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Diaquabis(5-carboxy-1*H*-pyrazole-3-carboxylato- κ^2N^2,O^3)cobalt(II) dihydrate

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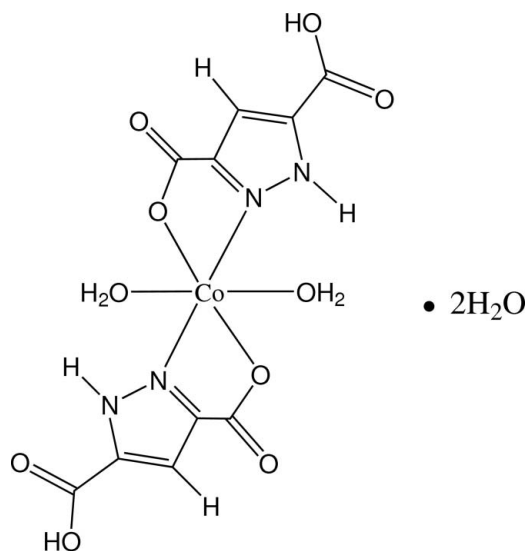
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(C-C) = 0.006$ Å; R factor = 0.048; wR factor = 0.142; data-to-parameter ratio = 11.6.

In the title complex, $[Co(C_5H_3N_2O_4)_2(H_2O)_2] \cdot 2H_2O$, the Co^{II} ion lies on an inversion center and is coordinated in a distorted octahedral environment. In the crystal structure, complex and water molecules are linked into a three-dimensional network by $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds.

Related literature

For a mononuclear zinc(II) complex with a pyrazole-3,5-dicarboxylato ligand, see: Xie *et al.* (2006) and for a cobalt(III) complex with a 5-carboxy-1*H*-pyrazole-3-carboxylato ligand, see: Xie *et al.* (2007). The 3,5-pyrazoledicarboxylic acid ligand is asymmetric and has six potential coordination sites which can act to link together metal centers through a number of bridging modes, see: King *et al.* (2004). A variety of complexes containing this ligand have been reported, see: Frisch & Cahill (2005); King *et al.* (2003, 2004); Li *et al.* (2005); Pan, Ching *et al.* (2001); Pan, Frydel *et al.* (2001).



Experimental

Crystal data

$[Co(C_5H_3N_2O_4)_2(H_2O)_2] \cdot 2H_2O$
 $M_r = 441.18$
 Monoclinic, $P2_1/c$
 $a = 10.030$ (3) Å
 $b = 12.483$ (4) Å
 $c = 6.827$ (2) Å
 $\beta = 108.641$ (4)°

$V = 809.9$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.14$ mm⁻¹
 $T = 291$ K
 $0.32 \times 0.27 \times 0.14$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.713$, $T_{max} = 0.854$

5748 measured reflections
 1502 independent reflections
 1331 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.142$
 $S = 1.12$
 1502 reflections
 129 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.84$ e Å⁻³
 $\Delta\rho_{min} = -0.44$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1—O5	2.065 (3)	O1—C1	1.262 (5)
Co1—N1	2.108 (3)	O2—C1	1.256 (5)
Co1—O1	2.120 (3)		
O5 ⁱ —Co1—O5	180	N1—Co1—O1 ⁱ	103.22 (11)
O5—Co1—N1	90.84 (12)	O5—Co1—O1	88.82 (12)
O5—Co1—N1 ⁱ	89.16 (12)	N1—Co1—O1	76.78 (11)
N1—Co1—N1 ⁱ	180	O1 ⁱ —Co1—O1	180
O5—Co1—O1 ⁱ	91.18 (12)		

 Symmetry code: (i) $-x + 1, -y + 2, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4 ⁱⁱ ···O2 ⁱⁱ	0.82	1.73	2.535 (4)	169
O5—H1W ⁱⁱⁱ ···O3 ⁱⁱⁱ	0.83	2.07	2.887 (4)	171
O5—H2W ^{iv} ···O2 ^{iv}	0.83	1.91	2.726 (4)	171
O6—H4W ^v ···O1 ^v	0.85 (11)	2.06 (11)	2.828 (5)	149 (10)
O6—H3W ^{vi} ···O3 ^{vi}	0.84	2.30	2.932 (5)	132
N2—H2 ^{vii} ···O6 ^{vii}	0.86	1.91	2.714 (5)	155

Symmetry codes: (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z$; (vi) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x, y + 1, z$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2869).

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supporting information

Acta Cryst. (2009). E65, m1009–m1010 [doi:10.1107/S1600536809029456]

Diaquabis(5-carboxy-1*H*-pyrazole-3-carboxylato- κ^2N^2,O^3)cobalt(II) dihydrate**Hui-Dong Xie, Li Jin and Cheng-Zhi Xie****S1. Comment**

In the past few decades, self-assembly processes involving metal ions and organic ligands directed by either metal coordination or hydrogen bonds have received a great deal of attention in the field of supramolecular chemistry and crystal engineering. The 3,5-pyrazoledicarboxylic acid ligand is asymmetric and has six potential coordination sites which can act to link together metal centers through a number of bridging modes (King *et al.*, 2004). A variety of complexes containing this ligand have been reported (Frisch *et al.*, 2005; King *et al.*, 2003, 2004; Pan, Ching *et al.*, 2001; Pan, Frydel *et al.*, 2001; Li *et al.*, 2005).

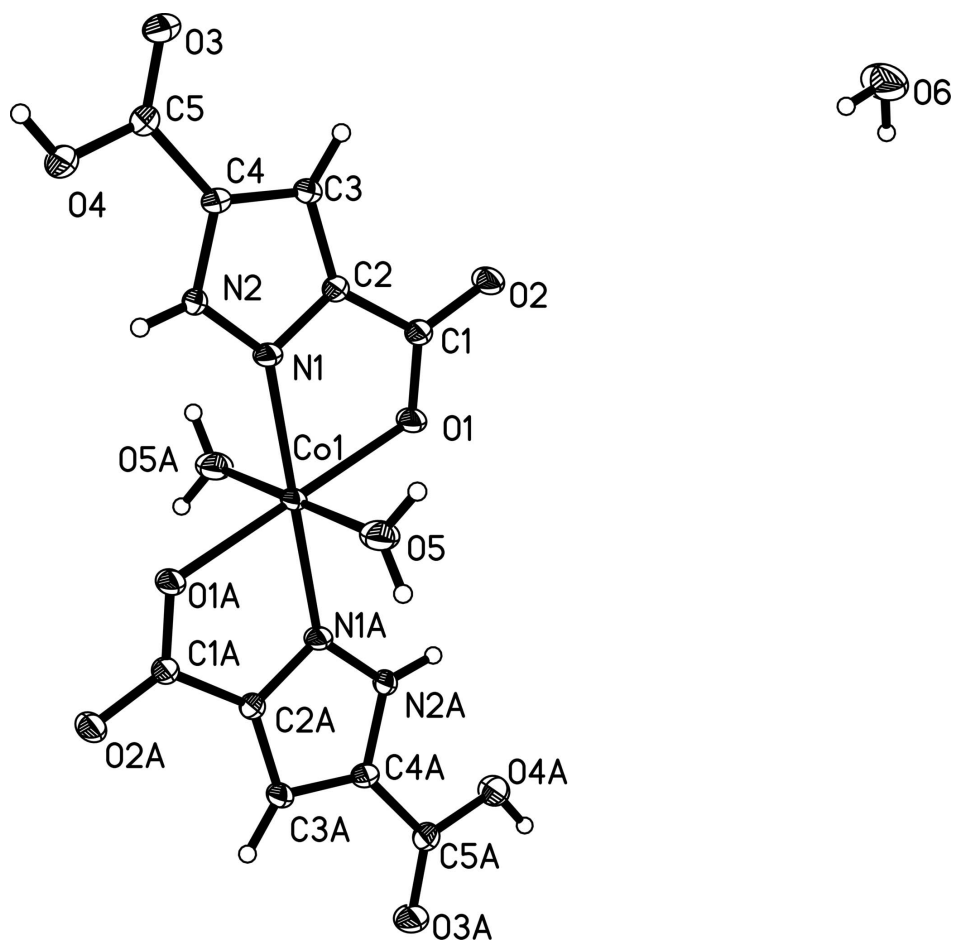
The molecular structure of the title complex, (I), is shown in Fig. 1. The Co^{II} ion is located on an inversion center and is coordinated in a distorted octahedral environment. The axial sites are occupied by water molecules and the equatorial plane is formed by two oxygen donors and two nitrogen donors from two chelating 5-carboxy-pyrazole-3-carboxylato ligands. In the crystal structure complex and water molecules are linked into a three-dimensional network by O-H \cdots O and N-H \cdots O hydrogen bonds.

S2. Experimental

A mixture of cobalt(II) nitrate (hexhydrate) (0.2 mmol, 58 mg), 3,5-pyrazoledicarboxylic acid (0.4 mmol, 62 mg) and H₂O (18.0 ml) in a 1:2:5000 molar ratio was sealed in a 25 ml stainless steel reactor with a Teflon liner. The autoclave was kept at 423 K for 3 d, then cooled to room temperature at a rate of 4 K/h. Orange block-shaped crystals of the title complex were collected by filtration for the structural analysis.

S3. Refinement

All H atoms bonded to C and N atoms were initially located in difference Fourier maps but were subsequently refined in a riding-model approximation with C—H = 0.93 Å, N—H = 0.86 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$. The O atoms bonded to the carboxylic group and the coordinated water atom were included in calculated positions and refined in a riding-model approximation with O—H = 0.82–0.83 Å and $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{O})$. One of the solvent water H atoms was included with O—H = 0.84; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ and the other H atom was refined isotropically.

**Figure 1**

The molecular structure of (I), with atom labels and 35% probability displacement ellipsoids for non-H atoms [symmetry code: (A) $-x+1, -y+2, -z$]. Only the unique solvent water molecule is shown.

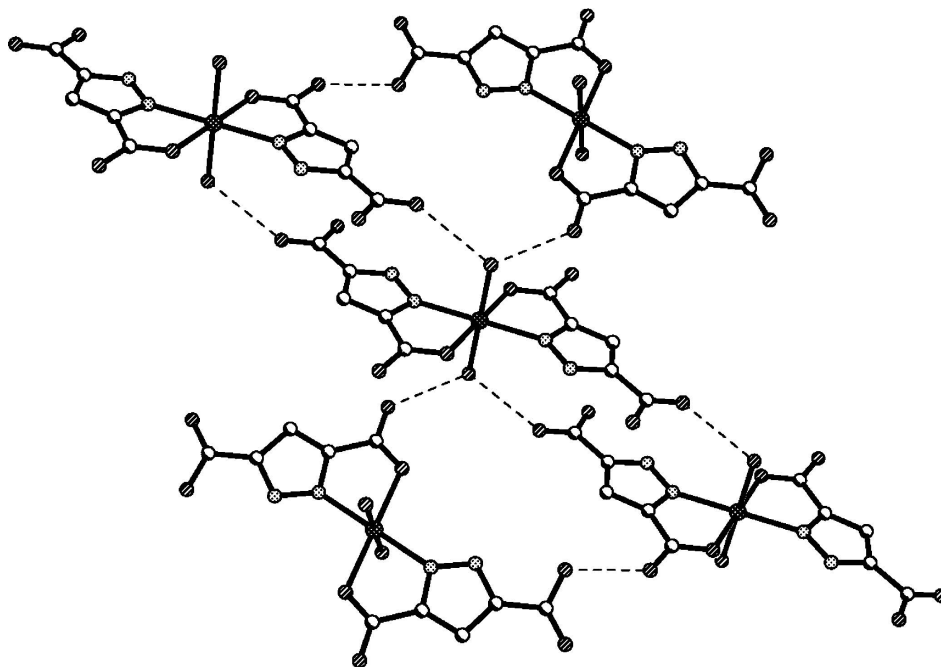


Figure 2

Part of the crystal structure of (I) showing the donor-acceptor distances of hydrogen bonds as dashed lines. H atoms have been omitted for clarity.

Diaquabis(5-carboxy-1*H*-pyrazole-3-carboxylato- κ^2N^2,O^3)cobalt(II) dihydrate

Crystal data

[Co(C₅H₃N₂O₄)₂(H₂O)₂] \cdot 2H₂O

$M_r = 441.18$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.030$ (3) Å

$b = 12.483$ (4) Å

$c = 6.827$ (2) Å

$\beta = 108.641$ (4)°

$V = 809.9$ (5) Å³

$Z = 2$

$F(000) = 450$

$D_x = 1.809$ Mg m⁻³

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

Cell parameters from 2747 reflections

$\theta = 2.7$ – 27.9°

$\mu = 1.14$ mm⁻¹

$T = 291$ K

Block, orange

$0.32 \times 0.27 \times 0.14$ mm

Data collection

Bruker SMART CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.713$, $T_{\max} = 0.854$

5748 measured reflections

1502 independent reflections

1331 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -12 \rightarrow 12$

$k = -15 \rightarrow 15$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.142$
 $S = 1.12$
 1502 reflections
 129 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 1.4115P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.84 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.44 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.5000	1.0000	0.0000	0.0227 (3)
O1	0.5183 (3)	0.8358 (2)	-0.0667 (5)	0.0308 (6)
O2	0.6657 (3)	0.6977 (2)	-0.0142 (5)	0.0337 (7)
O3	1.1998 (3)	0.9569 (3)	0.3134 (5)	0.0408 (8)
O4	1.0960 (3)	1.1105 (2)	0.3529 (5)	0.0366 (7)
H4	1.1772	1.1324	0.3977	0.055*
O5	0.4797 (3)	0.9554 (3)	0.2803 (5)	0.0378 (7)
H1W	0.4031	0.9594	0.3020	0.045*
H2W	0.5296	0.9069	0.3484	0.045*
O6	0.7621 (4)	0.2301 (3)	0.2670 (8)	0.0684 (13)
H3W	0.7617	0.2926	0.3116	0.082*
N1	0.7187 (3)	0.9727 (3)	0.1137 (5)	0.0238 (7)
N2	0.8371 (3)	1.0290 (2)	0.1925 (5)	0.0237 (7)
H2	0.8402	1.0958	0.2251	0.028*
C1	0.6402 (4)	0.7957 (3)	-0.0049 (6)	0.0239 (8)
C2	0.7586 (4)	0.8723 (3)	0.0850 (6)	0.0232 (7)
C3	0.9054 (4)	0.8646 (3)	0.1462 (6)	0.0255 (8)
H3	0.9595	0.8047	0.1422	0.031*
C4	0.9519 (4)	0.9668 (3)	0.2143 (6)	0.0246 (8)
C5	1.0964 (4)	1.0103 (3)	0.2981 (6)	0.0264 (8)
H4W	0.678 (12)	0.232 (9)	0.182 (18)	0.19 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0135 (4)	0.0169 (4)	0.0356 (4)	0.0024 (2)	0.0049 (3)	0.0001 (3)
O1	0.0156 (13)	0.0203 (13)	0.0522 (17)	0.0011 (10)	0.0046 (11)	-0.0035 (12)
O2	0.0203 (14)	0.0210 (14)	0.0535 (18)	0.0006 (10)	0.0031 (12)	-0.0062 (12)
O3	0.0198 (15)	0.0342 (16)	0.066 (2)	0.0006 (12)	0.0106 (14)	-0.0041 (15)
O4	0.0207 (14)	0.0269 (15)	0.0568 (19)	-0.0042 (11)	0.0048 (13)	-0.0063 (13)
O5	0.0292 (16)	0.0418 (17)	0.0443 (16)	0.0129 (13)	0.0143 (13)	0.0130 (14)
O6	0.041 (2)	0.0318 (19)	0.124 (4)	0.0026 (15)	0.014 (2)	-0.010 (2)
N1	0.0136 (15)	0.0210 (15)	0.0344 (17)	0.0010 (12)	0.0041 (12)	-0.0024 (12)
N2	0.0159 (15)	0.0154 (14)	0.0379 (17)	-0.0022 (12)	0.0059 (13)	-0.0025 (13)
C1	0.0170 (17)	0.0197 (18)	0.0327 (19)	-0.0005 (14)	0.0047 (15)	-0.0014 (14)
C2	0.0167 (17)	0.0185 (17)	0.0329 (19)	-0.0012 (14)	0.0056 (15)	-0.0014 (14)
C3	0.0171 (17)	0.0183 (18)	0.039 (2)	0.0018 (13)	0.0066 (15)	-0.0005 (15)
C4	0.0154 (17)	0.0236 (18)	0.0336 (19)	0.0010 (14)	0.0064 (14)	0.0008 (15)
C5	0.0205 (19)	0.0238 (19)	0.033 (2)	-0.0021 (14)	0.0065 (16)	0.0010 (15)

Geometric parameters (\AA , $^\circ$)

Co1—O5 ⁱ	2.065 (3)	O5—H2W	0.8277
Co1—O5	2.065 (3)	O6—H3W	0.8380
Co1—N1	2.108 (3)	O6—H4W	0.85 (11)
Co1—N1 ⁱ	2.108 (3)	N1—N2	1.336 (4)
Co1—O1 ⁱ	2.120 (3)	N1—C2	1.349 (5)
Co1—O1	2.120 (3)	N2—C4	1.358 (5)
O1—C1	1.262 (5)	N2—H2	0.8600
O2—C1	1.256 (5)	C1—C2	1.495 (5)
O3—C5	1.209 (5)	C2—C3	1.400 (5)
O4—C5	1.306 (5)	C3—C4	1.386 (5)
O4—H4	0.8200	C3—H3	0.9300
O5—H1W	0.8288	C4—C5	1.481 (5)
O5 ⁱ —Co1—O5	180	N2—N1—C2	106.3 (3)
O5 ⁱ —Co1—N1	89.16 (12)	N2—N1—Co1	138.6 (3)
O5—Co1—N1	90.84 (12)	C2—N1—Co1	114.8 (2)
O5 ⁱ —Co1—N1 ⁱ	90.84 (12)	N1—N2—C4	110.9 (3)
O5—Co1—N1 ⁱ	89.16 (12)	N1—N2—H2	124.6
N1—Co1—N1 ⁱ	180	C4—N2—H2	124.6
O5 ⁱ —Co1—O1 ⁱ	88.82 (12)	O2—C1—O1	124.1 (3)
O5—Co1—O1 ⁱ	91.18 (12)	O2—C1—C2	119.7 (3)
N1—Co1—O1 ⁱ	103.22 (11)	O1—C1—C2	116.2 (3)
N1 ⁱ —Co1—O1 ⁱ	76.78 (11)	N1—C2—C3	110.7 (3)
O5 ⁱ —Co1—O1	91.18 (12)	N1—C2—C1	114.8 (3)
O5—Co1—O1	88.82 (12)	C3—C2—C1	134.5 (3)
N1—Co1—O1	76.78 (11)	C4—C3—C2	104.3 (3)
N1 ⁱ —Co1—O1	103.22 (11)	C4—C3—H3	127.9
O1 ⁱ —Co1—O1	180	C2—C3—H3	127.9

C1—O1—Co1	116.9 (2)	N2—C4—C3	107.9 (3)
C5—O4—H4	109.5	N2—C4—C5	121.6 (3)
Co1—O5—H1W	121.4	C3—C4—C5	130.6 (3)
Co1—O5—H2W	119.8	O3—C5—O4	125.8 (4)
H1W—O5—H2W	111.9	O3—C5—C4	122.5 (3)
H3W—O6—H4W	95.7	O4—C5—C4	111.7 (3)
O5 ⁱ —Co1—O1—C1	92.3 (3)	Co1—N1—C2—C3	174.1 (3)
O5—Co1—O1—C1	-87.7 (3)	N2—N1—C2—C1	-179.5 (3)
N1—Co1—O1—C1	3.4 (3)	Co1—N1—C2—C1	-5.3 (4)
N1 ⁱ —Co1—O1—C1	-176.6 (3)	O2—C1—C2—N1	-171.3 (4)
O5 ⁱ —Co1—N1—N2	81.6 (4)	O1—C1—C2—N1	8.3 (5)
O5—Co1—N1—N2	-98.4 (4)	O2—C1—C2—C3	9.5 (7)
O1 ⁱ —Co1—N1—N2	-6.9 (4)	O1—C1—C2—C3	-170.8 (4)
O1—Co1—N1—N2	173.1 (4)	N1—C2—C3—C4	0.1 (4)
O5 ⁱ —Co1—N1—C2	-90.0 (3)	C1—C2—C3—C4	179.3 (4)
O5—Co1—N1—C2	90.0 (3)	N1—N2—C4—C3	-0.1 (4)
O1 ⁱ —Co1—N1—C2	-178.6 (3)	N1—N2—C4—C5	179.8 (3)
O1—Co1—N1—C2	1.4 (3)	C2—C3—C4—N2	0.0 (4)
C2—N1—N2—C4	0.2 (4)	C2—C3—C4—C5	-179.9 (4)
Co1—N1—N2—C4	-171.9 (3)	N2—C4—C5—O3	-178.0 (4)
Co1—O1—C1—O2	172.5 (3)	C3—C4—C5—O3	1.9 (7)
Co1—O1—C1—C2	-7.2 (4)	N2—C4—C5—O4	2.7 (5)
N2—N1—C2—C3	-0.2 (4)	C3—C4—C5—O4	-177.4 (4)

Symmetry code: (i) $-x+1, -y+2, -z$.

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H4 \cdots O2 ⁱⁱ	0.82	1.73	2.535 (4)	169
O5—H1W \cdots O3 ⁱⁱⁱ	0.83	2.07	2.887 (4)	171
O5—H2W \cdots O2 ^{iv}	0.83	1.91	2.726 (4)	171
O6—H4W \cdots O1 ^v	0.85 (11)	2.06 (11)	2.828 (5)	149 (10)
O6—H3W \cdots O3 ^{vi}	0.84	2.30	2.932 (5)	132
N2—H2 \cdots O6 ^{vii}	0.86	1.91	2.714 (5)	155

Symmetry codes: (ii) $-x+2, y+1/2, -z+1/2$; (iii) $x-1, y, z$; (iv) $x, -y+3/2, z+1/2$; (v) $-x+1, -y+1, -z$; (vi) $-x+2, y-1/2, -z+1/2$; (vii) $x, y+1, z$.