Crystal structure of $Na_4Co_{7-x}Al_{0.67x}(As_{1-y}P_yO_4)_6$ (x = 1.60; y = 0.116)

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The title compound, tetrasodium hepta(cobalt/aluminium) hexa(arsenate/phosphate), $Na_4Co_{5.40}Al_{1.07}(As_{0.883}P_{0.116}O_4)_6$, was prepared by a solid-state reaction. It is a new member of the family of isostructural compounds with the general formula $A_4M_7(XO_4)_6$ (A: Na, K; M: Ni, Co; X: P, As) that is most similar to $Na_4Co_{5.63}Al_{0.91}(AsO_4)_6$. The Co^{2+} ions in the title compound are substituted by Al^{3+} in a fully occupied octahedral site (site symmetry $2/m$) and a partially occupied tetrahedral site (site symmetry 2). A third octahedral site is fully occupied by Co^{2+} ions only. With regard to the P and As atoms, one site (site symmetry m) is simultaneously occupied by As and P, whereas in the second site there is only arsenic. The alkali cations are, as in the isostructural compounds, distributed over half-occupied crystallographic sites, with a positional disorder of one of them. The proposed structural model is based both on a careful investigation of the crystal data, as well as validation by means of bond-valence-sum (BVS) and charge-distribution (CHARDI) calculations. The correlation between the X-ray refinement and the validation results is discussed.

1. Chemical context

Metal-substituted aluminophosphates and aluminoarsenates form an important group of materials with many interesting properties such as molecular sieves, catalysts, *etc*. Li *et al.* (2012) reported the progress in heteroatom-containing aluminophosphate molecular sieves. With regard to their As homologues, one can cite $AlAsO_4$-5 and $AlAsO_4$-6, two aluminoarsenates with occluded ethylenediamine (Chen *et al.* 1990). The analogous cobalt compounds, such as ammonium-templated cobalt aluminophosphates with zeolite-like structures (Bontchev & Sevov, 1999), possess similar structural properties.

The title compound, $Na_4Co_{7-x}Al_{0.67x}(As_{1-y}P_yO_4)_6$ (x = 1.60; y = 0.116), was obtained during the exploration of the Na–Co–P–As–O system by solid-state reaction; as for many aluminophosphates, aluminum was incorporated from the reaction container. The chemical composition and crystal structure were determined by energy-dispersive X-ray spectroscopy (EDX) analysis (Fig. 1) and single-crystal X-ray diffraction; the proposed structural model is supported by validation tools by means of bond-valence-sum (BVS) calculations and charge-distribution (CHARDI) analysis (Brown, 2002; Adams, 2003, Nespolo, 2015, 2016; Eon & Nespolo, 2015). The correlation between the experimental and the validation results is discussed.
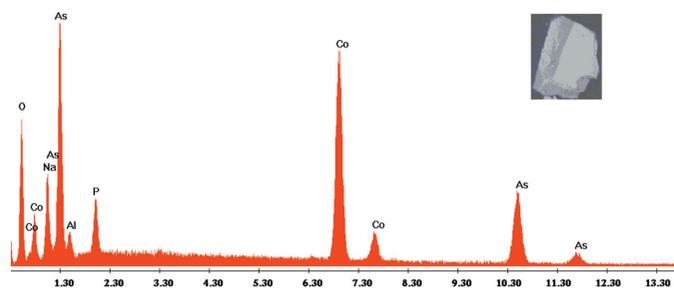

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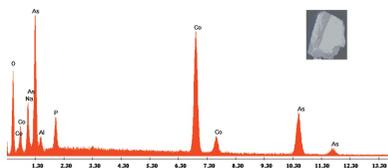
Figure 1
The EDX spectrum of the title compound. The inset shows the morphology of one crystal.

2. Structural commentary

The title compound is a new member of the isostructural compounds family with the general formula $A_4M_7(XO_4)_6$ (A: Na, K; M: Ni, Co; X: P, As) (Moring & Kostiner, 1986; Kobashi et al., 1998; Ben Smail et al., 1999; Marzouki et al., 2010, 2013).

The asymmetric unit of the title compound (I) (Fig. 2) contains seven metallic sites of which four are occupied by Na$^+$ cations (occupancies ranging from 0.23 to 0.50) with eight cations per unit cell, two others (denoted M_A and M_B) are simultaneously shared by Co^{2+} and Al^{3+} ions, and one is fully occupied by Co^{2+} ions: the same distribution is observed in the homologous arsenate Na$_4$Co$_{7-x}$Al$_{0.67x}$(AsO$_4$)$_6$ ($x = 1.37$) (II) (Marzouki et al., 2010).

3. Validation of the structural model using BVS and CHARDI

Two validation tools, BVS and CHARDI, are used to support and analyse the proposed structural model. Briefly, for a properly refined structure, the valences V according to the

Table 1
BVS and CHARDI analysis of cation polyhedra in the title compound (the structure described as being built of cation-centred polyhedra).

Cation	$q(i)\cdot$sof$i$	Vi	Qi	CNi	ECoNi
M_A	2.81	2.97	2.91	6	5.92
M_B	1.61	1.31	1.58	4	3.95
Co3	2.00	2.05	1.99	6	5.88
M_C	5.00	5.21	5.00	4	3.97
As2	5.00	5	5.09	4	3.98
Na1	0.50	0.51	0.49	5	4.53
Na2	0.50	0.52	0.49	7	6.18
Na31	0.23	0.23	0.23	7	6.06
Na32	0.27	0.28	0.27	6	5.31

Notes: M_A = Co$_{0.189}$Al$_{0.811}$; M_B = Co$_{0.605}$Al$_{0.135}$□$_{0.260}$; M_c = As$_{0.65}$P$_{0.35}$; q is the formal oxidation number; sof is the site-occupation factor; MAPD = 1% [the mean absolute percentage deviation MAPD measures the agreement between q and Q; for more information, see Nespolo (2016)].

BVS model and charges Q from the CHARDI analysis should agree with the oxidation states of the atoms (Brown, 2002; Adams, 2003, Nespolo, 2015, 2016; Eon & Nespolo, 2015).

The M_A site, with an octahedral environment by oxygen atoms, is fully occupied by the two cations with overall occupancy Co$_{0.189}$Al$_{0.811}$. This distribution scheme is confirmed by the validation tools, with a better convergence with the CHARDI model (Table 1). If compared to the homologous site in (II) with overall occupancy Co$_{0.286}$Al$_{0.714}$ (Marzouki et al., 2010), the average arithmetic distance in (I) (1.91 Å) is smaller than in (II) (1.96 Å) due to the higher fraction of the small cation (Al^{3+}) in (I).

For the M_B site with a tetrahedral coordination, the Co^{2+}/Al^{3+} distribution is based on the same observations as in (II), mainly if it is refined as partially occupied by just Co^{2+}, the charge neutrality is not achieved, and then a fraction of Al^{3+} was introduced in the M_B site yielding an overall occupancy distribution of Co$_{0.605}$Al$_{0.135}$□$_{0.260}$, with □ expressing the vacancy. The validation results for this particular distribution are: $V(M_B)$ = 1.31 and $Q(M_B)$ = 1.58, the theoretical value is 1.61 (Table 1). Finally, with regard to P and As atoms, the P/As substitutional disorder is observed in one of the two sites (M_C): P/As = 0.35/0.65; V = 5.21 and Q = 5.00.

The final result corresponds to the formula Na$_4$Co$_{5.40}$Al$_{1.07}$(As$_{0.883}$P$_{0.116}$O$_4$)$_6$. It is the first case in its
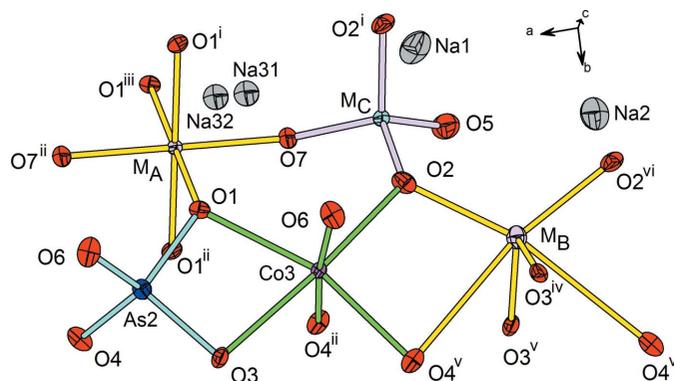

Figure 2
The asymmetric unit of (I), showing the atom-labelling scheme. The full coordination polyhedra are shown, including the corresponding symmetry-related O atoms. Displacement ellipsoids are drawn at the 50% probability level. [M_A = Co$_{0.189}$Al$_{0.811}$; M_B = Co$_{0.605}$Al$_{0.135}$□$_{0.260}$; M_C = As$_{0.65}$P$_{0.35}$. Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, -z$; (iii) $-x, -y, -z$; (iv) $-\frac{1}{2} - x, \frac{1}{2} - y, z$; (v) $-\frac{1}{2} - x, \frac{1}{2} - y, -z$; (vi) $-1 - x, y, -z$.]
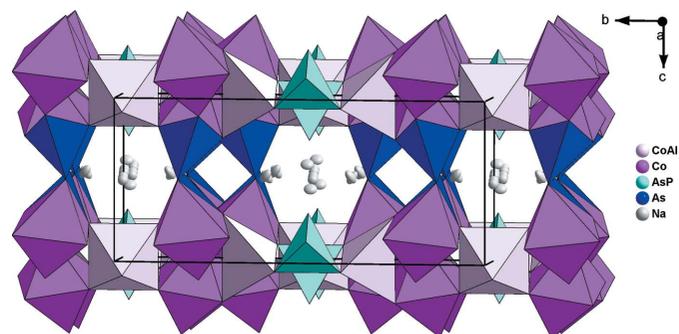

Figure 3
The structure of the title compound viewed appoximately along [100], showing the tunnels and the Na$^+$ cations.

Table 2
Experimental details.

Crystal data	
Chemical formula	$Na_4Co_{5.40}Al_{1.07}(As_{0.883}P_{0.116}O_4)_6$
M_r	1242.08
Crystal system, space group	Monoclinic, $C2/m$
Temperature (K)	293
a, b, c (Å)	10.5797 (2), 14.5528 (3), 6.6441 (3)
β (°)	105.608 (9)
V (Å^3)	985.23 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	13.60
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.055, 0.140
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2409, 1124, 894
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.083, 1.07
No. of reflections	1124
No. of parameters	117
No. of restraints	2
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.81, −0.85

Computer programs: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

homologous family which contains such a number of elements. The similarity to (II) (Marzouki *et al.*, 2010) is clear, the cell parameters of (I) are smaller than those of (II) as it contains more small elements than (II). The CHARDI method is extended, as for (II), to analyse the coordination polyhedra by means of the Effective Coordination Numbers (ECoN): the polyhedron distortion is more pronounced if the ECoN deviates more from the classical coordination number (CN).

The framework of the title compound is of an open character (Fig. 3). Its aptitude for sodium conduction through the tunnels appears to be possible, as shown in experimental and theoretical studies for the similar compound (II) (Marzouki *et al.*, 2013). These studies will be the subject of future works.

4. Synthesis and crystallization

A mixture of sodium nitrate, cobalt nitrate hexahydrate, $NH_4H_2XO_4$ (*X*: P, As) in the molar ratio Na:Co:P:As = 2:1:0.5:1 was dissolved in deionized water and then heated at 373 K to dehydration. After grinding, it was placed in a porcelain boat and first heated at 673 K in air for 24 h and then heated gradually to 1123 K for 1 d. Some pink parallelepiped-shaped crystals were isolated from the sample. A qualitative EDX analysis confirmed the presence of Na, Co, Al, As and O

(Fig. 1), with the aluminium diffusing from the reaction container.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The Co and Al atoms occupying the M_A and M_B sites, as well as the P and As atoms occupying the M_C site, were constrained using the EXYZ and EADP instructions of *SHELXL97* (Sheldrick, 2008). Three linear free variable restraints (SUMP) were required to restrain the sum of their occupation factors. The Na1 and Na2 cations are at half-occupancy sites and the two others (Na31 and Na32) with isotropic refinement have a total occupancy of 0.50 because, when refined freely, their occupations converged to these values.

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supporting information

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Computing details

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Tetrasodium hepta(cobalt/aluminium) hexa(arsenate/phosphate)

Crystal data

Na$_4$Co$_{5.40}$Al$_{1.07}$(As$_{0.883}$P$_{0.116}$O$_4$)$_6$	$F(000) = 1162$
$M_r = 1242.08$	$D_x = 4.187$ Mg m^{-3}
Monoclinic, $C2/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.5797$ (2) Å	Cell parameters from 25 reflections
$b = 14.5528$ (3) Å	$\theta = 12.0$–$14.8°$
$c = 6.6441$ (3) Å	$\mu = 13.60$ mm^{-1}
$\beta = 105.608$ (9)°	$T = 293$ K
$V = 985.23$ (7) Å^3	Parallelepiped, pink
$Z = 2$	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	894 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.027$
Absorption correction: ψ scan (North *et al.*, 1968)	$\theta_{max} = 27.0°$, $\theta_{min} = 2.4°$
	$h = -13\rightarrow13$
$T_{min} = 0.055$, $T_{max} = 0.140$	$k = -1\rightarrow18$
2409 measured reflections	$l = -8\rightarrow8$
1124 independent reflections	2 standard reflections every 120 reflections
	intensity decay: 1%

Refinement

Refinement on F^2	2 restraints
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 10.5538P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.083$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.81$ e Å^{-3}
1124 reflections	$\Delta\rho_{min} = -0.85$ e Å^{-3}
117 parameters	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Co1	0.0000	0.0000	0.0000	0.0064 (9)	0.189 (13)
Al1	0.0000	0.0000	0.0000	0.0064 (9)	0.811 (13)
Co2	−0.5000	0.16324 (13)	0.0000	0.0118 (6)	0.605 (9)
Al2	−0.5000	0.16324 (13)	0.0000	0.0118 (6)	0.135 (9)
Co3	−0.18046 (7)	0.18027 (5)	0.17925 (10)	0.0062 (2)	
As1	−0.32397 (10)	0.0000	−0.06479 (16)	0.0091 (4)	0.649 (7)
P1	−0.32397 (10)	0.0000	−0.06479 (16)	0.0091 (4)	0.351 (7)
As2	0.09963 (5)	0.17931 (4)	0.29004 (8)	0.00940 (18)	
Na1	−0.4220 (5)	−0.1148 (4)	−0.5048 (8)	0.0258 (12)	0.5
Na2	−0.6741 (7)	0.0000	−0.4195 (11)	0.0217 (16)	0.5
Na31	−0.084 (3)	0.0000	0.469 (3)	0.017 (2)*	0.229 (19)
Na32	−0.036 (2)	0.0000	0.487 (2)	0.017 (2)*	0.271 (19)
O1	−0.0101 (4)	0.0937 (3)	0.2026 (6)	0.0090 (8)	
O2	−0.3346 (4)	0.0895 (3)	0.0802 (6)	0.0127 (8)	
O3	−0.0063 (4)	0.2670 (3)	0.2696 (6)	0.0100 (8)	
O4	0.1921 (4)	0.2070 (3)	0.1327 (6)	0.0111 (8)	
O5	−0.4356 (6)	0.0000	−0.2789 (10)	0.0202 (14)	
O6	0.1900 (4)	0.1511 (3)	0.5228 (6)	0.0134 (9)	
O7	−0.1813 (6)	0.0000	−0.1116 (10)	0.0141 (13)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0061 (14)	0.0053 (15)	0.0075 (14)	0.000	0.0013 (9)	0.000
Al1	0.0061 (14)	0.0053 (15)	0.0075 (14)	0.000	0.0013 (9)	0.000
Co2	0.0103 (8)	0.0146 (10)	0.0102 (9)	0.000	0.0021 (6)	0.000
Al2	0.0103 (8)	0.0146 (10)	0.0102 (9)	0.000	0.0021 (6)	0.000
Co3	0.0065 (3)	0.0070 (4)	0.0048 (3)	0.0004 (3)	0.0007 (3)	0.0005 (3)
As1	0.0070 (5)	0.0067 (6)	0.0131 (6)	0.000	0.0019 (4)	0.000
P1	0.0070 (5)	0.0067 (6)	0.0131 (6)	0.000	0.0019 (4)	0.000
As2	0.0090 (3)	0.0115 (3)	0.0070 (3)	−0.0007 (2)	0.0010 (2)	0.0008 (2)
Na1	0.026 (3)	0.020 (3)	0.027 (3)	0.005 (2)	0.001 (2)	−0.011 (2)
Na2	0.022 (4)	0.029 (5)	0.018 (4)	0.000	0.012 (3)	0.000
O1	0.0112 (17)	0.0083 (19)	0.0072 (18)	−0.0014 (15)	0.0018 (14)	−0.0006 (16)
O2	0.0149 (19)	0.011 (2)	0.0122 (19)	−0.0039 (16)	0.0043 (15)	−0.0052 (17)
O3	0.0076 (18)	0.010 (2)	0.0112 (19)	0.0023 (16)	0.0002 (14)	−0.0004 (16)
O4	0.0150 (19)	0.016 (2)	0.0041 (18)	−0.0056 (17)	0.0050 (15)	−0.0040 (16)
O5	0.019 (3)	0.016 (4)	0.022 (3)	0.000	0.000 (3)	0.000
O6	0.0145 (19)	0.023 (2)	0.0022 (17)	0.0030 (18)	0.0009 (15)	−0.0017 (16)

O7	0.009 (3)	0.011 (3)	0.023 (3)	0.000	0.006 (2)	0.000

Geometric parameters (Å, º)

Co1—O7[i]	1.861 (6)	Na2—Na1[ix]	2.086 (8)
Co1—O7	1.861 (6)	Na2—Na1[xi]	2.086 (8)
Co1—O1	1.939 (4)	Na2—O5	2.443 (10)
Co1—O1[i]	1.939 (4)	Na2—Na31[xii]	2.49 (3)
Co1—O1[ii]	1.939 (4)	Na2—O5[ix]	2.572 (10)
Co1—O1[iii]	1.939 (4)	Na2—O2[iv]	2.584 (7)
Co2—O2[iv]	1.999 (4)	Na2—O2[xii]	2.584 (7)
Co2—O2	1.999 (4)	Na2—O6[xiii]	2.598 (6)
Co2—O3[v]	2.075 (4)	Na2—O6[xiv]	2.598 (6)
Co2—O3[vi]	2.075 (4)	Na2—Na32[xii]	2.98 (2)
Co3—O6[vii]	2.054 (4)	Na31—Na32[xv]	1.23 (5)
Co3—O2	2.064 (4)	Na31—Na31[xv]	1.72 (6)
Co3—O4[iii]	2.080 (4)	Na31—O6[xv]	2.473 (15)
Co3—O4[v]	2.092 (4)	Na31—O6[vii]	2.473 (15)
Co3—O1	2.171 (4)	Na31—Na2[xii]	2.49 (3)
Co3—O3	2.181 (4)	Na31—O1	2.524 (17)
As1—O5	1.586 (6)	Na31—O1[ii]	2.524 (17)
As1—O7	1.621 (6)	Na31—O1[vii]	2.536 (17)
As1—O2[ii]	1.642 (4)	Na31—O1[xv]	2.536 (17)
As1—O2	1.642 (4)	Na32—Na32[xv]	0.73 (4)
As2—O6	1.637 (4)	Na32—Na31[xv]	1.23 (5)
As2—O4	1.662 (4)	Na32—O1[vii]	2.408 (13)
As2—O3	1.680 (4)	Na32—O1[xv]	2.408 (13)
As2—O1	1.695 (4)	Na32—O1	2.407 (13)
Na1—O5	2.276 (7)	Na32—O1[ii]	2.407 (13)
Na1—O3[viii]	2.298 (7)	Na32—O6[xv]	2.727 (14)
Na1—O5[ix]	2.441 (7)	Na32—O6[vii]	2.727 (14)
Na1—O6[i]	2.545 (7)	Na32—Na2[xii]	2.98 (2)
Na1—O3[x]	2.572 (8)		
O7[i]—Co1—O7	180.0	O2[iv]—Co2—O3[vi]	105.15 (15)
O7[i]—Co1—O1	88.09 (17)	O2—Co2—O3[vi]	105.29 (15)
O7—Co1—O1	91.91 (17)	O3[v]—Co2—O3[vi]	121.5 (2)
O7[i]—Co1—O1[i]	91.91 (17)	O6[vii]—Co3—O2	86.29 (16)
O7—Co1—O1[i]	88.09 (17)	O6[vii]—Co3—O4[iii]	173.90 (16)
O1—Co1—O1[i]	180.0	O2—Co3—O4[iii]	88.41 (16)
O7[i]—Co1—O1[ii]	88.09 (17)	O6[vii]—Co3—O4[v]	96.19 (16)
O7—Co1—O1[ii]	91.91 (17)	O2—Co3—O4[v]	91.84 (17)
O1—Co1—O1[ii]	89.4 (2)	O4[iii]—Co3—O4[v]	80.95 (17)
O1[i]—Co1—O1[ii]	90.6 (2)	O6[vii]—Co3—O1	93.80 (16)
O7[i]—Co1—O1[iii]	91.91 (17)	O2—Co3—O1	102.77 (16)
O7—Co1—O1[iii]	88.09 (17)	O4[iii]—Co3—O1	90.31 (15)
O1—Co1—O1[iii]	90.6 (2)	O4[v]—Co3—O1	162.79 (16)
O1[i]—Co1—O1[iii]	89.4 (2)	O6[vii]—Co3—O3	96.40 (16)

O1^{ii}—Co1—O1^{iii}	180.0 (3)	O2—Co3—O3	174.29 (16)
O2^{iv}—Co2—O2	115.1 (3)	O4^{iii}—Co3—O3	89.15 (16)
O2^{iv}—Co2—O3^{v}	105.29 (15)	O4^{v}—Co3—O3	92.87 (16)
O2—Co2—O3^{v}	105.15 (15)	O1—Co3—O3	72.08 (15)

Symmetry codes: (i) −x, −y, −z; (ii) x, −y, z; (iii) −x, y, −z; (iv) −x−1, y, −z; (v) x−1/2, −y+1/2, z; (vi) −x−1/2, −y+1/2, −z; (vii) −x, y, −z+1; (viii) x−1/2, y−1/2, z−1; (ix) −x−1, −y, −z−1; (x) −x−1/2, y−1/2, −z; (xi) −x−1, y, −z−1; (xii) −x−1, −y, −z; (xiii) x−1, −y, z−1; (xiv) x−1, y, z−1; (xv) −x, −y, −z+1.