

The alluaudite-type crystal structures of $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$ and $\text{Ag}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$

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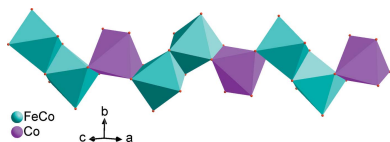
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Single crystals of the title compounds, disodium di(cobalt/iron) cobalt tris(orthovanadate), $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$, and disilver di(cobalt/iron) cobalt tris(orthovanadate), $\text{Ag}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$, were grown from a melt consisting of stoichiometric mixtures of three metallic cation precursors and vanadium pentoxide. The difficulty to distinguish between cobalt and iron by using X-ray diffraction alone forced us to explore several models, assuming an oxidation state of +II for Co and +III for Fe and a partial cationic disorder in the Wyckoff site $8f$ containing a mixture of Co and Fe with a statistical distribution for the Na compound and an occupancy ratio of 0.4875:0.5125 (Co:Fe) for the Ag compound. The alluaudite-type structure is made up from $[10\bar{1}]$ chains of $[(\text{Co,Fe})_2\text{O}_{10}]$ double octahedra linked by highly distorted $[\text{CoO}_6]$ octahedra *via* a common edge. The chains are linked through VO_4 tetrahedra, forming polyhedral sheets perpendicular to $[010]$. The stacking of the sheets defines two types of channels parallel to $[001]$ where the Na^+ cations (both with full occupancy) or Ag^+ cations (one with occupancy 0.97) are located.

1. Chemical context

The needs of the society on the ‘energy front’ is one of the greatest challenges for present and future times. Materials with three-dimensional framework structures delimiting channels, as built of transition metal cations and polyanions $(\text{XO}_4)^{n-}$, have become a subject of very intensive research worldwide since the discovery of the electrochemical activity of LiFePO_4 (Padhi *et al.*, 1997*a,b*). Hence, new transition metal-based materials adopting open three-dimensional framework structures have been synthesized and investigated by us over the last years. Thereby our attention has focused on the synthesis and characterization of new materials belonging to the family of alluaudites that, according to Moore (1971), has the general formula $A(1)A(2)M(1)M(2)_2(\text{XO}_4)_3$. The A sites may be occupied by larger mono- and/or divalent cations, while the M sites correspond to bi- or trivalent transition metal cations in an octahedral environment. Alluaudite-like compounds, having open-framework structures, allow a certain prediction of physical properties and promising practical applications in several fields. For instance, alluaudite-like compounds exhibit electronic and/or ionic conductivity, as has been shown by Warner *et al.* (1993, 1994), which make them worthy of investigating their electrochemical performance. Mainly, several alluaudite-like phosphates have been tested as anode and/or cathode materials in Li-ion and/or Na-ion batteries. For example, $\text{Li}_{0.78}\text{Na}_{0.22}\text{MnPO}_4$ was proposed by Kim *et al.* (2014) as a promising new positive electrode for



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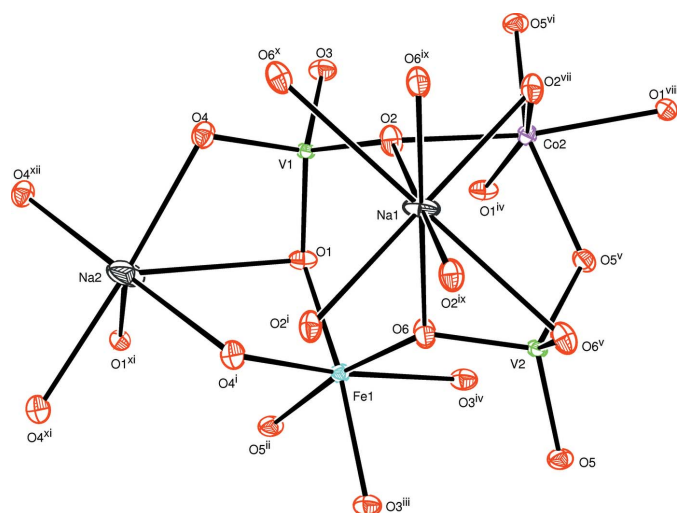


Figure 1
The principal building units in the structure of $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y + 1, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 2$; (iii) $x, y, z + 1$; (iv) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (v) $-x + 1, y, -z + \frac{3}{2}$; (vi) $x, y, z - 1$; (vii) $-x + 1, y, -z + \frac{1}{2}$; (viii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ix) $-x + 1, -y + 1, -z + 1$; (x) $x, -y + 1, z - \frac{1}{2}$; (xi) $-x + 2, y, -z + \frac{3}{2}$; (xii) $-x + 2, -y + 1, -z + 1$.]

Li-ion batteries. The sulfates $\text{Na}_{2.44}\text{Mn}_{1.79}(\text{SO}_4)_3$ (Dwibedi *et al.*, 2015) and $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ (Dwibedi *et al.*, 2016) were tested as electroactive materials for Na-ion batteries. In this context, we have investigated *pseudo*-ternary $\text{A}_2\text{O/MO/P}_2\text{O}_5$, *pseudo*-quaternary $\text{A}_2\text{O/MO/Fe}_2\text{O}_3/\text{P}_2\text{O}_5$, and more recently,

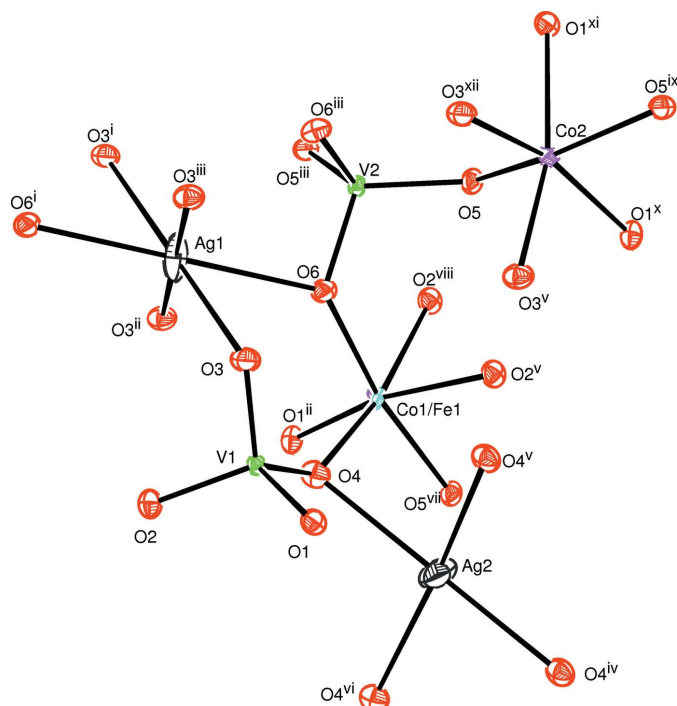


Figure 2
The principal building units in the structure of $\text{Ag}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y + 1, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 2$; (iii) $x, y, z + 1$; (iv) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (v) $-x + 1, y, -z + \frac{3}{2}$; (vi) $x, y, z - 1$; (vii) $-x + 1, y, -z + \frac{1}{2}$; (viii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ix) $-x + 1, -y + 1, -z + 1$; (x) $x, -y + 1, z - \frac{1}{2}$; (xi) $-x + 2, y, -z + \frac{3}{2}$; (xii) $-x + 2, -y + 1, -z + 1$.]

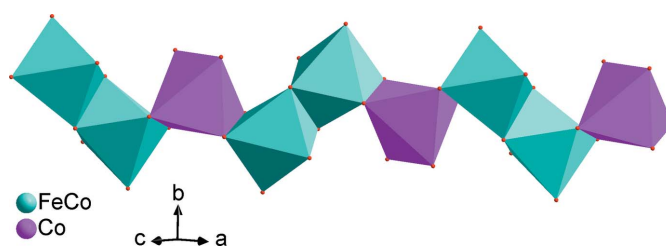


Figure 3
Edge-sharing octahedra forming an infinite zigzag chain running along $[10\bar{1}]$. Data from $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$.

$\text{A}_2\text{O/MO/Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ systems synthesized *via* hydrothermal or solid-state routes, resulting in new alluaudite-like phosphates $\text{AgMg}_3(\text{HPO}_4)_2\text{PO}_4$ (Assani *et al.*, 2011), $\text{NaMg}_3(\text{HPO}_4)_2\text{PO}_4$ (Ould Saleck *et al.*, 2015), $\text{Na}_2\text{Co}_2\text{Fe}(\text{PO}_4)_3$ (Bouraima *et al.*, 2015), $\text{Na}_{1.67}\text{Zn}_{1.67}\text{Fe}_{1.33}(\text{PO}_4)_3$ (Khmiyas *et al.*, 2015), and most lately, the first alluaudite-like vanadate $(\text{Na}_{0.70})(\text{Na}_{0.70}\text{Mn}_{0.30})(\text{Fe}^{3+}/\text{Fe}^{2+})_2\text{Fe}^{2+}(\text{VO}_4)_3$ (Benhsina *et al.*, 2016). As a continuation of our studies of phases with alluaudite-like structures, the present work reports details of the synthesis and crystal structures of the compounds $\text{M}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$ ($\text{M} = \text{Na}, \text{Ag}$).

2. Structural commentary

The two alluaudite-like vanadates, $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$ and $\text{Ag}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$, are isotypic. In the structure of $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$ all sites are fully occupied and only the cationic site on Wyckoff position 8f shows disorder with a statistical distribution of Co and Fe, assuming oxidation state +II for Co and +III for Fe. In the structure of $\text{Ag}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$ a small deficit in the Ag2 site was considered (occupancy 0.97) that is compensated by a slight excess of Fe (occupancy 0.51) compared with Co (occupancy 0.49) in the 8f mixed site, again under the assumption of oxidation state +II

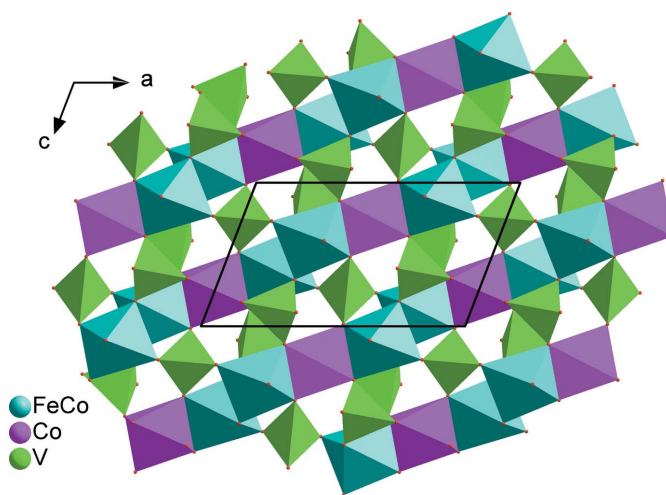


Figure 4
A sheet perpendicular to $[010]$, resulting from the connection of individual chains *via* VO_4 tetrahedra. Data from $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$.

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$\text{Na}_2(\text{Co}_{0.5}\text{Fe}_{0.5})_2\text{Co}(\text{VO}_4)_3$	$\text{Ag}_{1.97}(\text{Co}_{0.49}\text{Fe}_{0.51})_2\text{Co}(\text{VO}_4)_3$
M_r	564.51	730.96
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature (K)	296	296
a, b, c (Å)	11.7258 (2), 12.7819 (2), 6.8264 (1)	11.7846 (4), 12.8314 (4), 6.8064 (2)
β (°)	111.069 (1)	111.001 (1)
V (Å ³)	954.73 (3)	960.85 (5)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	7.85	11.60
Crystal size (mm)	0.32 × 0.25 × 0.19	0.34 × 0.22 × 0.17
Data collection		
Diffractometer	Bruker X8 APEX	Bruker X8 APEX
Absorption correction	Multi-scan (SADABS; Bruker, 2009)	Multi-scan (SADABS; Bruker, 2009)
T_{\min} , T_{\max}	0.572, 0.747	0.439, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17675, 2094, 1893	15366, 2113, 1987
R_{int}	0.047	0.039
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.806	0.806
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.054, 1.10	0.018, 0.041, 1.14
No. of reflections	2094	2113
No. of parameters	95	104
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.88, -1.00	0.80, -1.66

Computer programs: APEX2 and SAINT (Bruker, 2009), SHELXT2014 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2006) and publCIF (Westrip, 2010).

for Co and +III for Fe. The (Fe1,Co1) and Co2 sites have octahedral environments while the vanadium atoms are located in tetrahedral environments. The sequence of different polyhedra forming the principal building units are shown in Figs. 1 and 2. The mixed-occupied sites containing the

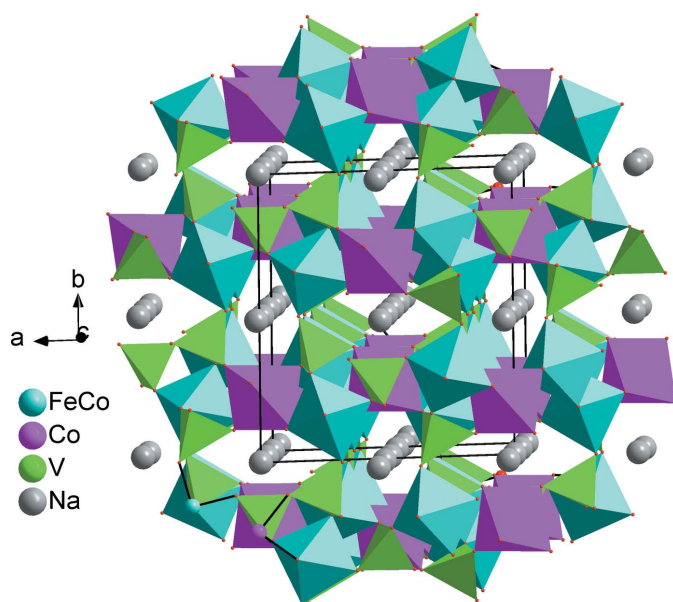


Figure 5
Polyhedral representation of $\text{Na}_2(\text{Fe/Co})_2\text{Co}(\text{VO}_4)_3$ showing sodium cations in the channels extending along [001].

(Fe1,Co1) atoms form $[(\text{Co,Fe})_2\text{O}_{10}]$ dimers through edge-sharing of a single octahedron and are linked by highly distorted $[\text{CoO}_6]$ octahedra. The linkage of alternating $[\text{CoO}_6]$ octahedra and $[(\text{Co,Fe})_2\text{O}_{10}]$ double octahedra leads to the formation of infinite chains along the $[10\bar{1}]$ direction (Fig. 3). The connection of these chains through VO_4 tetrahedra makes up sheets perpendicular to $[010]$, as shown in Fig. 4. The stacking of these sheets defines an open three-dimensional framework delimiting two types of channels parallel to $[001]$ where the M^+ cations ($M = \text{Na}, \text{Ag}$) are situated (Fig. 5). In the sodium compound, the Na1 site is coordinated by eight oxygen atoms with Na1—O distances in the range between 2.4118 (14) and 2.8820 (15) Å, while Na2 is surrounded by six oxygen atoms in a range between 2.4347 (14) and 2.780 (2) Å. In the silver compound, the Ag1 site is coordinated by six oxygen atoms in a range between 2.4244 (12) and 2.5960 (13) Å, whereas the Ag2 site is surrounded by four oxygen atoms in a range between 2.4708 (14) and 2.4779 (14) Å.

3. Synthesis and crystallization

The target compounds were obtained by solid-state reactions. A starting mixture of metallic iron (+ a few drops of HNO_3), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, NH_4VO_3 and NaNO_3 or AgNO_3 was mixed in molar ratios $M: \text{Co}: \text{Fe}: \text{V} = 2: 2: 1: 3$ ($M = \text{Na}$ or Ag). The mixture was placed in a platinum crucible and then heated gradually until melting (1253 K). Single crystals were obtained by cooling the molten product to room temperature at rate of

5 Kh⁻¹. The resulting mixtures contained pink crystals (for $M = \text{Na}$) or green crystals (for $M = \text{Ag}$) of a suitable size for the X-ray diffraction study. The powder X-ray diffraction patterns are in good agreement with the simulated patterns, generated from the final structure models of the two compounds (see supplementary material).

4. Refinement

Crystal data, data collection and structure refinement details for both structures are summarized in Table 1.

As a matter of fact, the distinction between cobalt and iron by X-ray diffraction is nearly impossible. Therefore we have examined several crystallographic models during crystal structure refinements of the title compounds. Based on the stoichiometric ratio of 1:2 for iron and cobalt in the starting materials, we assumed the same ratio in the crystal structures with oxidation states of +II for cobalt and +III for iron. In the final model, Fe1 and Co1 atoms are constrained to share the same general position $8f$ of the space group $C2/c$. Electrical neutrality and bond valence sum calculations of all atoms (Brown & Altermatt, 1985) in the structures are in reasonable agreement with the final models. Bond valence sums (in valence units) for $\text{Na}_2(\text{Fe}/\text{Co})_2\text{Co}(\text{VO}_4)_3$ are 1.07 for Na1, 0.86 for Na2, 2.24 for Co1, 1.97 for Co2, 2.69 for Fe1, 5.01 for V1, and 4.99 for V2. Values of the bond valence sums calculated for all oxygen atoms are between 1.90 and 2.07. Bond valence sums for $\text{Ag}_2(\text{Fe}/\text{Co})_2\text{Co}(\text{VO}_4)_3$ are 1.01 for Ag1, 0.72 for Ag2, 2.27 for Co1, 1.98 for Co2, 2.72 for Fe1, 4.99 for V1, and 4.94 for V2. The values of the O atoms are in the range 1.94 to 2.03. A very similar cationic distribution was observed by Yakubovich *et al.* (1977) in the alluaudite-type phosphate $\text{Na}_2(\text{Fe}^{3+}/\text{Fe}^{2+})_2\text{Fe}^{2+}(\text{PO}_4)_3$.

Refinement of $\text{Na}_2(\text{Fe}/\text{Co})_2\text{Co}(\text{VO}_4)_3$: Co1 and Fe1 were constrained to share the same site in a statistical occupation with common displacement parameters. Reflection (132) probably was affected by the beam-stop and was omitted from the refinement. The remaining electron densities (max/min) in the final Fourier map were 0.46 Å and 0.71 Å away from atoms Na1 and Na2, respectively.

Refinement of $\text{Ag}_2(\text{Fe}/\text{Co})_2\text{Co}(\text{VO}_4)_3$: The coordinates and displacement factors of Co1 and Fe1 atoms were refined independent from each other. An underoccupation of the Ag2 site was modelled with an occupancy of 0.97 which made it necessary to constrain the occupancies of the Co1 site (0.4875) and Fe1 site (0.5125) for electroneutrality. The remaining

electron densities (max/min) in the final Fourier map were 0.61 Å and 0.66 Å away from Ag2.

Acknowledgements

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supporting information

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE* (Bruker, 2009); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

(I) Disodium di(cobalt/iron) cobalt tris(orthovanadate)

Crystal data

$\text{Na}_2(\text{Co}\cdot\text{Fe})_2\text{Co}(\text{VO}_4)_3$
 $M_r = 564.51$
 Monoclinic, *C2/c*
 $a = 11.7258$ (2) Å
 $b = 12.7819$ (2) Å
 $c = 6.8264$ (1) Å
 $\beta = 111.069$ (1)°
 $V = 954.73$ (3) Å³
 $Z = 4$

$F(000) = 1068$
 $D_x = 3.927$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2094 reflections
 $\theta = 2.5\text{--}35.0^\circ$
 $\mu = 7.85$ mm⁻¹
 $T = 296$ K
 Block, pink
 $0.32 \times 0.25 \times 0.19$ mm

Data collection

Bruker X8 APEX
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2009)
 $T_{\min} = 0.572$, $T_{\max} = 0.747$

17675 measured reflections
 2094 independent reflections
 1893 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$
 $\theta_{\max} = 35.0^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -17 \rightarrow 18$
 $k = -20 \rightarrow 20$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.054$
 $S = 1.10$
 2094 reflections
 95 parameters

0 restraints
 $w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 2.754P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.88$ e Å⁻³
 $\Delta\rho_{\min} = -1.00$ e Å⁻³

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe1	0.79142 (2)	0.66131 (2)	0.88043 (4)	0.00595 (6)	0.5
Co1	0.79142 (2)	0.66131 (2)	0.88043 (4)	0.00595 (6)	0.5
Co2	0.5000	0.73184 (3)	0.2500	0.00727 (7)	
V1	0.77138 (3)	0.61298 (2)	0.38340 (4)	0.00555 (6)	
V2	0.5000	0.70722 (3)	0.7500	0.00629 (8)	
Na1	0.5000	0.5000	0.5000	0.0123 (2)	
Na2	1.0000	0.50245 (14)	0.7500	0.0257 (3)	
O1	0.84286 (13)	0.67273 (11)	0.6264 (2)	0.0102 (2)	
O2	0.62045 (12)	0.60248 (11)	0.3329 (2)	0.0116 (2)	
O3	0.78619 (13)	0.68309 (11)	0.1758 (2)	0.0113 (2)	
O6	0.61413 (13)	0.62261 (11)	0.7671 (2)	0.0120 (2)	
O5	0.53637 (12)	0.77735 (11)	0.9853 (2)	0.0104 (2)	
O4	0.84074 (13)	0.49296 (11)	0.4032 (2)	0.0108 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.00562 (10)	0.00715 (11)	0.00541 (10)	−0.00056 (7)	0.00237 (7)	−0.00051 (7)
Co1	0.00562 (10)	0.00715 (11)	0.00541 (10)	−0.00056 (7)	0.00237 (7)	−0.00051 (7)
Co2	0.00669 (14)	0.00821 (15)	0.00752 (13)	0.000	0.00330 (11)	0.000
V1	0.00559 (12)	0.00635 (12)	0.00449 (11)	−0.00001 (9)	0.00155 (9)	−0.00011 (8)
V2	0.00700 (17)	0.00647 (17)	0.00459 (15)	0.000	0.00113 (12)	0.000
Na1	0.0208 (6)	0.0070 (5)	0.0074 (4)	−0.0057 (4)	0.0030 (4)	−0.0015 (3)
Na2	0.0097 (5)	0.0565 (10)	0.0105 (5)	0.000	0.0031 (4)	0.000
O1	0.0115 (6)	0.0116 (6)	0.0074 (5)	−0.0037 (5)	0.0031 (4)	−0.0016 (4)
O2	0.0077 (5)	0.0107 (6)	0.0158 (6)	−0.0008 (4)	0.0035 (5)	0.0004 (5)
O3	0.0138 (6)	0.0126 (6)	0.0080 (5)	−0.0004 (5)	0.0043 (4)	0.0006 (4)
O6	0.0092 (6)	0.0098 (6)	0.0148 (6)	0.0012 (4)	0.0015 (5)	−0.0019 (5)
O5	0.0075 (5)	0.0156 (6)	0.0082 (5)	−0.0017 (5)	0.0028 (4)	−0.0025 (4)
O4	0.0102 (6)	0.0092 (6)	0.0129 (6)	0.0002 (4)	0.0042 (5)	−0.0015 (4)

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

Fe1—O6	2.0021 (14)	V2—O6 ^v	1.6917 (14)
Fe1—O1	2.0359 (14)	V2—O5	1.7531 (13)
Fe1—O4 ⁱ	2.0451 (14)	V2—O5 ^v	1.7531 (13)
Fe1—O5 ⁱⁱ	2.0497 (14)	Na1—O6	2.4118 (14)
Fe1—O3 ⁱⁱⁱ	2.0581 (14)	Na1—O6 ^{ix}	2.4119 (14)
Fe1—O3 ^{iv}	2.1633 (14)	Na1—O2 ^{ix}	2.4841 (14)

Co2—O5 ^v	2.0831 (14)	Na1—O2	2.4841 (14)
Co2—O5 ^{vi}	2.0831 (14)	Na1—O2 ⁱ	2.5626 (14)
Co2—O2	2.1153 (14)	Na1—O2 ^{vii}	2.5626 (14)
Co2—O2 ^{vii}	2.1153 (14)	Na1—O6 ^x	2.8820 (15)
Co2—O1 ^{iv}	2.1159 (13)	Na1—O6 ^v	2.8820 (15)
Co2—O1 ^{viii}	2.1159 (13)	Na2—O4 ^{xi}	2.4347 (14)
V1—O2	1.6823 (14)	Na2—O4	2.4347 (14)
V1—O4	1.7188 (14)	Na2—O4 ⁱ	2.4472 (15)
V1—O3	1.7374 (14)	Na2—O4 ^{xiii}	2.4472 (15)
V1—O1	1.7428 (13)	Na2—O1	2.780 (2)
V2—O6	1.6917 (14)	Na2—O1 ^{xi}	2.780 (2)
O6—Fe1—O1	105.84 (6)	O6—Na1—O2 ^{ix}	104.36 (5)
O6—Fe1—O4 ⁱ	90.98 (6)	O6 ^{ix} —Na1—O2 ^{ix}	75.63 (5)
O1—Fe1—O4 ⁱ	88.38 (6)	O6—Na1—O2	75.64 (5)
O6—Fe1—O5 ⁱⁱ	170.54 (6)	O6 ^{ix} —Na1—O2	104.37 (5)
O1—Fe1—O5 ⁱⁱ	78.91 (5)	O2 ^{ix} —Na1—O2	180.0
O4 ⁱ —Fe1—O5 ⁱⁱ	97.39 (6)	O6—Na1—O2 ⁱ	71.50 (5)
O6—Fe1—O3 ⁱⁱⁱ	91.12 (6)	O6 ^{ix} —Na1—O2 ⁱ	108.50 (5)
O1—Fe1—O3 ⁱⁱⁱ	161.29 (6)	O2 ^{ix} —Na1—O2 ⁱ	63.02 (6)
O4 ⁱ —Fe1—O3 ⁱⁱⁱ	99.39 (6)	O2—Na1—O2 ⁱ	116.98 (6)
O5 ⁱⁱ —Fe1—O3 ⁱⁱⁱ	83.21 (5)	O6—Na1—O2 ^{vii}	108.50 (5)
O6—Fe1—O3 ^{iv}	81.17 (6)	O6 ^{ix} —Na1—O2 ^{vii}	71.50 (5)
O1—Fe1—O3 ^{iv}	91.00 (5)	O2 ^{ix} —Na1—O2 ^{vii}	116.98 (6)
O4 ⁱ —Fe1—O3 ^{iv}	171.64 (6)	O2—Na1—O2 ^{vii}	63.02 (6)
O5 ⁱⁱ —Fe1—O3 ^{iv}	90.67 (6)	O2 ⁱ —Na1—O2 ^{vii}	180.0
O3 ⁱⁱⁱ —Fe1—O3 ^{iv}	83.72 (5)	O6—Na1—O6 ^x	121.93 (6)
O5 ^v —Co2—O5 ^{vi}	147.57 (8)	O6 ^{ix} —Na1—O6 ^x	58.07 (6)
O5 ^v —Co2—O2	108.15 (5)	O2 ^{ix} —Na1—O6 ^x	114.84 (4)
O5 ^{vi} —Co2—O2	97.18 (6)	O2—Na1—O6 ^x	65.16 (4)
O5 ^v —Co2—O2 ^{vii}	97.18 (6)	O2 ⁱ —Na1—O6 ^x	89.66 (4)
O5 ^{vi} —Co2—O2 ^{vii}	108.15 (5)	O2 ^{vii} —Na1—O6 ^x	90.34 (4)
O2—Co2—O2 ^{vii}	77.17 (8)	O6—Na1—O6 ^v	58.07 (6)
O5 ^v —Co2—O1 ^{iv}	85.04 (5)	O6 ^{ix} —Na1—O6 ^v	121.93 (6)
O5 ^{vi} —Co2—O1 ^{iv}	76.38 (5)	O2 ^{ix} —Na1—O6 ^v	65.16 (4)
O2—Co2—O1 ^{iv}	86.67 (5)	O2—Na1—O6 ^v	114.84 (4)
O2 ^{vii} —Co2—O1 ^{iv}	163.59 (6)	O2 ⁱ —Na1—O6 ^v	90.34 (4)
O5 ^v —Co2—O1 ^{viii}	76.38 (5)	O2 ^{vii} —Na1—O6 ^v	89.66 (4)
O5 ^{vi} —Co2—O1 ^{viii}	85.04 (5)	O6 ^x —Na1—O6 ^v	180.0
O2—Co2—O1 ^{viii}	163.59 (6)	O4 ^{xi} —Na2—O4	174.29 (11)
O2 ^{vii} —Co2—O1 ^{viii}	86.67 (5)	O4 ^{xi} —Na2—O4 ⁱ	91.26 (5)
O1 ^{iv} —Co2—O1 ^{viii}	109.60 (8)	O4—Na2—O4 ⁱ	88.87 (5)
O2—V1—O4	112.22 (7)	O4 ^{xi} —Na2—O4 ^{xii}	88.87 (5)
O2—V1—O3	106.27 (7)	O4—Na2—O4 ^{xii}	91.26 (5)
O4—V1—O3	109.96 (7)	O4 ⁱ —Na2—O4 ^{xiii}	177.25 (11)
O2—V1—O1	109.92 (7)	O4 ^{xi} —Na2—O1	121.82 (7)
O4—V1—O1	105.32 (7)	O4—Na2—O1	63.31 (5)
O3—V1—O1	113.29 (7)	O4 ⁱ —Na2—O1	65.58 (5)

O6—V2—O6 ^v	100.53 (10)	O4 ^{xii} —Na2—O1	112.08 (6)
O6—V2—O5	109.75 (7)	O4 ^{xi} —Na2—O1 ^{xi}	63.31 (5)
O6 ^v —V2—O5	108.41 (7)	O4—Na2—O1 ^{xi}	121.82 (7)
O6—V2—O5 ^v	108.42 (7)	O4 ⁱ —Na2—O1 ^{xi}	112.08 (6)
O6 ^v —V2—O5 ^v	109.75 (7)	O4 ^{xii} —Na2—O1 ^{xi}	65.58 (5)
O5—V2—O5 ^v	118.49 (10)	O1—Na2—O1 ^{xi}	76.92 (7)
O6—Na1—O6 ^{ix}	180.0		

Symmetry codes: (i) $x, -y+1, z+1/2$; (ii) $-x+3/2, -y+3/2, -z+2$; (iii) $x, y, z+1$; (iv) $-x+3/2, -y+3/2, -z+1$; (v) $-x+1, y, -z+3/2$; (vi) $x, y, z-1$; (vii) $-x+1, y, -z+1/2$; (viii) $x-1/2, -y+3/2, z-1/2$; (ix) $-x+1, -y+1, -z+1$; (x) $x, -y+1, z-1/2$; (xi) $-x+2, y, -z+3/2$; (xii) $-x+2, -y+1, -z+1$.

(II) Disilver di(cobalt/iron) cobalt tris(orthovanadate)

Crystal data

Ag_{1.97}(Co_{0.49}Fe_{0.51})₂Co(VO₄)₃

$M_r = 730.96$

Monoclinic, $C2/c$

$a = 11.7846$ (4) Å

$b = 12.8314$ (4) Å

$c = 6.8064$ (2) Å

$\beta = 111.001$ (1)°

$V = 960.85$ (5) Å³

$Z = 4$

$F(000) = 1350$

$D_x = 5.053$ Mg m⁻³

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

Cell parameters from 2113 reflections

$\theta = 2.4\text{--}35.0^\circ$

$\mu = 11.60$ mm⁻¹

$T = 296$ K

Block, green

$0.34 \times 0.22 \times 0.17$ mm

Data collection

Bruker X8 APEX
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.439$, $T_{\max} = 0.747$

15366 measured reflections

2113 independent reflections

1987 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 35.0^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -18 \rightarrow 18$

$k = -20 \rightarrow 20$

$l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.041$

$S = 1.14$

2113 reflections

104 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0093P)^2 + 2.3975P]$

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

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

$\Delta\rho_{\max} = 0.80$ e Å⁻³

$\Delta\rho_{\min} = -1.66$ e Å⁻³

Extinction correction: SHELXL2014

(Sheldrick, 2015b),

$Fc^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00190 (7)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ag1	0.0000	0.5000	0.0000	0.02187 (6)	
Ag2	0.5000	0.50840 (2)	0.7500	0.02578 (6)	0.97
Co1	0.2919 (4)	0.6616 (4)	0.3791 (8)	0.0066 (12)	0.4875
Fe1	0.2923 (4)	0.6620 (4)	0.3814 (8)	0.0061 (12)	0.5125
Co2	0.0000	0.73364 (2)	0.7500	0.00755 (6)	
V1	0.27106 (2)	0.38672 (2)	0.38255 (4)	0.00573 (5)	
V2	0.0000	0.70581 (3)	0.2500	0.00609 (6)	
O1	0.34160 (11)	0.32595 (9)	0.62391 (19)	0.0103 (2)	
O2	0.28472 (11)	0.31626 (10)	0.17435 (19)	0.0109 (2)	
O3	0.12124 (11)	0.39463 (10)	0.3352 (2)	0.0121 (2)	
O4	0.33731 (12)	0.50845 (9)	0.3988 (2)	0.0123 (2)	
O5	0.03699 (11)	0.77654 (10)	0.48520 (19)	0.0100 (2)	
O6	0.11558 (11)	0.62338 (9)	0.2663 (2)	0.0114 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.03724 (13)	0.01563 (9)	0.01248 (9)	-0.01172 (8)	0.00860 (8)	-0.00330 (6)
Ag2	0.01181 (9)	0.04845 (15)	0.01618 (10)	0.000	0.00390 (8)	0.000
Co1	0.0072 (18)	0.0061 (17)	0.0085 (18)	0.0017 (12)	0.0052 (12)	-0.0004 (12)
Fe1	0.0059 (17)	0.0082 (18)	0.0032 (15)	-0.0027 (12)	0.0007 (11)	-0.0007 (11)
Co2	0.00710 (12)	0.00870 (12)	0.00779 (13)	0.000	0.00380 (10)	0.000
V1	0.00651 (10)	0.00586 (10)	0.00488 (10)	0.00018 (7)	0.00212 (8)	0.00004 (7)
V2	0.00679 (14)	0.00648 (13)	0.00465 (14)	0.000	0.00161 (11)	0.000
O1	0.0119 (5)	0.0111 (5)	0.0081 (5)	0.0027 (4)	0.0038 (4)	0.0013 (4)
O2	0.0129 (5)	0.0121 (5)	0.0083 (5)	-0.0007 (4)	0.0045 (4)	-0.0007 (4)
O3	0.0094 (5)	0.0113 (5)	0.0156 (6)	0.0007 (4)	0.0045 (4)	-0.0005 (4)
O4	0.0132 (5)	0.0087 (5)	0.0156 (6)	-0.0002 (4)	0.0060 (5)	0.0010 (4)
O5	0.0091 (5)	0.0136 (5)	0.0078 (5)	-0.0018 (4)	0.0036 (4)	-0.0019 (4)
O6	0.0088 (5)	0.0103 (5)	0.0137 (5)	0.0000 (4)	0.0024 (4)	-0.0021 (4)

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

Ag1—O6 ⁱ	2.4244 (12)	Fe1—O1 ⁱⁱ	2.040 (6)
Ag1—O6	2.4244 (12)	Fe1—O5 ^{vii}	2.045 (5)
Ag1—O3 ⁱⁱ	2.5051 (13)	Fe1—O2 ^v	2.047 (5)
Ag1—O3 ⁱⁱⁱ	2.5051 (13)	Fe1—O2 ^{viii}	2.154 (5)
Ag1—O3	2.5960 (13)	Co2—O5 ^{ix}	2.0747 (12)
Ag1—O3 ⁱ	2.5960 (13)	Co2—O5	2.0748 (12)
Ag2—O4	2.4708 (14)	Co2—O1 ^x	2.1156 (12)
Ag2—O4 ^{iv}	2.4709 (14)	Co2—O1 ^{xi}	2.1156 (12)
Ag2—O4 ^v	2.4779 (14)	Co2—O3 ^{xiii}	2.1197 (13)
Ag2—O4 ^{vi}	2.4779 (14)	Co2—O3 ^v	2.1197 (13)
Co1—O6	2.001 (5)	V1—O3	1.6804 (13)
Co1—O1 ⁱⁱ	2.028 (6)	V1—O4	1.7319 (12)

Co1—O4	2.028 (5)	V1—O2	1.7363 (12)
Co1—O5 ^{vii}	2.053 (5)	V1—O1	1.7375 (12)
Co1—O2 ^v	2.061 (5)	V2—O6	1.6965 (12)
Co1—O2 ^{viii}	2.157 (5)	V2—O6 ⁱⁱⁱ	1.6965 (12)
Fe1—O6	2.007 (5)	V2—O5 ⁱⁱⁱ	1.7539 (12)
Fe1—O4	2.033 (5)	V2—O5	1.7539 (12)
O6 ⁱ —Ag1—O6	180.0	O6—Fe1—O5 ^{vii}	170.5 (3)
O6 ⁱ —Ag1—O3 ⁱⁱ	105.99 (4)	O4—Fe1—O5 ^{vii}	98.8 (2)
O6—Ag1—O3 ⁱⁱ	74.01 (4)	O1 ⁱⁱ —Fe1—O5 ^{vii}	79.3 (2)
O6 ⁱ —Ag1—O3 ⁱⁱⁱ	74.01 (4)	O6—Fe1—O2 ^v	90.7 (2)
O6—Ag1—O3 ⁱⁱⁱ	105.99 (4)	O4—Fe1—O2 ^v	100.2 (2)
O3 ⁱⁱ —Ag1—O3 ⁱⁱⁱ	180.0	O1 ⁱⁱ —Fe1—O2 ^v	162.1 (3)
O6 ⁱ —Ag1—O3	107.57 (4)	O5 ^{vii} —Fe1—O2 ^v	83.95 (17)
O6—Ag1—O3	72.43 (4)	O6—Fe1—O2 ^{viii}	81.09 (17)
O3 ⁱⁱ —Ag1—O3	116.87 (5)	O4—Fe1—O2 ^{viii}	170.3 (2)
O3 ⁱⁱⁱ —Ag1—O3	63.13 (5)	O1 ⁱⁱ —Fe1—O2 ^{viii}	90.6 (2)
O6 ⁱ —Ag1—O3 ⁱ	72.43 (4)	O5 ^{vii} —Fe1—O2 ^{viii}	90.5 (2)
O6—Ag1—O3 ⁱ	107.57 (4)	O2 ^v —Fe1—O2 ^{viii}	83.31 (18)
O3 ⁱⁱ —Ag1—O3 ⁱ	63.13 (5)	O5 ^{ix} —Co2—O5	149.23 (7)
O3 ⁱⁱⁱ —Ag1—O3 ⁱ	116.87 (5)	O5 ^{ix} —Co2—O1 ^x	85.91 (5)
O3—Ag1—O3 ⁱ	180.0	O5—Co2—O1 ^x	76.96 (5)
O4—Ag2—O4 ^{iv}	179.97 (6)	O5 ^{ix} —Co2—O1 ^{xi}	76.96 (5)
O4—Ag2—O4 ^v	87.12 (4)	O5—Co2—O1 ^{xi}	85.91 (5)
O4 ^{iv} —Ag2—O4 ^v	92.89 (4)	O1 ^x —Co2—O1 ^{xi}	111.91 (7)
O4—Ag2—O4 ^{vi}	92.89 (4)	O5 ^{ix} —Co2—O3 ^{xii}	96.48 (5)
O4 ^{iv} —Ag2—O4 ^{vi}	87.12 (4)	O5—Co2—O3 ^{xii}	107.40 (5)
O4 ^v —Ag2—O4 ^{vi}	169.99 (6)	O1 ^x —Co2—O3 ^{xii}	162.94 (5)
O6—Co1—O1 ⁱⁱ	105.6 (2)	O1 ^{xi} —Co2—O3 ^{xii}	85.03 (5)
O6—Co1—O4	90.1 (2)	O5 ^{ix} —Co2—O3 ^v	107.40 (5)
O1 ⁱⁱ —Co1—O4	89.02 (19)	O5—Co2—O3 ^v	96.48 (5)
O6—Co1—O5 ^{vii}	170.0 (3)	O1 ^x —Co2—O3 ^v	85.03 (5)
O1 ⁱⁱ —Co1—O5 ^{vii}	79.4 (2)	O1 ^{xi} —Co2—O3 ^v	162.94 (5)
O4—Co1—O5 ^{vii}	98.73 (19)	O3 ^{xii} —Co2—O3 ^v	78.12 (7)
O6—Co1—O2 ^v	90.4 (2)	O3—V1—O4	112.11 (6)
O1 ⁱⁱ —Co1—O2 ^v	161.7 (3)	O3—V1—O2	105.86 (6)
O4—Co1—O2 ^v	99.9 (2)	O4—V1—O2	110.50 (6)
O5 ^{vii} —Co1—O2 ^v	83.40 (18)	O3—V1—O1	108.79 (6)
O6—Co1—O2 ^{viii}	81.15 (16)	O4—V1—O1	107.01 (6)
O1 ⁱⁱ —Co1—O2 ^{viii}	90.9 (2)	O2—V1—O1	112.65 (6)
O4—Co1—O2 ^{viii}	170.8 (3)	O6—V2—O6 ⁱⁱⁱ	102.86 (8)
O5 ^{vii} —Co1—O2 ^{viii}	90.3 (2)	O6—V2—O5 ⁱⁱⁱ	108.27 (6)
O2 ^v —Co1—O2 ^{viii}	82.90 (17)	O6 ⁱⁱⁱ —V2—O5 ⁱⁱⁱ	109.38 (6)
O6—Fe1—O4	89.8 (2)	O6—V2—O5	109.37 (6)

O6—Fe1—O1 ⁱⁱ	105.0 (2)	O6 ⁱⁱⁱ —V2—O5	108.27 (6)
O4—Fe1—O1 ⁱⁱ	88.6 (2)	O5 ⁱⁱⁱ —V2—O5	117.68 (8)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x, -y+1, z-1/2$; (iii) $-x, y, -z+1/2$; (iv) $-x+1, y, -z+3/2$; (v) $x, -y+1, z+1/2$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+1/2, -y+3/2, -z+1$; (viii) $-x+1/2, y+1/2, -z+1/2$; (ix) $-x, y, -z+3/2$; (x) $-x+1/2, y+1/2, -z+3/2$; (xi) $x-1/2, y+1/2, z$; (xii) $-x, -y+1, -z+1$.