

Synthesis and crystal structures of two new lead(II) hexafluoroarsenates(V)

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Dedicated to the memory of fluorine chemist Dr. Karel Lutar (2 September 2000)

Abstract

In the system $\text{PbF}_2/\text{AsF}_5/\text{anhydrous hydrogen fluoride (aHF)}$ two new lead(II) hexafluoroarsenates(V) $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ and PbFAsF_6 were isolated. $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ is formed when the molar ratio $\text{AsF}_5:\text{PbF}_2$ is 2 or higher. It crystallizes in the space group $Pbcn$ with $a = 1058.3(3)$ pm, $b = 1520.9(6)$ pm, $c = 1079.4(3)$ pm, $V = 1.7374(10)$ nm³ and $Z = 8$. The HF molecule is directly connected to the Pb center, eight fluorine atoms from three different AsF_6^- ions (Pb–F distances ranging from 248(4) to 276(2) pm) and one further fluorine at 306(3) pm complete the coordination sphere. PbFAsF_6 is obtained when equimolar amounts of PbF_2 and AsF_5 react in aHF. PbFAsF_6 crystallizes in the space group $P\bar{1}$ with: $a = 466.10(10)$ pm, $b = 723.70(10)$ pm, $c = 747.40(10)$ pm, $\alpha = 105.930(10)^\circ$, $\beta = 101.49(2)^\circ$, $\gamma = 90.660(10)^\circ$, $V = 0.23698(7)$ nm³ and $Z = 2$. The basic unit in the structure of $\text{PbF}(\text{AsF}_6)$ consists of a four-membered ring of two Pb and two F atoms. The Pb atoms in the ring are further connected by two AsF_6^- units via *cis*-fluorine bridges, thus forming a $[\text{PbF}(\text{AsF}_6)]_2$ cluster, which interacts by additional Pb–F bonds thus forming a ribbon-like polymer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $\text{Pb}(\text{HF})(\text{AsF}_6)_2$; PbFAsF_6 ; Crystal structure; Synthesis; Infrared; Raman spectra

1. Introduction

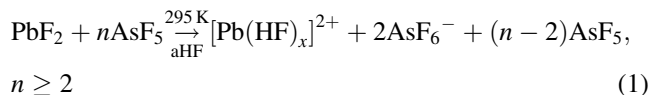
Metal(II) hexafluoroarsenates(V) are widely used as starting materials in coordination chemistry especially in sulfur dioxide as a solvent [1]. It was previously described that $\text{M}(\text{AsF}_6)_2$ can be readily prepared from MF_2 and AsF_5 in aHF [2,3], but, according to our experience, depending on the purity of the starting materials and the reaction conditions, usually a variety of phases are formed which make the characterization of pure compounds practically impossible without crystal structure determinations. Only a few crystal structures of metal(II) hexafluoroarsenates(V) are known to date. In $\text{Mn}(\text{AsF}_6)_2$ the Mn(II) shows the unusually high coordination number 8 in a pure fluorine environment [4]. The structure of $\text{SnF}_2 \cdot \text{AsF}_5$ consists of discrete cyclic $(\text{Sn}-\text{F})_3^{3+}$ cations and octahedral AsF_6^- anions [5]. The crystal structure of $\text{AgF}_2 \cdot \text{AsF}_5$ is built up from an infinite, fluorine-bridged $(\text{Ag}-\text{F})_n^{n+}$ chain and AsF_6^- octahedra cross-linked to these chains via further fluorine bridges [6]. These

few examples give an impression of the great structural variety of pure metal(II) hexafluoroarsenates(V), thus their synthesis and their crystal structure determination still present a challenge in the research work.

2. Results and discussion

2.1. Synthesis of $\text{Pb}(\text{HF})(\text{AsF}_6)_2$

The reaction between PbF_2 and excess of AsF_5 in aHF as solvent (reaction 1) yields a colorless solution of solvated Pb^{2+} cations and AsF_6^- anions.



A clear solution is obtained when the molar ratio between $\text{PbF}_2:\text{AsF}_5$ is reached. Excess of AsF_5 is not necessary although the reaction proceeds with a higher rate in aHF made acidic with excess of AsF_5 . $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ was obtained as a white solid after removal of excess AsF_5 and aHF. In [2] this compound was erroneously reported

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Table 1
Crystal data and structure refinement for Pb(HF)(AsF₆)₂ and PbFAsF₆

Empirical formula	HAs ₂ F ₁₃ Pb	AsF ₇ Pb
Formula weight	605.04	415.11
Temperature	173(2) K	173(2) K
Wavelength	71.073 pm	71.073 pm
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 1058.3(3) pm <i>b</i> = 1520.9(6) pm <i>c</i> = 1079.4(3) pm α = 90° β = 90° γ = 90°	<i>a</i> = 466.10(10) pm <i>b</i> = 723.70(10) pm <i>c</i> = 747.40(10) pm α = 105.930(10)° β = 101.49(2)° γ = 90.660(10)°
Volume	1.7374(10) nm ³	0.23698(7) nm ³
Z	8	2
Density (calculated)	4.626 Mg/m ³	5.817 Mg/m ³
Absorption coefficient	27.172 mm ⁻¹	42.603 mm ⁻¹
F(0 0 0)	2128	356
Crystal size	0.50 mm × 0.40 mm × 0.20 mm	0.40 mm × 0.20 mm × 0.10 mm
Theta range for data collection	2.68–24.97°	2.90–27.50°
Index ranges	−1 ≤ <i>h</i> ≤ 13, −19 ≤ <i>k</i> ≤ −12 ≤ <i>l</i> ≤ 1	−6 ≤ <i>h</i> ≤ 6, −9 ≤ <i>k</i> ≤ 9, −9 ≤ <i>l</i> ≤ 9
Reflections collected	1850	2048
Independent reflections	1355 [<i>R</i> (int) = 0.0584]	1070 [<i>R</i> (int) = 0.0825]
Completeness to theta	88.7%	98.3%
Absorption correction	Empirical (DIFABS)	Psi-scan
Maximum and minimum transmission	0.0740 and 0.0259	0.1002 and 0.0209
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1355/18/149	1070/0/83
Goodness-of-fit on <i>F</i> ²	1.099	1.127
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0800, <i>wR</i> ₂ = 0.1491	<i>R</i> ₁ = 0.0589, <i>wR</i> ₂ = 0.1379
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1408, <i>wR</i> ₂ = 0.1652	<i>R</i> ₁ = 0.0604, <i>wR</i> ₂ = 0.1393
Extinction coefficient	0.00033(9)	0.044(4)
Largest diffractometer peak and hole	2.156 and −1.783 e ⁻¹ Å ⁻³	4.299 and −4.908 e ⁻¹ Å ⁻³

as Pb(AsF₆)₂, as was shown by their identical X-ray powder diffraction pattern. The compound Pb(HF)(AsF₆)₂ is very soluble in aHF, single crystals were grown from saturated solutions. When Pb(HF)(AsF₆)₂ is redissolved in aHF partial solvolysis always takes place and besides the bulk of the crystals of Pb(HF)(AsF₆)₂, some shiny crystals of PbFAsF₆ were also spotted and picked up for X-ray analysis. The low solubility of PbFAsF₆ in comparison to the solubility of Pb(HF)(AsF₆)₂ contributes to this effect.

Details on data collection and the structure determination of Pb(HF)(AsF₆)₂ are given in Table 1. The X-ray powder diffraction pattern calculated from this structure matches the X-ray powder diffraction pattern obtained from the bulk of the sample (Table 2). Additional evidence for HF bonded to Pb(AsF₆)₂ is the higher weight of the final product than would be expected for only Pb(AsF₆)₂ only although this is not highly significant due to the low molecular weight of HF and the possible change of the weight of the PFA reaction vessel during the reaction. Chemical analysis shows free fluoride, further proof for the presence of HF since fluorine from AsF₆⁻ anions is not detected as free fluoride.

2.2. Crystal structure of Pb(HF)(AsF₆)₂

Selected bond distances and angles are given in Table 3. Fig. 1 shows the coordination spheres of the Pb center

and those of the three structurally different AsF₆⁻ ions. This difference is further illustrated by Figs. 2–4. As(1)F₆⁻ and As(3)F₆⁻ bridge to Pb centers with formation of

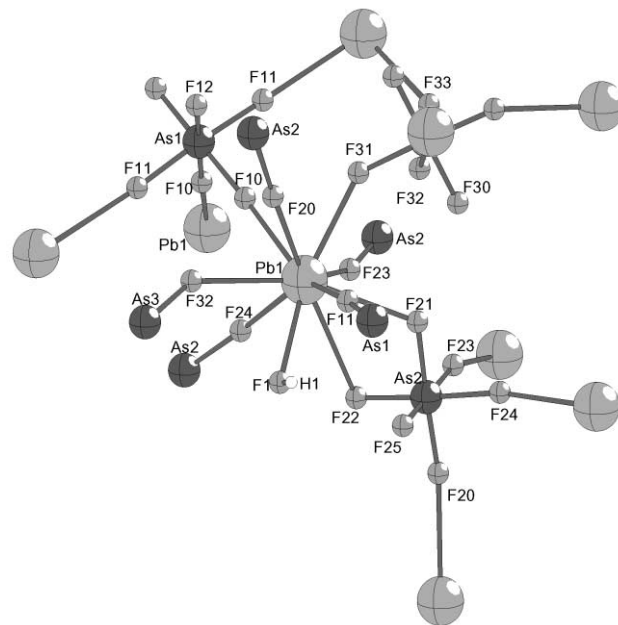


Fig. 1. Coordination sphere of the Pb center in the structure of Pb(HF)(AsF₆)₂.

Table 2
X-ray powder diffraction data for Pb(HF)(AsF₆)₂ and PbFAsF₆

Pb(HF)(AsF ₆) ₂				PbFAsF ₆			
<i>d</i> _{calc} (pm)	<i>I</i> ^a	<i>d</i> _{obs} (pm)	<i>I</i> ^b	<i>d</i> _{calc} (pm)	<i>I</i> ^a	<i>d</i> _{obs} (pm)	<i>I</i> ^b
458.4	200	459.0	m	369.2	1000	370.1	s
402.9	390	401.3	m	353.3	632		
377.8	1000	376.9	vs	351.3	645	352.5	vs (br)
348.9	181			346.7	718		
343.6	249	345.1	s	340.4	478	340.0	w
339.7	433			311.7	209		
338.4	284	335.8	s	308.7	535	309.4	m
325.2	402	323.6	m	291.5	274	291.4	m
310.8	153	309.6	w	282.9	259		
289.6	136	290.5	w	281.2	274	281.8	m
254.3	101			231.5	227	234.5	vw
251.5	51	251.9	w	224.6	215		
249.9	69			221.5	138	222.7	w
211.1	57			221.1	229		
210.5	81	211.4	vw	213.1	155		
209.6	67			212.9	144	213.1	vw
207.7	76			194.8	233		
205.2	60	205.8	vw	190.5	378	191.5	w
197.4	95			184.6	151		
196.3	142	196.0	m	184.5	101		
194.0	115			183.7	100	184.6	w
193.3	151	192.7	m	183.0	104		
184.4	106						
183.7	121						
182.0	121	182.3	m				
181.1	83						
176.9	64						
176.4	50	176.3	vw				

^a Calculated *d* values from the structures, only the strongest peaks are shown.

^b Intensities were estimated visually, very strong: vs, strong: s, medium: m, weak: w, very weak: vw, broad line: br.

16-membered heterocycles. Since each of these AsF₆[−] units is connected to four different Pb centers layers are formed. In As(3)F₆[−] the four meridional F's are involved in this interaction, in As(1)F₆[−] the two non-coordinating fluorines

are in *cis*-positions. Particularly interesting is the interaction of As(2)F₆[−] with the Pb centers. Taking into account the weak Pb–F(22) interaction (306(3) pm) the AsF₆[−] acts as a bidentate ligand with formation of a four-membered

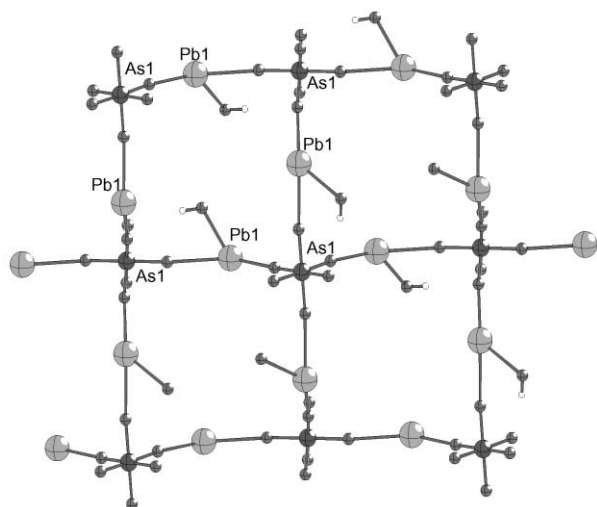


Fig. 2. Connection of Pb atoms via As(1)F₆[−] in Pb(HF)(AsF₆)₂.

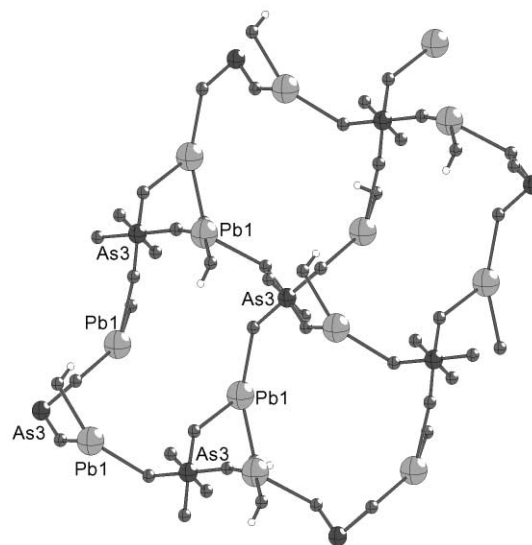


Fig. 3. Connection of Pb atoms via As(3)F₆[−] in Pb(HF)(AsF₆)₂.

Table 3
Selected bond lengths (pm) and angles (°) for Pb(HF)(AsF₆)₂^a

Pb–F			
Pb(1)–F(1)	248(4)	Pb(1)–F(32)#3	266(3)
Pb(1)–F(24)#1	251(2)	Pb(1)–F(11)#4	269.8(16)
Pb(1)–F(10)	252(2)	Pb(1)–F(21)	270.3(17)
Pb(1)–F(31)	258(2)	Pb(1)–F(20)#5	276(2)
Pb(1)–F(23)#2	263.1(18)	Pb(1)–F(22)	306(3)
AsF ₆ octahedra			
As(1)–F(12)#6	164(3)	F(12)#6–As(1)–F(12)	92
As(1)–F(12)	164(3)	F(12)#6–As(1)–F(10)	177.9(15)
As(1)–F(10)	172(2)	F(12)–As(1)–F(10)	89.7(12)
As(1)–F(10)#6	172(2)	F(10)–As(1)–F(10)#6	88.6(17)
As(1)–F(11)#6	174.7(17)	F(10)–As(1)–F(11)#6	86.9(11)
As(1)–F(11)	174.7(17)	F(11)#6–As(1)–F(11)	176.1(16)
As(2)–F(25)	166.0(19)	F(25)–As(2)–F(22)	92.5(10)
As(2)–F(22)	170.7(18)	F(22)–As(2)–F(21)	91.5(11)
As(2)–F(21)	171(2)	F(21)–As(2)–F(24)	85.9(11)
As(2)–F(20)	172(2)	F(21)–As(2)–F(20)	177.6(12)
As(2)–F(23)	172.5(18)	F(23)–As(2)–F(24)	87.9(10)
As(2)–F(24)	179(2)	F(22)–As(2)–F(24)	176.9(12)
As(3)–F(30)	161(4)	F(30)–As(3)–F(33)	180.0
As(3)–F(33)	162(9)	F(33)–As(3)–F(32)	87.2(15)
As(3)–F(32)	170(3)	F(32)–As(3)–F(32)#8	174(3)
As(3)–F(32)#8	170(3)	F(32)–As(3)–F(31)	89.4(10)
As(3)–F(31)#8	171.0(18)	F(31)#8–As(3)–F(31)	178.1(19)
As(3)–F(31)	171.0(18)	F(33)–As(3)–F(31)	90.9(10)

^a Symmetry transformations used to generate equivalent atoms: #1 *x*, *−y*, *z* + 1/2; #2 *−x*, *−y*, *−z*; #3 *−x* + 1/2, *−y* + 1/2, *z* + 1/2; #4 *−x* + 1/2, *−y* + 1/2, *z* − 1/2; #5 *−x* + 1/2, *y* + 1/2, *z*; #6 *−x*, *y*, *−z* + 1/2; #7 *x*, *−y*, *z* − 1/2; #8 *−x*, *y*, *−z* − 1/2.

ring, two of these basic units form eight-membered heterocycles.

The coordination number of the central Pb(1) is 10 if we consider bond distances up to 306 pm: one fluorine from a HF molecule and nine fluorines from the AsF₆[−] units. The distance Pb(1)–F(1) (fluorine from the HF molecule) is the shortest distance in the structure (248(4) pm). This is the second example of a complex where HF is bonded directly to a metal center [7], although hydrogen bonding to fluoride ions is well established [8,9]. For La(HF)₂(AsF₆)₃ we reported a La–F(H) distance of 246.6(3) pm [7]. The

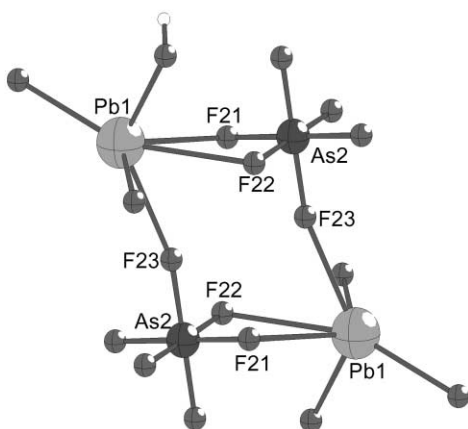
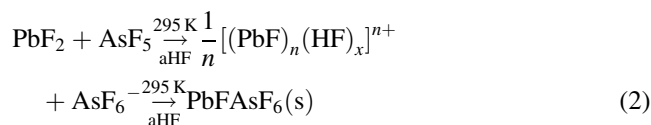


Fig. 4. Connection of Pb atoms via As(2)F₆[−] in Pb(HF)(AsF₆)₂.

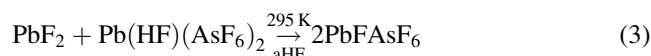
Pb–F(H) distance of 248(4) pm is only a little longer than the shortest Pb–F distance in PbF₂ (241 pm) [10]. As discussed previously each As(1)F₆[−] and As(3)F₆[−] coordinates four Pb atoms, the distances for the bridging As(1)–F are in the range from 172(2) to 174.7(17) pm and for As(3)–F from 170(3) to 171.0(18) pm. The terminal As–F distances are in the range from 161(4) to 164(3) pm as expected for terminal fluorines in the AsF₆[−] units. In the case of As(2) the As(2)–F distances are: 166.0(19) pm for the terminal F atom (F(25)) and 171(2) to 179(2) pm for the bridging ones. As(2)–F(22) is 170.7(18) pm, longer than expected for a terminal bond, a further indication for the weak interaction between F(22) and Pb(1).

2.3. Synthesis of PbFAsF₆

The reaction between PbF₂ and an equimolar amount of AsF₅ in aHF as solvent yields colorless solutions probably containing solvated (Pb – F)_nⁿ⁺ cations and AsF₆[−] anions (reaction 2), from which PbFAsF₆ precipitates. This compound is much less soluble in aHF than Pb(HF)(AsF₆)₂. Preliminary measurements show that it is even less soluble than PbF₂ itself.



It is possible that some Pb(HF)(AsF₆)₂ is formed during the reaction due to the higher local concentration of AsF₅ but this finally reacts with an excess of dissolved PbF₂ yielding PbFAsF₆ which precipitates. This was shown to be the case by a separate reaction between equimolar amounts of PbF₂ and Pb(HF)(AsF₆)₂ dissolved in aHF yielding PbFAsF₆ (reaction 3)



The X-ray powder diffraction pattern calculated from the structure of PbFAsF₆ matches the X-ray powder diffraction pattern of the bulk material obtained by reactions (2) and (3) (Table 2).

2.4. Crystal structure of the PbFAsF₆

Details on the data collection and selected bond distances and angles are given in Tables 1 and 4. The basic unit in the structure of PbFAsF₆ (Fig. 5) can be described as a four-membered ring of two Pb and two F atoms. The shortest distance in the ring Pb(1)–F(1) is 227.2(8) pm and the longer one F(1)–Pb(1)#2 is 251.5(8) pm. Two AsF₆[−] units further connect the Pb atoms in the ring via *cis*-fluorine bridges to form [PbF(AsF₆)₂] clusters. The distances between the Pb atoms and the F atoms from the AsF₆[−] unit are 264.6(8) pm (Pb(1)–F(2)) and 269.1(7) pm (Pb(1)–F(4)#2). The clusters are further connected by additional Pb–F (F(1)–Pb(1)#1)

Table 4
Selected bond lengths (pm) and angles ($^{\circ}$) for $\text{PbFAsF}_6^{\text{a}}$

$(\text{Pb} - \text{F})_n^{n+}$ environment			
$\text{F}(1) - \text{Pb}(1)$	227.2(8)	$\text{Pb}(1) - \text{F}(1) - \text{Pb}(1)\#1$	109.9(3)
$\text{F}(1) - \text{Pb}(1)\#1$	246.3(8)	$\text{Pb}(1) - \text{F}(1) - \text{Pb}(1)\#2$	110.7(3)
$\text{F}(1) - \text{Pb}(1)\#2$	251.5(8)	$\text{Pb}(1)\#1 - \text{F}(1) - \text{Pb}(1)\#2$	138.9(4)
$\text{Pb}(1) - \text{F}(1)\#1$	246.3(8)	$\text{F}(1) - \text{Pb}(1) - \text{F}(1)\#1$	70.1(3)
$\text{Pb}(1) - \text{F}(1)\#2$	251.5(8)	$\text{F}(1) - \text{Pb}(1) - \text{F}(1)\#2$	69.3(3)
$\text{Pb}(1) - \text{F}(2)$	264.6(8)	$\text{F}(1) - \text{Pb}(1) - \text{F}(2)$	71.3(3)
$\text{Pb}(1) - \text{F}(4)\#2$	269.1(7)		
$\text{Pb}(1) - \text{F}(5)\#3$	284.4(8)		
$\text{Pb}(1) - \text{F}(6)\#1$	298.9(9)		
$\text{Pb}(1) - \text{F}(7)\#4$	299.3(8)		
$\text{Pb}(1) - \text{F}(3)\#5$	307.1(9)		
AsF_6 octahedra			
$\text{As}(1) - \text{F}(2)$	172.5(8)	$\text{As}(1) - \text{F}(2) - \text{Pb}(1)$	135.6(4)
$\text{As}(1) - \text{F}(3)$	171.5(9)	$\text{F}(4) - \text{As}(1) - \text{F}(7)$	179.9(5)
$\text{As}(1) - \text{F}(4)$	171.3(7)	$\text{F}(5) - \text{As}(1) - \text{F}(6)$	178.3(4)
$\text{As}(1) - \text{F}(5)$	170.4(8)	$\text{F}(4) - \text{As}(1) - \text{F}(3)$	89.8(4)
$\text{As}(1) - \text{F}(6)$	172.0(8)	$\text{F}(5) - \text{As}(1) - \text{F}(2)$	90.7(4)
$\text{As}(1) - \text{F}(7)$	171.8(8)	$\text{F}(4) - \text{As}(1) - \text{F}(2)$	89.0(4)

^a Symmetry transformation used to generate equivalent atoms: #1 $-x, -y + 1, -z$; #2 $-x + 1, -y + 1, -z$; #3 $-x + 1, -y, -z$; #4 $-x, -y, -z$; #5 $x, y, z - 1$; #6 $x, y, z + 1$; #7 $x + 1, y, z + 1$.

bonds (246.3(8) pm) thus forming a ribbon-like polymer (Fig. 5).

The coordination number of Pb is 9 (Fig. 6), within the ribbon three coordination sites are occupied by the F atoms and three by fluorines from the bridging AsF_6^- units, two strong interactions (264.6(8) pm ($\text{Pb}(1) - \text{F}(2)$) and 269.1(7) pm ($\text{Pb}(1) - \text{F}(4)\#2$), respectively) and one weaker $\text{Pb}(1) - \text{F}(6)\#1$ (298.9(9) pm). The distances to three further F atoms from AsF_6^- of neighboring ribbons are in the range 284.4(8)–307.1(9) pm (Fig. 7).

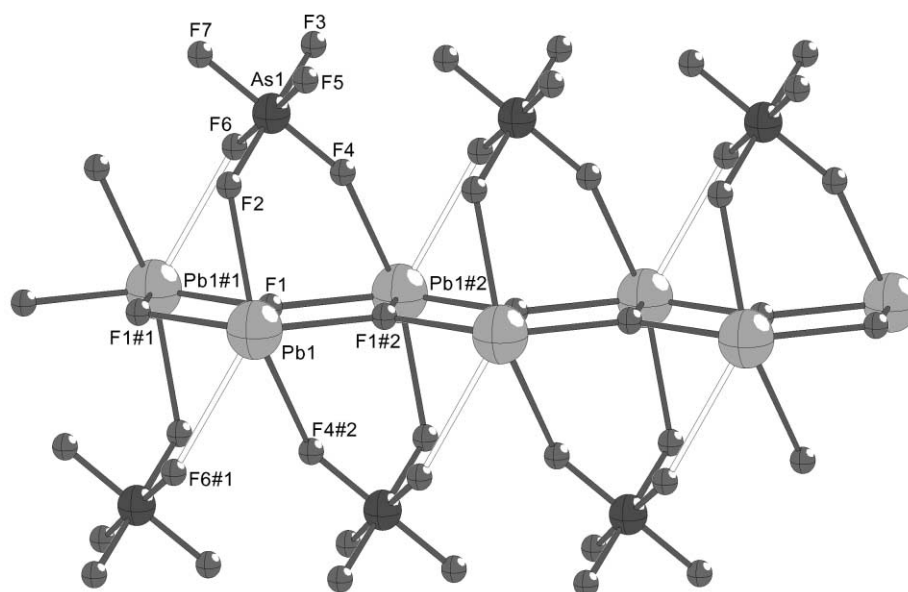


Fig. 5. Basic units in the structure of PbFAsF_6 .

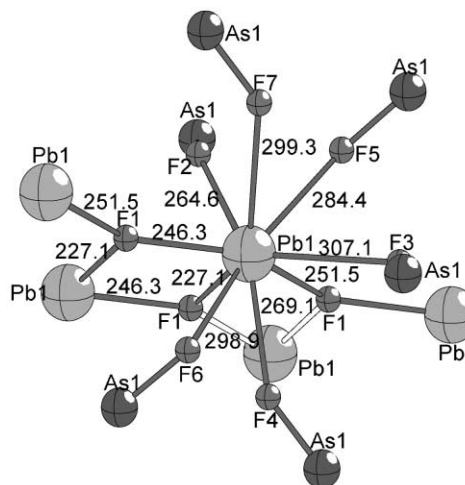


Fig. 6. Coordination sphere of the Pb center in PbFAsF_6 .

As discussed previously the shortest Pb–F distance in the $(\text{Pb} - \text{F})_n^{n+}$ polymeric ribbon is 227.2(8) pm, a distance not much longer than that expected for a pure covalent Pb–F bond (219 pm). A distance of 252 pm is expected for an ionic bond (CN = 7). Higher coordination numbers of metal centers increase their ionic radii, thus the expected distance for ionic Pb–F bonds increase to 265 pm (CN = 9) [11], similar to the distances to the bridging AsF_6^- within the $[\text{PbF}(\text{AsF}_6)]_2$ clusters.

Each AsF_6^- bridges six different Pb centers, due to their weak interaction the AsF_6^- anions have nearly regular O_h symmetry with all angles close to 90° . The As–F distances are in the range 170.4(8)–172.5(8) pm which is longer than expected for terminal fluorine atoms but shorter than expected for bridging ones.

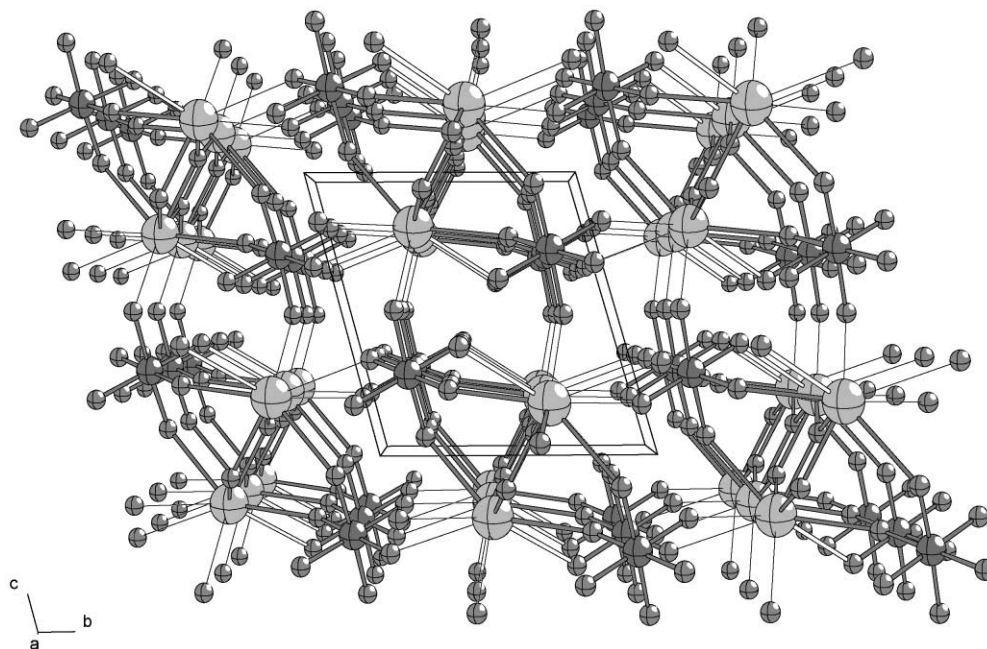


Fig. 7. Arrangement of the basic units in the structure of PbFAsF_6 .

2.5. Vibrational spectra of Pb(II) hexafluoroarsenates(V)

Infrared and Raman spectra are presented in Figs. 8 and 9 and Table 5. Vibrational frequencies of CsAsF_6 with AsF_6^- having O_h symmetry are also given in Table 5 for comparison [12]. For the octahedral AsF_6^- ion (O_h symmetry) three Raman active fundamental vibrations, ν_1 , ν_2 and ν_5 and two infrared active vibrations, ν_3 and ν_4 are expected [12]. Vibration ν_6 is both infrared and Raman inactive. In the compound PbFAsF_6 the X-ray studies on the single crystal show that the average As–F distance is 171.4 ± 0.8 pm and

AsF_6^- having nearly O_h symmetry. The vibrational data clearly support the picture obtained from the crystallographic studies (see Table 5). In the compound $\text{Pb(HF)(AsF}_6)_2$ the AsF_6^- octahedra are deformed due to a much stronger polarizing effect of naked Pb^{2+} cation in comparison to the less polarizing effect of the $(\text{Pb} - \text{F})_n^{n+}$ cation. As–F distances in AsF_6^- ions are in the range from 161(4) to 179(2) pm. In the vibrational spectra splitting of all As–F vibrations is observed due to a strong deformation of AsF_6^- ions. Bands at 300 cm^{-1} (R) and at 580 cm^{-1} (IR) in the case of PbFAsF_6 were assigned to the $\nu(\text{Pb} - \text{F})$ vibrations

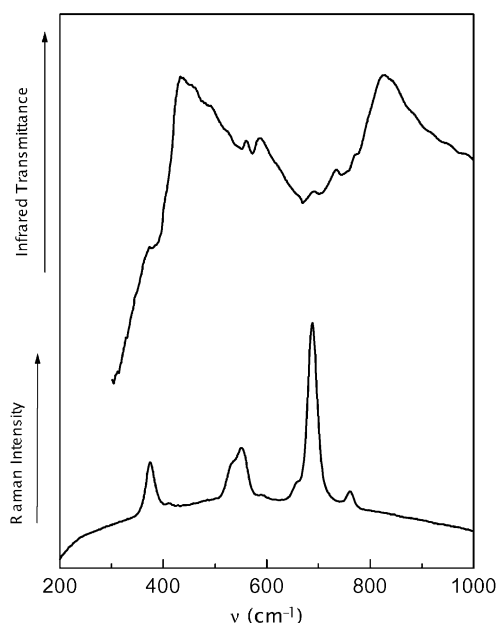


Fig. 8. Infrared and Raman spectra of $\text{Pb(HF)(AsF}_6)_2$.

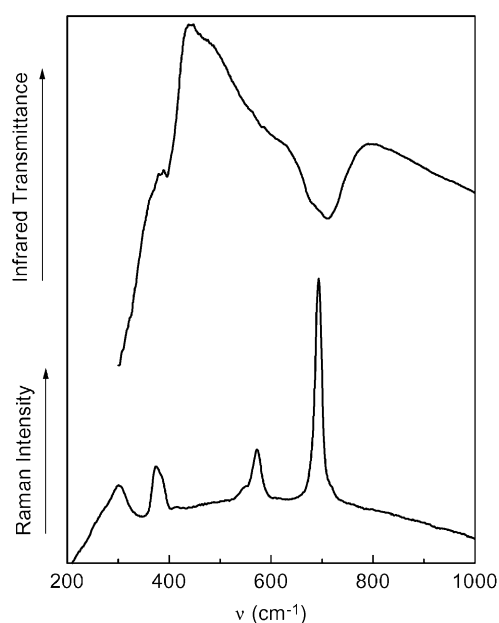


Fig. 9. Infrared and Raman spectra of PbFAsF_6 .

Table 5
Vibrational frequencies of lead(II) hexafluoroarsenates(V) and CsAsF₆^a

Pb(HF)(AsF ₆) ₂		PbFAsF ₆		CsAsF ₆ ^b		Assignment AsF ₆ ⁻ (O _h)
R	IR	R	IR	R	IR	
761 (0.8)	776 (sh) 759 (sh) 744 (s) 703 (vs)		710 (vs)		699 (s)	v ₃
689 (10)	669 (vs)	693 (10)	675 (sh)	685 (10)		v ₁
660 (1.1) 595 (0.1)			580 (sh)			
	572 (m) 553 (m)	572 (2.4)		576 (2.3)		v ₂
551 (2.7)		547 (0.6)				
531 (1.9)	520 (sh) 479 (sh) 447 (w)					
412 (0.1)			395 (s)		392 (m)	v ₄
		386 (0.5)				
374 (2.8)	378 (s)	373 (2.1) 300 (1.7)		372 (2.6)		v ₅

^a IR intensities: very strong: vs, strong: s, medium: m, shoulder: sh; Raman intensities are in parentheses.

^b [12].

on the basis of comparison. In the infrared spectrum of PbFSnF₃ the band at 562 cm⁻¹ has been assigned to the Pb–F⁺ cation [13] while in PbF₂ ν(Pb–F) is at 531.2 cm⁻¹ in the infrared spectrum [14] and at 239 cm⁻¹ in the Raman spectrum.¹

2.6. Conclusion

Depending on the amount of AsF₅ added to the suspension of PbF₂ in aHF two Pb(II) hexafluoroarsenates(V) can be synthesized. In strongly acidic aHF when the molar ratio between AsF₅ and PbF₂ is 2 or higher Pb(HF)(AsF₆)₂ is obtained. The reaction of equimolar amounts of PbF₂ and AsF₅ in aHF yields PbFAsF₆. This product can also be obtained by the reaction of equimolar amounts of PbF₂ and Pb(HF)(AsF₆)₂ dissolved in aHF.

3. Experimental

3.1. General experimental procedures

3.1.1. Apparatus, techniques and reagents

A nickel vacuum line and a Teflon vacuum system were used as previously described [4]. Non-volatile materials,

which are very sensitive to traces of moisture, were handled in the dry argon atmosphere of a glove box with maximum content of 0.1 ppm of water vapor (Mbraun, Garching, Germany). PFA reaction vessels equipped with Teflon valves and Teflon-covered stirring bars were used for the syntheses. T-shaped reaction vessels are constructed from two PFA tubes (16 mm i.d. × 19 mm o.d.) each drawn down to 8 mm i.d. × 10 mm o.d., joined at a right angle by a Teflon Swagelok T compression fitting and joined to a Teflon valve [15]. T-shaped PFA reaction vessels constructed from one large PFA tube (16 mm i.d.) and a smaller PFA tube (4 mm i.d.) joined at a right angle and equipped with a Teflon valve, were used for crystallization.

PbF₂ was used as purchased (Merck, Suprapur), aHF (Praxair, 99.9%) was treated with K₂NiF₆ for several days prior to use. AsF₅ was prepared by high-pressure fluorination of As₂O₃, a procedure previously described for PF₅ [16].

3.2. Synthesis of lead(II) hexafluoroarsenates(V)

3.2.1. Synthesis of Pb(HF)(AsF₆)₂

PbF₂ (1.378 g, 5.62 mmol) was weighed into a PFA reaction vessel equipped with a Teflon valve and a Teflon-coated stirring bar. Approximately 6 ml of aHF were added by condensation at 77 K. AsF₅ was slowly added at room temperature until a colorless solution was obtained. The reaction proceeded for 1 h at room temperature. Then aHF and excess of AsF₅ were removed at room temperature yielding a white solid. Mass balance of the reaction:

¹ Raman spectrum of PbF₂ (Merck) was taken in quartz capillary at the Department of Inorganic Chemistry and Technology, Institute Jožef Stefan, Slovenia.

calculated for $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ 3.400 g, calculated for $\text{Pb}(\text{AsF}_6)_2$ 3.288 g, obtained 3.344 g.

3.2.2. Synthesis of PbFAsF_6

The compound was synthesized by the reaction between PbF_2 (1.010 g, 4.12 mmol) and AsF_5 (0.756 g, 4.45 mmol) in aHF (5 ml) at room temperature. The amount of added AsF_5 was monitored by measuring the change of pressure in known volume. The weight of added AsF_5 was slightly higher than required for 1:1 mol ratio. The reaction took place for 24 h and the white solid and a colorless solution were obtained. After aHF was pumped away at room temperature PbFAsF_6 was obtained (1.739 g, 4.19 mmol).

PbF_2 (0.168 g, 0.69 mmol) was weighed into one arm of the T-shaped reaction vessel and $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ (0.390 g, 0.65 mmol) into the other one. Anhydrous HF (3–4 ml) was added to both starting compounds and reaction vessel was allowed to warm up to room temperature. The solution of PbF_2 was poured into solution of $\text{Pb}(\text{HF})(\text{AsF}_6)_2$. Reaction took place immediately and PbFAsF_6 was precipitated. The yield of the product was (0.552 g, 1.33 mmol).

3.2.3. Preparation of single crystals

Due to the high solubility of $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ in aHF, single crystals were grown from its aHF solution. In the T-shaped PFA reaction vessel the $\text{Pb}(\text{HF})(\text{AsF}_6)_2$ was dissolved in aHF in the wider tube and then poured into the narrower one. A small temperature gradient of 6 K was maintained by cooling the wider tube with cold water (~ 287 K) and keeping the narrower one at room temperature for 14 days. After aHF was removed the crystals were immersed in Kel-F oil in the glove box, selected under the microscope and transferred to the cold nitrogen stream (173 K) of the diffractometer. Under the microscope two different types of single crystals were observed. Crystal data showed that the majority of the sample crystallizes as $\text{Pb}(\text{HF})(\text{AsF}_6)_2$. A few selected crystals of the composition PbFAsF_6 were also found. PbFAsF_6 can be crystallized also from its aHF solution.

3.3. Compound characterization

3.3.1. Chemical analysis

Free and total fluoride ion contents were determined by an ion selective electrode [17,18]. Lead was determined by complexometric titration [19]. AsF_6^- was determined gravimetrically by precipitation with tetraphenylarsonium chloride [20]. Arsenic was determined by the ICP method [21].

3.3.2. Results of chemical analysis

Anal. Calcd. for $\text{Pb}(\text{HF})(\text{AsF}_6)_2$: Pb, 34.3; F_{total} , 40.8; F_{free} , 3.1; AsF_6^- , 62.5. Found: Pb, 34.5; F_{total} , 39.3; F_{free} , 1.5; AsF_6^- , 64.3. Anal. Calcd. for PbFAsF_6 : Pb, 49.9; F_{total} , 32.0; F_{free} , 4.6; As, 18.1; AsF_6^- , 45.5. Found: Pb, 46.7; F_{total} , 32.0; F_{free} , 3.6; As, 16.2; AsF_6^- , 47.4.

3.3.3. X-ray crystallography

X-ray powder diffraction photographs were taken in sealed quartz capillaries on a Debye–Scherrer camera, using Mo $K\alpha$ radiation and Zr filter. Crystal data were collected on a Siemens P4 diffractometer, details: $\omega - 2\theta$ scans; refinement based on F^2 ; $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR_2 = \{ \sum [w(F_0^2 - F_c^2)] / \sum [w(F_0^2)^2] \}^{1/2}$. Programs SHELX-97 [22] and DIAMOND² were used. Crystallographic data for the structures in this paper have been deposited with the Fachinformationzentrum Karlsruhe (FIZ) as supplementary publication nos. CSD 411787 and CSD 411788. Copies of the data can be obtained, free of charge, on application to FIZ, abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany.³

3.3.4. Infrared and Raman spectroscopy

Infrared spectra were taken on a Perkin-Elmer FT-IR 1710 spectrometer on powdered samples between AgCl windows in a leak-tight brass cell. Raman spectra of powdered samples in sealed quartz capillaries were taken on a Renishaw Raman Imaging Microscope System 1000, with the exiting line at 632.8 nm of a He–Ne laser.

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