

Synthesis and crystal structure of a two-dimensional Co^{II} coordination polymer: poly[(μ_3 -3-carboxybenzoato)(μ_2 -5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi[1,2,4-triazole])]cobalt(II)]

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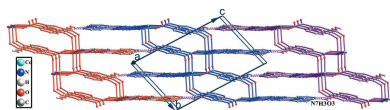
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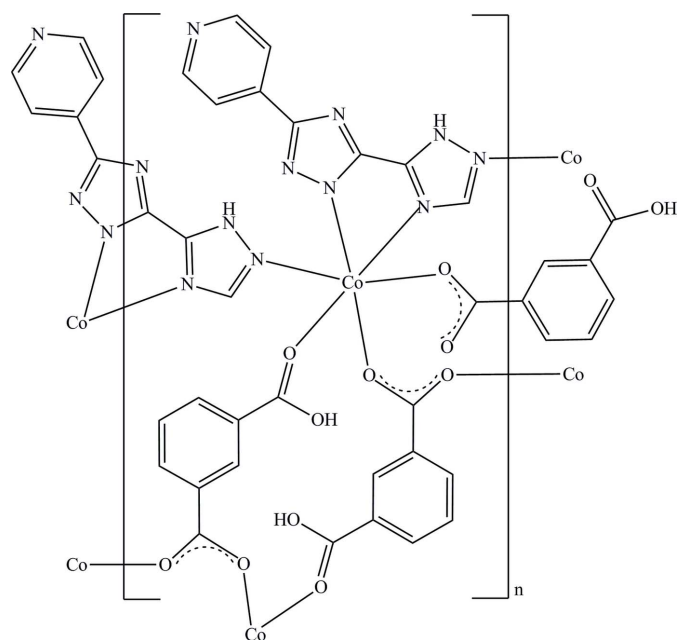
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In the title compound, [Co(C₈H₅O₄)(C₉H₆N₇)]_n, the divalent Co^{II} atom is six-coordinated to three N atoms from two symmetrical 5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi[1,2,4-triazole] (H₂pyttz) ligands and three O atoms from three symmetrical 3-carboxybenzoate (Hbdic) ligands, leading to a distorted {CoN₃O₃} octahedral coordination environment. Two Co^{II} cations are linked by four bridging carboxylate groups to generate a dinuclear [Co₂(CO₂)₄] unit. The dinuclear units are further connected into a chain along [010] *via* the Hbdic ligands. The other infinite chain, along [100], is formed through the H₂pyttz ligands. Finally, the two kinds of chains are cross-linked, by sharing the Co^{II} cations, into a two-dimensional network. In the crystal, adjacent layers are further linked by O–H···N hydrogen bonds into a three-dimensional framework.

1. Chemical context

In recent years, the design and synthesis of coordination polymers (CPs) or metal–organic frameworks (MOFs) have attracted great interest because of their fascinating architectures and potential applications in areas such as gas storage and separation, catalysis, fluorescence, magnetism, molecular recognition, conductivity *etc* (Kitagawa *et al.*, 2004; Zhou *et al.*, 2012; Cavka *et al.*, 2014; Zhang *et al.*, 2014; Huang *et al.*, 2017; Nath *et al.*, 2016; Ni *et al.*, 2017; Yi *et al.*, 2016; Sun *et al.*, 2016). It is well known that organic ligands play a crucial role in the rational design and synthesis of coordination polymers (Li & Sato, 2017; Sun & Sun, 2015). Among the many organonitrogen ligands, the rigid 5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi(1,2,4-triazole) ligand (H₂pyttz) attracted our attention for the following reasons. First, the H₂pyttz ligand possesses seven potential N-donor coordination sites and can exhibit various coordination modes. Second, the uncoordinated N atoms are helpful for the construction of hydrogen bonds. The hydrogen bonds not only increase the diversity of coordination polymer structures, but also enhance their stability. With an increasing interest in H₂pyttz organometallic systems, we report herein on the synthesis and crystal structure of the title compound [Co(C₈H₅O₄)(C₉H₆N₇)]_n, (I).





2. Structural commentary

The asymmetric unit of (I) contains one independent Co^{II} cation, one partially deprotonated Hpyttz^- ligand and one partial deprotonated Hbtc^- ligand. Notably, the deprotonated Hbtc^- ligand adopts two different coordination modes. The deprotonated carboxylate group has a bis(monodentate) coordination mode to bridge two Co^{II} centers while the undepronated carboxylic group adopts a monodentate mode. As shown in Fig. 1, the Co^{II} cation is six-coordinated to three carboxylic oxygen atoms from three symmetrical Hbtc^- ligands and three nitrogen atoms from two symmetrical Hpyttz^- ligands in a distorted $[\text{CoN}_3\text{O}_3]$ octahedral coordination geometry. Four bridging carboxylate groups link two Co^{II} cations to generate a dinuclear $[\text{Co}_2(\text{CO}_2)_4]$ unit, which is

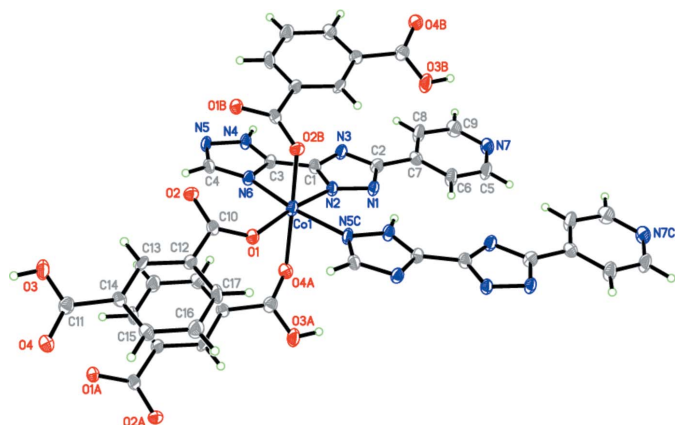


Figure 1
Coordination environment of the Co^{II} cation in (I) showing the atomic numbering scheme, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (A) $1 - x, -y, 1 - z$; (B) $1 - x, 1 - y, 1 - z$; (C) $-1 + x, y, z$].

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3}\cdots\text{N7}^i$	0.89 (5)	1.72 (5)	2.592 (4)	166 (5)

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

further connected into an infinite chain along the b -axis direction. There exist eight- and 16-membered metallamacrocycles in the chain structure. In the 16-membered metallamacrocycle, the dihedral angle between the two aromatic rings is 0° , indicating the parallel orientation of the two aromatic rings.

The other infinite linear chain is along the a -axis direction with a $\text{Co}\cdots\text{Co}$ distance of $6.5825(5) \text{\AA}$ and $\text{Co}-\text{Co}-\text{Co}$ angle of 180.00° and it is also generated through the coordination between the Hpyttz^- ligands and the Co^{II} cations. In the complex, the Hpyttz^- ligand is almost coplanar, with dihedral angles of $7.48(4)$, $6.87(4)$ and $4.43(4)^\circ$ between the pyridine and the two triazole rings, respectively. Finally, these two kinds of chains are cross-linked, by sharing the Co^{II} cations, into a two-dimensional network.

3. Supramolecular features

In the crystal, adjacent two-dimensional networks are packed parallel to each other in an $\cdots\text{AAAA}\cdots$ fashion (Fig. 2). It should be noted that the carboxylic oxygen atom O3 and the uncoordinated nitrogen atom N7 in adjacent networks interact with each other and form strong $\text{O3}-\text{H3}\cdots\text{N7}$ hydrogen bonds (Table 1), which further link the two-dimensional networks into a three-dimensional supramolecular architecture.

4. Database survey

A search of the Cambridge Structural Database (Version 5.37; Groom *et al.*, 2016) for 5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi(1,2,4-triazole) reveals five structures. Of these, there is only one Co^{II} coordination structure (ZOTDIX; Gong *et al.*, 2014). In this structure, the pyridyl nitrogen atom is not coordinated to the Co^{II} cation.

5. Synthesis and crystallization

A mixture of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.10 mmol), 5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi(1,2,4-triazole) (0.10 mmol), benzene-1,3-dicarboxylic acid (0.10 mmol) and H_2O (10 ml) was stirred at room temperature for 30 min. When the pH value had been adjusted to about 7.0 with 0.1 *M* NaOH, the mixture was sealed in a 20 ml Teflon-lined stainless-steel reactor and then heated to 433 K for 72 h under autogenous pressure, and then slowly cooled to room temperature at a rate of 5 K h^{-1} . Pink block-shaped crystals of the title complex were isolated, washed with distilled water, and dried in air (yield 52%).

Table 2
Experimental details.

Crystal data	
Chemical formula	[Co(C ₈ H ₅ O ₄)(C ₉ H ₆ N ₇)]
M_r	436.26
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	6.5825 (5), 9.0574 (12), 13.9842 (12)
α, β, γ (°)	74.214 (1), 84.690 (2), 82.303 (1)
V (Å ³)	793.69 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.13
Crystal size (mm)	0.20 × 0.18 × 0.15
Data collection	
Diffraction	Bruker SMART CCD area detector
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
T_{\min}, T_{\max}	0.797, 0.858
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5565, 3507, 2338
R_{int}	0.055
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.113, 1.09
No. of reflections	3507
No. of parameters	265
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.49, -0.59

Computer programs: SMART and SAINT (Bruker, 2008), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg & Putz, 2006).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms attached to C and N atoms were placed in calculated positions (C–H = 0.93 Å,

N–H = 0.86 Å) and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$, respectively. The carboxyl H atom was located in the difference Fourier-map and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Funding information

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References

- Brandenburg, K. & Putz, H. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2008). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cavka, J. H., Grande, C. A., Mondino, G. & Blom, R. (2014). *Ind. Eng. Chem. Res.* **53**, 15500–15507.
- Gong, Y., Yang, Y. X., Zhang, P., Gao, X. L., Yin, J. L. & Lin, J. H. (2014). *Dalton Trans.* **43**, 16928–16936.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Huang, Y.-B., Liang, J., Wang, X.-S. & Cao, R. (2017). *Chem. Soc. Rev.* **46**, 126–157.
- Kitagawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
- Li, G.-L. & Sato, O. (2017). *Acta Cryst.* **E73**, 993–995.
- Nath, I., Chakraborty, J. & Verpoort, F. (2016). *Chem. Soc. Rev.* **45**, 4127–4170.
- Ni, Z.-P., Liu, J.-L., Hoque, Md. N., Liu, W., Li, J.-Y., Chen, Y.-C. & Tong, M.-L. (2017). *Chem. Rev.* **335**, 28–43.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Sun, L., Campbell, M. G. & Dincă, M. (2016). *Angew. Chem. Int. Ed.* **55**, 3566–3579.
- Sun, Y.-X. & Sun, W.-Y. (2015). *CrystEngComm*, **17**, 4045–4063.
- Yi, F.-Y., Chen, D., Wu, M.-K., Han, L. & Jiang, H.-L. (2016). *ChemPlusChem*, **81**, 675–690.
- Zhang, Z., Yao, Z.-Z., Xiang, S. C. & Chen, B. L. (2014). *Energ. Environ. Sci.* **7**, 2868–2899.
- Zhou, H. C., Long, J. R. & Yaghi, O. M. (2012). *Chem. Rev.* **112**, 673–674.

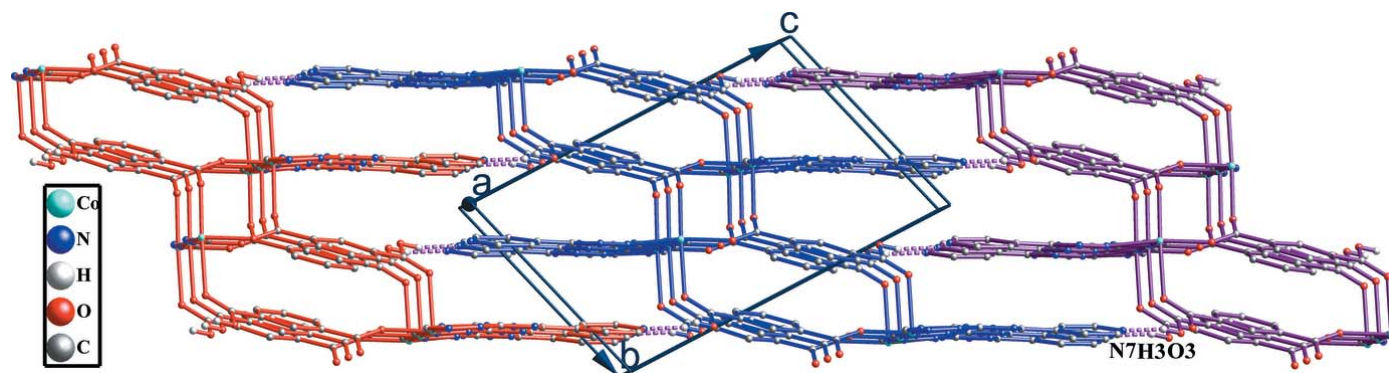


Figure 2

The three-dimensional structure of the title complex formed by the O–H···N hydrogen bonds (dashed lines) between adjacent networks (depicted in different colours). H atoms not involved in hydrogen bonds have been omitted for clarity.

supporting information

Acta Cryst. (2017). E73, 1779-1781 [https://doi.org/10.1107/S205698901701533X]

Synthesis and crystal structure of a two-dimensional Co^{II} coordination polymer: poly[(μ_3 -3-carboxybenzoato)[μ_2 -5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi[1,2,4-triazole]]cobalt(II)]

Chao-Jun Du, Xiao-Na Zhao and Bao-Yong Chen

Computing details

Data collection: *SMART* (Bruker, 2008); cell refinement: *SMART* (Bruker, 2008); data reduction: *S SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *DIAMOND* (Brandenburg & Putz, 2006).

Poly[(μ_3 -3-carboxybenzoato)[μ_2 -5-(pyridin-4-yl)-1*H*,2'*H*-3,3'-bi[1,2,4-triazole]]cobalt(II)]

Crystal data

[Co(C₈H₅O₄)(C₉H₆N₇)]

$M_r = 436.26$

Triclinic, *P* $\bar{1}$

$a = 6.5825$ (5) Å

$b = 9.0574$ (12) Å

$c = 13.9842$ (12) Å

$\alpha = 74.214$ (1)°

$\beta = 84.690$ (2)°

$\gamma = 82.303$ (1)°

$V = 793.69$ (14) Å³

$Z = 2$

$F(000) = 442$

$D_x = 1.825$ Mg m⁻³

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

Cell parameters from 1163 reflections

$\theta = 3.0\text{--}28.3^\circ$

$\mu = 1.13$ mm⁻¹

$T = 293$ K

Block, pink

0.20 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD area detector
diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

$T_{\min} = 0.797$, $T_{\max} = 0.858$

5565 measured reflections

3507 independent reflections

2338 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 28.4^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -8 \rightarrow 8$

$k = -11 \rightarrow 12$

$l = -16 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.113$

$S = 1.09$

3507 reflections

265 parameters

0 restraints

Primary atom site location: difference Fourier
map

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0172P)^2 + 0.0319P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.36855 (8)	0.42648 (8)	0.65379 (5)	0.02024 (18)
N1	0.2335 (5)	0.5770 (4)	0.8362 (3)	0.0196 (9)
N2	0.3746 (5)	0.5162 (4)	0.7767 (3)	0.0182 (9)
N3	0.5482 (5)	0.6182 (4)	0.8697 (3)	0.0210 (9)
N4	0.9301 (5)	0.5039 (4)	0.7413 (3)	0.0200 (9)
H4	0.9832	0.5434	0.7811	0.024*
N5	1.0369 (5)	0.4445 (4)	0.6689 (3)	0.0197 (9)
N6	0.7019 (5)	0.4259 (4)	0.6688 (3)	0.0191 (9)
N7	0.0562 (5)	0.8553 (5)	1.1093 (3)	0.0273 (10)
O1	0.3534 (4)	0.3140 (4)	0.5493 (2)	0.0209 (7)
O2	0.6377 (4)	0.3585 (4)	0.4500 (2)	0.0209 (7)
O3	0.8393 (5)	-0.0128 (4)	0.2340 (3)	0.0342 (10)
H3	0.917 (7)	-0.071 (6)	0.200 (4)	0.051*
O4	0.6280 (4)	-0.1888 (4)	0.2391 (2)	0.0257 (8)
C1	0.5576 (6)	0.5438 (5)	0.7995 (3)	0.0180 (10)
C2	0.3424 (6)	0.6368 (5)	0.8906 (3)	0.0199 (10)
C3	0.7332 (6)	0.4911 (5)	0.7405 (3)	0.0173 (10)
C4	0.8918 (6)	0.3997 (5)	0.6277 (3)	0.0206 (11)
H4A	0.9183	0.3542	0.5751	0.025*
C5	-0.0515 (6)	0.7829 (6)	1.0630 (4)	0.0280 (12)
H5	-0.1909	0.7793	1.0807	0.034*
C6	0.0347 (6)	0.7140 (6)	0.9909 (4)	0.0282 (12)
H6	-0.0461	0.6662	0.9598	0.034*
C7	0.2431 (6)	0.7154 (5)	0.9641 (3)	0.0209 (10)
C8	0.3536 (6)	0.7892 (6)	1.0130 (4)	0.0297 (12)
H8	0.4938	0.7923	0.9977	0.036*
C9	0.2573 (7)	0.8578 (6)	1.0842 (4)	0.0300 (13)
H9	0.3342	0.9075	1.1159	0.036*
C10	0.4755 (6)	0.2952 (5)	0.4773 (3)	0.0186 (10)
C11	0.6668 (6)	-0.0715 (6)	0.2607 (3)	0.0213 (10)
C12	0.4189 (6)	0.1867 (5)	0.4224 (3)	0.0173 (10)
C13	0.5649 (6)	0.1212 (5)	0.3625 (3)	0.0191 (10)
H13	0.6973	0.1499	0.3523	0.023*
C14	0.5117 (6)	0.0126 (5)	0.3179 (3)	0.0198 (10)
C15	0.3112 (6)	-0.0227 (5)	0.3286 (3)	0.0235 (11)

H15	0.2761	-0.0946	0.2982	0.028*
C16	0.1631 (6)	0.0470 (6)	0.3834 (4)	0.0285 (12)
H16	0.0276	0.0257	0.3880	0.034*
C17	0.2189 (6)	0.1497 (6)	0.4316 (3)	0.0239 (11)
H17	0.1206	0.1943	0.4706	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0155 (3)	0.0282 (4)	0.0212 (4)	-0.0045 (3)	0.0037 (2)	-0.0142 (3)
N1	0.0152 (18)	0.027 (2)	0.019 (2)	-0.0025 (16)	0.0041 (15)	-0.0124 (19)
N2	0.0152 (17)	0.022 (2)	0.019 (2)	-0.0014 (16)	0.0029 (15)	-0.0101 (19)
N3	0.0155 (18)	0.028 (2)	0.023 (2)	-0.0047 (16)	0.0039 (15)	-0.0132 (19)
N4	0.0158 (18)	0.030 (2)	0.019 (2)	-0.0041 (16)	0.0025 (15)	-0.0150 (19)
N5	0.0120 (17)	0.024 (2)	0.025 (2)	-0.0028 (16)	0.0053 (15)	-0.0112 (19)
N6	0.0159 (17)	0.027 (2)	0.019 (2)	-0.0039 (16)	0.0009 (15)	-0.0129 (19)
N7	0.031 (2)	0.029 (3)	0.025 (2)	-0.0022 (19)	0.0044 (18)	-0.016 (2)
O1	0.0245 (16)	0.0234 (19)	0.0183 (18)	-0.0064 (14)	0.0066 (13)	-0.0120 (15)
O2	0.0201 (15)	0.0205 (18)	0.0247 (19)	-0.0065 (13)	0.0016 (13)	-0.0096 (16)
O3	0.0267 (18)	0.041 (2)	0.043 (2)	-0.0092 (17)	0.0161 (16)	-0.029 (2)
O4	0.0300 (17)	0.026 (2)	0.026 (2)	-0.0057 (15)	0.0039 (14)	-0.0147 (17)
C1	0.018 (2)	0.022 (3)	0.016 (2)	-0.0021 (19)	0.0014 (17)	-0.008 (2)
C2	0.019 (2)	0.025 (3)	0.018 (3)	-0.006 (2)	0.0003 (18)	-0.010 (2)
C3	0.015 (2)	0.020 (3)	0.018 (2)	-0.0010 (18)	0.0004 (17)	-0.008 (2)
C4	0.017 (2)	0.022 (3)	0.026 (3)	0.000 (2)	0.0024 (19)	-0.014 (2)
C5	0.020 (2)	0.038 (3)	0.027 (3)	-0.004 (2)	0.010 (2)	-0.015 (3)
C6	0.021 (2)	0.042 (3)	0.027 (3)	-0.003 (2)	0.006 (2)	-0.021 (3)
C7	0.025 (2)	0.023 (3)	0.017 (3)	0.001 (2)	0.0010 (19)	-0.011 (2)
C8	0.017 (2)	0.044 (3)	0.034 (3)	-0.004 (2)	0.003 (2)	-0.022 (3)
C9	0.031 (3)	0.037 (3)	0.032 (3)	-0.009 (2)	0.002 (2)	-0.024 (3)
C10	0.016 (2)	0.016 (3)	0.023 (3)	0.0015 (19)	0.0000 (18)	-0.004 (2)
C11	0.022 (2)	0.026 (3)	0.016 (3)	-0.001 (2)	-0.0006 (18)	-0.007 (2)
C12	0.019 (2)	0.023 (3)	0.013 (2)	-0.0060 (19)	0.0008 (17)	-0.010 (2)
C13	0.016 (2)	0.025 (3)	0.019 (3)	-0.0109 (19)	0.0068 (17)	-0.009 (2)
C14	0.025 (2)	0.019 (3)	0.017 (2)	-0.004 (2)	0.0040 (18)	-0.008 (2)
C15	0.024 (2)	0.026 (3)	0.026 (3)	-0.008 (2)	0.002 (2)	-0.016 (2)
C16	0.021 (2)	0.038 (3)	0.033 (3)	-0.007 (2)	0.003 (2)	-0.019 (3)
C17	0.025 (2)	0.027 (3)	0.022 (3)	0.002 (2)	0.0048 (19)	-0.013 (2)

Geometric parameters (Å, °)

Co1—O1	2.012 (3)	O4—C11	1.244 (5)
Co1—O2 ⁱ	2.086 (3)	O4—Co1 ⁱⁱⁱ	2.262 (4)
Co1—N2	2.097 (3)	C1—C3	1.461 (5)
Co1—N5 ⁱⁱ	2.162 (3)	C2—C7	1.463 (5)
Co1—N6	2.223 (3)	C4—H4A	0.9300
Co1—O4 ⁱⁱⁱ	2.262 (4)	C5—C6	1.368 (5)
N1—C2	1.347 (5)	C5—H5	0.9300

N1—N2	1.352 (4)	C6—C7	1.389 (6)
N2—C1	1.345 (5)	C6—H6	0.9300
N3—C1	1.327 (5)	C7—C8	1.384 (6)
N3—C2	1.357 (5)	C8—C9	1.377 (6)
N4—C3	1.318 (5)	C8—H8	0.9300
N4—N5	1.368 (4)	C9—H9	0.9300
N4—H4	0.8600	C10—C12	1.502 (5)
N5—C4	1.320 (5)	C11—C14	1.495 (5)
N5—Co1 ^{iv}	2.162 (3)	C12—C17	1.387 (6)
N6—C3	1.338 (5)	C12—C13	1.395 (5)
N6—C4	1.345 (5)	C13—C14	1.394 (5)
N7—C5	1.339 (5)	C13—H13	0.9300
N7—C9	1.339 (5)	C14—C15	1.385 (5)
O1—C10	1.262 (5)	C15—C16	1.377 (5)
O2—C10	1.258 (5)	C15—H15	0.9300
O2—Co1 ⁱ	2.086 (3)	C16—C17	1.391 (6)
O3—C11	1.299 (5)	C16—H16	0.9300
O3—H3	0.89 (5)	C17—H17	0.9300
O1—Co1—O2 ⁱ	93.18 (12)	N5—C4—N6	113.9 (4)
O1—Co1—N2	172.28 (15)	N5—C4—H4A	123.1
O2 ⁱ —Co1—N2	94.31 (13)	N6—C4—H4A	123.1
O1—Co1—N5 ⁱⁱ	87.27 (12)	N7—C5—C6	122.8 (4)
O2 ⁱ —Co1—N5 ⁱⁱ	91.64 (13)	N7—C5—H5	118.6
N2—Co1—N5 ⁱⁱ	90.64 (12)	C6—C5—H5	118.6
O1—Co1—N6	105.23 (11)	C5—C6—C7	119.9 (4)
O2 ⁱ —Co1—N6	90.18 (13)	C5—C6—H6	120.1
N2—Co1—N6	76.64 (12)	C7—C6—H6	120.1
N5 ⁱⁱ —Co1—N6	167.25 (12)	C8—C7—C6	116.9 (4)
O1—Co1—O4 ⁱⁱⁱ	84.32 (12)	C8—C7—C2	121.6 (4)
O2 ⁱ —Co1—O4 ⁱⁱⁱ	177.47 (11)	C6—C7—C2	121.4 (4)
N2—Co1—O4 ⁱⁱⁱ	88.17 (13)	C9—C8—C7	120.4 (4)
N5 ⁱⁱ —Co1—O4 ⁱⁱⁱ	87.82 (13)	C9—C8—H8	119.8
N6—Co1—O4 ⁱⁱⁱ	90.88 (13)	C7—C8—H8	119.8
C2—N1—N2	105.2 (3)	N7—C9—C8	122.0 (4)
C1—N2—N1	105.6 (3)	N7—C9—H9	119.0
C1—N2—Co1	117.7 (3)	C8—C9—H9	119.0
N1—N2—Co1	136.0 (2)	O2—C10—O1	125.2 (4)
C1—N3—C2	100.7 (3)	O2—C10—C12	119.0 (4)
C3—N4—N5	109.5 (3)	O1—C10—C12	115.8 (4)
C3—N4—H4	125.2	O4—C11—O3	123.0 (4)
N5—N4—H4	125.2	O4—C11—C14	121.0 (4)
C4—N5—N4	103.0 (3)	O3—C11—C14	116.1 (4)
C4—N5—Co1 ^{iv}	135.8 (3)	C17—C12—C13	119.2 (4)
N4—N5—Co1 ^{iv}	121.0 (2)	C17—C12—C10	119.8 (4)
C3—N6—C4	103.5 (3)	C13—C12—C10	121.0 (4)
C3—N6—Co1	111.1 (2)	C14—C13—C12	119.8 (4)
C4—N6—Co1	144.9 (3)	C14—C13—H13	120.1

C5—N7—C9	118.1 (4)	C12—C13—H13	120.1
C10—O1—Co1	132.1 (3)	C15—C14—C13	119.8 (4)
C10—O2—Co1 ⁱ	120.5 (3)	C15—C14—C11	118.3 (4)
C11—O3—H3	108 (3)	C13—C14—C11	121.9 (4)
C11—O4—Co1 ⁱⁱⁱ	124.8 (3)	C16—C15—C14	120.9 (4)
N3—C1—N2	114.7 (3)	C16—C15—H15	119.5
N3—C1—C3	130.7 (4)	C14—C15—H15	119.5
N2—C1—C3	114.6 (3)	C15—C16—C17	119.1 (4)
N1—C2—N3	113.8 (3)	C15—C16—H16	120.5
N1—C2—C7	121.9 (4)	C17—C16—H16	120.5
N3—C2—C7	124.3 (4)	C12—C17—C16	121.1 (4)
N4—C3—N6	110.1 (3)	C12—C17—H17	119.5
N4—C3—C1	130.3 (4)	C16—C17—H17	119.5
N6—C3—C1	119.5 (3)		
C2—N1—N2—C1	-0.1 (5)	N1—C2—C7—C8	-173.9 (5)
C2—N1—N2—Co1	-169.6 (4)	N3—C2—C7—C8	5.4 (8)
C3—N4—N5—C4	0.5 (5)	N1—C2—C7—C6	8.8 (7)
C3—N4—N5—Co1 ^{iv}	-174.9 (3)	N3—C2—C7—C6	-171.9 (5)
C2—N3—C1—N2	-0.1 (5)	C6—C7—C8—C9	-0.4 (8)
C2—N3—C1—C3	177.7 (5)	C2—C7—C8—C9	-177.8 (5)
N1—N2—C1—N3	0.1 (5)	C5—N7—C9—C8	0.2 (8)
Co1—N2—C1—N3	171.9 (3)	C7—C8—C9—N7	0.5 (8)
N1—N2—C1—C3	-178.1 (4)	Co1 ⁱ —O2—C10—O1	-88.9 (5)
Co1—N2—C1—C3	-6.3 (5)	Co1 ⁱ —O2—C10—C12	91.8 (4)
N2—N1—C2—N3	0.0 (5)	Co1—O1—C10—O2	-6.3 (7)
N2—N1—C2—C7	179.3 (4)	Co1—O1—C10—C12	173.1 (3)
C1—N3—C2—N1	0.1 (5)	Co1 ⁱⁱⁱ —O4—C11—O3	104.3 (5)
C1—N3—C2—C7	-179.3 (5)	Co1 ⁱⁱⁱ —O4—C11—C14	-77.2 (5)
N5—N4—C3—N6	-0.6 (5)	O2—C10—C12—C17	-162.0 (4)
N5—N4—C3—C1	-176.6 (5)	O1—C10—C12—C17	18.6 (6)
C4—N6—C3—N4	0.4 (5)	O2—C10—C12—C13	18.4 (7)
Co1—N6—C3—N4	-173.6 (3)	O1—C10—C12—C13	-161.0 (4)
C4—N6—C3—C1	177.0 (4)	C17—C12—C13—C14	-4.1 (7)
Co1—N6—C3—C1	3.0 (5)	C10—C12—C13—C14	175.5 (4)
N3—C1—C3—N4	-0.2 (9)	C12—C13—C14—C15	3.9 (7)
N2—C1—C3—N4	177.7 (5)	C12—C13—C14—C11	-174.3 (4)
N3—C1—C3—N6	-175.9 (5)	O4—C11—C14—C15	-13.1 (7)
N2—C1—C3—N6	1.9 (6)	O3—C11—C14—C15	165.5 (4)
N4—N5—C4—N6	-0.2 (5)	O4—C11—C14—C13	165.1 (5)
Co1 ^{iv} —N5—C4—N6	174.1 (3)	O3—C11—C14—C13	-16.3 (7)
C3—N6—C4—N5	-0.1 (5)	C13—C14—C15—C16	-0.6 (7)
Co1—N6—C4—N5	170.1 (4)	C11—C14—C15—C16	177.7 (4)
C9—N7—C5—C6	-0.9 (8)	C14—C15—C16—C17	-2.5 (7)
N7—C5—C6—C7	1.0 (8)	C13—C12—C17—C16	1.0 (7)

C5—C6—C7—C8	-0.3 (7)	C10—C12—C17—C16	-178.6 (5)
C5—C6—C7—C2	177.1 (5)	C15—C16—C17—C12	2.3 (8)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H3...N7 ^v	0.89 (5)	1.72 (5)	2.592 (4)	166 (5)

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