

The novel arsenate $\text{Na}_4\text{Co}_{7-x}\text{Al}_{2/3x}\text{-(AsO}_4)_6$ ($x = 1.37$): crystal structure, charge-distribution and bond-valence-sum investigations

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The title compound, tetrasodium cobalt aluminium hexaarsenate, $\text{Na}_4\text{Co}_{7-x}\text{Al}_{2/3x}(\text{AsO}_4)_6$ ($x = 1.37$), is isostructural with $\text{K}_4\text{Ni}_7(\text{AsO}_4)_6$; however, in its crystal structure, some of the Co^{2+} ions 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. One of the two independent tetrahedral As atoms and two of its attached O atoms reside on a mirror plane, as do two of the three independent Na^+ cations, all of which are present at half-occupancy. The proposed structural model based on a careful investigation of the crystal data is supported by charge-distribution (CHARDI) analysis and bond-valence-sum (BVS) calculations. The correlation between the X-ray refinement and the validation results is discussed.

Comment

Metal-substituted aluminophosphates constitute an interesting group of materials widely used as molecular sieves with catalytic and adsorptive properties. The cobalt analogue compounds possess the same structural properties, for example, the mixed cobalt aluminium phosphate $\text{K}(\text{Co}^{\text{II}},\text{Al})_2(\text{PO}_4)_2$, which contains only tetrahedrally coordinated Co/Al sites and a three-dimensional system of interconnected tunnels (Chen *et al.*, 1997), and the two ammonium-templated cobalt aluminophosphates $(\text{NH}_4)_2[(\text{OH})_{0.95}(\text{H}_2\text{O})_{0.05}]_2[\text{Co}_{0.05}\text{Al}_{0.95}]_2(\text{PO}_4)_2$ and $(\text{NH}_4)[(\text{OH})_{0.95}(\text{H}_2\text{O})_{0.05}][\text{Co}_{0.025}\text{Al}_{0.975}]_2 \cdot 2\text{H}_2\text{O}$ with zeolite-like structures (Bontchev & Sevov, 1999). During an exploration of the Na–Co–As–O system, and in an attempt to prepare the arsenic homologue of $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ (Kobashi *et al.*, 1998), the new compound $\text{Na}_4\text{Co}_{7-x}\text{Al}_{2/3x}(\text{AsO}_4)_6$ ($x = 1.37$), (I), was isolated and its composition determined by single-crystal X-ray diffraction. It should be

noted that, as for the three already mentioned aluminophosphates, the incorporation of aluminium from the reaction container could occur. We report herein the synthesis and crystal structure of (I), together with charge-distribution (CHARDI) and bond-valence-sum (BVS) calculations that validate the X-ray composition.

The asymmetric unit of (I) (Fig. 1) contains six metallic sites of which three are half-occupied by Na^+ cations (eight cations per unit cell), two others (denoted $M1$ and $M2$) are simultaneously shared by Co^{2+} and Al^{3+} ions, and one is fully occupied by Co^{2+} ions. The fact that Co^{2+} and Al^{3+} ions are distributed over the two M positions was determined based on examination of the displacement ellipsoids, residual peaks and interatomic distances. Aluminium cations share with cobalt the $2b$ Wyckoff position at the centre of an octahedron with a fully occupied scheme and this position with overall occupancy $\text{Co}_{0.286}\text{Al}_{0.714}$ is denoted as $M1$. The substitution of the smaller Al^{3+} cations results in a reduction of the $M1\text{—O}$ bond distances compared to what would be found in a pure Co^{2+} octahedron, thus supporting the mixing of Co^{2+} and Al^{3+} at this site.

For the second site, denoted $M2$, the $\text{Co}^{2+}/\text{Al}^{3+}$ ions are tetrahedrally coordinated by O atoms with an arithmetic average distance of $\langle M2\text{—O} \rangle = 2.13 \text{ \AA}$. As the interatomic distances are notably larger than those of a pure Co^{2+} tetrahedron [such as that in the phosphorus homologue (Kobashi *et al.*, 1998), in which $\langle \text{Co—O} \rangle = 2.01 \text{ \AA}$], the displacement parameters were large for a fully occupied cobalt site, and a deep hole of -3.44 e \AA^{-3} was localized in the difference Fourier map at a distance of 0.52 \AA from the $M2$ position; therefore, the $M2$ site was initially refined as being partially occupied by cobalt ions, yielding an occupancy of just under 72%. If the site is partially occupied by just Co^{2+} , this occupancy is insufficient to achieve charge neutrality in the empirical formula that would then arise, $[\text{Na}_4\text{Co}_{5.715}\text{Al}_{0.715}(\text{AsO}_4)_6]$.

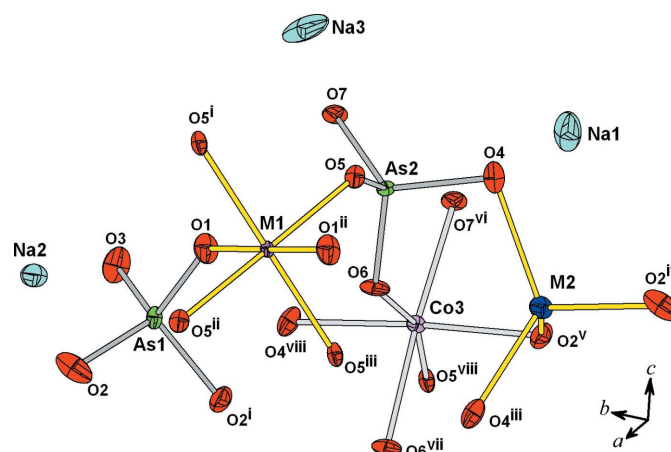


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Some symmetry-related O atoms are included to show the full coordination polyhedra around the Co/Al and As atoms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y + 1, z$; (ii) $-x, -y + 1, -z$; (iii) $-x, y, -z$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z$; (vi) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, z$.]

Many propositions are possible to ensure the electroneutrality of (I), *viz.* the existence of some vacancies in the O-atom positions, the oxidation of a small amount of Co^{2+} to Co^{3+} , and aliovalent occupation of the same site other than *M1* by Co^{2+} and Al^{3+} ions. These hypotheses were then tested one by one. Although the presence of heavy atoms makes the refinement of O-atom occupancies not very reliable, these occupancy factors have been refined and did not show significant deviation from full occupation, so the first hypothesis was then excluded.

To check the second proposition, one should first know the thermal decomposition behaviour of the cobalt source, cobalt acetate tetrahydrate (Grimes & Fitch, 1991; Alshehri *et al.*, 2000; Tang & Chen, 2007). The atmospheres used in the decomposition studies include vacuum, flowing gas and self-generated atmospheres, and the end product is influenced by the atmosphere and the conditions used.

Assuming the decomposition process produced CoO as a final product, as suggested by Grimes & Fitch (1991), within the Ellingham approximation the oxygen pressure needed to transform CoO to Co_3O_4 at 1153 K was evaluated from the thermodynamic data to be about 3.27 bar (1 bar = 10^5 Pa). This is much higher than the P_{O_2} in air of 0.2 bar, so we can deduce that the reaction to give partial oxidation of Co^{2+} to Co^{3+} is thermodynamically impossible under the conditions of our reaction. This does not exclude the existence of other oxidation reactions, but such a mechanism remains less probable. Indeed, to the best of our knowledge, there is only one cobalt arsenate, $\text{Co}_8\text{As}_3\text{O}_{16}$ (Krishnamachari & Calvo, 1970), where this particular transformation has been proposed because of the deviation from stoichiometry.

The third mechanism was then retained to fulfill the electroneutrality. In the final refinement, a fraction of Al^{3+} was introduced in the *M2* site and the two ions were assumed to be statistically distributed in the fractionally occupied *M2* site to yield an overall occupancy distribution of $\text{Co}_{0.672}\text{Al}_{0.101}\square_{0.230}$, with \square expressing the vacancy. The result thus obtained corresponds to the formula $\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.91}(\text{AsO}_4)_6$. A similar distribution in a tetrahedral site has been reported in the structure of Co^{2+} -stabilized β'' -alumina, $\text{Co}_{0.350}\text{Al}_{0.558}\square_{0.092}$ (Chen *et al.*, 1986).

The obtained structural model of (I) was submitted to both charge-distribution (CD) (Nespolo *et al.*, 2001; Nespolo, 2001) and BVS analyses (Brown, 2002; Adams, 2003). The cation charges Q from the CD analysis and valences V according to the BVS model are reported in Table 1. The CD method has been mainly used to validate structures, as in the nonstoichiometric mixed oxide YbFeMnO_4 (Nespolo *et al.*, 2000), the oxygen-deficient arsenate $\text{Na}_7\text{As}_{11}\text{O}_{31}$ (Guesmi *et al.*, 2006) and the mixed-valent cobalt phosphate $\text{Li}_{4.03}\text{Co}_{1.97}(\text{P}_2\text{O}_7)_2$ (Kouass *et al.*, 2010); bond-valence analysis has also been used for structural validation and seems to be an important tool to model ionic conduction pathways (*e.g.* Mazza, 2001; Adams, 2006; Ouerfelli *et al.*, 2008).

The computed charges (Q) from the CD analysis are in good agreement with the charges of all the cation sites and the structural model is thus validated, as shown by the dispersion

factor of 5% which measures the deviation of the computed charges (Q) with respect to the formal oxidation numbers. The rejection of the oxygen vacancy hypothesis to ensure electroneutrality is also supported, as the computed anion charges are consistent with the expected ones (dispersion factor 9%), with the exception of a slight under- and over-bonding on O1 and O2, respectively [$Q(\text{O1}) = -1.841$ and $Q(\text{O2}) = -2.095$]. Looking to the BVS results, and mainly to the cation valences, although the BVS validation tool does not contain an internal criterion as for the CD analysis (q/Q ratio close to 1), the structural model is supported, particularly the cation distribution on the *M1* site. The exception is the significant deviation observed for the partially occupied *M2* site. Such a result is expected since the BVS model rarely confirms the valence of sites partially occupied by metal cations such as Al^{3+} or transition metal ions as in the investigated compound. For example, the valence of the partially occupied Co^{2+} site (site-occupation factor = 0.728) in $\text{Co}_{0.95}\text{As}_{3.62}\text{O}_{16}$ (Krishnamachari & Calvo, 1973) is calculated by BVS to be only 1.30 v.u. (valence unit), lower than the occupancy-based value of 1.46. This is not the case for alkali cations where sometimes it is difficult to distinguish between the first and the second coordination sphere and their BVS valences in most cases are close to the expected values. In summary, the structural model is supported by associating the results of the crystal structure refinement to the CD and BVS investigations.

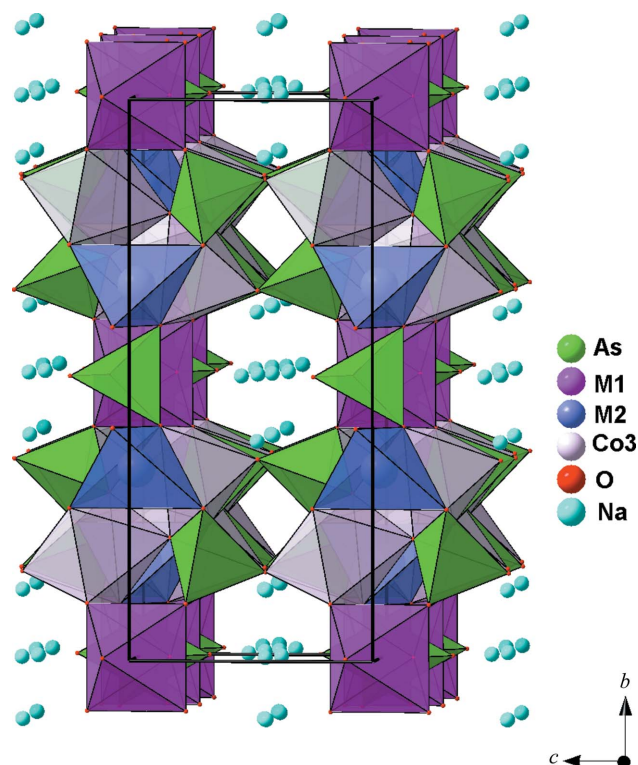


Figure 2
The structure of $\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.91}(\text{AsO}_4)_6$, viewed near the $[100]$ direction, showing the tunnels.

The investigated compound is a new member of the family of isostructural phases that includes $\text{Na}_4\text{Ni}_7(\text{PO}_4)_6$ (Moring & Kostiner, 1986), $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ (Kobashi *et al.*, 1998) and $\text{K}_4\text{Ni}_7(\text{AsO}_4)_6$ (Ben Smail *et al.*, 1999). In addition to the Co/Al-centred polyhedra, the structure contains two independent arsenic-centred tetrahedra. All the polyhedra show limited degrees of distortion with respect to ideal geometries, as indicated by their effective coordination numbers (ECoN) (Table 1). The distortion is a bit more pronounced for the octahedra than for the tetrahedra based on these results.

The three-dimensional centrosymmetric framework (Fig. 2) delimits tunnels running along the [100] direction and communicating along the *b* axis through quadrilateral windows. These voids accommodate the Na^+ cations which are, as in the isostructural compounds, distributed in three independent positions, one located at the periphery and two special positions at the centre of the tunnels. The dimensions of the hexagonal sections of the tunnels are $4.46 \times 4.82 \text{ \AA}$ measured between O atoms; the O3 atoms coordinated only to As1 tetrahedra point to the centre of tunnels at a shortest distance of 2.93 \AA . The framework of (I) is thus of open character and the motion of sodium cations through the tunnels seems feasible. This possibility is to be confirmed by electrical measurements in future work.

Experimental

A mixture of sodium carbonate, cobalt acetate tetrahydrate and As_2O_5 in an Na:Co:As molar ratio of 4:7:6 was placed in a porcelain boat and first heated at 673 K in air for 24 h and then heated gradually to 1153 K for 3 d. Some pink parallelepiped crystals were isolated from the sample. A qualitative EDX (energy-dispersive X-ray spectroscopy) analysis detected the presence of Na, Co, Al, As and O, with the aluminium diffusing from the reaction container. A polycrystalline powder of (I) was obtained by treating a stoichiometric mixture of the above reagents with Al_2O_3 as the aluminium source. The powder X-ray diffraction pattern was in agreement with the single-crystal structure.

Crystal data

$\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.91}(\text{AsO}_4)_6$	$V = 1033.2 (6) \text{ \AA}^3$
$M_r = 1281.94$	$Z = 2$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 10.744 (4) \text{ \AA}$	$\mu = 14.20 \text{ mm}^{-1}$
$b = 14.847 (3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 6.722 (3) \text{ \AA}$	$0.25 \times 0.25 \times 0.22 \text{ mm}$
$\beta = 105.51 (3)^\circ$	

Data collection

Enraf–Nonius CAD-4 diffractometer	1157 independent reflections
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	1042 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.040$, $T_{\max} = 0.044$	$R_{\text{int}} = 0.028$
1584 measured reflections	2 standard reflections every 120 min intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	117 parameters
$wR(F^2) = 0.068$	2 restraints
$S = 1.13$	$\Delta\rho_{\text{max}} = 0.90 \text{ e \AA}^{-3}$
1157 reflections	$\Delta\rho_{\text{min}} = -0.91 \text{ e \AA}^{-3}$

Table 1
CHARDI and BVS analysis of cation polyhedra in $\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.91}(\text{AsO}_4)_6$.

Cation	<i>q</i> .sof	<i>Q</i>	<i>V</i>	CN	ECoN
M1	2.714	2.810	2.701	6	5.912
M2	1.647	1.567	1.020	4	3.978
Co3	2.00	1.990	1.981	6	5.898
As1	5.00	5.033	5.011	4	3.990
As2	5.00	5.001	4.870	4	3.983
Na1	0.50	0.498	0.471	5	4.589
Na2	0.50	0.501	0.413	7	6.437
Na3	0.50	0.504	0.471	6	5.970

Notes: M1 = $\text{Co}_{0.286}\text{Al}_{0.714}$; M2 = $\text{Co}_{0.672}\text{Al}_{0.101}\square_{0.226}$; *q* is the formal oxidation number; sof is the site-occupation factor; sodium CNs for $d(\text{Na}-\text{O})^{\text{max}} = 3.00 \text{ \AA}$; $\sigma = [\sum_i (q_i - Q_i)^2 / N - 1]^{1/2} = 0.047$.

The Co and Al atoms occupying the M1 and M2 sites were constrained [using the EXYZ and EADP instructions of *SHELXL97* (Sheldrick, 2008)] to have the same positional and displacement parameters. Two linear free variable restraints (SUMP) were required to restrain the sum of their occupation factors. Noting the difference between the displacement parameters of the M1 and M2 sites, we believe that the relatively large displacement parameters for the latter are reasonable since the M2 site is fractionally occupied. The same relationship has been observed in $\text{Co}_{6.95}\text{As}_{3.62}\text{O}_{16}$ (Krishnamachari & Calvo, 1973) in which the following parameters were reported: for Co1, site-occupation factor = 0.7275 and $U_{\text{eq}} = 0.0107 (2) \text{ \AA}^2$; for Co2, site-occupation factor = 1.0 and $U_{\text{eq}} = 0.0075 (2) \text{ \AA}^2$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1995); cell refinement: *CAD-4 EXPRESS*; 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, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3262). Services for accessing these data are described at the back of the journal.

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