

**Hexafluoro-, heptafluoro-, and octafluoro- salts, and  $[M_nF_{5n+1}]^-$  ( $n = 2, 3, 4$ ) polyfluorometallates of singly charged metal cations,  $Li^+ - Cs^+$ ,  $Cu^+$ ,  $Ag^+$ ,  $In^+$  and  $Tl^+$**

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**Abstract**

Keywords: hexafluorometallates, heptafluorometallates, octafluorometallates, polyfluorometallates, crystal structures

**1. Introduction**

Monofluorides ( $AF$ ) and pentafluorides ( $MF_5$ ) form a variety of compounds with general formulas  $AMF_6$ ,  $A_2MF_7$ ,  $A_3MF_8$ ,  $AM_2F_{11}$ ,  $AM_3F_{16}$  and  $AM_4F_{21}$ . The largest group represents  $AMF_6$  compounds, where more than 100 compounds have been reported (Table 1). Their crystal structures were last time completely reviewed in sixties [1,2] and briefly discussed in Refs. [3] and [4]. Since that time a large number of publications about crystal data of  $AMF_6$  compounds were published. Because of that and because of some discrepancies with different data a complete review concerning the crystal structure of  $AMF_6$  compounds was made. Additionally, known literature data about other phases in  $AF-MF_5$  systems ( $A_2MF_7$ ,  $A_3MF_8$ ,  $AM_2F_{11}$ ,  $AM_3F_{16}$  and  $AM_4F_{21}$ ) are included.

## 2. $AMF_6$ compounds

The structures of  $AMF_6$  compounds are divided in NaCl- and CsCl-types. NaCl-type has a (6,6)-coordination and is found for the salt of which the radius ratio  $r(\text{cation}) / r(\text{anion})$  is small. CsCl-type has an (8,8)-coordination and occurs for the salt with a large radius ratio. Since the  $MF_6$  anion is not perfectly spherical, its orientation is affected again by the size of cation and probably by the hardness of it. By the difference in the orientational manner of anions, structural variety occurs for both the NaCl- and CsCl type salts. The orientation of anions varies the coordination number of fluorine atoms around the cation from six found for  $LiSbF_6$  (NaCl-type) and  $NaSbF_6$  structure (NaCl-type) to twelve for  $KOsF_6$  structure (CsCl-type). Some of the hexafluorophosphates and arsenates exhibit orientational disorders. The coordination numbers varies from six to twelve in the local structure of these compounds. Among them, compounds like  $CsPF_6$  (NaCl-type) exhibit a fixed twelve coordination number in spite of the presence of disorder. Some of the salts are polymorphic and phase transitions have been reported (see Legend under Table 1). Some of the structure data are based on only powder diffraction work in the middle of last century. Re-classification in this review has been made mostly based on the reported single crystal data.

Table 1  
Structural types of  $A^I M^V F_6$  compounds

|    |                           | P                                  | As                                  | V        | Rh       | Ru                  | Au       | Pt       | Ir                  | Os                  | Re                  | Sb                                          | Mo       | W        | Nb                      | Ta                      | Bi                                |
|----|---------------------------|------------------------------------|-------------------------------------|----------|----------|---------------------|----------|----------|---------------------|---------------------|---------------------|---------------------------------------------|----------|----------|-------------------------|-------------------------|-----------------------------------|
|    | Ionic radius <sup>I</sup> | 0.52                               | 0.60                                | 0.68     | 0.69     | 0.705               | 0.71     | 0.71     | 0.71                | 0.715               | 0.72                | 0.74                                        | 0.75     | 0.76     | 0.78                    | 0.78                    | 0.90                              |
| Li | 0.90                      | <i>a</i>                           | <i>a</i>                            | <i>a</i> | <i>a</i> | <i>a</i>            | <i>a</i> | <i>a</i> | <i>a</i>            | <i>a</i>            | <i>a</i>            | <i>a</i>                                    | <i>a</i> | <i>a</i> | <i>a</i>                | <i>a</i>                | <i>a</i>                          |
| Cu | 0.91                      | /                                  | <i>a</i>                            | /        | /        | /                   | /        | /        | /                   | /                   | /                   | <i>a</i>                                    | /        | /        | /                       | /                       | /                                 |
| Na | 0.116                     | <i>b</i> <sup>II</sup>             | <i>a</i>                            | <i>a</i> | <i>a</i> | <i>a</i>            | <i>a</i> | /        | <i>a</i>            | <i>a</i>            | <i>b</i>            | <i>b</i>                                    | <i>b</i> | <i>b</i> | <i>b</i>                | <i>b</i>                | <i>a</i>                          |
| Ag | 0.129                     | <i>c</i>                           | <i>c</i>                            | <i>d</i> | /        | <i>d</i>   <i>e</i> | <i>a</i> | /        | <i>d</i>   <i>e</i> | <i>d</i>   <i>e</i> | /                   | <i>e</i>                                    | /        | /        | <i>h</i>                | <i>h</i>                | <i>d</i>                          |
| K  | 0.152                     | <i>g</i> <sup>III</sup>   <i>f</i> | <i>g</i> <sup>IV</sup>   <i>f</i>   | <i>f</i> | <i>f</i> | <i>f</i>            | <i>f</i> | <i>f</i> | <i>f</i>            | <i>f</i>            | <i>d</i>   <i>f</i> | <i>e</i> <sup>V</sup>   <i>d</i>   <i>f</i> | <i>d</i> | <i>d</i> | <i>d</i>                | <i>d</i>                | <i>e</i> <sup>VI</sup>   <i>d</i> |
| In |                           | <i>g</i>                           | <i>f</i>                            | /        | /        | /                   | /        | /        | /                   | /                   | /                   | /                                           | /        | /        | /                       | /                       | /                                 |
| Tl | 0.164                     | <i>g</i>                           | <i>f</i>                            | <i>f</i> | /        | <i>f</i>            | /        | /        | /                   | /                   | /                   | <i>f</i>                                    | <i>f</i> | /        | <i>f</i> <sup>VII</sup> | <i>f</i> <sup>VII</sup> | /                                 |
| Rb | 0.166                     | <i>g</i>                           | <i>f</i> <sup>VIII</sup>   <i>g</i> | <i>f</i> | <i>f</i> | <i>f</i>            | <i>f</i> | <i>f</i> | <i>f</i>            | <i>f</i>            | <i>f</i>            | <i>f</i> <sup>VIII</sup>                    | <i>f</i> | <i>f</i> | <i>f</i> <sup>IX</sup>  | <i>f</i> <sup>IX</sup>  | <i>f</i>                          |
| Cs | 0.181                     | <i>g</i> <sup>X</sup>              | <i>f</i> <sup>VIII</sup>   <i>g</i> | <i>f</i> | <i>f</i> | <i>f</i>            | <i>f</i> | <i>f</i> | <i>f</i>            | <i>f</i>            | <i>f</i>            | <i>f</i> <sup>VIII</sup>                    | <i>f</i> | <i>f</i> | <i>f</i> <sup>IX</sup>  | <i>f</i> <sup>IX</sup>  | <i>f</i>                          |

*a* =  $LiSbF_6$ -type ; *b* =  $NaSbF_6$ -type; *c* =  $AgPF_6$ -type; *d* =  $KNbF_6$ -/ $KSbF_6$ (I)-types; *e* =  $AgSbF_6$ -type; *f* =  $KOsF_6$ -type; *g* =  $CsPF_6$ -type; *h* =  $AgTaF_6$ -type.

<sup>I</sup>Shanon ionic radii / Å.[5] Information about some high-temperature phases not included in Table 1 and structural transitions in dependence of temperature could be found in: <sup>II</sup>Ref. [6,7], <sup>III</sup>Ref. [7], <sup>IV</sup>Ref. [8], <sup>V</sup>Ref. [9], <sup>VI</sup>Ref.[10], <sup>VII</sup>Ref.[11], <sup>VIII</sup>Ref. [12], <sup>IX</sup>Ref.[13], <sup>X</sup>Ref. [7,14].

## 2.1 LiSbF<sub>6</sub>–structural type (Fig. 1)

All the LiMF<sub>6</sub> and Cu<sup>I</sup>MF<sub>6</sub> compounds (although only two examples are so far known for the latter [15],[16]) crystallize in this structure. In the series of NaMF<sub>6</sub>, irregularity is observed in the radius ratio rule. LiSbF<sub>6</sub> structure mostly appears for NaMF<sub>6</sub> of which the ionic radius of *M* is small (<0.72 Å). However, NaPF<sub>6</sub> which is the salt with the smallest MF<sub>6</sub> anion in Table 2 does not crystallize in LiSbF<sub>6</sub> structure but in NaSbF<sub>6</sub> structure as a stable form at ambient conditions [7]. On the other hand, NaBiF<sub>6</sub> with the largest MF<sub>6</sub> anion appeared in the Table 2 crystallizes in LiSbF<sub>6</sub> structure rather than in NaSbF<sub>6</sub> structure. In the AgMF<sub>6</sub> series, only AgAuF<sub>6</sub> is known to crystallize in LiSbF<sub>6</sub> structure. The structure is the result of the (6,6) coordination of NaCl–type for the combination of small atomic cations and large hexafluoroanions as in the case of NaSbF<sub>6</sub>–type. It is regarded to a slightly twisted NaSbF<sub>6</sub> structure so as to elongate the diagonal of the pseudo NaCl–type lattice for the effective packing of ions. MF<sub>6</sub><sup>–</sup> anions tilt towards the edge of the rhombohedron (17° in the case of LiSbF<sub>6</sub>). The cation is coordinated by six fluorine atoms from the six different MF<sub>6</sub><sup>–</sup> anions. A–F–M chain is not straight but bent (148° in the case of LiSbF<sub>6</sub>).

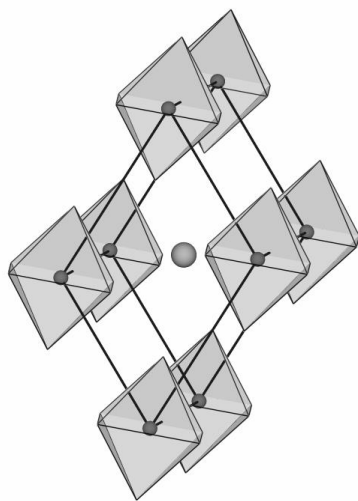


Fig. 1. The rhombohedral unit cell and structure of LiSbF<sub>6</sub>–structural type.

Table 2 LiSbF<sub>6</sub>-type (rhombohedral,  $R\bar{3}$ , No.148,  $Z = 1$ , C.N.(A<sup>I</sup>, M<sup>V</sup>) = 6)

|                                  | Lattice Constants |                  |                      |                   | $V / \text{\AA}^3$<br><sup>a)</sup> | Structural Data <sup>b)</sup>           | Ref.       |
|----------------------------------|-------------------|------------------|----------------------|-------------------|-------------------------------------|-----------------------------------------|------------|
|                                  | Hexagonal setting |                  | Rhombohedral setting |                   |                                     |                                         |            |
|                                  | $a / \text{\AA}$  | $c / \text{\AA}$ | $a / \text{\AA}$     | $\alpha / ^\circ$ |                                     |                                         |            |
| LiPF <sub>6</sub>                | 4.932(2)          | 12.658(4)        | 5.09                 | 57.954            | 88.9                                | structure; single crystal               | [17]       |
|                                  | 4.932(2)          | 12.641(5)        | 5.086                | 58.012            | 88.8                                | unit cell; powder data <sup>c)</sup>    | [18]       |
|                                  | 4.933(1)          | 12.657(2)        | 5.090                | 57.966            | 88.9                                | unit cell; powder data <sup>d)</sup>    | [18]       |
| LiAsF <sub>6</sub>               | 5.016(1)          | 13.028(4)        | 5.220                | 57.435            | 94.6                                | structure; powder data                  | [17]       |
| LiVF <sub>6</sub>                | 5.00              | 13.33            | 5.30                 | 56.3              | 96.3                                | unit cell; powder data                  | [1,2]      |
| LiRhF <sub>6</sub>               | 5.02018(7)        | 13.5588(3)       | 5.369                | 55.745            | 98.6                                | single crystal/SPDD <sup>e)</sup>       | [19,20,21] |
| LiRuF <sub>6</sub>               | 5.07397(8)        | 13.5244(3)       | 5.376                | 56.314            | 100.5                               | structure; SPDD data <sup>e)</sup>      | [19,20]    |
| LiAuF <sub>6</sub>               | 5.00337(5)        | 13.7160(2)       | 5.410                | 55.091            | 99.1                                | structure; SPDD data                    | [19,20]    |
|                                  | 4.994(1)          | 13.624(2)        | 5.379                | 55.315            | 98.1                                | unit cell; powder data                  | [22]       |
| LiPtF <sub>6</sub>               | 5.02686(4)        | 13.6559(2)       | 5.398                | 55.497            | 99.6                                | structure; SPDD data <sup>e)</sup>      | [19,20]    |
| LiIrF <sub>6</sub>               | 5.06148(4)        | 13.6260(2)       | 5.401                | 55.855            | 100.8                               | single crystal and SPDD <sup>e)</sup>   | [19,20,21] |
| LiOsF <sub>6</sub>               | 5.10558(6)        | 13.6106(2)       | 5.410                | 56.307            | 102.4                               | structure; SPDD data <sup>e)</sup>      | [20]       |
|                                  | 5.1111(8)         | 13.625(4)        | 5.416                | 56.308            | 102.7                               | structure; single crystal <sup>f)</sup> | [20]       |
|                                  | 5.0512(3)         | 13.5932(9)       | 5.388                | 55.901            | 100.12                              | structure; single crystal <sup>g)</sup> | [19,20]    |
| LiReF <sub>6</sub> <sup>h)</sup> | 5.057             | 13.735           | 5.43                 | 55.5              | 101.4                               | unit cell; powder data                  | [1,2,19]   |
| LiSbF <sub>6</sub>               | 5.18(2)           | 13.60(2)         | 5.43                 | 56.97             | 105.3                               | structure; single crystal               | [17,23]    |
| LiMoF <sub>6</sub>               | 5.190             | 13.585           | 5.43                 | 57.1              | 105.6                               | unit cell; powder data                  | [1,19]     |
| LiWF <sub>6</sub>                | 5.234             | 13.606           | 5.45                 | 57.4              | 107.6                               | unit cell; powder data                  | [1,2,19]   |
| LiNbF <sub>6</sub>               | 5.31810(3)        | 13.5861(2)       | 5.471                | 58.155            | 110.9                               | structure; SPDD data <sup>e)</sup>      | [19,20]    |
| LiTaF <sub>6</sub>               | 5.32006(8)        | 13.6178(3)       | 5.481                | 58.070            | 111.26                              | structure; SPDD data <sup>e)</sup>      | [19,20]    |
| LiBiF <sub>6</sub>               | 5.181             | 13.99            | 5.540                | 55.76             | 108.4                               | structure, powder data                  | [17,25]    |
| CuAsF <sub>6</sub>               | 5.13              | 13.87            | 5.49(1)              | 55.7(1)           | 105.3                               | unit cell; powder data                  | [15]       |
| CuSbF <sub>6</sub>               | 5.304(4)          | 14.53(1)         | 5.730                | 55.138            | 118.0                               | structure; single crystal               | [16]       |
| NaAsF <sub>6</sub>               | 5.336             | 13.979           | 5.586                | 57.06             | 114.9                               | unit cell; powder data                  | [1]        |
| NaVF <sub>6</sub>                | 5.330             | 14.144           | 5.629                | 56.55             | 116.0                               | unit cell; powder data                  | [1,2]      |
| NaRhF <sub>6</sub>               | 5.24              | 14.62            | 5.74                 | 54.36             | 115.9                               | unit cell; powder data                  | [24]       |
| NaRuF <sub>6</sub>               | 5.31              | 14.77            | 5.80                 | 54.49             | 120.2                               | unit cell; powder data                  | [24]       |
| NaAuF <sub>6</sub>               | 5.237(2)          | 15.042(4)        | 5.855                | 53.13             | 119.1                               | unit cell; powder data                  | [22]       |
| NaIrF <sub>6</sub>               | 5.37              | 14.70            | 5.80                 | 55.2              | 122.5                               | unit cell; powder data                  | [1,2]      |
| NaOsF <sub>6</sub>               | 5.37              | 14.70            | 5.80                 | 55.2              | 122.5                               | unit cell; powder data                  | [1,2]      |
| NaBiF <sub>6</sub>               | 5.468             | 15.16            | 5.958                | 54.64             | 130.4                               | structure: powder data                  | [17,25]    |
| AgAuF <sub>6</sub>               | 5.2840(2)         | 15.0451(6)       | 5.870                | 53.498            | 121.3                               | unit cell; SPDD data <sup>e)</sup>      | [19,26]    |

<sup>a)</sup>Volume is given for rhombohedral unit cell. <sup>b)</sup>Where not stated otherwise, data were collected by powder or single crystal X-ray diffraction methods. <sup>c)</sup>LiPF<sub>6</sub> prepared by the reaction between the elemental F<sub>2</sub> and equimolar mixture of LiF and P. <sup>d)</sup>LiPF<sub>6</sub> prepared by the reaction of LiF with PF<sub>5</sub> in anhydrous HF. <sup>e)</sup>SPDD = synchrotron X-ray powder diffraction data at 299 K. <sup>f)</sup>Data collected at 293 K. <sup>g)</sup>Data collected at 129 K. <sup>h)</sup>The authenticity of this compound is doubtful (see Ref. [19]).

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## 2.2 NaSbF<sub>6</sub>–structural type (Fig. 2)

NaSbF<sub>6</sub> structure with the highest symmetry among the AMF<sub>6</sub> structures is not widely spread and found only for the sodium hexafluorometallates of transition metals with limited ionic radii of 0.72 to 0.78 Å. There occurs of a NaCl–type arrangement of the cations and anions. *A–F–M* chain is straight without the tilt of MF<sub>6</sub> units. NaPF<sub>6</sub> is the only exception in this series which crystallizes in NaSbF<sub>6</sub> structure in spite of the small size of phosphorus atom. The structure of this compound was originally classified as “NaPF<sub>6</sub> type” with the same space group, but with inclined anions with an eight–fold orientational disorder. The recent result based on the single crystal X–ray diffraction analysis however, supports NaSbF<sub>6</sub>–type for the structure of this salt [7]. Coordination number of the fluorine atoms around the cation is six.

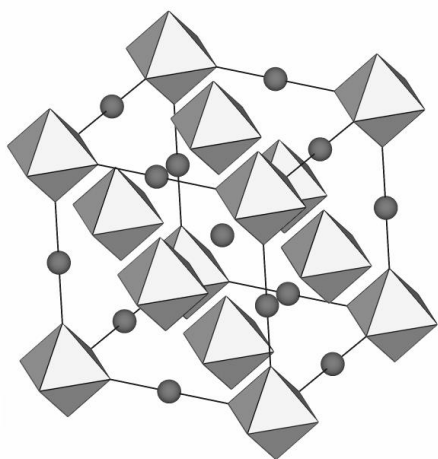


Fig. 2. The cubic unit cell and structure of NaSbF<sub>6</sub>–structural type.

Table 3

NaSbF<sub>6</sub>–type (cubic,  $Fm\bar{3}m$ , No. 225,  $Z = 4$ , C.N.(A<sup>I</sup>) = 6) (previously NaPF<sub>6</sub>–type)

|                    | Lattice Constants<br>$a / \text{\AA}$ | $V / \text{\AA}^3$ | Structural Data <sup>a)</sup> | Ref.      |
|--------------------|---------------------------------------|--------------------|-------------------------------|-----------|
| NaPF <sub>6</sub>  | 7.6140(5)                             | 441.41(4)          | structure; single crystal     | [1,7]     |
| NaReF <sub>6</sub> | 8.18                                  | 547.3              | unit cell; powder data        | [1,2]     |
| NaSbF <sub>6</sub> | 8.184(5)                              | 547.3              | structure; powder data        | [2,17,27] |
| NaMoF <sub>6</sub> | 8.194                                 | 550.2              | unit cell; powder data        | [1,2]     |
| NaWF <sub>6</sub>  | 8.18                                  | 547.3              | unit cell; powder data        | [1,2]     |
| NaNbF <sub>6</sub> | 8.26                                  | 563.6              | unit cell; powder data        | [1,2]     |
|                    | 8.28                                  | 567.7              | unit cell; powder data        | [28]      |
| NaTaF <sub>6</sub> | 8.28                                  | 567.7              | unit cell; powder data        | [1,2]     |

<sup>a)</sup>Data were collected by powder or single crystal X–ray diffraction methods.

### 2.3 Structures of cubic $APF_6$ and $AAsF_6$ with orientational disorders of the anions (Figs. 3 and 4)

Some of the structures of  $AMF_6$  ( $M = P, As$ ) in Table 4 were originally reported as “ $KPF_6$ -type” and later renamed to  $CsPF_6$  structure of the  $Pa\bar{3}$  space symmetry. This structure could be described by starting from  $NaSbF_6$ -type ( $Fm\bar{3}m$ ), then rotating the octahedral  $PF_6$  anion by  $60^\circ$  around the three-fold axis of the lattice (the diagonal direction of the unit cell). The choice of the three-fold axis out of four of them for the rotation is uniquely determined for each  $PF_6^-$  to keep the cubic symmetry. By the rotation, two fluorine atoms from each  $PF_6^-$  equally coordinate to one cation, increasing the coordination number to 12 as a total. As a result, the space symmetry descends to  $Pa\bar{3}$  and the lattice becomes primitive. However, the single crystal structure recently determined for some salts revealed that the lattices of these compounds are actually not primitive but preserve face-centered cubic symmetry. This is caused by the random choice of the rotation axis of each  $PF_6^-$  out of the four three-fold axes.[7] As a result, twenty-four sites for fluorine atoms around a phosphorus atom, corresponding to a special position (96k), are equally occupied with the occupancy ratio of 0.25. Coordination of the  $A^+$  cation by fluorine atoms is unchanged by the rotation. The coordination number of  $A^+$  cation is still 12.

Another type of  $AMF_6$  that possesses  $Fm\bar{3}m$  symmetry is found for  $AgPF_6$  and  $AgAsF_6$  [29]. In this case, the disorder occurs by the choice of the three four-fold rotational axes with the rotation of  $45^\circ$  from the original position in  $NaSbF_6$  structure. Twenty-four sites for fluorine atoms around four  $PF_6^-$  anions corresponding two special positions (24e and 48h) are equally occupied with the occupancy ratio of 0.33. The averaged coordination number of fluorine atoms around the cation is calculated to be 10 as a sum of them at 24e (2) and 48h (8).

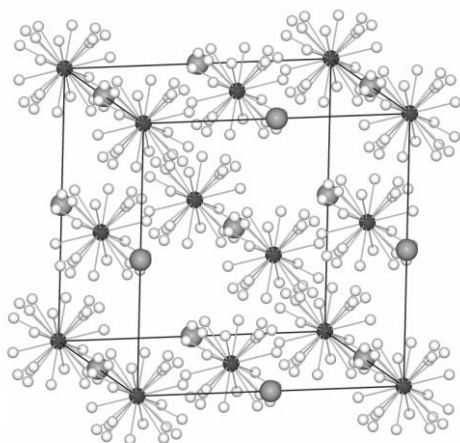


Fig. 3. The cubic unit cell and structure of  $CsPF_6$ -structural type with disordered  $PF_6$  units.

The structures of the cubic  $\text{APF}_6$  and  $\text{AAsF}_6$  in Table 4 have not been determined in detail unless otherwise noted. It has not been clarified either if some of the  $\text{PF}_6$  and/or  $\text{AsF}_6$  salts crystallize in the former  $\text{CsPF}_6$  structure ( $Pa\bar{3}$ ) in which no disorders occur in the orientation of  $\text{PF}_6^-$  or  $\text{AsF}_6^-$ . Single crystal X-ray or neutron powder diffraction study is necessary for further discussions on the detailed structure of these compounds.

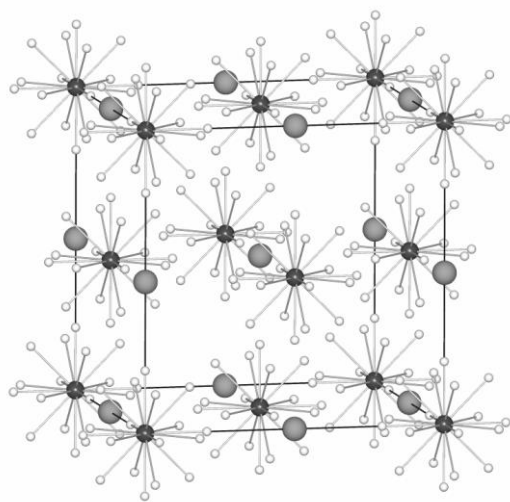


Fig. 4. The cubic unit cell and structure of  $\text{AgPF}_6$ —structural type with disordered  $\text{PF}_6$  units.

Table 4

Cubic  $\text{AMF}_6$  ( $M = \text{P, As}$ ),  $Fm\bar{3}m$ , No. 225,  $Z = 4$ , C.N.(A<sup>1</sup>) = 10 (for  $\text{AgPF}_6$  type), 12 (for  $\text{CsPF}_6$  type); previously classified as  $Pa\bar{3}$   $\text{CsPF}_6$ -type

|                  | Lattice Constants<br>$a / \text{\AA}$ | $V / \text{\AA}^3$ | Structure type  | Structural Data <sup>a)</sup>           | Ref       |
|------------------|---------------------------------------|--------------------|-----------------|-----------------------------------------|-----------|
| $\text{AgPF}_6$  | 7.5508(7)                             | 430.51(12)         | $\text{AgPF}_6$ | structure; single crystal               | [7,29,30] |
| $\text{AgAsF}_6$ | 7.7548(21)                            | 466.34(37)         | $\text{AgPF}_6$ | structure; single crystal               | [29,30]   |
| $\text{KPF}_6$   | 7.7891(7)                             | 472.57(6)          | $\text{CsPF}_6$ | structure; single crystal <sup>b)</sup> | [7]       |
| $\text{KAsF}_6$  | 8.0560                                | 522.83             |                 | unit cell; powder data                  | [8]       |
| $\text{InPF}_6$  | 8.07(2)                               | 524.9              |                 | unit cell; powder data                  | [31]      |
| $\text{TlPF}_6$  | 7.94                                  | 500.6              |                 | structure; powder data                  | [1]       |
| $\text{RbPF}_6$  | 7.887(8)                              | 490.6(8)           | $\text{CsPF}_6$ | unit cell; single crystal               | [7]       |
| $\text{RbAsF}_6$ | 8.246(4)                              | 560.7              |                 | unit cell; powder data                  | [12]      |
| $\text{CsPF}_6$  | 8.197(2)                              | 550.9(2)           | $\text{CsPF}_6$ | structure; single crystal <sup>c)</sup> | [7]       |
| $\text{CsAsF}_6$ | 8.384(5)                              | 589.3              |                 | unit cell; powder data                  | [12]      |

<sup>a)</sup>Data were collected by powder or single crystal X-ray diffraction methods. <sup>b)</sup>For high-pressure behaviour of the cubic phase of  $\text{KPF}_6$  see Ref. [32]. <sup>c)</sup>For other possible high-temperature modifications see Ref. [7].

## 2.4 Tetragonal KSbF<sub>6</sub> (T) –structural types and similar structures (Fig. 5)

There seems to be some confusion in the literature structures of this type. Some sources describe this structure as one structural type, [3] meanwhile others as two different types [4]. There is a group of  $AMF_6$  compounds classified as  $KNbF_6$  structure [2]. In these compounds,  $MF_6$  octahedra are significantly compressed ( $O_h$  to  $D_{3d}$ ), *cis* F–M–F angle being about 45°. However, if the fluorine atoms located at  $4e$  in  $P\bar{4}c2$  (No. 116) are repositioned to  $4f$ , the  $MF_6$  anions recover their octahedral shape. The reported space groups of  $KSbF_6$  (T) [33],  $AgTaF_6$  [30], and  $KNbF_6$  [34] are  $P\bar{4}2m$ ,  $P4_2/mcm$  and  $P\bar{4}c2$ , respectively. However, their structures are the same except the difference in the manner of slight deformation of the  $MF_6$  octahedron (in the case of  $KNbF_6$ , fluorine atoms should be repositioned). Further examination is necessary to check the structural differences in these compounds. Especially, unusual deformation of  $MF_6$  in the  $KNbF_6$  structure should be carefully re-examined. Cations and anions form CsCl-type arrangement with (8,8) coordination. Doubling of the CsCl cell along the *c*-axis is due to different orientations of  $MF_6$  octahedra that are slightly compressed along this axis ( $O_h$  to  $D_{2h}$ ). The cation is coordinated by four F(1) from four different  $MF_6$  and eight F(2) from the other four different  $MF_6$ , forming a dodecahedral coordination. The coordination number varies by the definition. In the case of  $AgTaF_6$  for example, the distance Ta–F(2) (2.46(2) Å) is shorter than Ta–F(1) (2.91(3) Å). Therefore the coordination number based on the closest approach of the F atoms is eight.

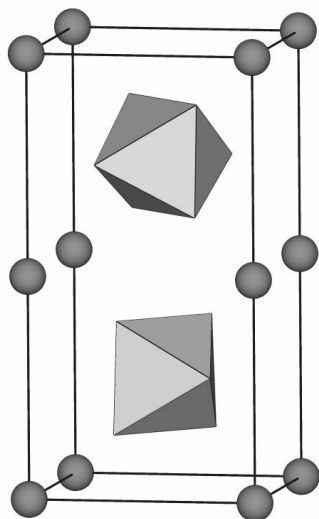


Fig. 5. The tetragonal unit cell and structure of  $KSbF_6$  (T)–structural type. The origin is set at the K position.

Table 5  
Tetragonal  $AMF_6$ ,  $Z = 2$ , C.N.(A<sup>1</sup>) = 8–12

|                    | Lattice Constants |                  | $V / \text{\AA}^3$ | Space group  | Structural Data <sup>a)</sup> | Ref.         |
|--------------------|-------------------|------------------|--------------------|--------------|-------------------------------|--------------|
|                    | $a / \text{\AA}$  | $c / \text{\AA}$ |                    |              |                               |              |
| AgVF <sub>6</sub>  | 4.90              | 9.42             | 226.2              | $P\bar{4}c2$ | unit cell; powder data        | [1,2]        |
| AgRuF <sub>6</sub> | 4.85              | 9.54             | 224.4              | $P\bar{4}c2$ | unit cell; powder data        | [1,2]        |
| AgIrF <sub>6</sub> | 4.85              | 9.70             | 228.2              | $P\bar{4}c2$ | unit cell; powder data        | [1,2]        |
| AgOsF <sub>6</sub> | 4.92              | 9.58             | 231.8              | $P\bar{4}c2$ | unit cell; powder data        | [1,2]        |
| AgBiF <sub>6</sub> | 5.079(2)          | 9.552(3)         | 246.4              | $P\bar{4}2m$ | unit cell; powder data        | [19]         |
| AgNbF <sub>6</sub> | 4.9780(10)        | 9.6040(10)       | 237.99(12)         | $P4_2/mcm$   | unit cell; single crystal     | [30]         |
| AgTaF <sub>6</sub> | 4.9949(4)         | 9.6051(8)        | 239.64(6)          | $P4_2/mcm$   | structure; single crystal     | [30]         |
| KReF <sub>6</sub>  | 5.044             | 10.09            | 256.8              | $P\bar{4}c2$ | unit cell; powder data        | [1,2]        |
| KSbF <sub>6</sub>  | 5.16(1)           | 10.07(2)         | 267.86             | $P\bar{4}2m$ | structure; single crystal     | [9,10,17,33] |
| KMoF <sub>6</sub>  | 5.085             | 9.97             | 257.8              | $P\bar{4}c2$ | unit cell; powder data        | [2]          |
| KWF <sub>6</sub>   | 5.105             | 10.09            | 263                | $P\bar{4}c2$ | unit cell; powder data        | [2]          |
| KNbF <sub>6</sub>  | 5.18(2)           | 10.05(2)         | 269.8              | $P\bar{4}c2$ | structure; single crystal     | [10,34]      |
|                    | 5.18              | 10.08            | 270.5              |              | unit cell; powder data        | [43]         |
| KTaF <sub>6</sub>  | 5.20(2)           | 10.05(2)         | 271.8              | $P\bar{4}c2$ | structure; single crystal     | [1,2,34]     |
| KBiF <sub>6</sub>  | 5.248             | 10.07            | 277.34             | $P\bar{4}c2$ | structure; powder data        | [10,17]      |

<sup>a)</sup>Data were collected by powder or single crystal X-ray diffraction methods.

## 2.5 AgSbF<sub>6</sub>–structural type and similar structures (Fig. 6)

The array of cations and anions is a CsCl-type with no compression. Therefore the  $SbF_6^-$  anion is a regular octahedron, which contrasts to that in the tetragonal  $AMF_6$ . Four orientations of  $SbF_6^-$  octahedron occur, the unit cell being a cube with a doubled lattice constant containing eight  $SbF_6^-$  anions forming (8,8) coordination. However, six fluorine atoms from six different  $SbF_6^-$  out of eight coordinate to a silver atom. In Table 6, only the structure of AgSbF<sub>6</sub> has been determined by single crystal X-ray diffraction [30]. The same space group,  $Ia\bar{3}$ , was originally proposed also for the KSbF<sub>6</sub> as a low temperature form (high temperature form is tetragonal), however, different space groups such as  $I23$  or  $I2_13$  were proposed later. The structure of the potassium salts should be re-examined to confirm the structural difference from the silver salts (Table 6).

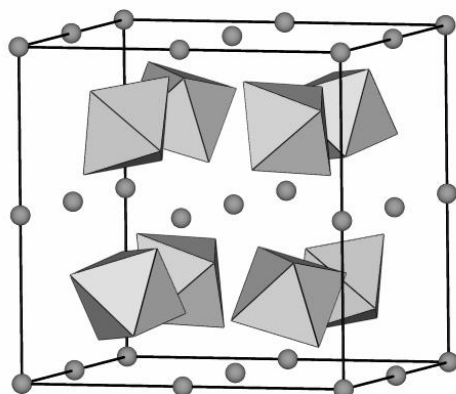


Fig. 6. The cubic unit cell and structure of  $\text{AgSbF}_6$ -structural type. The origin is set at the Ag position.

Table 6

$\text{AgSbF}_6$ -type (cubic,  $Ia\bar{3}$ , No. 206,  $Z = 8$ , C.N.(A<sup>1</sup>) = 6)

|                  | Lattice<br>Constants<br>$a / \text{\AA}$ | $V / \text{\AA}^3$ | Space group        | Structural Data <sup>b)</sup>        | Ref.    |
|------------------|------------------------------------------|--------------------|--------------------|--------------------------------------|---------|
| $\text{AgRuF}_6$ | 9.653(10)                                | 899.5(14)          | $Ia\bar{3}$        | unit cell; powder data               | [19]    |
| $\text{AgIrF}_6$ | 9.704(2)                                 | 913.80(28)         | $Ia\bar{3}$        | unit cell; powder data               | [19]    |
| $\text{AgOsF}_6$ | 9.7318(9)                                | 921.68(13)         | $Ia\bar{3}$        | unit cell; powder data               | [19]    |
| $\text{AgSbF}_6$ | 9.857(5)                                 | 957.7(7)           | $Ia\bar{3}$        | unit cell; powder data               | [19]    |
| $\text{AgSbF}_6$ | 9.7985(4)                                | 940.76(12)         | $Ia\bar{3}$        | structure; single crystal            | [30]    |
| $\text{KSbF}_6$  | 10.176(8)                                | 1053.7(12)         | $I23$ or $I2_13^a$ | unit cell; powder data <sup>c)</sup> | [9,17]  |
| $\text{KBiF}_6$  | 10.34                                    | 1105.51            | $Ia\bar{3}$        | structure; powder data               | [10,17] |

<sup>a)</sup>Initially proposed space group symmetry  $Ia\bar{3}$  was it was later ruled out [9] and new space groups  $I23$  or  $I2_13$  proposed. <sup>b)</sup>Data were collected by powder or single crystal X-ray diffraction methods. <sup>c)</sup>Data collected at 268 K.

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## 2.7 $\text{KOsF}_6$ - structural type (Fig. 7)

This structure is found for some  $\text{KMF}_6$  compounds and for the majority of  $\text{AMF}_6$  compounds with  $A^+$  cations where the radii are larger than 1.5  $\text{\AA}$ . The structure is derived from the CsCl-type arrangement of cations and anions with a rhombohedral distortion. Compression of the CsCl cubic cell along the cell diagonal yields rhombohedral cell with the distortion angle ( $\alpha$ ) which ranges from 95 to 98°. Two fluorine atoms from each  $\text{MF}_6$  anion at the corner of the unit cell are arranged to equally coordinate the central cation. A cation is equally coordinated by 12 fluorine atoms as a total. The cations and fluorine atoms form together

a cubic close packing arrangement in which the former are coordinated by six of the latter in the same layer, three of them above the layer and another three below.

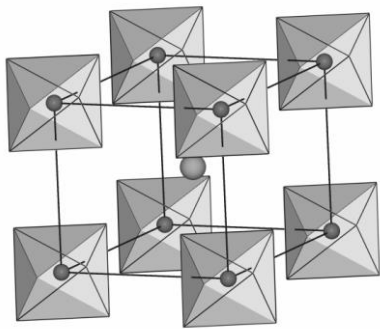


Fig. 7. The rhombohedral unit cell and structure of KOsF<sub>6</sub> –structural type.

Table 7  
KOsF<sub>6</sub>-type (rhombohedral,  $R\bar{3}$ , No.148,  $Z = 1$ , C.N.(A<sup>I</sup>) = 12)

|                    | Lattice Constants |           |                      |           | V / Å <sup>3 a)</sup> | Structural Data <sup>b)</sup>           | Ref.         |
|--------------------|-------------------|-----------|----------------------|-----------|-----------------------|-----------------------------------------|--------------|
|                    | Hexagonal setting |           | Rhombohedral setting |           |                       |                                         |              |
|                    | a / Å             | c / Å     | a / Å                | α / °     |                       |                                         |              |
| KPF <sub>6</sub>   | 7.09              | 7.79      | 4.85                 | 94        | 113.2                 | unit cell; powder data                  | [1]          |
| KAsF <sub>6</sub>  | 7.39(1)           | 7.32(1)   | 4.92                 | 97.49     | 115.4                 | structure; single crystal               | [35,8,17]    |
| KVF <sub>6</sub>   | 7.38              | 7.38      | 4.92                 | 97.2      | 116.0                 | unit cell; powder data                  | [1,2]        |
| KRhF <sub>6</sub>  | 7.46              | 7.36      | 4.96                 | 97.62     | 118.2                 | unit cell; powder data                  | [24]         |
|                    | 7.4060(2)         | 7.2714(2) | 4.915                | 97.772    | 115.13                | structure, single crystal <sup>c)</sup> | [20]         |
| KRuF <sub>6</sub>  | 7.46              | 7.41      | 4.97                 | 97.4      | 119.0                 | unit cell; powder data                  | [2,24]       |
|                    | 7.465             | 7.414     | 4.968(1)             | 97.40(1)  | 119.3                 | unit cell; powder data                  | [36]         |
| KAuF <sub>6</sub>  | 7.348(8)          | 7.198(8)  | 4.874                | 97.84     | 112.2                 | unit cell; powder data                  | [22]         |
|                    | 7.49              | 7.27      | 4.936(5)             | 97.96(3)  | 116.4                 | unit cell; powder data                  | [37]         |
|                    | 7.496(3)          | 7.315(3)  | 4.967                | 97.966    | 118.7                 | structure, single crystal <sup>d)</sup> | [38]         |
| KPtF <sub>6</sub>  | 7.45              | 7.40      | 4.96                 | 97.4      | 118.7                 | unit cell; powder data                  | [2,37,36,39] |
| KIrF <sub>6</sub>  | 7.474             | 7.524     | 4.9744(7)            | 97.399(9) | 119.7                 | unit cell; powder data                  | [36]         |
| KOsF <sub>6</sub>  | 7.486             | 7.487     | 4.991(1)             | 97.18(2)  | 121.1                 | structure; powder data                  | [1,2,40]     |
| KReF <sub>6</sub>  | 7.530             | 7.537     | 5.012(4)             | 97.15(4)  | 123.4                 | unit cell; powder data                  | [36]         |
| InAsF <sub>6</sub> | 7.58(2)           | 7.90(1)   | 5.108                | 95.813    | 131.1                 | unit cell; powder data                  | [31]         |
| TlAsF <sub>6</sub> | 7.55              | 7.59      | 5.04                 | 97.0      | 124.9                 | unit cell; powder data                  | [1]          |
| TlVF <sub>6</sub>  | 7.53              | 7.99      | 5.10                 | 95.2      | 130.9                 | unit cell; powder data                  | [1,2]        |
| TlRuF <sub>6</sub> | 7.60              | 7.74      | 5.09                 | 96.6      | 129.0                 | unit cell; powder data                  | [1,2]        |
| TlSbF <sub>6</sub> | 7.67              | 7.95      | 5.16                 | 96.0      | 135.0                 | structure; powder data                  | [1]          |
| TlMoF <sub>6</sub> | 7.631             | 7.885     | 5.135                | 96.13     | 132.5                 | unit cell; powder data                  | [1,2]        |

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|                    |                  |                  |                  |                   |                |                                                  |                  |
|--------------------|------------------|------------------|------------------|-------------------|----------------|--------------------------------------------------|------------------|
| TlNbF <sub>6</sub> | 7.662<br>7.766   | 7.853<br>7.960   | 5.142<br>5.21    | 96.37<br>96.37    | 133.1<br>138.6 | unit cell; powder data<br>unit cell; powder data | [1,2,11]<br>[13] |
| TlTaF <sub>6</sub> | 7.672            | 7.881            | 5.148            | 96.34             | 133.9          | unit cell; powder data                           | [1,2]            |
| RbAsF <sub>6</sub> | 7.497(1)         | 7.589(1)         | 5.013            | 96.783            | 123.1          | structure; single crystal                        | [12]             |
| RbVF <sub>6</sub>  | 7.51             | 7.55             | 5.01             | 97.0              | 122.7          | unit cell; powder data                           | [1,2]            |
| RbRhF <sub>6</sub> | 7.61             | 7.62             | 5.06             | 97.14             | 127.4          | unit cell; powder data                           | [24]             |
| RbRuF <sub>6</sub> | 7.59             | 7.66             | 5.07             | 96.88             | 127.4          | unit cell; powder data                           | [2,24]           |
| RbAuF <sub>6</sub> | 7.638(4)         | 7.608(4)         | 5.087            | 97.309            | 128.1          | unit cell; powder data                           | [22]             |
| RbPtF <sub>6</sub> | 7.61             | 7.65             | 5.08             | 97.0              | 127.9          | unit cell; powder data                           | [2]              |
| RbIrF <sub>6</sub> | 7.639            | 7.682            | 5.105            | 97.0              | 129.4          | unit cell; powder data                           | [1,2]            |
| RbOsF <sub>6</sub> | 7.64             | 7.75             | 5.106            | 96.74             | 130.5          | unit cell; powder data                           | [1,2]            |
| RbReF <sub>6</sub> | 7.64             | 7.75             | 5.11             | 96.7              | 130.5          | unit cell; powder data                           | [1,2]            |
| RbSbF <sub>6</sub> | 7.670(1)         | 7.861(2)         | 5.145            | 96.373            | 133.5          | structure, single crystal                        | [1,12]           |
| RbMoF <sub>6</sub> | 7.63             | 7.79             | 5.11             | 96.13             | 130.6          | unit cell; powder data                           | [1,2]            |
| RbWF <sub>6</sub>  | 7.72             | 7.69             | 5.14             | 97.6              | 132.2          | unit cell; powder data                           | [1,2]            |
| RbNbF <sub>6</sub> | 7.66             | 7.85             | 5.14             | 96.4              | 133.1          | unit cell; powder data                           | [13,11]          |
| RbTaF <sub>6</sub> | 7.663            | 7.848            | 5.14             | 96.4              | 133.1          | unit cell; powder data                           | [1]              |
| RbBiF <sub>6</sub> | 7.712            | 7.889            | 5.171            | 96.44             | 135.4          | structure; powder data                           | [25,17]          |
| CsAsF <sub>6</sub> | 7.723(1)         | 8.050(1)         | 5.204            | 95.806            | 138.6          | structure; single crystal                        | [12]             |
| CsVF <sub>6</sub>  | 7.80             | 8.04             | 5.24             | 96.2              | 141.2          | unit cell; powder data                           | [1]              |
| CsRhF <sub>6</sub> | 7.81             | 8.02             | 5.24             | 96.31             | 141.2          | unit cell; powder data                           | [24]             |
| CsRuF <sub>6</sub> | 7.80             | 8.07             | 5.25             | 96.3              | 141.7          | unit cell; powder data                           | [2,24]           |
| CsAuF <sub>6</sub> | 7.640(5)<br>7.81 | 8.133(6)<br>8.00 | 5.204<br>5.24(1) | 95.34<br>96.43(5) | 137.0<br>140.9 | unit cell; powder data<br>unit cell; powder data | [22]<br>[37]     |
| CsPtF <sub>6</sub> | 7.86             | 8.05             | 5.27             | 96.4              | 143.4          | unit cell; powder data                           | [2]              |
| CsIrF <sub>6</sub> | 7.85             | 8.08             | 5.27             | 96.2              | 143.6          | unit cell; powder data                           | [1,2]            |
| CsOsF <sub>6</sub> | 7.85             | 8.12             | 5.28             | 96.1              | 144.5          | unit cell; powder data                           | [1,2]            |
| CsReF <sub>6</sub> | 7.853(1)         | 8.140(1)         | 5.284            | 95.996            | 144.9          | structure; single crystal <sup>9)</sup>          | [14,41]          |
| CsSbF <sub>6</sub> | 7.904(1)         | 8.261(1)         | 5.330            | 95.717            | 149.0          | structure; single crystal                        | [41,42,17]       |
| CsMoF <sub>6</sub> | 7.86             | 8.15             | 5.29             | 96.0              | 145.4          | unit cell; powder data                           | [1,2]            |
| CsWF <sub>6</sub>  | 7.85             | 8.30             | 5.31             | 95.5              | 147.7          | unit cell; powder data                           | [1,2]            |
| CsNbF <sub>6</sub> | 7.97             | 8.07             | 5.32             | 95.8              | 147.9          | unit cell; powder data                           | [2,13]           |
| CsTaF <sub>6</sub> | 7.96             | 8.17             | 5.32             | 95.8              | 149.3          | unit cell; powder data                           | [2]              |
| CsBiF <sub>6</sub> | 7.930            | 8.274            | 5.345            | 95.76             | 150.1          | structure; powder data                           | [25,17]          |

<sup>a)</sup>Volume is given for rhombohedral unit cell. <sup>b)</sup>Data were collected by powder or single crystal X-ray diffraction methods. <sup>c)</sup>Data collected at 158 K; <sup>d)</sup>Data collected at 200 K. <sup>e)</sup>Data collected at 293 K.

### 3. A<sub>2</sub>MF<sub>7</sub> compounds

Table 8.  
Known A<sub>2</sub>MF<sub>7</sub> compounds

|    | Nb                                   | Ta                                      | W                       | Sb        | Bi        |
|----|--------------------------------------|-----------------------------------------|-------------------------|-----------|-----------|
| Li | Ref. [43]                            | /                                       | /                       | /         | /         |
| Na | Ref. [43,44]                         | Ref. [45,46]                            | /                       | /         | Ref. [53] |
| K  | Refs. [43,44,47,48,49] <sup>a)</sup> | Refs. [45,46,48,49,50,51] <sup>a)</sup> | Ref. [52] <sup>a)</sup> | Ref. [53] | Ref. [53] |
| Rb | Ref. [13,44]                         | Ref. [46,54]                            | Ref.[52]                | /         | Ref. [53] |
| Cs | Ref. [13]                            | Ref. [46,54]                            | /                       | Ref. [53] | Ref. [53] |
| Tl | Ref. [11,13]                         | Ref. [46]                               | /                       | /         | /         |

<sup>a)</sup>Crystal structure known.

Known  $A_2MF_7$  compounds are given in Table 8. The most investigated compounds are  $K_2NbF_7$  and  $K_2TaF_7$ , because of their use as initial materials for metals production. The available data about  $K_2TaF_7$  preparation, main properties and structure have been recently reviewed.[50]  $K_2TaF_7$  crystallizes in the monoclinic space group  $P2_1/c$  (No. 14) with  $Z = 4$  (Table 9).[48]

Table 9.  
Crystal data of  $A_2MF_7$  compounds

|             | Crystal system            | Structural Data <sup>a)</sup>                                                                                      |                              | Ref.    |
|-------------|---------------------------|--------------------------------------------------------------------------------------------------------------------|------------------------------|---------|
| $Na_2NbF_7$ | monoclinic                | $a = 5.38 \text{ \AA}$<br>$b = 11.84 \text{ \AA}$<br>$c = 8.03 \text{ \AA}$<br>$\beta = 90^\circ$                  | unit cell;<br>powder data    | [43]    |
| $K_2NbF_7$  | monoclinic                | $a = 5.846(3) \text{ \AA}$<br>$b = 12.693(6) \text{ \AA}$<br>$c = 8.515(4) \text{ \AA}$<br>$\beta = 90.0(1)^\circ$ | structure,<br>single crystal | [47]    |
| $Rb_2NbF_7$ | monoclinic                | $a = 10.60 \text{ \AA}$<br>$b = 10.10 \text{ \AA}$<br>$c = 9.65 \text{ \AA}$<br>$\beta = 99.5^\circ$               | unit cell;<br>powder data    | [13]    |
| $Cs_2NbF_7$ | monoclinic                | $a = 11.50 \text{ \AA}$<br>$b = 10.97 \text{ \AA}$<br>$c = 9.08 \text{ \AA}$<br>$\beta = 95^\circ$                 | unit cell;<br>powder data    | [13]    |
| $Tl_2NbF_7$ | rhombohedral              | $a = 10.97 \text{ \AA}$<br>$\alpha = 9.25^\circ$                                                                   | unit cell;<br>powder data    | [11,13] |
| $Na_2TaF_7$ | isomorphous to $K_2TaF_7$ |                                                                                                                    | powder data                  | [45,46] |
| $K_2TaF_7$  | monoclinic                | $a = 5.8559(6) \text{ \AA}$<br>$b = 12.708(1) \text{ \AA}$<br>$c = 8.5125(9) \text{ \AA}$<br>$\beta = 90.17^\circ$ | structure,<br>single crystal | [48,50] |
| $K_2WF_7$   | orthorhombic              | $a = 9.800(2) \text{ \AA}$<br>$b = 5.736(11) \text{ \AA}$<br>$c = 11.723(2) \text{ \AA}$                           | structure,<br>single crystal | [52]    |

<sup>a)</sup>Data were collected by powder or single crystal X-ray diffraction methods.

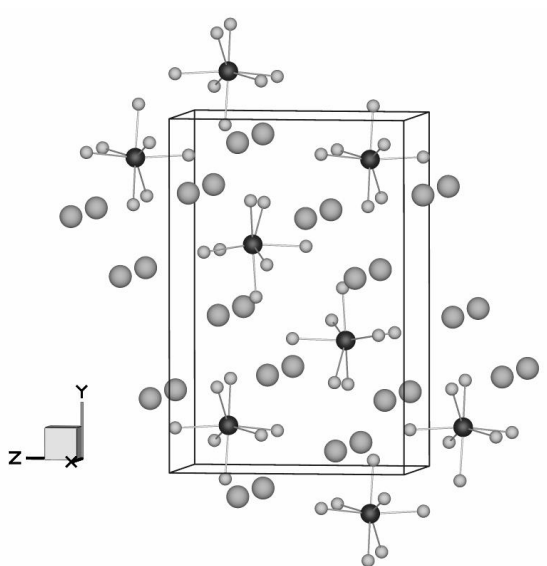


Fig. 8. Part of the crystal structure  $K_2TaF_7$ .

The crystal structure of  $K_2TaF_7$  consists from potassium cations and  $TaF_7^{2-}$  anions (Fig. 8). Below 150 K,  $TaF_7^{2-}$  anion is built as trigonal prism with six fluorine atoms in the vertices. The seventh fluorine atom is placed above the centre of rectangular face of the prism.[50] With increasing temperature deformation of  $TaF_7^{2-}$  anions occurs.[50]

Crystal structures of  $K_2NbF_7$  and  $K_2WF_7$  were also determined by single crystal X-ray diffraction. The former is isostructural to  $K_2TaF_7$ , meanwhile  $K_2WF_7$  crystallizes in an orthorhombic crystal system (Table 9), space group  $Pnma$  (No. 62) with  $Z = 4$ . [52] In  $K_2WF_7$  structure, the tungsten atom is surrounded by an array of seven fluoride ligands in a distorted trigonal prism where one of the rectangular faces is capped by the seventh fluorine atom.[52] Two of the fluorine atoms are unequally disordered between two sets of positions (Fig. 9). Potassium cations are 11-coordinated with fluorine atoms, which is in contrast with  $K_2NbF_7$  and  $K_2TaF_7$  structures, both of which contain 9-coordinate potassium cations.

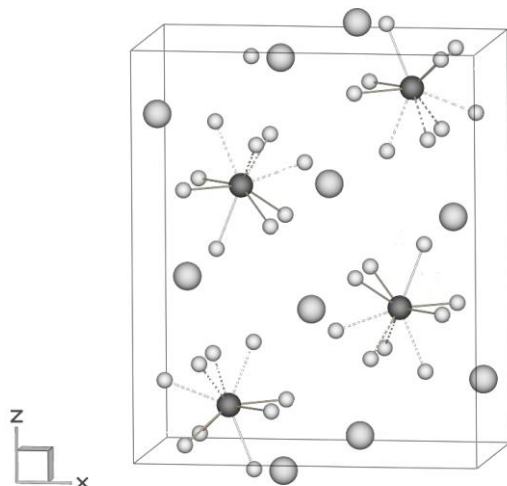


Fig. 9. Part of the crystal structure of  $K_2WF_7$  (dashed lines represent bonds between tungsten and two pairs of disordered fluorine atoms).

For the rest of known  $A_2NbF_7$  ( $A = Li$ , [43]  $Na$ , [43]  $Rb$ , [13]  $Cs$ , [13] and  $Tl$  [11, 13]) compounds only lattice parameters were reported.  $Na_2NbF_7$  is reported to be isostructural to  $K_2NbF_7$ . [43]

In the case of other  $A_2TaF_7$  ( $A = Na$ ,  $Rb$ ,  $Cs$ ,  $Tl$ ) salts, sodium compound is reported to be isomorphous to  $K_2TaF_7$ . [45]

Reports about mixed-alkali-cation niobium and tantalum heptafluoro complexes ( $NaANbF_7$ ,  $A = K$ ,  $Rb$ ;  $NaATaF_7$ ,  $A = K$ ,  $Rb$ ,  $Cs$ ) also exist. [55]

$Rb_2WF_7$  was characterized by Raman spectroscopy, [52] meanwhile  $SbF_7^{2-}$  and  $BiF_7^{2-}$  salts were studied by vibrational spectroscopy and *ab initio* electronic structure calculations. [53] They possess pentagonal bipyramidal, highly fluxional structures of  $D_{5h}$  symmetry.

#### 4. $A_3MF_8$ compounds

Table 10  
Known  $A_3MF_8$  compounds.

|    | Nb           | Ta                            | Mo        | W               |
|----|--------------|-------------------------------|-----------|-----------------|
| Li | Ref. [43]    | /                             | /         | /               |
| Na | Ref. [43]    | Ref. [45,46,56] <sup>a)</sup> | /         | Ref. [52]       |
| K  | Ref. [43,44] | [46]                          | Ref. [57] | Ref. [52,57,58] |
| Rb | Ref. [13]    | /                             | /         | Ref. [52]       |
| Cs | Ref. [13]    | /                             | /         | /               |
| Tl | Ref. [11,13] | /                             | /         | /               |

<sup>a)</sup>Crystal structure known.

Known  $A_3MF_8$  compounds are given in Table 11. The complete crystal structure determinations was made only for  $Na_3TaF_8$ . [56] It crystallizes in a monoclinic space group  $C2/c$  (No. 15) with  $Z = 4$  (Table 12). The structure consists of  $Na^+$  cations and  $TaF_8^{3-}$  anions (Fig. 10).

Table 11  
Crystal data of  $A_3MF_8$  compounds

|             | Crystal system                 | Structural Data <sup>a)</sup>                                                                       | Ref.                                 |
|-------------|--------------------------------|-----------------------------------------------------------------------------------------------------|--------------------------------------|
| $Na_3NbF_8$ | isostructural with $Na_3TaF_8$ | powder data                                                                                         | [43]                                 |
| $Rb_3NbF_8$ | monoclinic                     | $a = 10.65 \text{ \AA}$<br>$b = 9.40 \text{ \AA}$<br>$c = 8.58 \text{ \AA}$<br>$\beta = 91.2^\circ$ | unit cell;<br>powder data<br>[13]    |
| $Cs_3NbF_8$ | monoclinic                     | $a = 11.20 \text{ \AA}$<br>$b = 9.85 \text{ \AA}$<br>$c = 8.93 \text{ \AA}$<br>$\beta = 91.5^\circ$ | unit cell;<br>powder data<br>[13]    |
| $Tl_3NbF_8$ | hexagonal                      | $a = 8.59 \text{ \AA}$<br>$c = 6.69 \text{ \AA}$                                                    | unit cell;<br>powder data<br>[13]    |
| $Na_3TaF_8$ | monoclinic                     | $a = 11.52 \text{ \AA}$<br>$b = 5.38 \text{ \AA}$<br>$c = 11.21 \text{ \AA}$<br>$\beta = 120^\circ$ | structure,<br>single crystal<br>[56] |
| $K_3MoF_8$  | cubic                          | $a = 14.1 \text{ \AA}$                                                                              | unit cell;<br>powder data<br>[57]    |
| $K_3WF_8$   | rhombohedral                   | $a = 9.75 \text{ \AA}$<br>$\alpha = 86.4^\circ$                                                     | unit cell;<br>powder data<br>[58]    |

<sup>a)</sup>Data were collected by powder or single crystal X-ray diffraction methods.

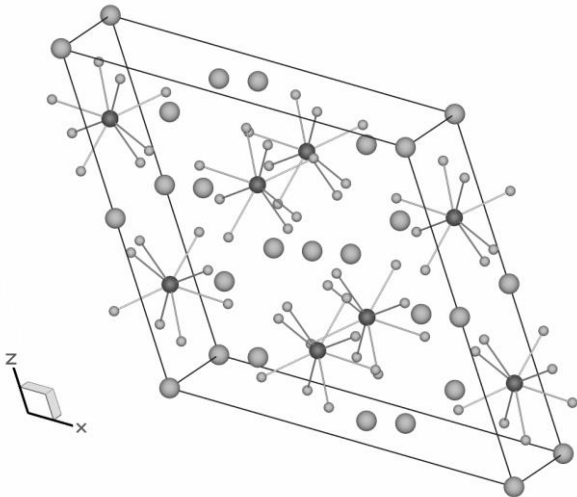


Fig. 10. Part of the crystal structure of  $Na_3TaF_8$ .

For other compounds only lattice parameters determined from powder data are available. (Table 12)  $\text{Na}_3\text{NbF}_8$  is reported to be isostructural with  $\text{Na}_3\text{TaF}_8$ . [13]  $\text{Rb}_3\text{NbF}_8$  and  $\text{Cs}_3\text{NbF}_8$  appear to be isostructural, but different from  $\text{Tl}_3\text{NbF}_8$ . [13]  $\text{K}_3\text{WF}_8$  is reported to be rhombohedral. There are no available structural data about other  $\text{A}_3\text{WF}_8$  ( $\text{A} = \text{Na}, \text{Rb}$ ) compounds. Together with  $\text{K}_3\text{WF}_8$  they were characterized by their Raman spectra in the molten FLINAK eutectic melt. [52]

## 5. $\text{AM}_2\text{F}_{11}$ compounds

Known  $\text{AM}_2\text{F}_{11}$  compounds are given in Table 13.  $\text{AV}_2\text{F}_{11}$  ( $\text{A} = \text{K}, \text{Cs}$ ) [59],  $\text{CsTa}_2\text{F}_{11}$  [63,64] and  $\text{CsBi}_2\text{F}_{11}$  [60] were characterized by vibrational spectroscopy only.

Table 12  
Known  $\text{AM}_2\text{F}_{11}$  compounds.

|    | V         | Nb                | Ta            | Sb                      | Bi        |
|----|-----------|-------------------|---------------|-------------------------|-----------|
| Ag | /         | /                 | /             | Ref. [61] <sup>a)</sup> | /         |
| K  | Ref. [59] | Ref. [43]         | /             | Ref. [62] <sup>a)</sup> | /         |
| Rb | /         | Ref. [13]         | /             | Ref. [62]               | /         |
| Cs | Ref. [59] | Refs. [13, 63,64] | Refs. [63,64] | Ref. [62] <sup>a)</sup> | Ref. [60] |
| Tl | /         | Ref. [11,13]      | /             | Ref. [62]               | /         |

<sup>a)</sup>Crystal structure known.

For  $\text{ANb}_2\text{F}_{11}$  ( $\text{A} = \text{Rb}, \text{Cs}, \text{Tl}$ ) compounds there are only lattice parameters reported (Table 13), [13].

Most extensive studies were made in  $\text{AF-SbF}_5$  system where crystal structures of  $\text{ASb}_2\text{F}_{11}$  ( $\text{A} = \text{Ag}, \text{K}, \text{Cs}$ ) were determined. [61,62]

Table 13  
Crystal data of  $\text{AM}_2\text{F}_{11}$  compounds

|                                            | Crystal system | Structural Data <sup>a)</sup>                                                                                               |                                            | Ref. |
|--------------------------------------------|----------------|-----------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|------|
| $\text{RbNb}_2\text{F}_{11}$ <sup>b)</sup> | rhombohedral   | $a = 12.76 \text{ \AA}$<br>$\alpha = 91.2^\circ$                                                                            | unit cell;<br>powder data                  | [13] |
| $\text{CsNb}_2\text{F}_{11}$               | rhombohedral   | $a = 12.47 \text{ \AA}$<br>$\alpha = 91.30^\circ$                                                                           | unit cell;<br>powder data                  | [13] |
| $\text{TlNb}_2\text{F}_{11}$ <sup>b)</sup> | rhombohedral   | $a = 10.70 \text{ \AA}$<br>$\alpha = 94.5^\circ$                                                                            | unit cell;<br>powder data                  | [13] |
| $\text{AgSb}_2\text{F}_{11}$               | orthorhombic   | $a = 10.91.80(7) \text{ \AA}$<br>$b = 12.4628(8) \text{ \AA}$<br>$c = 38.802(3) \text{ \AA}$                                | structure,<br>single crystal <sup>c)</sup> | [61] |
| $\text{KSb}_2\text{F}_{11}$                | orthorhombic   | $a = 11.4165(8) \text{ \AA}$<br>$b = 12.7996(9) \text{ \AA}$<br>$c = 39.485(3) \text{ \AA}$                                 | structure,<br>single crystal <sup>c)</sup> | [62] |
| $\text{CsSb}_2\text{F}_{11}$               | monoclinic     | $a = 7.7410(14) \text{ \AA}$<br>$b = 14.2541(17) \text{ \AA}$<br>$c = 9.5130(15) \text{ \AA}$<br>$\beta = 113.226(6)^\circ$ | structure,<br>single crystal <sup>c)</sup> | [62] |

<sup>a)</sup>Data were collected by powder or single crystal X-ray diffraction methods. <sup>b)</sup>At high temperature there is a phase transition to cubic phase. <sup>c)</sup>Data collected at 250 K.

Crystals of  $\text{KSb}_2\text{F}_{11}$  are orthorhombic (space group  $Pbca$  and  $Z = 24$ ) and isostructural to  $\text{AgSb}_2\text{F}_{11}$ . (Table 14) The complex structure of  $\text{ASb}_2\text{F}_{11}$  ( $A = \text{Ag, K}$ ) reveals three crystallographic non-equivalent  $[\text{Sb}_2\text{F}_{11}]^-$  anions highly distorted from ideal  $D_{4h}$  symmetry. There are also three crystallographic non-equivalent  $A^+$  ( $A = \text{Ag, K}$ ) cations in the crystal structure of corresponding  $[\text{Sb}_2\text{F}_{11}]^-$  salts. The coordination of  $\text{K/Ag}$  atoms in  $\text{ASb}_2\text{F}_{11}$  ( $A = \text{Ag, K}$ ) can be written as eight for two  $A^+$  cations (C.N. = 8) and nine for the third one (C.N. = 9).

$\text{CsSb}_2\text{F}_{11}$  crystallizes monoclinic with the unit cell parameters given in Table 14, space group  $P2_1/n$  (No. 14) and having  $Z = 4$ . The packing diagram is depicted in Fig. 11.

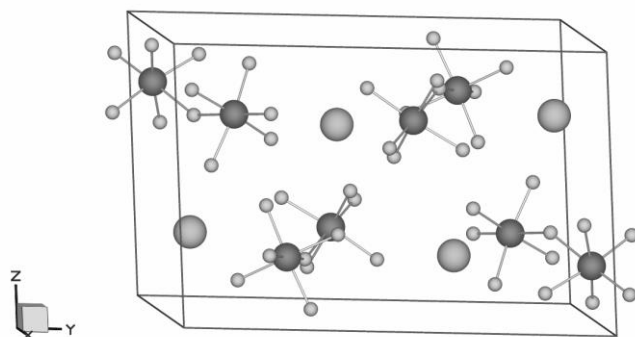


Fig. 11. Packing diagram of  $\text{CsSb}_2\text{F}_{11}$ .

The structure of  $\text{CsSb}_2\text{F}_{11}$  is ionic consisting of discrete  $[\text{Sb}_2\text{F}_{11}]^-$  anions and  $\text{Cs}^+$  cations adopt a simple packing arrangement. As in the case of  $\text{KSb}_2\text{F}_{11}$  the  $\text{Sb}_2\text{F}_{11}^-$  anion in  $\text{CsSb}_2\text{F}_{11}$  is highly distorted from ideal  $D_{4h}$  symmetry. Cesium atom is surrounded by 12 fluorine atoms.

The X-ray powder diffraction photographs indicate that  $\text{RbSb}_2\text{F}_{11}$  and  $\text{TlSb}_2\text{F}_{11}$  are isostructural and distinguish from crystal structure of  $\text{KSb}_2\text{F}_{11}$  or  $\text{CsSb}_2\text{F}_{11}$ , respectively.[62]

## 6. $\text{AM}_3\text{F}_{16}$ and $\text{AM}_4\text{F}_{21}$ compounds

The reports about  $\text{AM}_3\text{F}_{16}$  and  $\text{AM}_4\text{F}_{21}$  compounds are scarce (Table 14).

Table 14  
Known  $\text{AM}_3\text{F}_{16}$  and  $\text{AM}_4\text{F}_{21}$  compounds.

|    | $\text{AM}_3\text{F}_{16}$ |                         | $\text{AM}_4\text{F}_{21}$ |
|----|----------------------------|-------------------------|----------------------------|
|    | Nb                         | Sb                      | Nb                         |
| K  | Ref. [43]                  | /                       | /                          |
| Rb | Ref. [13]                  | /                       | /                          |
| Cs | /                          | Ref. [62] <sup>a)</sup> | Ref. [13]                  |
| Tl | Ref. [11,13]               | /                       | /                          |

<sup>a)</sup>Crystal structure known.

$[\text{Nb}_3\text{F}_{16}]^-$ -salts were partly characterized by their powder X-ray diffraction patterns.[13,43]  $\text{CsSb}_3\text{F}_{16}$  was completely structurally characterized on single crystal.[62]  $\text{CsSb}_3\text{F}_{16}$  crystallizes orthorhombic at 200 K, with  $a = 22.07(3) \text{ \AA}$ ,  $b = 7.726(11) \text{ \AA}$ ,  $c = 16.05(3) \text{ \AA}$ , and  $Z = 8$ , space group  $Pca2_1$  (No. 29). The crystal structure of  $\text{CsSb}_3\text{F}_{16}$  reveals two crystallographic non-equivalent  $[\text{Sb}_3\text{F}_{16}]^-$  anions adopting a *cis*-fluorine-bridged geometry (Fig. 12). The packing diagram is depicted in Fig. 13.

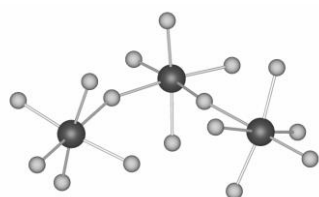


Fig. 12.  $[\text{Sb}_3\text{F}_{16}]^-$  anion adopting a *cis*-fluorine-bridged geometry in the crystal structure of  $\text{CsSb}_3\text{F}_{16}$ .

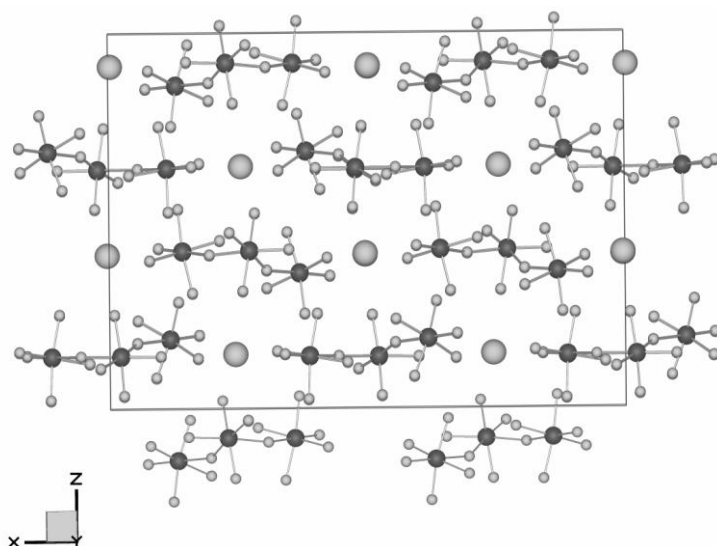


Fig. 13. Packing diagram for  $\text{CsSb}_3\text{F}_{16}$ .

There are also two crystallographic non-equivalent  $\text{Cs}^+$  cations in the crystal structure of  $\text{CsSb}_3\text{F}_{16}$ . These cations are surrounded by 12 fluorine atoms.

The only reported example of  $\text{AM}_4\text{F}_{21}$  compound is  $\text{CsNb}_4\text{F}_{21}$ . [13] The indexation of its powder X-ray diffraction pattern gave rhombohedral unit cell ( $a = 9.52 \text{ \AA}$ ,  $\alpha = 88.8^\circ$ ).

## 7. Conclusions

## Acknowledgement

One of the authors (Z. M.) gratefully acknowledge the Slovenian Research Agency (ARRS) for the financial support of the present study within the research program: P1-0045 Inorganic Chemistry and Technology.

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