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Li₂PtF₆ revisited

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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{Pt}-\text{F}) = 0.004$ Å; R factor = 0.019; wR factor = 0.052; data-to-parameter ratio = 13.5.

In comparison with previous structure determinations of Li₂PtF₆, dilithium hexafluoridoplatinate(IV) [Graudejus *et al.* (2000). *Inorg. Chem.* **39**, 2794–2800; Henkel & Hoppe (1968). *Z. Anorg. Allg. Chem.* **359**, 160–177], the current study revealed the Li atom to be refined with anisotropic displacement parameters, thus allowing for a higher overall precision of the model. Li₂PtF₆ adopts the trirutile structure type with site symmetries of $2.mm$, $m.mm$, $..m$ and $m.2m$ for the Li, Pt and the two F sites. The Pt–F distances in the slightly distorted PtF₆ octahedron are essentially similar with 1.936 (4) and 1.942 (6) Å, and the equatorial F–Pt–F angles range from 82.2 (2) to 97.8 (2)°. The Li–F distances in the somewhat more distorted LiF₆ octahedron are 1.997 (15) and 2.062 (15) Å, with equatorial F–Li–F angles ranging from 76.3 (7) to 99.71 (17)°.

Related literature

Henkel & Hoppe (1968) reported on the synthesis of Li₂PtF₆ by direct fluorination of (NH₄)₂PtCl₆ and Li₂CO₃. The obtained yellow Li₂PtF₆ was characterized by powder X-ray diffraction and reported to crystallize in the monoclinic crystal system. Graudejus *et al.* (2000) obtained Li₂PtF₆ in the form of yellow and air-stable crystals from the reaction of LiF with Pt in anhydrous HF under UV-photolysis of F₂. The reported space group and unit cell parameters are in accordance with the current redetermination. However, a low precision of the Pt–F bond lengths of only ± 0.01 Å was obtained due to many unobserved reflections even at the 2σ level. For synthetic details for the preparation of PtF₄, see: Müller & Serafin (1992).

Experimental*Crystal data*

Li ₂ PtF ₆	$Z = 2$
$M_r = 322.97$	Mo $K\alpha$ radiation
Tetragonal, $P4_2/mmm$	$\mu = 35.71 \text{ mm}^{-1}$
$a = 4.6427$ (1) Å	$T = 150$ K
$c = 9.1234$ (2) Å	$0.05 \times 0.05 \times 0.04 \text{ mm}$
$V = 196.65$ (1) Å ³	

Data collection

Oxford Diffraction Xcalibur3 diffractometer	5829 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	257 independent reflections
$T_{\min} = 0.148$, $T_{\max} = 1.000$	184 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	19 parameters
$wR(F^2) = 0.052$	$\Delta\rho_{\text{max}} = 2.51 \text{ e \AA}^{-3}$
$S = 1.17$	$\Delta\rho_{\text{min}} = -1.33 \text{ e \AA}^{-3}$
257 reflections	

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5032).

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supporting information

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S1. Experimental

Single-crystalline Li₂PtF₆ was obtained by the reaction of LiF and PtF₄ in platinum tubes. LiF was purified and dried in a stream of F₂:Ar 1:1 at 573 K for 24 hours. PtF₄ was synthesized according to literature procedures (Müller & Serafin, 1992). A stoichiometric mixture of the compounds was heated in a sealed platinum ampoule (jacketed in an evacuated fused silica tube) to 973 K with a rate of 30 K/d. After three weeks the ampoule was slowly cooled to room temperature and opened in an argon filled glove box. Yellow crystals of Li₂PtF₆ were obtained.

S2. Refinement

The highest residual electron density is 0.85 Å from atom Pt1. Structure data have also been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), with depository number CSD-414496.

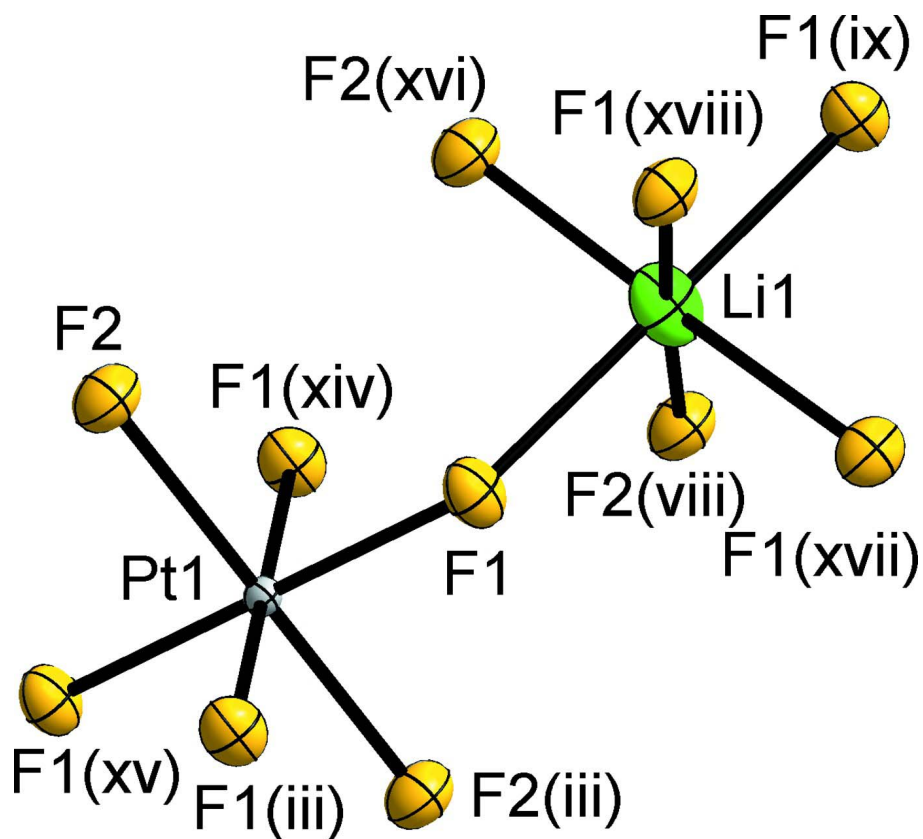
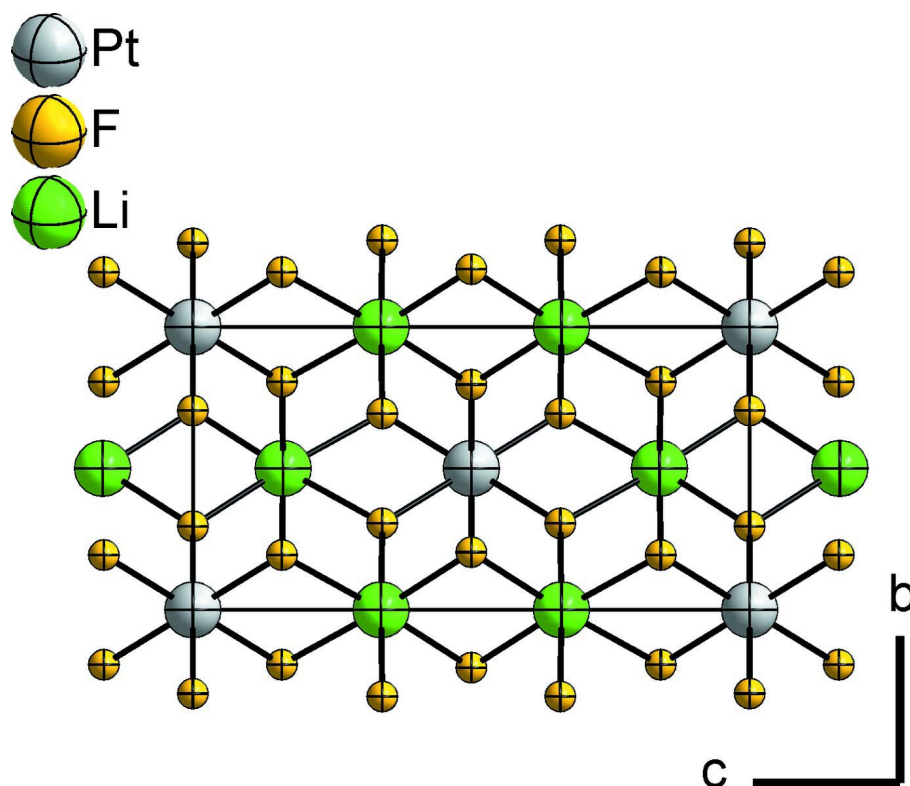


Figure 1

View of the coordination polyhedra around Pt and Li. Displacement ellipsoids are shown at the 70% probability level.

[Symmetry codes: (iii) $-x, -y, z$; (viii) $x + 1, y, z$; (ix) $-x + 1, -y + 1, z$; (xiv) $y, x, -z$; (xv) $-y, -x, -z$; (xvi) $-x, 1 - y, z$; (xvii) $x + 1/2, -y + 1/2, -z + 1/2$; (xviii) $-x + 1/2, y + 1/2, -z + 1/2$.]

**Figure 2**

The unit cell of Li_2PtF_6 viewed along $[100]$, with all atoms displayed as spheres with arbitrary radii.

Dilithium hexafluoridoplatinate(IV)

Crystal data

Li_2PtF_6

$M_r = 322.97$

Tetragonal, $P4_2/mnm$

Hall symbol: $-P\ 4n\ 2n$

$a = 4.6427(1)\ \text{\AA}$

$c = 9.1234(2)\ \text{\AA}$

$V = 196.65(1)\ \text{\AA}^3$

$Z = 2$

$F(000) = 276$

$D_x = 5.454\ \text{Mg m}^{-3}$

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

Cell parameters from 3453 reflections

$\theta = 4.4\text{--}34.6^\circ$

$\mu = 35.71\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Cuboid, yellow

$0.05 \times 0.05 \times 0.04\ \text{mm}$

Data collection

Oxford Diffraction Xcalibur3
diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: $16.0238\ \text{pixels mm}^{-1}$

φ and ω scans

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford Diffraction, 2007)

$T_{\min} = 0.148$, $T_{\max} = 1.000$

5829 measured reflections

257 independent reflections

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

$R_{\text{int}} = 0.062$

$\theta_{\max} = 34.7^\circ$, $\theta_{\min} = 4.5^\circ$

$h = -7 \rightarrow 7$

$k = -7 \rightarrow 7$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.052$
 $S = 1.17$
 257 reflections
 19 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 2.1946P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.51 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.33 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.041 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.0000	0.0000	0.0000	0.0056 (2)
F1	0.1939 (6)	0.1939 (6)	0.1599 (4)	0.0149 (7)
F2	-0.2958 (10)	0.2958 (10)	0.0000	0.0164 (11)
Li1	0.5000	0.5000	0.162 (2)	0.019 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.0054 (2)	0.0054 (2)	0.0061 (2)	0.00022 (14)	0.000	0.000
F1	0.0170 (11)	0.0170 (11)	0.0105 (13)	-0.0029 (15)	-0.0009 (10)	-0.0009 (10)
F2	0.0165 (18)	0.0165 (18)	0.016 (2)	0.004 (2)	0.000	0.000
Li1	0.024 (6)	0.024 (6)	0.010 (7)	-0.006 (7)	0.000	0.000

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

Pt1—F1 ⁱ	1.936 (4)	F1—Li1 ^{iv}	2.062 (15)
Pt1—F1 ⁱⁱ	1.936 (4)	F2—Li1 ^{vi}	1.997 (15)
Pt1—F1 ⁱⁱⁱ	1.936 (4)	F2—Li1 ^{vii}	1.997 (15)
Pt1—F1	1.936 (4)	Li1—F2 ^{vi}	1.997 (15)
Pt1—F2 ⁱ	1.942 (6)	Li1—F2 ^{viii}	1.997 (15)
Pt1—F2	1.942 (6)	Li1—F1 ^{ix}	2.010 (4)
Pt1—Li1 ^{iv}	3.081 (19)	Li1—F1 ^x	2.062 (15)
Pt1—Li1 ^v	3.081 (19)	Li1—F1 ^{xi}	2.062 (15)
F1—Li1	2.010 (4)	Li1—Li1 ^{xii}	2.96 (4)

F1 ⁱ —Pt1—F1 ⁱⁱ	82.2 (2)	F2 ^{vi} —Li1—F2 ^{viii}	84.3 (8)
F1 ⁱ —Pt1—F1 ⁱⁱⁱ	97.8 (2)	F2 ^{vi} —Li1—F1 ^{ix}	89.5 (4)
F1 ⁱⁱ —Pt1—F1 ⁱⁱⁱ	180.0 (3)	F2 ^{viii} —Li1—F1 ^{ix}	89.5 (4)
F1 ⁱ —Pt1—F1	180.0	F2 ^{vi} —Li1—F1	89.5 (4)
F1 ⁱⁱ —Pt1—F1	97.8 (2)	F2 ^{viii} —Li1—F1	89.5 (4)
F1 ⁱⁱⁱ —Pt1—F1	82.2 (2)	F1 ^{ix} —Li1—F1	178.8 (11)
F1 ⁱ —Pt1—F2 ⁱ	90.0	F2 ^{vi} —Li1—F1 ^x	176.0 (7)
F1 ⁱⁱ —Pt1—F2 ⁱ	90.0	F2 ^{viii} —Li1—F1 ^x	99.71 (17)
F1 ⁱⁱⁱ —Pt1—F2 ⁱ	90.0	F1 ^{ix} —Li1—F1 ^x	90.5 (4)
F1—Pt1—F2 ⁱ	90.0	F1—Li1—F1 ^x	90.5 (4)
F1 ⁱ —Pt1—F2	90.0	F2 ^{vi} —Li1—F1 ^{xi}	99.71 (17)
F1 ⁱⁱ —Pt1—F2	90.0	F2 ^{viii} —Li1—F1 ^{xi}	176.0 (7)
F1 ⁱⁱⁱ —Pt1—F2	90.0	F1 ^{ix} —Li1—F1 ^{xi}	90.5 (4)
F1—Pt1—F2	90.0	F1—Li1—F1 ^{xi}	90.5 (4)
F2 ⁱ —Pt1—F2	180.00 (19)	F1 ^x —Li1—F1 ^{xi}	76.3 (7)

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