



# HF molecules and poly(hydrogen fluoride) anions as ligands to metal centers

Melita Tramšek\*, Evgeny Goreschnik, Matic Lozinšek, Boris Žemva

Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

## ARTICLE INFO

### Article history:

Received 14 May 2009

Received in revised form 9 June 2009

Accepted 9 June 2009

Available online 21 June 2009

### Keywords:

HF

Poly(hydrogen fluoride) anions

Crystal structures

Coordination compounds

Review

## ABSTRACT

The paper is dealing with the two sets of the coordination compounds:

- the coordination compounds in which anhydrous HF is acting as a ligand to the metal ions
- the compounds in which poly(hydrogen–fluoride) anions of the type  $H_nF_{n+1}^-$  ( $n = 1, 2, 3$ ) are coordinated to the metal centers and connecting them in the 3D structures.

The main purpose of this work is the review of the above mentioned compounds which were recently isolated in our laboratory. The coordination of the metal centers and their connection in the three-dimensional network are illustrated with their crystal structures. A very brief review of the achievements of some other groups is also mentioned where it is appropriate.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Anhydrous hydrogen fluoride<sup>1</sup> (HF) is very versatile solvent in the inorganic fluorine chemistry and it is frequently used in the preparation of various inorganic compounds. The preparation of the coordination compounds of the type  $M^n(AF_6)_n$ , where M is a metal in the oxidation state  $n$  and A is P, As, Sb, Bi, Nb, Ta, Ru etc., is performed in HF as a solvent. In these compounds the metal center is practically “naked” because of the bulky  $AF_6^-$  anions therefore also the molecules of the solvent could act as ligands to the metal center. It is surprising that the first such compound in the solid state was isolated only a decade ago. [1] Since then several examples of this type of the compounds were prepared and properly characterized. The compounds published before 2006 have been described in the review paper. [2] Only the compounds isolated and characterized after 2006 are the subject of this review.

HF molecules in a basic medium, where  $F^-$  anions are present, yield poly(hydrogen–fluoride) anions of the type  $(H_nF_{n+1})^-$ . The compounds in which metal centers are coordinated with anions like  $HF_2^-$ ,  $H_2F_3^-$ ,  $H_3F_4^-$  will be also described here. In this paper the review of such compounds, mostly isolated and characterized in our laboratory, will be given besides some representative examples from the other groups.

We are well aware that other interesting fields of fluorine chemistry are dealing with compounds containing poly(hydrogen–

fluoride) anions. One of these fields is the chemistry of “room-temperature ionic liquid (RTIL)”. [3]

## 2. Coordination compounds with HF molecule(s) as ligand(s) to the metal center

### 2.1. $[Sr(HF)_3](TaF_6)_2$

First only the structures of the coordination compounds of the type  $[M(HF)_x](AF_6)_2$ , (M is a metal in the oxidation state +2 and A = As, Sb) were reported. Recently we prepared and structurally characterized the coordination compounds with A = Ta, Ru. The compound  $[Sr(HF)_3](TaF_6)_2$  was prepared by direct fluorination of Ta metal, first with HF to  $TaF_3$  and then with elemental fluorine in anhydrous HF and in the presence of the corresponding amount of  $SrF_2$  (Ta:SrF<sub>2</sub> = 2:1). [4] The coordination sphere of  $Sr^{2+}$  cation consists of nine fluorine atoms and adopts the shape of tri-capped trigonal prism. Six fluorine atoms belong to  $TaF_6^-$  anions and three fluorine atoms are from HF molecules. All three HF molecules are located on the same triangular face.  $TaF_6^-$  are bridging, forming infinitive double layers which are further interconnected by  $F-H \cdots F(Ta)$  hydrogen bonds (2.813 Å) (Fig. 1).

### 2.2. $[Ba(HF)](RuF_6)_2$

The compound  $Ba(RuF_6)_2$  was prepared in the same way as described in the case of  $Sr(TaF_6)_2$ . The compound  $[Ba(HF)](RuF_6)_2$  crystallizes from HF solution of  $Ba(RuF_6)_2$ . Ba atom in the compound  $[Ba(HF)](RuF_6)_2$  is coordinated to 10 fluorine atoms (Fig. 2). Eight fluorine atoms are from  $RuF_6^-$  anions and one from HF molecule. One of the  $RuF_6^-$  anion is coordinated to metal center

\* Corresponding author. Tel.: +386 1 477 33 01; fax: +386 1 477 31 55.

E-mail addresses: [melita.tramsek@ijs.si](mailto:melita.tramsek@ijs.si) (M. Tramšek), [evgeny.goreschnik@ijs.si](mailto:evgeny.goreschnik@ijs.si) (E. Goreschnik), [matic.lozinsek@ijs.si](mailto:matic.lozinsek@ijs.si) (M. Lozinšek), [boris.zemva@ijs.si](mailto:boris.zemva@ijs.si) (B. Žemva).

<sup>1</sup> HF throughout of this paper stands for anhydrous HF.

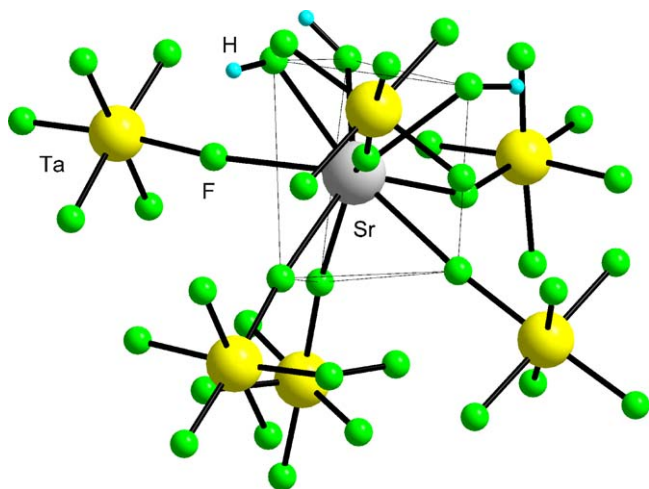


Fig. 1. Coordination sphere of the Sr metal in the compound  $[\text{Sr}(\text{HF})_3](\text{TaF}_6)_2$ .

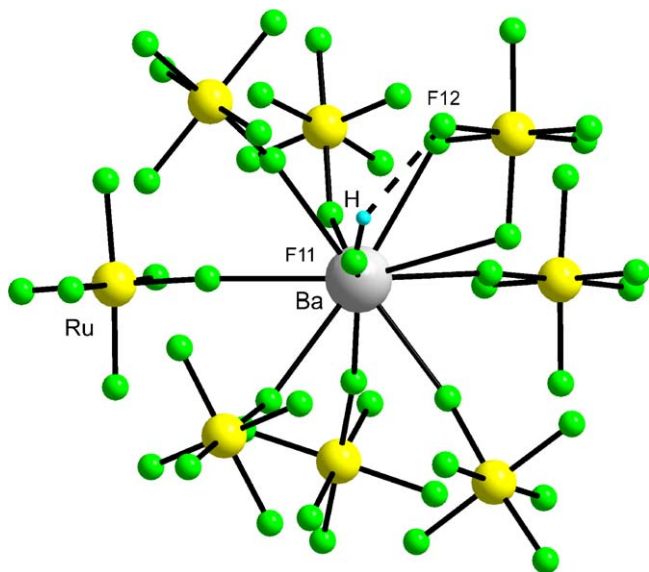


Fig. 2. Coordination sphere of Ba atom in  $[\text{Ba}(\text{HF})](\text{RuF}_6)_2$ . The hydrogen bond F11–F12 distance is 2.889 Å.

with two fluorine atoms (chelate). Ba atoms are connected *via*  $\text{RuF}_6$  moieties into three-dimensional network. The hydrogen bond distance  $\text{F}-\text{H}\cdots\text{F}(\text{Ru})$  to the  $\text{RuF}_6$  unit coordinated to the same Ba atom is 2.889 Å.

### 2.3. $[\text{Sr}(\text{HF})](\text{BF}_4)_2$

The coordination compounds of the type  $[\text{M}^n(\text{HF})_x](\text{BF}_4)_n$  are less common than those with  $\text{AsF}_6^-$  or  $\text{SbF}_6^-$  anions. For HF molecule it is more difficult to compete in the coordination to metal centre with  $\text{BF}_4^-$  than with  $\text{AF}_6^-$ . The main reason for such behavior is that the negative charge on F ligands in  $\text{BF}_4^-$  is higher as in  $\text{AF}_6^-$  anions. The structure of  $[\text{Sr}(\text{HF})](\text{BF}_4)_2$  was determined by X-ray single crystal technique.[4] Nine fluorine atoms form tri-capped trigonal prism around Sr atom (Fig. 3). Interesting feature of this structure is that fluorine atom from HF molecule acts as a bridge between two Sr atoms. Additionally, H atom is also involved in a formation of strong  $\text{F}-\text{H}\cdots\text{F}(\text{B})$  (2.47 Å) hydrogen bond. This value is close to those in crystalline HF (2.49 Å). [5] Two crystallographically different  $\text{BF}_4^-$  anions have also different

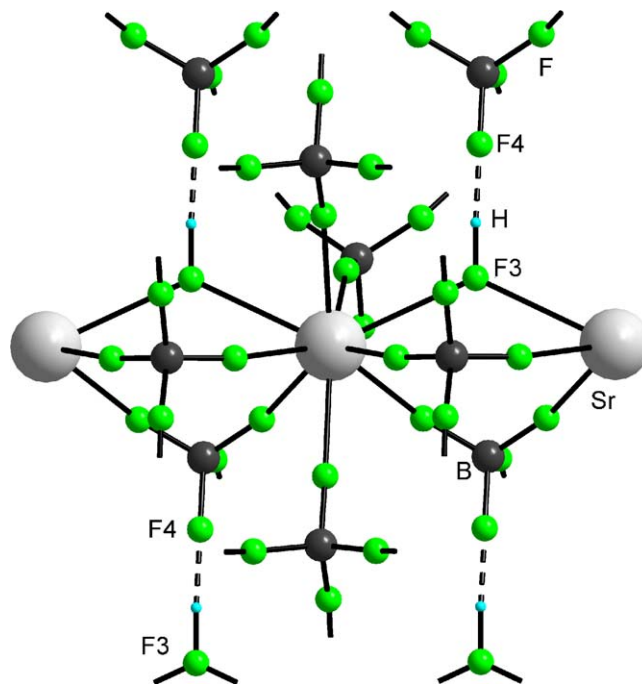


Fig. 3. Coordination sphere of Sr atom in  $[\text{Sr}(\text{HF})](\text{BF}_4)_2$  and connection between Sr atoms *via* HF molecules. The hydrogen bond F3–F4 distance is 2.47 Å.

surroundings. One of  $\text{BF}_4^-$  units is connected to four Sr atoms while the other connects three Sr atoms. The fourth fluorine atom is involved in the hydrogen bond. Because of the bridging function of  $\text{BF}_4^-$  anions and HF molecules complex three-dimensional structure appears.

### 2.4. $[\text{LnF}(\text{HF})](\text{BF}_4)_2$

Rare earth trifluorides react with  $\text{BF}_3$  in HF at room temperature yielding the products with the composition  $[\text{LnF}(\text{HF})](\text{BF}_4)_2$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}$ ). Single crystals of  $[\text{LnF}(\text{HF})](\text{BF}_4)_2$  ( $\text{Ln} = \text{Pr}, \text{Nd}$ ) and  $\text{La}(\text{BF}_4)_3$  were prepared so far. [6] The structures of  $[\text{LnF}(\text{HF})](\text{BF}_4)_2$  consist from zig-zag Ln–F chains connected *via*  $\text{BF}_4^-$  anions and HF molecules into the three-dimensional network. Similar to the  $[\text{Sr}(\text{HF})](\text{BF}_4)_2$  also in this case the strong hydrogen bond between HF molecule and fluorine atom from  $\text{BF}_4^-$  anion was found ( $\text{F}-\text{H}\cdots\text{F}(\text{B})$ : 2.475 Å in the case of Pr; 2.483 Å in the case of Nd).

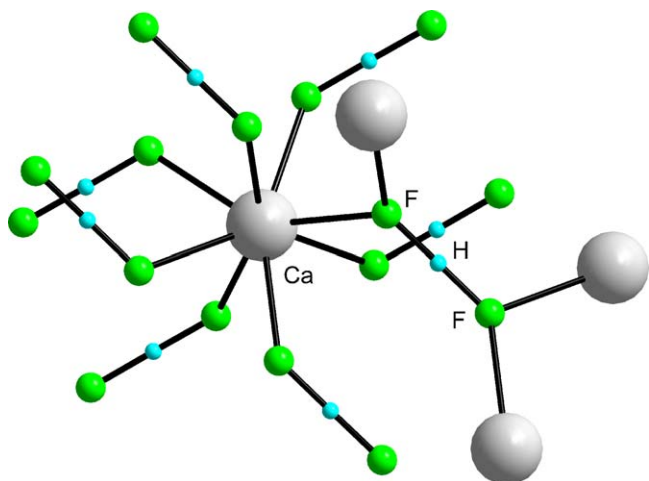
## 3. Coordination compounds with poly(hydrogen–fluoride) anions

### 3.1. Coordination compounds with $\text{HF}_2^-$ anions

#### 3.1.1. General introduction

The bifluoride anion  $\text{HF}_2^-$  is the smallest and the most common adduct of HF molecule with  $\text{F}^-$  anion and exhibits the strongest hydrogen bond. The most “simple” cases are alkaline metal bifluorides. The structures of  $\text{MHF}_2$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) and  $\text{Rb}_5\text{F}_4(\text{HF}_2)\cdot 2\text{H}_2\text{O}$  have been determined.  $\text{HF}_2^-$  anion has a linear structure with F–F distance ranging from 2.277 to 2.281 Å. [7] The unusually short F–F distance of 2.213 Å [8] in  $\text{NMe}_4\text{HF}_2$  ion was reinvestigated and a new slightly higher value for F–F distance (2.256 Å) was obtained. [9]

In the case of the compounds of alkaline earth metals with  $\text{HF}_2^-$  anions the structures of the compounds  $\text{SrF}(\text{HF}_2)$  and  $\text{BaF}(\text{HF}_2)$  were determined. [10] The coordination sphere around alkaline earth cations is tri-capped trigonal prism with four  $\text{F}^-$  and five



**Fig. 4.** Coordination sphere of Ca in  $\text{Ca}(\text{HF}_2)_2$  and the example of  $\text{HF}_2^-$  bonded to four Ca centers. The F–F' distances in the  $\text{HF}_2^-$  anions are 2.283 Å.

$\text{HF}_2^-$  anions. The F–F distances are 2.269 Å for Sr and 2.281 Å for Ba compound.

### 3.1.2. Coordination compounds with $\text{HF}_2^-$ anion isolated in our laboratory

Recently the compound  $\text{Ca}(\text{HF}_2)_2$  was prepared by dissolving  $\text{CaF}_2$  in anhydrous HF. The compound can be prepared also as a by-product in the system  $\text{CaF}_2\text{--PF}_5\text{--HF}$  and at the partial decomposition of the compound  $\text{Ca}(\text{RuF}_6)_2 \cdot n\text{XeF}_2$  in HF. [11] The main feature of the compound  $\text{Ca}(\text{HF}_2)_2$  is that Ca atom is homoleptically coordinated by  $\text{HF}_2^-$  anions. Calcium atom is coordinated by eight fluorine atoms from eight  $\text{HF}_2^-$  moieties and each anion is bonded to four metal centers (Fig. 4.) A three-dimensional network of Ca atoms bonded via  $\text{HF}_2^-$  units is formed.  $\text{HF}_2^-$  is symmetrical but slightly bent with F–F distances being 2.283 Å and angle F–H–F being 177.1°.

$\text{Ba}_4\text{F}_4(\text{HF}_2)(\text{PF}_6)_3$  and  $\text{Pb}_2\text{F}_2(\text{HF}_2)(\text{PF}_6)$  represent another type of compounds in which beside  $\text{HF}_2^-$  anions also  $\text{F}^-$  and  $\text{PF}_6^-$  anions are present. [11] Compounds were synthesized in the system  $\text{MF}_2\text{--PF}_5\text{--HF}$ . The excess of  $\text{PF}_5$  was used and the reaction proceeded at room temperature. The main feature of both compounds is the formation of polymeric zig-zag ribbon composed of metal cation and fluoride anion. Similar  $(\text{MF}^+)_n$  ribbon was found in the compound  $\text{PbF}(\text{AsF}_6)$ . [12] In the case of Ba compound infinite

$(\text{BaF}^+)_n$  ribbons are connected by  $\text{HF}_2^-$  anions into slabs. These slabs are “capped” by strongly bonded  $\text{PF}_6^-$  anions, and in between are located weakly bonded  $\text{PF}_6^-$  units (Fig. 5). In the compound  $\text{Pb}_2\text{F}_2(\text{HF}_2)(\text{PF}_6)$  zig-zag ribbons are linked with  $\text{HF}_2^-$  anions into infinite double layers. Weakly bonded  $\text{PF}_6^-$  units are located between the layers (Fig. 6). The  $\text{HF}_2^-$  anions in both compounds are again symmetric with F–F distance 2.28 Å in the case of Ba compound and 2.32 Å in the case of Pb compound. In both cases each fluorine atom in the  $\text{HF}_2^-$  anion is bonded to two metal atoms.

### 3.1.3. Some other examples of the coordination compounds with $\text{HF}_2^-$ anion

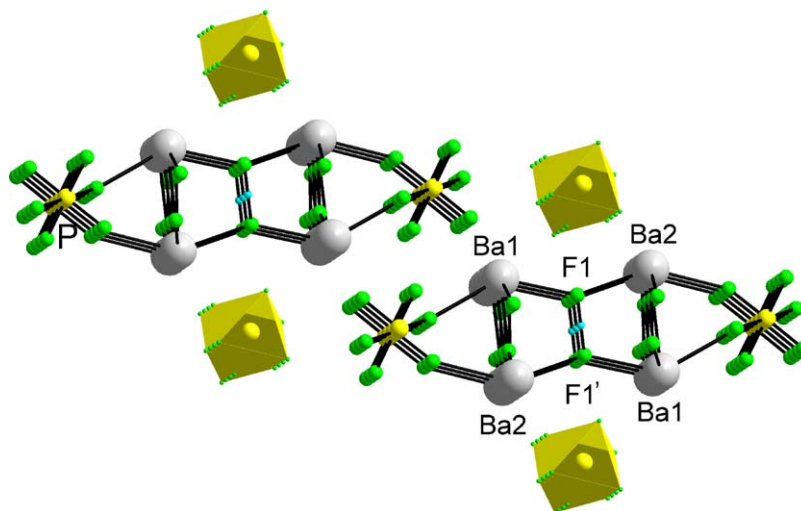
Several studies have been done recently on the copper pyrazine coordination polymers. Compounds  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$  [13],  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$  and  $[\text{Cu}_2\text{F}(\text{HF})(\text{HF}_2)(\text{pyz})_4](\text{SbF}_6)_2$  [14] were structurally characterized. In these compounds Cu atoms are connected by the  $\text{HF}_2^-$  anions as described above. The anion  $\text{HF}_2^-$  is symmetrical with the F–F distance 2.260 Å in the case of  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$  and 2.266 Å in the case of  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$ . In the compound  $[\text{Cu}_2\text{F}(\text{HF})(\text{HF}_2)(\text{pyz})_4](\text{SbF}_6)_2$  the anion  $\text{HF}_2^-$  has symmetric H–F bond lengths (1.142 Å) and a non-linear H–F–H angle of 171°. These compounds are interesting because of their magnetic behavior similar as in the case of paramagnetic Mn compound  $\text{pipzH}_2[\text{MnF}_4(\text{HF}_2)]$ . [15] In the compound  $\text{pipzH}_2[\text{MnF}_4(\text{HF}_2)]$  manganese is coordinated by six fluorine atoms: four from  $\text{F}^-$  and two from  $\text{HF}_2^-$ . The anion  $\text{HF}_2^-$  is symmetrical with a typical F–F distance of 2.281 Å.

The examples of the  $\text{HF}_2^-$  anion, which connects two metal centers, has been found earlier in the structures of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{NbF}_4(\text{AsF}_3)_2]_2 \cdot [(\eta^5\text{-C}_5\text{Me}_5)\text{NbF}_4(\text{HF})\text{AsF}_3]_2$  [16] and the isotypical compounds of  $[\text{Cu}_2(\text{HF}_2)(\text{H}_2\text{O})_8][\text{MF}_6] \cdot 2\text{H}_2\text{O}$  (M = Fe [17], Al [18]). It has been recognized also as a ligand in the transition metal complexes of Mo [19], W [20] and Pt [21].

## 3.2. Coordination compounds with $\text{H}_2\text{F}_3^-$ anions

### 3.2.1. General introduction

Coordination compounds with the  $\text{H}_2\text{F}_3^-$  anion are less common than those with the  $\text{HF}_2^-$  anion. The  $\text{H}_2\text{F}_3^-$  anion in the solid state exhibit bent (V shape) structure with two HF molecules linked to the central F atom ( $\text{F}^-$  anion) via strong hydrogen bonds. It could also be written as  $[\text{F}(\text{HF})_2]^-$  anion. Several examples of the compounds with  $\text{H}_2\text{F}_3^-$  anions should be mentioned here together with the F–F distances and the F–F–F angles:  $[\text{Co}(\text{py})_4\text{F}_2][\text{H}_2\text{F}_3]$ : 2.222 and 2.232 Å, 123.3° [22],  $\text{KH}_2\text{F}_3$ :



**Fig. 5.** Structure of  $\text{Ba}_4\text{F}_4(\text{HF}_2)(\text{PF}_6)_3$ . The F–F' distance in the  $\text{HF}_2^-$  is 2.28 Å.

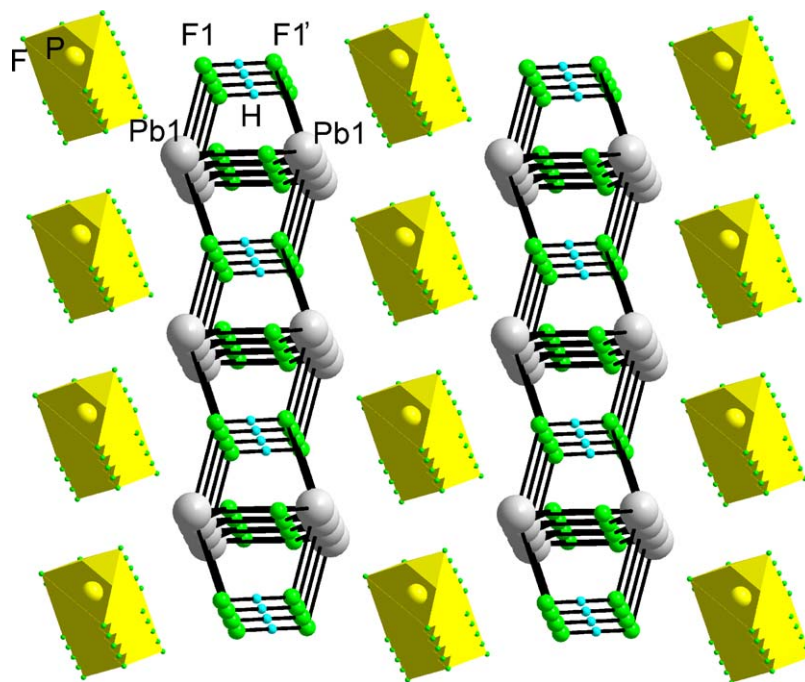


Fig. 6. Structure of  $\text{Pb}_2\text{F}_2(\text{HF}_2)(\text{PF}_6)$ . The F–F' distance in the  $\text{HF}_2^-$  is 2.32 Å.

from 2.29 to 2.35 Å,  $130^\circ$  and  $139^\circ$  [23] and  $\text{KF}\cdot 2.5\text{HF}$ : 2.352 and 2.323 Å,  $107^\circ$  [24],  $\text{CsH}_2\text{F}_3$ : 2.30–2.34 Å,  $141.2^\circ$  and  $148.4^\circ$  [9]  $\{[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}\}^-[\text{H}_2\text{F}_3]^-1.5\text{CH}_2\text{Cl}_2$ : 2.273 and 2.325 Å,  $117.5^\circ$  [25]. In the  $(\text{CH}_3)_4\text{NF}\cdot 2\text{HF}$  the F–F distances and the F–F–F angles were 2.316 and 2.302 Å,  $123^\circ$  [26] and later refined to 2.322 and 2.316 Å [9]. In the study of the amine-poly(hydrogen-fluoride) the solid state structures of  $\text{Me}_3\text{N}\cdot 3\text{HF}$  (F–F distance 2.371 Å and F–F–F angle  $97.9^\circ$ ) and  $\text{Et}_3\text{N}\cdot 3\text{HF}$  (F–F distance 2.351 Å and F–F–F angle  $119.7^\circ$ ) were determined [27].

The average F–F bond length in the  $\text{H}_2\text{F}_3^-$  anion is longer as in the  $\text{HF}_2^-$  anion as a consequence of central F atom acting as a double acceptor. The molecule is not very rigid and it bends according to the specific packing in the crystal structure.

### 3.2.2. Coordination compounds with $\text{H}_2\text{F}_3^-$ anion isolated in our laboratory

The compounds of the type  $\text{M}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{AF}_6)$  ( $\text{M} = \text{Ca}$ ,  $\text{A} = \text{As}$ ;  $\text{M} = \text{Sr}$ ,  $\text{A} = \text{As}$ ,  $\text{P}$ ) [28] represent the first known examples of the compounds with  $\text{H}_2\text{F}_3^-$  and  $\text{HF}_2^-$  anions in the molecule. They can be prepared by the reaction of  $\text{MF}_2$  and  $\text{M}(\text{AsF}_6)_2$  in the mole ratio 3:1 in HF (Ca compound) or by the reaction of  $\text{MF}_2$  and  $\text{AsF}_5$  in the mole ratio 2:1 in HF (Ca, Sr compounds).  $\text{Sr}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{PF}_6)$  crystallizes out of the HF solution in the system  $\text{SrF}_2\text{--XeF}_2\text{--PF}_5$ . The  $\text{H}_2\text{F}_3^-$  and  $\text{HF}_2^-$  anions simultaneously bridge metal centers forming close packed three-dimensional network of polymeric compounds. These compounds are isotypical. They have nine fluorine atoms around the metal centers which are connected by two  $\text{HF}_2^-$  anions and fluorine atom from the  $\text{H}_2\text{F}_3^-$  anion. The second way of the connection between metal centers is via  $\text{HF}_2^-$  anions and  $\text{AF}_6$  units (Fig. 7). The anion  $\text{HF}_2^-$  in all three structures is asymmetric with hydrogen atom being closer to the one fluorine atom and the F–F distances being  $\sim 2.28$  Å.

The anion  $\text{H}_2\text{F}_3^-$ , formed by the interaction of  $\text{F}^-$  anion with two HF molecules from neighboring layer, is characterized by the F–F distance and the F–F–F angle. In the case of  $\text{M}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{AF}_6)$  the F–F distances in the  $\text{H}_2\text{F}_3^-$  range from 2.406 to 2.422 Å and the angles F–F–F range from  $95.1^\circ$  to  $97.7^\circ$ . The longer distances and the smaller F–F–F angles in the  $\text{H}_2\text{F}_3^-$ , compared to the other cases, are probably the consequence of the close packing in the described

compounds. The most interesting in the described structures is their stabilization by the small anions  $\text{HF}_2^-$  and  $\text{H}_2\text{F}_3^-$  which together with the  $\text{AF}_6$  units interconnect calcium or strontium atoms in a close packed three-dimensional network.

### 3.3. Coordination compounds with $\text{H}_3\text{F}_4^-$ anions

#### 3.3.1. General introduction

The single crystal structures determined on the compounds with the  $\text{H}_3\text{F}_4^-$  anions are less numerous than those with the  $\text{HF}_2^-$  anions. Some previously published examples should be mentioned here.  $\text{KF}\cdot 2.5\text{HF}$  can also be written as  $\text{K}_2(\text{H}_2\text{F}_3)(\text{H}_3\text{F}_4)$  and the  $\text{H}_3\text{F}_4^-$  anion can be formulated as  $[(\text{FH})\text{FH}(\text{HF})]^-$  [24]. Two HF molecules are bonded via hydrogen bond (F–F distances being 2.402 and 2.441 Å) to one fluorine atom each of the central  $\text{HF}_2^-$  ion (F–F distance being 2.281 Å). Two terminal hydrogen bonds are oriented *cis* to each

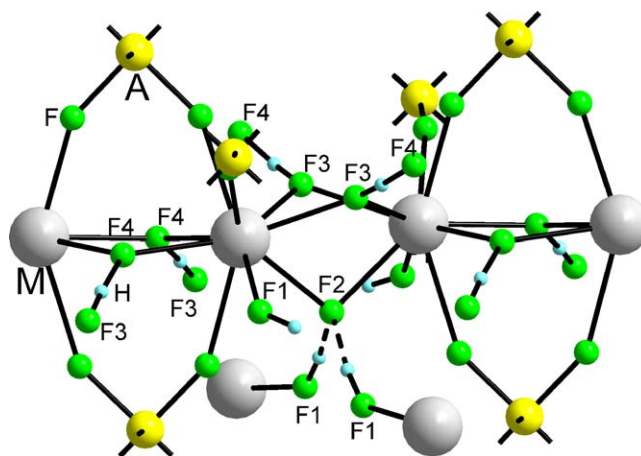
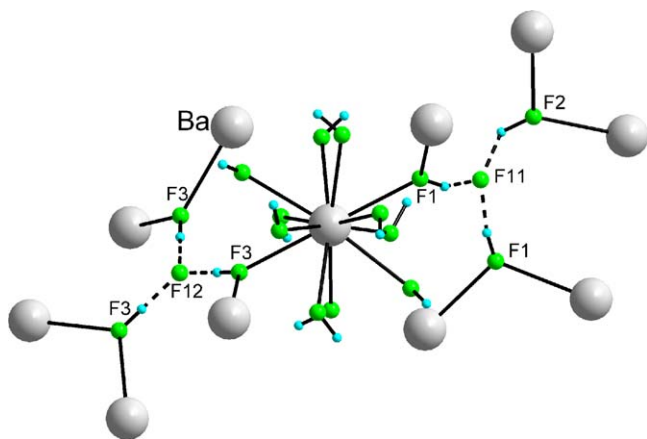


Fig. 7. Structure of  $\text{M}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{AF}_6)$ .  $\text{Ca}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{AsF}_6)$ : F3–F4 distance in  $\text{HF}_2^-$  is 2.285 Å and F1–F2 distance in  $\text{H}_2\text{F}_3^-$  is 2.422 Å.  $\text{Sr}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{AsF}_6)$ : F3–F4 distance in  $\text{HF}_2^-$  is 2.281 Å and F1–F2 distance in  $\text{H}_2\text{F}_3^-$  is 2.406 Å.  $\text{Sr}_2(\text{H}_2\text{F}_3)(\text{HF}_2)_2(\text{PF}_6)$ : F3–F4 distance in  $\text{HF}_2^-$  is 2.273 Å and F1–F2 distance in  $\text{H}_2\text{F}_3^-$  is 2.408 Å.



**Fig. 8.** Coordination of Ba center in  $\text{Ba}(\text{H}_3\text{F}_4)_2$  and bridging role of  $\text{H}_3\text{F}_4^-$  anions. Distances and angles in  $\text{H}_3\text{F}_4^-$ : F3–F12: 2.323 Å, F3–F12–F3:  $120^\circ$ , F1–F11: 2.344 Å, F2–F11: 2.332 Å, F1–F11–F1:  $106.4^\circ$ , F2–F11–F1:  $125.0^\circ$  Å.

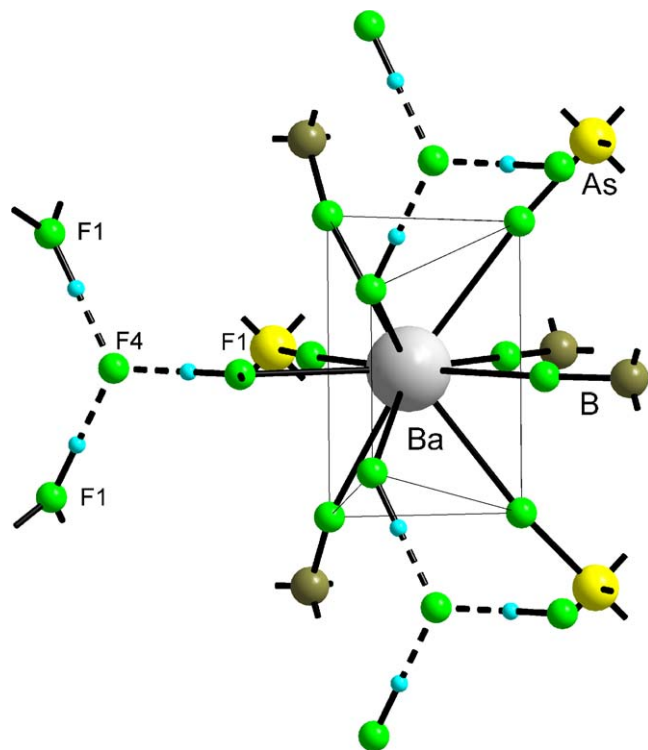
other. The anion exhibit so called unbranched-chain geometry which was also found in  $\text{H}_2\text{O}\cdot 4\text{HF}$  [29]. The other example is  $\text{KF}\cdot 3\text{HF}$  which can be formulated as  $\text{KH}_3\text{F}_4$  and the anion can be written as  $[\text{F}(\text{HF})_3]^-$ . It exhibit trigonal planar geometry (branched-chain) with the F–F distance of 2.401 Å and the F–F–F angles of  $120^\circ$ . In the  $\text{Me}_3\text{N}\cdot 4\text{HF}$  and  $\text{Et}_3\text{N}\cdot 4\text{HF}$  the anions  $\text{H}_3\text{F}_4^-$  are virtually planar and in the branched-chain form  $[\text{F}(\text{HF})_3]^-$ . The F–F distances in these compounds range from 2.365 to 2.406 Å and the angles F–F–F are in the range from  $106.4^\circ$  to  $143.2^\circ$  [27]. Some of the other examples of compounds in which the  $\text{H}_3\text{F}_4^-$  anion could be formulated as  $[\text{F}(\text{HF})_3]^-$  are  $\text{NOF}\cdot 3\text{HF}$  [30],  $\text{Me}_4\text{NF}\cdot 3\text{HF}$  [26],  $3\text{IF}_5\cdot \text{CsF}\cdot 3\text{HF}$  [31],  $\text{K}_3\text{BiCl}_6\cdot 2\text{KCl}\cdot \text{KF}\cdot 3\text{HF}$  [32] and  $\text{NH}_3\cdot 4\text{HF}$  [33].

Another interesting example of the metal coordinated by the  $\text{H}_3\text{F}_4^-$  anion is found in the compound  $[\text{CuAg}(\text{H}_3\text{F}_4)(\text{pyz})_5](\text{SbF}_6)_2$ , which is bimetallic and contains an ordered arrangement of octahedrally coordinated  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  cations and the bridging  $\text{H}_3\text{F}_4^-$  anions. The  $\text{H}_3\text{F}_4^-$  anion is geometrically unique in that it has a rhombic-like motif and forms a bridge between  $\text{Cu}^{2+}$  ions. Because of disorder, three of the four H positions are randomly occupied [14].

### 3.3.2. Coordination compounds with $\text{H}_3\text{F}_4^-$ anion isolated in our laboratory

An example of the compound in which metal centers are bridged *via* the  $\text{H}_3\text{F}_4^-$  is  $\text{Ba}(\text{H}_3\text{F}_4)_2$ . The coordination sphere of Ba atom in  $\text{Ba}(\text{H}_3\text{F}_4)_2$  consists of 12 fluorine atoms from HF molecules forming regular icosahedra. Each HF molecule acts as a bridge between two metal centers (Fig. 8) [34]. Three-dimensional network with two kinds of infinite channels is formed. In these channels fluorine anions ( $\text{F}^-$ ) are bonded with three H(F) atoms resulting in formation on the  $\text{H}_3\text{F}_4^-$  anions which can be formulated as  $[\text{F}(\text{HF})_3]^-$ . There are two crystallographically independent  $\text{H}_3\text{F}_4^-$  anions. One exhibits the regular planar-trigonal geometry with all F–F distances of 2.323 Å and F–F–F angles of  $120^\circ$ . In the other  $\text{H}_3\text{F}_4^-$  anion the planar-trigonal geometry is distorted with F–F distances being 2.332 and 2.344 Å (two times) and angles of  $106.4^\circ$  and  $125^\circ$  (two times).

In the recently characterized compound  $\text{Ba}_2(\text{BF}_4)_2(\text{AsF}_6)(\text{H}_3\text{F}_4)$  beside the  $\text{H}_3\text{F}_4^-$  anion also additional two anions were found: tetrahedral  $\text{BF}_4^-$  and octahedral  $\text{AsF}_6^-$ . [35] The compound can be prepared by the reaction of the corresponding amounts of  $\text{Ba}(\text{BF}_4)_2$ ,  $\text{Ba}(\text{AsF}_6)_2$  and  $\text{BaF}_2$ . The barium environment in the shape of tetra-capped trigonal prism involves 10 fluorine atoms from four  $\text{BF}_4^-$ , three  $\text{AsF}_6^-$  and three  $\text{H}_3\text{F}_4^-$  anions (Fig. 9). All fluorine atoms from  $\text{AsF}_6^-$ ,  $\text{BF}_4^-$ , and  $\text{H}_3\text{F}_4^-$  with exception of the central fluorine atom in the  $\text{H}_3\text{F}_4^-$  moiety, act as  $\mu_2$ -bridges yielding a complex three-



**Fig. 9.** Coordination sphere of Ba atom in  $\text{Ba}_2(\text{BF}_4)_2(\text{AsF}_6)(\text{H}_3\text{F}_4)$ . Distances and angles in  $\text{H}_3\text{F}_4^-$ : F1–F4: 2.340 Å, F1–F4–F1:  $120^\circ$ .

dimensional structural network. The  $\text{H}_3\text{F}_4^-$  anion exhibits regular trigonal planar geometry with the F–F distances of 2.340 Å and the F–F–F angles of  $120^\circ$ . Each terminal fluorine atom connects a pair of Ba atoms. These six Ba atoms form a trigonal prism, while in the case of  $\text{Ba}(\text{H}_3\text{F}_4)_2$  they form nearly regular hexagon.

## 4. Experimental procedure

The detailed experimental procedures for the syntheses and characterization of the compounds mentioned in this review can be found in the corresponding cited literature. Here, only basic experimental techniques are given.

Volatile materials (anhydrous HF,  $\text{AsF}_5$ ,  $\text{PF}_5$ ,  $\text{BF}_3$ ) were manipulated in an all-Teflon vacuum line equipped with Teflon valves. Non-volatile materials that were sensitive to traces of moisture were handled in an argon atmosphere in a dry box (maximum water content was less than 1 ppm). FEP reaction vessels, equipped with a Teflon valve and a Teflon-covered stirring bar were used for the syntheses. T-shaped reaction vessels constructed from PFA tubes of different diameters joined at right angle and equipped with a Teflon valve were used for crystallization.

Single crystal data of the compounds, prepared in our laboratory, were collected using a Mercury CCD area detector coupled to a Rigaku AFC7 diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation.

## Acknowledgement

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

## References

- [1] Z. Mazej, H. Borrmann, K. Lutar, B. Žemva, *Inorg. Chem.* 37 (1998) 5912–5914.
- [2] M. Tramšek, B. Žemva, *J. Fluorine Chem.* 127 (2006) 1275–1284.

- [3] T. Tsuda, R. Hagiwara, *J. Fluorine Chem.* 129 (2008) 4–13.
- [4] T. Bunič, M. Tramšek, E. Goresnik, B. Žemva, *Acta. Chim. Slov.* 55 (2008) 788–792.
- [5] M. Atoji, W.N. Lipscomb, *Acta Crystallogr.* 7 (1954) 173–175.
- [6] Z. Mazej, E. Goresnik, K. Hironaka, Y. Katayama, R. Hagiwara, *Z. Anorg. Allg. Chem.*, (2009) doi:10.1002/zaac.200900123.
- [7] S.I. Troyanov, *Crystallogr. Rep.* 50 (2005) 773–778.
- [8] W.W. Wilson, K.O. Christe, J.-A. Feng, R. Bau, *Can. J. Chem.* 67 (1989) 1898–1901.
- [9] S.I. Troyanov, I.V. Morozov, E. Kemnitz, *Z. Anorg. Allg. Chem.* 631 (2005) 1651–1654.
- [10] W. Massa, E. Herdtweck, *Acta Crystallogr.* C39 (1983) 509–512.
- [11] T. Bunič, M. Tramšek, E. Goresnik, Boris Žemva, *J. Solid State Chem.* 181 (2008) 2318–2324.
- [12] M. Tramšek, E. Lork, R. Mews, B. Žemva, *J. Fluorine Chem.* 110 (2001) 123–131.
- [13] J.L. Manson, M.M. Conner, J.A. Schlueter, T. Lancaster, S.J. Blundell, M.L. Brooks, F.L. Pratt, T. Papageorgiou, A.D. Bianchi, J. Wosnitza, M.-H. Whangbo, *Chem. Commun.* (2006) 4894–4896.
- [14] J.L. Manson, J.A. Schlueter, K.A. Funk, H.I. Southerland, B. Twamley, T. Lancaster, S.J. Blundell, P.J. Baker, F.L. Pratt, J. Singelton, R.D. McDonald, P.A. Goddard, P. Sengupta, C.D. Batista, L. Ding, C. Lee, M.-H. Whangbo, I. Franke, S. Cox, C. Baines, D. Trial, *J. Am. Chem. Soc.* 131 (2009) 6733–6747.
- [15] U. Bentrup, K. Harms, W. Massa, J. Pebler, *Solid State Sci.* 2 (2000) 373–376.
- [16] H.W. Roesky, M. Sotoodeh, Y.M. Xu, F. Schrumpf, M. Noltemeyer, *Z. Anorg. Allg. Chem.* 580 (1990) 131–138.
- [17] A. Le Bail, A.-M. Mercier, *Acta Crystallogr.* E65 (2009) i23–i24.
- [18] M. Weil, *Acta Crystallogr.* E65 (2009) i29.
- [19] V.J. Murphy, T. Hascall, J.Y. Chen, G. Parkin, *J. Am. Chem. Soc.* 118 (1996) 7428–7429.
- [20] V.J. Murphy, D. Rabinovich, T. Hascall, W.T. Klooster, T.F. Koetzle, G. Parkin, *J. Am. Chem. Soc.* 120 (1998) 4372–4387.
- [21] N.A. Jasim, R.N. Perutz, *J. Am. Chem. Soc.* 122 (2000) 8685–8693.
- [22] J. Holzbock, W. Sawodny, U. Thewalt, *Z. Anorg. Allg. Chem.* 626 (2000) 2563–2568.
- [23] J.D. Forrester, M.E. Senko, A. Zalkin, D.H. Tempelton, *Acta Crystallogr.* 16 (1963) 58–62.
- [24] D. Mootz, D. Boenigk, *J. Am. Chem. Soc.* 108 (1986) 6634–6636.
- [25] T. Mathieson, A. Schier, H. Schmidbaur, *Z. Naturforsch.* 55b (2000) 1000–1004.
- [26] D. Mootz, D. Boenigk, *Z. Anorg. Allg. Chem.* 544 (1987) 159–166.
- [27] D. Wiechert, D. Mootz, R. Franz, G. Siegmund, *Chem. Eur. J.* 4 (1998) 1043–1047.
- [28] M. Tramšek, G. Tavčar, T. Bunič, P. Benkič, B. Žemva, *J. Fluorine Chem.* 126 (2005) 1088–1094.
- [29] D. Mootz, W. Poll, *Z. Anorg. Allg. Chem.* 484 (1982) 158–164.
- [30] D. Mootz, W. Poll, *Z. Naturforsch.* B 39 (1984) 1300–1305.
- [31] A.R. Mahjoub, D. Leopold, K. Seppelt, *Eur. J. Solid State Inorg. Chem.* 29 (1992) 635–647.
- [32] A.A. Udovenko, R.L. Davidovich, *Koord. Khim.* 17 (1991) 1545–1546.
- [33] D. Mootz, W. Poll, *Z. Naturforsch.* B 39 (1984) 290–297.
- [34] T. Bunič, M. Tramšek, E. Goresnik, B. Žemva, *Solid State Sci.* 8 (2006) 927–931.
- [35] M. Lozinšek, T. Bunič, E. Goresnik, A. Meden, M. Tramšek, G. Tavčar, B. Žemva, *J. Solid State Chem.*, submitted for publication.