metal-organic compounds

trans-Diaquabis[5-carboxy-2-(3-pyridyl)-1*H*-imidazole-4-carboxylato-$\kappa^2 N^3,O^4$]-cobalt(II)

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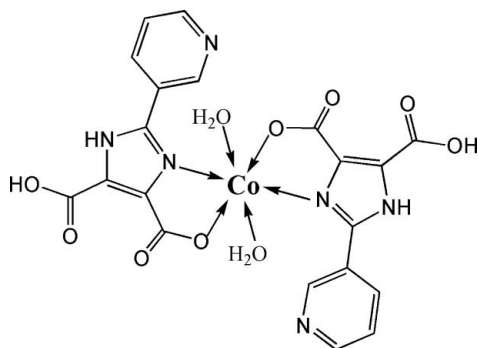Correspondence e-mail: zhanqg2001@yahoo.com.cn

In the title complex, $[Co(C_{10}H_6N_3O_4)_2(H_2O)_2]$, the Co^{II} atom is located on an inversion centre and displays a distorted octahedral coordination geometry defined by two *N,O*-bidentate ligands in the equatorial plane and two water molecules in the axial positions. The conformation is stabilized by intramolecular O—H···O hydrogen bonds. Intermolecular N—H···O hydrogen bonds link the molecules into chains, which are further connected by intermolecular O—H···O and O—H···N hydrogen-bonding interactions, forming a two-dimensional supramolecular network parallel to (110).

Related literature

For general background to the design and synthesis of coordination polymers based on 1*H*-imidazole-4,5-dicarboxylic acid, see: Gu *et al.* (2010); Wang *et al.* (2010). For related complexes with 5-carboxy-2-(3-pyridyl)-1*H*-imidazole-4-carboxylate, see: Chen (2008); Liu *et al.* (2009); Jing *et al.* (2010, 2011); Zhou *et al.* (2011).

Experimental

Crystal data

$[Co(C_{10}H_6N_3O_4)_2(H_2O)_2]$	γ = 67.755 (2)°
M_r = 559.32	V = 531.12 (12) Å³
Triclinic, $P\bar{1}$	Z = 1
a = 7.0240 (9) Å	Mo $K\alpha$ radiation
b = 8.8770 (12) Å	μ = 0.88 mm⁻¹
c = 9.3240 (12) Å	T = 298 K
α = 81.598 (2)°	0.32 × 0.28 × 0.26 mm
β = 83.290 (2)°	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	2936 measured reflections
	2052 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	1589 reflections with $I > 2\sigma(I)$
T_{min} = 0.765, T_{max} = 0.803	R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	170 parameters
$wR(F^2)$ = 0.104	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 0.30 e Å⁻³
2052 reflections	$\Delta\rho_{min}$ = −0.33 e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2ⁱ	0.82	1.65	2.465 (3)	176
N2—H2···O4ⁱ	0.86	2.00	2.840 (3)	166
O5—H5A···O3ⁱⁱ	0.85	2.07	2.918 (3)	173
O5—H5B···N3ⁱⁱⁱ	0.85	2.02	2.784 (3)	150

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, L.-Z. (2008). *Acta Cryst.* E**64**, m1286.
Gu, Z.-G., Cai, Y.-P., Fang, H.-C., Zhou, Z.-Y., Thallapally, P.-K., Tian, J., Liu, J. & Exarhos, G.-J. (2010). *Chem. Commun.* **46**, 5373–5375.
Jing, X.-M., Meng, H., Li, G.-H., Yu, Y., Huo, Q.-S., Eddaoudi, M. & Liu, Y.-L. (2010). *Cryst. Growth Des.* **10**, 3489–3495.
Jing, X.-M., Zhao, T.-T., Zheng, B., Peng, Y., Yan, Y., Huo, Q.-S. & Liu, Y.-L. (2011). *Inorg. Chem. Commun.* **14**, 22–25.
Liu, W., Zhang, G., Li, X., Wu, B.-L. & Zhang, H.-Y. (2009). *Acta Cryst.* E**65**, m938–m939.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, S., Zhao, T.-T., Li, G.-H., Wojtas, L., Huo, Q.-S., Eddaoudi, M. & Liu, Y.-L. (2010). *J. Am. Chem. Soc.* **132**, 18038–18041.
Zhou, R.-S., Song, J.-F., Li, Y.-B., Xu, C.-Y. & Yang, X.-F. (2011). *Z. Anorg. Allg. Chem.* **637**, 251–256.

supporting information

trans-Diaquabis[5-carboxy-2-(3-pyridyl)-1*H*-imidazole-4-carboxylato-κ^2N^3,O^4]cobalt(II)

Qing-Guang Zhan

S1. Comment

In recent years, the design and synthesis of novel metal-organic coordination polymers based on *N*-heterocyclic carboxylic acids have provoked much attention owing to their structure diversity and their potential applications as functional materials. Particular attention has been paid to the 1H-imidazole-4,5-dicarboxylic acid (H_3IDC) ligand, because it can coordinate with metal ions in diverse coordination fashions to produce a series of complexes with different structures and interesting properties (Gu *et al.*, 2010; Wang *et al.*, 2010). In this work, a very close analogue ligand of H_3IDC, 5-carboxy-2-(3-pyridyl)-1H-imidazole-4-carboxylate (H_3PyIDC), has been chosen to prepare new coordination polymers. Up to now, only two 0D clusters (Chen, 2008; Liu *et al.*, 2009), one 1D chain (Jing *et al.*, 2011), one 2D layer (Zhou *et al.*, 2011), and one 3D network (Jing *et al.*, 2010) constructed by the H_3PyIDC ligand have been reported. For example, Chen (2008) and Liu *et al.* (2009) have described the structures of the mononuclear complexes [Mn(H₂PyIDC)₂(H₂O)₂] and [Fe(H₂PyIDC)₂(H₂O)₂], in which both the manganese(II) and iron(II) ions show octahedral coordinations with the H₂PyIDC ligands. A new complex [Co(H₂PyIDC)₂(H₂O)₂], (I), which is isostructural with the manganese(II) and iron(II) analogues, is presented in this paper.

   As illustrated in Fig. 1, the molecule of (I) is a discrete neutral monomer, with an asymmetric unit that contains one-half of the [Co(H₂PyIDC)₂(H₂O)₂] formula unit. The Co atom lies on an inversion center and is six-coordinated with two nitrogen and two oxygen atoms from two chelating H₂PIDC ligands in the equatorial plane, and two coordinated water molecules in axial positions, forming a slightly distorted octahedral geometry. The Co–N (2.215 (2) Å) and Co–O nond distances (2.061 (2)–2.098 (2)Å) are similar to the M–O and M–N bond lengths (M = Mn, Fe) observed in the corresponding isotypic structures. The conformation of the complex is stabilized by intramolecular O—H···O hydrogen bonds. In the crystal structure, intermolecular N–H···O hydrogen bonds (Table 1) link the molecules into one-dimensional chains as shown in Fig. 2. The chains are further connected by two types of hydrogen bonds O–H···O and O–H···N involving the coordinated water molecule, the carboxylate group and the uncoordinated pyridine N atoms, resulting in a two-dimensional supramolecular network (Fig. 3).

S2. Experimental

A mixture of CoCl₂.6H₂O (47.6 mg, 0.2 mmol), H₃PyIDC (46.6 mg, 0.2 mmol), 8 ml H₂O, and 0.1 mL Et₃N was sealed in a 15 mL Teflon-lined stainless steel autoclave, heated at 443 K for 72 h, and then slowly cooled to room temperature at a rate of 5 K h⁻¹. Brown block-shaped crystals of (I) were obtained with a yield of 28% after washing with distilled water and drying in air.

S3. Refinement

Water H atoms were located in a difference Fourier map and refined with distance restraints of O—H = 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(O). Other H atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic), O—H = 0.82 Å and N—H = 0.86 Å with U_{iso}(H) = 1.2 U_{eq}(C, N) or U_{iso}(H) = 1.5 U_{eq}(O).
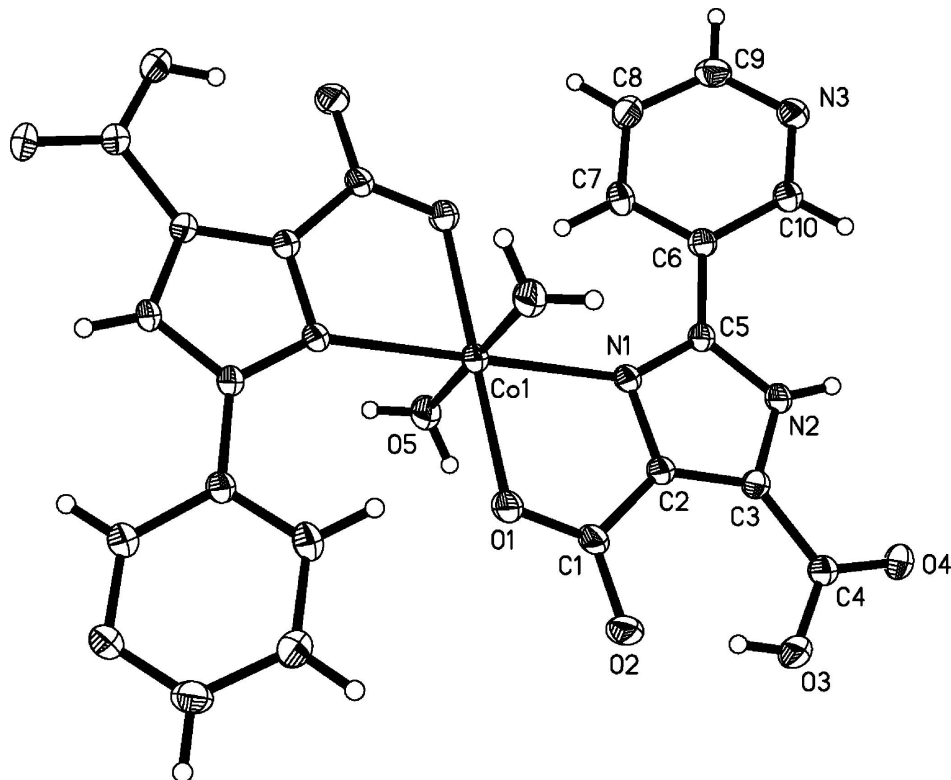

Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. Unlabelled atoms are related to the labelled atoms by the symmetry operation 2-x, -y, 1-z.
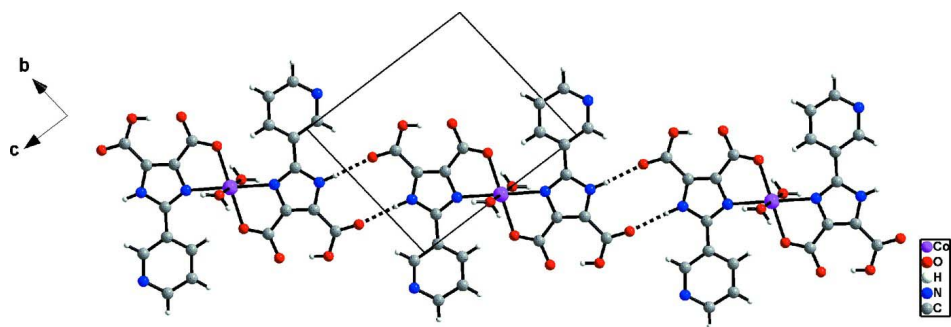

Figure 2

Crystal packing of the title compound viewed down the *a* axis, showing the one-dimensional chain structure. Hydrogen bonds are shown as dashed lines.
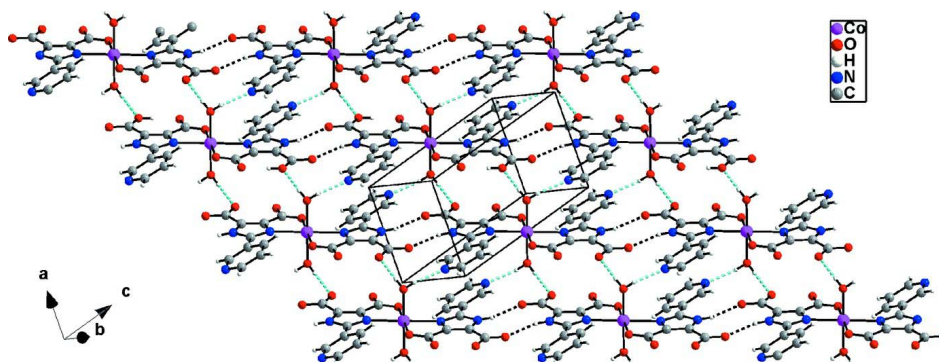
Figure 3

Crystal packing of the title compound showing the two-dimensional hydrogen-bonding network (dashed lines).

***trans*-Diaquabis[5-carboxy-2-(3-pyridyl)-1*H*-imidazole-4- carboxylato-κ^2N^3,O^4]cobalt(II)**

Crystal data

[Co(C$_{10}$H$_6$N$_3$O$_4$)$_2$(H$_2$O)$_2$]	$Z = 1$
$M_r = 559.32$	$F(000) = 285$
Triclinic, $P\bar{1}$	$D_x = 1.749$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.0240$ (9) Å	Cell parameters from 860 reflections
$b = 8.8770$ (12) Å	$\theta = 2.2$–24.9°
$c = 9.3240$ (12) Å	$\mu = 0.88$ mm^{-1}
$\alpha = 81.598$ (2)°	$T = 298$ K
$\beta = 83.290$ (2)°	Block, brown
$\gamma = 67.755$ (2)°	0.32 × 0.28 × 0.26 mm
$V = 531.12$ (12) Å^3	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	2936 measured reflections
Radiation source: fine-focus sealed tube	2052 independent reflections
Graphite monochromator	1589 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.2°$
	$h = -8 \rightarrow 8$
$T_{min} = 0.765$, $T_{max} = 0.803$	$k = -10 \rightarrow 6$
	$l = -10 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.3865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
2052 reflections	
170 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.33$ 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Co1	1.0000	0.0000	0.5000	0.0352 (2)
O3	0.5734 (4)	0.6730 (3)	0.6242 (2)	0.0470 (6)
H3	0.6370	0.6154	0.5601	0.071*
N2	0.6548 (4)	0.2945 (3)	0.8556 (2)	0.0313 (6)
H2	0.5996	0.3198	0.9404	0.038*
O1	0.9299 (4)	0.2412 (3)	0.4017 (2)	0.0432 (6)
N1	0.8176 (4)	0.1439 (3)	0.6778 (2)	0.0310 (6)
O2	0.7771 (4)	0.5056 (3)	0.4308 (2)	0.0463 (6)
O4	0.4586 (4)	0.6330 (3)	0.8526 (2)	0.0511 (7)
C3	0.6630 (5)	0.4031 (4)	0.7370 (3)	0.0309 (7)
C5	0.7482 (5)	0.1401 (4)	0.8172 (3)	0.0295 (7)
O5	0.7336 (3)	−0.0027 (3)	0.4303 (2)	0.0456 (6)
H5A	0.6363	0.0901	0.4178	0.055*
H5B	0.7239	−0.0620	0.3698	0.055*
C4	0.5565 (5)	0.5820 (4)	0.7409 (3)	0.0359 (8)
N3	0.7778 (4)	−0.1290 (3)	1.1669 (3)	0.0395 (7)
C1	0.8292 (5)	0.3538 (4)	0.4769 (3)	0.0358 (8)
C10	0.7591 (5)	−0.0006 (4)	1.0681 (3)	0.0357 (7)
H10	0.7395	0.0988	1.1006	0.043*
C2	0.7669 (5)	0.3071 (4)	0.6286 (3)	0.0307 (7)
C6	0.7672 (5)	−0.0064 (4)	0.9188 (3)	0.0302 (7)
C9	0.8085 (5)	−0.2721 (4)	1.1191 (3)	0.0408 (8)
H9	0.8238	−0.3634	1.1865	0.049*
C8	0.8181 (5)	−0.2887 (4)	0.9732 (3)	0.0413 (8)
H8	0.8411	−0.3901	0.9436	0.050*
C7	0.7934 (5)	−0.1542 (4)	0.8716 (3)	0.0381 (8)
H7	0.7943	−0.1628	0.7732	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0425 (4)	0.0304 (4)	0.0199 (3)	0.0005 (3)	0.0020 (2)	−0.0042 (2)
O3	0.0634 (17)	0.0283 (12)	0.0362 (13)	−0.0031 (12)	0.0034 (12)	−0.0062 (10)
N2	0.0357 (15)	0.0312 (14)	0.0193 (12)	−0.0042 (12)	0.0043 (10)	−0.0056 (10)
O1	0.0519 (15)	0.0365 (13)	0.0219 (11)	0.0020 (11)	0.0086 (10)	−0.0030 (10)
N1	0.0381 (15)	0.0277 (13)	0.0184 (12)	−0.0038 (12)	0.0022 (10)	−0.0016 (10)

O2	0.0629 (16)	0.0325 (13)	0.0277 (12)	−0.0056 (12)	0.0065 (11)	0.0050 (10)
O4	0.0706 (18)	0.0352 (13)	0.0320 (13)	0.0002 (12)	0.0022 (12)	−0.0142 (10)
C3	0.0337 (17)	0.0270 (16)	0.0239 (15)	−0.0026 (13)	0.0012 (12)	−0.0043 (12)
C5	0.0319 (17)	0.0280 (16)	0.0217 (14)	−0.0035 (13)	0.0014 (12)	−0.0047 (12)
O5	0.0465 (14)	0.0443 (14)	0.0339 (12)	−0.0005 (11)	−0.0039 (10)	−0.0109 (10)
C4	0.0436 (19)	0.0300 (17)	0.0261 (16)	−0.0045 (15)	−0.0011 (14)	−0.0043 (14)
N3	0.0473 (17)	0.0373 (16)	0.0261 (13)	−0.0089 (13)	0.0000 (12)	0.0001 (12)
C1	0.0409 (19)	0.0346 (18)	0.0198 (15)	−0.0019 (15)	0.0016 (13)	−0.0014 (13)
C10	0.0412 (19)	0.0343 (18)	0.0261 (15)	−0.0083 (15)	0.0008 (13)	−0.0044 (13)
C2	0.0357 (18)	0.0269 (16)	0.0217 (14)	−0.0036 (14)	0.0010 (12)	−0.0026 (12)
C6	0.0311 (17)	0.0298 (16)	0.0227 (14)	−0.0055 (13)	0.0047 (12)	−0.0025 (12)
C9	0.043 (2)	0.0353 (18)	0.0373 (18)	−0.0102 (16)	−0.0024 (15)	0.0064 (15)
C8	0.050 (2)	0.0316 (18)	0.0390 (19)	−0.0113 (16)	0.0023 (15)	−0.0070 (15)
C7	0.044 (2)	0.0421 (19)	0.0241 (15)	−0.0118 (16)	0.0048 (14)	−0.0074 (14)

Geometric parameters (Å, º)

Co1—O5ⁱ	2.061 (2)	C3—C2	1.374 (4)
Co1—O5	2.061 (2)	C3—C4	1.481 (4)
Co1—O1	2.098 (2)	C5—C6	1.465 (4)
Co1—O1ⁱ	2.098 (2)	O5—H5A	0.8500
Co1—N1	2.215 (2)	O5—H5B	0.8499
Co1—N1ⁱ	2.215 (2)	N3—C10	1.332 (4)
O3—C4	1.279 (4)	N3—C9	1.339 (4)
O3—H3	0.8200	C1—C2	1.479 (4)
N2—C5	1.358 (4)	C10—C6	1.394 (4)
N2—C3	1.368 (4)	C10—H10	0.9300
N2—H2	0.8600	C6—C7	1.384 (4)
O1—C1	1.243 (4)	C9—C8	1.381 (4)
N1—C5	1.334 (3)	C9—H9	0.9300
N1—C2	1.374 (4)	C8—C7	1.380 (4)
O2—C1	1.276 (4)	C8—H8	0.9300
O4—C4	1.223 (4)	C7—H7	0.9300
O5ⁱ—Co1—O5	180.0	Co1—O5—H5A	115.6
O5ⁱ—Co1—O1	89.88 (10)	Co1—O5—H5B	127.2
O5—Co1—O1	90.12 (10)	H5A—O5—H5B	107.7
O5ⁱ—Co1—O1ⁱ	90.12 (10)	O4—C4—O3	124.5 (3)
O5—Co1—O1ⁱ	89.88 (10)	O4—C4—C3	119.0 (3)
O1—Co1—O1ⁱ	180.0	O3—C4—C3	116.5 (3)
O5ⁱ—Co1—N1	90.05 (9)	C10—N3—C9	117.7 (3)
O5—Co1—N1	89.95 (9)	O1—C1—O2	124.0 (3)
O1—Co1—N1	78.08 (8)	O1—C1—C2	117.3 (3)
O1ⁱ—Co1—N1	101.92 (8)	O2—C1—C2	118.7 (3)
O5ⁱ—Co1—N1ⁱ	89.95 (9)	N3—C10—C6	123.8 (3)
O5—Co1—N1ⁱ	90.05 (9)	N3—C10—H10	118.1
O1—Co1—N1ⁱ	101.92 (8)	C6—C10—H10	118.1
O1ⁱ—Co1—N1ⁱ	78.08 (8)	N1—C2—C3	110.8 (2)

N1—Co1—N1^i	180.00 (7)	N1—C2—C1	119.0 (3)
C4—O3—H3	109.5	C3—C2—C1	130.2 (3)
C5—N2—C3	108.6 (2)	C7—C6—C10	117.7 (3)
C5—N2—H2	125.7	C7—C6—C5	121.9 (3)
C3—N2—H2	125.7	C10—C6—C5	120.4 (3)
C1—O1—Co1	117.58 (19)	N3—C9—C8	122.3 (3)
C5—N1—C2	105.3 (2)	N3—C9—H9	118.9
C5—N1—Co1	146.4 (2)	C8—C9—H9	118.9
C2—N1—Co1	107.94 (17)	C7—C8—C9	119.7 (3)
N2—C3—C2	104.8 (3)	C7—C8—H8	120.1
N2—C3—C4	121.4 (3)	C9—C8—H8	120.1
C2—C3—C4	133.6 (3)	C8—C7—C6	118.7 (3)
N1—C5—N2	110.5 (2)	C8—C7—H7	120.6
N1—C5—C6	126.5 (3)	C6—C7—H7	120.6
N2—C5—C6	123.0 (2)		
O5^i—Co1—O1—C1	−88.7 (3)	Co1—O1—C1—C2	−0.4 (4)
O5—Co1—O1—C1	91.3 (3)	C9—N3—C10—C6	0.8 (5)
N1—Co1—O1—C1	1.4 (2)	C5—N1—C2—C3	−1.2 (4)
N1^i—Co1—O1—C1	−178.6 (2)	Co1—N1—C2—C3	−176.6 (2)
O5^i—Co1—N1—C5	−84.2 (4)	C5—N1—C2—C1	178.0 (3)
O5—Co1—N1—C5	95.8 (4)	Co1—N1—C2—C1	2.6 (3)
O1—Co1—N1—C5	−174.0 (4)	N2—C3—C2—N1	1.3 (4)
O1^i—Co1—N1—C5	6.0 (4)	C4—C3—C2—N1	−172.9 (3)
O5^i—Co1—N1—C2	87.8 (2)	N2—C3—C2—C1	−177.8 (3)
O5—Co1—N1—C2	−92.2 (2)	C4—C3—C2—C1	8.0 (6)
O1—Co1—N1—C2	−2.0 (2)	O1—C1—C2—N1	−1.7 (5)
O1^i—Co1—N1—C2	178.0 (2)	O2—C1—C2—N1	178.3 (3)
C5—N2—C3—C2	−0.9 (3)	O1—C1—C2—C3	177.3 (3)
C5—N2—C3—C4	174.2 (3)	O2—C1—C2—C3	−2.7 (6)
C2—N1—C5—N2	0.6 (4)	N3—C10—C6—C7	0.9 (5)
Co1—N1—C5—N2	172.7 (3)	N3—C10—C6—C5	−179.1 (3)
C2—N1—C5—C6	−179.1 (3)	N1—C5—C6—C7	−23.7 (5)
Co1—N1—C5—C6	−7.0 (6)	N2—C5—C6—C7	156.7 (3)
C3—N2—C5—N1	0.2 (4)	N1—C5—C6—C10	156.4 (3)
C3—N2—C5—C6	179.9 (3)	N2—C5—C6—C10	−23.3 (5)
N2—C3—C4—O4	−0.4 (5)	C10—N3—C9—C8	−0.9 (5)
C2—C3—C4—O4	173.0 (4)	N3—C9—C8—C7	−0.7 (5)
N2—C3—C4—O3	−179.9 (3)	C9—C8—C7—C6	2.4 (5)
C2—C3—C4—O3	−6.5 (6)	C10—C6—C7—C8	−2.5 (5)
Co1—O1—C1—O2	179.7 (3)	C5—C6—C7—C8	177.6 (3)

Symmetry code: (i) −x+2, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯O2	0.82	1.65	2.465 (3)	176

N2—H2···O4[ii]	0.86	2.00	2.840 (3)	166
O5—H5*A*···O3[iii]	0.85	2.07	2.918 (3)	173
O5—H5*B*···N3[iv]	0.85	2.02	2.784 (3)	150

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