inorganic compounds

Octahedral–tetrahedral framework structures of InAsO$_4$·H$_2$O and PbIn(AsO$_4$)(AsO$_3$OH)

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Indium arsenate(V) monohydrate, InAsO$_4$·H$_2$O, (I), crystallizes in the structure type of MnMoO$_4$·H$_2$O. The structure is built of In$_2$O$_8$(H$_2$O)$_2$ dimers (mean In—O = 2.150 Å), corner-linked to slightly distorted AsO$_4$ tetrahedra (mean As—O = 1.686 Å). The linkage results in a three-dimensional framework, with small voids into which the apical water ligand of the InO$_5$(H$_2$O) octahedron points. The hydrogen bonds in (I) are of medium strength. Lead(II) indium arsenate(V) hydrogen arsenate(V), PbIn(AsO$_4$)(AsO$_3$OH), (II), represents the first reported lead indium arsenate. It is characterized by a framework structure of InO$_6$ octahedra corner-linked to AsO$_4$ and AsO$_3$OH tetrahedra. The resulting voids are occupied by Pb$_2$O$_{10}$(OH)$_2$ dimers built of two edge-sharing highly distorted PbO$_6$(OH) polyhedra (mean Pb—O = 2.623 Å). The compound is isotypic with PbFe^{III}(AsO$_4$)-(AsO$_3$OH). The average In—O bond length in (II) is 2.157 Å. In both arsenates, all atoms are in general positions.

Comment

InAsO$_4$·H$_2$O, [indium arsenate(V) monohydrate], (I), and PbIn(AsO$_4$)(AsO$_3$OH), [lead(II) indium arsenate(V) hydrogen arsenate(V)], (II), were obtained during an ongoing systematic study of the crystallography and crystal chemistry of metal–M^{III} arsenates (M = Al, Ga, In, Sc, Cr and Fe), which have been synthesized by hydrothermal methods.

Compound (I) is a previously unknown indium arsenate compound. It has a triclinic crystal structure (space group $P\bar{1}$) and is isotypic with its Sc analogue ScAsO$_4$·H$_2$O (Kolitsch & Schwendtner, 2004), its phosphate analogue InPO$_4$·H$_2$O (Tang & Lachgar, 1998), the vanadate schubnelite Fe^{III}VO$_4$·H$_2$O (Schindler & Hawthorne, 1999), and the molybdates and tungstates $M^{II}XO_4$·H$_2$O (M = Mg and Mn; X = Mo and W; Clearfield et al., 1985; Amberg et al., 1988).

Other known indium arsenates(V) are InAsO$_4$·2H$_2$O (Chen et al., 2002; Tang et al., 2002) and InAsO$_4$. The former adopts the structure type of variscite (AlPO$_4$·2H$_2$O) and is also known in nature as the mineral yanomatite (Botelho et al.,

1994). The crystal structure of InAsO$_4$ appears to be unknown, although its unindexed X-ray powder diffraction pattern (Ezhova et al., 1977) suggests it may be isostructural with orthorhombic InPO$_4$ (Mooney, 1956).

The asymmetric unit of (I) contains one crystallographically non-equivalent In atom, one As atom and five O atoms, all of which are located in general positions (Figs. 1 and 2). The ligand OW5 represents a water molecule. The In atom is octahedrally coordinated to six O ligands (including OW5), with an average In—O bond length of 2.150 Å (Table 1). The somewhat distorted InO$_5$(H$_2$O) octahedron shares one O1–O1′ edge with another crystallographically equivalent octahedron, thus forming an In$_2$O$_8$(H$_2$O)$_2$ dimer. As expected from In–In repulsion across the shared edge, this edge represents the shortest O—O distance within the dimeric unit. The In$_2$O$_8$(H$_2$O)$_2$ dimers are corner-linked to slightly distorted AsO$_4$ tetrahedra (mean As—O = 1.686 Å). The

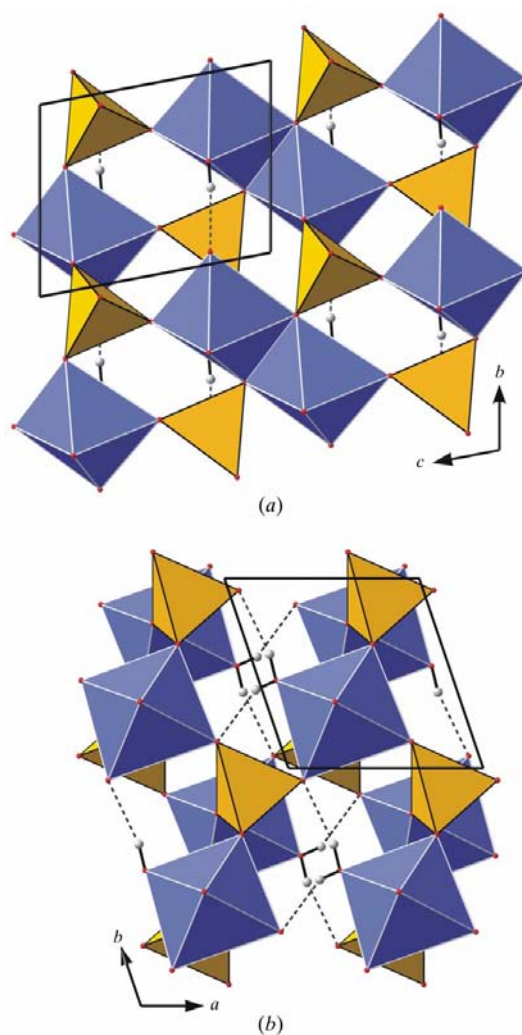**Figure 1**
A view of InAsO$_4$·H$_2$O along (a) [010] and (b) [001]. Slightly distorted AsO$_4$ tetrahedra are corner-linked to In$_2$O$_8$(H$_2$O)$_2$ dimers, which are built of two edge-sharing InO$_5$(H$_2$O) octahedra. The medium-strong hydrogen bonds are shown as dashed lines. The unit cell is outlined.

linkage results in a three-dimensional framework with small voids into which the apical water ligand (OW5) of the $InO_5(H_2O)$ octahedron points.

The positions of the H atoms in (I) are close to those in $MgMoO_4·H_2O$ (Amberg *et al.*, 1988). The hydrogen bonds are of medium strength (Table 2). The hydrogen-bonding schemes in isotypic $InPO_4·H_2O$ and $ScAsO_4·H_2O$ are practically identical to that in (I). Bond-valence sums for all atoms 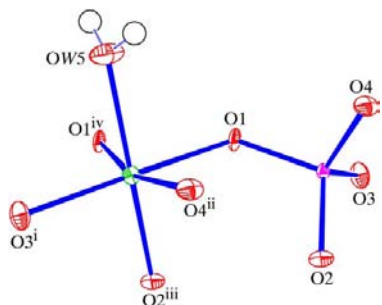were calculated using the bond-valence parameters of Brese & O'Keeffe (1991). The bond-valence sums are 3.09 (In), 4.99 (As), 2.02 (O1), 1.80 (O2), 1.97 (O3), 1.81 (O4) and 0.49 v.u. (valence units) (OW5), and thus are all reasonably close to ideal valencies. The somewhat undersaturated O2 and O4 ligands are acceptors of the two hydrogen bonds (Table 2).

Compound (I) represents the first inorganic compound containing an $In_2O_8(H_2O)_2$ dimer. A closely related, equally unique, $In_2O_9(H_2O)$ dimer is present in $In_2(HPO_3)_3(H_2O)$ (Yi *et al.*, 2005). In contrast, water-free In_2O_{10} dimers have been reported in several indium compounds, such as α-$LiIn(MoO_4)_2$ (Velikodnyi *et al.*, 1980), $CaIn_2(PO_4)_2(HPO_4)$ (Tang & Lachgar, 1996), $Na_3In_2(PO_4)_3$ and $Na_3In_2(AsO_4)_3$ (Lii & Ye, 1997), and $In_2O(PO_4)$ (Thauern & Glaum, 2004).

The unit-cell volume of (I) is slightly smaller than that of the Sc analogue $ScAsO_4·H_2O$ [201.21 (6) Å^3; Kolitsch & Schwendtner, 2004], which is not the result that would be expected from the slightly larger ionic radius of six-coordinate In^{III} (the average In—O bond length is 2.141 Å, while the average Sc—O bond is 2.105 Å; Baur, 1981). However, the change in the unit-cell parameters shows a fairly irregular behaviour. In (I), *a* and *c* are smaller than in $ScAsO_4·H_2O$, whereas *b* is larger; the three angles differ by only 0.2–0.3°. Apparently, the polyhedral connectivity in (I) results in a more efficient space filling.

$PbIn(AsO_4)(AsO_3OH)$, (II), is the first lead(II) indium arsenate(V) reported. Its monoclinic crystal structure (space group $P2_1/n$) is a three-dimensional framework (Figs. 3 and 4) based on the corner-linkage of distorted AsO_4 and AsO_3OH tetrahedra (mean As—O = 1.695 and 1.688 Å, respectively), with slightly distorted InO_6 octahedra (mean In—O = 2.157 Å). Voids in the framework are occupied by $Pb_2O_{10}(OH)_2$ dimers, which are built of two edge-sharing symmetrically equivalent $PbO_6(OH)$ polyhedra [Pb···Pb = 4.069 (1) Å]. The coordination number of the Pb atom is unambiguous; there are seven oxygen ligands within 2.88 Å (mean Pb—O = 2.623 Å), whereas the eighth O-atom neighbour is at a distance of 3.365 (9) Å. The $PbO_6(OH)$ polyhedron is highly distorted and the distinct tendency for a one-sided coordination environment indicates that the lone electron pair on the Pb^{II} cation is stereochemically active; the

Figure 2
The connectivity in $InAsO_4·H_2O$, showing the atom-labelling scheme and 70% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) −*x*, −*y*, −*z*; (iii) −*x* + 1, −*y*, −*z*; (iv) −*x* + 1, −*y* + 1, −*z*.]
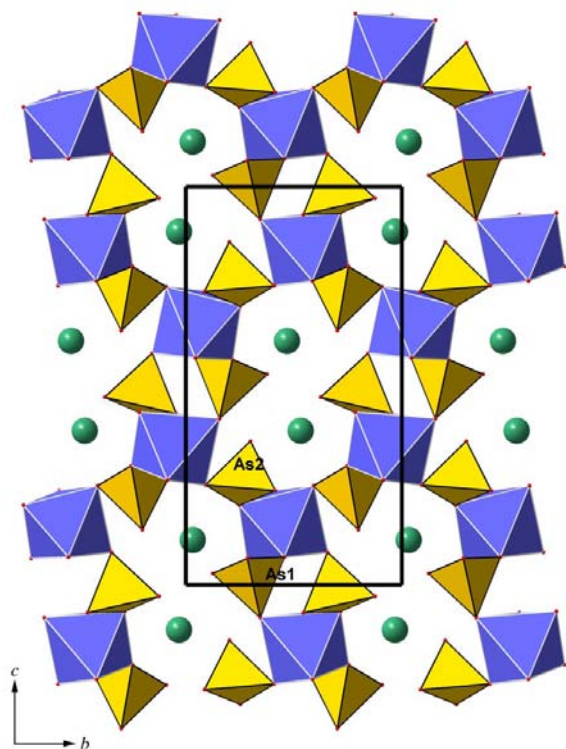

Figure 3
A view of $PbIn(AsO_4)(AsO_3OH)$ along [100]. AsO_4 and AsO_3OH tetrahedra are corner-linked to InO_6 octahedra. Voids in the resulting octahedral–tetrahedral framework are occupied by $Pb_2O_{10}(OH)_2$ dimers, which are built of two edge-sharing highly distorted $PbO_6(OH)$ polyhedra [Pb···Pb = 4.069 (1) Å]. The unit cell is outlined.

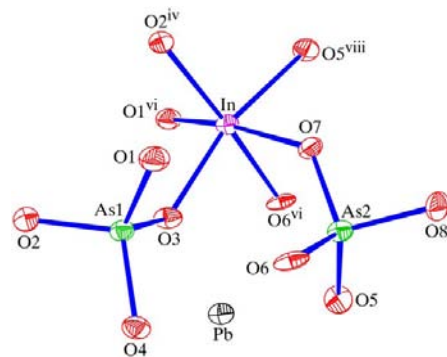**Figure 4**
The connectivity in $PbIn(AsO_4)(AsO_3OH)$, showing the atom-labelling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (iv) −*x* + 1, −*y* + 1, −*z*; (vi) *x* + 1, *y*, *z*; (viii) −*x* + $\frac{3}{2}$, *y* + $\frac{1}{2}$, −*z* + $\frac{1}{2}$.]

electron pair points toward the remaining void space within the framework. The Pb-containing voids in the framework are arranged to form channels parallel to [100] (Fig. 3). A view along the b axis (not shown) reveals a layer-like arrangement of tetrahedra and octahedra, as often encountered in mixed octahedral–tetrahedral framework structures. $PbIn(AsO_4)(AsO_3OH)$ is isotypic with $PbFe^{III}(AsO_4)(AsO_3OH)$ (Effenberger et al., 1996). The crystal structure of the phosphate analogue $PbIn(PO_4)(PO_3OH)$ (Belokoneva et al., 2001) shows only weak relations to that of (II).

Interestingly, the structure type of $PbM^{III}(AsO_4)(AsO_3OH)$ (M = Fe and In) is related to that of $(H_3O)Fe(HPO_4)_2$ (Vencato et al., 1989). The latter has similar unit-cell parameters ($a = 5.191$ Å, $b = 8.748$ Å, $c = 14.448$ Å and $\beta = 94.81°$) and a similar topology, albeit a different space group ($P2_1/c$). The structure type of $(H_3O)Fe(HPO_4)_2$ is adopted by several other acid phosphates and arsenates [see overview by Schwendtner & Kolitsch (2004)].

The very long As2—O8 bond in (II) (Table 3) confirms that atom O8 represents an OH group belonging to an AsO_3OH tetrahedron (cf. Ferraris & Ivaldi, 1984). The hydrogen bonding is strong, as the distance between donor atom O8 (OH) and the only possible acceptor atom (O2) is fairly short [2.614 (13) Å]. In isotypic $PbFe^{III}(AsO_4)(AsO_3OH)$ (Effenberger et al., 1996), the corresponding O···O distance is slightly longer [2.648 (10) Å]. The hydrogen bonds serve to reinforce the walls of the voids hosting the $Pb_2O_{10}(OH)_2$ dimers. Bond-valence sums for all atoms in (II) were calculated using the bond-valence parameters of Krivovichev & Brown (2001) for Pb—O bonds, and of Brese & O'Keeffe (1991) for the remaining bonds. The values obtained, 1.93 (Pb), 3.03 (In), 4.86 (As1), 4.96 (As2), 1.85 (O1), 1.74 (O2, the acceptor of a strong hydrogen bond), 2.04 (O3), 1.91 (O4), 1.97 (O5), 2.05 (O6), 1.97 (O7) and 1.26 v.u. (O8 = OH), are all close to ideal valencies.

Experimental

The title compounds were prepared by a hydrothermal method (Teflon-lined stainless steel bombs, 493 K, 7 d, slow furnace cooling) from mixtures of distilled water, arsenic acid, In_2O_3 [for (I) and (II)], Li_2CO_3 [for (I)] and yellow PbO [for (II)]. The final pH values of the reacted solutions were about 1 and 2 for (I) and (II), respectively. Compound (I) formed tiny colourless pseudo-rhombohedral crystals. Compound (II) formed tiny colourless indistinct (grain-like) crystals, associated with very minor amounts of synthetic schultenite (PbHAsO_4) as tiny rectangular platelets.

Compound (I)

Crystal data

$InAsO_4 \cdot H_2O$	$Z = 2$
$M_r = 271.76$	$D_x = 4.598$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.500$ (1) Å	Cell parameters from 1409
$b = 5.720$ (1) Å	reflections
$c = 6.685$ (1) Å	$\theta = 2.0–32.5°$
$\alpha = 98.90$ (3)°	$\mu = 14.28$ mm^{-1}
$\beta = 94.60$ (3)°	$T = 293$ (2) K
$\gamma = 107.55$ (3)°	Pseudo-rhombohedral, colourless
$V = 196.30$ (7) Å^3	$0.05 \times 0.05 \times 0.03$ mm

Data collection

Nonius KappaCCD diffractometer	1427 independent reflections
φ and ω scans	1405 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.013$
(HKL SCALEPACK;	$\theta_{max} = 32.5°$
Otwinowski et al., 2003)	$h = -8 \rightarrow 8$
$T_{min} = 0.535$, $T_{max} = 0.674$	$k = -8 \rightarrow 8$
2799 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0067P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.013$	$+ 0.2212P]$
$wR(F^2) = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.20$	$(\Delta/\sigma)_{max} < 0.001$
1427 reflections	$\Delta\rho_{max} = 0.91$ e Å^{-3}
73 parameters	$\Delta\rho_{min} = -0.77$ e Å^{-3}
All H-atom parameters refined	Extinction correction: SHELXL97
	Extinction coefficient: 0.0355 (12)

Table 1
Selected interatomic distances (Å) for (I).

In—O3^i	2.0731 (14)	In—O1^{iv}	2.2173 (16)
In—O4^{ii}	2.1203 (16)	As—O3	1.6600 (15)
In—O2^{iii}	2.1298 (14)	As—O2	1.6816 (13)
In—OW5	2.1667 (16)	As—O4	1.6834 (13)
In—O1	2.1945 (13)	As—O1	1.7173 (13)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x, -y, -z$; (iii) $-x+1, -y, -z$; (iv) $-x+1, -y+1, -z$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
OW5—H1···O4^v	0.76 (4)	2.02 (4)	2.771 (2)	167 (4)
OW5—H2···O2^{ii}	0.70 (4)	2.08 (4)	2.728 (2)	154 (4)

Symmetry codes: (ii) $-x, -y, -z$; (v) $-x, -y+1, -z$.

Compound (II)

Crystal data

$PbIn(AsO_4)(AsO_3OH)$	$D_x = 5.911$ Mg m^{-3}
$M_r = 600.86$	Mo $K\alpha$ radiation
Monoclinic, $P12_1/n1$	Cell parameters from 2570
$a = 4.955$ (1) Å	reflections
$b = 8.591$ (2) Å	$\theta = 2.0–30.0°$
$c = 15.874$ (3) Å	$\mu = 38.05$ mm^{-1}
$\beta = 92.38$ (3)°	$T = 293$ (2) K
$V = 675.2$ (2) Å^3	Irregular fragment, colourless
$Z = 4$	$0.03 \times 0.03 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer	1903 independent reflections
φ and ω scans	1445 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.040$
(SCALEPACK;	$\theta_{max} = 30.0°$
Otwinowski et al., 2003)	$h = -6 \rightarrow 6$
$T_{min} = 0.357$, $T_{max} = 0.467$	$k = -12 \rightarrow 12$
3677 measured reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 1P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
1903 reflections	$\Delta\rho_{max} = 3.95$ e Å^{-3}
109 parameters	$\Delta\rho_{min} = -1.91$ e Å^{-3}
H-atom parameters not defined	

Table 3
Selected interatomic distances (Å) for (II).

Pb—O4^{vi}	2.373 (9)	In—O5^{viii}	2.150 (9)
Pb—O3	2.477 (9)	In—O7	2.161 (9)
Pb—O6^{vi}	2.531 (9)	In—O6^{vi}	2.240 (9)
Pb—O4^{iii}	2.616 (9)	As1—O1	1.679 (10)
Pb—O7^{vii}	2.664 (9)	As1—O2	1.695 (9)
Pb—O5	2.821 (10)	As1—O4	1.696 (9)
Pb—O8^{vii}	2.880 (10)	As1—O3	1.710 (9)
Pb—O2^{iii}	3.365 (9)	As2—O6	1.659 (9)
In—O1^{vi}	2.105 (10)	As2—O5	1.675 (9)
In—O2^{iv}	2.143 (8)	As2—O7	1.688 (9)
In—O3	2.143 (9)	As2—O8	1.730 (9)

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

The atomic coordinates of ScAsO4·H2O (Kolitsch & Schwendtner, 2004) were used as the starting parameters for the final refinement of (I). H atoms were refined freely (see Table 2 for refined O—H distances). The atomic coordinates of PbFe^{III}(AsO4)(AsO3OH) (Effenberger *et al.*, 1996) were used as the starting parameters for the final refinement of (II). The H atom could not be located. A total of 52 reflections were omitted from the data set of (II) because these were strongly affected by overlap with reflections from about two extremely small additional grains intergrown with the measured crystal grain. The highest electron-density peak in the difference map of (II) is 0.86 Å from the Pb site and the deepest hole is 0.77 Å from the Pb site.

For both compounds, data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *DENZO* (Otwinowski *et al.*, 2003) and *SCALE-PACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1060). Services for accessing these data are described at the back of the journal.

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