



Na_{1.85}Mg_{1.85}In_{1.15}(PO₄)₃ and Ag_{1.69}Mg_{1.69}In_{1.31}(PO₄)₃ with alluaudite-type structures

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Single crystals of two new phosphates, sodium magnesium indium(III) tris(orthophosphate) and silver magnesium indium(III) tris(orthophosphate), were obtained from solid-state reactions. The two phosphates are isotypic and exhibit alluaudite-type structures. They are characterized by a cationic disorder of the Mg and In sites and a partial occupation of the Na and Ag sites, respectively. The structure of both phosphates is made up of chains of edge-sharing [(Mg,In)O₆] octahedra extending parallel to [10 $\bar{1}$]. Adjacent chains are linked by PO₄ tetrahedra to form a three-dimensional framework delimiting two types of channels parallel to [001] in which the monovalent cations are situated. The coordination numbers of the Na⁺ cations are 6 and 8, and for both Ag⁺ cations 6. The corresponding coordination spheres are considerably distorted.

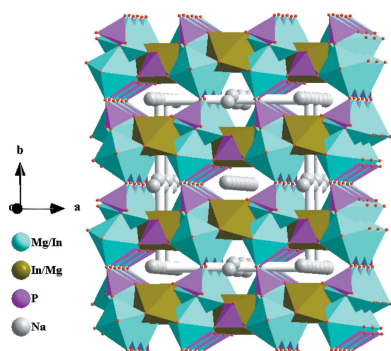
1. Chemical context

The crystal structure of the mineral alluaudite was determined by Moore (1971). Since then, many new members of this structure type, including phosphates, arsenates, molybdates, sulfates and, more recently, vanadates have been synthesized and structurally characterized. The growing interest in these kinds of materials is related to their interesting physical properties, in particular in electrochemistry and battery research. For example, the phosphate Na₂Ni₂Fe(PO₄)₃ (Essehli *et al.*, 2015) is a promising cathode in sodium batteries since its electrochemical behaviour is comparable to that of LiFePO₄. In this context, alluaudite-type phosphates such as Na_{1.67}Zn_{1.67}Fe_{1.33}(PO₄)₃ (Khmiyas *et al.*, 2015), Ag_{1.655}Co_{1.647}Fe_{1.352}(PO₄)₃ (Bouraima *et al.*, 2017) and the vanadate (Na_{0.7})(Na_{0.70}, Mn_{0.30})(Fe³⁺, Fe²⁺)₂Fe²⁺(VO₄)₃ (Benhsina *et al.*, 2016) have been investigated by our group.

In the present work, the synthesis and structure determination of two new magnesium-based alluaudite-type phosphates with composition Na_{1.85}Mg_{1.85}In_{1.15}(PO₄)₃ (I) and Ag_{1.69}Mg_{1.69}In_{1.31}(PO₄)₃ (II) are reported.

2. Structural commentary

In the crystal structures of the two isotypic phosphates (I) and (II), site Na1 (Ag1) shows full occupancy and is located on an inversion centre (Wyckoff position 4*b*), and one mixed-occupied (Mg/In)₂ site [occupancy ratio Mg:In = 0.51:0.49 for (I) and 0.314:0.686 for (II)], the second partially occupied Na2



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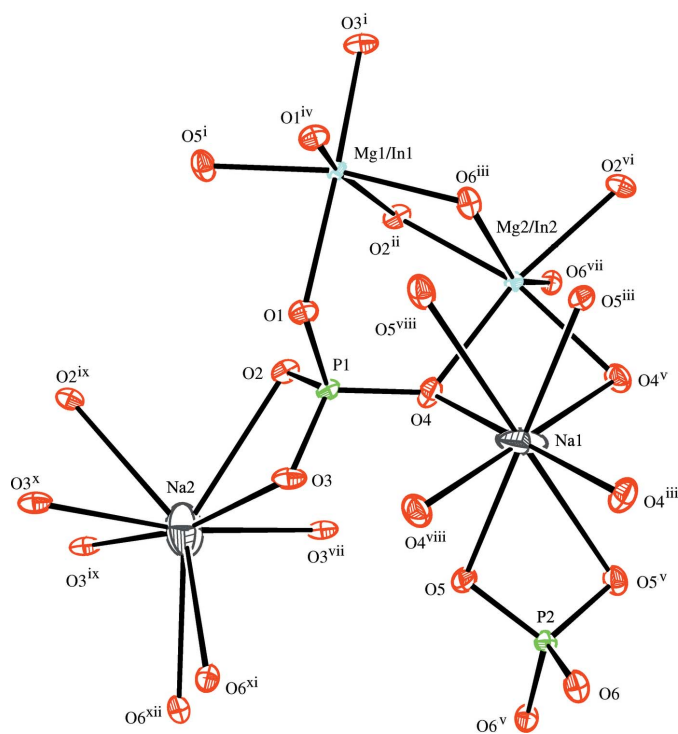


Figure 1
The principal building units in the structure of $\text{Na}_{1.85}\text{Mg}_{1.85}\text{In}_{1.15}(\text{PO}_4)_3$, (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z$; (v) $-x + 1, y, -z + \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $x, -y + 1, z + \frac{1}{2}$; (viii) $x, -y + 1, z - \frac{1}{2}$; (ix) $-x + 2, y, -z + \frac{3}{2}$; (x) $-x + 2, -y + 1, -z + 1$; (xi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (xii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$.]

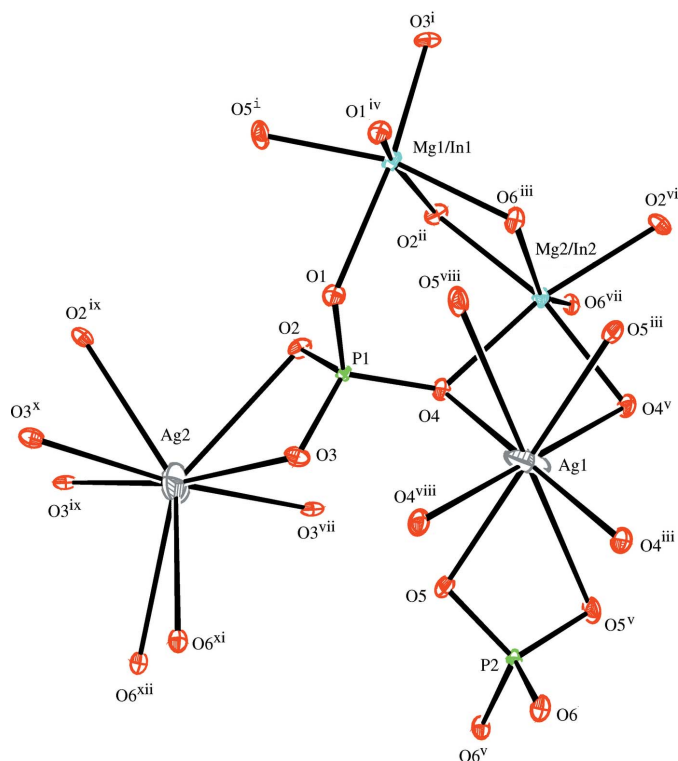


Figure 2
The principal building units in the structure of $\text{Ag}_{1.69}\text{Mg}_{1.69}\text{In}_{1.31}(\text{PO}_4)_3$, (II). Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as in Fig. 1.

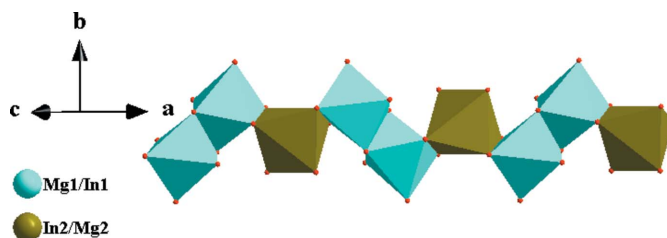


Figure 3
Edge-sharing $[(\text{Mg}/\text{In})_2\text{O}_6]$ octahedra and $[(\text{Mg}/\text{In})_1]_2\text{O}_{10}$ dimers forming an infinite chain extending parallel to $[00\bar{1}]$. Data taken from (I).

(Ag2) site [occupancy 0.848 (9) for (I) and 0.6988 for (II)] and the P1 site are located on twofold rotation axes ($4e$) of space group type $C2/c$. There is another mixed-occupancy (Mg,In)1 site in a general position ($8f$) with occupancy ratios Mg:In = 0.68:0.32 for (I) and 0.687 (2):0.314 (2) for (II). This kind of cationic disorder is a characteristic feature of alluaudite-type structures. The principal building units in the crystal structures of (I) and (II) are $[(\text{Mg}/\text{In})\text{O}_6]$ and $[(\text{Mg},\text{In})_2\text{O}_6]$ octahedra and two PO_4 tetrahedra (Figs. 1 and 2). Two $[(\text{Mg}/\text{In})\text{O}_6]$ octahedra are linked together by a common edge into an $[(\text{Mg}/\text{In})_1]_2\text{O}_{10}$ dimer. These dimers are connected through edge-sharing with $[(\text{Mg}/\text{In})_2\text{O}_6]$ octahedra into undulating chains extending parallel to $[10\bar{1}]$ (Fig. 3). Adjacent chains are linked together by P1O_4 and P2O_4 tetrahedra into (010) sheets, as shown in Fig. 4. Neighbouring sheets are finally fused into a three-dimensional framework structure by P1O_4 tetrahedra. This framework delimits two types of hexagonal channels oriented parallel to $[001]$, in which the Na^+ (for (I) or Ag^+ (for (II) cations are located (Fig. 5). The Na–O distances fall in the range 2.307 (2)–2.960 (2) Å with coordination numbers of six for Na1 and eight for Na2, while those for Ag–O vary between 2.345 (2) and 2.963 (2) Å, with coordination numbers of six for both Ag^+ cations.

3. Database Survey

The presence of disordered alkali metal or other cations in the channels of alluaudite-type structures is a concomitant feature

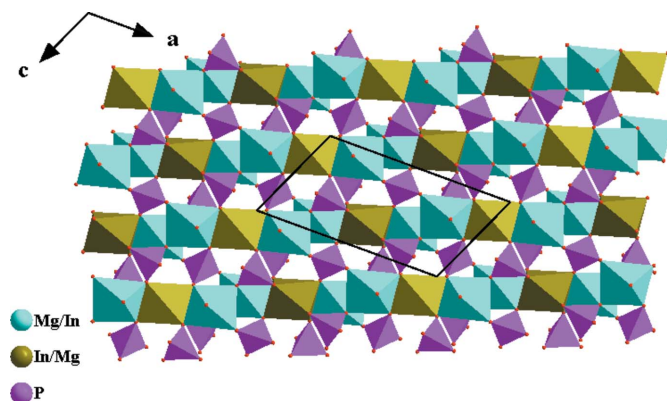


Figure 4
 $[(\text{Mg}/\text{In})\text{O}_6]$ octahedra and PO_4 tetrahedra forming a sheet extending parallel to (010). Data taken from (I).

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	Na _{1.85} Mg _{1.85} In _{1.15} (PO ₄) ₃	Ag _{1.69} Mg _{1.69} In _{1.31} (PO ₄) ₃
<i>M_r</i>	504.46	658.40
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.9796 (13), 12.6935 (13), 6.5239 (7)	12.0273 (3), 12.8120 (3), 6.5061 (2)
β (°)	114.555 (3)	114.519 (1)
<i>V</i> (Å ³)	902.33 (17)	912.14 (4)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	3.82	7.59
Crystal size (mm)	0.31 × 0.24 × 0.20	0.30 × 0.27 × 0.23
Data collection		
Diffractometer	Bruker X8 APEXII	Bruker X8 APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.596, 0.748	0.404, 0.748
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	21364, 2076, 2012	13615, 1827, 1818
<i>R_{int}</i>	0.026	0.027
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.819	0.781
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.058, 1.29	0.022, 0.053, 1.25
No. of reflections	2076	1827
No. of parameters	97	97
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.64, -0.88	2.32, -1.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS2016* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

of the cationic disorder at the octahedral sites, as observed for example in Cu_{1.35}Fe₃(PO₄)₃ (Warner *et al.*, 1993), (Na_{0.38},Ca_{0.31})MgFe₂(PO₄)₃ (Zid *et al.*, 2005), K_{0.53}Mn_{2.37}Fe_{1.24}(PO₄)₃ (Hidouri & Ben Amara, 2011), NaFe_{3.67}(PO₄)₃ (Korzenski *et al.*, 1998), Na_{1.25}Mg_{1.10}Fe_{1.90}

(PO₄)₃ (Hidouri *et al.*, 2008), Na_{1.50}Mn_{2.48}Al_{0.85}(PO₄)₃ (Hatert, 2006), Na_{1.79}Mg_{1.79}Fe_{1.21}(PO₄)₃ (Hidouri *et al.*, 2003), Na_{1.67}Zn_{1.67}Fe_{1.33}(PO₄)₃ (Khmiya *et al.*, 2015) or Ag_{1.655}Co_{1.647}Fe_{1.352}(PO₄)₃ (Bouraima *et al.*, 2017).

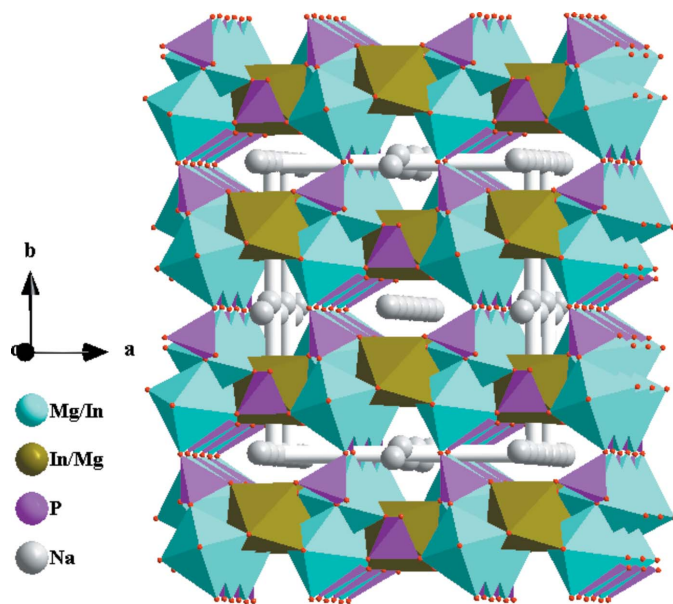


Figure 5
Polyhedral representation of the crystal structure of (I) showing Na⁺ cations situated in the two types of channels parallel to [001].

4. Synthesis and crystallization

Single crystals of (I) and (II) were grown by solid-state reactions. The starting mixtures comprising of Mg(NO₃)₂·6H₂O (Sigma–Aldrich, 97%), InI₃ (Ventron, 99%), NH₄H₂PO₄ (Alfa Aesar, 98%), ANO₃ (*A* = Na or Ag) (NaNO₃: Acros Organics, 99%; AgNO₃: Sigma–Aldrich, 99%) were weighted in molar ratios *A*:Zn:In:P = 2:2:1:3 and placed in a platinum crucible. After intermediate grinding and temperature treatments at 573, 673, 773 and 873 K in a platinum crucible, both mixtures were heated at 1373 K above the melting temperatures. The crucibles were then cooled slowly to 1093 K at a rate of 5 K h⁻¹, followed by cooling to room temperature after switching off the furnace. Transparent, colourless crystals with a blocky form were isolated from the two final products. The bulk products were not checked for phase purity.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. In the initial stages of the refinements the occupancies of the disordered sodium (Na₂) or silver (Ag₂) sites were refined freely and the mixed-occupancy (Mg/In) sites were refined under consideration of full occu-

pancy for each of these sites. The obtained occupancy rates of Mg:In were rounded and subsequently fixed for charge-neutrality of the compounds. The maximum and minimum electron densities are located 0.55 Å from Mg2 and 0.38 Å from P1 for (I) and 0.78 and 0.59 Å, respectively, from Ag2 for (II).

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Na_{1.85}Mg_{1.85}In_{1.15}(PO₄)₃ and Ag_{1.69}Mg_{1.69}In_{1.31}(PO₄)₃ with alluaudite-type structures

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXS2016* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Sodium magnesium indium(III) tris(orthophosphate) (I)

Crystal data

Na_{1.85}Mg_{1.85}In_{1.15}(PO₄)₃

$M_r = 504.46$

Monoclinic, *C2/c*

$a = 11.9796$ (13) Å

$b = 12.6935$ (13) Å

$c = 6.5239$ (7) Å

$\beta = 114.555$ (3)°

$V = 902.33$ (17) Å³

$Z = 4$

$F(000) = 960$

$D_x = 3.713$ Mg m⁻³

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

Cell parameters from 2076 reflections

$\theta = 2.5$ – 35.6 °

$\mu = 3.82$ mm⁻¹

$T = 296$ K

Block, colourless

$0.31 \times 0.24 \times 0.20$ mm

Data collection

Bruker X8 APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.596$, $T_{\max} = 0.748$

21364 measured reflections

2076 independent reflections

2012 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 35.6$ °, $\theta_{\min} = 2.5$ °

$h = -19 \rightarrow 19$

$k = -20 \rightarrow 20$

$l = -10 \rightarrow 4$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.058$

$S = 1.29$

2076 reflections

97 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0082P)^2 + 5.6344P]$

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

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

$\Delta\rho_{\max} = 0.64$ e Å⁻³

$\Delta\rho_{\min} = -0.88$ 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)
Mg1	0.71903 (3)	0.84384 (2)	0.13247 (5)	0.00578 (6)	0.68
In1	0.71903 (3)	0.84384 (2)	0.13247 (5)	0.00578 (6)	0.32
In2	0.500000	0.73266 (2)	0.250000	0.00619 (6)	0.51
Mg2	0.500000	0.73266 (2)	0.250000	0.00619 (6)	0.49
P1	0.76657 (4)	0.60997 (4)	0.37446 (8)	0.00665 (8)	
P2	0.500000	0.29168 (6)	0.250000	0.00702 (11)	
Na1	0.500000	0.500000	0.000000	0.0261 (4)	
Na2	1.000000	0.4813 (2)	0.750000	0.0369 (8)	0.848 (9)
O1	0.77790 (14)	0.67695 (12)	0.1877 (2)	0.0092 (2)	
O2	0.83997 (14)	0.66480 (12)	0.6061 (2)	0.0096 (2)	
O3	0.82556 (15)	0.50207 (12)	0.3858 (3)	0.0126 (3)	
O4	0.62982 (14)	0.60255 (13)	0.3291 (3)	0.0128 (3)	
O5	0.59943 (14)	0.36515 (12)	0.2450 (3)	0.0124 (3)	
O6	0.45840 (13)	0.22035 (12)	0.0372 (2)	0.0099 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.00607 (11)	0.00594 (11)	0.00620 (11)	−0.00056 (8)	0.00342 (8)	−0.00092 (8)
In1	0.00607 (11)	0.00594 (11)	0.00620 (11)	−0.00056 (8)	0.00342 (8)	−0.00092 (8)
In2	0.00700 (12)	0.00580 (11)	0.00657 (11)	0.000	0.00360 (9)	0.000
Mg2	0.00700 (12)	0.00580 (11)	0.00657 (11)	0.000	0.00360 (9)	0.000
P1	0.00876 (19)	0.00636 (18)	0.00521 (17)	−0.00120 (14)	0.00328 (15)	−0.00039 (14)
P2	0.0072 (3)	0.0077 (3)	0.0054 (2)	0.000	0.0018 (2)	0.000
Na1	0.0375 (9)	0.0121 (6)	0.0156 (6)	0.0017 (6)	−0.0020 (6)	0.0029 (5)
Na2	0.0228 (11)	0.0569 (17)	0.0235 (11)	0.000	0.0020 (8)	0.000
O1	0.0121 (6)	0.0098 (6)	0.0062 (5)	−0.0004 (5)	0.0044 (5)	0.0014 (4)
O2	0.0136 (6)	0.0099 (6)	0.0053 (5)	−0.0027 (5)	0.0039 (5)	−0.0017 (4)
O3	0.0189 (7)	0.0062 (5)	0.0135 (6)	0.0003 (5)	0.0077 (5)	−0.0009 (5)
O4	0.0109 (6)	0.0136 (6)	0.0156 (7)	−0.0035 (5)	0.0072 (5)	−0.0016 (5)
O5	0.0090 (6)	0.0111 (6)	0.0155 (7)	−0.0012 (5)	0.0036 (5)	0.0053 (5)
O6	0.0083 (5)	0.0131 (6)	0.0076 (5)	0.0007 (5)	0.0026 (4)	−0.0026 (5)

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

Mg1—O5 ⁱ	1.9992 (16)	P2—O6 ^v	1.5558 (15)
Mg1—O3 ⁱ	2.0690 (16)	P2—O6	1.5558 (15)
Mg1—O2 ⁱⁱ	2.1030 (15)	Na1—O5 ⁱⁱⁱ	2.3068 (15)
Mg1—O6 ⁱⁱⁱ	2.1099 (15)	Na1—O5	2.3068 (15)

Mg1—O1 ^{iv}	2.1207 (14)	Na1—O4	2.4387 (16)
Mg1—O1	2.2144 (15)	Na1—O4 ⁱⁱⁱ	2.4388 (16)
In2—O4 ^v	2.1783 (17)	Na1—O4 ^{viii}	2.6072 (15)
In2—O4	2.1784 (17)	Na1—O4 ^v	2.6072 (15)
In2—O2 ⁱⁱ	2.1807 (15)	Na1—O5 ^{viii}	2.9603 (17)
In2—O2 ^{vi}	2.1807 (15)	Na1—O5 ^v	2.9603 (17)
In2—O6 ^{vii}	2.2115 (15)	Na2—O3	2.4401 (17)
In2—O6 ⁱⁱⁱ	2.2115 (15)	Na2—O3 ^{ix}	2.4401 (17)
P1—O3	1.5287 (16)	Na2—O3 ^x	2.5955 (17)
P1—O1	1.5373 (15)	Na2—O3 ^{vii}	2.5955 (17)
P1—O4	1.5419 (16)	Na2—O6 ^{xi}	2.856 (3)
P1—O2	1.5609 (15)	Na2—O6 ^{xii}	2.856 (3)
P2—O5	1.5238 (16)	Na2—O2	2.913 (3)
P2—O5 ^v	1.5238 (16)	Na2—O2 ^{ix}	2.913 (3)
O5 ⁱ —Mg1—O3 ⁱ	95.94 (6)	O5—Na1—O4 ^{viii}	72.41 (6)
O5 ⁱ —Mg1—O2 ⁱⁱ	111.05 (6)	O4—Na1—O4 ^{viii}	111.56 (7)
O3 ⁱ —Mg1—O2 ⁱⁱ	86.09 (6)	O4 ⁱⁱⁱ —Na1—O4 ^{viii}	68.44 (7)
O5 ⁱ —Mg1—O6 ⁱⁱⁱ	162.43 (6)	O5 ⁱⁱⁱ —Na1—O4 ^v	72.41 (6)
O3 ⁱ —Mg1—O6 ⁱⁱⁱ	99.50 (6)	O5—Na1—O4 ^v	107.59 (6)
O2 ⁱⁱ —Mg1—O6 ⁱⁱⁱ	78.50 (6)	O4—Na1—O4 ^v	68.44 (7)
O5 ⁱ —Mg1—O1 ^{iv}	87.10 (6)	O4 ⁱⁱⁱ —Na1—O4 ^v	111.56 (7)
O3 ⁱ —Mg1—O1 ^{iv}	100.00 (6)	O4 ^{viii} —Na1—O4 ^v	180.0
O2 ⁱⁱ —Mg1—O1 ^{iv}	160.31 (6)	O5 ⁱⁱⁱ —Na1—O5 ^{viii}	52.70 (6)
O6 ⁱⁱⁱ —Mg1—O1 ^{iv}	82.03 (6)	O5—Na1—O5 ^{viii}	127.30 (6)
O5 ⁱ —Mg1—O1	81.05 (6)	O4—Na1—O5 ^{viii}	85.86 (5)
O3 ⁱ —Mg1—O1	174.39 (6)	O4 ⁱⁱⁱ —Na1—O5 ^{viii}	94.14 (5)
O2 ⁱⁱ —Mg1—O1	90.57 (6)	O4 ^{viii} —Na1—O5 ^{viii}	66.27 (5)
O6 ⁱⁱⁱ —Mg1—O1	84.22 (6)	O4 ^v —Na1—O5 ^{viii}	113.73 (5)
O1 ^{iv} —Mg1—O1	84.63 (6)	O5 ⁱⁱⁱ —Na1—O5 ^v	127.30 (6)
O4 ^v —In2—O4	81.40 (8)	O5—Na1—O5 ^v	52.70 (6)
O4 ^v —In2—O2 ⁱⁱ	165.44 (6)	O4—Na1—O5 ^v	94.14 (5)
O4—In2—O2 ⁱⁱ	86.40 (6)	O4 ⁱⁱⁱ —Na1—O5 ^v	85.86 (5)
O4 ^v —In2—O2 ^{vi}	86.40 (6)	O4 ^{viii} —Na1—O5 ^v	113.73 (5)
O4—In2—O2 ^{vi}	165.44 (6)	O4 ^v —Na1—O5 ^v	66.27 (5)
O2 ⁱⁱ —In2—O2 ^{vi}	106.70 (8)	O5 ^{viii} —Na1—O5 ^v	180.0
O4 ^v —In2—O6 ^{vii}	90.87 (6)	O3—Na2—O3 ^{ix}	167.61 (15)
O4—In2—O6 ^{vii}	113.19 (6)	O3—Na2—O3 ^x	98.29 (5)
O2 ⁱⁱ —In2—O6 ^{vii}	86.65 (5)	O3 ^{ix} —Na2—O3 ^x	80.70 (5)
O2 ^{vi} —In2—O6 ^{vii}	74.72 (5)	O3—Na2—O3 ^{vii}	80.70 (5)
O4 ^v —In2—O6 ⁱⁱⁱ	113.19 (6)	O3 ^{ix} —Na2—O3 ^{vii}	98.29 (5)
O4—In2—O6 ⁱⁱⁱ	90.87 (6)	O3 ^x —Na2—O3 ^{vii}	170.69 (14)
O2 ⁱⁱ —In2—O6 ⁱⁱⁱ	74.72 (5)	O3—Na2—O6 ^{xi}	73.60 (6)
O2 ^{vi} —In2—O6 ⁱⁱⁱ	86.65 (5)	O3 ^{ix} —Na2—O6 ^{xi}	118.42 (10)
O6 ^{vii} —In2—O6 ⁱⁱⁱ	148.70 (8)	O3 ^x —Na2—O6 ^{xi}	84.80 (7)
O3—P1—O1	110.04 (9)	O3 ^{vii} —Na2—O6 ^{xi}	103.66 (8)
O3—P1—O4	112.79 (9)	O3—Na2—O6 ^{xii}	118.42 (10)
O1—P1—O4	108.57 (9)	O3 ^{ix} —Na2—O6 ^{xii}	73.60 (6)

O3—P1—O2	106.82 (9)	O3 ^x —Na2—O6 ^{xii}	103.66 (8)
O1—P1—O2	108.72 (8)	O3 ^{vii} —Na2—O6 ^{xii}	84.80 (7)
O4—P1—O2	109.83 (9)	O6 ^{xi} —Na2—O6 ^{xii}	52.60 (8)
O5—P2—O5 ^v	104.53 (13)	O3—Na2—O2	54.35 (6)
O5—P2—O6 ^v	114.33 (8)	O3 ^{ix} —Na2—O2	114.22 (10)
O5 ^v —P2—O6 ^v	107.48 (9)	O3 ^x —Na2—O2	109.91 (9)
O5—P2—O6	107.48 (9)	O3 ^{vii} —Na2—O2	61.95 (6)
O5 ^v —P2—O6	114.33 (8)	O6 ^{xi} —Na2—O2	126.98 (4)
O6 ^v —P2—O6	108.82 (12)	O6 ^{xii} —Na2—O2	146.30 (5)
O5 ⁱⁱⁱ —Na1—O5	180.0	O3—Na2—O2 ^{ix}	114.22 (10)
O5 ⁱⁱⁱ —Na1—O4	99.83 (6)	O3 ^{ix} —Na2—O2 ^{ix}	54.35 (6)
O5—Na1—O4	80.17 (6)	O3 ^x —Na2—O2 ^{ix}	61.95 (6)
O5 ⁱⁱⁱ —Na1—O4 ⁱⁱⁱ	80.17 (6)	O3 ^{vii} —Na2—O2 ^{ix}	109.91 (9)
O5—Na1—O4 ⁱⁱⁱ	99.83 (6)	O6 ^{xi} —Na2—O2 ^{ix}	146.30 (5)
O4—Na1—O4 ⁱⁱⁱ	180.0	O6 ^{xii} —Na2—O2 ^{ix}	126.98 (4)
O5 ⁱⁱⁱ —Na1—O4 ^{viii}	107.59 (6)	O2—Na2—O2 ^{ix}	73.83 (9)

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

Silver magnesium indium(III) tris(orthophosphate) (II)

Crystal data

Ag_{1.69}Mg_{1.69}In_{1.31}(PO₄)₃

$M_r = 658.40$

Monoclinic, *C2/c*

$a = 12.0273$ (3) Å

$b = 12.8120$ (3) Å

$c = 6.5061$ (2) Å

$\beta = 114.519$ (1)°

$V = 912.14$ (4) Å³

$Z = 4$

$F(000) = 1219$

$D_x = 4.794$ Mg m⁻³

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

Cell parameters from 1827 reflections

$\theta = 2.5$ – 33.7 °

$\mu = 7.59$ mm⁻¹

$T = 296$ K

Block, colourless

$0.30 \times 0.27 \times 0.23$ mm

Data collection

Bruker X8 APEXII

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.404$, $T_{\max} = 0.748$

13615 measured reflections

1827 independent reflections

1818 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 33.7$ °, $\theta_{\min} = 2.5$ °

$h = -18$ → 18

$k = -20$ → 20

$l = -10$ → 7

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.053$

$S = 1.25$

1827 reflections

97 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0071P)^2 + 8.2996P]$

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

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

$\Delta\rho_{\max} = 2.32$ e Å⁻³

$\Delta\rho_{\min} = -1.36$ e Å⁻³

Extinction correction: SHELXL2016

(Sheldrick, 2015*b*),

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

Extinction coefficient: 0.00143 (15)

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)
In1	0.71633 (3)	0.84600 (3)	0.12503 (6)	0.0061 (2)	0.314 (2)
Mg1	0.71633 (3)	0.84600 (3)	0.12503 (6)	0.0061 (2)	0.687 (2)
Mg2	0.500000	0.73554 (2)	0.250000	0.00583 (9)	0.314 (2)
In2	0.500000	0.73554 (2)	0.250000	0.00583 (9)	0.686 (2)
Ag1	0.500000	0.500000	0.000000	0.02109 (10)	
Ag2	1.000000	0.48627 (5)	0.750000	0.03258 (15)	0.6988
P1	0.76583 (5)	0.61258 (4)	0.37509 (9)	0.00362 (10)	
P2	0.500000	0.29241 (6)	0.250000	0.00404 (13)	
O1	0.77898 (15)	0.67881 (13)	0.1901 (3)	0.0064 (3)	
O2	0.84069 (15)	0.66448 (13)	0.6096 (3)	0.0065 (3)	
O3	0.81775 (16)	0.50301 (13)	0.3825 (3)	0.0096 (3)	
O4	0.62999 (15)	0.60993 (13)	0.3340 (3)	0.0080 (3)	
O5	0.60107 (15)	0.36446 (13)	0.2501 (3)	0.0094 (3)	
O6	0.45894 (15)	0.22207 (13)	0.0360 (3)	0.0062 (3)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
In1	0.00587 (16)	0.00690 (16)	0.00638 (17)	−0.00070 (10)	0.00336 (11)	−0.00109 (10)
Mg1	0.00587 (16)	0.00690 (16)	0.00638 (17)	−0.00070 (10)	0.00336 (11)	−0.00109 (10)
Mg2	0.00560 (13)	0.00642 (13)	0.00604 (13)	0.000	0.00297 (9)	0.000
In2	0.00560 (13)	0.00642 (13)	0.00604 (13)	0.000	0.00297 (9)	0.000
Ag1	0.03303 (18)	0.00978 (13)	0.01314 (14)	0.00397 (10)	0.00229 (11)	0.00201 (9)
Ag2	0.0127 (2)	0.0291 (3)	0.0406 (3)	0.000	−0.00429 (19)	0.000
P1	0.0037 (2)	0.0038 (2)	0.0036 (2)	−0.00040 (15)	0.00170 (17)	−0.00038 (15)
P2	0.0035 (3)	0.0051 (3)	0.0031 (3)	0.000	0.0010 (2)	0.000
O1	0.0069 (6)	0.0084 (6)	0.0043 (6)	−0.0004 (5)	0.0027 (5)	0.0011 (5)
O2	0.0084 (6)	0.0072 (6)	0.0034 (6)	−0.0025 (5)	0.0020 (5)	−0.0018 (5)
O3	0.0106 (7)	0.0043 (6)	0.0142 (8)	0.0006 (5)	0.0055 (6)	−0.0022 (5)
O4	0.0052 (6)	0.0078 (6)	0.0120 (7)	0.0002 (5)	0.0045 (6)	0.0009 (5)
O5	0.0055 (6)	0.0091 (7)	0.0129 (8)	−0.0018 (5)	0.0032 (6)	0.0031 (6)
O6	0.0052 (6)	0.0091 (6)	0.0043 (6)	−0.0006 (5)	0.0019 (5)	−0.0014 (5)

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

In1—O5 ⁱ	2.0146 (17)	Ag1—O5 ^{viii}	2.9625 (19)
In1—O3 ⁱ	2.0495 (17)	Ag1—O5 ^v	2.9625 (19)
In1—O1 ⁱⁱ	2.0985 (16)	Ag2—O3	2.4934 (19)
In1—O2 ⁱⁱⁱ	2.1098 (17)	Ag2—O3 ^{ix}	2.4934 (19)

In1—O6 ^{iv}	2.1140 (16)	Ag2—O3 ^x	2.6713 (18)
In1—O1	2.2518 (17)	Ag2—O3 ^{vii}	2.6713 (18)
Mg2—O4	2.1502 (17)	Ag2—O2 ^{ix}	2.8751 (18)
Mg2—O4 ^v	2.1503 (17)	Ag2—O2	2.8751 (18)
Mg2—O2 ⁱⁱⁱ	2.1665 (16)	Ag2—O6 ^{xi}	2.9558 (18)
Mg2—O2 ^{vi}	2.1665 (16)	Ag2—O6 ^{xii}	2.9558 (18)
Mg2—O6 ^{vii}	2.1827 (16)	P1—O3	1.5290 (17)
Mg2—O6 ^{iv}	2.1827 (16)	P1—O1	1.5335 (17)
Ag1—O5	2.3450 (17)	P1—O4	1.5425 (17)
Ag1—O5 ^{iv}	2.3451 (17)	P1—O2	1.5624 (17)
Ag1—O4 ^{iv}	2.5162 (17)	P2—O5 ^v	1.5261 (17)
Ag1—O4	2.5162 (17)	P2—O5	1.5261 (17)
Ag1—O4 ^{viii}	2.6449 (17)	P2—O6	1.5569 (17)
Ag1—O4 ^v	2.6449 (17)	P2—O6 ^v	1.5569 (17)
O5 ⁱ —In1—O3 ⁱ	93.91 (7)	O4 ^{viii} —Ag1—O5 ^{viii}	68.99 (5)
O5 ⁱ —In1—O1 ⁱⁱ	86.84 (7)	O4 ^v —Ag1—O5 ^{viii}	111.01 (5)
O3 ⁱ —In1—O1 ⁱⁱ	102.20 (7)	O5—Ag1—O5 ^v	52.97 (7)
O5 ⁱ —In1—O2 ⁱⁱⁱ	110.35 (7)	O5 ^{iv} —Ag1—O5 ^v	127.03 (7)
O3 ⁱ —In1—O2 ⁱⁱⁱ	87.27 (7)	O4 ^{iv} —Ag1—O5 ^v	84.06 (5)
O1 ⁱⁱ —In1—O2 ⁱⁱⁱ	159.96 (6)	O4—Ag1—O5 ^v	95.94 (5)
O5 ⁱ —In1—O6 ^{iv}	160.79 (7)	O4 ^{viii} —Ag1—O5 ^v	111.01 (5)
O3 ⁱ —In1—O6 ^{iv}	104.16 (7)	O4 ^v —Ag1—O5 ^v	68.99 (5)
O1 ⁱⁱ —In1—O6 ^{iv}	83.05 (6)	O5 ^{viii} —Ag1—O5 ^v	180.0
O2 ⁱⁱⁱ —In1—O6 ^{iv}	77.49 (6)	O3—Ag2—O3 ^{ix}	170.14 (8)
O5 ⁱ —In1—O1	79.17 (7)	O3—Ag2—O3 ^x	101.46 (5)
O3 ⁱ —In1—O1	170.47 (7)	O3 ^{ix} —Ag2—O3 ^x	78.02 (5)
O1 ⁱⁱ —In1—O1	84.09 (6)	O3—Ag2—O3 ^{vii}	78.02 (5)
O2 ⁱⁱⁱ —In1—O1	89.01 (6)	O3 ^{ix} —Ag2—O3 ^{vii}	101.46 (5)
O6 ^{iv} —In1—O1	83.56 (6)	O3 ^x —Ag2—O3 ^{vii}	174.11 (7)
O4—Mg2—O4 ^v	83.10 (9)	O3—Ag2—O2 ^{ix}	116.17 (5)
O4—Mg2—O2 ⁱⁱⁱ	85.00 (6)	O3 ^{ix} —Ag2—O2 ^{ix}	54.71 (5)
O4 ^v —Mg2—O2 ⁱⁱⁱ	166.46 (6)	O3 ^x —Ag2—O2 ^{ix}	62.21 (5)
O4—Mg2—O2 ^{vi}	166.46 (6)	O3 ^{vii} —Ag2—O2 ^{ix}	112.62 (5)
O4 ^v —Mg2—O2 ^{vi}	84.99 (6)	O3—Ag2—O2	54.71 (5)
O2 ⁱⁱⁱ —Mg2—O2 ^{vi}	107.51 (9)	O3 ^{ix} —Ag2—O2	116.17 (5)
O4—Mg2—O6 ^{vii}	111.55 (6)	O3 ^x —Ag2—O2	112.62 (5)
O4 ^v —Mg2—O6 ^{vii}	90.29 (6)	O3 ^{vii} —Ag2—O2	62.21 (5)
O2 ⁱⁱⁱ —Mg2—O6 ^{vii}	88.11 (6)	O2 ^{ix} —Ag2—O2	74.85 (7)
O2 ^{vi} —Mg2—O6 ^{vii}	74.86 (6)	O3—Ag2—O6 ^{xi}	73.59 (5)
O4—Mg2—O6 ^{iv}	90.29 (6)	O3 ^{ix} —Ag2—O6 ^{xi}	115.97 (5)
O4 ^v —Mg2—O6 ^{iv}	111.55 (6)	O3 ^x —Ag2—O6 ^{xi}	83.88 (5)
O2 ⁱⁱⁱ —Mg2—O6 ^{iv}	74.86 (6)	O3 ^{vii} —Ag2—O6 ^{xi}	101.50 (5)
O2 ^{vi} —Mg2—O6 ^{iv}	88.11 (6)	O2 ^{ix} —Ag2—O6 ^{xi}	145.67 (5)
O6 ^{vii} —Mg2—O6 ^{iv}	151.18 (9)	O2—Ag2—O6 ^{xi}	127.48 (4)
O4—Mg2—O5 ^{iv}	83.64 (6)	O3—Ag2—O6 ^{xii}	115.97 (5)
O5—Ag1—O5 ^{iv}	180.0	O3 ^{ix} —Ag2—O6 ^{xii}	73.59 (5)
O5—Ag1—O4 ^{iv}	98.18 (6)	O3 ^x —Ag2—O6 ^{xii}	101.50 (5)

O5 ^{iv} —Ag1—O4 ^{iv}	81.82 (6)	O3 ^{vii} —Ag2—O6 ^{xii}	83.88 (5)
O5—Ag1—O4	81.82 (6)	O2 ^{ix} —Ag2—O6 ^{xii}	127.48 (4)
O5 ^{iv} —Ag1—O4	98.17 (6)	O2—Ag2—O6 ^{xii}	145.67 (5)
O4 ^{iv} —Ag1—O4	180.0	O6 ^{xi} —Ag2—O6 ^{xii}	50.87 (6)
O5—Ag1—O4 ^{viii}	70.42 (6)	O3—P1—O1	111.04 (10)
O5 ^{iv} —Ag1—O4 ^{viii}	109.58 (6)	O3—P1—O4	112.00 (10)
O4 ^{iv} —Ag1—O4 ^{viii}	67.05 (7)	O1—P1—O4	108.85 (9)
O4—Ag1—O4 ^{viii}	112.95 (7)	O3—P1—O2	107.32 (10)
O5—Ag1—O4 ^v	109.58 (6)	O1—P1—O2	109.01 (9)
O5 ^{iv} —Ag1—O4 ^v	70.42 (6)	O4—P1—O2	108.55 (10)
O4 ^{iv} —Ag1—O4 ^v	112.95 (7)	O5 ^v —P2—O5	105.56 (14)
O4—Ag1—O4 ^v	67.05 (7)	O5 ^v —P2—O6	113.12 (9)
O4 ^{viii} —Ag1—O4 ^v	180.00 (5)	O5—P2—O6	107.91 (9)
O5—Ag1—O5 ^{viii}	127.03 (7)	O5 ^v —P2—O6 ^v	107.91 (9)
O5 ^{iv} —Ag1—O5 ^{viii}	52.97 (7)	O5—P2—O6 ^v	113.12 (9)
O4 ^{iv} —Ag1—O5 ^{viii}	95.94 (5)	O6—P2—O6 ^v	109.26 (13)
O4—Ag1—O5 ^{viii}	84.06 (5)		

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