Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis and crystal structure of poly[(3-amino-1,2,4-triazole)(μ_3-1*H*-benzimidazole-5,6-dicarboxylato)cobalt(II)]

Chen Zhao, Yi Li, Jin-Sheng Xiao, Peng-Dan Zhang, Xue-Qian Wu* and Qiang Chen

Beijing Key Laboratory for Green Catalysis and Separation and Department of Environmental Chemical Engineering, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, People's Republic of China. *Correspondence e-mail: wuxueqiansnail@emails.bjut.edu.cn

Received 29 April 2021
Accepted 6 June 2021

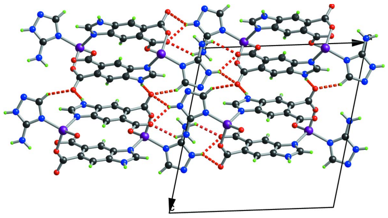
Edited by G. Díaz de Delgado, Universidad de Los Andes, Venezuela

Keywords: crystal structure; coordination polymer; mixed-ligands synthetic strategy; imidazole; dicarboxylic acid.

CCDC reference: 1996100

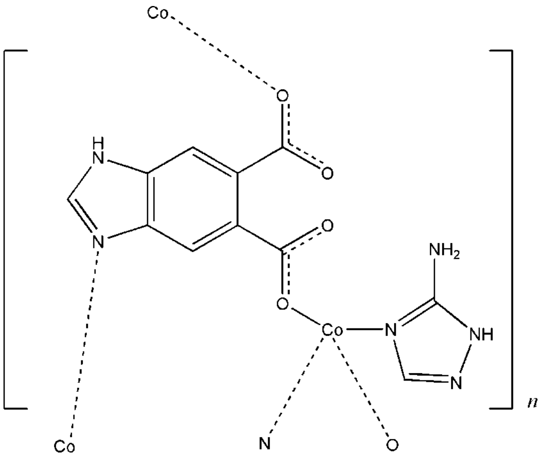
Supporting information: this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title coordination polymer, $[Co(C_9H_4N_2O_4)(C_2H_4N_4)]_n$ or $[Co(L_1)(L_2)]_n$, consists of one crystallographically independent Co^{2+} centre, one $L_1{}^{2-}$ ligand and one L_2 ligand (L_1 = 1*H*-benzimidazole-5,6-dicarboxylic acid, L_2 = 3-amino-1,2,4-triazole). The Co^{2+} centre is coordinated by two carboxylato-*O* atoms from two independent $L_1{}^{2-}$ ligands and two nitrogen atoms from L_2 and another L_1 ligand. Thus, the metal center adopts a four-coordinate mode, forming a tetrahedral geometry. Interestingly, through the combination of two $L_1{}^{2-}$, two L_2 ligands and two Co^{2+} ions, a basic repeating unit is constructed, resulting in the formation of a one-dimensional straight chain structure. These chains are further expanded to the final three-dimensional framework *via* N—H$\cdots$O hydrogen-bonding interactions.



1. Chemical context

Over the past two decades, coordination polymers (CPs) have been demonstrated to represent a new type of crystalline organic–inorganic hybrid materials, and are unique in terms of their potentially high porosities, tunable pores, and diverse compositions (Du *et al.*, 2013; Kitagawa *et al.*, 2007; Cui *et al.*, 2016). These features have enabled CPs to be constructed with great potential for various applications, such as gas adsorption/separation (Zhao *et al.*, 2018), chemical sensing (Huang *et al.*, 2017), heterogeneous catalysis (He *et al.*, 2020) and energy storage/conversion (Lu *et al.*, 2020). Meanwhile, the crystalline nature of CPs allows for the accurate determination of their structures using X-ray diffraction techniques and further, the revealing of structure–property relationships. The great potential of these compounds certainly promotes the development of synthetic strategies for new CPs. It has been demonstrated that many efficient synthetic routes, including metal exchange (Wang *et al.*, 2017), ligand substitution (Han *et al.*, 2014), directional construction based on secondary building units (SBUs) (Zou *et al.*, 2016), and topology-guided reticular chemistry principles (Wang *et al.*, 2016) have shown some advantages in fabricating new CPs with multiple structures and functionalities. In addition to the methods mentioned above, the mixed-ligands strategy is also considered to be an important approach for the integration of the properties of related ligands into a single coordination polymer and hence expansion of the structural diversity of CPs (Macreadie *et al.*, 2020). In this context, we report the synthesis and crystal structure of the title coordination polymer poly[(3-amino-1,2,4-triazole)(μ_3-1*H*-benzimidazole-5,6-dicarboxylato)cobalt(II)] (**1**), which was prepared by the solvothermal method using two simple ligands and a cobalt salt.



2. Structural commentary

The title coordination polymer (**1**) crystallizes in the monoclinic system, $P2_1/c$ space group, and its asymmetric unit contains one Co^{2+} center, one L_1^{2-} anion and one L_2 ligand (Fig. 1). The metal center adopts a typical tetrahedral linkage geometry to coordinate with two carboxylato-*O* atoms from two independent L_1^{2-} ligands and two nitrogen atoms, one from L_2 and another from an L_1 ligand. Interestingly, through the combination of two L_1^{2-}, two L_2 ligands and two Co^{2+} ions, a basic repeating unit is constructed, resulting in the formation of a one-dimensional straight chain structure (as shown in Fig. 2). These chains are further connected *via* hydrogen bonding interactions (Fig. 3), generating a three-dimensional framework.

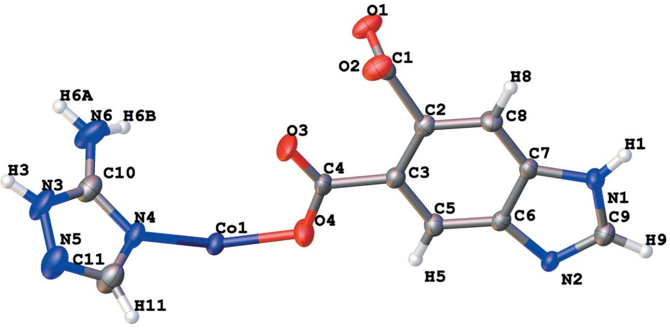


Figure 1
A view of the asymmetric unit of the title coordination polymer showing the atom numbering with displacement ellipsoids drawn at the 50% probability level.

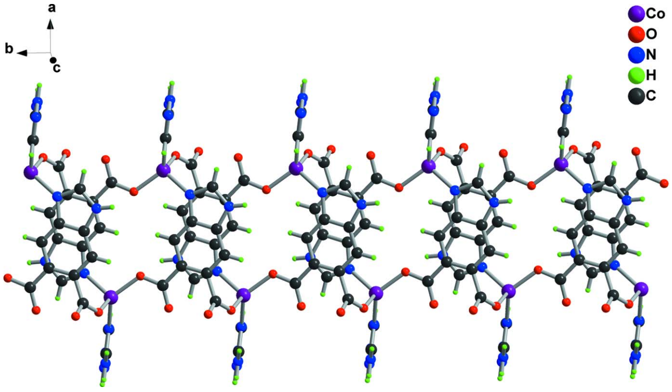


Figure 2
A view of the one-dimensional straight chain structure within the coordination polymer.

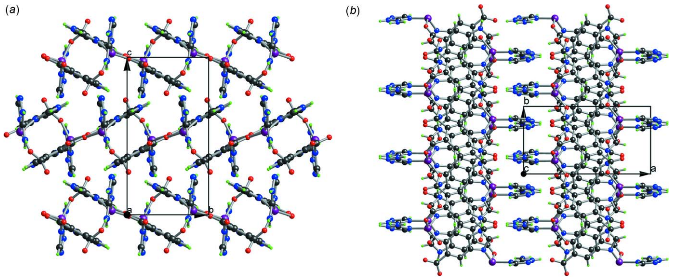


Figure 3
Structure of the title coordination polymer viewed along the (*a*) *a* axis and (*b*) *c* axis, respectively.

3. Supramolecular features

As mentioned above, extensive hydrogen-bonding interactions in the crystal of the title coordination polymer are observed, the numerical values of which are presented in Table 1. As shown in Fig. 4, each chain is linked to adjacent chains by N1—H1⋯O1 hydrogen bonds into infinite layer structures parallel to the *bc* plane. Meanwhile, these layers are

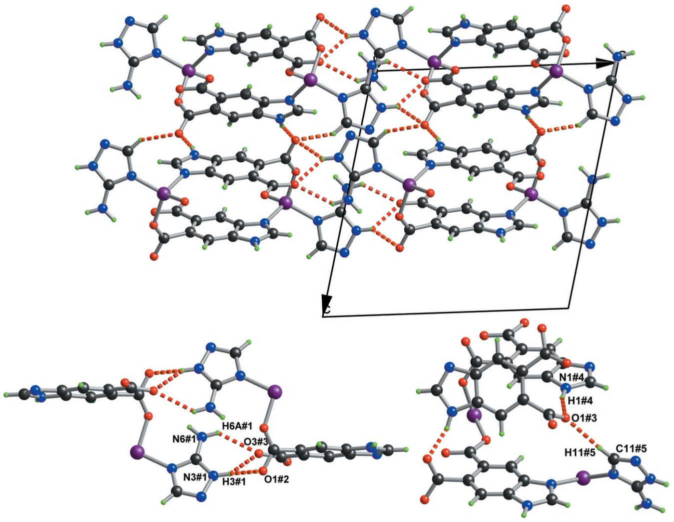


Figure 4
A view of the hydrogen bonds in the title coordination polymer. Intramolecular hydrogen bonds are omitted for clarity [symmetry codes: (#1) $-1 + x, y, z$; (#2) $1 - x, 1 - y, 1 - z$; (#3) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (#4) $-1 + x, 1 + y, z$; (#5) $-x, 1 - y, 1 - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^{i}	0.86	1.84	2.675 (4)	163
N3—H3$\cdots$O1^{ii}	0.86	2.48	3.104 (4)	130
N3—H3$\cdots$O3^{ii}	0.86	2.08	2.811 (4)	142
N6—H6$A\cdots$O3^{ii}	0.86	2.35	3.036 (5)	136
N6—H6$B\cdots$O2^{iii}	0.86	2.23	2.946 (5)	141
C5—H5$\cdots$O4^{iv}	0.93	2.58	3.312 (4)	136
C9—H9$\cdots$N5^{v}	0.93	2.48	3.332 (5)	152
C11—H11$\cdots$O1^{vi}	0.93	2.41	3.215 (5)	145

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

linked by other intermolecular hydrogen bonds (*e.g.*, N3—H3$\cdots$O3 and N6—H6$A\cdots$O3), resulting in the formation of the final three-dimensional supramolecular network. Due to the regular distribution of Co^{2+} metal sites, the high density of nitrogen atoms in the structure, and the packing arrangement of the supramolecular network, the coordination polymer has the potential to work as a molecular catalyst or to serve as the precursor material for preparing an electrocatalyst.

4. Database survey

A search of the Cambridge Crystallographic Database (CSD version 5.42, update of Feb 2021, Groom *et al.*, 2016) for structures with 1*H*-benzimidazole-5,6-dicarboxylate gave 372 hits of which some are coordination polymers with prominent free pore space (also known as metal-organic frameworks, MOFs). For example, Li and co-workers reported a new three-dimensional non-interpenetrating metal–organic framework (BARKUD01), featuring one-dimensional nanotube channels and exhibiting excellent gas separation performances (Li *et al.*, 2017). There are some Co^{2+} complexes containing only ligand L_1 [refcodes AJIKIO (Fu *et al.*, 2009), NUCGUO (Wei *et al.*, 2009), ROMRUH (Xu *et al.*, 2009), ROMRUH01 (Wei *et al.*, 2009), ROMRUH02 (Shi *et al.*, 2012), SILZAP (Lo *et al.*, 2007), SOGCEX (Gao *et al.*, 2008), and YOTFET (Song *et al.*, 2009)]. However, none of these exhibit a tetrahedral geometry around the Co atom. A zinc complex (BOVQUZ; Li *et al.*, 2009) displays a tetrahedral coordination around the metal center. By using cyclopentadienyliron dicarbonyl dimer as a starting material, two new Fe^{II}-based MOFs have been constructed (HOHBEN and HOHBIR; Li *et al.*, 2014). As a typical imidazole-carboxylate ligand, 1*H*-benzimidazole-5,6-dicarboxylate could bind rare earth/transition-metal centers with multiple coordination modes, which provides an ideal platform for the preparation of various coordination polymers, such as BASTOG (Sun *et al.*, 2010), EHETAO (Jin *et al.*, 2016) and FELBAC (Chai *et al.*, 2018).

5. Synthesis and crystallization

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (20 mg, 0.069 mmol), 1*H*-benzimidazole-5,6-dicarboxylic acid (10 mg, 0.049 mmol), 3-amino-1,2,4-triazole (10 mg, 0.119 mmol), DMA (2 mL) and H_2O (2 mL) were added to a 20 mL vial. The reaction system was then heated at 373 K for 72 h in an oven. Purple block-shaped crystals of the title compound suitable for X-ray analysis were obtained.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(C_9H_4N_2O_4)(C_2H_4N_4)]$
M_r	347.16
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	279
a, b, c (Å)	13.3368 (8), 6.8727 (4), 13.6015 (10)
β (°)	103.478 (7)
V (Å^3)	1212.38 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.45
Crystal size (mm)	0.06 × 0.05 × 0.04
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, AtlasS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.979, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5618, 2475, 1839
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.098, 1.03
No. of reflections	2475
No. of parameters	199
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions (N—H = 0.86 Å, C—H = 0.93 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(N,C)$

Funding information

The authors gratefully acknowledge financial support from the National Innovation and Entrepreneurship Training Program of Beijing University of Technology for College Students (GJDC-2019-01-43).

References

Chai, J., Wang, P., Jia, J., Ma, B., Sun, J., Tao, Y., Zhang, P., Wang, L. & Fan, Y. (2018). *Polyhedron*, **141**, 369–376.

Cui, Y., Li, B., He, H., Zhou, W., Chen, B. & Qian, G. (2016). *Acc. Chem. Res.* **49**, 483–493.

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

Du, M., Li, C.-P., Liu, C.-S. & Fang, S.-M. (2013). *Coord. Chem. Rev.* **257**, 1282–1305.

Fu, J.-D., Tang, Z.-W., Yuan, M.-Y. & Wen, Y.-H. (2009). *Acta Cryst.* E**65**, m1657.

Gao, Q., Gao, W.-H., Zhang, C.-Y. & Xie, Y.-B. (2008). *Acta Cryst.* E**64**, m928.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Han, Y., Li, J.-R., Xie, Y. & Guo, G. (2014). *Chem. Soc. Rev.* **43**, 5952–5981.

He, T., Huang, Z., Yuan, S., Lv, X.-L., Kong, X.-J., Zou, X., Zhou, H.-C. & Li, J.-R. (2020). *J. Am. Chem. Soc.* **142**, 13491–13499.

Huang, R.-W., Wei, Y.-S., Dong, X.-Y., Wu, X.-H., Du, C.-X., Zang, S.-Q. & Mak, T. C. W. (2017). *Nat. Chem.* **9**, 689–697.

Jin, J., Chen, C., Gao, Y., Zhao, R., Wang, X., Lü, C., Chi, Y. & Niu, S. (2016). *J. Solid State Chem.* **235**, 193–201.

Kitagawa, S. & Matsuda, R. (2007). *Coord. Chem. Rev.* **251**, 2490–2509.

Li, J.-T., Li, J., Song, L.-M. & Ji, X.-H. (2017). *Inorg. Chem. Commun.* **83**, 88–91.

Li, Q., Tian, C., Zhang, H., Qian, J. & Du, S. (2014). *CrystEngComm*, **16**, 9208–9215.

Li, Z.-Y., Dai, J.-W. & Yue, S.-T. (2009). *Acta Cryst.* E**65**, m775.

Lo, Y.-L., Wang, W.-C., Lee, G.-A. & Liu, Y.-H. (2007). *Acta Cryst.* E**63**, m2657–m2658.

Lu, X.-F., Xia, B.-Y., Zang, S.-Q. & Lou, X.-W. (2020). *Angew. Chem.* **132**, 4662–4678.

Macreadie, L. K., Babarao, R., Setter, C. J., Lee, S. J., Qazvini, O. T., Seeber, A. J., Tsanaktsidis, J., Telfer, S. G., Batten, S. R. & Hill, M. R. (2020). *Angew. Chem. Int. Ed.* **59**, 6090–6098.

Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.

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

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

Shi, Z.-F., Li, L. & Niu, S.-Y. (2012). *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **42**, 818–822.

Song, W.-D., Wang, H., Li, S.-J., Qin, P.-W. & Hu, S.-W. (2009). *Acta Cryst.* E**65**, m702.

Sun, Y.-G., Wu, Y.-L., Xiong, G., Smet, P. F., Ding, F., Guo, M.-Y., Zhu, M.-C., Gao, E. J., Poelman, D. & Verpoort, F. (2010). *Dalton Trans.* **39**, 11383–11395.

Wang, J.-H., Zhang, Y., Li, M., Yan, S., Li, D. & Zhang, X.-M. (2017). *Angew. Chem. Int. Ed.* **56**, 6478–6482.

Wang, X., Lu, W., Gu, Z.-Y., Wei, Z. & Zhou, H.-C. (2016). *Chem. Commun.* **52**, 1926–1929.

Wei, Y., Yu, Y., Sa, R., Li, Q. & Wu, K. (2009). *CrystEngComm*, **11**, 1054–1060.

Xu, K. & Yu, L.-P. (2009). *Acta Cryst.* E**65**, m295.

Zhao, X., Wang, Y., Li, D.-S., Bu, X. & Feng, P. (2018). *Adv. Mater.* **30**, 1705189.

Zou, R., Li, P.-Z., Zeng, Y.-F., Liu, J., Zhao, R., Duan, H., Luo, Z., Wang, J.-G., Zou, R. & Zhao, Y. (2016). *Small*, **12**, 2334–2343.

supporting information

Acta Cryst. (2021). E**77**, 714-717   [https://doi.org/10.1107/S2056989021005867]

Synthesis and crystal structure of poly[(3-amino-1,2,4-triazole)(μ_3-1*H*-benzimidazole-5,6-dicarboxylato)cobalt(II)]

Chen Zhao, Yi Li, Jin-Sheng Xiao, Peng-Dan Zhang, Xue-Qian Wu and Qiang Chen

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Poly[(3-amino-1,2,4-triazole)(μ_3-1*H*-benzimidazole-5,6-dicarboxylato)cobalt(II)]

Crystal data

$[Co(C_9H_4N_2O_4)(C_2H_4N_4)]$
$M_r = 347.16$
Monoclinic, $P2_1/c$
$a = 13.3368\ (8)$ Å
$b = 6.8727\ (4)$ Å
$c = 13.6015\ (10)$ Å
$\beta = 103.478\ (7)°$
$V = 1212.38\ (14)$ Å^3
$Z = 4$
$F(000) = 700$
$D_x = 1.902$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1697 reflections
$\theta = 4.3–26.7°$
$\mu = 1.45$ mm^{-1}
$T = 279$ K
Block, purple
0.06 × 0.05 × 0.04 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer
Graphite monochromator
Detector resolution: 10.3376 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)
$T_{min} = 0.979$, $T_{max} = 1.000$
5618 measured reflections
2475 independent reflections
1839 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 26.4°$, $\theta_{min} = 3.3°$
$h = -14 \rightarrow 16$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.098$
$S = 1.03$
2475 reflections
199 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.6634P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.75360 (3)	0.69451 (6)	0.52745 (4)	0.02172 (16)
O2	0.76917 (18)	−0.1847 (3)	0.40067 (19)	0.0298 (6)
O1	0.74157 (18)	0.0171 (3)	0.27211 (19)	0.0303 (6)
O4	0.66113 (18)	0.4785 (3)	0.4920 (2)	0.0328 (6)
O3	0.77486 (18)	0.2754 (4)	0.4537 (2)	0.0418 (7)
N2	0.3154 (2)	0.1240 (4)	0.3922 (2)	0.0203 (6)
N1	0.3399 (2)	−0.1552 (4)	0.3188 (2)	0.0254 (7)
H1	0.326047	−0.266046	0.289464	0.030*
N4	0.9004 (2)	0.6928 (4)	0.6053 (2)	0.0264 (7)
C4	0.6862 (3)	0.3188 (5)	0.4544 (3)	0.0216 (8)
C7	0.4351 (2)	−0.0655 (5)	0.3432 (2)	0.0197 (7)
C6	0.4188 (2)	0.1110 (5)	0.3892 (2)	0.0190 (7)
C8	0.5319 (2)	−0.1215 (5)	0.3322 (3)	0.0223 (8)
H8	0.541882	−0.239926	0.302707	0.027*
N3	1.0667 (2)	0.7206 (5)	0.6511 (3)	0.0402 (9)
H3	1.129713	0.736543	0.647408	0.048*
C1	0.7158 (3)	−0.0546 (5)	0.3456 (3)	0.0210 (8)
C3	0.5986 (2)	0.1848 (5)	0.4132 (2)	0.0205 (7)
C9	0.2731 (3)	−0.0376 (5)	0.3493 (3)	0.0254 (8)
H9	0.203572	−0.067057	0.340978	0.031*
C2	0.6129 (2)	0.0051 (5)	0.3665 (2)	0.0198 (7)
C5	0.5008 (2)	0.2361 (5)	0.4240 (3)	0.0215 (8)
H5	0.490570	0.353422	0.454314	0.026*
N5	1.0361 (2)	0.6888 (5)	0.7393 (3)	0.0449 (9)
N6	0.9921 (3)	0.7490 (5)	0.4760 (3)	0.0491 (10)
H6A	1.051093	0.765185	0.461830	0.059*
H6B	0.936808	0.749236	0.428430	0.059*
C10	0.9863 (3)	0.7234 (5)	0.5721 (3)	0.0300 (9)
C11	0.9367 (3)	0.6734 (6)	0.7073 (3)	0.0380 (10)
H11	0.893449	0.650912	0.750793	0.046*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0156 (3)	0.0225 (3)	0.0273 (3)	−0.0014 (2)	0.00539 (19)	−0.0020 (2)
O2	0.0248 (13)	0.0346 (14)	0.0315 (15)	0.0118 (12)	0.0097 (11)	0.0126 (12)
O1	0.0273 (14)	0.0316 (14)	0.0369 (16)	0.0087 (12)	0.0178 (12)	0.0121 (12)
O4	0.0234 (14)	0.0270 (14)	0.0481 (17)	−0.0055 (12)	0.0083 (12)	−0.0114 (13)
O3	0.0146 (13)	0.0519 (18)	0.061 (2)	−0.0066 (13)	0.0135 (13)	−0.0209 (15)

N2	0.0151 (14)	0.0249 (15)	0.0214 (16)	−0.0029 (13)	0.0057 (12)	−0.0010 (13)
N1	0.0206 (15)	0.0259 (16)	0.0307 (18)	−0.0053 (13)	0.0080 (13)	−0.0088 (13)
N4	0.0142 (14)	0.0321 (17)	0.0327 (18)	−0.0010 (13)	0.0047 (13)	0.0032 (14)
C4	0.0197 (18)	0.0233 (18)	0.0228 (19)	−0.0069 (15)	0.0068 (14)	−0.0014 (15)
C7	0.0200 (18)	0.0199 (17)	0.0197 (18)	−0.0035 (15)	0.0055 (14)	−0.0002 (14)
C6	0.0175 (17)	0.0200 (17)	0.0201 (18)	−0.0007 (15)	0.0060 (14)	0.0020 (14)
C8	0.0229 (18)	0.0186 (17)	0.026 (2)	0.0030 (16)	0.0069 (15)	−0.0033 (15)
N3	0.0159 (16)	0.062 (2)	0.043 (2)	−0.0036 (16)	0.0083 (15)	0.0089 (18)
C1	0.0222 (18)	0.0175 (17)	0.0239 (19)	−0.0018 (15)	0.0067 (15)	−0.0053 (15)
C3	0.0184 (17)	0.0233 (18)	0.0199 (18)	−0.0012 (15)	0.0046 (14)	0.0005 (15)
C9	0.0190 (18)	0.0292 (19)	0.028 (2)	−0.0019 (16)	0.0052 (15)	−0.0012 (16)
C2	0.0178 (17)	0.0223 (18)	0.0187 (18)	0.0024 (15)	0.0030 (14)	0.0041 (15)
C5	0.0203 (18)	0.0196 (17)	0.0240 (19)	−0.0011 (15)	0.0041 (15)	−0.0003 (15)
N5	0.0260 (18)	0.068 (3)	0.039 (2)	−0.0059 (17)	0.0032 (16)	0.0083 (19)
N6	0.0297 (19)	0.084 (3)	0.038 (2)	0.0013 (19)	0.0161 (16)	0.010 (2)
C10	0.0228 (19)	0.031 (2)	0.038 (2)	0.0027 (17)	0.0099 (17)	0.0063 (18)
C11	0.026 (2)	0.055 (3)	0.034 (2)	−0.001 (2)	0.0066 (17)	0.010 (2)

Geometric parameters (Å, º)

Co1—O2$^{\rm i}$	1.968 (2)	C7—C8	1.390 (4)
Co1—O4	1.919 (2)	C6—C5	1.384 (4)
Co1—N2$^{\rm ii}$	2.016 (3)	C8—H8	0.9300
Co1—N4	1.997 (3)	C8—C2	1.381 (5)
O2—C1	1.272 (4)	N3—H3	0.8600
O1—C1	1.234 (4)	N3—N5	1.372 (5)
O4—C4	1.287 (4)	N3—C10	1.331 (5)
O3—C4	1.222 (4)	C1—C2	1.521 (5)
N2—C6	1.392 (4)	C3—C2	1.422 (5)
N2—C9	1.319 (4)	C3—C5	1.392 (5)
N1—H1	0.8600	C9—H9	0.9300
N1—C7	1.380 (4)	C5—H5	0.9300
N1—C9	1.337 (4)	N5—C11	1.300 (5)
N4—C10	1.342 (5)	N6—H6A	0.8600
N4—C11	1.366 (5)	N6—H6B	0.8600
C4—C3	1.490 (5)	N6—C10	1.339 (5)
C7—C6	1.405 (5)	C11—H11	0.9300
O2$^{\rm i}$—Co1—N2$^{\rm ii}$	111.64 (11)	N5—N3—H3	124.4
O2$^{\rm i}$—Co1—N4	100.15 (11)	C10—N3—H3	124.4
O4—Co1—O2$^{\rm i}$	107.41 (11)	C10—N3—N5	111.1 (3)
O4—Co1—N2$^{\rm ii}$	105.49 (11)	O2—C1—C2	119.0 (3)
O4—Co1—N4	128.46 (11)	O1—C1—O2	122.3 (3)
N4—Co1—N2$^{\rm ii}$	103.38 (11)	O1—C1—C2	118.6 (3)
C1—O2—Co1$^{\rm iii}$	130.8 (2)	C2—C3—C4	122.0 (3)
C4—O4—Co1	123.3 (2)	C5—C3—C4	118.4 (3)
C6—N2—Co1$^{\rm ii}$	129.5 (2)	C5—C3—C2	119.6 (3)
C9—N2—Co1$^{\rm ii}$	124.0 (2)	N2—C9—N1	113.5 (3)

C9—N2—C6	104.9 (3)	N2—C9—H9	123.2
C7—N1—H1	126.4	N1—C9—H9	123.2
C9—N1—H1	126.4	C8—C2—C1	115.8 (3)
C9—N1—C7	107.3 (3)	C8—C2—C3	121.5 (3)
C10—N4—Co1	129.0 (3)	C3—C2—C1	122.6 (3)
C10—N4—C11	103.3 (3)	C6—C5—C3	119.4 (3)
C11—N4—Co1	127.6 (3)	C6—C5—H5	120.3
O4—C4—C3	115.0 (3)	C3—C5—H5	120.3
O3—C4—O4	123.5 (3)	C11—N5—N3	102.1 (3)
O3—C4—C3	121.4 (3)	H6A—N6—H6B	120.0
N1—C7—C6	105.3 (3)	C10—N6—H6A	120.0
N1—C7—C8	132.6 (3)	C10—N6—H6B	120.0
C8—C7—C6	122.1 (3)	N3—C10—N4	108.5 (3)
N2—C6—C7	109.0 (3)	N3—C10—N6	124.8 (4)
C5—C6—N2	131.2 (3)	N6—C10—N4	126.7 (3)
C5—C6—C7	119.8 (3)	N4—C11—H11	122.5
C7—C8—H8	121.2	N5—C11—N4	115.1 (4)
C2—C8—C7	117.5 (3)	N5—C11—H11	122.5
C2—C8—H8	121.2		

Co1—O4—C4—O3	13.1 (5)	C7—C8—C2—C1	−175.4 (3)
Co1—O4—C4—C3	−168.4 (2)	C5—C3—C2—C8	−0.6 (5)
C9—N1—C7—C8	178.0 (4)	C4—C3—C2—C8	177.4 (3)
C9—N1—C7—C6	−0.2 (4)	C5—C3—C2—C1	175.7 (3)
C9—N2—C6—C5	−179.1 (4)	C4—C3—C2—C1	−6.3 (5)
Co1^{ii}—N2—C6—C5	−13.5 (5)	O1—C1—C2—C8	98.3 (4)
C9—N2—C6—C7	−0.3 (4)	O2—C1—C2—C8	−77.6 (4)
Co1^{ii}—N2—C6—C7	165.4 (2)	O1—C1—C2—C3	−78.3 (4)
N1—C7—C6—C5	179.3 (3)	O2—C1—C2—C3	105.8 (4)
C8—C7—C6—C5	0.8 (5)	N2—C6—C5—C3	178.5 (3)
N1—C7—C6—N2	0.3 (4)	C7—C6—C5—C3	−0.2 (5)
C8—C7—C6—N2	−178.2 (3)	C2—C3—C5—C6	0.1 (5)
N1—C7—C8—C2	−179.2 (3)	C4—C3—C5—C6	−177.9 (3)
C6—C7—C8—C2	−1.2 (5)	C10—N3—N5—C11	0.2 (4)
Co1^{iii}—O2—C1—O1	173.7 (2)	N5—N3—C10—N6	−179.1 (4)
Co1^{iii}—O2—C1—C2	−10.5 (4)	N5—N3—C10—N4	−0.3 (4)
O3—C4—C3—C5	174.7 (3)	C11—N4—C10—N3	0.3 (4)
O4—C4—C3—C5	−3.8 (5)	Co1—N4—C10—N3	176.1 (2)
O3—C4—C3—C2	−3.3 (5)	C11—N4—C10—N6	179.1 (4)
O4—C4—C3—C2	178.2 (3)	Co1—N4—C10—N6	−5.1 (6)
C6—N2—C9—N1	0.2 (4)	N3—N5—C11—N4	0.0 (5)
Co1^{ii}—N2—C9—N1	−166.5 (2)	C10—N4—C11—N5	−0.2 (5)
C7—N1—C9—N2	0.0 (4)	Co1—N4—C11—N5	−176.1 (3)
C7—C8—C2—C3	1.1 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{iv}	0.86	1.84	2.675 (4)	163
N3—H3···O1^{v}	0.86	2.48	3.104 (4)	130
N3—H3···O3^{v}	0.86	2.08	2.811 (4)	142
N6—H6*A*···O3^{v}	0.86	2.35	3.036 (5)	136
N6—H6*B*···O2^{i}	0.86	2.23	2.946 (5)	141
C5—H5···O4^{ii}	0.93	2.58	3.312 (4)	136
C5—H5···O4	0.93	2.37	2.698 (4)	100
C9—H9···N5^{vi}	0.93	2.48	3.332 (5)	152
C11—H11···O1^{vii}	0.93	2.41	3.215 (5)	145

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