Journal of Solid State Chemistry 181 (2008) 2318–2324

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis and structural investigation of the compounds containing HF_2^- anions: $Ca(HF_2)_2$, $Ba_4F_4(HF_2)(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$

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ARTICLE INFO

Article history:
Received 15 February 2008
Received in revised form
23 April 2008
Accepted 5 May 2008
Available online 16 May 2008

Keywords:
Poly-(hydrogen fluorides)
Hydrogen bonding
Crystal structure
Raman spectrum
$(MF)_n^+$ ribbon
Homoleptic HF environment

ABSTRACT

Three new compounds $Ca(HF_2)_2$, $Ba_4F_4(HF_2)(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$ were obtained in the system metal(II) fluoride and anhydrous HF (aHF) acidified with excessive PF_5. The obtained polymeric solids are slightly soluble in aHF and they crystallize out of their aHF solutions. $Ca(HF_2)_2$ was prepared by simply dissolving CaF_2 in a neutral aHF. It represents the second known compound with homoleptic HF environment of the central atom besides $Ba(H_3F_4)_2$. The compounds $Ba_4F_4(HF_2)(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$ represent two additional examples of the formation of a polymeric zigzag ladder or ribbon composed of metal cation and fluoride anion $(MF^+)_n$ besides $PbF(AsF_6)$, the first isolated compound with such zigzag ladder. The obtained new compounds were characterized by X-ray single crystal diffraction method and partly by Raman spectroscopy. $Ba_4F_4(HF_2)(PF_6)_3$ crystallizes in a triclinic space group $P\bar{1}$ with $a = 4.5870(2)$ Å, $b = 8.8327(3)$ Å, $c = 11.2489(3)$ Å, $\alpha = 67.758(9)^\circ$, $\beta = 84.722(12)$, $\gamma = 78.283(12)^\circ$, $V = 413.00(3)$ Å^3 at 200 K, $Z = 1$ and $R = 0.0588$. $Pb_2F_2(HF_2)(PF_6)$ at 200 K: space group $P\bar{1}$, $a = 4.5722(19)$ Å, $b = 4.763(2)$ Å, $c = 8.818(4)$ Å, $\alpha = 86.967(10)^\circ$, $\beta = 76.774(10)^\circ$, $\gamma = 83.230(12)^\circ$, $V = 185.55(14)$ Å^3, $Z = 1$ and $R = 0.0937$. $Pb_2F_2(HF_2)(PF_6)$ at 293 K: space group $P\bar{1}$, $a = 4.586(2)$ Å, $b = 4.781(3)$ Å, $c = 8.831(5)$ Å, $\alpha = 87.106(13)^\circ$, $\beta = 76.830(13)^\circ$, $\gamma = 83.531(11)^\circ$, $V = 187.27(18)$ Å^3, $Z = 1$ and $R = 0.072$. $Ca(HF_2)_2$ crystallizes in an orthorhombic *Fddd* space group with $a = 5.5709(6)$ Å, $b = 10.1111(9)$ Å, $c = 10.5945(10)$ Å, $V = 596.77(10)$ Å^3 at 200 K, $Z = 8$ and $R = 0.028$.

1. Introduction

It has been known for a long time that the metal fluorides form complex salts with HF [1,2]. These salts are important inorganic compounds that have found extensive use at the inorganic synthesis in the laboratory and in the engineering, e.g., in the production of elemental fluorine and hydrogen fluoride [3]. They contain HF_2^- bifluoride anions, which are characterized by the shortest hydrogen bond known to date. The investigation of the crystal structures of the bifluorides and other salts with H_nF_{n+1} anions is of particular importance in the elucidation of the nature of a strong hydrogen bonding. The structures of the acidic fluorides of the general formula MHF_2 (M = Li, Na, K, Rb, Cs) and $Rb_5F_4(HF_2)\cdot 2H_2O$ have been determined [4].

In the recent years, we have synthesized compounds with poly-(hydrogen fluoride) anions bonded as ligands to the metal cation: $M_2(H_2F_3)(HF_2)_2(AF_6)$ (M = Ca, A = As; M = Sr, A = As, P) [5]. In these polymeric compounds, $H_2F_3^-$ and HF_2^- anions bridge metal centers forming close packed three-dimensional networks. Various compounds with HF acting as a ligand bonded directly to the metal center of the general formula $[M^{n+}(HF)_x](AF_6)_n$ are also known. The first such compound was $[La(HF)_2](AsF_6)_3$ [6]. Recently, the following compounds were isolated and characterized: $[Pb(HF)](AsF_6)_2$ [7], $[Cd(HF)](AsF_6)_2$ [8], $[M(HF)_2](SbF_6)_2$ (M = Mg, Ca) [9], $[Ca(HF)_6](AsF_6)_2$, $[Ca(HF)](AsF_6)_2$ [10], $[Au(HF)_2](SbF_6)_2\cdot 2HF$ [11], $[(OsO_3F)(HF)_2](AsF_6)_2$ [12], $[Hg_2(OH_2)_2](SbF_6)_2\cdot 4HF$ [13] and $[Ir(CO)_6](SbF_6)_3\cdot 4HF$ [14].

2. Experimental

2.1. General experimental procedures

A nickel vacuum line and Teflon vacuum system were used as previously described [15]. Volatile materials (aHF, PF_5) were manipulated in an all-Teflon vacuum line equipped with Teflon valves. Non-volatile materials 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 vapor (MBraun, Garching, Germany). A FEP reaction vessel equipped with a Teflon valve and a Teflon-covered mixing bar was used for the syntheses. The

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doi:10.1016/j.jssc.2008.05.013

crystals were grown in a crystallization vessel made from a T-shaped FEP reaction vessel, constructed from one 16 mm i.d. and one 4 mm i.d. FEP tubes joint at a right angle and equipped with a Teflon valve.

2.2. *Reagents*

PbF_2, CaF_2 (Merck, Suprapur), BaF_2 (Alfa Aesar, 99.99%) and fluorine (Solvay, 99.98%) were used as purchased. PF_5 was prepared by fluorination of P_2O_5 powder under high-pressure as previously described [16]. Its purity was checked by IR spectroscopy. Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use. Caution: anhydrous hydrogen fluoride and PF_5 must be handled in a well-ventilated hood and protective clothing must be worn all the times! The experimentalist must become familiar with these reagents and the hazards associated with them. Fresh tubes of calcium gluconate gel should always be at hand for the fast treatment of skin exposed to these reagents. For treatment of HF injuries, see Ref. [17].

2.3. *Syntheses*

The compounds $Ca(HF_2)_2$, $Pb_2F_2(HF_2)(PF_6)$ and $Ba_4F_4(HF_2)(PF_6)_3$ were synthesized in the system MF_2–PF_5–aHF. The metal(II) fluoride (M = Ca, Ba, Pb) was weighed into the reaction vessel inside the dry box. The reaction vessel was evacuated and then cooled down to −196 °C. Anhydrous HF was added by sublimation. Then the reaction vessel was warmed up to room temperature and weighed. Suspension was cooled again in liquid nitrogen and excess of PF_5 was added. The reaction proceeded at room temperature. After the reaction aHF and excessive PF_5 were carefully removed at temperature around −30 °C. The obtained products in the case of Ba and Pb are loosing PF_5 in a dynamic vacuum at room temperature. Details of the syntheses are CaF_2 (0.166 g, 2.13 mmol), PF_5 (0.321 g, 2.55 mmol), product (0.385 g, 3.2 mmol); PbF_2 (0.448 g, 1.83 mmol), PF_5 (0.243 g, 1.93 mmol), product (0.636 g, 1.00 mmol); BaF_2 (0.259 g, 1.47 mmol), PF_5 (0.107 g, 0.848 mmol), product (0.557 g, 0.51 mmol).

$Ca(HF_2)_2$ could also be prepared by direct reaction between CaF_2 (0.0943 g, 1.21 mmol) and HF (3.5 mL), product (0.150 g, 1.27 mmol). $Ca(HF_2)_2$ was also found as by-product of the partial decomposition of $Ca(RuF_6)_2 \cdot nXeF_2$ in aHF solution.

2.4. *Preparation of single crystals*

The 100–200 mg of the compounds $Ca(HF_2)_2$, $Pb_2F_2(HF_2)(PF_6)$ and $Ba_4F_4(HF_2)(PF_6)_3$ obtained during the syntheses (see Section 2.3) were transferred in the dry box into the FEP crystallization vessel. Anhydrous HF was added and a saturated solution was prepared. This solution was decanted into a narrower part of the reaction vessel, which was left at room temperature while the wider part was cooled with tap water. In this way, a small temperature gradient was achieved. The crystallization proceeded for several days. Crystals were isolated by pumping off aHF on the vacuum line at room temperature. Inside the dry box, the crystals were put in a perfluorinated oil (ABCR, FO5960), selected under the microscope outside of the dry box and transferred into the cold nitrogen stream at the X-ray diffractometer. One of $Pb_2F_2(HF_2)(PF_6)$ crystals was placed in the capillary and its structure determination has been performed also at room temperature.

Crystals of $Ba_4F_4(HF_2)(PF_6)_3$ were grown also directly from the reaction mixture. BaF_2 (0.088 g, 0.502 mmol) was added into the crystallization vessel which was cooled with liquid nitrogen and

Table 2
Selected bond distances (Å) in $Ba_4F_4(HF_2)(PF_6)_3$

Ba1–F3	2.276(11)	Ba2–F2	2.325(12)
Ba1–F2^{i}	2.450(12)	Ba2–F3	2.410(12)
Ba1–F1	2.475(12)	Ba2–F1^{iv}	2.516(12)
Ba1–F2	2.478(12)	Ba2–F3^{v}	2.525(12)
Ba1–F11	2.775(11)	Ba2–F15	2.587(11)
Ba1–F22	2.984(14)	Ba2–F23^{vi}	2.878(13)
Ba1–F16	3.050(13)	Ba2–F14^{vii}	2.914(13)
Ba1–F13^{ii}	3.050(12)	Ba2–F12	2.927(12)
Ba1–F21	3.160(14)	Ba2–F22^{iv}	3.125(15)
Ba1–F13^{iii}	3.163(12)	Ba2–F21^{viii}	3.221(14)
Ba1–F16^{ii}	3.237(13)	Ba2–F23^{iv}	3.245(13)
Ba1–F14^{ii}	3.364(18)	Ba2–F11^{v}	3.502(23)
P1–F11^{v}	1.594(12)	P2–F21^{x}	1.587(13)
P1–F12^{ix}	1.596(13)	P2–F21^{i}	1.587(13)
P1–F13	1.600(13)	P2–F22^{xi}	1.595(14)
P1–F14	1.615(13)	P2–F22	1.595(14)
P1–F15	1.622(13)	P2–F23	1.603(13)
P1–F16	1.634(13)	P2–F23^{xi}	1.603(13)

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

Table 1
Crystal data and structure refinement of $Ba_4F_4(HF_2)(PF_6)_3$, $Pb_2F_2(HF_2)(PF_6)$ and $Ca(HF_2)_2$

Formula	$Ba_4F_{24}HP_3$	$Pb_2F_{10}HP$	$Pb_2F_{10}HP$	CaF_4H_2
Fw	1099.24	636.362	*636.362*	118.088
T (K)	200	200	*293*	200
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Fddd*
a (Å)	4.5870(2)	4.5722(19)	*4.586(2)*	5.5709(6)
b (Å)	8.8327(3)	4.763(2)	*4.781(3)*	10.1111(9)
c (Å)	11.2489(3)	8.818(4)	*8.831(5)*	10.5945(10)
α (deg)	67.758(9)	86.967(10)	*87.106(13)*	90
β (deg)	84.722(12)	76.774(10)	*76.830(13)*	90
γ (deg)	78.283(12)	83.230(12)	*83.531(11)*	90
V (Å^3)	413.00(3)	185.55(14)	*187.27(18)*	596.77(10)
Z	1	1	*1*	8
$D_{calculated}$ (g/cm^3)	4.42	5.695	*5.643*	2.629
λ (Å)	0.71069	0.71069	*0.71069*	0.71069
μ (mm^{-1})	9.943	45.661	*45.242*	2.007
$R1^{a}$; $wR2$	0.0588; 0.1761	0.0937; 0.2466	*0.072*; *0.192*	0.028; 0.0679
GOF	1.145	1.073	*1.08*	1.205

[a] $R1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR2 = [w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$, $GOF = [\sum w(F_o^2 - F_c^2)^2)/N_o - N_p)]^{1/2}$, where N_o is no. of reflns and N_p is no. of refined parameters.

Table 3
Selected bond distances (Å) in $Pb_2F_2(HF_2)(PF_6)$

Pb1–F2	*2.307(15)* *2.312(12)*	Pb1–F12^{iii}	*3.22(3)* *3.26(3)*
Pb1–F2^{i}	*2.460(17)* *2.459(14)*	Pb1–F11^{iii}	*3.30(2)* *3.30(2)*
Pb1–F2^{ii}	*2.473(16)* *2.469(15)*	Pb1–F13^{iii}	*3.37(3)* *3.41(3)*
Pb1–F1	*2.48(2)* *2.474(16)*	P1–F13^{iv}	*1.566(16)* *1.619(13)*
Pb1–F1^{iii}	*2.55(2)* *2.582(16)*	P1–F13	*1.566(16)* *1.619(13)*
Pb1–F13^{vi}	*2.92(3)* *2.85(3)*	P1–F12	*1.587(18)* *1.602(17)*
Pb1–F11^{vii}	*2.99(3)* *3.01(3)*	P1–F12^{iv}	*1.587(18)* *1.602(17)*
Pb1–F12	*2.99(3)* *2.97(3)*	P1–F11^{iv}	*1.597(18)* *1.579(17)*
		P1–F11	*1.597(18)* *1.579(17)*

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y, -z+1$; (iii) $x, y+1, z$; (iv) $-x, -y-1, -z$; (v) $x, y-1, z$; (vi) $1+x, 1+y, z$; (vii) $1-x, -1-y, -z$.
Regular font: data at 200 K; italic font: data at room temperature.

aHF was added by sublimation. Then the crystallization vessel was warmed up to room temperature and weighed. Solution was cooled again in liquid nitrogen and excess of PF_5 (0.332 g, 2.63 mmol) was added. The saturated solution was decanted into the narrower part of the reaction vessel, which was left at room temperature while the wider part was cooled with tap water. Crystals were isolated by pumping off aHF and PF_5 at −35 °C.

2.5. *Crystal structure determination*

Data were collected on Rigaku AFC7S diffractometer equipped by Mercury CCD area detector using graphite monochromated Mo$K\alpha$ radiation. The treatment of all data was performed using CrystalClear program package [18]. The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was applied to all datasets. All structures were solved by direct methods using SIR-92 [19] program implemented in program package TeXsan [20] and refined with SHELXL-97 [21] software (program packages TeXsan and WinGX [22]). In the case of $Pb_2F_2(HF_2)(PF_6)$ compound, majority of checked crystals

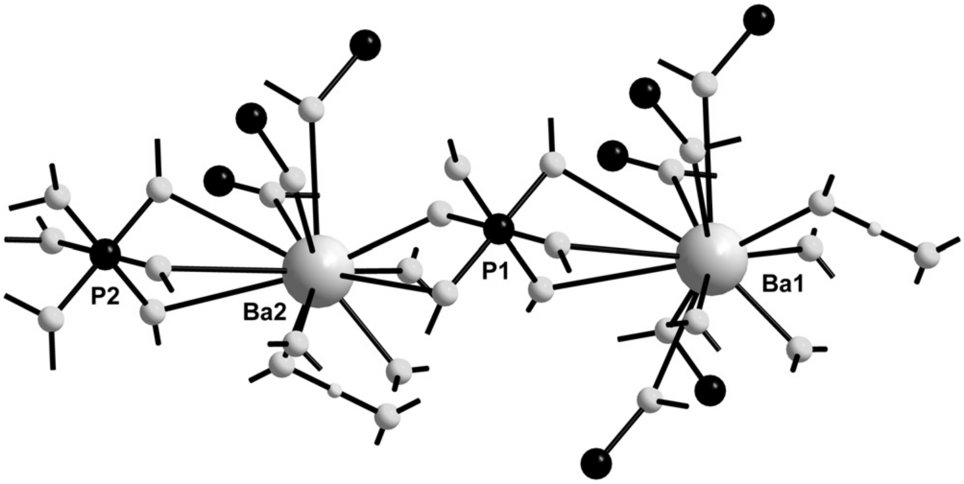

Fig. 1. Coordination of barium atoms and bridging function of PF_6^- anions in $Ba_4F_4(HF_2)(PF_6)_3$.

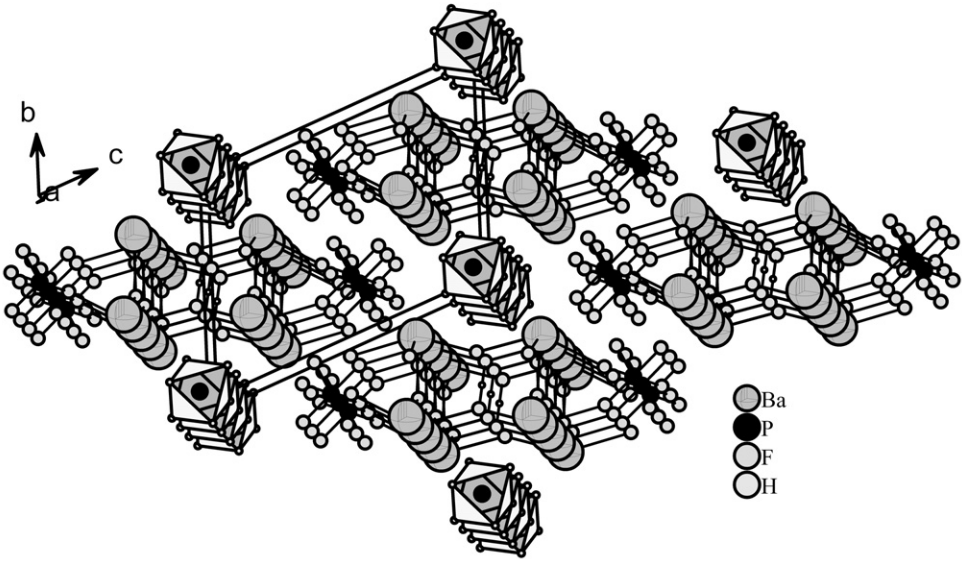

Fig. 2. Packing in the structure of $Ba_4F_4(HF_2)(PF_6)_3$.

demonstrate a reproducible affinity to twinning with the rotating of sub-domains on 180° around *a*-axis. The data were treated using Twinsolve [23] software, and hklf5 reflections file was generated. The final refinement has led to 0.23:0.77 ratio of twin domains. In this compound, as well as in the compound $Ba_4F_4(HF_2)(PF_6)_3$, the positions of hydrogen atoms were found on the basis of the geometrical reasons. In the case of the compound $Ca(HF_2)_2$, the positions of the hydrogen atoms were found on a difference Fourier map. The figures were prepared using DIAMOND 3.1 software [24]. The crystal data and the details of structure refinement for these compounds are given in Table 1, selected bond distances for compounds $Pb_2F_2(HF_2)(PF_6)$ and $Ba_4F_4(HF_2)(PF_6)_3$ are placed in Tables 2 and 3.

2.6. Raman spectroscopy

Raman spectra of the powdered samples in the 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. Geometry for all Raman experiments was 180° back scattering with a laser power of 25 mW.

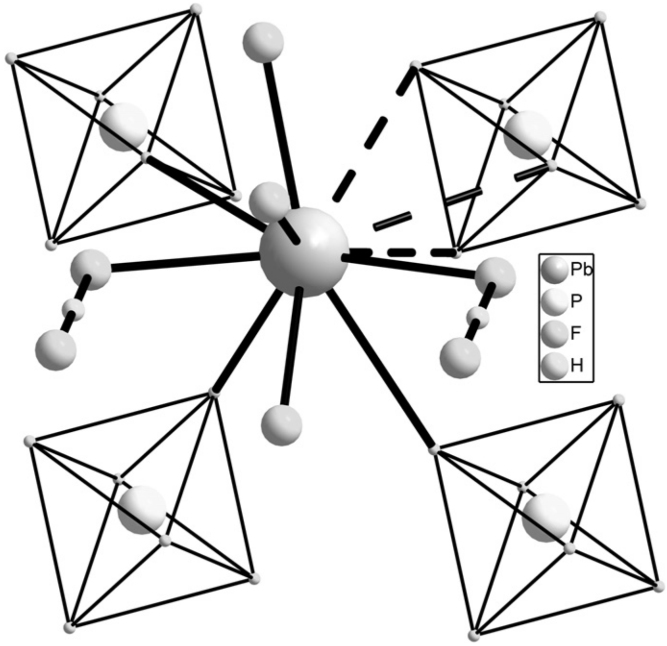

Fig. 3. Coordination sphere of the lead atom in $Pb_2F_2(HF_2)(PF_6)$.

3. Results and discussion

3.1. Syntheses

In the case of the compounds $Ba_4F_4(HF_2)(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$, the corresponding metal(II) fluoride reacted with PF_5 and HF in aHF solution yielding first $M(PF_6)_2$ or $M(PF_6)_2(HF)_n$ derivatives, which are stable in the presence of excessive PF_5. After the excess of PF_5 was pumped away, these compounds start to decompose in now neutral aHF. PF_6^- anions (RuF_6^- in the case of Ca derivative) could be a source of F^- anions in the solution. Because of the competition between metal centers and hydrogen atoms for bonding with fluoride anions, the metal coordination sphere containing F^-, HF_2^- and, possibly, HF and PF_6^- moieties forms. The crystallization process completely removed the solvent from the metal environment with a formation of the title compounds. The equations for such a process could be written as follows:

$$4Ba(PF_6)_2 + HF \rightarrow Ba_4F_4(HF_2)(PF_6)_3 + 5PF_5\uparrow$$
$$2Pb(PF_6)_2 + HF \rightarrow Pb_2F_2(HF_2)(PF_6) + 3PF_5\uparrow.$$

The crystals of the compound $Ca(HF_2)_2$ were found in three different reaction systems: CaF_2–HF, CaF_2–PF_5–HF and CaF_2–RuF_5–XeF_2–HF. The main reason for obtaining the same compound in all three systems is rather low solubility of $Ca(HF_2)_2$ and its relatively high stability.

3.2. Crystal structures

3.2.1. Description of crystal structure of $Ba_4F_4(HF_2)(PF_6)_3$

The crystal structure of the compound $Ba_4F_4(HF_2)(PF_6)_3$ contains two crystallographically independent barium atoms. The coordination sphere of Ba1 atom includes 12 fluorine atoms: one F center belongs to HF_2^- moiety, three other are F^- anions, five fluorine atoms are from five mono-dentate PF_6^- anions and the last three F atoms are from tri-dentate PF_6^- unit. Ba1–F distances vary from 2.276(11) to 2.478(12) Å, Ba1–F(HF_2^-) bond length is 2.475(12) Å. The Ba1–F(PF_6^-) distances appear to be much longer (2.775(11) to 3.36(2) Å). The environment of Ba2 also consists of

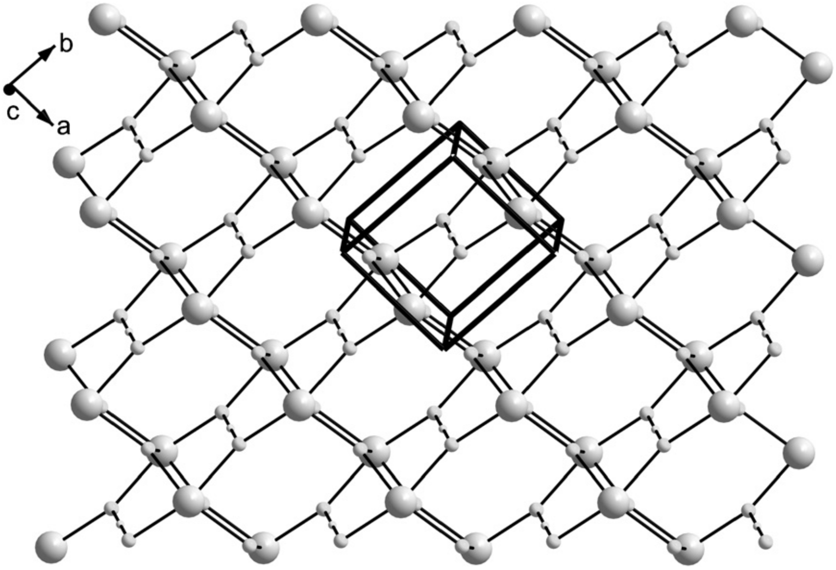

Fig. 4. Double layers in $Pb_2F_2(HF_2)(PF_6)$.

12 F centers: one from HF_2^- unit, three F^- anions, three fluorine atoms from three mono-dentate PF_6^- anions, two from bi-dentate PF_6^- moiety and three more from tri-dentate PF_6^- unit (Fig. 1) with the bond distances of 2.325(12)–2.525(12), 2.516(12) and 2.587(11)–3.50(2) Å for the bonds Ba2–F, Ba2–F(HF_2^-) and Ba2–F(PF_6^-), respectively (Table 2). The last value coincides practically with the sum of Van der Waals radii of Ba and F atoms (3.47 Å). Ba cations and F^- anions form infinite ribbons. Similar infinite metal-fluoride fragments were found earlier in PbF(AsF_6) [7]. These ribbons, in turn, are interconnected by HF_2^- anions into infinite slabs oriented along *a*-axis. Each HF_2^- unit is linked to four barium atoms located roughly on the common plane. The HF_2^- anion demonstrates symmetrical geometry with hydrogen atom located on inversion center and F···F distance of 2.28(2) Å. The crystallografically independent PF_6^- anions differ in the coordination behavior. In P(1)F_6 anion, connected to seven Ba cations, four F centers demonstrate μ_3-bridging functions, and two other are μ_2-bridges. In the case of P2 anion, all fluorine atoms act as μ_3-bridges, and the P(2)F_6 anion is bound to eight metal centers. Because of the difference in the shortest Ba–F(PF_6^-) bond lengths, P(1)F_6^- anion will be described as strongly bonded (Ba–F_{min} 2.59(1) Å, shown as balls-and-sticks), and P(2)F_6^- moiety as weakly bonded (Ba–F_{min} 2.88(2) Å, drawn in polyhedra style) to the metal centers. Mentioned above slabs are "capped" by strongly bonded PF_6^- anions, and in between are located weakly bonded PF_6^- units (Fig. 2).

3.2.2. *Description of crystal structure of $Pb_2F_2(HF_2)(PF_6)$*

In the structure of $Pb_2F_2(HF_2)(PF_6)$, lead atom possess coordination number 8+3: two F atoms belong to two HF_2^- moieties with the Pb–F distances of 2.48(2) and 2.55(2) Å, three other are F^- anions (Pb–F 2.307(15)–2.473(16) Å), three fluorine atoms are from three mono-dentate PF_6^- anions (Pb–F 2.92(2)–2.99(2) Å) and three more from tri-dentate PF_6^- unit (Pb–F 3.27(3)–3.36(3) Å) (Fig. 3; Table 3). Metal and fluorine atoms also form infinite double ribbons. Contrary to previously discussed structure, HF_2 moieties link such ribbons into infinite double layers (Fig. 4). Weakly bonded PF_6^- anions are located between these puckered layers (Fig. 5). Each F center act as μ_2-bridge, and PF_6^- unit is connected to six lead atoms. Similarly to $Ba_4F_4(PF_6)_3HF_2$ structure symmetrical HF_2 unit with F···F distance of 2.32(4) Å is bound to four metal centers located roughly on the common plane.

3.2.3. *Description of crystal structure of $Ca(HF_2)_2$*

$Ca(HF_2)_2$ compound represents a unique case of homoleptic HF environment of Ca atom. Each cation is surrounded by eight F atoms from eight HF_2^- moieties (Fig. 6). Because of the location of the metal atom at 8a Wyckoff position with 222 symmetry, Ca–F distances form two sets of 4 × 2.3492(11) and 4 × 2.3678(11) Å.

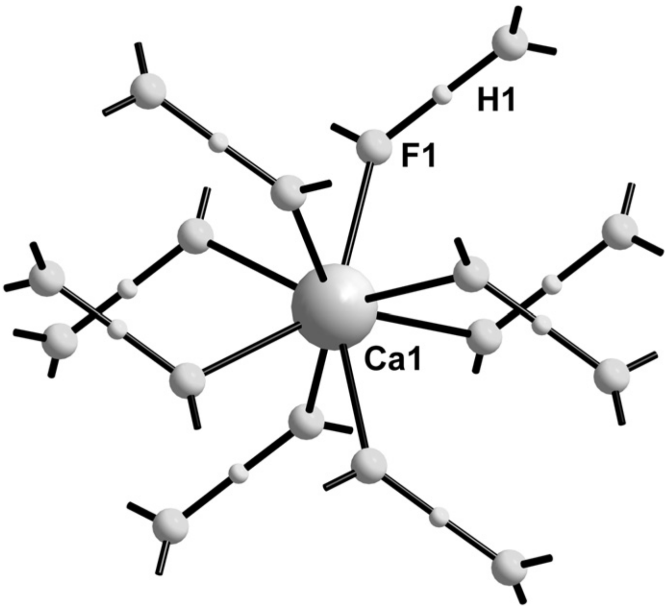

Fig. 6. Homoleptic environment of Ca atoms and bridging role of HF_2 anions in $Ca(HF_2)_2$.

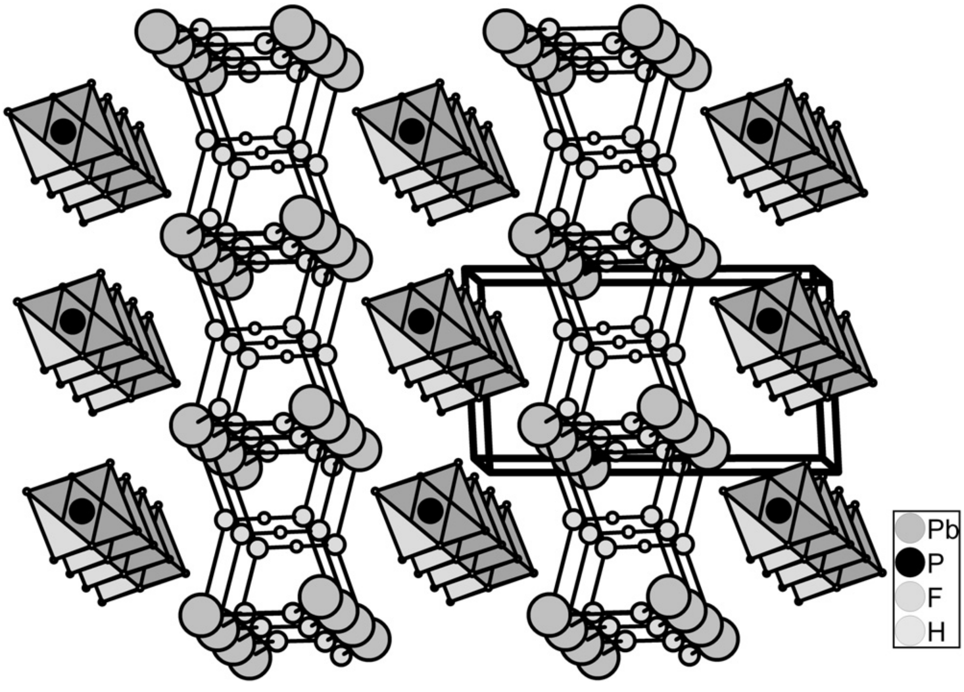

Fig. 5. Packing diagram of $Pb_2F_2(HF_2)(PF_6)$.

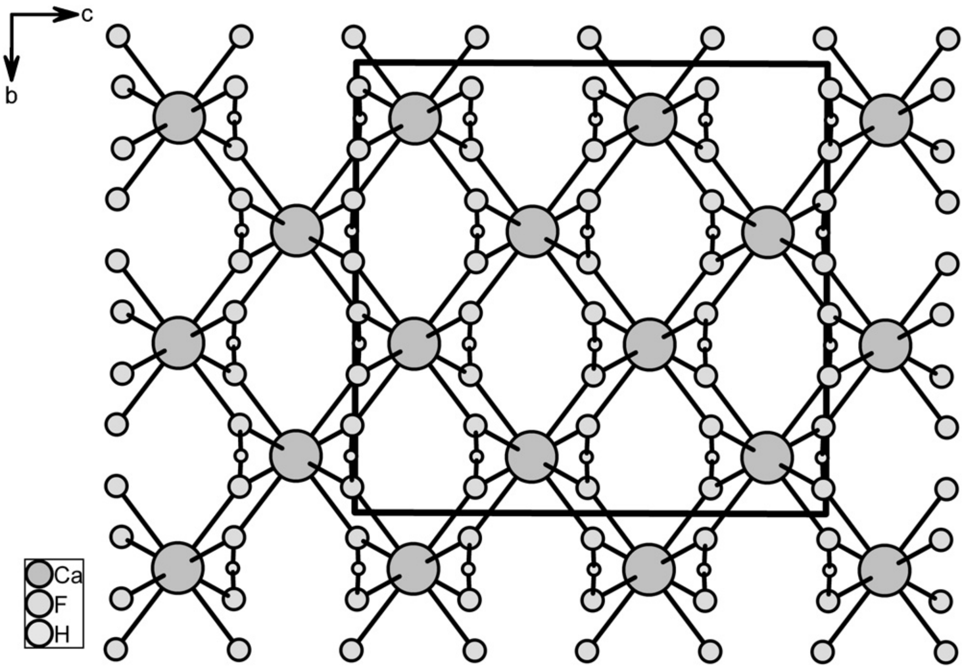

Fig. 7. 3D network in $Ca(HF_2)_2$.

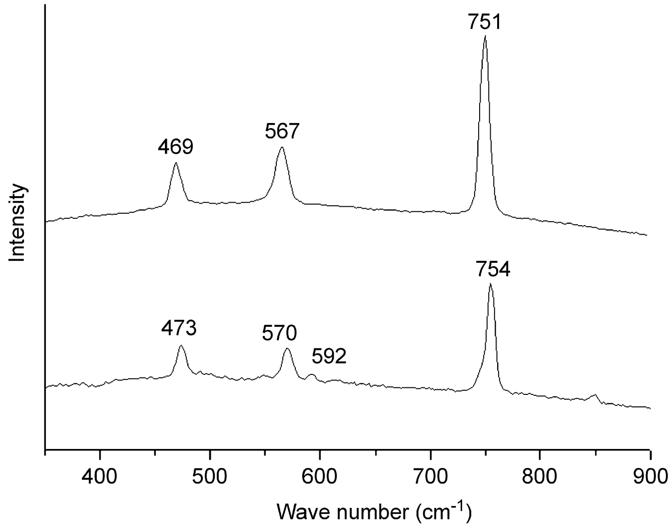

Fig. 8. Raman spectra of $Pb_2F_2(HF_2)(PF_6)$ (top) and $Ba_4F_4(HF_2)(PF_6)_3$ (bottom).

In turn, each anion is bonded to four metal centers. Fluorine atoms of the HF_2^- anion are related through a crystallographic two-fold axis and the hydrogen atom was refined on the special position on axes 2. The F$\cdots$F distance of 2.283(2) Å) in HF_2^- moiety is practically the same as in $Ba_4F_4 \cdot HF_2(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$ is very similar to that in KHF_2 (2.277(6) Å), and is somewhat longer than that in the crystal structure of $[N(CH_3)_4][HF_2]$ (2.213(4) Å) [25]. Contrary to earlier discussed structures of $Ba_4F_4 \cdot HF_2(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$ compounds, metal atoms bonded to one HF_2^- unit, are mutually oriented in tetrahedral manner, resulting in a formation of complicated 3D structure (Fig. 7).

3.3. *Raman spectra*

In the case of O_h symmetry of the PF_6^- anion ν_1 is found at $756\,cm^{-1}$, ν_2 at 570 and $580\,cm^{-1}$ and ν_5 at 468, 475 and $480\,cm^{-1}$ [26]. In the Raman spectrum of $Ba_4F_4(HF_2)(PF_6)_3$, the band at $754\,cm^{-1}$ can be confidentially assigned to ν_1 of PF_6^- while the vibrations at 570 and $473\,cm^{-1}$ could be assigned to ν_2 and ν_5 of PF_6^- anion, respectively. The weak band at $592\,cm^{-1}$ could be assigned to $\nu_1(\Sigma_g^+)\nu_{sym}$) of the anion HF_2^- (Fig. 8). In $[N(CH_3)_4]HF_2$ the peak at $576\,cm^{-1}$ [25], in $NaHF_2$ the peak at $630\,cm^{-1}$ [27] and in $Sr_2(H_2F_3)(HF_2)_2(AsF_6)$ the peak at $620\,cm^{-1}$ [5] were assigned to the symmetric HF_2^- anion.

In the Raman spectrum of $Pb_2F_2(HF_2)(PF_6)$, the peaks at 751, 567 and $469\,cm^{-1}$ could be assigned to ν_1, ν_2 and ν_5 of PF_6^- anion, respectively. The peak which could be assigned to ν_1 of the anion HF_2^- is either too weak to be seen or the compound decomposed in the laser beam.

In the case of $Ca(HF_2)_2$, we were not able to obtain a reasonable Raman spectrum.

4. Supplementary material

Further details of the crystal structure investigation(s) can 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 CSD-419141 for $Pb_2F_2(HF_2)(PF_6)$ at 293 K, CSD-419142 for $Pb_2F_2(HF_2)(PF_6)$ at 200 K, CSD-419143 for $Ba_4F_4(HF_2)(PF_6)_3$, CSD-419144 for $Ca(HF_2)_2$.

Acknowledgment

The authors gratefully acknowledge to the Slovenian Research Agency (ARRS) for the financial support of the Research Program P1-0045 (Inorganic Chemistry and Technology).

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