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Diaquabis(2-pyridylphosphonato *N*-oxide-κ^2O^1,O^2)cobalt(II)

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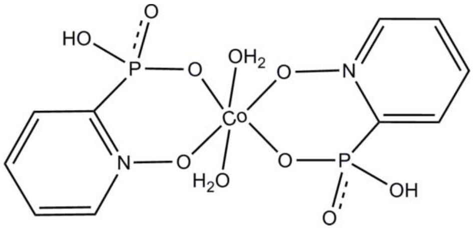
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.051; wR factor = 0.109; data-to-parameter ratio = 14.6.

In the title complex, $[Co(C_5H_5NO_4P)_2(H_2O)_2]$, the Co^{II} ion, which lies on a crystallographic inversion center, is coordinated by four O atoms from two bidentate 2-phosphonatopyridine *N*-oxide ligands and two O atoms from two water ligands in a slightly distorted octahedral environment. Molecules are interlinked by three O—H⋯O hydrogen bonds and one weak C—H⋯O interaction, forming a three-dimensional supramolecular structure.

Related literature

For new open frameworks based on metal pyridylphosphonates, see: Ayyappan *et al.* (2001). For two-dimensional Cu-phosphonates, see: Ma *et al.* (2006). For one-dimensional Cu-phosphonates containing bridging ligands, see: Ma *et al.* (2007). For catalytic and magnetic properties of metal phosphonates, see: Cao *et al.* (1992). For the layered structures of monophosphonic acids and transition metal ions, see Clearfield (1998). For a tetraaqua-Co(II)-4-hydroxypyridine-2,6-dicarboxylate structure, see: Cui *et al.* (2006). For weak C—H⋯O hydrogen-bonding contacts, see: Desiraju & Steiner (2001). For the synthesis of the ligand (2-pyridyl-*N*-oxide)phosphonic acid, see: McCabe *et al.* (1987).



Experimental

Crystal data

$[Co(C_5H_5NO_4P)_2(H_2O)_2]$
M_r = 443.10
Monoclinic, $P2_1/n$
a = 4.7899 (10) Å
b = 12.075 (2) Å
c = 14.162 (3) Å
β = 99.51 (3)°
V = 807.8 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.32 mm^{-1}
T = 293 (2) K
0.5 × 0.3 × 0.2 mm

Data collection

Rigaku SCX mini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.625, T_{max} = 0.766
8068 measured reflections
1848 independent reflections
1373 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.109
S = 1.05
1848 reflections
127 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.084 (2)	Co1—O4	2.131 (2)
Co1—O1*W*	2.099 (3)		
O1—Co1—O1*W*	89.93 (11)	O1*W*—Co1—O4	91.55 (10)
O1—Co1—O4	87.91 (9)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*W*—H1*WB*⋯O1^{i}	0.77 (4)	2.15 (5)	2.803 (4)	142 (4)
O3—H3*A*⋯O2^{ii}	0.85 (4)	1.68 (4)	2.516 (3)	171 (4)
O1*W*—H1*WA*⋯O4^{ii}	0.77 (4)	2.00 (4)	2.719 (4)	155 (4)
C3—H3⋯O2^{iii}	0.93	2.52	3.449 (5)	178

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2126).

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supporting information

Acta Cryst. (2008). E**64**, m1550–m1551 [doi:10.1107/S1600536808037185]

Diaquabis(2-pyridylphosphonato *N*-oxide-κ^2O^1,O^2)cobalt(II)

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S1. Comment

The chemistry of metal phosphonates has received an increasing attention in recent years for their new architectures and properties in catalysis, ion exchange and magnetic materials (Cao *et al.*, 1992). It has been well known that the mono-phosphonic acid RPO$_3$H$_2$, where R represents an alkyl or aryl group, prefer to form layered structures with transition metal ions (Clearfield 1998). There are some metal phosphonates reported during the past several years which contain pyridyl groups (Ayyappan *et al.* (2001); Ma *et al.* (2006); Ma *et al.* (2007). The present paper is concerned with the crystal structure of a new cobalt phosphonate complex with a (2-pyridyl-*N*-oxide)phosphonate ligand.

The asymmetric unit contains half of the [$Co(C_5H_4NOPO_3H)_2(H_2O)_2$] molecule. As shown in Fig. 1, atom Co1 lies on an inversion centre and is coordinated by four O atoms [O1, O1^i, O4 and O4^i] from two ligands, and two O atoms from two aqua ligands, thereby forming a slightly distorted CoO$_6$ octahedral coordination geometry. The Co1—O1 and the Co1—O4 distances (Table 1) are close to the value observed in [CoL_2(H$_2$O)$_4$] [2.0653 (12) Å, and the Co—O(H$_2$O) distance in the title structure is close to the value observed in the Co-tetraaqua compound [2.0764 (13) Å with L = 4-hydroxy-pyridine-2,6-dicarboxylate (Cui *et al.*, 2006)] (Table 1). The *cisoid* angles of CoO$_6$ (Table 1) are close to 90°. The phosphonate serves as a chelating ligand using one pyridyl N-oxide acceptor O atom and one phosphonate oxygen atom. One phosphonate oxygen is protonated with the P1—O3 distance 1.560 (3) Å.

In the complex, three classic intermolecular O—H···O hydrogen-bonds exist between the water molecule and a phosphonate O atom, the water molecule and a pyridyl N-oxide acceptor O atom, and between two phosphonate O atoms (Fig. 1, Table 2). Thus, the molecules are interlinked by these hydrogen bonds, forming a one-dimensional chain structure along the *a*-axis (Fig.2). Additionally, weak intermolecular C—H···O hydrogen bonding contacts (Desiraju & Steiner, 2001) link these chains to form a three-dimensional supramolecular network (Fig. 3).

S2. Experimental

The synthesis of the ligand (2-pyridyl-*N*-oxide)phosphonic acid, see: McCabe *et al.* (1987). The (2-pyridyl-*N*-oxide)phosphonic acid (0.0176 g, 0.1 mmol) was dissolved in distilled water (5 ml), and was added a solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.0240 g, 0.01 mmol) in distilled water (2 ml). The mixture was stirred at room temperature for 5 h and then filtered. Slow evaporation of the solvent gave pink crystals. (Yield 45%).

S3. Refinement

Carbon-bound H atoms were positioned geometrically (C—H = 0.93 Å), and were included in the refinement in the riding mode approximation, with U_{iso}(H) = 1.2U_{eq}(C). The water H atoms and P—O—H H atom were located in a difference Fourier map and restrained to 0.77 (4) Å and 0.85 (4) Å, respectively, with U_{iso}(H) refined between 1.0 and 1.8U_{eq}(O).

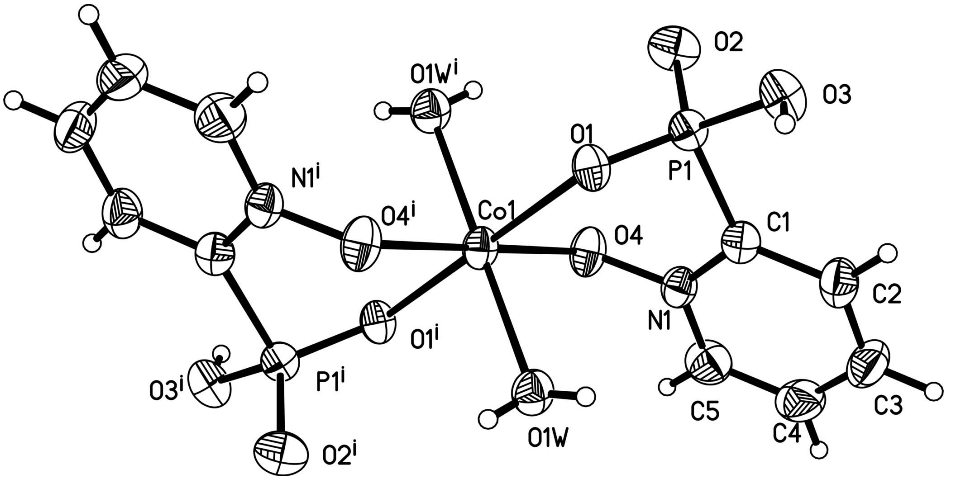

Figure 1

A view of the compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 40% probability level. [Symmetry code i = (-*x*, -*y*, -*z* + 1)]

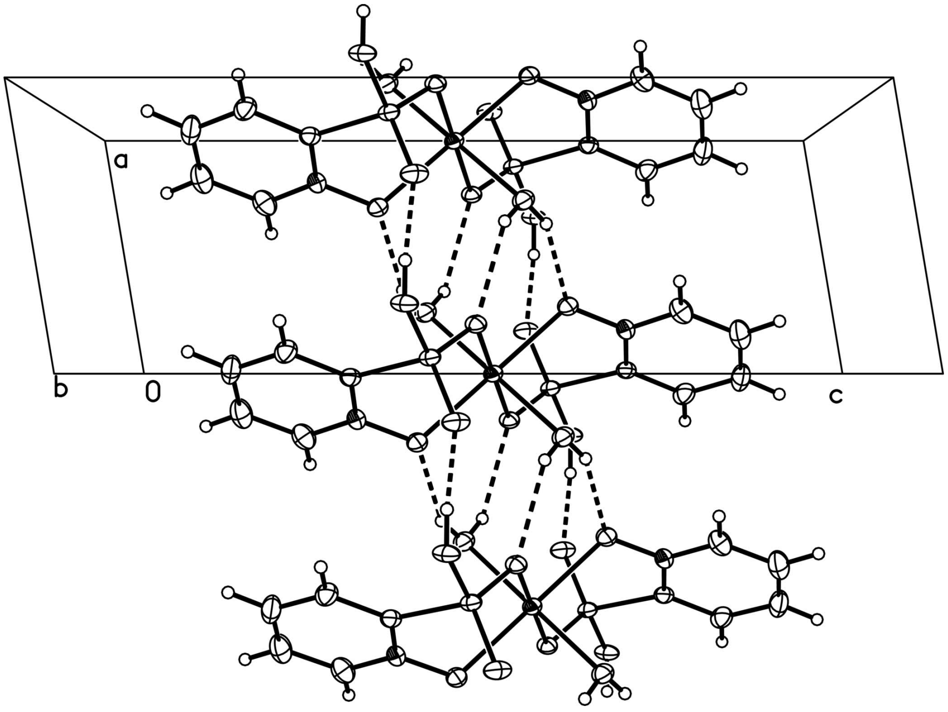

Figure 2

One-dimensional supramolecular chain structure with classic O—H···O hydrogen bonds shown with dashed lines, running along the *a* axis.

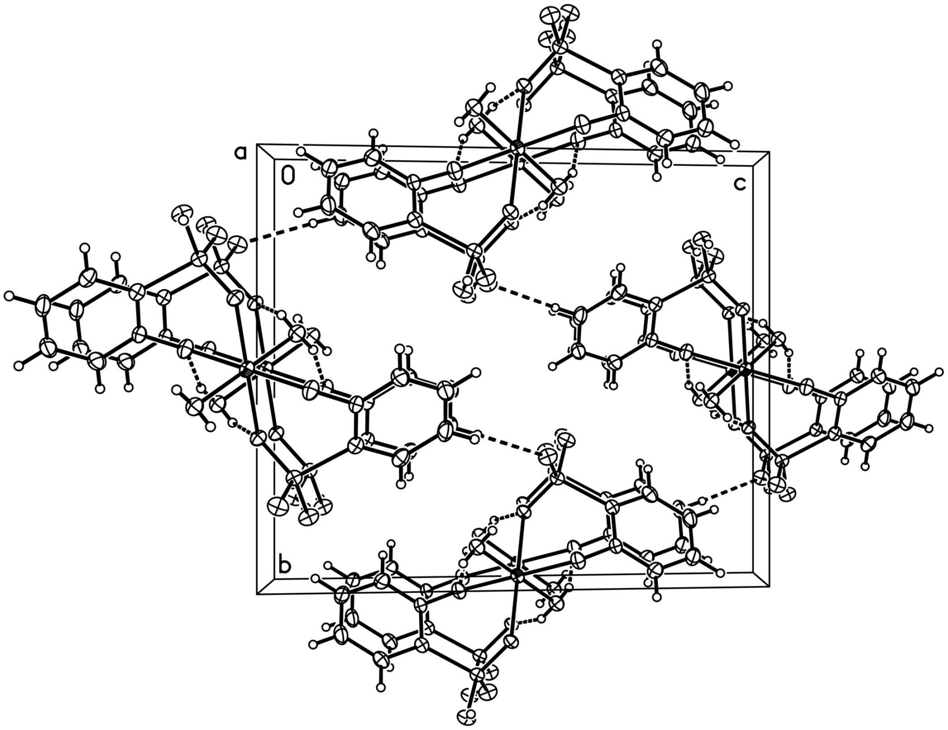

Figure 3

The cell packing diagram indicating weak C—H···O links with dashed lines, viewed down the *a* axis.

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Crystal data

$[Co(C_5H_5NO_4P)_2(H_2O)_2]$
$M_r = 443.10$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 4.7899$ (10) Å
$b = 12.075$ (2) Å
$c = 14.162$ (3) Å
$\beta = 99.51$ (3)°
$V = 807.8$ (3) Å^3
$Z = 2$
$F(000) = 450$
$D_x = 1.822$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6955 reflections
$\theta = 3.4$–27.7°
$\mu = 1.32$ mm^{-1}
$T = 293$ K
Needle, pink
0.5 × 0.3 × 0.2 mm

Data collection

Rigaku MACHINE?
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
dtfind.ref scans
Absorption correction: multi-scan
  (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.625$, $T_{max} = 0.766$
8068 measured reflections
1848 independent reflections
1373 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$h = -6 \rightarrow 6$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.1404P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1848 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.45$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Co1	0.0000	0.0000	0.5000	0.0251 (2)
P1	0.06589 (18)	0.23457 (7)	0.41631 (6)	0.0247 (2)
O1	0.2057 (5)	0.14984 (17)	0.48661 (15)	0.0265 (5)
O2	−0.1949 (5)	0.2903 (2)	0.43729 (17)	0.0367 (6)
O3	0.2811 (5)	0.3247 (2)	0.39564 (18)	0.0328 (6)
H3A	0.455 (9)	0.307 (3)	0.406 (3)	0.055 (14)*
O4	−0.2925 (5)	0.0442 (2)	0.37548 (16)	0.0326 (6)
O1W	0.2669 (6)	−0.0782 (3)	0.4170 (2)	0.0317 (6)
H1WA	0.362 (8)	−0.043 (3)	0.389 (3)	0.031 (12)*
H1WB	0.362 (9)	−0.120 (4)	0.449 (3)	0.057 (17)*
N1	−0.1928 (6)	0.0750 (2)	0.29606 (19)	0.0281 (7)
C1	−0.0157 (7)	0.1641 (3)	0.3010 (2)	0.0273 (8)
C2	0.0908 (8)	0.1928 (3)	0.2193 (3)	0.0365 (9)
H2	0.2141	0.2525	0.2210	0.044*
C3	0.0168 (9)	0.1342 (3)	0.1355 (3)	0.0450 (10)
H3	0.0910	0.1534	0.0811	0.054*
C4	−0.1695 (9)	0.0462 (4)	0.1332 (3)	0.0465 (11)
H4	−0.2257	0.0071	0.0767	0.056*
C5	−0.2703 (9)	0.0173 (3)	0.2146 (3)	0.0407 (10)
H5	−0.3930	−0.0426	0.2138	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0192 (4)	0.0303 (4)	0.0261 (4)	−0.0024 (3)	0.0050 (3)	0.0041 (3)

P1	0.0175 (5)	0.0272 (5)	0.0299 (5)	−0.0009 (4)	0.0049 (4)	0.0017 (4)
O1	0.0208 (12)	0.0281 (12)	0.0301 (13)	−0.0053 (10)	0.0031 (10)	0.0049 (10)
O2	0.0216 (14)	0.0389 (15)	0.0494 (16)	0.0026 (12)	0.0056 (12)	−0.0042 (12)
O3	0.0177 (14)	0.0330 (14)	0.0464 (16)	−0.0028 (12)	0.0010 (12)	0.0074 (11)
O4	0.0244 (14)	0.0436 (15)	0.0301 (13)	−0.0085 (11)	0.0050 (11)	0.0067 (11)
O1W	0.0271 (15)	0.0354 (16)	0.0339 (16)	−0.0008 (14)	0.0084 (13)	0.0033 (13)
N1	0.0279 (16)	0.0325 (16)	0.0232 (15)	0.0009 (14)	0.0020 (12)	0.0032 (12)
C1	0.0207 (18)	0.0320 (19)	0.0288 (18)	0.0021 (16)	0.0033 (15)	0.0034 (15)
C2	0.035 (2)	0.040 (2)	0.037 (2)	0.0009 (18)	0.0113 (18)	0.0096 (17)
C3	0.056 (3)	0.053 (3)	0.028 (2)	0.011 (2)	0.0147 (19)	0.0060 (18)
C4	0.062 (3)	0.044 (2)	0.031 (2)	0.010 (2)	0.002 (2)	−0.0053 (18)
C5	0.046 (3)	0.037 (2)	0.037 (2)	−0.0031 (19)	−0.0016 (19)	−0.0040 (17)

Geometric parameters (Å, º)

Co1—O1	2.084 (2)	O1W—H1WA	0.77 (4)
Co1—O1^{i}	2.084 (2)	O1W—H1WB	0.77 (4)
Co1—O1W^{i}	2.099 (3)	N1—C5	1.346 (4)
Co1—O1W	2.099 (3)	N1—C1	1.365 (4)
Co1—O4	2.131 (2)	C1—C2	1.383 (5)
Co1—O4^{i}	2.131 (2)	C2—C3	1.377 (5)
P1—O2	1.491 (2)	C2—H2	0.9300
P1—O1	1.505 (2)	C3—C4	1.384 (6)
P1—O3	1.560 (3)	C3—H3	0.9300
P1—C1	1.826 (3)	C4—C5	1.367 (5)
O3—H3A	0.85 (4)	C4—H4	0.9300
O4—N1	1.345 (3)	C5—H5	0.9300
O1—Co1—O1^{i}	180.0	N1—O4—Co1	119.04 (18)
O1—Co1—O1W^{i}	90.07 (11)	Co1—O1W—H1WA	120 (3)
O1^{i}—Co1—O1W^{i}	89.93 (11)	Co1—O1W—H1WB	108 (3)
O1—Co1—O1W	89.93 (11)	H1WA—O1W—H1WB	108 (4)
O1^{i}—Co1—O1W	90.07 (11)	O4—N1—C5	119.2 (3)
O1W^{i}—Co1—O1W	180.000 (1)	O4—N1—C1	118.6 (3)
O1—Co1—O4	87.91 (9)	C5—N1—C1	122.2 (3)
O1^{i}—Co1—O4	92.09 (9)	N1—C1—C2	117.8 (3)
O1W^{i}—Co1—O4	88.45 (10)	N1—C1—P1	116.9 (2)
O1W—Co1—O4	91.55 (10)	C2—C1—P1	125.3 (3)
O1—Co1—O4^{i}	92.09 (9)	C3—C2—C1	120.9 (4)
O1^{i}—Co1—O4^{i}	87.91 (9)	C3—C2—H2	119.5
O1W^{i}—Co1—O4^{i}	91.55 (10)	C1—C2—H2	119.5
O1W—Co1—O4^{i}	88.45 (10)	C2—C3—C4	119.2 (4)
O4—Co1—O4^{i}	180.00 (9)	C2—C3—H3	120.4
O2—P1—O1	118.07 (14)	C4—C3—H3	120.4
O2—P1—O3	108.89 (15)	C5—C4—C3	119.5 (4)
O1—P1—O3	111.28 (14)	C5—C4—H4	120.2
O2—P1—C1	109.02 (15)	C3—C4—H4	120.2
O1—P1—C1	106.32 (14)	N1—C5—C4	120.3 (4)

O3—P1—C1	101.99 (15)	N1—C5—H5	119.9
P1—O1—Co1	119.01 (13)	C4—C5—H5	119.9
P1—O3—H3A	117 (3)		

O2—P1—O1—Co1	68.83 (18)	O4—N1—C1—P1	−0.7 (4)
O3—P1—O1—Co1	−164.20 (13)	C5—N1—C1—P1	179.3 (3)
C1—P1—O1—Co1	−53.93 (18)	O2—P1—C1—N1	−68.0 (3)
O1W^{i}—Co1—O1—P1	−78.04 (16)	O1—P1—C1—N1	60.3 (3)
O1W—Co1—O1—P1	101.96 (16)	O3—P1—C1—N1	176.9 (2)
O4—Co1—O1—P1	10.41 (15)	O2—P1—C1—C2	113.0 (3)
O4^{i}—Co1—O1—P1	−169.59 (15)	O1—P1—C1—C2	−118.7 (3)
O1—Co1—O4—N1	52.1 (2)	O3—P1—C1—C2	−2.0 (3)
O1^{i}—Co1—O4—N1	−127.9 (2)	N1—C1—C2—C3	0.9 (5)
O1W^{i}—Co1—O4—N1	142.2 (2)	P1—C1—C2—C3	179.9 (3)
O1W—Co1—O4—N1	−37.8 (2)	C1—C2—C3—C4	0.8 (6)
Co1—O4—N1—C5	121.0 (3)	C2—C3—C4—C5	−1.8 (6)
Co1—O4—N1—C1	−59.0 (3)	O4—N1—C5—C4	−179.3 (3)
O4—N1—C1—C2	178.3 (3)	C1—N1—C5—C4	0.7 (5)
C5—N1—C1—C2	−1.7 (5)	C3—C4—C5—N1	1.1 (6)

Symmetry code: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WB*···O1^{ii}	0.77 (4)	2.15 (5)	2.803 (4)	142 (4)
O3—H3*A*···O2^{iii}	0.85 (4)	1.68 (4)	2.516 (3)	171 (4)
O1*W*—H1*WA*···O4^{iii}	0.77 (4)	2.00 (4)	2.719 (4)	155 (4)
C3—H3···O2^{iv}	0.93	2.52	3.449 (5)	178

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) *x*+1/2, −*y*+1/2, *z*−1/2.