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Review

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

The AMF_6, A_2MF_7, A_3MF_8, AM_2F_{11}, AM_3F_{16} and AM_4F_{21} compounds (A = Li, Na, K, Rb, Cs, Cu, Ag, In, Tl; M = P, As, V, Rh, Ru, Au, Pt, Ir, Os, Re, Sb, Mo, W, Nb, Ta, Bi) are reviewed.

Some of the structural data of the AMF_6 compounds are based just on powder diffraction work from the middle of the last century. The crystal structure types of AMF_6 compounds have been re-classified in this review, based mainly on single crystal data. The crystal structure types of AMF_6 compounds can be classified into six main groups: $LiSbF_6$ type, $NaSbF_6$ type, structures of cubic APF_6 and $AAsF_6$ with orientational disorder of the anions, tetragonal $KSbF_6$ (T) types and similar structures, $AgSbF_6$ type and similar structures, and $KOsF_6$ type.

Reported crystal structures of A_2MF_7, A_3MF_8, AM_2F_{11}, AM_3F_{16} and AM_4F_{21} compounds are limited. K_2MF_7 (M = Nb, Ta) crystallizes in the monoclinic and K_2WF_7 in the orthorhombic crystal system. Among the A_3MF_8 compounds the complete crystal structure has been determined only for Na_3TaF_8, which is monoclinic. The only known examples of crystal structures of AM_2F_{11} compounds are ASb_2F_{11} (A = Ag, K, Cs). Crystals of KSb_2F_{11} are orthorhombic and isostructural to $AgSb_2F_{11}$, while $CsSb_2F_{11}$ is monoclinic. $CsSb_3F_{16}$ is the only example of a structurally characterized AM_3F_{16} compound. Its crystals are orthorhombic. For the rest of the known A_2MF_7, A_3MF_8, AM_2F_{11}, AM_3F_{16} and AM_4F_{21} compounds, only lattice parameters are known.

Keywords: Hexafluorometallates; Heptafluorometallates; Octafluorometallates; Polyfluorometallates; Crystal structures

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Contents

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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 comprises the AMF_6 compounds, more than 100 of which have been reported (Table 1). The last complete review of their crystal structures dates from the 1960s [1,2] with subsequent brief discussion in Refs. [3,4]. Since then many crystal structures of AMF_6 compounds have been published. Because of this, and because of some discrepancies in the published data, we have carried out a comprehensive review of the crystal structures of AMF_6 compounds and proposed a modified classification. Additionally, literature data relating to other phases in AF–MF_5 systems (A_2MF_7, A_3MF_8, AM_2F_{11}, AM_3F_{16} and AM_4F_{21}) have been included. In these systems only the chemistry of tantalum and niobium was recently reviewed [5].

2. AMF_6 compounds

The structures of AMF_6 compounds can be divided into NaCl and CsCl types. The NaCl type has (6,6)-coordination which is found for the salt whose radius ratio, *r*(cation)/*r*(anion), is small. The CsCl type has (8,8)-coordination and occurs in salts with a large radius ratio. Since the MF_6 anion is not perfectly spherical, its orientation is also affected by the size of the cation and probably by its hardness. Due to differences in the orientation of the anions, a variety of structures are found in both NaCl and CsCl type salts. Depending on the orientation of the anions, the coordination number of fluorine atoms around the cation varies from six, for $LiSbF_6$ (NaCl type) and $NaSbF_6$ (NaCl type) structures, to 12 for the $KOsF_6$ structure (CsCl type). Some of the hexafluorophosphates and arsenates exhibit orientational disorders. The coordination numbers vary from 6 to 12 in the local structure of these compounds. Among them, compounds like $CsPF_6$ (NaCl type) exhibit a fixed 12 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 structures are based only on powder diffraction work from the middle of the 20th century. In this review, we have reclassified the published structures, based mainly on single crystal data.

2.1. $LiSbF_6$ structural type (*Fig. 1*)

All the $LiMF_6$ and Cu^IMF_6 compounds (although only two examples are so far known for the latter [16,17]) crystallize in this structure. In the series of $NaMF_6$, irregularity is observed in the radius ratio rule. $LiSbF_6$ structure is found mainly for $NaMF_6$ whose ionic radius of M is small (<0.72 Å). However, $NaPF_6$, which is the salt with the smallest $[MF_6]^-$ anion in Table 2, crystallizes not in the $LiSbF_6$ but in the $NaSbF_6$ structure, as a stable form under ambient conditions [8]. On the other hand, $NaBiF_6$, with the largest $[MF_6]^-$ anion,

Table 1
Structural types of $A^IM^VF_6$ compounds

	P (0.52[a])	As (0.60[a])	V (0.68[a])	Rh (0.69[a])	Ru (0.705[a])	Au (0.71[a])	Pt (0.71[a])	Ir (0.71[a])	Os (0.715[a])	Re (0.72[a])	Sb (0.74[a])	Mo (0.75[a])	W (0.76[a])	Nb (0.78[a])	Ta (0.78[a])	Bi (0.90[a])
Li (0.90)	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
Cu (0.91)	–	a	–	–	–	–	–	–	–	–	a	–	–	–	–	–
Na (0.116)	b [7,8]	a	a	a	a	a	–	a	a	b	b	b	b	b	b	a
Ag (0.129)	c	c	d	–	d, e	a	–	d, e	d, e	–	e	–	–	h	h	d
K (0.152)	g [8], f	g [9], f	f	f	f	f	f	f	f	d, f	e [10], d, f	d	d	d	d	e [11], d
In	g	f	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tl (0.164)	g	f	f	–	f	–	–	–	–	–	f	f	–	f [12]	f [12]	–
Rb (0.166)	g	f [13], g	f	f	f	f	f	f	f	f	f [13]	f	f	f [14]	f [14]	f
Cs (0.181)	g [8,15]	f [13], g	f	f	f	f	f	f	f	f	f [13]	f	f	f [14]	f [14]	f

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. Information about some high-temperature phases not included in Table 1 and structural transitions in dependence of temperature could be found in Refs. [7–15].

[a] Shanon ionic radii (Å) [6].

Table 2
LiSbF$_6$ type (rhombohedral, $R\bar{3}$, no. 148, $Z = 1$, C.N. (A^{I}, M^{V}) = 6)

	Lattice constants				V (Å^3)[a]	Structural data[b]	References
	Hexagonal setting		Rhombohedral setting				
	a (Å)	c (Å)	a (Å)	α (°)			
LiPF$_6$	4.932(2)	12.658(4)	5.09	57.954	88.9	Structure; single crystal	[18]
	4.932(2)	12.641(5)	5.086	58.012	88.8	Unit cell; powder data[c]	[19]
	4.933(1)	12.657(2)	5.090	57.966	88.9	Unit cell; powder data[d]	[19]
LiAsF$_6$	5.016(1)	13.028(4)	5.220	57.435	94.6	Structure; powder data	[18]
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]	[20–22]
LiRuF$_6$	5.07397(8)	13.5244(3)	5.376	56.314	100.5	Structure; SPDD data[e]	[20,21]
LiAuF$_6$	5.00337(5)	13.7160(2)	5.410	55.091	99.1	Structure; SPDD data	[20,21]
	4.994(1)	13.624(2)	5.379	55.315	98.1	Unit cell; powder data	[23]
LiPtF$_6$	5.02686(4)	13.6559(2)	5.398	55.497	99.6	Structure; SPDD data[e]	[20,21]
LiIrF$_6$	5.06148(4)	13.6260(2)	5.401	55.855	100.8	Single crystal and SPDD[e]	[20–22]
LiOsF$_6$	5.10558(6)	13.6106(2)	5.410	56.307	102.4	Structure; SPDD data[e]	[21]
	5.1111(8)	13.625(4)	5.416	56.308	102.7	Structure; single crystal[f]	[21]
	5.0512(3)	13.5932(9)	5.388	55.901	100.12	Structure; single crystal[g]	[20,21]
LiReF$_6$[h]	5.057	13.735	5.43	55.5	101.4	Unit cell; powder data	[1,2,20]
LiSbF$_6$	5.18(2)	13.60(2)	5.43	56.97	105.3	Structure; single crystal	[18,24]
LiMoF$_6$	5.190	13.585	5.43	57.1	105.6	Unit cell; powder data	[1,20]
LiWF$_6$	5.234	13.606	5.45	57.4	107.6	Unit cell; powder data	[1,2,20]
LiNbF$_6$	5.31810(3)	13.5861(2)	5.471	58.155	110.9	Structure; SPDD data[e]	[20,21]
LiTaF$_6$	5.32006(8)	13.6178(3)	5.481	58.070	111.26	Structure; SPDD data[e]	[20,21]
LiBiF$_6$	5.181	13.99	5.540	55.76	108.4	Structure; powder data	[18,26]
CuAsF$_6$	5.13	13.87	5.49(1)	55.7(1)	105.3	Unit cell; powder data	[16]
CuSbF$_6$	5.304(4)	14.53(1)	5.730	55.138	118.0	Structure; single crystal	[17]
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	[25]
NaRuF$_6$	5.31	14.77	5.80	54.49	120.2	Unit cell; powder data	[25]
NaAuF$_6$	5.237(2)	15.042(4)	5.855	53.13	119.1	Unit cell; powder data	[23]
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	[18,26]
AgAuF$_6$	5.2840(2)	15.0451(6)	5.870	53.498	121.3	Unit cell; SPDD data[e]	[20,27]

[a] Volume is given for the rhombohedral unit cell.
[b] Data were collected by powder or single crystal X-ray diffraction methods.
[c] LiPF$_6$ prepared by reaction between elemental F$_2$ and an equimolar mixture of LiF and P.
[d] LiPF$_6$ prepared by reacting LiF with PF$_5$ 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. [20]).

crystallizes in the LiSbF$_6$ rather than the NaSbF$_6$ structure (Table 2). In the AgMF$_6$ series, only AgAuF$_6$ is known to crystallize in the LiSbF$_6$ structure. The structure is the result of (6,6)-coordination of NaCl-type for the combination of small atomic cations and large hexafluoroanions, as in the case of NaSbF$_6$-type. It is regarded as an NaSbF$_6$ structure, slightly twisted so as to elongate the diagonal of the pseudo NaCl-type lattice for the effective packing of ions. $[MF_6]^-$ anions tilt towards the edge of the rhombohedron (17° in the case of LiSbF$_6$). The cation is coordinated by six fluorine

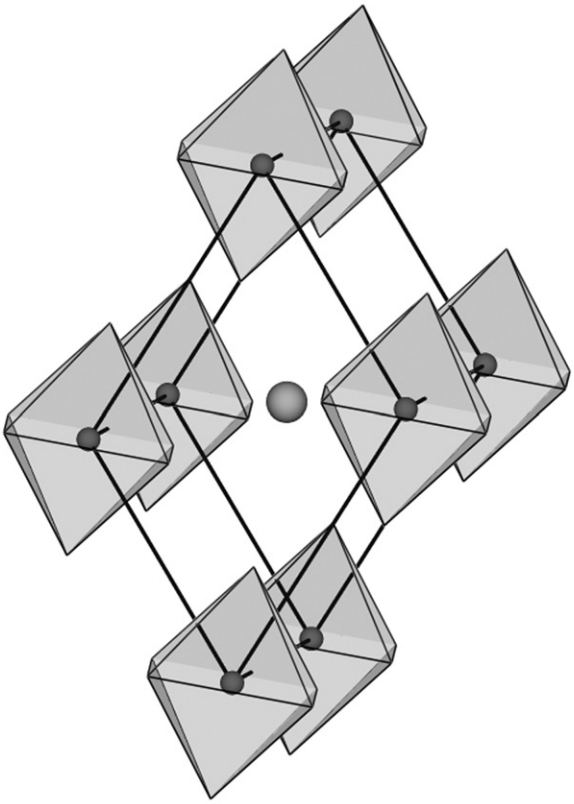

Fig. 1. The rhombohedral unit cell and structure of $LiSbF_6$ structural type.

atoms from the six different $[MF_6]^-$ anions. The A–F–M chain is not straight, but bent (148° in the case of $LiSbF_6$) (Fig. 1).

2.2. $NaSbF_6$ structural type (Fig. 2)

The $NaSbF_6$ structure, which has the highest symmetry of the AMF_6 structures, is not widespread and is found only for the sodium hexafluorometallates of transition metals with limited ionic radii of 0.72–0.78 Å. They contain an NaCl type arrangement of the cations and anions. The A–F–M chain is straight, without the tilt of MF_6 units. $NaPF_6$ is the only exception in this series, crystallizing in $NaSbF_6$ structure in spite of the small size of the phosphorus atom. The structure of this compound was originally classified as "$NaPF_6$ type" with the same space group, but with inclined anions with an eight-fold orientational disorder. The recent result, however, based on single crystal X-ray diffraction analysis, supports the $NaSbF_6$ type [8]. The coordination number of the fluorine atoms around the cation is 6 (Fig. 2) (Table 3).

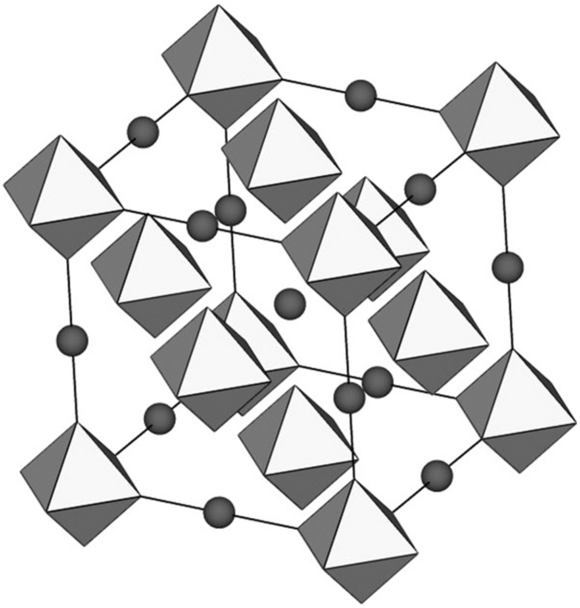

Fig. 2. The cubic unit cell and structure of $NaSbF_6$ structural type.

2.3. Structures of cubic APF_6 and $AAsF_6$ with orientational disorder 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 retermed $CsPF_6$ structure with $Pa\bar{3}$ 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 three-fold axis out of four for the rotation is uniquely

Table 3
$NaSbF_6$ type (cubic, $Fm\bar{3}m$, no. 225, $Z = 4$, C.N. (A^I) = 6) (previously $NaPF_6$ type)

	Lattice constants, a (Å)	V (Å^3)	Structural data[a]	References
$NaPF_6$	7.6140(5)	441.41(4)	Structure; single crystal	[1,8]
$NaReF_6$	8.18	547.3	Unit cell; powder data	[1,2]
$NaSbF_6$	8.184(5)	547.3	Structure; powder data	[2,18,28]
$NaMoF_6$	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 8.28	563.6 567.7	Unit cell; powder data Unit cell; powder data	[1,2] [29]
$NaTaF_6$	8.28	567.7	Unit cell; powder data	[1,2]

[a] Data were collected by powder or single crystal X-ray diffraction methods.

Table 4
Cubic AMF_6 (M = P, As), $Fm\overline{3}m$, no. 225, $Z = 4$, C.N. (A^I) = 10 (for $AgPF_6$ type), 12 (for $CsPF_6$ type); previously classified as $Pa\overline{3}$ $CsPF_6$ type

	Lattice constants, *a* (Å)	*V* (Å^3)	Structure type	Structural data[a]	References
$AgPF_6$	7.5508(7)	430.51(12)	$AgPF_6$	Structure; single crystal	[8,30,31]
$AgAsF_6$	7.7548(21)	466.34(37)	$AgPF_6$	Structure; single crystal	[30,31]
KPF_6	7.7891(7)	472.57(6)	$CsPF_6$	Structure; single crystal[b]	[8]
$KAsF_6$	8.0560	522.83		Unit cell; powder data	[9]
$InPF_6$	8.07(2)	524.9		Unit cell; powder data	[32]
$TlPF_6$	7.94	500.6		Structure; powder data	[1]
$RbPF_6$	7.887(8)	490.6(8)	$CsPF_6$	Unit cell; single crystal	[8]
$RbAsF_6$	8.246(4)	560.7		Unit cell; powder data	[13]
$CsPF_6$	8.197(2)	550.9(2)	$CsPF_6$	Structure; single crystal[c]	[8]
$CsAsF_6$	8.384(5)	589.3		Unit cell; powder data	[13]

[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. [33].
[c] For other possible high-temperature modifications see Ref. [8].

determined for each $[PF_6]^-$ to maintain the cubic symmetry. By the rotation, two fluorine atoms from each PF_6^- coordinate equally to one cation, increasing the coordination number to a total of 12. As a result, the space symmetry descends to $Pa\overline{3}$ and the lattice becomes primitive. However, the single crystal structure recently determined for some salts has 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 [8]. As a result, the 24 sites for fluorine atoms around a phosphorus atom, corresponding to a special position (96k), are equally occupied, with an 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 (Figs. 3 and 4).

Another type of AMF_6 that possesses $Fm\overline{3}m$ symmetry is found for $AgPF_6$ and $AgAsF_6$ [30]. In this case, the disorder results from the choice of the three four-fold rotational axes with a rotation of 45° from the original position in the $NaSbF_6$ structure. The 24 sites for fluorine atoms around a phosphorus atom, corresponding to two special positions (24e and 48h), are equally occupied with an occupancy ratio of 0.33. The averaged

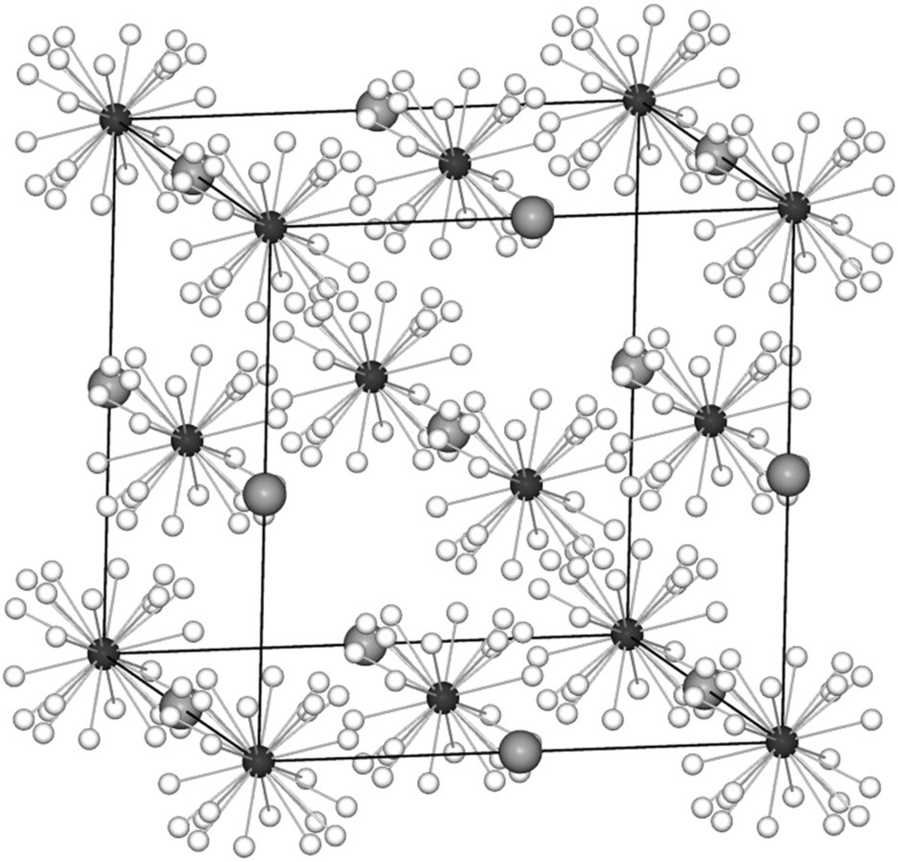

Fig. 3. The cubic unit cell and structure of $CsPF_6$ structural type with disordered PF_6 units.

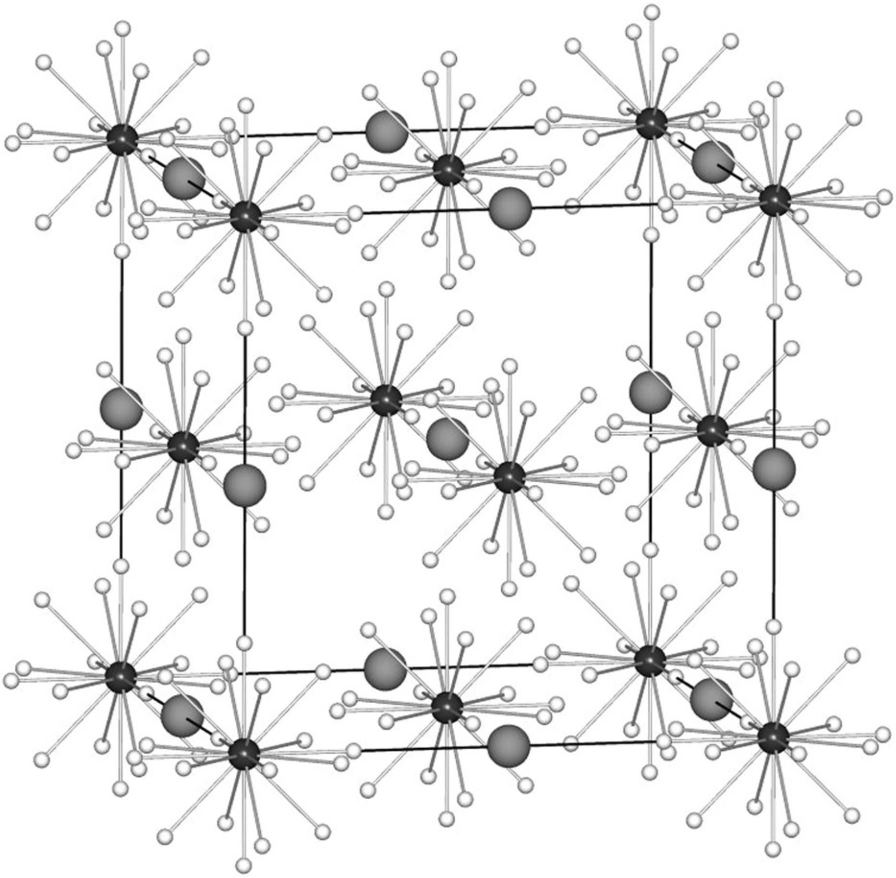

Fig. 4. The cubic unit cell and structure of $AgPF_6$ type with disordered PF_6 units.

Table 5
Tetragonal AMF_6, $Z = 2$, C.N. (A^I) = 8–12

	Lattice constants		V (Å^3)	Space group	Structural data[a]	References
	a (Å)	c (Å)				
$AgVF_6$	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	[20]
$AgNbF_6$	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	[10,11,18,34]
$KMoF_6$	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) 5.18	10.05(2) 10.08	269.8 270.5	$P\bar{4}c2$	Structure; single crystal Unit cell; powder data	[11,35] [44]
$KTaF_6$	5.20(2)	10.05(2)	271.8	$P\bar{4}c2$	Structure; single crystal	[1,2,35]
$KBiF_6$	5.248	10.07	277.34	$P\bar{4}c2$	Structure; powder data	[11,18]

[a] Data were collected by powder or single crystal X-ray diffraction methods.

coordination number of fluorine atoms around the cation is 10, the sum of those at 24e (2) and those at 48h (8).

The structures of the cubic APF_6 and $AAsF_6$ compounds in Table 4 have not been determined in detail unless otherwise noted. It has also not been clarified whether some of the $[PF_6]^-$ and/or $[AsF_6]^-$ salts crystallize in the structure formerly determined for $CsPF_6$ ($Pa\bar{3}$), in which no disorder occurs in the orientation of $[PF_6]^-$ or $[AsF_6]^-$. A single crystal X-ray or neutron powder diffraction study is necessary for further clarification of the detailed structure of these compounds (Table 4).

2.4. *Tetragonal $KSbF_6$ (T) structural types and similar structures (Fig. 5)*

There is some confusion as to the structure of this group of compounds, some sources reporting one structural type [3], and others 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}), the *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) [34], $AgTaF_6$ [31], and $KNbF_6$ [35] are $P\bar{4}2m$, $P4_2/mcm$, and $P\bar{4}c2$, respectively. However, their structures are the same, except for differences in the manner of the 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 between these compounds. In particular, the unusual deformation of MF_6 in the $KNbF_6$ structure should be carefully re-examined. Cations and anions form a CsCl-type arrangement with (8,8)-coordination. Doubling of the CsCl cell along the *c*-axis is due to different orientations of the 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 MF_6, forming a dodecahedral coordination. The coordination number varies according to 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). Thus the coordination number based on the closest approach of the F atoms is 8 (Table 5) (Fig. 5).

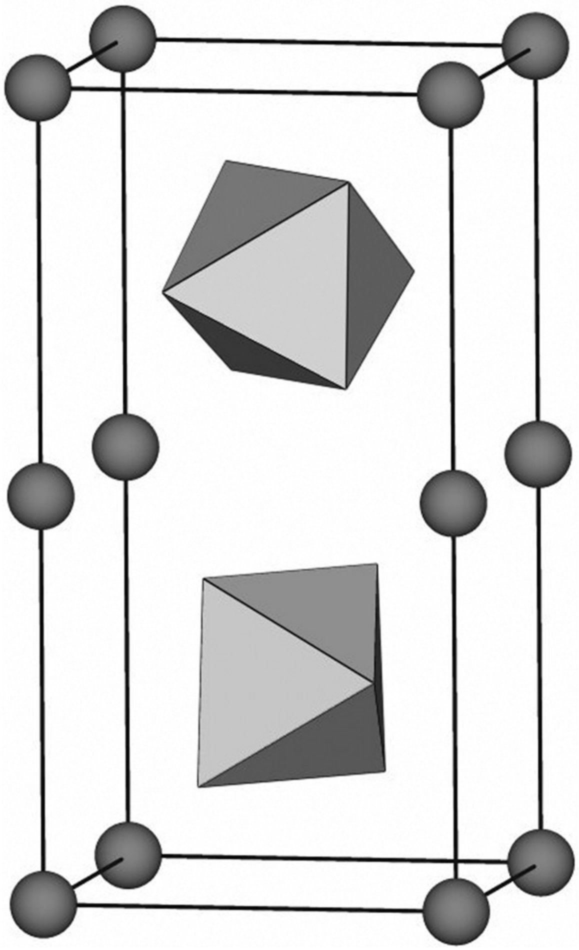

Fig. 5. The tetragonal unit cell and structure of $KSbF_6$ (T) structural type. The origin is set at the K position.

2.5. *$AgSbF_6$ structural type and similar structures (Fig. 6)*

The array of cations and anions here is CsCl type with no compression. The $[SbF_6]^-$ anion is thus a regular octahedron, which contrasts with that in the tetragonal AMF_6. Four orientations of the 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 $AgSbF_6$ has been determined by

Table 6
$AgSbF_6$ type (cubic, $Ia\bar{3}$, no. 206, $Z = 8$, C.N. $(A^I) = 6$)

	Lattice constants, *a* (Å)	*V* (Å^3)	Space group	Structural data[a]	References
$AgRuF_6$	9.653(10)	899.5(14)	$Ia\bar{3}$	Unit cell; powder data	[20]
$AgIrF_6$	9.704(2)	913.80(28)	$Ia\bar{3}$	Unit cell; powder data	[20]
$AgOsF_6$	9.7318(9)	921.68(13)	$Ia\bar{3}$	Unit cell; powder data	[20]
$AgSbF_6$	9.857(5)	957.7(7)	$Ia\bar{3}$	Unit cell; powder data	[20]
$AgSbF_6$	9.7985(4)	940.76(12)	$Ia\bar{3}$	Structure; single crystal	[31]
$KSbF_6$	10.176(8)	1053.7(12)	$I23$ or $I2_13$[b]	Unit cell; powder data[c]	[10,18]
$KBiF_6$	10.34	1105.51	$Ia\bar{3}$	Structure; powder data	[11,18]

[a] Data were collected by powder or single crystal X-ray diffraction methods.

[b] The initially proposed space group symmetry $Ia\bar{3}$ was later ruled out [10] and new space groups $I23$ or $I2_13$ proposed.

[c] Data collected at 268 K.

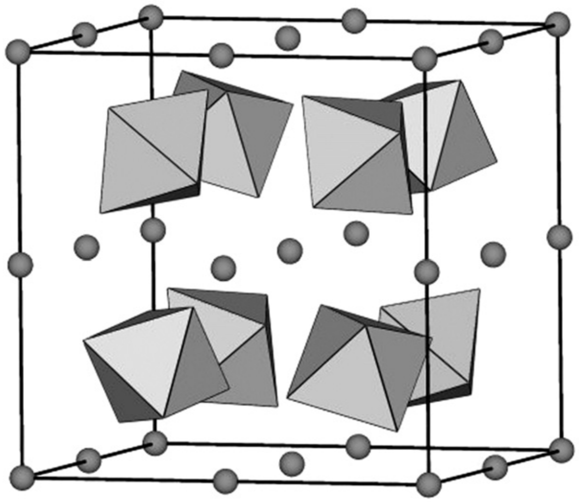

Fig. 6. The cubic unit cell and structure of $AgSbF_6$ structural type. The origin is set at the Ag position.

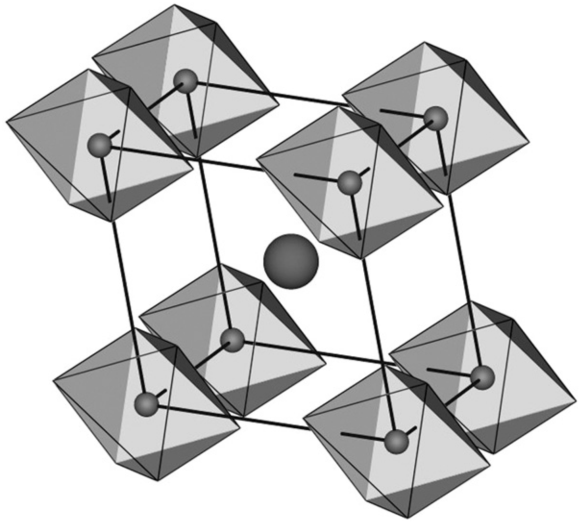

Fig. 7. The rhombohedral unit cell and structure of $KOsF_6$ structural type.

single crystal X-ray diffraction [31]. The same space group, $Ia\overline{3}$, was originally proposed also for $KSbF_6$ as a low-temperature form (the high-temperature form is tetragonal), however, different space groups such as $I23$ or $I2_13$ were later proposed. The structure of the potassium salts should be re-examined to confirm the structural difference from the silver salts (Table 6) (Fig. 6).

2.6. $KOsF_6$ structural type (Fig. 7)

This structure is found for some KMF_6 compounds and for the majority of AMF_6 compounds whose A^+ cations have radii larger than 1.5 Å. The structure is derived from the CsCl type arrangement of cations and anions with rhombohedral distortion. Compression of the CsCl cubic cell along the cell diagonal yields a rhombohedral cell with a distortion angle (α) that ranges from 95° to 98°. Two fluorine atoms from each $[MF_6]^-$ anion at the corner of the unit cell are arranged to coordinate equally to the central cation. The cation is equally coordinated by a total of 12 fluorine atoms. The cations and fluorine atoms together form 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 three below (Fig. 7) (Table 7).

Table 7
$KOsF_6$ type (rhombohedral, $R\overline{3}$, no. 148, $Z = 1$, C.N. (A^I) = 12)

	Lattice constants				V (Å^3)[a]	Structural data[b]	References
	Hexagonal setting		Rhombohedral setting				
	a (Å)	c (Å)	a (Å)	α (°)			
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	[36,9,18]
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	[25]
	7.4060(2)	7.2714(2)	4.915	97.772	115.13	Structure; single crystal[c]	[21]
$KRuF_6$	7.46	7.41	4.97	97.4	119.0	Unit cell; powder data	[2,25]
	7.465	7.414	4.968(1)	97.40(1)	119.3	Unit cell; powder data	[37]
$KAuF_6$	7.348(8)	7.198(8)	4.874	97.84	112.2	Unit cell; powder data	[23]
	7.49	7.27	4.936(5)	97.96(3)	116.4	Unit cell; powder data	[38]
	7.496(3)	7.315(3)	4.967	97.966	118.7	Structure; single crystal[d]	[39]
$KPtF_6$	7.45	7.40	4.96	97.4	118.7	Unit cell; powder data	[2,38,37,40]
$KIrF_6$	7.474	7.524	4.9744(7)	97.399(9)	119.7	Unit cell; powder data	[37]
$KOsF_6$	7.486	7.487	4.991(1)	97.18(2)	121.1	Structure; powder data	[1,2,41]
$KReF_6$	7.530	7.537	5.012(4)	97.15(4)	123.4	Unit cell; powder data	[37]
$InAsF_6$	7.58(2)	7.90(1)	5.108	95.813	131.1	Unit cell; powder data	[32]
$TlAsF_6$	7.55	7.59	5.04	97.0	124.9	Unit cell; powder data	[1]

Table 7 (*Continued*)

	Lattice constants				V (Å^3)[a]	Structural data[b]	References
	Hexagonal setting		Rhombohedral setting				
	a (Å)	c (Å)	a (Å)	α (°)			
$TlVF_6$	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]
$TlNbF_6$	7.662	7.853	5.142	96.37	133.1	Unit cell; powder data	[1,2,12]
	7.766	7.960	5.21	96.37	138.6	Unit cell; powder data	[14]
$TlTaF_6$	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	[13]
$RbVF_6$	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	[25]
$RbRuF_6$	7.59	7.66	5.07	96.88	127.4	Unit cell; powder data	[2,25]
$RbAuF_6$	7.638(4)	7.608(4)	5.087	97.309	128.1	Unit cell; powder data	[23]
$RbPtF_6$	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	[1,13]
$RbMoF_6$	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	[14,12]
$RbTaF_6$	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	[26,18]
$CsAsF_6$	7.723(1)	8.050(1)	5.204	95.806	138.6	Structure; single crystal	[13]
$CsVF_6$	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	[25]
$CsRuF_6$	7.80	8.07	5.25	96.3	141.7	Unit cell; powder data	[2,25]
$CsAuF_6$	7.640(5)	8.133(6)	5.204	95.34	137.0	Unit cell; powder data	[23]
	7.81	8.00	5.24(1)	96.43(5)	140.9	Unit cell; powder data	[38]
$CsPtF_6$	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[e]	[14,42]
$CsSbF_6$	7.904(1)	8.261(1)	5.330	95.717	149.0	Structure; single crystal	[42,43,18]
$CsMoF_6$	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	[2,14]
$CsTaF_6$	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	[26,18]

[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. A_2MF_7 compounds

Known A_2MF_7 compounds are given in Table 8. The most investigated are K_2NbF_7 and K_2TaF_7, because of their use as starting materials for the production of metals. The available data about K_2TaF_7 preparation, main properties and structure have been reviewed recently [51]. K_2TaF_7 crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $Z = 4$ (Table 9) [49].

The crystal structure of K_2TaF_7 consists of potassium cations and $[TaF_7]^{2-}$ anions (Fig. 8). Below 150 K, the $[TaF_7]^{2-}$ anion is built as a trigonal prism with six fluorine atoms at the vertices.

Table 8
Known A_2MF_7 compounds

	Nb	Ta	W	Sb	Bi
Li	[44]	–	–	–	–
Na	[44,45]	[46,47]	–	–	[54]
K	[44,45,48–50][a]	[46,47,49–52][a]	[53][a]	[54]	[54]
Rb	[14,45]	[47,55]	[53]	–	[54]
Cs	[14]	[47,55]	–	[54]	[54]
Tl	[12,14]	[47]	–	–	–

[a] Crystal structure known.

Table 9
Crystal data of A_2MF_7 compounds

	Crystal system	Structural data[a]		References
Na_2NbF_7	Monoclinic	$a = 5.38$ Å, $b = 11.84$ Å, $c = 8.03$ Å, $\beta = 90°$	Unit cell; powder data	[44]
K_2NbF_7	Monoclinic	$a = 5.846(3)$ Å, $b = 12.693(6)$ Å, $c = 8.515(4)$ Å, $\beta = 90.0(1)°$	Structure; single crystal	[48]
Rb_2NbF_7	Monoclinic	$a = 10.60$ Å, $b = 10.10$ Å, $c = 9.65$ Å, $\beta = 99.5°$	Unit cell; powder data	[14]
Cs_2NbF_7	Monoclinic	$a = 11.50$ Å, $b = 10.97$ Å, $c = 9.08$ Å, $\beta = 95°$	Unit cell; powder data	[14]
Tl_2NbF_7	Rhombohedral	$a = 10.97$ Å, $\alpha = 9.25°$	Unit cell; powder data	[12,14]
Na_2TaF_7	Isomorphous to K_2TaF_7		Powder data	[46,47]
K_2TaF_7	Monoclinic	$a = 5.8559(6)$ Å, $b = 12.708(1)$ Å, $c = 8.5125(9)$ Å, $\beta = 90.17°$	Structure; single crystal	[49,51]
K_2WF_7	Orthorhombic	$a = 9.800(2)$ Å, $b = 5.736(11)$ Å, $c = 11.723(2)$ Å	Structure; single crystal	[53]

[a] Data were collected by powder or single crystal X-ray diffraction methods.

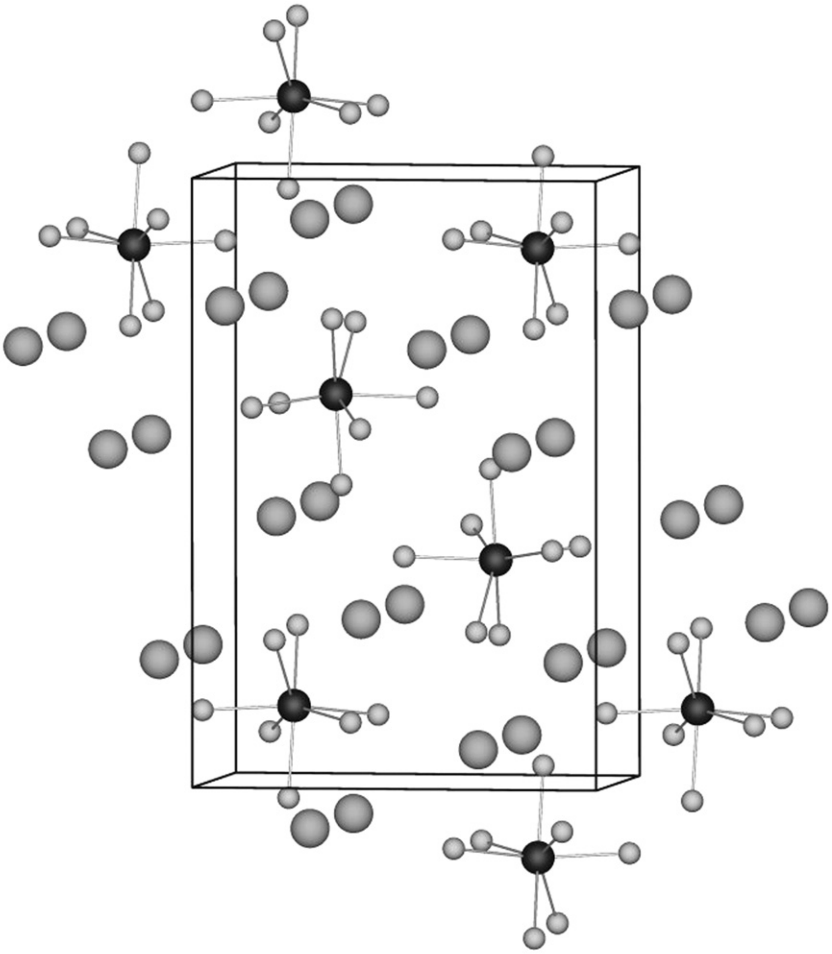

Fig. 8. The monoclinic unit cell and structure of K_2MF_7 structural type (M = Nb, Ta).

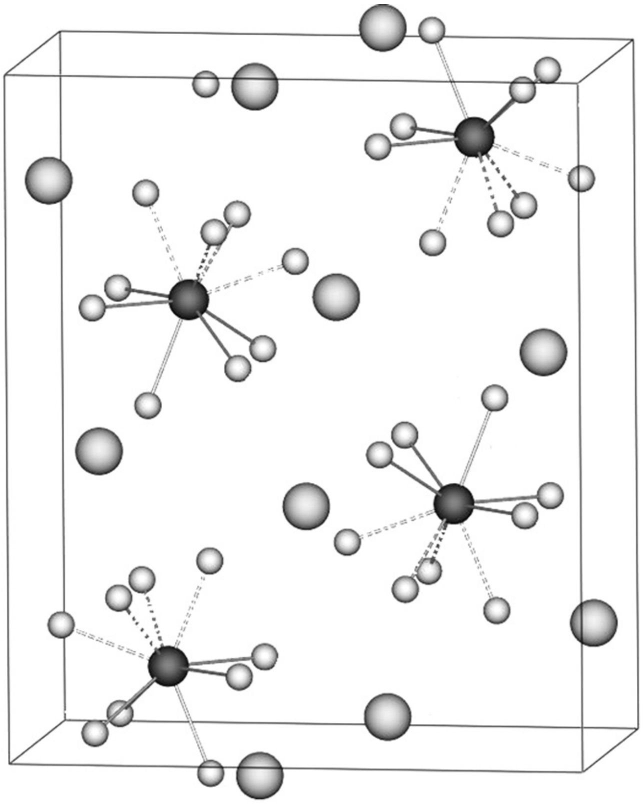

Fig. 9. The orthorhombic unit cell and structure of K_2WF_7 (dashed lines represent bonds between tungsten and two pairs of disordered fluorine atoms).

The seventh fluorine atom is placed above the centre of the rectangular face of the prism (i.e., mono-capped trigonal prism with c_{2v} symmetry) [51]. With increasing temperature, the $[TaF_7]^{2-}$ anions deform [51].

Crystal structures of K_2NbF_7 and K_2WF_7 have also been determined by single crystal X-ray diffraction. The former is isostructural with K_2TaF_7, while K_2WF_7 crystallizes in an orthorhombic crystal system (Table 9), space group *Pnma* (no. 62) with $Z = 4$ [53]. In the K_2WF_7 structure, the tungsten atom is surrounded by an array of seven fluoride ligands in a distorted trigonal prism, in which one of the rectangular faces is capped by the seventh fluorine atom [53]. Two of the fluorine atoms are unequally disordered between two sets of positions (Fig. 9). Potassium cations are 11-coordinated with fluorine atoms, in contrast to the K_2NbF_7 and K_2TaF_7 structures, both of which contain 9-coordinate potassium cations.

For the rest of the known A_2NbF_7 (A = Li [44], Na [44], Rb [14], Cs [14], and Tl [12,14]) compounds only lattice parameters have been reported. Na_2NbF_7 is reported to be isostructural with K_2NbF_7 [44].

In the case of the other A_2TaF_7 (A = Na, Rb, Cs, Tl) salts, the sodium compound is reported to be isomorphous to K_2TaF_7 [46].

Mixed alkali cation niobium and tantalum heptafluoro complexes ($NaANbF_7$, A = K, Rb; $NaATaF_7$, A = K, Rb, Cs) have also been reported [56].

Rb_2WF_7 was characterized by Raman spectroscopy [53], and $[SbF_7]^{2-}$ and $[BiF_7]^{2-}$ salts by vibrational spectroscopy and *ab initio* electronic structure calculations [54]. They possess pentagonal bipyramidal structures of D_{5h} symmetry (Table 10).

Table 10
Known A_3MF_8 compounds

	Nb	Ta	Mo	W
Li	[44]	–	–	–
Na	[44]	[46,47,57][a]	–	[53]
K	[44,45]	[47]	[58]	[53,58,59]
Rb	[14]	–	–	[53]
Cs	[14]	–	–	–
Tl	[12,14]	–	–	–

[a] Crystal structure known.

4. A_3MF_8 compounds

Known A_3MF_8 compounds are listed in Table 11. A complete crystal structure has been determined only for Na_3TaF_8 [57]. It crystallizes in a monoclinic space group *C*2/*c* (no. 15) with $Z = 4$ (Table 12). The structure consists of Na^+ cations and $[TaF_8]^{3-}$ anions (Fig. 10). The $[TaF_8]^{3-}$ anion assumes a configuration close to that of the square Archimedean antiprism of symmetry D_{4d} [57].

For the other compounds only lattice parameters, determined from powder data, are available (Table 11). Na_3NbF_8 is reported to be isostructural with Na_3TaF_8 [14]. Rb_3NbF_8 and Cs_3NbF_8 appear to be isostructural, but different from Tl_3NbF_8 [14]. K_3WF_8 is reported to be rhombohedral. No structural data are available for other A_3WF_8 (A = Na, Rb) compounds. Together with K_3WF_8, they were characterized by their Raman spectra in the molten FLINAK eutectic melt [53].

Table 11
Crystal data of A_3MF_8 compounds

	Crystal system	Structural data[a]		References
Na_3NbF_8	Isostructural with Na_3TaF_8		Powder data	[44]
Rb_3NbF_8	Monoclinic	$a = 10.65$ Å, $b = 9.40$ Å, $c = 8.58$ Å, $\beta = 91.2°$	Unit cell; powder data	[14]
Cs_3NbF_8	Monoclinic	$a = 11.20$ Å, $b = 9.85$ Å, $c = 8.93$ Å, $\beta = 91.5°$	Unit cell; powder data	[14]
Tl_3NbF_8	Hexagonal	$a = 8.59$ Å, $c = 6.69$ Å	Unit cell; powder data	[14]
Na_3TaF_8	Monoclinic	$a = 11.52$ Å, $b = 5.38$ Å, $c = 11.21$ Å, $\beta = 120.55°$	Structure; single crystal	[57]
K_3MoF_8	Cubic	$a = 14.1$ Å	Unit cell; powder data	[58]
K_3WF_8	Rhombohedral	$a = 9.75$ Å, $\alpha = 86.4°$	Unit cell; powder data	[59]

[a] Data were collected by powder or single crystal X-ray diffraction methods.

Table 12
Known AM_2F_{11} compounds

	V	Nb	Ta	Sb	Bi
Ag	–	–	–	[62][a]	–
K	[60]	[44]	–	[63][a]	–
Rb	–	[14]	–	[63]	–
Cs	[60]	[14,64,65]	[64,65]	[63][a]	[61]
Tl	–	[12,14]	–	[63]	–

[a] Crystal structure known.

5. AM_2F_{11} compounds

The known AM_2F_{11} compounds are listed in Table 13. AV_2F_{11} (A = K, Cs) [60], $CsTa_2F_{11}$ [64,65] and $CsBi_2F_{11}$ [60] have been characterized only by vibrational spectroscopy.

For ANb_2F_{11} (A = Rb, Cs, Tl) compounds, only lattice parameters have been reported (Table 13) [14].

The AF–SbF_5 system is the most extensively studied, and crystal structures of ASb_2F_{11} (A = Ag, K, Cs) have been determined [62,63].

Crystals of KSb_2F_{11} are orthorhombic (space group *Pbca* and $Z = 24$) and isostructural with $AgSb_2F_{11}$ (Table 14). The complex structure of ASb_2F_{11} (A = Ag, K) reveals three crystallographically non-equivalent $[Sb_2F_{11}]^-$ anions, highly distorted from the ideal D_{4h} or D_{4d} symmetries, which differ only in the angular orientation of the SbF_5 units relative to each other [65]. There are also three crystallographically non-equivalent A^+ (A = Ag, K) cations in the crystal structure of the corresponding $[Sb_2F_{11}]^-$ salts. The coordination of K/Ag atoms in ASb_2F_{11} (A = Ag, K) can be written as 8 for two A^+ cations and 9 for the third one.

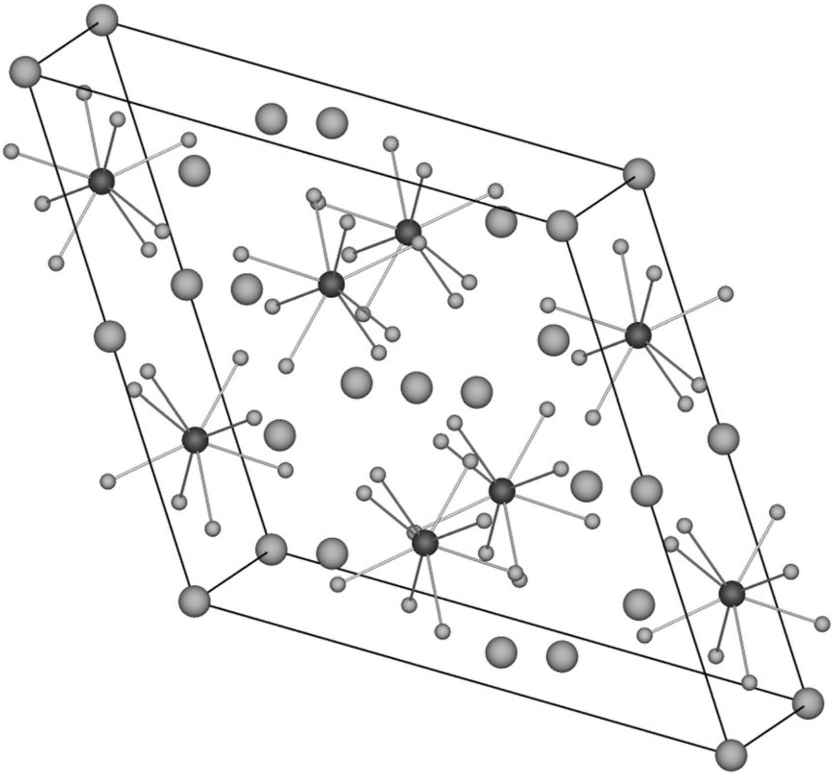

Fig. 10. The monoclinic unit cell and structure of Na_3TaF_8.

Table 13
Crystal data of AM_2F_{11} compounds

	Crystal system	Structural data[a]		References
$RbNb_2F_{11}$[b]	Rhombohedral	$a = 12.76$ Å, $\alpha = 91.2^\circ$	Unit cell; powder data	[14]
$CsNb_2F_{11}$	Rhombohedral	$a = 12.47$ Å, $\alpha = 91.30^\circ$	Unit cell; powder data	[14]
$TlNb_2F_{11}$[b]	Rhombohedral	$a = 10.70$ Å, $\alpha = 94.5^\circ$	Unit cell; powder data	[14]
$AgSb_2F_{11}$	Orthorhombic	$a = 10.91.80(7)$ Å, $b = 12.4628(8)$ Å, $c = 38.802(3)$ Å	Structure; single crystal[c]	[62]
KSb_2F_{11}	Orthorhombic	$a = 11.4165(8)$ Å, $b = 12.7996(9)$ Å, $c = 39.485(3)$ Å	Structure; single crystal[c]	[63]
$CsSb_2F_{11}$	Monoclinic	$a = 7.7410(14)$ Å, $b = 14.2541(17)$ Å, $c = 9.5130(15)$ Å, $\beta = 113.226(6)^\circ$	Structure; single crystal[c]	[63]

[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.

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

	AM_3F_{16}		AM_4F_{21}
	Nb	Sb	Nb
K	[44]	–	–
Rb	[14]	–	–
Cs	–	[63][a]	[14]
Tl	[12,14]	–	–

[a] Crystal structure known.

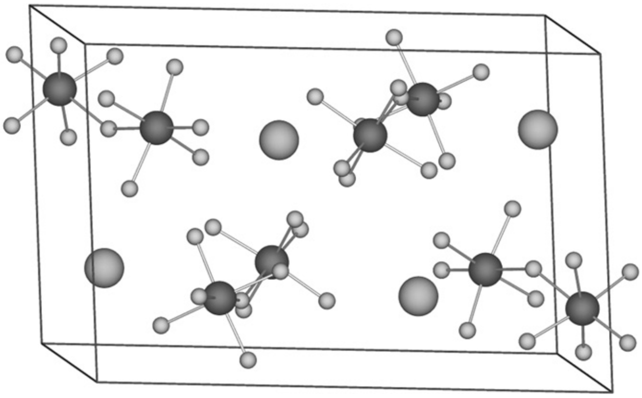

Fig. 11. Packing diagram of $CsSb_2F_{11}$.

$CsSb_2F_{11}$ crystallizes in a monoclinic form with the unit cell parameters given in Table 14, space group $P2_1/n$ (no. 14) and $Z = 4$. The packing diagram is depicted in Fig. 11.

The structure of $CsSb_2F_{11}$ is ionic, consisting of discrete $[Sb_2F_{11}]^-$ anions and Cs^+ cations. As in the case of KSb_2F_{11}, the $[Sb_2F_{11}]^-$ anion in $CsSb_2F_{11}$ is highly distorted from ideal D_{4h}/D_{4d} symmetry and is similar/identical to the lowest energy structure in the gas phase [66]. The caesium atom is surrounded by 12 fluorine atoms.

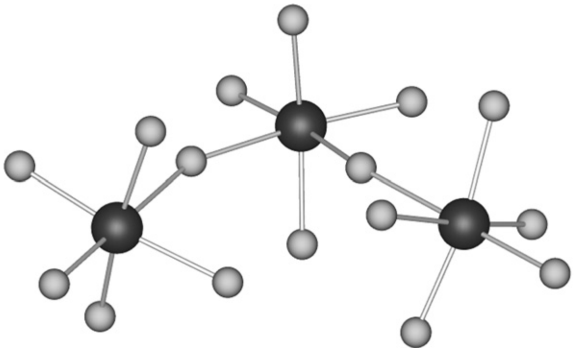

Fig. 12. The $[Sb_3F_{16}]^-$ anion adopts a *cis* fluorine-bridged geometry in the crystal structure of $CsSb_3F_{16}$.

The X-ray powder diffraction photographs indicate that $RbSb_2F_{11}$ and $TlSb_2F_{11}$ are isostructural and are distinguished from the crystal structures of KSb_2F_{11} and $CsSb_2F_{11}$, respectively [63].

6. AM_3F_{16} and AM_4F_{21} compounds

Little structural data is available for AM_3F_{16} and AM_4F_{21} compounds (Table 14).

$[Nb_3F_{16}]^-$-salts were partially characterized by their powder X-ray diffraction patterns [14,44]. The structure of $CsSb_3F_{16}$ was however determined by single crystal analysis [63]. It

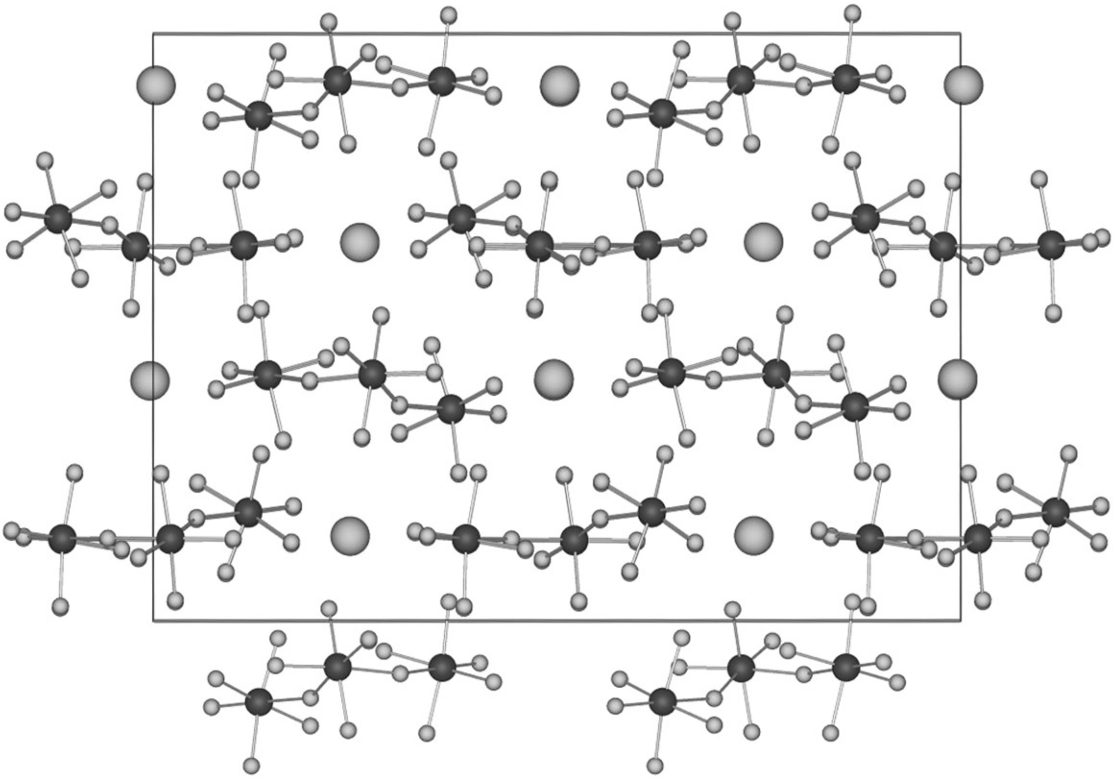

Fig. 13. Packing diagram for $CsSb_3F_{16}$.

crystallizes in an orthorhombic unit cell at 200 K, with $a = 22.07(3)$ Å, $b = 7.726(11)$ Å, $c = 16.05(3)$ Å, and $Z = 8$, space group $Pca2_1$ (no. 29). The crystal structure of $CsSb_3F_{16}$ reveals two crystallographically non-equivalent $[Sb_3F_{16}]^-$ anions that adopt a *cis* fluorine-bridged geometry (Fig. 12). The packing diagram is shown in Fig. 13.

There are also two crystallographically non-equivalent Cs^+ cations in the crystal structure of $CsSb_3F_{16}$. These cations are each surrounded by 12 fluorine atoms.

The only reported example of an AM_4F_{21} compound in the AF–MF_5 system is $CsNb_4F_{21}$ [14]. The indexing of its powder X-ray diffraction pattern gave a rhombohedral unit cell ($a = 9.52$ Å, $\alpha = 88.8°$). The geometry of the $[M_4F_{21}]^-$ anion has only been determined for M = Sb in $Xe_2Sb_4F_{21}$ [67].

7. Conclusions

The A(I)–M(V) fluorocomplexes AMF_6, A_2MF_7, A_3MF_8, AM_2F_{11}, AM_3F_{16} and AM_4F_{21}, whose structures have been completely or partially determined, are reviewed here [where A = Li, Na, K, Rb, Cs, Cu, Ag, In, Tl; M = P, As, V, Rh, Ru, Au, Pt, Ir, Os, Re, Sb, Mo, W, Nb, Ta, Bi]. Even for AMF_6, there are some compounds whose structures are still unknown. The structures of some AMF_6 compounds are still based only on powder diffraction studies causing confusion and ambiguity and leaving a degree of uncertainty as to the structure of some of them. Single crystal determination is necessary to clarify the classification of their structures. This applies particularly to the A_2MF_7, A_3MF_8, AM_2F_{11}, AM_3F_{16} and AM_4F_{21} compounds in the AF–MF_5 systems and to the geometry of the corresponding $[M_nF_{5n+1}]^-$ ($n = 2$, 3, 4) anions, for which data are still limited. Here it is necessary to add that the effect of the cation–anion contacts on the structure of $[Sb_2F_{11}]^-$ anion was extensively studied by Wilner and Aubke in the transition metal carbonyl chemistry [68–71].

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