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Hexafluoro-, heptafluoro-, and octafluoro-salts, and [MF] (n=2, 3, 4) polyfluorometallates of singly charged metal cations, Li-Cs, Cu, Ag, In and Tl

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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 ^I	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> ^{II}	<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> ^{III} <i>f</i>	<i>g</i> ^{IV} <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> ^V <i>d</i> <i>f</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>e</i> ^{VI} <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> ^{VII}	<i>f</i> ^{VII}	/
Rb	0.166	<i>g</i>	<i>f</i> ^{VIII} <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> ^{VIII}	<i>f</i>	<i>f</i>	<i>f</i> ^{IX}	<i>f</i> ^{IX}	<i>f</i>
Cs	0.181	<i>g</i> ^X	<i>f</i> ^{VIII} <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> ^{VIII}	<i>f</i>	<i>f</i>	<i>f</i> ^{IX}	<i>f</i> ^{IX}	<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.

^IShanon 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: ^{II}Ref. [6,7], ^{III}Ref. [7], ^{IV}Ref. [8], ^VRef. [9], ^{VI}Ref.[10], ^{VII}Ref.[11], ^{VIII}Ref. [12], ^{IX}Ref.[13], ^XRef. [7,14].

2.1 LiSbF₆-structural type (Fig. 1)

All the LiMF₆ and Cu^IMF₆ compounds (although only two examples are so far known for the latter [15],[16]) crystallize in this structure. In the series of NaMF₆, irregularity is observed in the radius ratio rule. LiSbF₆ structure mostly appears for NaMF₆ of which the ionic radius of *M* is small (<0.72 Å). However, NaPF₆ which is the salt with the smallest MF₆ anion in Table 2 does not crystallize in LiSbF₆ structure but in NaSbF₆ structure as a stable form at ambient conditions [7]. On the other hand, NaBiF₆ with the largest MF₆ anion appeared in the Table 2 crystallizes in LiSbF₆ structure rather than in NaSbF₆ structure. In the AgMF₆ series, only AgAuF₆ is known to crystallize in LiSbF₆ 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 NaSbF₆-type. It is regarded to a slightly twisted NaSbF₆ structure so as to elongate the diagonal of the pseudo NaCl-type lattice for the effective packing of ions. MF₆⁻ anions tilt towards the edge of the rhombohedron (17° in the case of LiSbF₆). The cation is coordinated by six fluorine atoms from the six different MF₆⁻ anions. A–F–M chain is not straight but bent (148° in the case of LiSbF₆).

Fig. 1. The rhombohedral unit cell and structure of LiSbF₆-structural type.

Table 2 LiSbF₆-type (rhombohedral, $R\bar{3}$, No.148, $Z = 1$, C.N.(A^I, M^V) = 6)

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

^{a)}Volume is given for rhombohedral unit cell. ^{b)}Where not stated otherwise, data were collected by powder or single crystal X-ray diffraction methods. ^{c)}LiPF₆ prepared by the reaction between the elemental F₂ and equimolar mixture of LiF and P. ^{d)}LiPF₆ prepared by the reaction of LiF with PF₅ in anhydrous HF. ^{e)}SPDD = synchrotron X-ray powder diffraction data at 299 K. ^{f)}Data collected at 293 K. ^{g)}Data collected at 129 K. ^{h)}The authenticity of this compound is doubtful (see Ref. [19]).

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2.2 NaSbF₆–structural type (Fig. 2)

NaSbF₆ structure with the highest symmetry among the AMF_6 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_6 units. NaPF₆ is the only exception in this series which crystallizes in NaSbF₆ structure in spite of the small size of phosphorus atom. The structure of this compound was originally classified as “NaPF₆ 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 NaSbF₆–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 NaSbF₆–structural type.

Table 3

NaSbF₆–type (cubic, $Fm\bar{3}m$, No. 225, $Z = 4$, C.N.(A^I) = 6) (previously NaPF₆–type)

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

^{a)}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° 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° 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 APF_6 and AAsF_6 in Table 4 have not been determined in detail unless otherwise noted. It has not been clarified either if some of the PF_6^- and/or AsF_6^- salts crystallize in the former CsPF_6 structure ($Pa\bar{3}$) in which no disorders occur in the orientation of PF_6^- or 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 AgPF_6 -structural type with disordered PF_6 units.

Table 4

Cubic AMF_6 ($M = \text{P, As}$), $Fm\bar{3}m$, No. 225, $Z = 4$, C.N.(A¹) = 10 (for AgPF_6 type), 12 (for CsPF_6 type); previously classified as $Pa\bar{3}$ CsPF_6 -type

	Lattice Constants $a / \text{\AA}$	$V / \text{\AA}^3$	Structure type	Structural Data ^{a)}	Ref
AgPF_6	7.5508(7)	430.51(12)	AgPF_6	structure; single crystal	[7,29,30]
AgAsF_6	7.7548(21)	466.34(37)	AgPF_6	structure; single crystal	[29,30]
KPF_6	7.7891(7)	472.57(6)	CsPF_6	structure; single crystal ^{b)}	[7]
KAsF_6	8.0560	522.83		unit cell; powder data	[8]
InPF_6	8.07(2)	524.9		unit cell; powder data	[31]
TlPF_6	7.94	500.6		structure; powder data	[1]
RbPF_6	7.887(8)	490.6(8)	CsPF_6	unit cell; single crystal	[7]
RbAsF_6	8.246(4)	560.7		unit cell; powder data	[12]
CsPF_6	8.197(2)	550.9(2)	CsPF_6	structure; single crystal ^{c)}	[7]
CsAsF_6	8.384(5)	589.3		unit cell; powder data	[12]

^{a)}Data were collected by powder or single crystal X-ray diffraction methods. ^{b)}For high-pressure behaviour of the cubic phase of KPF_6 see Ref. [32]. ^{c)}For other possible high-temperature modifications see Ref. [7].

2.4 Tetragonal KSbF₆ (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 , $Z = 2$, $C.N.(A^I) = 8-12$

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

^{a)}Data were collected by powder or single crystal X-ray diffraction methods.

2.5 AgSbF₆—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 AgSbF₆ has been determined by single crystal X-ray diffraction [30]. The same space group, $Ia\bar{3}$, was originally proposed also for the KSbF₆ 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 AgSbF_6 -structural type. The origin is set at the Ag position.

Table 6

AgSbF_6 -type (cubic, $Ia\bar{3}$, No. 206, $Z = 8$, C.N.(A^1) = 6)

	Lattice Constants	$V / \text{\AA}^3$	Space group	Structural Data ^{b)}	Ref.
	$a / \text{\AA}$				
AgRuF_6	9.653(10)	899.5(14)	$Ia\bar{3}$	unit cell; powder data	[19]
AgIrF_6	9.704(2)	913.80(28)	$Ia\bar{3}$	unit cell; powder data	[19]
AgOsF_6	9.7318(9)	921.68(13)	$Ia\bar{3}$	unit cell; powder data	[19]
AgSbF_6	9.857(5)	957.7(7)	$Ia\bar{3}$	unit cell; powder data	[19]
AgSbF_6	9.7985(4)	940.76(12)	$Ia\bar{3}$	structure; single crystal	[30]
KSbF_6	10.176(8)	1053.7(12)	$I23$ or $I2_13^a)$	unit cell; powder data ^{c)}	[9,17]
KBiF_6	10.34	1105.51	$Ia\bar{3}$	structure; powder data	[10,17]

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

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2.7 KOsF_6 - structural type (Fig. 7)

This structure is found for some KMF_6 compounds and for the majority of 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 (α) which ranges from 95 to 98° . Two fluorine atoms from each 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_6 —structural type.

Table 7

KOsF_6 -type (rhombohedral, $R\bar{3}$, No.148, $Z = 1$, C.N.(A^I) = 12)

RKF ₆ -type (rhombohedral, R $\bar{3}$, No.148, Z = 1, C.N.(A) = 12)	Lattice Constants				$V / \text{\AA}^3$ ^{a)}	Structural Data ^{b)}	Ref.
	Hexagonal setting		Rhombohedral setting				
	$a / \text{\AA}$	$c / \text{\AA}$	$a / \text{\AA}$	$\alpha / ^\circ$			
KPF ₆	7.09	7.79	4.85	94	113.2	unit cell; powder data	[1]
KAsF ₆	7.39(1)	7.32(1)	4.92	97.49	115.4	structure; single crystal	[35,8,17]
KVF ₆	7.38	7.38	4.92	97.2	116.0	unit cell; powder data	[1,2]
KRhF ₆	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 ^{c)}	[20]
KRuF ₆	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 ₆	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 ^{d)}	[38]
KPtF ₆	7.45	7.40	4.96	97.4	118.7	unit cell; powder data	[2,37,36,39]
KIrF ₆	7.474	7.524	4.9744(7)	97.399(9)	119.7	unit cell; powder data	[36]
KOsF ₆	7.486	7.487	4.991(1)	97.18(2)	121.1	structure; powder data	[1,2,40]
KReF ₆	7.530	7.537	5.012(4)	97.15(4)	123.4	unit cell; powder data	[36]
InAsF ₆	7.58(2)	7.90(1)	5.108	95.813	131.1	unit cell; powder data	[31]
TlAsF ₆	7.55	7.59	5.04	97.0	124.9	unit cell; powder data	[1]
TlVF ₆	7.53	7.99	5.10	95.2	130.9	unit cell; powder data	[1,2]
TlRuF ₆	7.60	7.74	5.09	96.6	129.0	unit cell; powder data	[1,2]
TlSbF ₆	7.67	7.95	5.16	96.0	135.0	structure; powder data	[1]
TlMoF ₆	7.631	7.885	5.135	96.13	132.5	unit cell; powder data	[1,2]

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

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

3. A₂MF₇ compounds

Table 8.
Known A₂MF₇ 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] ^{a)}	Refs. [45,46,48,49,50,51] ^{a)}	Ref. [52] ^{a)}	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]	/	/	/

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

^{a)}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] ^{a)}	/	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]	/	/	/

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

^{a)}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) Na_3NbF_8 is reported to be isostructural with Na_3TaF_8 . [13] Rb_3NbF_8 and Cs_3NbF_8 appear to be isostructural, but different from Ti_3NbF_8 . [13] K_3WF_8 is reported to be rhombohedral. There are no available structural data about other A_3WF_8 ($\text{A} = \text{Na}, \text{Rb}$) compounds. Together with K_3WF_8 they were characterized by their Raman spectra in the molten FLINAK eutectic melt. [52]

5. AM_2F_{11} compounds

Known AM_2F_{11} compounds are given in Table 13. AV_2F_{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 AM_2F_{11} compounds.

	V	Nb	Ta	Sb	Bi
Ag	/	/	/	Ref. [61] ^{a)}	/
K	Ref. [59]	Ref. [43]	/	Ref. [62] ^{a)}	/
Rb	/	Ref. [13]	/	Ref. [62]	/
Cs	Ref. [59]	Refs. [13, 63,64]	Refs. [63,64]	Ref. [62] ^{a)}	Ref. [60]
Tl	/	Ref. [11,13]	/	Ref. [62]	/

^{a)}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 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 AM_2F_{11} compounds

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

^{a)}Data were collected by powder or single crystal X-ray diffraction methods. ^{b)}At high temperature there is a phase transition to cubic phase. ^{c)}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 $\text{ASb}_2\text{F}_{11}$ ($A = \text{Ag}, \text{K}$) 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^+ ($A = \text{Ag}, \text{K}$) cations in the crystal structure of corresponding $[\text{Sb}_2\text{F}_{11}]^-$ salts. The coordination of K/Ag atoms in $\text{ASb}_2\text{F}_{11}$ ($A = \text{Ag}, \text{K}$) 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 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. AM_3F_{16} and AM_4F_{21} compounds

The reports about AM_3F_{16} and AM_4F_{21} compounds are scarce (Table 14).

Table 14
Known AM_3F_{16} and AM_4F_{21} compounds.

	AM_3F_{16}		AM_4F_{21}
	Nb	Sb	Nb
K	Ref. [43]	/	/
Rb	Ref. [13]	/	/
Cs	/	Ref. [62] ^{a)}	Ref. [13]
Tl	Ref. [11,13]	/	/

^{a)}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 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 AM_4F_{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

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