

CALCIUM HEXAFLUOROARSENATES WITH METAL COORDINATED HF MOLECULES

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Abstract

Two calcium hexafluoroarsenates(V) with metal coordinated HF were structurally characterised: $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ and $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$. $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ crystallizes in a monoclinic crystal system, space group $P2_1/c$, with $a = 962.4(6)$ pm, $b = 926.4(5)$ pm and $c = 1059.2(7)$ pm, $\beta = 104.161(13)^\circ$, $V = 0.9157(10)$ nm³ and $Z = 4$. $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ crystallizes in a monoclinic crystal system, space group $P2_1/c$, with $a = 1004.9(5)$ pm, $b = 1498.7(7)$ pm and $c = 984.0(5)$ pm, $\beta = 109.56(11)^\circ$, $V = 1.3965(12)$ nm³ and $Z = 4$.

Key words: calcium, hexafluoroarsenates, hydrogen fluorid

Introduction

Metal fluorides dissolve in anhydrous hydrogen fluoride (aHF) acidified with Lewis acids (AsF_5 , SbF_5) yielding solutions of solvated cations and relatively weakly coordinated corresponding anions.¹ Several years ago the first structure with HF coordinated directly to the metal center was determined: $\text{La}(\text{HF})(\text{AsF}_6)_3$.² Since then several examples of metal hexafluoroarsenates and antimonates with coordinated HF were found: $\text{Pb}(\text{HF})(\text{AsF}_6)_2$,³ $\text{Ca}(\text{HF})_2(\text{SbF}_6)_2$,⁴ $\text{Mg}(\text{HF})_2(\text{SbF}_6)_2$,⁴ $[(\text{OsO}_3\text{F})(\text{HF})_2](\text{AsF}_6)_2$,⁵ $\text{Au}(\text{HF})_2(\text{SbF}_6)_2$,⁶ and $\text{Cd}(\text{HF})(\text{AsF}_6)_2$.⁷

$\text{Ca}(\text{HF})(\text{AsF}_6)_2$ and $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ present new examples of metal HF coordinated compounds. $\text{Ca}(\text{HF})(\text{AsF}_6)_2$, which is isostructural with $\text{Cd}(\text{HF})(\text{AsF}_6)_2$ ⁷ has been briefly mentioned in a review paper.⁸ Details of structure determination for both compounds are given here for the first time.

Results and discussion

$\text{Ca}(\text{AsF}_6)_2$ can be prepared by the reaction between CaF_2 and AsF_5 in aHF solvent as described in the literature.⁹ The lattice energy of $\text{Ca}(\text{AsF}_6)_2$ is rather low as a consequence of the relatively large volume of AsF_6^- (110 Å³ 10). The AsF_6^- anion is a

weak Lewis base, so even poor Lewis base solvents, such as aHF, can provide sufficient solvation energy to dissolve the $\text{Ca}(\text{AsF}_6)_2$ salt to form solvated $[\text{Ca}(\text{HF})_n]^{2+}$ cations and AsF_6^- anions. Molecules of the solvent, in this case HF, remain coordinated to the metal center during the process of crystallisation and help to stabilise crystal packing. This seems to be important in the cases of the compounds with low lattice energy, which cannot fully compensate the energy needed for the desolvation of the cation. In the type of compounds $\text{M}(\text{L})(\text{AF}_6)_2$ ($\text{L} = \text{HF}, \text{XeF}_2$) which were recently synthesised in our laboratory calcium compounds shows the largest variety of the structural types found so far. In the system $\text{Ca}^{2+}/\text{XeF}_2/\text{AsF}_6^-$ three compounds were found: $\text{Ca}_2(\text{XeF}_2)_9(\text{AsF}_6)_2$,¹¹ $[\text{Ca}(\text{XeF}_2)_4](\text{AsF}_6)_2$ and $[\text{Ca}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_2$.¹² In the first two compounds layer structure arrangement was found, while for the latter 3D structure type was determined. In these cases, the mole ratio between metal center Ca^{2+} and ligand molecule XeF_2 was important in the reaction and crystallisation process. Similarly, parameters that influence stability of the $[\text{Ca}(\text{HF})_n]^{2+}$ coordination sphere must play important role in the reaction system of $\text{Ca}^{2+}/\text{HF}/\text{AsF}_6^-$. Crystals with compositions $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ were found in the crystallization vessel after crystallisation of the $[\text{Ca}(\text{XeF}_2)_4](\text{AsF}_6)_2$ (see details in the experimental section), while after crystallization from saturated aHF solution of the $\text{Ca}(\text{AsF}_6)_2$, crystals with composition $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ were obtained.

Calcium atom in the $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ is coordinated to nine fluorine atoms in the form of tricapped trigonal prism (Figure 1a). Six of the fluorine atoms in the apexes of the trigonal prism arise from six AsF_6 units with the Ca-F distances in the range of 231.5–246.2 pm. Additionally, two AsF_6 units act as bidentate ligands interacting with calcium atoms via second fluorine atom placed over the rectangular faces (F23 and F13) of the trigonal prism at distances 267.8 pm and 277.3 pm. Fluorine atom from HF molecule is placed over the third rectangular face of the trigonal prism (Ca1-F1 is 239.6 pm). AsF_6 units are distorted due to the interactions with calcium atoms as is clearly seen from the range of distances and angles (see Table 1).

Calcium atoms are further connected *via* two crystallographically different AsF_6 units, forming square rings with composition $[\text{Ca}_2(\text{AsF}_6)_2]^{2+}$. The square rings are alternately connected by trans bridges of AsF_6 units forming zigzag ladders (Figure 1b). Described ladders runs in the [1,1,1] direction. Each Ca atom from the [1,1,1] ladder is

part of an identical ladder running in the $[-1,-1,-1]$ direction. Calcium atoms connect both types of ladders in a 3D network, where channels are formed along a axis.

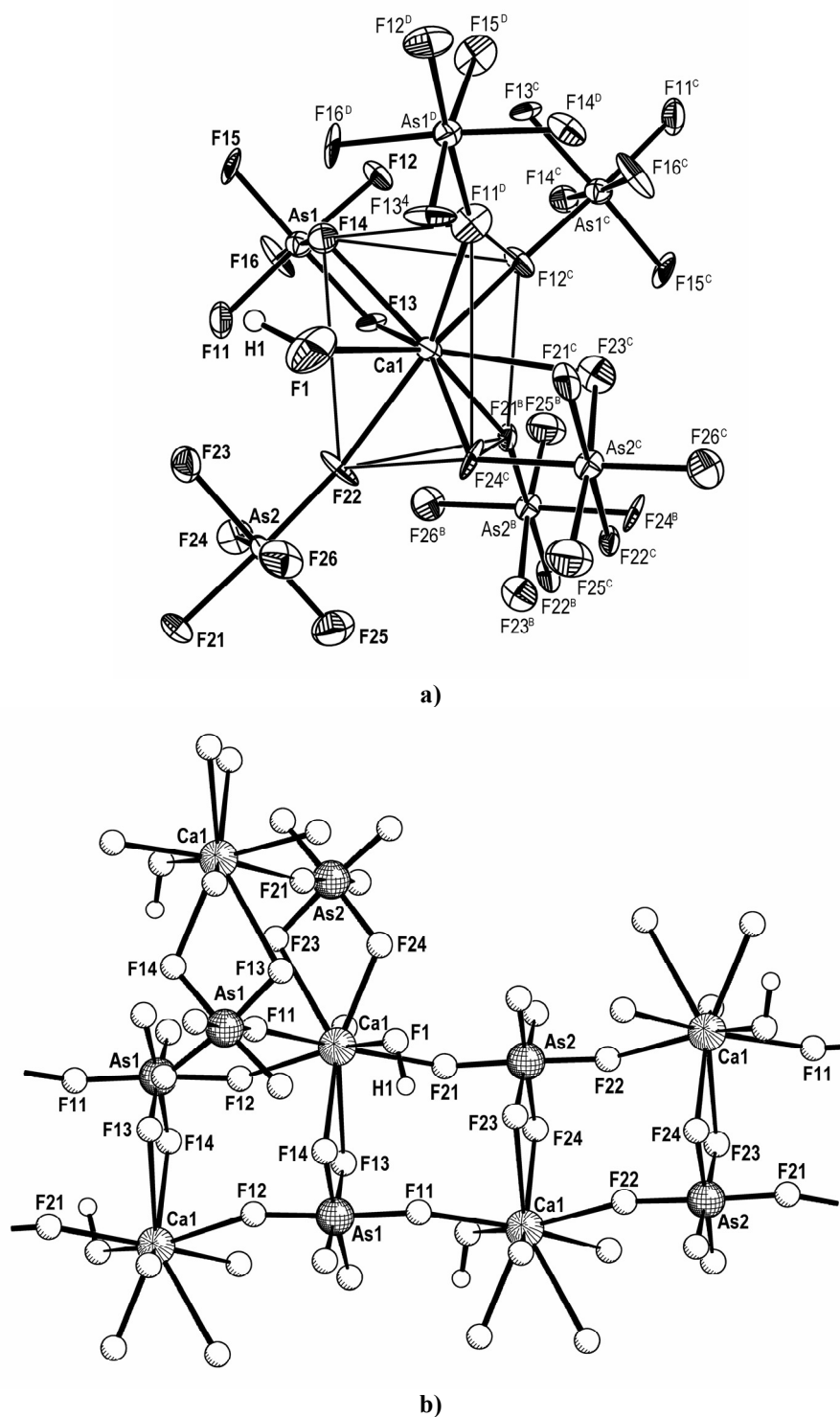


Figure 1. a) Coordination of Ca and b) Rings in the structure of $\text{Ca}(\text{HF})(\text{AsF}_6)_2$;
Symmetry operations: B $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; C $-x, -y, -z$; D $x, -y - \frac{1}{2}, z - \frac{1}{2}$.

HF molecules coordinated via fluorine atom directly to calcium atom are placed in these channels. Distances between F1 atom and surrounding atoms that could be involved in hydrogen bonding of HF molecule are given in Table 2. Distances F1...F for atoms F11, F13, F14, F21, F26 are short, but these atoms are involved in the bridging interactions As-F-Ca and are regarded to similar structures $[\text{Mg}(\text{HF})_2](\text{SbF}_6)_2$ and $[\text{Ca}(\text{HF})_2](\text{SbF}_6)_6$ ⁴ usually not involved in hydrogen bonding. Terminal fluorine atoms on the AsF_6^- (F25, F16', F25, F16, F26, F15) units seem to be more appropriate for hydrogen bonds. Lengthening of the As-F bond in the case of hydrogen bond can be expected, which gives us the most likely candidates: F1-H1...F16 and F1-H1...F16'. The F1...F16 distance is shorter than F...F16' but according to small angle Ca1-F1...F16 (90.7 °C) with respect to the angle Ca1-F1...F16' (111.0°), hydrogen atom was placed between F1...F16'. Nevertheless disorder of the HF molecule cannot be excluded.

Table 1. Selected distances and angles in $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ and $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$.

$\text{Ca}(\text{HF})(\text{AsF}_6)_2$				$\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$			
Distance [pm]		Angle [°]		Distance [pm]		Angle [°]	
Ca1-F1	239.6(9)			Ca1-F1	245(3)		
Ca1-F11	234.7(10)			Ca1-F2	227(3)		
Ca1-F12	238.2(9)			Ca1-F3	253(2)		
Ca1-F13	277.3(11)			Ca1-F4	242(3)		
Ca1-F14	246.2(10)			Ca1-F5	239(2)		
Ca1-F21	236.4(8)			Ca1-F6	236(3)		
Ca1-F22	238.5(8)			Ca1-F11	250(2)		
Ca1-F23	267.8(11)			Ca1-F23	259(3)		
Ca1-F24	231.5(9)						
As1-F11	176.8(9)	F11-As1-F12	176.0(5)	As1-F11	173.8(19)	F11-As1-F13	89.1(11)
As1-F12	172.3(8)	F12-As1-F14	87.0(5)	As1-F12	171(2)	F12-As1-F11	178.8(11)
As1-F13	172.7(9)	F13-As1-F11	89.3(4)	As1-F13	172(2)	F13-As1-F15	178.1(10)
As1-F14	172.5(9)	F14-As1-F16	176.2(5)	As1-F14	170(2)	F14-As1-F11	90.0(13)
As1-F15	168.6(8)	F15-As1-F13	173.4(5)	As1-F15	173(2)	F15-As1-F12	91.9(12)
As1-F16	171.6(8)	F16-As1-F12	95.4(4)	As1-F16	169(2)	F16-As1-F13	90.0(12)
As2-F21	173.7(7)	F21-As2-F24	90.7(4)	As2-F21	172(2)	F21-As2-F22	178.4(14)
As2-F22	172.1(8)	F22-As2-F21	177.5(5)	As2-F22	169(3)	F22-As2-F25	89.3(15)
As2-F23	172.7(9)	F23-As2-F24	82.6(5)	As2-F23	171(2)	F23-As2-F25	179.5(11)
As2-F24	175.4(8)	F24-As2-F22	88.4(4)	As2-F24	170(2)	F24-As2-F23	90.2(14)
As2-F25	167.4(10)	F25-As2-F23	174.2(5)	As2-F25	172(2)	F25-As2-F21	90.6(14)
As2-F26	166.5(10)	F26-As2-F24	176.2(5)	As2-F26	171.0(18)	F26-As2-F23	90.2(13)

Table 2. Distances F(H)⋯F [pm] in Ca(HF)(AsF₆)₂.

F1-F14	293.1	F1-F23	320.6	F1-F24	281.1	F1-F13	320.4
F1-F21	330.1	F1-F25'	337.2	F1-F11	299.2	F1-F15'	329.7
F1-F26	311.1	F1-F16'	337.3	F1-F16	298.3	F1-F26'	334.9

Calcium in the Ca(HF)₆(AsF₆)₂ is coordinated to eight fluorine atoms in the form of Archimedian antiprism. Six of fluorine atoms arise from HF molecules and two from two bridging AsF₆ units (Figure 2). Two calcium atoms are connected via AsF₆ units (*cis*) into the ring (dimer) with composition [Ca₂(As(1)F₆)₂]²⁺. Distances Ca-F(H) are in the range of 227 pm to 253 pm, while the Ca-F(As) distances are 250 pm and 259 pm. Charge of the calcium is compensated by free As(2)F₆ units.

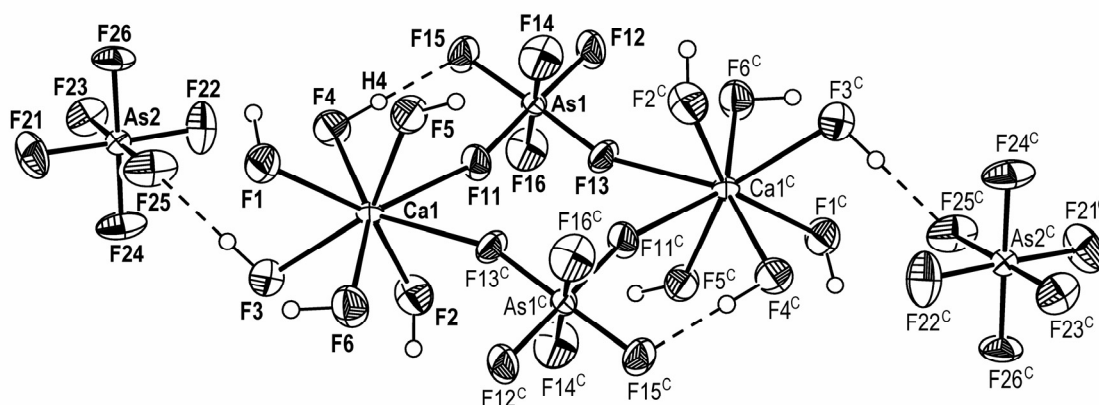


Figure 2. Ring [Ca₂(As(1)F₆)₂]²⁺ and two As(2)F₆ units in the structure of the Ca(HF)₆(AsF₆)₂
 Symmetry operations: ^B'-x, y + 1/2, -z + 1/2'; ^C'-x, -y, -z'; ^D'x, -y - 1/2, z - 1/2'

Symmetry of the space group (*P*2₁/*c*) defines the position of the dimers in the crystal packing, so layers of the rings ([Ca₂(As(1)F₆)₂]²⁺), perpendicular to the *b* axis, are formed (Figure 3). Those layers sandwich the layer of free AsF₆ units, which interconnect dimers with electrostatic interactions and hydrogen bonds.

Distances F(H)⋯F, which can be involved in the hydrogen bonds are given in Table 3. On the basis of surrounding F atoms and slight elongation of the As-F distances hydrogen atoms can be placed between F6 and F21, F3 and F25 and F4 and F15.

The other possible hydrogen bonds, which involve interactions of HF molecules with surrounding fluorine atoms, were tentative defined also on the similarity basis with known structures of the poly-hydrogen fluoride anions. In the crystal structure of

anhydrous hydrogen fluoride the angle $F'\cdots F\cdots F''$ is 120° ¹³ and an average angle of $H_2F_3^-$ anion in $KF \cdot 2HF$ is 135° .¹⁴ Angles $F'\cdots F\cdots F''$ in the proposed hydrogen bond interactions are in the range from 101.9 to 128.7° (smaller angles in the range from 62° to 93.5° were considered as less likely), so it is reasonable to expect that they form stable structural moieties.

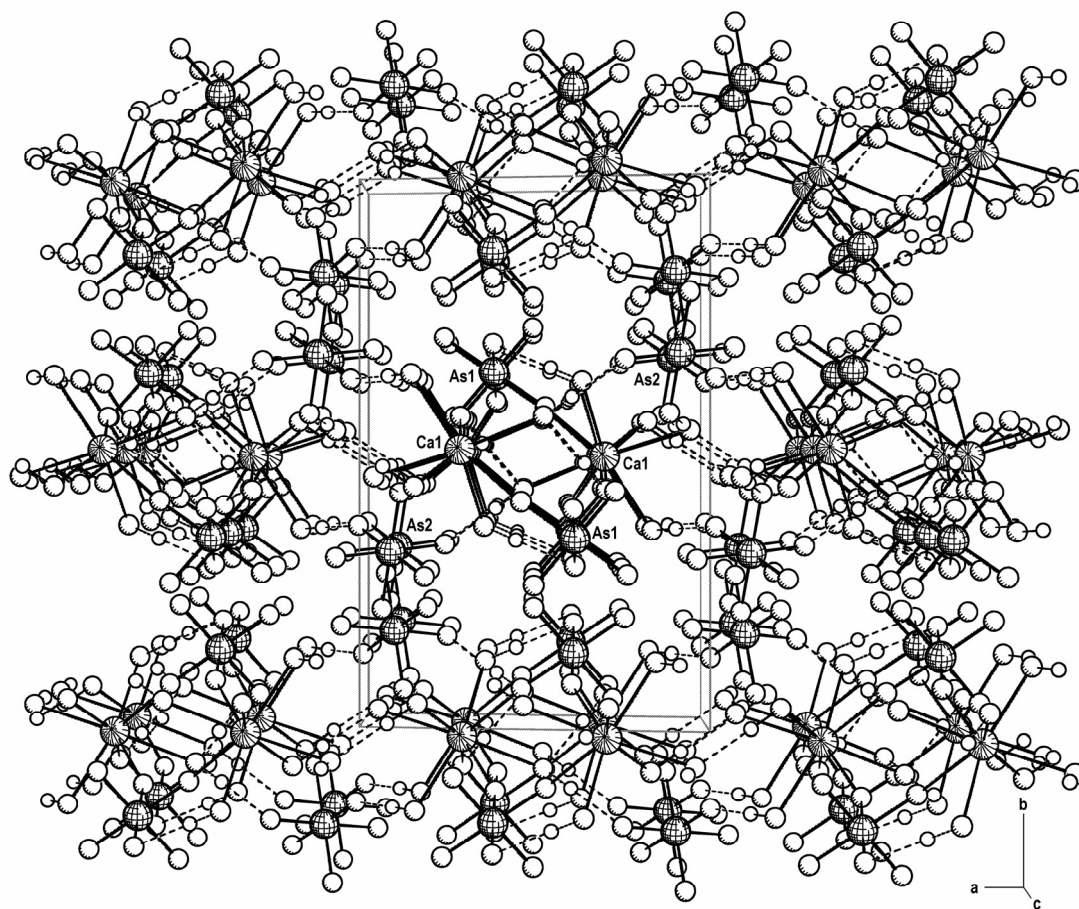


Figure 3. Packing in the structure of $Ca(HF)_6(AsF_6)_2$.

Table 3. Distances $F(H)\cdots F$ [pm] in $Ca(HF)_6(AsF_6)_2$.

F1-F5	301.1	F2-F23	323.9	F4-F5	303.7	F5-F26	296.4
F1-F25	300.1	F2-F26	327.1	F4-F22	280.1	F5-F14	323.3
F1-F21	305.3	F3-F2	298.7	F4-F16	283.6	F6-F21	283.0
F2-F3	298.7	F3-F23	278.4	F4-F15	298.4	F6-F24	289.0
F2-F21	307.9	F3-F21	286.0	F5-F1	301.0	F6-F12	303.0
F2-F14	321.7	F3-F25	300.0	F5-F4	303.7		

As already mentioned calcium and cadmium compounds with one HF coordinated to the metal are isostructural and 3D network crystal packing is found as in the several other cases: $\text{Ca}(\text{HF})_2(\text{SbF}_6)_2$, $\text{Mg}(\text{HF})_2(\text{SbF}_6)_2$,⁴ $\text{La}(\text{HF})_2(\text{AsF}_6)_3$.² In the crystal packing of $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$, formation of the dimer is interesting. This means, that first solvation sphere of Ca^{2+} cation is almost preserved in the crystal packing and that under certain condition of crystallisation, formation of $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ is favorite enough without additional cation-anion contacts in the solid. Nevertheless, those are required to raise free energy of crystal formation in the case of $\text{Ca}(\text{HF})(\text{AsF}_6)_2$, where calcium solvation sphere have to be almost completely removed.

Conclusions

Two calcium hexafluoroarsenates(V) with metal HF coordinated molecules were structurally characterised: $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ and $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$. The structural diversity of compounds with same cation, ligand and anion is illustrated.

Experimental

A nickel vacuum line and Teflon vacuum system were used as previously described.¹⁵ Non-volatile materials, which were very sensitive to traces of moisture, were handled in the dry argon atmosphere in a glove box with maximum content of 0.1 ppm of water vapour (MBraun, Garching, Germany).

CaF_2 was used as purchased (Merck, Suprapur), anhydrous HF (aHF) (Praxair, 99.9%) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use. AsF_5 was prepared by high-pressure fluorination of As_2O_3 , using a procedure previously described for PF_5 .¹⁶ $\text{Ca}(\text{AsF}_6)_2$ was prepared by the reaction of CaF_2 (1.004 g, 12.89 mmol) and excessive AsF_5 (6.011 g, 35.38 mmol) in aHF as previously described.⁹ AsF_5 and aHF were pumped off on the vacuum line and $\text{Ca}(\text{AsF}_6)_2$ was isolated (5.379 g, 12.87 mmol) and characterized by X ray powder diffraction data and chemical analysis: Calcd for $\text{Ca}(\text{AsF}_6)_2$: Ca 9.6, As 35.9, F 54.6, AsF_6^- 90.4. Found: Ca 9.6, As 35.7, F 53.6, AsF_6^- 90.0.

Crystals were prepared in the T shaped reaction vessel constructed from large (16 mm i.d.) and smaller (4 mm i.d.) FEP tubes joined at right angle and equipped with a Teflon valve and were grown from aHF solution by the procedure previously

described.¹² In both cases crystals were immersed in perfluorinated oil in the dry box and were selected under the microscope and transferred into the cold nitrogen stream at the diffractometer. Crystals of $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ were found in the same crystallization batch as crystals of $[\text{Ca}(\text{XeF}_2)_4](\text{AsF}_6)_2$, only several months later, after they were isolated and stored in the dry-box. Crystals with composition $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ were grown from the saturated aHF solution of $\text{Ca}(\text{AsF}_6)_2$ (aprox.: 0.080 g of $\text{Ca}(\text{AsF}_6)_2$ and aprox. 4 mL aHF). In this case crystals were isolated by a quick removal of aHF on the vacuum line and they were transferred in the diffractometer within the one hour.

Table 4. Crystal data and Structure refinement for $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ and $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$.

Parameter	$\text{Ca}(\text{HF})(\text{AsF}_6)_2$	$\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$
fw	437.93	537.97
temp (K)	200(2)	200(2)
space group	$P2_1/c$	$P2_1/c$
<i>a</i> (pm)	962.4(6)	1004.9(5)
<i>b</i> (pm)	926.4(5)	1498.7(7)
<i>c</i> (pm)	1059.2(7)	984.0(5)
β (°)	104.161(13)	109.56(11)
<i>V</i> (nm ³)	0.9157(10)	1.3965(12)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g/cm ³)	3.177	2.559
λ (pm)	71.069	71.069
μ (mm ⁻¹)	8.038	5.345
Data measured/unique	6648/2269	10435/3380
<i>R</i> _{int}	0.064	0.083
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0825; 0.1410	0.0750; 0.1840
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.1381; 0.1619	0.1222; 0.2029
Refined Parameters	149	190

Both single crystal data sets were collected using a Mercury CCD area detector coupled to a Rigaku AFC7 diffractometer with graphite monochromated Mo-K α radiation. The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied to both data sets. All calculations during the data processing were performed using the CrystalClear software suite.¹⁷ Structures were solved using direct methods¹⁸ and expanded using Fourier techniques. Full-matrix least squares refinement of *F*² against all reflections was performed using the SHELX 97

program.¹⁹ Hydrogen atoms could not be located from the difference Fourier map. The most probable hydrogen positions have been suggested on the basis of the acceptor atoms around HF molecules to which they (HF) could donate hydrogen bond. Those positions were not included in the refinement of the structural parameters. More details on the data collection and structure determinations are given in Table 4.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers: Ca(HF)(AsF₆)₂: CSD-414129, Ca(HF)₆(AsF₆)₂: CSD-414130.

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Povzetek

Kalcijeva heksafluoroarzenata(V): $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ in $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ sta bila karakterizirana z rentgensko strukturno analizo. $\text{Ca}(\text{HF})(\text{AsF}_6)_2$ kristalizira v monoklinskem kristalnem sistemu, prostorska skupina $P2_1/c$, $a = 962.4(6)$ pm, $b = 926.4(5)$ pm in $c = 1059.2(7)$ pm, $\beta = 104.161(13)^\circ$, $V = 0.9157(10)$ nm³ in $Z = 4$. $\text{Ca}(\text{HF})_6(\text{AsF}_6)_2$ kristalizira v monoklinskem kristalnem sistemu, prostorska skupina $P2_1/c$, $a = 1004.9(5)$ pm, $b = 1498.7(7)$ pm in $c = 984.0(5)$ pm, $\beta = 109.59(11)^\circ$, $V = 1.3965(12)$ nm³ in $Z = 4$.