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Bis(2-methylanilinium) diaquabis[dihydrogendiphosphato(2−)]cobaltate(II)

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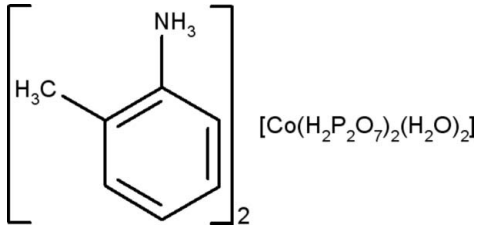
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.078; data-to-parameter ratio = 24.8.

In the title cobalt(II) complex with 2-methylanilinium and diphosphate, $(C_7H_{10}N)_2[Co(H_2P_2O_7)_2(H_2O)_2]$, a three-dimensional network is built up from anionic layers of $[Co(H_2P_2O_7)_2(H_2O)_2]^{2-}$ units and 2-methylanilinium cations located between these layers. The dihydrogendiphosphate groups present a bent eclipsed conformation, while the Co^{2+} ions lie on inversion centers. An intricate network of O—H···O and N—H···O hydrogen bonds is established between the different components, assuring the cohesion of the network with other interactions, being of electrostatic and van der Waals nature.

Related literature

For organic-inorganic transition metal frameworks, see: Cheetham *et al.* (1999); Clearfield (1998). For the role played by diphosphates in interactions between metal centers, see: Xu *et al.* (2008). For related structures, see: Essehli *et al.* (2006); Gharbi *et al.* (1994); Gharbi & Jouini (2004).



Experimental

Crystal data

$(C_7H_{10}N)_2[Co(H_2P_2O_7)_2(H_2O)_2]$
M_r = 663.19
Triclinic, $P\overline{1}$
a = 7.440 (4) Å
b = 7.455 (2) Å
c = 11.747 (3) Å
α = 91.92 (3)°
β = 94.09 (5)°
γ = 104.67 (2)°
V = 627.8 (4) Å^3
Z = 1
Ag $K\alpha$ radiation
μ = 0.53 mm^{-1}
T = 298 K
0.33 × 0.26 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
4678 measured reflections
4486 independent reflections
3911 reflections with $I > 2\sigma(I)$
R_{int} = 0.008
2 standard reflections
frequency: 120 min
intensity decay: 7%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.078
S = 1.08
4486 reflections
181 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O3^{i}	0.82	1.75	2.5712 (17)	177
O2—H2···O7^{ii}	0.82	1.71	2.522 (2)	169
O8—H2*W*···O2^{iii}	0.842 (9)	1.978 (10)	2.8199 (18)	179 (3)
O8—H1*W*···O4^{i}	0.842 (9)	2.202 (13)	3.020 (2)	164 (3)
N1—H1*A*···O7^{iii}	0.89	1.89	2.7788 (18)	177
N1—H1*B*···O5	0.89	2.31	3.0083 (19)	135
N1—H1*B*···O1^{iv}	0.89	2.48	3.105 (2)	127
N1—H1*C*···O3^{i}	0.89	1.94	2.821 (2)	168

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2278).

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supporting information

Acta Cryst. (2009). E**65**, m1487 [https://doi.org/10.1107/S1600536809044079]

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S1. Comment

Organic inorganic transition metal frameworks can be usefully employed in diverse areas, such as shape selective catalysis or adsorption (Cheetham *et al.*, 1999; Clearfield, 1998). In such compounds the transition metal plays a key role for building interesting topologies with one-, two- or three-dimensional networks. In these atomic arrangements, the transition element is coordinated generally to ligands *via* several donor atoms such as oxygen or nitrogen. In recent years, many researchers have focused on diphosphates because they are powerful ligands that can link metal ions through their oxygen atoms, and can play an essential role in the interaction between the metallic centers (Xu *et al.*, 2008).

The title compound, is built up from a diaquabis[dihydrogendiphosphato(2)]cobaltate(II) anion and two organic 2-methylanilinium cations (Fig. 1). A half of the complex anion and one organic cation constitute the asymmetric unit of (I).

The metal complex anions, interconnected *via* hydrogen bonds involving the two hydroxyl groups of $H_2P_2O_7^{2-}$ and the water molecule, develop a thick bi-dimensional layer of formula $[Co(H_2P_2O_7)_2(H_2O)_2]^{2n-}$ perpendicular to the *c* axis (Fig. 2). The protonated organic cations 2-$CH_3C_6H_4NH_3^+$ are anchored between these layers .

With regard to the inorganic arrangement, the Co atom is located on an inversion center and is surrounded by two symmetry related dihydrogendiphosphate ligands with a bent eclipsed conformation as seen by the P1—O4—P2 angle of 129.26 (7)% , and two water molecules in an octahedral coordination. Four external O atoms, OE, in the basal plane from two bidendate $[H_2P_2O_7]$ groups and the two remaining O atoms, OW, in the apical positions from the water molecule give a slightly distorted CoO_6 octahedron. Within this octahedron, the Co—O distances range from 2.057 (1) to 2.149 (1) Å with Cu—OW distances longer than those of Co—OE. A similar coordination geometry around the central atom has also been observed in other $M^{II}O_6$ octahedra, M^{II} = Co or Ni, in organic diphosphate compounds (Essehli *et al.*, 2006; Gharbi *et al.*, 1994; Gharbi *et al.*, 2004).

Analysis of hydrogen bonds within (I), revealed an intricate network of O—H···O and N—H···O bonds which along with other interactions (electrostatic and Van der Waals) stabilize the whole structure. The O—H···O contacts, with O—H···O distances ranging from 2.522 (2) to 3.020 (2) Å, link the complex anions while the N—H···O bonds linking the anions and cations are weaker since the N—H···O distances are longer, ranging from 2.779 (2) to 3.105 (2) Å. These H-bonds (Table 1) participate in the cohesion of the three-dimensional network (Fig 2).

S2. Experimental

Crystals of the title compound were prepared by adding an ethanol solution (10 ml) of 2-methylaniline (7.52 mmol) dropwise to a mixture of $H_4P_2O_7$ (3.75 mmol) and $CoCl_2$ (1.88 mmol) in water (20 ml). Good quality green prisms were obtained after a slow evaporation during few days at ambient temperature. The diphosphoric acid, $H_4P_2O_7$, was produced from $Na_4P_2O_7$ by using an ion-exchange resin (Amberlite IR 120).

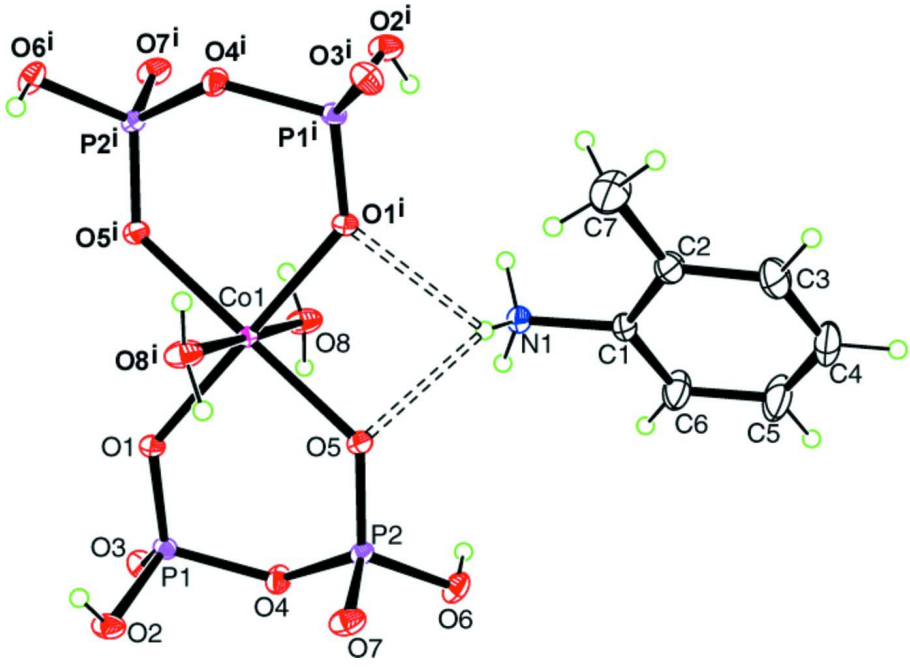

Figure 1

An *ORTEP* view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are represented as dashed lines.[Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.]

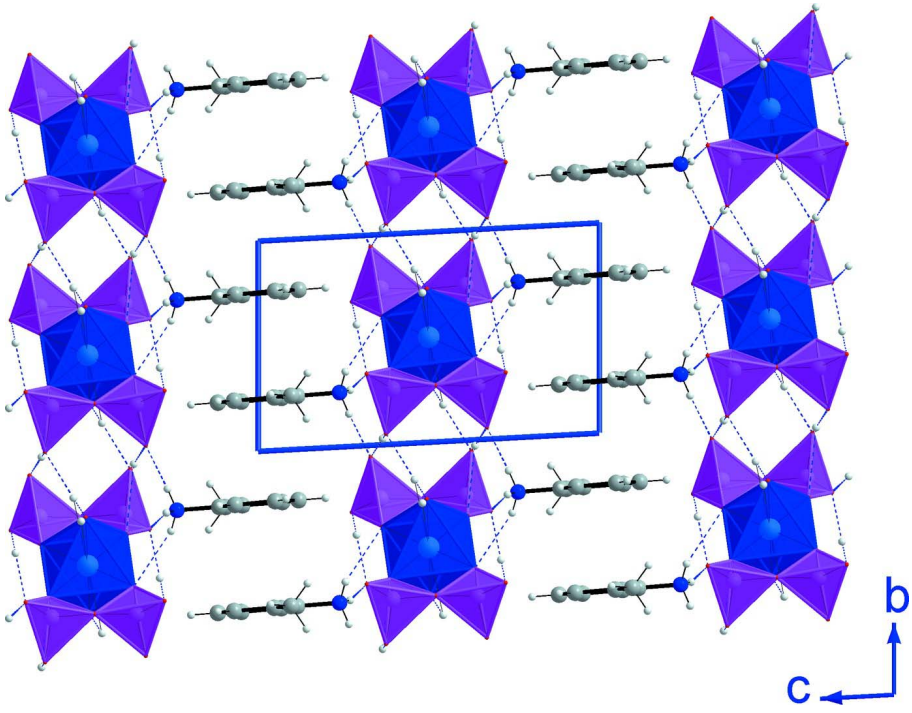

Figure 2

Projection of (I) along the *a* axis.

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Crystal data

$(C_7H_{10}N)_2[Co(H_2P_2O_7)_2(H_2O)_2]$
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Triclinic, $P\overline{1}$
$a = 7.440$ (4) Å
$b = 7.455$ (2) Å
$c = 11.747$ (3) Å
$\alpha = 91.92$ (3)°
$\beta = 94.09$ (5)°
$\gamma = 104.67$ (2)°
$V = 627.8$ (4) Å^3
$Z = 1$
$F(000) = 341$
$D_x = 1.754$ Mg m^{-3}
Ag $K\alpha$ radiation, $\lambda = 0.56085$ Å
Cell parameters from 25 reflections
$\theta = 9$–11°
$\mu = 0.53$ mm^{-1}
$T = 298$ K
Prism, pink
0.33 × 0.26 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: Enraf Nonius FR590
Graphite monochromator
Non–profiled ω scans
4678 measured reflections
4486 independent reflections
3911 reflections with $I > 2\sigma(I)$
$R_{int} = 0.008$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 17$
2 standard reflections every 120 min
intensity decay: 7%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.078$
$S = 1.08$
4486 reflections
181 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.209P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e 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_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.5000	0.01548 (6)
P1	0.21765 (4)	0.73669 (4)	0.39318 (3)	0.01617 (7)
P2	0.27309 (4)	0.74457 (4)	0.64170 (3)	0.01643 (7)

O1	0.37007 (14)	0.64107 (14)	0.38682 (8)	0.02204 (18)
O2	0.29044 (15)	0.94783 (14)	0.37491 (11)	0.0272 (2)
H2	0.4017	0.9718	0.3647	0.041*
O3	0.04241 (14)	0.65899 (15)	0.31845 (9)	0.0253 (2)
O4	0.15097 (14)	0.73056 (16)	0.52080 (9)	0.02389 (19)
O5	0.39173 (14)	0.61111 (14)	0.63563 (8)	0.02138 (18)
O6	0.11785 (15)	0.68728 (15)	0.72493 (9)	0.0258 (2)
H6	0.0630	0.5776	0.7116	0.039*
O7	0.37403 (15)	0.94287 (14)	0.67018 (10)	0.0275 (2)
O8	0.25633 (15)	0.27064 (15)	0.49415 (11)	0.0291 (2)
N1	0.29299 (18)	0.25923 (18)	0.76160 (10)	0.0234 (2)
H1A	0.3161	0.1554	0.7340	0.035*
H1B	0.3821	0.3566	0.7445	0.035*
H1C	0.1832	0.2687	0.7308	0.035*
C1	0.2890 (2)	0.2541 (2)	0.88612 (12)	0.0242 (3)
C2	0.4492 (2)	0.2523 (2)	0.95316 (14)	0.0313 (3)
C3	0.4354 (3)	0.2471 (3)	1.07075 (16)	0.0469 (5)
H3	0.5407	0.2471	1.1184	0.056*
C4	0.2716 (4)	0.2419 (4)	1.11818 (16)	0.0550 (6)
H4	0.2668	0.2390	1.1970	0.066*
C5	0.1146 (3)	0.2411 (4)	1.04945 (18)	0.0579 (6)
H5	0.0026	0.2356	1.0815	0.069*
C6	0.1229 (3)	0.2486 (3)	0.93204 (15)	0.0439 (5)
H6A	0.0173	0.2499	0.8849	0.053*
C7	0.6297 (3)	0.2562 (4)	0.90335 (19)	0.0530 (6)
H7A	0.6174	0.1429	0.8587	0.079*
H7B	0.7264	0.2685	0.9639	0.079*
H7C	0.6609	0.3596	0.8555	0.079*
H2W	0.266 (3)	0.174 (2)	0.458 (2)	0.052 (7)*
H1W	0.149 (2)	0.287 (4)	0.481 (2)	0.070 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01533 (10)	0.01613 (11)	0.01672 (11)	0.00681 (8)	0.00249 (8)	0.00182 (8)
P1	0.01346 (13)	0.01654 (13)	0.01897 (14)	0.00477 (10)	0.00046 (10)	0.00225 (10)
P2	0.01503 (13)	0.01627 (13)	0.01831 (14)	0.00417 (10)	0.00368 (10)	−0.00060 (10)
O1	0.0232 (4)	0.0268 (5)	0.0211 (4)	0.0146 (4)	0.0039 (3)	0.0048 (3)
O2	0.0226 (5)	0.0166 (4)	0.0435 (6)	0.0046 (3)	0.0094 (4)	0.0045 (4)
O3	0.0192 (4)	0.0266 (5)	0.0276 (5)	0.0033 (4)	−0.0058 (4)	0.0029 (4)
O4	0.0175 (4)	0.0356 (5)	0.0208 (4)	0.0104 (4)	0.0031 (3)	0.0036 (4)
O5	0.0249 (4)	0.0240 (4)	0.0188 (4)	0.0124 (4)	0.0029 (3)	0.0005 (3)
O6	0.0244 (5)	0.0267 (5)	0.0252 (5)	0.0023 (4)	0.0113 (4)	−0.0023 (4)
O7	0.0236 (5)	0.0172 (4)	0.0402 (6)	0.0018 (4)	0.0081 (4)	−0.0043 (4)
O8	0.0194 (5)	0.0226 (5)	0.0449 (6)	0.0051 (4)	0.0037 (4)	−0.0048 (4)
N1	0.0260 (5)	0.0274 (6)	0.0187 (5)	0.0100 (4)	0.0022 (4)	0.0020 (4)
C1	0.0268 (6)	0.0295 (7)	0.0181 (5)	0.0105 (5)	0.0013 (5)	0.0029 (5)
C2	0.0302 (7)	0.0405 (8)	0.0249 (7)	0.0136 (6)	−0.0025 (5)	0.0005 (6)

C3	0.0520 (11)	0.0671 (14)	0.0254 (8)	0.0252 (10)	−0.0082 (7)	0.0032 (8)
C4	0.0703 (15)	0.0815 (17)	0.0207 (7)	0.0315 (13)	0.0095 (8)	0.0077 (9)
C5	0.0507 (12)	0.101 (2)	0.0299 (9)	0.0290 (13)	0.0178 (8)	0.0089 (11)
C6	0.0314 (8)	0.0799 (15)	0.0262 (7)	0.0233 (9)	0.0067 (6)	0.0074 (8)
C7	0.0297 (9)	0.0902 (18)	0.0426 (10)	0.0239 (10)	−0.0023 (8)	−0.0015 (11)

Geometric parameters (Å, º)

Co1—O1	2.0574 (12)	N1—C1	1.4667 (18)
Co1—O1^{i}	2.0574 (12)	N1—H1A	0.8900
Co1—O5	2.0752 (12)	N1—H1B	0.8900
Co1—O5^{i}	2.0752 (12)	N1—H1C	0.8900
Co1—O8	2.1491 (14)	C1—C6	1.375 (2)
Co1—O8^{i}	2.1491 (14)	C1—C2	1.384 (2)
P1—O1	1.4892 (11)	C2—C3	1.394 (2)
P1—O3	1.4919 (14)	C2—C7	1.496 (3)
P1—O2	1.5570 (11)	C3—C4	1.368 (3)
P1—O4	1.6108 (12)	C3—H3	0.9300
P2—O5	1.4909 (11)	C4—C5	1.371 (3)
P2—O7	1.4933 (12)	C4—H4	0.9300
P2—O6	1.5529 (13)	C5—C6	1.387 (3)
P2—O4	1.6160 (13)	C5—H5	0.9300
O2—H2	0.8200	C6—H6A	0.9300
O6—H6	0.8200	C7—H7A	0.9600
O8—H2W	0.842 (9)	C7—H7B	0.9600
O8—H1W	0.842 (9)	C7—H7C	0.9600
O1—Co1—O1^{i}	180.00 (4)	Co1—O8—H1W	121 (2)
O1—Co1—O5	90.50 (5)	H2W—O8—H1W	111 (2)
O1^{i}—Co1—O5	89.50 (5)	C1—N1—H1A	109.5
O1—Co1—O5^{i}	89.50 (5)	C1—N1—H1B	109.5
O1^{i}—Co1—O5^{i}	90.50 (5)	H1A—N1—H1B	109.5
O5—Co1—O5^{i}	180.00 (3)	C1—N1—H1C	109.5
O1—Co1—O8	91.82 (6)	H1A—N1—H1C	109.5
O1^{i}—Co1—O8	88.18 (6)	H1B—N1—H1C	109.5
O5—Co1—O8	86.64 (6)	C6—C1—C2	122.21 (15)
O5^{i}—Co1—O8	93.36 (6)	C6—C1—N1	118.02 (14)
O1—Co1—O8^{i}	88.18 (6)	C2—C1—N1	119.77 (14)
O1^{i}—Co1—O8^{i}	91.82 (6)	C1—C2—C3	116.73 (17)
O5—Co1—O8^{i}	93.36 (6)	C1—C2—C7	122.34 (15)
O5^{i}—Co1—O8^{i}	86.64 (6)	C3—C2—C7	120.94 (17)
O8—Co1—O8^{i}	180.0	C4—C3—C2	122.00 (18)
O1—P1—O3	117.53 (7)	C4—C3—H3	119.0
O1—P1—O2	110.90 (7)	C2—C3—H3	119.0
O3—P1—O2	109.47 (7)	C3—C4—C5	119.95 (18)
O1—P1—O4	109.65 (7)	C3—C4—H4	120.0
O3—P1—O4	104.33 (7)	C5—C4—H4	120.0
O2—P1—O4	103.91 (7)	C4—C5—C6	119.9 (2)

O5—P2—O7	115.99 (7)	C4—C5—H5	120.1
O5—P2—O6	112.76 (7)	C6—C5—H5	120.1
O7—P2—O6	108.25 (7)	C1—C6—C5	119.22 (18)
O5—P2—O4	108.51 (6)	C1—C6—H6A	120.4
O7—P2—O4	108.93 (7)	C5—C6—H6A	120.4
O6—P2—O4	101.36 (7)	C2—C7—H7A	109.5
P1—O1—Co1	134.55 (7)	C2—C7—H7B	109.5
P1—O2—H2	109.5	H7A—C7—H7B	109.5
P1—O4—P2	129.26 (7)	C2—C7—H7C	109.5
P2—O5—Co1	132.40 (6)	H7A—C7—H7C	109.5
P2—O6—H6	109.5	H7B—C7—H7C	109.5
Co1—O8—H2W	114.2 (17)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O3^{ii}	0.82	1.75	2.5712 (17)	177
O2—H2···O7^{iii}	0.82	1.71	2.522 (2)	169
O8—H2*W*···O2^{iv}	0.84 (1)	1.98 (1)	2.8199 (18)	179 (3)
O8—H1*W*···O4^{ii}	0.84 (1)	2.20 (1)	3.020 (2)	164 (3)
N1—H1*A*···O7^{iv}	0.89	1.89	2.7788 (18)	177
N1—H1*B*···O5	0.89	2.31	3.0083 (19)	135
N1—H1*B*···O1^{i}	0.89	2.48	3.105 (2)	127
N1—H1*C*···O3^{ii}	0.89	1.94	2.821 (2)	168

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