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Lithium Hexafluoroarsenate Monohydrate, $LiAsF_6.H_2O$

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Abstract

$LiAsF_6.H_2O$ crystallizes with the $NaPF_6.H_2O$ structure type. $[AsF_6]^-$ anions with nearly ideal octahedral geometry (As—F 1.71–1.72 Å) and water molecules form chains *via* weak F···H—O hydrogen bonds. The complex anions and water molecules exhibit a CsCl-like arrangement, with the octahedral holes partially occupied by Li^+ cations.

Comment

$LiAsF_6.H_2O$ crystallizes with the $NaPF_6.H_2O$ structure type (space group *Imma*, $Z = 4$). The structure type was first described by Bode (Bode, 1954; Bode & Teufer, 1956) with atomic coordinates determined by Weissenberg film methods. The P/As atoms situated at the origin of the unit cell form the centres of nearly regular octahedra of F^- ions (Fig. 1). Even though the site symmetry of the complex anions is only $2/m$, the F—As—F angles deviate by only 0.03° from ideal octahedral values. The As—F distances are 1.707 (2) (2×) and 1.722 (1) Å (4×). These values correspond to the distances found in the anhydrous alkali metal hexafluoroarsenates $RbAsF_6$ (1.713 Å) and $CsAsF_6$ (1.714 Å), which crystallize with the $LiSbF_6$ structure type (Loss & Röhr, 1998). While the As—F distances in $(H_3O)AsF_6$ (Mootz & Wiebcke, 1986) are also in the same range (1.701–1.742 Å, somewhat influenced by strong hydrogen bonding), the data for $NaAsF_6$ [1.78 (4) Å; Loss & Röhr, 1998] and $LiAsF_6$ [1.74 (4) Å; Röhr & Kniep, 1994] are uncertain because they are derived from powder data by Rietveld refinement.

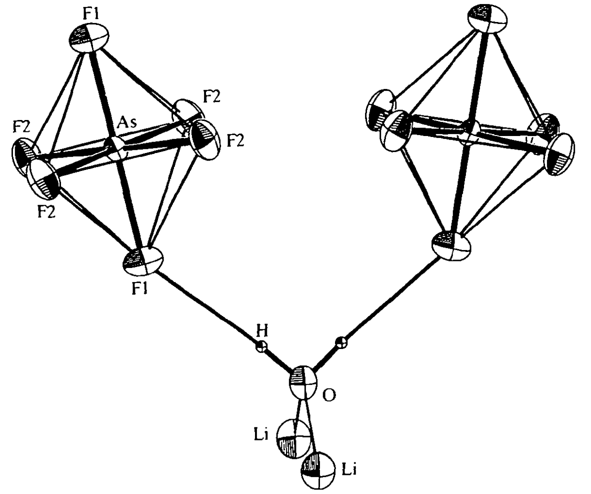

Fig. 1. A view of the $[AsF_6]^-$ octahedra and a connecting water molecule (50% probability ellipsoids).

In the crystal structure of the title compound, the O atoms of the water molecules are tetrahedrally coordinated by two H atoms and two Li^+ cations. The $[AsF_6]^-$ anions are connected to the water molecules *via* weak linear two-centre hydrogen bonds (Falk & Knop, 1973), with F1···O distances of 2.99 (1) Å and F1···H—O angles of 175 (3)°, to form chains running along the [010] direction (Fig. 2). The octahedra in the chains are alternately tilted with respect to the *c* axis

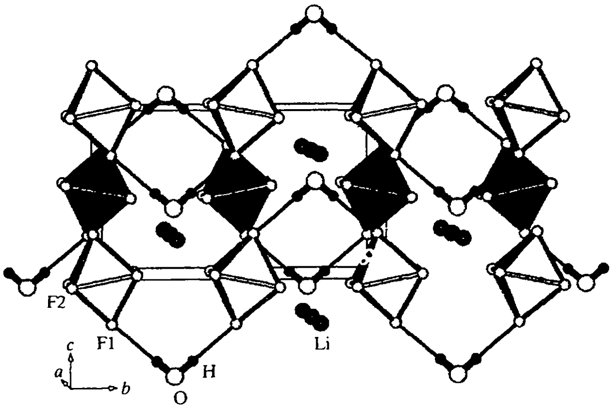

Fig. 2. The crystal structure of $LiAsF_6.H_2O$ viewed down [100], with chains of water-connected $[AsF_6]^-$ octahedra running along [010] at a height of $x = 0$ (light grey) and $x = \frac{1}{2}$ (dark grey).

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by ±11.3°. In the isotypic sodium hexafluorophosphate monohydrate $NaPF_6.H_2O$, the tilting is less pronounced (±3.8°). The Li^+ cations in $LiAsF_6.H_2O$ are arranged in chains running parallel to [100]. They are coordinated by four F [2.051 (1) Å] and two O [2.151 (1) Å] atoms, thus showing the same coordination number as in the water-free compound $LiAsF_6$.

As in $LiAsF_6$ and the low-temperature phase of $(H_3O)AsF_6$, the complex anions are packed in a simple cubic arrangement. In the compounds which contain only one cation [*i.e.* the low-temperature form of $(H_3O)AsF_6$, $LiAsF_6$, $NaAsF_6$, $RbAsF_6$, *etc.*, with the $LiSbF_6$ structure type, and $NaSbF_6$ (Sowa, 1997), KPF_6, $RbPF_6$, *etc.*, with the $NaSbF_6$ structure type], cations and complex anions form a distorted CsCl arrangement. In the crystal structure of the monohydrate, the water molecules are substituted at the positions of the cations. The Li^+ ions are situated in distorted octahedral holes in the packing of $[AsF_6]^-$ and H_2O.

The relationship between the CsCl and $NaPF_6.H_2O$ structure types is shown in Fig. 3; $[AsF_6]^-$ and water molecules form a CsCl-like arrangement, of which eight unit cells are shown. Li^+ cations are situated at octahedral interstices, forming zigzag –Li–O–Li–O–Li– chains running along [100] (*i.e.* [101] in CsCl), one at a height of $y = \frac{1}{4}$ and one at $y = \frac{3}{4}$. The orthorhombic unit cell of $LiAsF_6.H_2O$ can be transformed into the distorted CsCl structure ($a = 4.866$, $b = 5.247$, $c = 4.866$ Å, $\alpha = 90$, $\beta = 79.47$ and $\gamma = 90°$) by the matrix ($\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},0$; $\frac{1}{2},0,-\frac{1}{2}$).

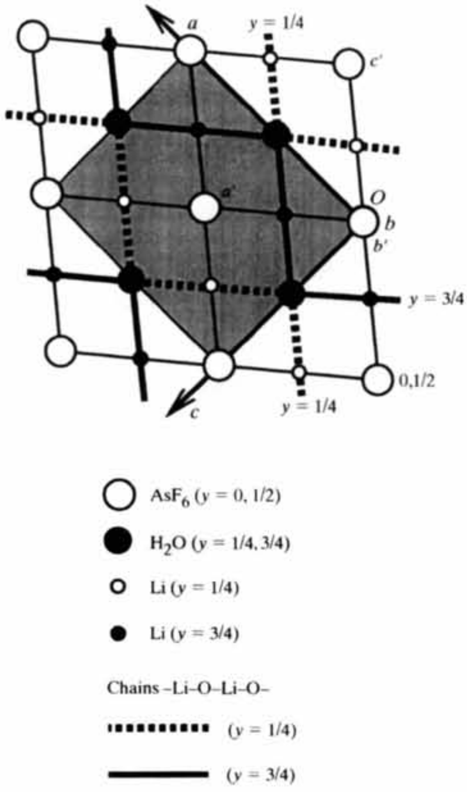

Fig. 3. The relationship between the unit cells of CsCl and $LiAsF_6.H_2O$.

Experimental

Commercially available $LiAsF_6$ (Aldrich, 98%) was recrystallized from 2-propanol at room temperature by slow evaporation of the solvent and dried *in vacuo* for 5 h. After dissolving this $LiAsF_6$ in liquid SO_2 (dried over P_4O_{10}), the solvent was slowly evaporated in a helium atmosphere using a temperature gradient (238–450 K) between two joined Schlenk flasks. After two months, needle-shaped colourless crystals of the title compound were obtained. As the crystals did not lose any water when stored under vacuum, it seems probable that $LiAsF_6$ cannot be dried completely *in vacuo*, so that the substance contained some water when used; experiments with controlled addition of water are in progress.

Crystal data

$LiAsF_6.H_2O$
$M_r = 213.88$
Orthorhombic
Imma
$a = 7.4845\ (9)$ Å
$b = 10.4936\ (10)$ Å
$c = 6.2217\ (5)$ Å
$V = 488.65\ (8)$ Å^3
$Z = 4$
$D_x = 2.907$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13.2\text{–}31.2°$
$\mu = 7.011$ mm^{-1}
$T = 293\ (2)$ K
Ellipsoid
$0.2 \times 0.1 \times 0.1$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*DATCOR*; Reibenspies, 1989)
$T_{\min} = 0.387$, $T_{\max} = 0.496$
593 measured reflections
593 independent reflections

465 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 34.92°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 16$
$l = -10 \rightarrow 0$
3 standard reflections
frequency: 720 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.056$
$S = 1.085$
593 reflections
32 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.0132P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.016$ e Å^{-3}
$\Delta\rho_{\min} = -0.751$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0153 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)*

U_{iso} for H1, $U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
As	0	0	0	0.01445 (11)
O1	0	1/4	0.5796 (4)	0.0223 (4)
H1	0	0.193 (4)	0.489 (5)	0.040 (12)
F1	0	0.0318 (2)	0.2690 (2)	0.0312 (3)
F2	0.16259 (14)	0.61379 (10)	0.0383 (2)	0.0284 (2)
Li	1/4	1/4	3/4	0.0273 (11)

Table 2. *Selected geometric parameters (Å, °)*

As—F1	1.707 (2)	O1—Li	2.1507 (12)
As—F2^{i}	1.7215 (10)	Li—F2^{ii}	2.0509 (10)
F1—As—F1^{iii}	180	F2^{i}—As—F2^{iv}	180
F1—As—F2^{i}	90.01 (5)	F2^{i}—As—F2^{v}	90.03 (8)
F1^{iii}—As—F2^{i}	89.99 (5)	F2^{iv}—As—F2^{v}	89.97 (8)

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

The initial model for the refinement was based on the coordinates for the isostructural compound $NaPF_6.H_2O$ (Bode & Teufer, 1956).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *HELENA* (Spek, 1996). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWXTL* (Finger & Kroeker, 1997). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1259). Services for accessing these data are described at the back of the journal.

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