Crystal structure of poly[[hexaqua-1κ⁴O,2κ²O-bis(μ₃-pyridine-2,4-dicarboxylato-1κO²:2κ²N,O²';1'κO⁴)cobalt(II)-strontium(II)] dihydrate]

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In the title polymeric complex, {[CoSr(C₇H₃NO₄)₂(H₂O)₆]·2H₂O}ₙ, the Co^{II} ion, which is situated on a crystallographic centre of inversion, is six-coordinated by two O atoms and two N atoms from two pyridine-2,4-dicarboxylate (pydc²⁻) ligands and two terminal water molecules in a slightly distorted octahedral geometry, to form a *trans*-[Co(pydc)₂(H₂O)₂]²⁻ unit. The Sr^{II} ion, situated on a C_2 axis, is coordinated by four O atoms from four pydc²⁻ ligands and four water molecules. The coordination geometry of the Sr^{II} atom can be best described as a distorted dodecahedron. Each Sr^{II} ion bridges four [Co(pydc)₂(H₂O)₂]²⁻ units by four COO⁻ groups of four pydc²⁻ ligands to form a three-dimensional network structure. Two additional solvent water molecules are observed in the crystal structure and are connected to the three-dimensional coordination polymer by O—H···O hydrogen bonds. Further intra- and intermolecular O—H···O hydrogen bonds consolidate the overall structure.

Keywords: crystal structure; heterometallic complex; pyridine-2,4-dicarboxylic acid heterometallic complex.

CCDC reference: 761895

1. Related literature

For similar heterometallic complexes, see: Chen *et al.* (2014, 2015); Gil de Muro *et al.* (1999); Li *et al.* (1989); Mege-Revil & Price (2013); Zasurskaya *et al.* (2000, 2001, 2006); Zhang (1993); Zhang *et al.* (1992).
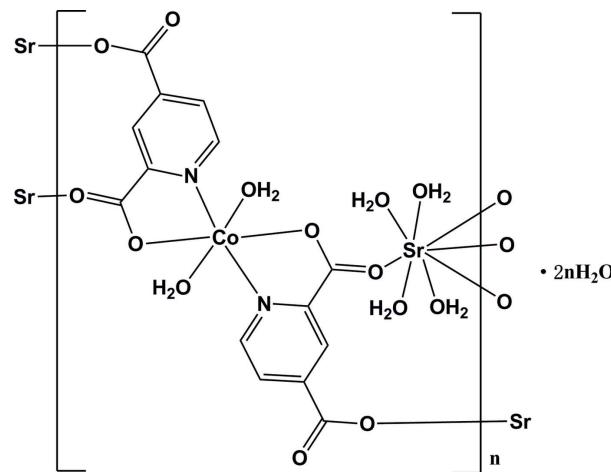
2. Experimental

2.1. Crystal data

[CoSr(C₇H₃NO₄)₂(H₂O)₆]·2H₂O
$M_r = 620.89$
Monoclinic, $C2/c$
$a = 18.628$ (4) Å
$b = 6.8742$ (14) Å
$c = 19.101$ (4) Å
$\beta = 118.77$ (3)°

$V = 2144.0$ (8) Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.35$ mm⁻¹
$T = 293$ K
$0.20 \times 0.18 \times 0.15$ mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.554$, $T_{max} = 0.634$

14907 measured reflections
1892 independent reflections
1776 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.055$
$S = 1.04$
1892 reflections
180 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.25$ e Å⁻³
$\Delta\rho_{min} = -0.46$ e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O4^i	0.78 (3)	2.00 (3)	2.7672 (19)	168 (2)
O5—H5B···O3^{ii}	0.79 (3)	1.96 (3)	2.734 (2)	165 (3)
O6—H6B···O8^{iii}	0.77 (3)	2.07 (4)	2.833 (3)	173 (3)
O7—H7A···O5^{iv}	0.77 (3)	2.57 (3)	3.233 (3)	145 (3)
O7—H7B···O2^v	0.85 (4)	2.39 (3)	3.170 (2)	153 (3)
O8—H8A···O6^{vi}	0.75 (5)	2.50 (5)	3.238 (3)	167 (5)
O8—H8B···O3	0.82 (6)	2.04 (6)	2.831 (3)	164 (6)
O6—H6A···O1	0.77 (3)	2.03 (3)	2.781 (2)	164 (3)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

data reports

Supporting information for this paper is available from the IUCr electronic archives (Reference: IM2469).

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supporting information

Crystal structure of poly[[hexaqua-1*κ⁴O*,2*κ²O*-bis(*µ₃*-pyridine-2,4-dicarboxyl-ato-1*κO²*:2*κ²N,O²′*;1′*κO⁴*)cobalt(II)strontium(II)] dihydrate]

Zhaojun Yu, Peng Jiang and Yanmei Chen

S1. Introduction

As an N,O-containing ligand, pyridine-2,4-dicarboxylic acid (pydc) possesses different binding sites with specific affinities to discriminate different metal ions. It coordinates to alkaline earth metals by using the oxygen atoms to form 'complex-ligands′, and the 'complex-ligands′ then bind with other metal ions to generate heterometallic coordination polymers. In our previous work, two heterometallic complexes containing Co^{II} and Sr^{II} ions were reported (Chen *et al.*, 2015; Chen *et al.*, 2014). As a continuation of our previous work, in this paper a new Co—Sr-pydc complex is reported.

## S2. Experimental

S2.1. Synthesis and crystallization

A mixture of pyridine-2,4-dicarboxylic acid (0.0337 g, 0.2 mmol), Sr(OH)$_2$·8 H$_2$O (0.0262 g, 0.1 mmol), Co(OAc)$_2$·4H$_2$O (0.0244 g,0.1 mmol), and H$_2$O (2 ml) was sealed in a pyrex-bottle (8 ml) and heated to 90°C for 2 days. The tube was then cooled to room temperature, generating yellow rod crystals. Yield: 0.0225 g (37%, based on Co). Elemental analysis calc. for C$_{14}$H$_{22}$CoN$_2$O$_{16}$Sr: C, 27.08; H, 3.57; N, 4.51%. Found: C,27.32; H, 3.57; N, 4.53%.

S2.2. Refinement

H atoms bonded to C atoms of the pyridine ring were positioned geometrically and refined as riding atoms, with C—H = 0.97 Å, and with U$_{iso}$(H) = 1.2 U$_{eq}$(C). The water H atoms were located from a difference Fourier map and refined with restraints of O—H = 0.86 (1) Å and U$_{iso}$(H) = 1.5 U$_{eq}$(O).

S3. Results and discussion

In the title polymeric complex, [C$_{14}$H$_{18}$CoN$_2$O$_{14}$Sr]n·2n H$_2$O, the Co^{II} ion, which is situated on a crystallographic centre of inversion, is six-coordinated by two oxygen atoms and two nitrogen atoms from two pyridine-2,4-dicarboxylate (pydc^{2-}) ligands and two terminal water molecules in a slightly distorted octahedral geometry, to form a *trans*-[Co(pydc)$_2$(H$_2$O)$_2$]$^{2-}$ unit. The Sr^{II} ion being situated on the C_2-axis is coordinated by four oxygen atoms from four pydc^{2-} ligands and four water molecules. The coordination geometry of the Sr^{II} atom can be best described as a distorted dodecahedron. Each Sr^{II} ion bridges four [Co(pydc)$_2$(H$_2$O)$_2$]$^{2-}$ units by four COO$^-$ groups of four pydc^{2-} ligands to form a three-dimensional network structure. The structure is also built up by hydrogen bond interactions between coordinated water molecules and carboxylic groups of pydc^{2-} ligands. Sovent water molecules are connected to the 3-D network by three intermolecular hydrogen bond interactions O6—H6B⋯O8, O8—H8A⋯O6 and O3—H8B⋯O3.
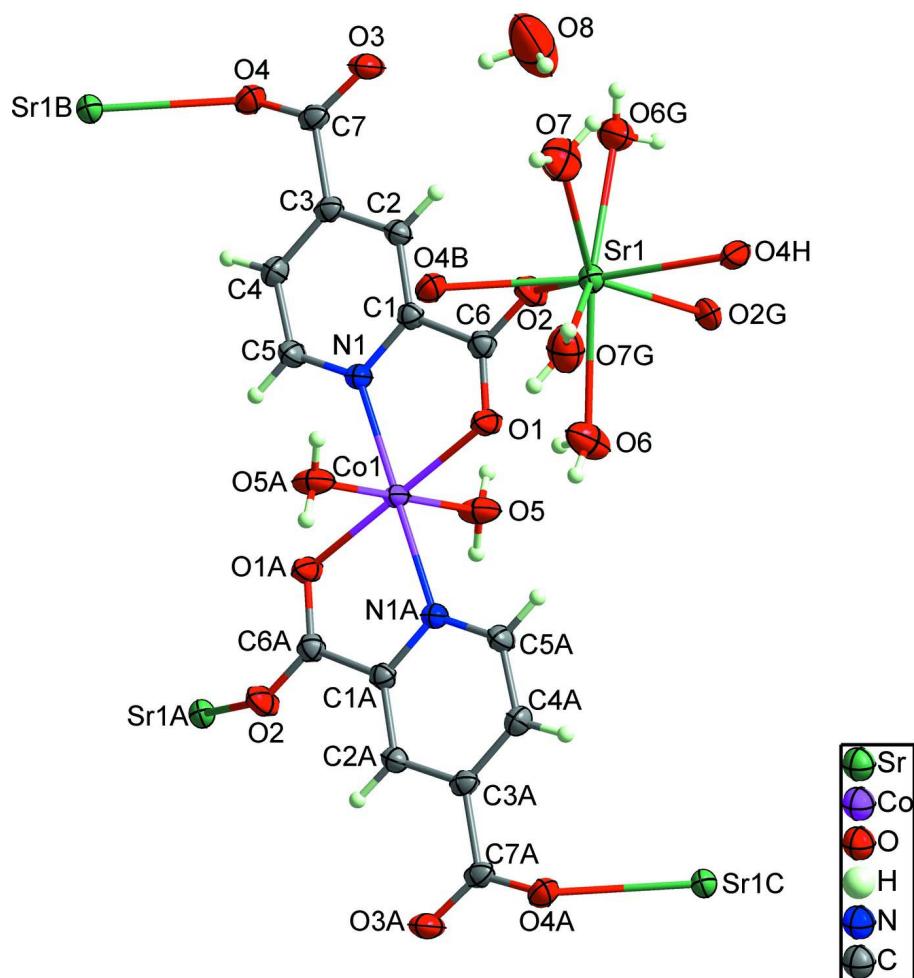
Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: A: -x,-y + 1,-z + 1; B: -x + 1/2,-y + 1/2,-z + 1; C: x - 1/2,y + 1/2,z; G: -x,y,-z + 1/2; H: x - 1/2,1/2 - y,z - 1/2.
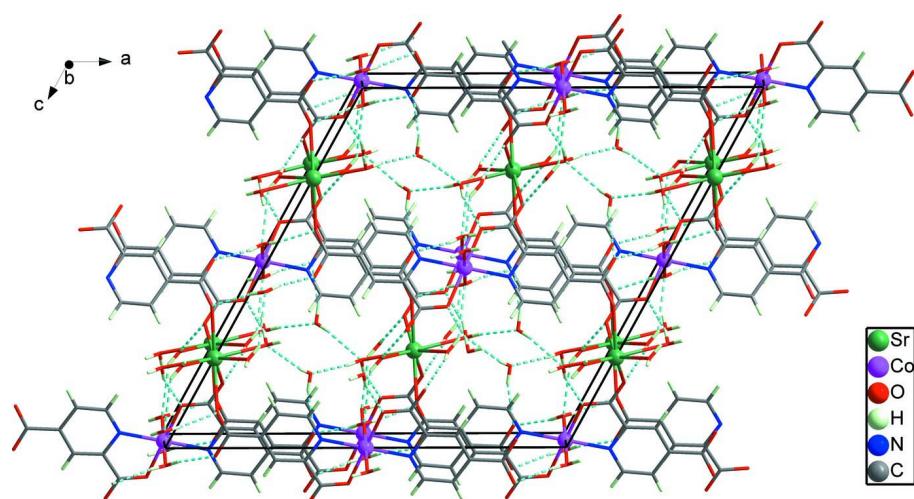
Figure 2

The packing diagram for the title compound, viewed down the *b*-axis, with hydrogen bonds drawn as dashed lines.

Poly[[hexaqua-1κ^4O,2κ^2O-bis(μ_3-pyridine-2,4-dicarboxylato-1κ^4O^2:2$\kappa^2N,O^{2'}$;1′κO^4)cobalt(II)strontium(II)] dihydrate]

Crystal data

[CoSr(C$_7$H$_3$NO$_4$)$_2$(H$_2$O)$_6$]·2H$_2$O	$F(000) = 1252$
$M_r = 620.89$	$D_x = 1.924$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1892 reflections
$a = 18.628$ (4) Å	$\theta = 2.4$–25.0°
$b = 6.8742$ (14) Å	$\mu = 3.35$ mm^{-1}
$c = 19.101$ (4) Å	$T = 293$ K
$\beta = 118.77$ (3)°	Block, yellow
$V = 2144.0$ (8) Å^3	$0.20 \times 0.18 \times 0.15$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	14907 measured reflections
Radiation source: fine-focus sealed tube	1892 independent reflections
Graphite monochromator	1776 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
$T_{min} = 0.554$, $T_{max} = 0.634$	$h = -22 \rightarrow 22$
	$k = -7 \rightarrow 8$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.020$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 2.0752P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1892 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
180 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

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. During the refinement, the command 'omit -3 50′ was used to omit the reflections above 50 degree.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Sr1	0.0000	0.01264 (3)	0.2500	0.02146 (10)
Co1	0.0000	0.5000	0.5000	0.01990 (11)
O1	−0.00844 (7)	0.38635 (19)	0.39640 (7)	0.0266 (3)
O2	0.06342 (8)	0.3272 (2)	0.33384 (7)	0.0315 (3)
O4	0.42018 (7)	0.5817 (2)	0.60160 (7)	0.0305 (3)
O3	0.36287 (8)	0.4710 (2)	0.47716 (9)	0.0317 (3)
O5	−0.03083 (9)	0.7721 (2)	0.44277 (9)	0.0331 (3)
H5A	0.0016 (16)	0.826 (4)	0.4351 (14)	0.050*
H5B	−0.0549 (15)	0.844 (4)	0.4563 (14)	0.050*
O6	−0.11541 (10)	0.1289 (3)	0.28103 (10)	0.0449 (4)
H6A	−0.0932 (18)	0.204 (5)	0.3145 (18)	0.067*
H6B	−0.143 (2)	0.067 (5)	0.2920 (19)	0.067*
O7	0.07800 (11)	−0.3050 (3)	0.24138 (10)	0.0465 (4)
H7A	0.0880 (19)	−0.302 (5)	0.2065 (18)	0.070*
H7B	0.0788 (19)	−0.423 (5)	0.2552 (18)	0.070*
N1	0.12275 (9)	0.5227 (2)	0.52456 (9)	0.0200 (3)
C1	0.13299 (11)	0.4627 (2)	0.46297 (10)	0.0186 (3)
C2	0.20789 (11)	0.4628 (2)	0.46526 (10)	0.0203 (4)
H2	0.2125	0.4217	0.4212	0.024*
C3	0.27660 (11)	0.5250 (2)	0.53410 (11)	0.0199 (4)
C4	0.26621 (10)	0.5851 (3)	0.59769 (10)	0.0243 (4)
H4	0.3108	0.6272	0.6448	0.029*
C5	0.18875 (10)	0.5820 (3)	0.59040 (10)	0.0250 (4)
H5	0.1824	0.6234	0.6335	0.030*
C6	0.05723 (10)	0.3868 (2)	0.39153 (10)	0.0210 (4)
C7	0.35996 (11)	0.5254 (2)	0.53790 (11)	0.0222 (4)
O8	0.27133 (18)	0.4156 (6)	0.30992 (15)	0.1108 (11)
H8A	0.239 (3)	0.339 (8)	0.295 (3)	0.166*
H8B	0.289 (3)	0.430 (8)	0.358 (3)	0.166*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sr1	0.02048 (15)	0.02650 (15)	0.01701 (14)	0.000	0.00871 (11)	0.000
Co1	0.01467 (19)	0.0272 (2)	0.01995 (19)	−0.00072 (11)	0.01003 (15)	−0.00234 (12)
O1	0.0171 (6)	0.0390 (7)	0.0237 (6)	−0.0033 (5)	0.0099 (5)	−0.0083 (5)
O2	0.0295 (7)	0.0452 (8)	0.0233 (6)	−0.0070 (6)	0.0154 (6)	−0.0120 (6)
O4	0.0171 (6)	0.0449 (8)	0.0262 (7)	−0.0022 (6)	0.0079 (5)	0.0046 (6)
O3	0.0247 (7)	0.0431 (8)	0.0344 (8)	0.0008 (6)	0.0199 (6)	−0.0043 (6)
O5	0.0305 (7)	0.0300 (8)	0.0512 (9)	0.0033 (6)	0.0295 (7)	0.0058 (6)
O6	0.0445 (9)	0.0566 (11)	0.0438 (9)	−0.0198 (7)	0.0294 (8)	−0.0190 (8)
O7	0.0529 (10)	0.0425 (9)	0.0410 (9)	0.0015 (8)	0.0201 (8)	−0.0091 (7)
N1	0.0175 (8)	0.0242 (8)	0.0202 (8)	0.0004 (5)	0.0106 (6)	−0.0009 (5)
C1	0.0190 (8)	0.0183 (8)	0.0198 (9)	0.0007 (7)	0.0103 (7)	0.0015 (7)
C2	0.0218 (9)	0.0213 (8)	0.0217 (9)	0.0014 (7)	0.0135 (7)	0.0002 (7)

C3	0.0181 (9)	0.0183 (8)	0.0247 (9)	0.0024 (6)	0.0115 (8)	0.0048 (6)
C4	0.0191 (8)	0.0303 (10)	0.0208 (8)	−0.0007 (7)	0.0075 (7)	−0.0007 (7)
C5	0.0216 (9)	0.0353 (10)	0.0198 (8)	0.0000 (8)	0.0114 (7)	−0.0052 (7)
C6	0.0213 (8)	0.0206 (9)	0.0208 (8)	0.0007 (7)	0.0099 (7)	0.0004 (6)
C7	0.0184 (9)	0.0214 (9)	0.0278 (10)	0.0032 (7)	0.0119 (8)	0.0072 (7)
O8	0.0901 (19)	0.191 (3)	0.0507 (13)	−0.065 (2)	0.0334 (14)	−0.0089 (17)

Geometric parameters (Å, º)

Co1—O1^i	2.0619 (12)	O7—H7B	0.85 (4)
Co1—O1	2.0619 (12)	N1—C5	1.331 (2)
Co1—O5	2.1025 (15)	N1—C1	1.344 (2)
Co1—O5^i	2.1025 (15)	C1—C2	1.375 (3)
Co1—N1	2.1072 (16)	C1—C6	1.507 (2)
Co1—N1^i	2.1072 (16)	C2—C3	1.389 (3)
O1—C6	1.271 (2)	C2—H2	0.9300
O2—C6	1.232 (2)	C3—C4	1.382 (3)
O4—C7	1.255 (2)	C3—C7	1.519 (2)
O3—C7	1.245 (2)	C4—C5	1.382 (2)
O5—H5A	0.78 (3)	C4—H4	0.9300
O5—H5B	0.79 (3)	C5—H5	0.9300
O6—H6A	0.77 (3)	O8—H8A	0.75 (5)
O6—H6B	0.77 (3)	O8—H8B	0.82 (6)
O7—H7A	0.77 (3)		
O1^i—Co1—O1	180.0	C1—N1—Co1	112.24 (12)
O1^i—Co1—O5	92.14 (6)	N1—C1—C2	122.78 (16)
O1—Co1—O5	87.86 (6)	N1—C1—C6	115.66 (15)
O1^i—Co1—O5^i	87.86 (6)	C2—C1—C6	121.51 (15)
O1—Co1—O5^i	92.14 (6)	C1—C2—C3	119.27 (16)
O5—Co1—O5^i	180.0	C1—C2—H2	120.4
O1^i—Co1—N1	100.66 (6)	C3—C2—H2	120.4
O1—Co1—N1	79.34 (6)	C4—C3—C2	117.96 (16)
O5—Co1—N1	92.61 (6)	C4—C3—C7	121.99 (16)
O5^i—Co1—N1	87.39 (6)	C2—C3—C7	120.05 (16)
O1^i—Co1—N1^i	79.34 (6)	C5—C4—C3	119.22 (16)
O1—Co1—N1^i	100.66 (6)	C5—C4—H4	120.4
O5—Co1—N1^i	87.39 (6)	C3—C4—H4	120.4
O5^i—Co1—N1^i	92.61 (6)	N1—C5—C4	123.02 (16)
N1—Co1—N1^i	180.0	N1—C5—H5	118.5
C6—O1—Co1	115.97 (11)	C4—C5—H5	118.5
Co1—O5—H5A	118.5 (19)	O2—C6—O1	124.93 (16)
Co1—O5—H5B	116.3 (18)	O2—C6—C1	118.35 (15)
H5A—O5—H5B	112 (3)	O1—C6—C1	116.71 (14)
H6A—O6—H6B	108 (3)	O3—C7—O4	125.23 (17)
H7A—O7—H7B	109 (3)	O3—C7—C3	117.19 (17)
C5—N1—C1	117.74 (15)	O4—C7—C3	117.58 (16)
C5—N1—Co1	130.01 (12)	H8A—O8—H8B	109 (5)

O5—Co1—O1—C6	90.49 (13)	C7—C3—C4—C5	179.75 (16)
N1—Co1—O1—C6	−2.57 (12)	C1—N1—C5—C4	0.3 (3)
O5—Co1—N1—C5	96.46 (16)	Co1—N1—C5—C4	178.77 (13)
O1—Co1—N1—C1	2.35 (11)	C3—C4—C5—N1	0.3 (3)
O5—Co1—N1—C1	−84.97 (12)	Co1—O1—C6—O2	−179.05 (14)
C5—N1—C1—C2	−0.8 (3)	Co1—O1—C6—C1	2.30 (19)
Co1—N1—C1—C2	−179.57 (13)	N1—C1—C6—O2	−178.92 (16)
C5—N1—C1—C6	176.84 (15)	C2—C1—C6—O2	−1.3 (3)
Co1—N1—C1—C6	−1.93 (18)	N1—C1—C6—O1	−0.2 (2)
N1—C1—C2—C3	0.8 (3)	C2—C1—C6—O1	177.49 (16)
C6—C1—C2—C3	−176.73 (15)	C4—C3—C7—O3	−179.09 (16)
C1—C2—C3—C4	−0.2 (2)	C2—C3—C7—O3	1.0 (2)
C1—C2—C3—C7	179.75 (15)	C4—C3—C7—O4	0.4 (2)
C2—C3—C4—C5	−0.3 (3)	C2—C3—C7—O4	−179.53 (16)

Symmetry code: (i) −x, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O4ii	0.78 (3)	2.00 (3)	2.7672 (19)	168 (2)
O5—H5B···O3iii	0.79 (3)	1.96 (3)	2.734 (2)	165 (3)
O6—H6B···O8iv	0.77 (3)	2.07 (4)	2.833 (3)	173 (3)
O7—H7A···O5v	0.77 (3)	2.57 (3)	3.233 (3)	145 (3)
O7—H7B···O2vi	0.85 (4)	2.39 (3)	3.170 (2)	153 (3)
O8—H8A···O6vii	0.75 (5)	2.50 (5)	3.238 (3)	167 (5)
O8—H8B···O3	0.82 (6)	2.04 (6)	2.831 (3)	164 (6)
O6—H6A···O1	0.77 (3)	2.03 (3)	2.781 (2)	164 (3)

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