{vi}	15.5 (6)
O2—C1—C2—C7	169.5 (3)	O1—C1—C2—C3	164.0 (3)
O2—C1—O1—Co1	-123.4 (3)	O1—C1—C2—C7	-13.6 (6)
O2—C1—O1—Co2 ⁱⁱⁱ	-1.0 (3)	O1—C1—O2—Co2 ⁱⁱⁱ	1.1 (3)
C3—C2—C7—C6	-4.3 (5)	N1—C9—C10—O5	22.0 (5)
C3—C2—C7—N1	178.9 (3)	N1—C9—C10—O6	-158.6 (3)
C3—C4—C5—C6	-2.6 (6)	N1—C13—C12—O7	27.9 (4)
C3—C4—C5—C8	176.6 (3)	N1—C13—C12—O8	-154.3 (3)
C4—C5—C6—C7	0.2 (6)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9A \cdots O3 ^{vii}	0.87	1.93	2.701 (4)	146

O9—H9B···O2 ^{viii}	0.87	2.00	2.809 (4)	153
O10—H10A···O12	0.89	1.98	2.849 (10)	164
O10—H10B···O5	0.92	2.02	2.798 (4)	141

Symmetry codes: (vii) $-x, -y, -z$; (viii) $x-1, y-1, z$.