

A novel In_3O_{16} fragment in
 $\text{Cs}_3\text{In}_3(\text{PO}_4)_4$ Igor V. Zatovsky,^{a*} Vyacheslav N. Baumer,^b Nataliya Yu. Strutynska,^a Nikolay S. Slobodyanik^a and Oleg V. Shishkin^b^aDepartment of Inorganic Chemistry, Taras Shevchenko National University, 64 Volodymyrska Street, 01601 Kyiv, Ukraine, and ^bSTC 'Institute for Single Crystals', National Academy of Science of Ukraine, 60 Lenin Avenue, 61001 Kharkiv, Ukraine
Correspondence e-mail: zvigov@yandex.ru

Received 17 February 2010

Accepted 13 May 2010

Online 17 June 2010

The double phosphate $\text{Cs}_3\text{In}_3(\text{PO}_4)_4$, prepared by a flux technique, features a fragment of composition In_3O_{16} formed by three corner-sharing InO_6 polyhedra. The central In atom resides on a twofold rotation axis, while the other two In atoms are on general positions. The O atoms in this fragment also belong to PO_4 tetrahedra, which link the structure into an overall three-dimensional anionic In–O–P network that is penetrated by tunnels running along *c*. Two independent Cs^+ cations reside inside the tunnels, one of which sits on a centre of inversion. In general, the organization of the framework is similar to that of $\text{K}_3\text{In}_3(\text{PO}_4)_4$, which also contains an In_3O_{16} fragment. However, in the latter case the unit consists of one InO_7 polyhedron and one InO_6 polyhedron sharing an edge, with a third InO_6 octahedron connected *via* a shared corner. Calculations of the Voronoi–Dirichlet polyhedra of the alkali metals give coordination schemes for Cs of [9+2] and [8+4] ($\bar{1}$ symmetry), and for K of [8+1], [7+2] and [7+2]. This structural analysis shows that the coordination requirements of the alkali metals residing inside the tunnels cause the difference in the In_3O_{16} geometry.

Comment

Complex salts of indium with tetrahedrally coordinated oxoanions, *e.g.* phosphates, molybdates and tungstates, represent a rich structural chemistry due to the special ability of indium to create building blocks with different types of condensation and linkage of InO_6 polyhedra. In spite of this, the formation of isolated InO_6 octahedra is also quite common, for example, in $\text{Li}_3\text{In}_2(\text{PO}_4)_3$ (Genkina *et al.*, 1987) and $\text{K}_5\text{In}(\text{MoO}_4)_4$ (Kudin *et al.*, 1981). Much more unusual condensed units involving edge-sharing indium polyhedra giving infinite one-dimensional chains are found in InPO_4 (Peltier *et al.*, 1998) and $M^{\text{I}}\text{In}(\text{WO}_4)_2$ ($M = \text{Na}$ or Ag ; Kravchenko, 1971; Pakhomov *et al.*, 1977), while corner-sharing InO_6 polyhedra resulting in a chain have been observed in $\text{RbInPO}_4(\text{OH})$ (Lii,

1996). Units consisting of isolated dimers of edge-sharing InO_6 polyhedra were found in $\text{InPO}_4 \cdot \text{H}_2\text{O}$ (Tang & Lachgar, 1998), $\text{Na}_3\text{In}_2(\text{PO}_4)_3$ (Lii & Ye, 1997) and $\text{CaIn}_2(\text{PO}_4)_2\text{HPO}_4$ (Tang & Lachgar, 1996). Recently, the structure of a new double phosphate, $\text{K}_3\text{In}_3(\text{PO}_4)_4$, involving a fragment of composition In_3O_{16} formed by condensed InO_x ($x = 6$ or 7) polyhedra, has been reported (Yang *et al.*, 2009). Here, we have found a similar In_3O_{16} unit, but with some notable differences, in the new double phosphate $\text{Cs}_3\text{In}_3(\text{PO}_4)_4$, (I).

The asymmetric unit of (I) contains two phosphate groups, two In atoms, with In1 on a twofold rotation axis and In2 on a general position, and two Cs^+ cations, *viz.* Cs1 on a general position and Cs2 on a centre of inversion (Fig. 1). Each InO_6 polyhedron is linked to two In_2O_6 *via* shared corners, resulting in a fragment of composition In_3O_{16} (Fig. 2*a*). The oxygen environment of In1 provides three pairs of In–O distances, while the environment of In2 is more irregular, with a broader range of six In–O distances (Table 1). Both indium polyhedra exhibit their maximum bond length for the bridging linkage $\text{In1} - \text{O2} - \text{In2}$.

Each P1O_4 tetrahedron (Fig. 3*a*) has a common edge with one In_2O_6 octahedron (*via* atoms O2^{i} and O4^{i}) and coordinates in a monodentate manner to In1^{xiv} (*via* atom O2^{i}) and the second In2^{i} (*via* atom O1^{i}) within the In_3O_{16} fragment, while the fourth corner (*via* atom O3^{i}) assembles with the neighbouring group of three In_3O_{16} units (In2 , In1^{xiv} and In2^{i} are in one fragment, while In2^{xiii} , In1 and In2^{xiv} are in another fragment; symmetry codes are given in the caption to Fig. 3). The second P2O_4 tetrahedron coordinates in a monodentate manner to In1 and In2^{xiii} , giving a six-membered $-\text{In1} - \text{O8} - \text{P2} - \text{O5} - \text{In2}^{\text{xiii}} - \text{O2}^{\text{iii}} -$ ring, as well as to In2 and In2^{iv} (*via* atoms O6 and O7) of adjacent fragments. As a result of these linkages, infinite rows of composition $[\text{In}_3\text{P}_4\text{O}_{16}]_{\infty}$ are formed along the *c* direction (Fig. 3*b*). Consequently, a three-dimensional framework is created involving hexagonal tunnels along *c*, where two types of Cs^+ cations reside (Fig. 4).

The frameworks of (I) and $\text{K}_3\text{In}_3(\text{PO}_4)_4$, (II) (Yang *et al.*, 2009), are similar. Both structures possess the anionic sublattice $[\text{In}_3\text{P}_4\text{O}_{16}]_{\infty}$, built up from In_3O_{16} blocks which are interlinked by phosphate tetrahedra in a similar way. The main difference lies in the principles of indium polyhedra condensation. In (II), the building block consists of one InO_7 and two

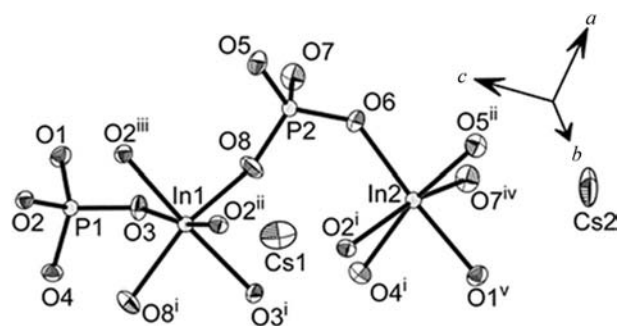


Figure 1

A connected set of numbered atoms of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $x, -y, z - \frac{1}{2}$; (iii) $-x, -y, -z + 2$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $x, y, z - 1$.]

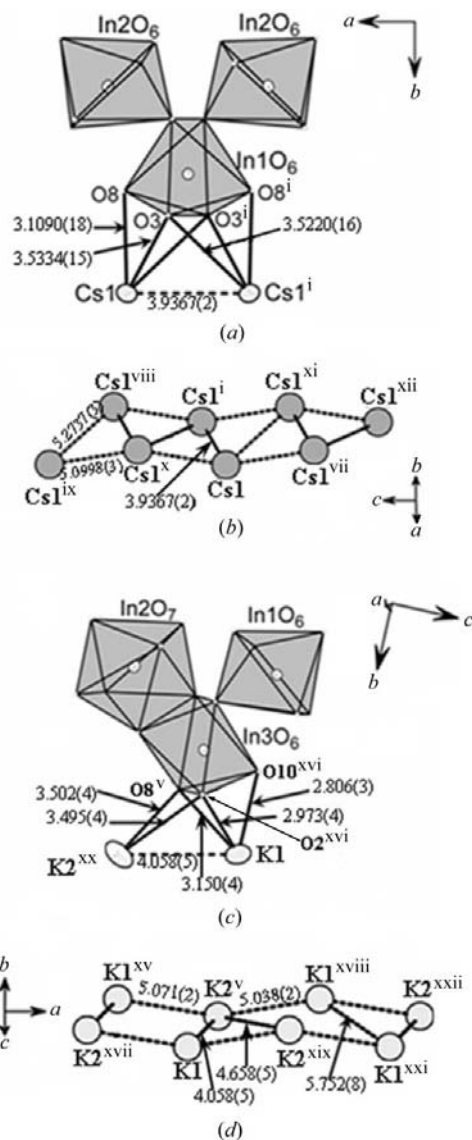


Figure 2
 (a)/(c) The difference in assemblage of In₃O₁₆ with alkali metals and (b)/(d) the principle of location of these alkali metals along the *c* axis in (I) or along the *a* axis in (II). [Symmetry codes for (I): (i) $-x, y, -z + \frac{3}{2}$; (vii) $x, -y + 1, z - \frac{1}{2}$; (viii) $-x, -y + 1, -z + 2$; (ix) $x, y, z + 1$; (x) $x, -y + 1, z + \frac{1}{2}$; (xi) $-x, -y + 1, -z + 1$; (xii) $-x, y, -z + \frac{1}{2}$; symmetry codes for (II): (v) $x, y, z - 1$; (xv) $-x + 2, -y + 3, -z$; (xvi) $-x + 2, -y + 2, -z + 1$; (xvii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (xviii) $-x + 3, -y + 3, -z$; (xix) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (xx) $x + \frac{3}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (xxi) $x + 1, y, z$; (xxii) $x + 1, y, z - 1$.]

InO₆ interlinked by a common edge and a corner (Fig. 2c), respectively, giving a wider range of In–O distances [2.063 (2)–2.388 (3) Å]. The In···In distances in (II) are 3.583 (3) and 3.603 (2) Å, respectively, compared with the In1···In2(*x, y, -z + 1*) distance of 3.6719 (2) Å in (I).

The key role in the local symmetry of the In₃O₁₆ fragment in these anionic lattices is played by the alkali counter-ion. In (II), the K⁺ cations occupy three independent positions, while in (I) the Cs⁺ cations reside in only two sites (Fig. 4). One common type of alkali metal site [Cs2 in (I) and K3 in (II)] nestles in the cavities in the walls of the tunnels. Another type, including Cs1 in (I) (Fig. 2b) and K1 and K2 in (II) (Fig. 2d), resides inside the windows of these tunnels. All alkali metals in

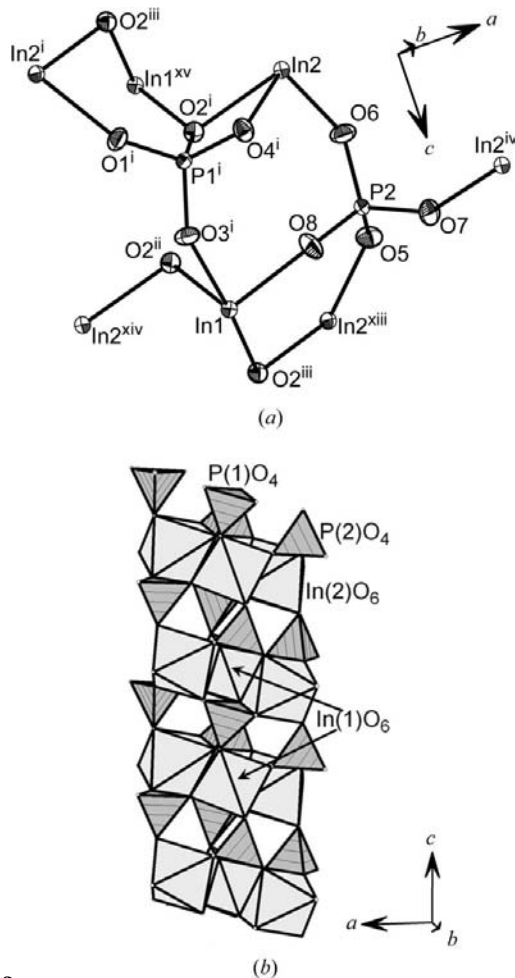


Figure 3
 (a) Assemblage of PO₄ tetrahedra within and between In₃O₁₆ units in (I). (b) The resulting infinite rows of [In₃P₄O₁₆]_∞ in (I). The arrows point to various symmetry-related positions of the indicated polyhedra. [Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $x, -y, z - \frac{1}{2}$; (iii) $-x, -y, -z + 2$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (xiii) $x, -y, z + \frac{1}{2}$; (xiv) $-x, -y, -z + 1$.]

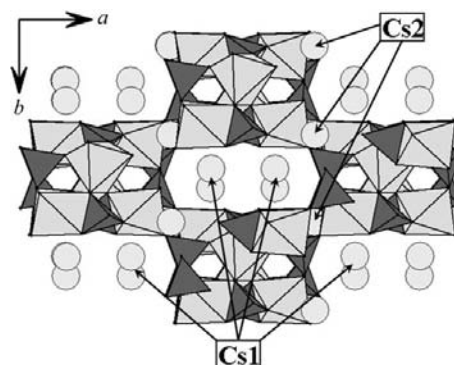


Figure 4
 Cs⁺ cation locations relative to the anionic In₃P₄O₁₆ sublattice in (I). The arrows point to various symmetry-related positions of the Cs atoms.

both structures are surrounded by four nearest In₃O₁₆ fragments. However, the details of the caesium and potassium coordination are different and that influences the geometry of the In₃O₁₆ units.

The nearest Cs–O environment in (I) might be considered as nine- (Cs1) and eightfold (Cs2), having a cut-off distance of

3.55 Å, while K in (II) presents K₁O₈, K₂O₇ and K₃O₇ coordination environments including all bonds up to 3.35 Å. For a more precise determination of the coordination numbers (CN) of the alkali metals, the method of construction of Voronoi–Dirichlet polyhedra (VDP) was applied through the *DIRICHLET* program included in the *TOPOS* package (Blatov *et al.*, 1995). Analysis of solid angles (Ω) was applied in the range of distances $M-O < 4.1$ Å ($M = K, Cs$), neglecting those corresponding to $\Omega < 1.5^\circ$ (Blatov *et al.*, 1998). The coordination schemes for Cs1 and Cs2 are described as [9+2] [Cs–O = 3.0046 (16)–3.854 (2) Å] and [8+4] [Cs–O = 2.8814 (16)–3.9367 (2) Å]. For (II), the potassium polyhedra are described as K₁O₉ [8+1], with eight K–O contacts in the range 2.668 (4)–3.257 (3) Å and the longest of 3.864 (4) Å with solid angle $\Omega = 3.23^\circ$, K₂O₇ [7+2], with K–O = 2.646 (5)–3.502 (4) Å, and K₃O₇ [7+2], with seven nearest K–O contacts 2.564 (3)–3.192 (4) Å and two longer contacts of 3.439 (3) and 3.709 (3) Å, with solid angles $\Omega = 5.64$ and 3.29° , respectively.

Structural analysis based on the proposed scheme of coordination shows that the coordination requirements of the alkali metal cations residing inside the tunnels of (I) and (II) (K1, K2 or Cs1) affect the geometry of the In₃O₁₆ fragment. In (II), the K1 cations form three bonds with one face of the In₁O₆ octahedron (Fig. 2c), while the neighbouring K2 atom has two much more remote contacts [K–O = 3.495 (4) and 3.502 (4) Å] with an edge of the same octahedron. By contrast, two Cs1 cations in (I) each share one face of the same indium octahedron through three O atoms (Fig. 2a). The latter arrangement appears due to the ability of caesium to create much longer and stronger ‘ion-covalent’ Cs–O bonds. This leads to a rotation of the central In₁O₆ octahedron and, as a result, to the ‘rupture’ of one of In–O bonds in (II), providing a decrease in the CN of one indium polyhedron from 7 to 6. The appearance of additional alkali metal contacts with indium polyhedra also affects the contact distances between nearest Cs⁺ cations [3.937 (1) Å] compared with those of K1 and K2 in (II) [4.058 (5) Å] (Figs. 2b and 2d).

Experimental

Crystals of (I) were prepared during investigation of the Cs₂O–P₂O₅–In₂O₃–CuO molten system by spontaneous crystallization from a melt with ratios Cs:P = 1.3, In:P = 0.2 and In:Cu = 1.0. A mixture of Cs₃P₃O₉ (1.667 g), Cs₂CO₃ (0.384 g), In₂O₃ (0.218 g) and CuO (0.250 g) was placed in a platinum crucible and heated to 1223 K. The melt obtained was kept at this temperature for 3 h and then cooled to 923 K at a rate of 30 K h^{−1}. Colourless prismatic crystals of (I) were leached out with a small amount of water. The compound can only be prepared in the presence of copper ions.

Crystal data

Cs ₃ In ₃ (PO ₄) ₄	$V = 1642.63$ (3) Å ³
$M_r = 1123.07$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.4370$ (2) Å	$\mu = 11.20$ mm ^{−1}
$b = 10.0498$ (1) Å	$T = 293$ K
$c = 9.9473$ (1) Å	0.20 × 0.10 × 0.01 mm
$\beta = 91.485$ (1)°	

Table 1
Selected bond lengths (Å).

In1–O8	2.0968 (14)	Cs1–O7 ^{vi}	3.2225 (17)
In1–O3	2.1396 (15)	Cs1–O6 ^{iv}	3.5025 (16)
In1–O2 ⁱⁱ	2.1971 (14)	Cs1–O4 ^{viii}	3.5050 (15)
In2–O7 ^{iv}	2.0744 (15)	Cs1–O3 ⁱ	3.5220 (16)
In2–O6	2.1136 (16)	Cs1–O3	3.5334 (15)
In2–O5 ⁱⁱ	2.1166 (15)	Cs1–O7	3.7162 (17)
In2–O1 ^v	2.1748 (15)	Cs1–O4 ^{vii}	3.854 (2)
In2–O4 ⁱ	2.1953 (14)	Cs2–O5 ⁱⁱ	2.8814 (16)
In2–O2 ⁱ	2.2473 (14)	Cs2–O7 ^{iv}	3.0529 (17)
Cs1–O4 ⁱ	3.0046 (16)	Cs2–O1 ^v	3.1104 (15)
Cs1–O5 ^{vi}	3.0426 (16)	Cs2–O6 ⁱⁱ	3.4008 (17)
Cs1–O8	3.1090 (18)	Cs2–O3 ^{iv}	3.6161 (15)
Cs1–O1 ^{vii}	3.1256 (16)	Cs2–O8 ^v	3.937 (2)

Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $x, -y, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $x, y, z - 1$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (vii) $x, -y + 1, z - \frac{1}{2}$; (viii) $-x, -y + 1, -z + 2$.

Data collection

Kuma KM-4/Oxford Xcalibur diffractometer with an Oxford Sapphire3 detector	27935 measured reflections 5338 independent reflections 4413 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{int} = 0.061$
$T_{min} = 0.213, T_{max} = 0.896$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	121 parameters
$wR(F^2) = 0.070$	$\Delta\rho_{max} = 2.77$ e Å ^{−3}
$S = 1.04$	$\Delta\rho_{min} = -2.75$ e Å ^{−3}
5338 reflections	

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the ICDD for financial support (grant No. 03-02).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3240). Services for accessing these data are described at the back of the journal.

References

- Blatov, V. A., Pogilyakova, L. V. & Serezhkin, V. N. (1998). *Z. Kristallogr.* **213**, 202–209.
- Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (1995). *Acta Cryst.* **A51**, 909–916.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Version 3.1f. Crystal Impact GbR, Bonn, Germany.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Genkina, E. A., Muradyan, L. A., Maksimov, B. A., Merinov, B. V. & Sigarev, S. E. (1987). *Kristallografiya*, **32**, 74–78.
- Kravchenko, V. B. (1971). *Zh. Strukt. Khim.* **12**, 1108–1110.
- Kudin, O. V., Efremov, V. A., Trunov, V. K. & Velikodnyi, Y. A. (1981). *Zh. Neorg. Khim.* **26**, 2734–2739.
- Lii, K.-H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 815–818.
- Lii, K.-H. & Ye, J. (1997). *J. Solid State Chem.* **131**, 131–137.
- Oxford Diffraction (2009). *CrysAlis Pro*. Version 1.171.33.31. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Pakhomov, V. J., Fedorov, P. M. & Okunera, A. S. (1977). *Koord. Khim.* **3**, 765–767.

Peltier, V., Deniard, P., Brec, R. & Marchand, R. (1998). *C. R. Acad. Sci.* **1**, 57–62.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Tang, X.-J. & Lachgar, A. (1996). *Z. Anorg. Allg. Chem.* **622**, 513–517.

Tang, X.-J. & Lachgar, A. (1998). *Inorg. Chem.* **37**, 6181–6185.
Yang, S.-L., Zhang, H., Xie, Z., Zhao, D., Zhang, W.-L. & Cheng, W.-D. (2009).
J. Solid State Chem. **182**, 855–861.