

# Crystal structure of $\text{Na}_4\text{Co}_{7-x}\text{Al}_{0.67x}(\text{As}_{1-y}\text{P}_y\text{O}_4)_6$ ( $x = 1.60$ ; $y = 0.116$ )

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Received 3 March 2016

Accepted 9 March 2016

Edited by I. D. Brown, McMaster University, Canada

**Keywords:** crystal structure;  $\text{Na}_4\text{Co}_{5.40}\text{Al}_{1.07}(\text{As}_{0.883}\text{P}_{0.116}\text{O}_4)_6$ ; bond-valence sum; charge distribution.

**CCDC reference:** 1462882

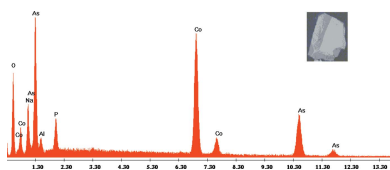
**Supporting information:** this article has supporting information at journals.iucr.org/e

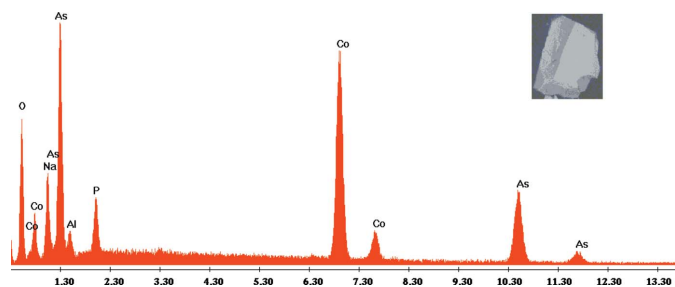
The title compound, tetrasodium hepta(cobalt/aluminium) hexa(arsenate/phosphate),  $\text{Na}_4\text{Co}_{5.40}\text{Al}_{1.07}(\text{As}_{0.883}\text{P}_{0.116}\text{O}_4)_6$ , was prepared by a solid-state reaction. It is a new member of the family of isostructural compounds with the general formula  $A_4M_7(\text{XO}_4)_6$  ( $A$ : Na, K;  $M$ : Ni, Co;  $X$ : P, As) that is most similar to  $\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.91}(\text{AsO}_4)_6$ . The  $\text{Co}^{2+}$  ions in the title compound are substituted by  $\text{Al}^{3+}$  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  $\text{Co}^{2+}$  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  $\text{AlAsO}_4\cdot 5$  and  $\text{AlAsO}_4\cdot 6$ , 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,  $\text{Na}_4\text{Co}_{7-x}\text{Al}_{0.67x}(\text{As}_{1-y}\text{P}_y\text{O}_4)_6$  ( $x = 1.60$ ;  $y = 0.116$ ), 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.





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

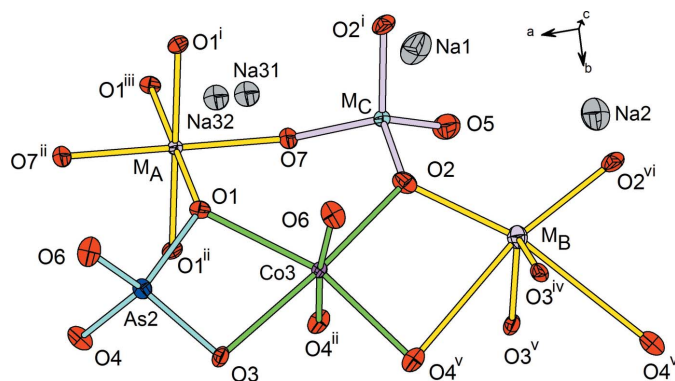
## 2. Structural commentary

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  $Na_4Co_{7-x}Al_{0.67x}(AsO_4)_6$  ( $x = 1.37$ ) (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



**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. [ $M_A = Co_{0.189}Al_{0.811}$ ;  $M_B = Co_{0.605}Al_{0.135}\square_{0.260}$ ;  $M_C = As_{0.65}P_{0.35}$ . 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)  $-1 - x, y, -z$ .]

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

Cation	$q(i)$ -sofi	$V_i$	$Q_i$	CNi	ECoNi
$M_A$	2.81	2.97	2.91	6	5.92
$M_B$	1.61	1.31	1.58	4	3.95
$Co_3$	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

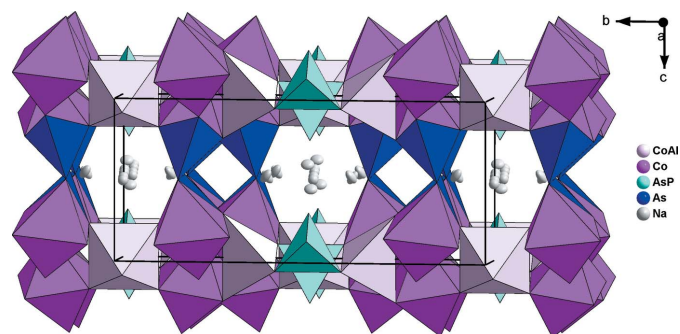
Notes:  $M_A = Co_{0.189}Al_{0.811}$ ;  $M_B = Co_{0.605}Al_{0.135}\square_{0.260}$ ;  $M_C = As_{0.65}P_{0.35}$ ;  $q$  is the formal oxidation number; sofi is the site-occupation factor; MAPD = 1% [the mean absolute percentage deviation MAPD measures the agreement between  $q$  and  $Q$ ; for more 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  $Co_{0.605}Al_{0.135}\square_{0.260}$ , with  $\square$  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  $Na_4Co_{5.40}Al_{1.07}(As_{0.883}P_{0.116}O_4)_6$ . It is the first case in its



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

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	Na <sub>4</sub> Co <sub>5.40</sub> Al <sub>1.07</sub> (As <sub>0.883</sub> P <sub>0.116</sub> O <sub>4</sub> ) <sub>6</sub>
<i>M<sub>r</sub></i>	1242.08
Crystal system, space group	Monoclinic, <i>C2/m</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.5797 (2), 14.5528 (3), 6.6441 (3)
$\beta$ (°)	105.608 (9)
<i>V</i> (Å <sup>3</sup> )	985.23 (7)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	13.60
Crystal size (mm)	0.30 × 0.20 × 0.20
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	$\psi$ scan (North <i>et al.</i> , 1968)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.055, 0.140
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	2409, 1124, 894
<i>R</i> <sub>int</sub>	0.027
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.638
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	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 <sup>-3</sup> )	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<sub>4</sub>H<sub>2</sub>XO<sub>4</sub> (*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<sub>A</sub>* and *M<sub>B</sub>* sites, as well as the P and As atoms occupying the *M<sub>C</sub>* 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.

#### Acknowledgements

The authors are grateful to Professor M. F. Zid, Université Tunis El Manar, Faculté des Sciences, for the X-ray data and to Professor M. Nespolo, Kyoto University, Faculty of Sciences, for fruitful discussions.

#### References

- Adams, S. (2003). *softBV*. University of Göttingen, Germany. <http://kristall.uni-mki.gwdg.de/softBV/>.
- Ben Smail, R., Driss, A. & Jouini, T. (1999). *Acta Cryst.* **C55**, 284–286.
- Bontchev, R. P. & Sevov, S. C. (1999). *J. Mater. Chem.* **9**, 2679–2682.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry – The Bond Valence Model. IUCr Monographs on Crystallography*, 12. Oxford University Press.
- Chen, J., Xu, R., Xu, Y. & Qiu, J. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3319–3323.
- Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
- Eon, J.-G. & Nespolo, M. (2015). *Acta Cryst.* **B71**, 34–47.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Kobashi, D., Kohara, S., Yamakawa, J. & Kawahara, A. (1998). *Acta Cryst.* **C54**, 7–9.
- Li, J., Yu, J. & Xu, R. (2012). *Proc. R. Soc. A*, **468**, 1955–1967.
- Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
- Marzouki, R., Guesmi, A. & Driss, A. (2010). *Acta Cryst.* **C66**, i95–i98.
- Marzouki, R., Guesmi, A., Zid, M. F. & Driss, A. (2013). *J. Inorg. Chem.* pp. 9–16.
- Moring, J. & Kostiner, E. (1986). *J. Solid State Chem.* **62**, 105–111.
- Nespolo, M. (2015). *CHARDI-2015*. <http://www.crystallography.fr/chardi>.
- Nespolo, M. (2016). *Acta Cryst.* **B72**, 51–66.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2016). E72, 495-497 [doi:10.1107/S205698901600400X]

## Crystal structure of $\text{Na}_4\text{Co}_{7-x}\text{Al}_{0.67x}(\text{As}_{1-y}\text{P}_y\text{O}_4)_6$ ( $x = 1.60$ ; $y = 0.116$ )

Chokri Issaoui, Hammouda Chebbi and Abderrahmen Guesmi

### 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 *pubCIF* (Westrip, 2010).

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

#### Crystal data

$\text{Na}_4\text{Co}_{5.40}\text{Al}_{1.07}(\text{As}_{0.883}\text{P}_{0.116}\text{O}_4)_6$

$M_r = 1242.08$

Monoclinic,  $C2/m$

$a = 10.5797$  (2) Å

$b = 14.5528$  (3) Å

$c = 6.6441$  (3) Å

$\beta = 105.608$  (9)°

$V = 985.23$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 1162$

$D_x = 4.187$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 12.0\text{--}14.8^\circ$

$\mu = 13.60$  mm<sup>-1</sup>

$T = 293$  K

Parallelepiped, pink

$0.30 \times 0.20 \times 0.20$  mm

#### Data collection

Enraf-Nonius CAD-4  
diffractometer

$\omega/2\theta$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$T_{\min} = 0.055$ ,  $T_{\max} = 0.140$

2409 measured reflections

1124 independent reflections

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

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -13 \rightarrow 13$

$k = -1 \rightarrow 18$

$l = -8 \rightarrow 8$

2 standard reflections every 120 reflections

intensity decay: 1%

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.083$

$S = 1.07$

1124 reflections

117 parameters

2 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 10.5538P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.81$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.85$  e Å<sup>-3</sup>

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)

07	0.009 (3)	0.011 (3)	0.023 (3)	0.000	0.006 (2)	0.000
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*Geometric parameters (Å, °)*

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

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O1 <sup>ii</sup> —Co1—O1 <sup>iii</sup>	180.0 (3)	O2—Co3—O3	174.29 (16)
O2 <sup>iv</sup> —Co2—O2	115.1 (3)	O4 <sup>iii</sup> —Co3—O3	89.15 (16)
O2 <sup>iv</sup> —Co2—O3 <sup>v</sup>	105.29 (15)	O4 <sup>v</sup> —Co3—O3	92.87 (16)
O2—Co2—O3 <sup>v</sup>	105.15 (15)	O1—Co3—O3	72.08 (15)

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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)  $-x, -y, -z+1$ .