

# Synthesis, crystal structure and charge-distribution validation of a new alluaudite-type phosphate, $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$

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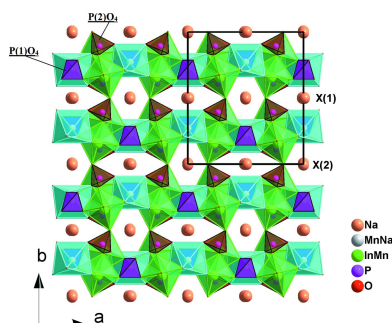
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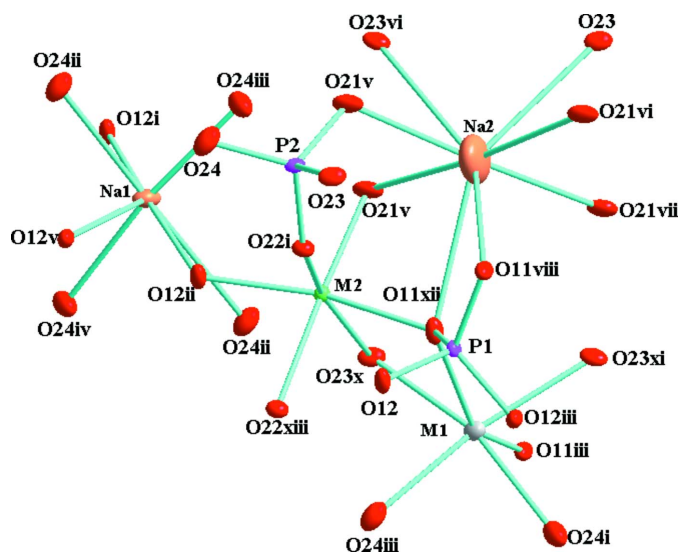
$\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$ , sodium manganese indium tris(phosphate) (2.22/0.87/1.68), was obtained in the form of single crystals by a flux method and was structurally characterized by single-crystal X-ray diffraction. The compound belongs to the alluaudite structure type (space group  $C2/c$ ) with general formula  $X(2)X(1)M(1)M(2)_2(\text{PO}_4)_3$ . The  $X(2)$  and  $X(1)$  sites are partially occupied by sodium [occupancy 0.7676 (17) and 1/2] while the  $M(1)$  and  $M(2)$  sites are fully occupied within a mixed distribution of sodium/manganese(II) and manganese(II)/indium, respectively. The three-dimensional anionic framework is built up on the basis of  $M(2)_2\text{O}_{10}$  dimers that share opposite edges with  $M(1)\text{O}_6$  octahedra, thus forming infinite chains extending parallel to  $[10\bar{1}]$ . The linkage between these chains is ensured by  $\text{PO}_4$  tetrahedra through common vertices. The three-dimensional network thus constructed delimits two types of hexagonal channels, resulting from the catenation of  $M(2)_2\text{O}_{10}$  dimers,  $M(1)\text{O}_6$  octahedra and  $\text{PO}_4$  tetrahedra through edge- and corner-sharing. The channels are occupied by  $\text{Na}^+$  cations with coordination numbers of seven and eight.

## 1. Chemical context

The general structural formula of alluaudite-type phosphates is  $[A(2)A(2)][A(1)A(1)'A(1)''_2]M(1)M(2)_2(\text{PO}_4)_3$  (Hatert *et al.*, 2000); in the majority of natural alluaudites, the large crystallographic  $A$  sites are occupied by  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Mn}^{2+}$ , and the distorted-octahedrally surrounded  $M$  sites are occupied by  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$  (Moore & Ito, 1979). Alluaudite-type phosphates are frequently used for practical applications such as corrosion inhibition, passivation of metal surfaces, or catalysis (Korzenski *et al.*, 1998; Kacimi *et al.*, 2005). Furthermore, as a result of the presence of channels, alluaudite-type compounds exhibit electronic and/or ionic conductivity properties (Warner *et al.*, 1994; Durio *et al.*, 2002). The possibility of inserting variable amounts of lithium into the channels of the alluaudite structure also makes the  $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}^{3+}_2(\text{PO}_4)_3$  and  $(\text{Na}_{1-x}\text{Li}_x)_{1.5}\text{Mn}_{1.5}\text{Fe}^{3+}_{1.5}(\text{PO}_4)_3$  compounds of value as potential battery materials (Hatert *et al.*, 2004; Trad *et al.*, 2018). A number of indium-bearing alluaudite-like compounds have also been synthesized, *i.e.*  $\text{NaCdIn}_2(\text{PO}_4)_3$  (Antenucci *et al.*, 1993),  $\text{Na}_3\text{In}_2(\text{PO}_4)_3$  (Lii & Ye, 1997), and  $\text{NaMn}(\text{Fe}_{1-x}\text{In}_x)_2(\text{PO}_4)_3$  (Hatert *et al.*, 2003). In this paper, we report the structural study of a new alluaudite-type phosphate,  $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$ , which was obtained



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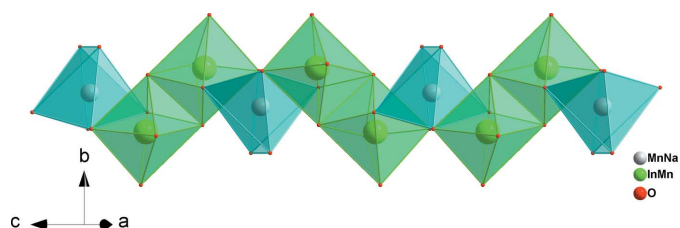


**Figure 1**  
The principal building units of the alluaudite-type phosphate  $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$  with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $x + 1, y, z + 1$ ; (iii)  $x + 1, y, z + \frac{3}{2}$ ; (iv)  $x, y, z - \frac{3}{2}$ ; (v)  $x, y, z - \frac{1}{2}$ ; (vi)  $x, y, z + \frac{3}{2}$ ; (vii)  $x, y, z + 2$ ; (viii)  $x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{3}{2}$ ; (ix)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (x)  $x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$ ; (xi)  $x + \frac{1}{2}, y + \frac{1}{2}, z + 1$ ; (xii)  $x - \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$ ; (xiii)  $x + \frac{1}{2}, y + \frac{1}{2}, z + 2$ ; (xiv)  $x + 1, y, z$ .]

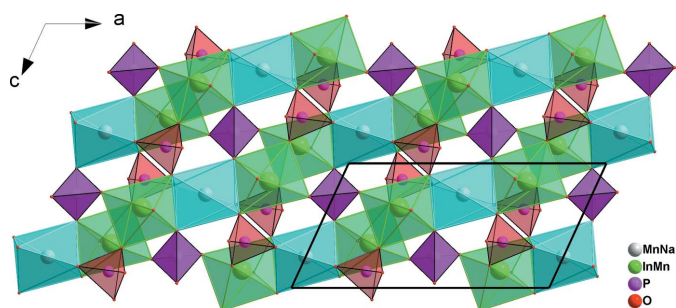
during our investigation of the  $\text{Na}_3\text{PO}_4\text{-Mn}_3(\text{PO}_4)_2\text{-InPO}_4$  quasi system.

## 2. Structural commentary

The principal building units (Fig. 1) of the three-dimensional framework structure of  $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$  are mixed-occupancy (Mn, Na) [=  $M(1)$ ; site symmetry 2] and (Mn1, In) [=  $M(2)$ ] sites with distorted octahedral environments and two phosphate tetrahedra (P1 and P2); the two sites associated with  $\text{Na}^+$  cations (Na1; Na2 with site symmetry 2) are partially occupied and are situated in the resulting voids. By edge-sharing, the (Mn,In) $\text{O}_6$  octahedra form (Mn,In) $\text{O}_{10}$  dimers, which are linked by highly distorted (Mn,Na) $\text{O}_6$  octahedra into infinite zigzag chains along  $[10\bar{1}]$  (Fig. 2). The connection of these chains through vertices belonging to  $\text{P1O}_4$  and  $\text{P2O}_4$  tetrahedra gives layers perpendicular to  $[010]$  (Fig. 3), which, in turn, are linked into the three-dimensional framework by sharing corners with phosphate tetrahedra. This framework accommodates two types of channels extending parallel to  $[001]$  in which the  $\text{Na}^+$  cations are located (Fig. 4).

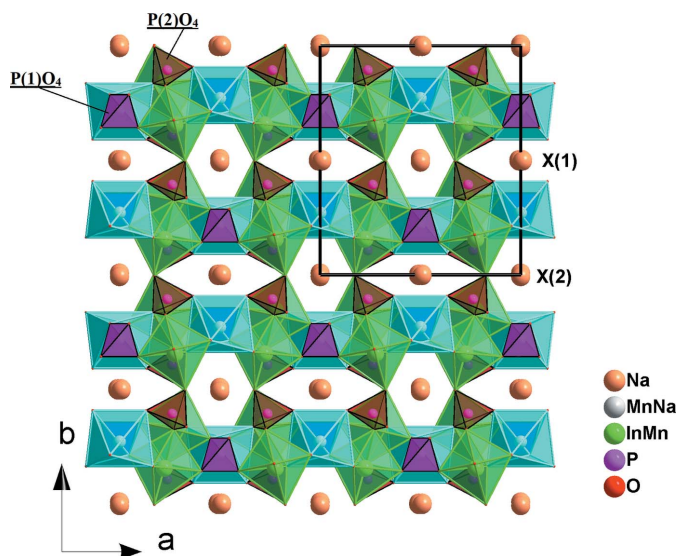


**Figure 2**  
Infinite zigzag chain extending parallel to  $[10\bar{1}]$ , built of edge-sharing  $M(2)\text{O}_{10}$  and  $M(1)\text{O}_6$  units.



**Figure 3**  
The connection of individual chains *via*  $\text{PO}_4$  tetrahedra to give sheets perpendicular to  $[010]$ .

The mean  $\langle M1\text{-O} \rangle$  distance of 2.329 Å is between those of 2.23 and 2.42 Å predicted by the sums of the ionic radii (Shannon, 1976) for  $\text{Mn}^{2+}$  and  $\text{Na}^+$  cations in an octahedral environment. The mean  $\langle M2\text{-O} \rangle$  distance of 2.150 Å is between the mean distance of 2.142 Å observed for  $\text{In}^{3+}$  in an octahedral environment in  $\text{NaCuIn}(\text{PO}_4)_2$  (Benhsina *et al.*, 2020) and 2.238 Å for  $\text{Mn}^{2+}$  in the same coordination in  $\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$  (Hidouri & Ben Amara, 2011). The  $\text{PO}_4$  tetrahedra show a slight distortion, as indicated by the range of P–O bond lengths [1.538 (2)–1.550 (2) Å for  $\text{P1O}_4$  and 1.520 (3)–1.566 (2) Å for  $\text{P2O}_4$ ], with mean bond lengths of  $\langle \text{P1-O} \rangle = 1.544$  (2) Å and  $\langle \text{P2-O} \rangle = 1.546$  (2) Å, consistent with 1.537 Å as calculated by Baur (1974) for the orthophosphate group. The coordination spheres of the two crystallographically distinct Na sites (Fig. 1) in the channels were defined under the assumption of a maximum Na–O distance  $L_{\text{max}} = 3.13$  Å, suggested by Donnay & Allmann (1970). The environment around Na1 consists of seven O atoms with distances varying from 2.35 (3) to 2.99 (3) Å, and Na2 is bound to eight O atoms with distances in the range 2.510 (3)–2.928 (6) Å.



**Figure 4**  
Projection of the  $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$  structure along the  $[001]$  direction showing channels occupied by the  $\text{Na}^+$  cations.

**Table 1**

CHARDI and BVS analysis of cations in  $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$ .

$M1 = \text{Mn/Na}$ ,  $M2 = \text{Mn/In}$ ,  $q$  = formal oxidation number,  $\text{sof}(i)$  = site-occupation factor,  $Q(i)$  = calculated charges, CN = coordination number, ECoN = number of effective coordination,  $d_{\text{ar}}$  = arithmetic average distance to oxygen atoms and  $d_{\text{med}}$  = weighted average distance to oxygen atoms.

Cation	$q.\text{sof}(i)$	$Q(i)$	$V(i).\text{sof}(i)$	CN( $i$ )	ECoN( $i$ )	$d_{\text{average}}$	$d_{\text{med}}$
Na1	0.50	0.50	0.542	7	5.56	2.550	2.428
Na2	0.77	0.75	0.716	8	6.70	2.738	2.653
M1	1.54	1.56	1.421	6	6.00	2.329	2.330
M2	2.84	2.84	2.696	6	5.87	2.150	2.141
P1	5.00	4.92	4.873	4	4.00	1.544	1.544
P2	5.00	5.05	4.844	4	3.98	1.546	1.545

The refined structure model is confirmed by (i) the bond-valence method (Brown & Altermatt, 1985; Brown, 2002) and (ii) the charge-distribution (Chardi) method (Nespolo, 2015, 2016). The Chardi method is a development of Pauling's concept of bond strength (Pauling, 1929). Instead of the empirical parameters used in the bond-valence approach, it exploits the experimental bond lengths deduced from the structural study to compute a non-integer coordination number (effective coordination number = ECoN) around a PC atom (atom placed at the center of a polyhedron,  $q > 0$ ), which is coordinated by V atoms (atoms located at the vertices;  $q < 0$ );  $q$  is the formal oxidation number. ECoN takes into account not only the number of V atoms around a given PC atom, but also their weight in terms of relative distances. Calculated charges  $Q(i)$  and valences  $V(i)$  are in good agreement with the formal oxidation number ( $q$ ) multiplied by occupancy rates. The dispersion factor MAPD,  $\text{MAPD} = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_i - Q_i}{q_i} \right|$ , which measures the mean absolute percentage deviation, is 1% for the calculated cationic charges. The variation of the ECoN value with respect to the traditional coordination number indicates the degree of distortion. The results of the two validation models are compiled in Table 1.

### 3. Synthesis and crystallization

Commercially available  $\text{NaNO}_3$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{MoO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  were mixed in stoichiometric ratios of 2:1:1:1:2 and dissolved in aqueous nitric acid. The resulting solution was then evaporated by heating at 353 K. The obtained dry residue was ground in an agate mortar, and then heated increasingly in an open platinum crucible up to 873 K. The sample was then reground and mixed with sodium dimolybdate  $\text{Na}_2\text{Mo}_2\text{O}_7$  in the molar ratio P:Mo = 2:1. The mixture was heated for 1 h at 1243 K to give a melt that was subsequently cooled down to room temperature at a rate of 10 K h<sup>-1</sup>. Brown hexagonally shaped crystals were obtained by washing the final product with hot water in order to dissolve the flux.

### 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The bond lengths involving  $M1-O$

**Table 2**

Experimental details.

Crystal data	$\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$
Chemical formula	575.82
$M_r$	Monoclinic, $C2/c$
Crystal system, space group	293
Temperature (K)	12.412 (2), 12.855 (2), 6.599 (1)
$a, b, c$ (Å)	114.727 (2)
$\beta$ (°)	956.4 (3)
$V$ (Å <sup>3</sup> )	4
$Z$	Mo $K\alpha$
Radiation type	5.81
$\mu$ (mm <sup>-1</sup> )	0.29 × 0.17 × 0.11
Crystal size (mm)	
Data collection	
Diffractometer	Nonius Kappa CCD
Absorption correction	Part of the refinement model ( $\Delta F$ ) (Parkin <i>et al.</i> , 1995)
$T_{\text{min}}, T_{\text{max}}$	0.178, 0.222
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	1183, 1183, 1172
$R_{\text{int}}$	0.034
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.680
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.054, 1.31
No. of reflections	1183
No. of parameters	102
No. of restraints	3
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.73, -0.83

Computer programs: *KappaCCD Server Software* (Nonius, 1997), *HKL SCALEPACK* and *DENZO* (Otwinovski & Minor, 1997), *SIR92* (Altomare *et al.*, 1993), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 1999).

and  $M2-O$  are those between the mean Na-O and Mn-O and the mean In-O and Mn-O bond lengths, respectively. We used EADP, EXYZ and SUMP constraints within *SHELXL2018/3* (Sheldrick, 2015) for the mixed-occupied  $M1$  [refined ratio Mn:Na = 0.5438 (14):0.4562 (14)] and  $M2$  [refined ratio In:Mn = 0.8443 (5):0.1557 (5)] sites. Na2 shows an occupancy of 0.7676 (17), and free refinement of the occupancy of Na1 resulted in a value very close to 0.5. For the final refinement, this value was fixed at 0.5, and all other occupancies were refined to ensure electrical neutrality of the compound. The remaining maximum and minimum electron densities are located 0.74 Å from P2 and 1.07 Å from O24, respectively.

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## supporting information

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## Synthesis, crystal structure and charge-distribution validation of a new alluaudite-type phosphate, $\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$

Abdessalem Badri, Inmaculada Alvarez-Serrano, María Luisa López and Mongi Ben Amara

### Computing details

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinovski & Minor, 1997); data reduction: *HKL DENZO* (Otwinovski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

### Sodium manganese indium tris(phosphate) (2.22/0.87/1.68)

#### Crystal data

$\text{Na}_{2.22}\text{Mn}_{0.87}\text{In}_{1.68}(\text{PO}_4)_3$

$M_r = 575.82$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 12.412\ (2)\ \text{\AA}$

$b = 12.855\ (2)\ \text{\AA}$

$c = 6.599\ (1)\ \text{\AA}$

$\beta = 114.727\ (2)^\circ$

$V = 956.4\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 1100$

$D_x = 4.115\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 3.2\text{--}28.9^\circ$

$\mu = 5.81\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, brown

$0.29 \times 0.17 \times 0.11\ \text{mm}$

#### Data collection

Nonius Kappa CCD

diffractometer

Graphite monochromator

non-profiled  $\omega/2\tau$  scans

Absorption correction: part of the refinement

model ( $\Delta F$ )

(Parkin *et al.*, 1995)

$T_{\min} = 0.178$ ,  $T_{\max} = 0.222$

1183 measured reflections

1183 independent reflections

1172 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 28.9^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -16 \rightarrow 14$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 8$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.054$

$S = 1.31$

1183 reflections

102 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

$w = 1/[\sigma^2(F_o^2) + (0.0135P)^2 + 7.1094P]$

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

$(\Delta/\sigma)_{\max} = 0.023$

$\Delta\rho_{\max} = 0.73\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.83\ \text{e \AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Na1	0.492 (3)	0.003 (3)	0.013 (5)	0.017 (2)	0.5
Na2	0	−0.0079 (4)	0.75	0.0586 (13)	0.7676 (17)
Mn	0.5	0.22924 (8)	0.25	0.0128 (2)	0.5438 (14)
Na	0.5	0.22924 (8)	0.25	0.0128 (2)	0.4562 (14)
In	0.22327 (2)	0.15486 (2)	0.64458 (4)	0.00781 (9)	0.8443 (5)
Mn1	0.22327 (2)	0.15486 (2)	0.64458 (4)	0.00781 (9)	0.1557 (5)
P1	0.5	0.21702 (9)	0.75	0.0075 (2)	
O11	0.5471 (2)	0.2867 (2)	0.9611 (4)	0.0138 (5)	
O12	0.4072 (2)	0.14288 (19)	0.7683 (4)	0.0140 (5)	
P2	0.23767 (7)	0.10662 (6)	1.13105 (13)	0.00841 (17)	
O21	0.1736 (3)	0.0029 (2)	1.1238 (4)	0.0172 (5)	
O22	0.2293 (2)	0.17542 (19)	1.3198 (4)	0.0112 (5)	
O23	0.1663 (2)	0.16388 (19)	0.9065 (4)	0.0139 (5)	
O24	0.3668 (2)	0.0921 (2)	1.1731 (5)	0.0206 (6)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Na1	0.023 (7)	0.013 (3)	0.012 (5)	0.004 (4)	0.005 (3)	−0.002 (3)
Na2	0.027 (2)	0.073 (3)	0.055 (3)	0	−0.0025 (19)	0
Mn	0.0146 (5)	0.0121 (5)	0.0141 (5)	0	0.0083 (4)	0
Na	0.0146 (5)	0.0121 (5)	0.0141 (5)	0	0.0083 (4)	0
In	0.00802 (13)	0.00782 (13)	0.00813 (14)	0.00050 (8)	0.00390 (10)	0.00093 (8)
Mn1	0.00802 (13)	0.00782 (13)	0.00813 (14)	0.00050 (8)	0.00390 (10)	0.00093 (8)
P1	0.0062 (5)	0.0092 (5)	0.0055 (5)	0	0.0008 (4)	0
O11	0.0097 (11)	0.0174 (12)	0.0121 (11)	0.0005 (9)	0.0024 (9)	−0.0062 (9)
O12	0.0083 (11)	0.0139 (12)	0.0184 (13)	−0.0007 (9)	0.0042 (10)	0.0045 (9)
P2	0.0131 (4)	0.0069 (4)	0.0063 (4)	0.0012 (3)	0.0051 (3)	0.0005 (3)
O21	0.0287 (14)	0.0080 (11)	0.0163 (13)	0.0006 (10)	0.0108 (11)	0.0008 (9)
O22	0.0154 (12)	0.0105 (11)	0.0081 (11)	−0.0003 (9)	0.0053 (9)	−0.0005 (9)
O23	0.0232 (13)	0.0120 (12)	0.0079 (11)	0.0027 (9)	0.0079 (10)	0.0021 (9)
O24	0.0201 (14)	0.0249 (14)	0.0206 (14)	0.0084 (11)	0.0124 (11)	0.0071 (11)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Na1—O12 <sup>i</sup>	2.35 (3)	Mn—O23 <sup>xi</sup>	2.330 (3)
Na1—O12 <sup>ii</sup>	2.38 (3)	Mn—O11 <sup>iii</sup>	2.335 (3)
Na1—O24 <sup>iii</sup>	2.38 (3)	Mn—O11 <sup>i</sup>	2.335 (3)
Na1—O24 <sup>iv</sup>	2.45 (3)	In—O12	2.084 (2)

Na1—O24 <sup>i</sup>	2.489 (18)	In—O21 <sup>v</sup>	2.107 (3)
Na1—O24 <sup>ii</sup>	2.811 (17)	In—O23	2.127 (3)
Na1—O12 <sup>v</sup>	2.99 (3)	In—O11 <sup>xii</sup>	2.144 (2)
Na2—O21	2.510 (3)	In—O22 <sup>i</sup>	2.192 (2)
Na2—O21 <sup>vi</sup>	2.510 (3)	In—O22 <sup>xiii</sup>	2.246 (2)
Na2—O21 <sup>v</sup>	2.616 (3)	P1—O12	1.538 (2)
Na2—O21 <sup>vii</sup>	2.616 (3)	P1—O12 <sup>iii</sup>	1.538 (2)
Na2—O23 <sup>vi</sup>	2.901 (5)	P1—O11 <sup>iii</sup>	1.550 (2)
Na2—O23	2.901 (5)	P1—O11	1.550 (2)
Na2—O11 <sup>viii</sup>	2.928 (6)	P2—O24	1.520 (3)
Na2—O11 <sup>ix</sup>	2.928 (6)	P2—O21	1.543 (3)
Mn—O24 <sup>i</sup>	2.323 (3)	P2—O23	1.557 (3)
Mn—O24 <sup>iii</sup>	2.323 (3)	P2—O22	1.566 (2)
Mn—O23 <sup>x</sup>	2.330 (3)		
O12 <sup>i</sup> —Na1—O12 <sup>ii</sup>	172.0 (8)	O21 <sup>vii</sup> —Na2—O11 <sup>ix</sup>	84.12 (12)
O12 <sup>i</sup> —Na1—O24 <sup>iii</sup>	100.6 (13)	O23 <sup>vi</sup> —Na2—O11 <sup>ix</sup>	145.72 (9)
O12 <sup>ii</sup> —Na1—O24 <sup>iii</sup>	80.8 (10)	O23—Na2—O11 <sup>ix</sup>	123.11 (7)
Na1 <sup>xiv</sup> —Na1—O24 <sup>iv</sup>	73 (10)	O11 <sup>viii</sup> —Na2—O11 <sup>ix</sup>	51.21 (13)
O12 <sup>i</sup> —Na1—O24 <sup>iv</sup>	79.9 (10)	O24 <sup>i</sup> —Mn—O24 <sup>iii</sup>	81.29 (13)
O12 <sup>ii</sup> —Na1—O24 <sup>iv</sup>	97.6 (12)	O24 <sup>i</sup> —Mn—O23 <sup>x</sup>	164.09 (10)
O24 <sup>iii</sup> —Na1—O24 <sup>iv</sup>	172.4 (9)	O24 <sup>iii</sup> —Mn—O23 <sup>x</sup>	86.16 (9)
O12 <sup>i</sup> —Na1—O24 <sup>i</sup>	76.2 (8)	O24 <sup>i</sup> —Mn—O23 <sup>xi</sup>	86.16 (9)
O12 <sup>ii</sup> —Na1—O24 <sup>i</sup>	111.7 (10)	O24 <sup>iii</sup> —Mn—O23 <sup>xi</sup>	164.09 (10)
O24 <sup>iii</sup> —Na1—O24 <sup>i</sup>	76.9 (7)	O23 <sup>x</sup> —Mn—O23 <sup>xi</sup>	107.74 (13)
O24 <sup>iv</sup> —Na1—O24 <sup>i</sup>	110.6 (11)	O24 <sup>i</sup> —Mn—O11 <sup>iii</sup>	91.16 (9)
O12 <sup>i</sup> —Na1—O24 <sup>ii</sup>	102.3 (8)	O24 <sup>iii</sup> —Mn—O11 <sup>iii</sup>	117.37 (9)
O12 <sup>ii</sup> —Na1—O24 <sup>ii</sup>	69.7 (6)	O23 <sup>x</sup> —Mn—O11 <sup>iii</sup>	85.95 (9)
O24 <sup>iii</sup> —Na1—O24 <sup>ii</sup>	102.7 (9)	O23 <sup>xi</sup> —Mn—O11 <sup>iii</sup>	72.40 (9)
O24 <sup>iv</sup> —Na1—O24 <sup>ii</sup>	69.8 (6)	O24 <sup>i</sup> —Mn—O11 <sup>i</sup>	117.37 (9)
O24 <sup>i</sup> —Na1—O24 <sup>ii</sup>	178.4 (15)	O24 <sup>iii</sup> —Mn—O11 <sup>i</sup>	91.16 (9)
O12 <sup>i</sup> —Na1—O12 <sup>v</sup>	135.0 (10)	O23 <sup>x</sup> —Mn—O11 <sup>i</sup>	72.40 (9)
O12 <sup>ii</sup> —Na1—O12 <sup>v</sup>	51.9 (6)	O23 <sup>xi</sup> —Mn—O11 <sup>i</sup>	85.95 (9)
O24 <sup>iii</sup> —Na1—O12 <sup>v</sup>	96.7 (9)	O11 <sup>iii</sup> —Mn—O11 <sup>i</sup>	143.12 (14)
O24 <sup>iv</sup> —Na1—O12 <sup>v</sup>	88.1 (10)	O12—In—O21 <sup>v</sup>	101.37 (10)
O24 <sup>i</sup> —Na1—O12 <sup>v</sup>	67.8 (5)	O12—In—O23	111.59 (10)
O24 <sup>ii</sup> —Na1—O12 <sup>v</sup>	113.8 (11)	O21 <sup>v</sup> —In—O23	85.28 (10)
O21—Na2—O21 <sup>vi</sup>	173.7 (3)	O12—In—O11 <sup>xii</sup>	159.80 (10)
O21—Na2—O21 <sup>v</sup>	80.14 (8)	O21 <sup>v</sup> —In—O11 <sup>xii</sup>	95.68 (10)
O21 <sup>vi</sup> —Na2—O21 <sup>v</sup>	99.71 (8)	O23—In—O11 <sup>xii</sup>	80.34 (10)
O21—Na2—O21 <sup>vii</sup>	99.71 (8)	O12—In—O22 <sup>i</sup>	84.96 (10)
O21 <sup>vi</sup> —Na2—O21 <sup>vii</sup>	80.14 (8)	O21 <sup>v</sup> —In—O22 <sup>i</sup>	100.43 (10)
O21 <sup>v</sup> —Na2—O21 <sup>vii</sup>	177.2 (3)	O23—In—O22 <sup>i</sup>	161.27 (10)
O21—Na2—O23 <sup>vi</sup>	119.88 (19)	O11 <sup>xii</sup> —In—O22 <sup>i</sup>	81.35 (9)
O21 <sup>vi</sup> —Na2—O23 <sup>vi</sup>	54.39 (10)	O12—In—O22 <sup>xiii</sup>	80.47 (9)
O21 <sup>v</sup> —Na2—O23 <sup>vi</sup>	115.22 (16)	O21 <sup>v</sup> —In—O22 <sup>xiii</sup>	176.57 (10)
O21 <sup>vii</sup> —Na2—O23 <sup>vi</sup>	62.40 (10)	O23—In—O22 <sup>xiii</sup>	91.36 (9)
O21—Na2—O23	54.39 (10)	O11 <sup>xii</sup> —In—O22 <sup>xiii</sup>	83.08 (9)

O21 <sup>vi</sup> —Na2—O23	119.88 (19)	O22 <sup>i</sup> —In—O22 <sup>xiii</sup>	82.57 (9)
O21 <sup>v</sup> —Na2—O23	62.40 (10)	O12—P1—O12 <sup>iii</sup>	103.4 (2)
O21 <sup>vii</sup> —Na2—O23	115.22 (16)	O12—P1—O11 <sup>iii</sup>	114.56 (13)
O23 <sup>vi</sup> —Na2—O23	80.89 (17)	O12 <sup>iii</sup> —P1—O11 <sup>iii</sup>	107.48 (14)
O21—Na2—O11 <sup>viii</sup>	115.83 (18)	O12—P1—O11	107.48 (14)
O21 <sup>vi</sup> —Na2—O11 <sup>viii</sup>	70.36 (11)	O12 <sup>iii</sup> —P1—O11	114.56 (13)
O21 <sup>v</sup> —Na2—O11 <sup>viii</sup>	84.12 (12)	O11 <sup>iii</sup> —P1—O11	109.4 (2)
O21 <sup>vii</sup> —Na2—O11 <sup>viii</sup>	98.43 (14)	O24—P2—O21	112.98 (16)
O23 <sup>vi</sup> —Na2—O11 <sup>viii</sup>	123.11 (7)	O24—P2—O23	111.62 (15)
O23—Na2—O11 <sup>viii</sup>	145.71 (9)	O21—P2—O23	107.34 (15)
O21—Na2—O11 <sup>ix</sup>	70.36 (11)	O24—P2—O22	109.88 (15)
O21 <sup>vi</sup> —Na2—O11 <sup>ix</sup>	115.83 (18)	O21—P2—O22	107.94 (14)
O21 <sup>v</sup> —Na2—O11 <sup>ix</sup>	98.43 (14)	O23—P2—O22	106.81 (14)

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