

Silver diaquacobalt(II) catena-borodiphosphate(V) hydrate, (Ag_{0.79}Co_{0.11})-Co(H₂O)₂[BP₂O₈]₂·0.67H₂O

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{O}-\text{B}) = 0.009$ Å; disorder in main residue; R factor = 0.040; wR factor = 0.093; data-to-parameter ratio = 12.6.

The structure of the title compound, (Ag_{0.79}Co_{0.11})Co(H₂O)₂[BP₂O₈]₂·0.67H₂O is isotypic to that of its recently published counterparts AgMg(H₂O)₂[BP₂O₈]₂·H₂O and (Ag_{0.57}Ni_{0.22})-Ni(H₂O)₂[BP₂O₈]₂·0.67H₂O. It consists of infinite borophosphate helical ribbons [BP₂O₈]³⁻, built up from alternate BO₄ and PO₄ tetrahedra arranged around the 6₅ screw axes. The vertex-sharing BO₄ and PO₄ tetrahedra form a spiral ribbon of four-membered rings in which BO₄ and PO₄ groups alternate. The ribbons are connected through slightly distorted CoO₄(H₂O)₂ octahedra whose four O atoms belong to the phosphate groups. The resulting three-dimensional framework is characterized by hexagonal channels running along [001] in which the remaining water molecules are located. The main difference between the Mg-containing and the title structure lies in the filling ratio of Wyckoff positions 6a and 6b in the tunnels. The refinement of the occupancy rate of the site 6a shows that it is occupied by water at 67%, while the refinement of that of the site 6b shows that this site is partially occupied by 78.4% Ag and 10.8% Co, for a total of 82.2%. The structure is stabilized by O—H...O hydrogen bonds between water molecules and O atoms that are part of the helices.

Related literature

For the isotypic Mg and Ni analogues, see: Zouihri *et al.* (2011*a,b*); Menezes *et al.* (2008). For other similar borophosphates, see: Kniep *et al.* (1997, 1998); Ewald *et al.* (2007); Lin *et al.* (2008). For ionic radii, see: Shannon (1976).

Experimental

Crystal data

(Ag _{0.79} Co _{0.11})Co(H ₂ O) ₂ [BP ₂ O ₈] ₂ ·0.67H ₂ O	$V = 1213.5$ (4) Å ³
$M_r = 398.78$	$Z = 6$
Hexagonal, $P6_522$	Mo $K\alpha$ radiation
$a = 9.4321$ (11) Å	$\mu = 4.63$ mm ⁻¹
$c = 15.750$ (4) Å	$T = 296$ K
	$0.16 \times 0.12 \times 0.10$ mm

Data collection

Bruker APEXII CCD detector diffractometer	7995 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	974 independent reflections
$T_{\min} = 0.519$, $T_{\max} = 0.630$	748 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.096$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.093$	$\Delta\rho_{\text{max}} = 0.83$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.54$ e Å ⁻³
974 reflections	Absolute structure: Flack (1983),
77 parameters	340 Friedel pairs
1 restraint	Flack parameter: -0.05 (5)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A...O4 ⁱ	0.86	1.89	2.748 (6)	178
O5—H5B...O2	0.86	1.90	2.750 (6)	171
O6—H6A...O5 ⁱⁱ	0.88	2.44	3.139 (11)	137

Symmetry codes: (i) $-x + y, -x + 1, z + \frac{1}{5}$; (ii) $x - y + 1, -y + 2, -z + 2$.

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: ORTEP-3 for Windows (Farrugia, 1997) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2019).

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supporting information

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Silver diaquacobalt(II) *catena*-borodiphosphate(V) hydrate, (Ag_{0.79}Co_{0.11})Co(H₂O)₂[BP₂O₈]·0.67H₂O

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S1. Comment

A large group of borophosphates is known with a molar ratio of B:P = 1:2 and helical structure type, which consist of loop branched chain anions built from tetrahedral BO₄ and PO₄ units (Kniep *et al.*, (1998); Menezes *et al.*, (2008) and Lin *et al.* (2008)).

The aim of this work is the synthesis and the crystal structure of a new borophosphate-hydrate (Ag_{0.79}Co_{0.11})Co(H₂O)₂[BP₂O₈],0.67(H₂O), which is isotypic to the analogue nickel and magnesium borophosphates (Ag_{0.57}Ni_{0.22})Ni(H₂O)₂[BP₂O₈],0.67(H₂O); AgMg(H₂O)₂[BP₂O₈],H₂O recently published (Zouihri *et al.*, 2011*a*, 2011*bM^{(I)}M^{(II)}(H_2O)_2[BP_2O_8] \cdot H_2O ($M^{(I)}$ =Li, Na, K, NH₄⁺; $M^{(II)}$ = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd) (Kniep *et al.*, (1997) and Ewald *et al.*, (2007)).*

The anionic partial structure of the title compound contains one-dimensional infinite helices, [BP₂O₈]³⁻, which are wound around 6₅ axis. It is built up from alternate borate (BO₄) and phosphate (PO₄) tetrahedra, forming a spiral ribbon. The Co²⁺ cations have a slightly distorted octahedral oxygen coordination by four oxygen atoms from the phosphate anion and by two from water molecules as shown in Fig.1. The ribbons are interconnected through CoO₄(H₂O)₂ octahedra. The resulting 3-D framework shows hexagonal tunnels running along *c* direction where water molecules are located (Fig.2).

The main difference between the structure of this compound and that of his counterpart AgMg(H₂O)₂[BP₂O₈],H₂O lies in the filling ratio of the Wyckoff positions 6*a* and 6*b* in tunnels. Indeed, in this work, the refinement of the occupancy rate of the sites 6*a* and 6*b* (space group P6₅22) shows that the first is occupied by water at 67% and the second is partially occupied by 78.4% of Ag and 10.8% of Co for a total of 82.2%. Note that in this case, the sum of the occupancie rate is restrained to fit the charge balance. While in the case of AgMg(H₂O)₂[BP₂O₈],H₂O structure these two sites are completely occupied by H₂O and Ag⁺ respectively.

It is interesting to compare the lattice parameters and volumes of title compound (Table 1) with some borophosphates of this family like AgMg(H₂O)₂[BP₂O₈],H₂O ($a = 9.4577$ (4) Å, $c = 15.830$ (2)Å and $V = 1226.4$ (2)Å³) and (Ag_{0.57}Ni_{0.22})Ni(H₂O)₂[BP₂O₈],0.67(H₂O) ($a = 9.3848$ (6) Å, $c = 15.841$ (2)Å and $V = 1208.3$ (2)Å³). The ionic radii of Mg_{II}, Co_{II}, and Ni_{II} in the octahedral site are 0.72 Å, 0.74 Å and 0.69 Å, respectively (Shannon, 1976). The difference between these values is very small, therefore the filling rate of 6*a* and 6*b* sites by (Ag/ M_{II}) and H₂O, respectively, leads to the variation of the lattice parameters and volumes of these compounds. Indeed the obtained values for the title compound are between these of the two precedents borophosphates as expected.

The structure is stabilized by O—H···O hydrogen bonds between water molecules and O atoms that are part of the helices (Table 2).

S2. Experimental

The title borophosphate compound was hydrothermally synthesized at 453 °K for 7 days in a 25 ml Teflon-lined steel autoclave from the mixture of CoCO_3 , H_3BO_3 , H_3PO_4 (85%), AgNO_3 and 5 ml of distilled water in the molar ratio of 1:4:6:1:165. The reaction product was separated by filtration, washed with hot water and dried in air. The pink hexagonal bipyramid crystals obtained were up to 0.15 mm in length. Except for boron and hydrogen the presence of the elements were additionally confirmed by EDAX measurements. Indeed, the results of semi quantitative EDAX measurements are: Element, in At %: BK = 22.45; OK = 59.13; PK = 8.88; Ag L = 4.68, Co = 4.87 K. These values show a large excess of boron which is not surprising because the excess of boron comes from the synthesis of crystals.

S3. Refinement

The highest peak and the minimum peak in the difference map are at 0.89 Å and 0.98 Å respectively from Ag1 and P atoms. The O-bound H atom is initially located in a difference map and refined with O—H distance restraints of 0.86 (1). In the last cycle there is refined in the riding model approximation with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$. The 340 Friedel opposite reflections are not merged.

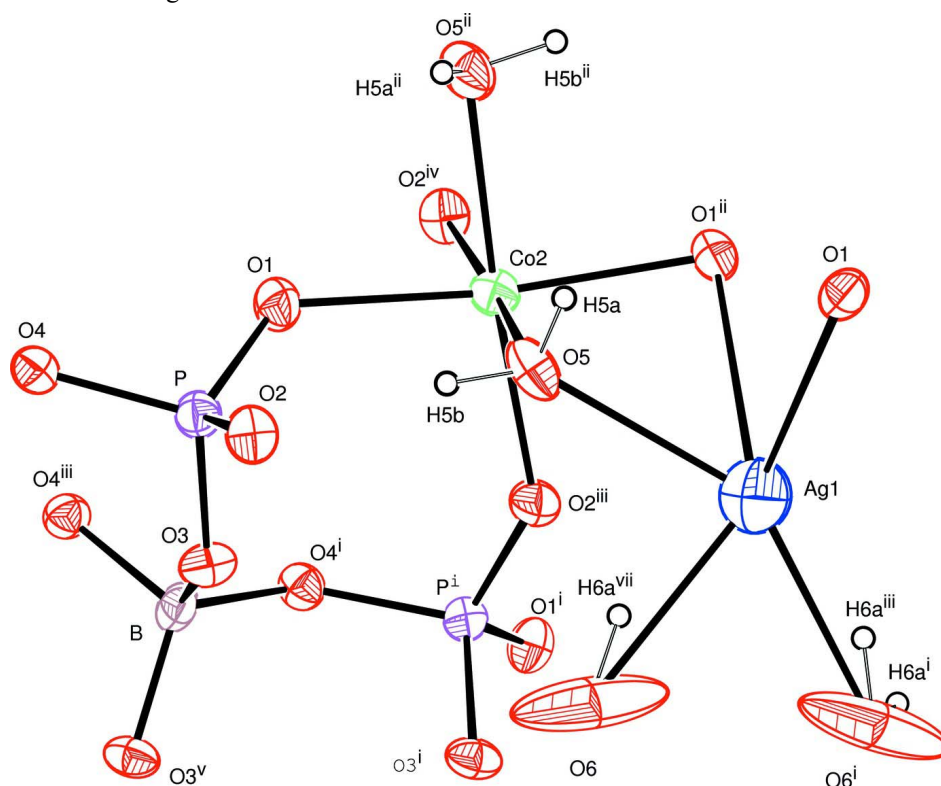


Figure 1

Partial plot of $(\text{Ag}_{0.79}\text{Co}_{0.11})\text{Co}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot 0.67(\text{H}_2\text{O})$ crystal structure showing polyhedra linkage. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-y + 1, -x + 1, -z + 13/6$; (ii) $y - 1, -x + y, z + 1/6$; (iii) $y - 1, x, -z + 5/3$; (iv) $x, x - y + 1, -z + 11/6$; (v) $-x + y - 1, y, -z + 3/2$; (vi) $-x, -x + y, -z + 4/3$; (vii) $y, x + 1, -z + 5/3$; (viii) $x - y + 1, -y + 2, -z + 2$.

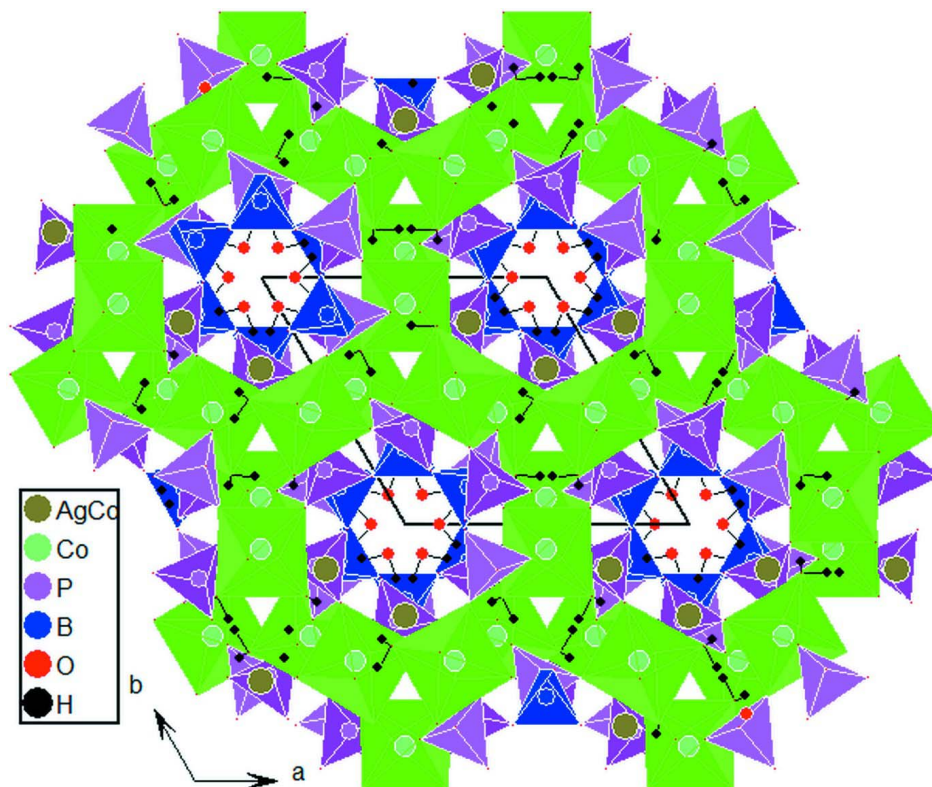


Figure 2

Projection view of the $(\text{Ag}_{0.79}\text{Co}_{0.11})\text{Co}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.67(\text{H}_2\text{O})$ framework structure showing tunnel running along c direction where water molecules are located.

Silver diaquacobalt(II) catena-borodiphosphate(V) hydrate

Crystal data

$(\text{Ag}_{0.79}\text{Co}_{0.11})\text{Co}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.67\text{H}_2\text{O}$

$M_r = 398.78$

Hexagonal, $P6_522$

Hall symbol: P 65 2 (0 0 1)

$a = 9.4321 (11) \text{ \AA}$

$c = 15.750 (4) \text{ \AA}$

$V = 1213.5 (4) \text{ \AA}^3$

$Z = 6$

$F(000) = 1155$

$D_x = 3.274 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 974 reflections

$\theta = 2.8\text{--}27.9^\circ$

$\mu = 4.63 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism, pink

$0.16 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker APEXII CCD detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1999)

$T_{\min} = 0.519$, $T_{\max} = 0.630$

7995 measured reflections

974 independent reflections

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

$R_{\text{int}} = 0.096$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -12 \rightarrow 11$

$k = -10 \rightarrow 12$

$l = -15 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.093$
 $S = 1.07$
 974 reflections
 77 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.3662P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.83 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 340 Friedel
 pairs
 Absolute structure parameter: $-0.05 (5)$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ag1	0.18406 (7)	0.81594 (7)	1.0833	0.0491 (4)	0.784 (3)
Co1	0.18406 (7)	0.81594 (7)	1.0833	0.0491 (4)	0.1082 (16)
Co2	0.10332 (14)	0.55166 (7)	0.9167	0.0195 (3)	
P	0.16844 (18)	0.77958 (17)	0.75218 (11)	0.0176 (3)	
B	-0.1524 (6)	0.6952 (12)	0.7500	0.019 (2)	
O1	0.1357 (6)	0.6203 (5)	0.7906 (2)	0.0224 (11)	
O2	0.3146 (5)	0.9298 (5)	0.7861 (2)	0.0214 (10)	
O3	0.0203 (5)	0.8048 (5)	0.7667 (3)	0.0195 (10)	
O4	0.1833 (5)	0.7642 (5)	0.6541 (2)	0.0184 (9)	
O5	0.2914 (5)	0.8033 (5)	0.9461 (3)	0.0263 (11)	
H5A	0.3808	0.8058	0.9599	0.039*	
H5B	0.3104	0.8472	0.8965	0.039*	
O6	0.1183 (13)	1.0000	1.0000	0.099 (6)	0.67
H6A	0.2180	1.0790	0.9885	0.148*	0.67

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0534 (6)	0.0534 (6)	0.0438 (7)	0.0292 (6)	-0.0038 (5)	-0.0038 (5)
Co1	0.0534 (6)	0.0534 (6)	0.0438 (7)	0.0292 (6)	-0.0038 (5)	-0.0038 (5)
Co2	0.0187 (6)	0.0184 (5)	0.0214 (5)	0.0093 (3)	0.000	0.0008 (5)
P	0.0170 (8)	0.0188 (8)	0.0170 (7)	0.0090 (6)	0.0001 (7)	0.0000 (7)
B	0.021 (4)	0.022 (5)	0.014 (4)	0.011 (3)	0.004 (4)	0.000

O1	0.028 (3)	0.022 (2)	0.018 (2)	0.012 (2)	0.0026 (18)	0.0037 (17)
O2	0.017 (2)	0.020 (2)	0.022 (2)	0.006 (2)	-0.0012 (17)	0.0000 (18)
O3	0.014 (2)	0.016 (2)	0.027 (2)	0.0063 (18)	-0.0020 (17)	-0.0056 (18)
O4	0.019 (2)	0.018 (2)	0.019 (2)	0.0094 (19)	-0.0011 (16)	0.0008 (16)
O5	0.022 (2)	0.026 (3)	0.027 (2)	0.009 (2)	-0.0065 (18)	0.0060 (19)
O6	0.032 (6)	0.075 (11)	0.204 (17)	0.038 (6)	-0.043 (6)	-0.085 (12)

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

Ag1—O5 ⁱ	2.414 (4)	P—O3	1.547 (4)
Ag1—O5	2.414 (4)	P—O4	1.564 (4)
Ag1—O6 ⁱ	2.489 (8)	B—O3 ^v	1.452 (7)
Ag1—O6	2.490 (8)	B—O3	1.452 (7)
Co2—O1	2.063 (4)	B—O4 ⁱⁱⁱ	1.475 (7)
Co2—O1 ⁱⁱ	2.063 (4)	B—O4 ^{vi}	1.475 (7)
Co2—O2 ⁱⁱⁱ	2.084 (4)	O2—Co2 ^{vii}	2.084 (4)
Co2—O2 ^{iv}	2.084 (4)	O4—B ^{vi}	1.475 (7)
Co2—O5	2.188 (4)	O5—H5A	0.8601
Co2—O5 ⁱⁱ	2.188 (4)	O5—H5B	0.8600
P—O2	1.497 (4)	O6—Ag1 ^{viii}	2.490 (8)
P—O1	1.502 (4)	O6—H6A	0.8785
O5 ⁱ —Ag1—O5	132.1 (2)	O1—P—O3	110.2 (3)
O5 ⁱ —Ag1—O6 ⁱ	79.6 (2)	O2—P—O4	111.0 (2)
O5—Ag1—O6 ⁱ	147.77 (18)	O1—P—O4	106.7 (2)
O5 ⁱ —Ag1—O6	147.77 (18)	O3—P—O4	106.8 (2)
O5—Ag1—O6	79.6 (2)	O3 ^v —B—O3	103.8 (7)
O6 ⁱ —Ag1—O6	69.9 (4)	O3 ^v —B—O4 ⁱⁱⁱ	113.5 (2)
O1—Co2—O1 ⁱⁱ	165.3 (3)	O3—B—O4 ⁱⁱⁱ	112.5 (2)
O1—Co2—O2 ⁱⁱⁱ	100.77 (16)	O3 ^v —B—O4 ^{vi}	112.5 (2)
O1 ⁱⁱ —Co2—O2 ⁱⁱⁱ	89.30 (16)	O3—B—O4 ^{vi}	113.5 (2)
O1—Co2—O2 ^{iv}	89.30 (16)	O4 ⁱⁱⁱ —B—O4 ^{vi}	101.5 (7)
O1 ⁱⁱ —Co2—O2 ^{iv}	100.77 (17)	P—O1—Co2	128.7 (3)
O2 ⁱⁱⁱ —Co2—O2 ^{iv}	94.3 (3)	P—O2—Co2 ^{vii}	139.9 (3)
O1—Co2—O5	87.21 (16)	B—O3—P	129.9 (4)
O1 ⁱⁱ —Co2—O5	82.44 (16)	B ^{vi} —O4—P	130.2 (4)
O2 ⁱⁱⁱ —Co2—O5	87.56 (18)	Co2—O5—Ag1	96.38 (15)
O2 ^{iv} —Co2—O5	176.30 (15)	Co2—O5—H5A	109.6
O1—Co2—O5 ⁱⁱ	82.44 (16)	Ag1—O5—H5A	101.7
O1 ⁱⁱ —Co2—O5 ⁱⁱ	87.21 (16)	Co2—O5—H5B	101.0
O2 ⁱⁱⁱ —Co2—O5 ⁱⁱ	176.31 (15)	Ag1—O5—H5B	141.3
O2 ^{iv} —Co2—O5 ⁱⁱ	87.56 (18)	H5A—O5—H5B	104.5
O5—Co2—O5 ⁱⁱ	90.8 (3)	Ag1—O6—Ag1 ^{viii}	106.6 (5)
O2—P—O1	115.7 (3)	Ag1—O6—H6A	99.5
O2—P—O3	106.1 (3)	Ag1 ^{viii} —O6—H6A	20.2

Symmetry codes: (i) $-y+1, -x+1, -z+13/6$; (ii) $x, x-y+1, -z+11/6$; (iii) $y-1, -x+y, z+1/6$; (iv) $y-1, x, -z+5/3$; (v) $-x+y-1, y, -z+3/2$; (vi) $-x, -x+y, -z+4/3$; (vii) $y, x+1, -z+5/3$; (viii) $x-y+1, -y+2, -z+2$.

Hydrogen-bond geometry (Å, °)

<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>
O5—H5A \cdots O4 ^{ix}	0.86	1.89	2.748 (6)	178
O5—H5B \cdots O2	0.86	1.90	2.750 (6)	171
O6—H6A \cdots O5 ^{viii}	0.88	2.44	3.139 (11)	137

Symmetry codes: (viii) $x-y+1, -y+2, -z+2$; (ix) $-x+y, -x+1, z+1/3$.