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Crystal Structure and Bonding in Transition-Metal Fluoro Compounds

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Contents

I. *Introduction*

The most electronegative element, fluorine, gives rise to the most ionic ligands. Such ligands are among the smallest and most rigid. These features make the crystal structures of metal fluorides comparatively simple and mainly governed by geometric and electrostatic principles. This class of compounds is therefore well suited for checking the usefulness and the limits of, for example, rigid-sphere concepts (in which radius ratios predetermine coordination numbers) and at the same time the validity of Pauling's rules, which postulate local balance of charges.[1,2]

In addition to collective properties, such as size and charge, the ions have individual properties, mainly determined by their electronic configuration. Transition-metal ions in particular are expected to affect the crystal structures of their compounds through a variety of electronic effects, such as covalency, back-bonding, spin state, or generally ligand field splitting, and—most dramatically—Jahn–Teller distortion. The better we know to what degree purely geometric and electrostatic principles predetermine crystal structures, the more admissible it becomes to interpret deviations from these expectations as being caused by bonding and electronic effects (which generally only modify the basic structural patterns).

To demonstrate the structural influence of the factors mentioned we will concentrate on 3d transition-metal fluorides. Most of the structure types occurring in this class of compounds will be tabulated, provided they have been determined by X-ray single-crystal work; no attempt will be made to specify the huge variety of isomorphs reported to date. Instead, examples will be selected to illustrate certain principles of structure and bonding. Most of these concern polynary compounds, including some hydrates for the study of hydrogen bridge effects.

The literature is covered up to 1986, which was the centenary year of the isolation of fluorine by Moissan. On that occasion a special report appeared on the first 100 years of fluorine chemistry; the reader is referred to it for the many interesting aspects of the chemistry of this element.[3] More especially, in the field of chemistry and physics of inorganic solid fluorides, a recent publication edited by Hagenmuller[4] will provide the information on such important topics as preparative methods, high oxidation states, or physical properties, all of which are absent in the present article. Structural reviews giving more details also exist, including those on lanthanide and actinide fluorides.[5–10]

II. *Coordination Behavior in Fluoride Structures*

A. Coordination around "Central" Cations

In most oxidation states of d transition-metal ions M, the radius ratio r_M:r_F falls within the range 0.41–0.73, i.e., just the stability field of octahedral coordination. This coordination is in fact observed in the majority of cases and it is quite unaffected by the F:M stoichiometry of the compound. Exceptions involve cations with the d^8 and even d^9 electronic configurations, especially those of the heavier elements, which in fluorides, too, often show the square-planar coordination usually

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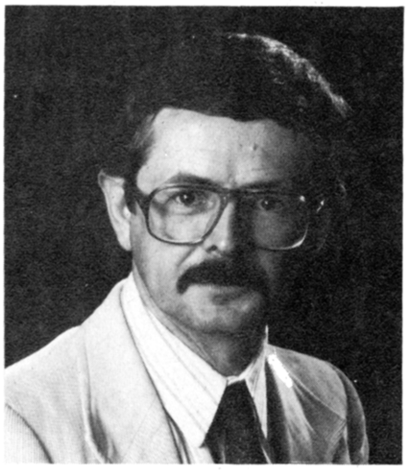
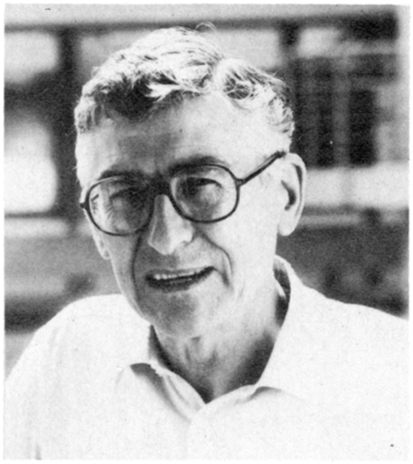


Werner Massa was born in 1944 and grew up in Riedlingen, Germany. He received his Dipl. Chem. (1969) and doctoral degrees (1972) at the University of Tübingen, where he worked in the group of Professor W. Rüdorff. In 1977 he joined the laboratory of Professor D. Babel at the University of Marburg. Since 1979 he has been directing the laboratory of X-ray crystal structure determination of the Fachbereich Chemie. After his Habilitation in 1982 he was appointed Privatdozent at the University of Marburg, where he currently is teaching. His research interests are structural chemistry, magnetism, and hydrogen bonding in inorganic solid fluorides of transition metals, especially of the Jahn–Teller active ion Mn(III).



Dietrich Babel was born 1930 in Bonn, Germany, and received his Dipl. Chem. (1958) and Dr. rer. nat. (1961) degrees at the University of Tübingen, where he was advised by Professor W. Rüdorff. After spending one term (1961/1962) with Professor W. Hoppe in Munich, to get acquainted with the techniques of X-ray single-crystal structure determination, he went back to Tübingen. He completed his Habilitation (1968) there, became a staff member (1969) in the Department of Inorganic Structural Chemistry in Tübingen, and then got a call (1970) to a chair of Inorganic Chemistry at the Philipps-University of Marburg, where he was appointed Professor (1971). He was a member of the Sonderforschungsbereich 127 "Crystal Structure and Chemical Bonding" (1974–1986) and during two periods (1977/1978 and 1986/1987) dean of the Fachbereich Chemie in Marburg. For a sabbatical leave (1981) he was absent one term for Bordeaux, at Professor P. Hagenmuller's Institute. His research interests are in the general area of solid-state chemistry, with special emphasis on crystal structure systematics and magnetochemistry, investigated mostly at transition-metal fluorides and cyanides.

found for these configurations.[10-16] On the other hand, there are rare cases of tetrahedral 4-coordination, e.g., in the scheelite type structure of $CaZnF_4$.[17] In fact, zinc is a central cation with a well-known preference for tetrahedral sites.

TABLE I. Fluoride Crystal Structures Containing Isolated $[MF_6]$octahedra

	prototype	CN of A ion	space group	Z	ref
AMF_6	$LiSbF_6$	Li: 6	$R\bar{3}$	1	19
	$NaSbF_6$	Na: 6	$Fm3m$	4	20
	$KNbF_6$	K: 8	$P\bar{4}c2$	2	21, 22
	$KOsF_6$	K: 12	$R\bar{3}$	1	23, 24
	$BaSiF_6$	Ba: 12	$R\bar{3}m$	1	24–26
A_2MF_6	Li_2ZrF_6	Li: 6	$P\bar{3}1m$	1	27, 28
	Na_2SiF_6	Na: 6	$P321$	3	29, 30
	Na_2SnF_6	Na: 6	$P2_1/c$	2	28, 31
	K_2GeF_6	K: 12	$P\bar{3}m1$	1	32
	K_2MnF_6	K: 12	$P6_3mc$	2	33
	K_2SiF_6	K: 12	$Fm3m$	4	34
	$CaLiAlF_6$	Ca: 6, Li: 6	$P\bar{3}1c$	2	35
	$SrLiFeF_6$	Sr: 6+2, Li: 6	$P2_1/c$	4	36
	$BaLiCrF_6$	Ba: 12, Li: 4	$P2_1/c$	4	37
A_3MF_6	α-Li_3AlF_6	Li: 6	$Pna2_1$	4	38
	β-Li_3VF_6	Li: 6 and 4	$C2/c$	12	39
	Na_3AlF_6	Na: 6+6 and 6	$P2_1/n$	2	40–42
	Rb_3TlF_6	Rb: 10 and 8	$I4/mmm$	2	43
	K_3MoF_6	K: 12 and 6	$Fm3m$	4	44
	Hg_3NbF_6	Hg chains	$I4_1/amd$	4	45
		Hg layers	$P\bar{3}1m$	1	46
	$Na_3Li_3Al_2F_{12}$	Na: 8, Li: 4	$Ia3d$	8	47, 48
	K_2NaAlF_6	K: 12, Na: 6	$Fm3m$	4	49–51
	K_2LiAlF_6	K: 12, Li: 6	$P3m1$	3	52, 53
	Cs_2NaCrF_6	Cs: 12, Na: 6	$R\bar{3}m$	6	54–56
	Cs_2LiGaF_6	Cs: 12, Li: 6	$P\bar{3}m1$	1	54
A_2MF_7	Ca_2AlF_7	Ca: 7 and 7+1	$Pnma$	4	57
	Pb_2RhF_7	Pb: 7+2 and 8+2	$P2_1/c$	4	58
	$BaCaCrF_7$	Ba: 12, Ca: 8	$P2/n$	4	59

While the number of transition-metal fluorides exhibiting coordination numbers (CN) smaller than 6 is quite limited, coordination numbers *higher* than 6 are more frequent. They occur with the larger cations, which in addition to some d elements as zirconium and hafnium typically comprise the f-series elements of the lanthanides and actinides. However, neither the structures found for the fluorides of these elements[7,8] nor others with CN $\neq$ 6 will be dealt with in this paper.

When dealing with the d transition-metal fluorides, we shall pay less attention to the well-known structures of binary compounds MF_n (n = 2–6)[9] and to those derived from the latter by substitution of differently charged cations, e.g., trirutiles like $LiM^{II}M^{III}F_6$ or VF_3- and ReO_3-type related structures like $LiSbF_6$ and $NaSbF_6$, respectively. Though a large number of compounds adopting these (pseudo)binary structures are known,[10] the structural variety in this class is rather limited. This is even more true of the structures of the alkali-metal and alkaline-earth fluorides AF and AF_2, respectively, the most common binary components of ternary transition-metal fluorides A_mMF_n. The simplest illustration of structural monotony in binary fluorides is the rock salt structure adopted by all the alkali-metal fluorides AF, regardless of the broad radius ratio range, which varies from $r_A/r_F = 0.57$ in LiF to 1.26 in CsF. This demonstrates the constraints imposed by stoichiometry, i.e., the composition of a compound, which is the most important of the factors influencing the geometry of a structure. Even the relative-size effect is controlled by the composition, which provides the number and proportion of building units to set up a structure.

B. Countercations in Polynary Fluorides

When going from binary to ternary compounds A_mMF_n, both cations, A and M, have access to more fluoride anions than before and therefore get a better chance to display differences in their coordination behavior according to their radius ratios r_A/r_F and r_M/r_F. As already mentioned, the result is nearly invariably octahedral coordination for the d transition-metal ions, which form negatively charged $[MF_6]$ units, isolated or linked (see later). The remaining positive elements A then play the role of countercations and influence the arrangement of these units in such a way as to achieve an optimum AF_n coordination. The resulting CNs of alkali-metal ions observed in a vast variety of polynary fluorides—unlike the constant CN 6 in the binary alkali-metal fluorides—are well differentiated and clearly follow the radius ratio r_A/r_F given for the element. The larger ions, K^+, Rb^+, and Cs^+, tend to close-pack with the similarly sized fluoride ion and therefore prefer CN 12. With only a few exceptions they exhibit at least 8-coordination. The smallest alkali-metal ion, Li^+, on the other hand, is generally only 6- or even 4-coordinated in polynary fluorides. In most fluoride compounds the sodium ion, Na^+, exhibits CNs between 6 and 8, consistent with its intermediate size. A similar gradation is observed for the alkaline-earth ions from Mg^{2+} (CN 6) to Ba^{2+} (CN 12). In Table I the CN of the countercations is shown for illustration.

III. Geometrical Features of Octahedrally Coordinated Fluoro Compounds

A. Isolated $[MF_6]$ Groups

Table I contains the most important structures reported for ternary and quaternary fluorides exhibiting isolated $[MF_6]^{m-}$ octahedra. These are generally formed if the stoichiometric ratio F:M ≥ 6, except for M in oxidation state +2.[18]

1. The Group of Cryolites and Elpasolites

As in most ternary compounds of general composition A_mMF_6, isolated octahedral $[MF_6]$ groups are also present in the "cryolites" A_3MF_6 and more especially in the "elpasolites" A_2BMF_6, named after the mineral K_2NaAlF_6.[49] This group of compounds is chosen here to show the size effect of the constituent ions ($r_A > r_B > r_M$) on the resulting structure.

When the two alkali-metal ions are different, A and B, the cryolite structure becomes cubic. This is generally not the case if they are both the same. The true cryolites Na_3MF_6 are monoclinic.[40–42] Most of the corresponding compounds with the larger alkali-metal ions have complicated superstructures of varying complexity, the majority of which have not yet been solved.[60,61]

The reason why (with some exceptions, especially involving high-temperature phases) only the elpasolites A_2BMF_6 adopt the idealized cubic cryolite structure is obviously purely geometric: the size difference between the large (A) and the small (B) ions matches the difference between the 12- and 6-coordinated cavities provided by the cubic structure shown in Figure 1.

The geometric conditions for the appearance of cubic symmetry and the relations between ionic radii and lattice constants in elpasolites are discussed in the following.

a. The Tolerance Factor and Its Geometrical Meaning. The elpasolite structure is a perovskite superstructure with doubled cell edge. It results from substitution of the two M^{II} cations in $A^I_2M^{II}M^{II}F_6$ by two unlike ions $B^I + M^{III}$, which order, because of differences in charge and size, on the octahedral sites in $A^I_2B^IM^{III}F_6$. The radius ratio relation for the perovskites, known as the Goldschmidt tolerance factor,[62] is therefore also applicable to the elpasolites. It turns out that elpasolites are cubic if their tolerance factor $t = 2^{1/2}(r_A + r_F)/(r_M + r_B + 2r_F)$ lies within the limits $0.88 \leq t \leq 1.00$.[10,63] The upper limit, $t = 1$, means that all cations are in contact with anions. As a result, in both rows of ions, that along the cell edge ($r_M + r_B + 2r_F = a_e/2$) and the other along the cell diagonal (projected on the edge: $2^{1/2}(r_A + r_F) = a_d/2$), the radii add up to the same value, which should be identical with the observed lattice constant, $a_0 = a_e = a_d$. However, the cubic structure tolerates loss of diagonal contact, as shown by the lower limit of $t = a_d/a_e = 0.88$.

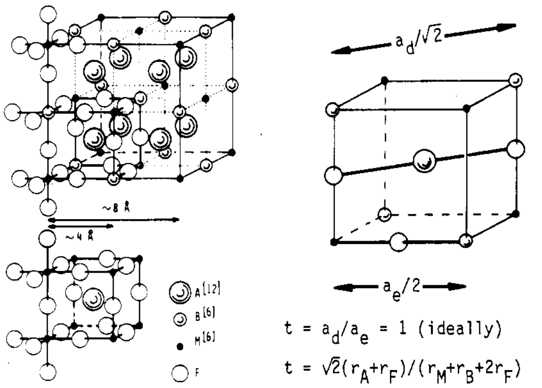


Figure 1. Structure of cubic elpasolites A_2BMF_6 as related to AMF_3 perovskites and the geometrical meaning of Goldschmidt's tolerance factor *t*.

In practice, it is often found, especially for compounds in the lower tolerance factor range, that the observed lattice constants are smaller than calculated from the edge-row ionic radii, $a_0 < a_e$. In fact single-crystal structure analyses and spectroscopic studies provide evidence of anion displacements from the ideal positions on the cell edges, such displacements accounting for some contraction.[51] However, if these details are disregarded, another idea, well-known from Vegard's rule,[2] may be applied to account for a variation of lattice constants: Since the cell dimensions of solid solutions are generally determined from those of the constituents according to their proportion, the lattice constants of the elpasolites should depend on the atom dimensions both along the edge and along the diagonal.

b. Ionic Radii and Lattice Constants of Elpasolites. The foregoing assumption leads to the simple expression $a = (a_d + a_e)/2$. For example, with the above definitions, and using the well-accepted Shannon radii[64] for the appropriate CNs and $r_F = 128.5$ pm, for Rb_2KFeF_6 ($t = 0.89$) $a_d = 849.9$ and $a_e = 919.0$ pm yield $a = 884.5$ pm, compared to the observed lattice constant $a_0 = 886.7$ pm (powder work) and 886.9 pm (single crystal).[51,63] In other words, the mean value of the diagonal and the edge radii sums, the ratio of which is the tolerance factor, gives a better approximation to the observed constant than either component alone.

Explicitly, this expression for predicting the cubic elpasolite lattice constants becomes $a = 2^{1/2}r_A + r_B + r_M + (2 + 2^{1/2})r_F$, which is a linear combination of ionic cavities inside the analogous M_2X_6 frameworks of both compounds, to which it is not specially bonded (see Figure 2). Quite recently, even a pyrochlore without any space fillers has been reported, viz., a new modification of FeF_3.[171]

Unlike in the perovskite framework, which contains one cavity (of CN 12) per MX_3 unit, in the modified pyrochlores two MX_3 units = M_2X_6 provide only one, still larger (CN 18) cavity. Consistent with these geometric conditions the modified pyrochlore structure is preferably adopted by cesium fluoro compounds $CsM^{II}M^{III}F_6$.[67] In the perovskites the smallest unit of three-dimensional linking consists of eight octahedra, centered at the corners of a cube (=the crystallographic cell). The cube contains the countercation A. In the pyrochlores the smallest unit comprises only four corner-sharing octahedra. The octahedral centers form a tetrahedron which remains empty, but four of these units are arranged once more tetrahedrally within the crystallographic cell and surround the countercations A as shown in Figure 2.

The tetragonal and hexagonal bronze structures already mentioned[184,185] are intermediate between the cubic and the tetrahedral array of octahedral centers, which here form trigonal prisms as the smallest units of three-dimensional linking. In between these units there are cavities of CNs 12 and 15 (TTB) and of 18 (HTB) for large A ions. However, the number of cavities is now reduced to 0.6 and 0.33 per MF_3 unit, respectively, and often even fewer are occupied.[167,190–192]

An interesting feature of the bronzes and of the cubic pyrochlores $AM^{II}M^{III}F_6$ is the random distribution of the di- and tervalent M cations over one and the same crystallographic equipoint. Only a limited number of noncubic pyrochlores are known, in which the different M cations are ordered. Surprisingly, all mixed-valence fluorides, like $NH_4Fe_2F_6$ or $CsNi_2F_6$,[172–175] belong to these ordered pyrochlores, of which at least two types exist.

Using a sample prepared from the iron fluorides with natural ^{57}Fe abundance and another enriched with $^{57}FeF_3$, a recent Mössbauer study has shown that the ion ordering in the orthorhombic mixed-valence $CsFe_2F_6$ proceeds via electron transfer.[193] The cubic, ionically disordered high-temperature phase can thus transform without cationic displacement at lower temperature to a phase of lower symmetry but with the M^{II} and M^{III} cations ordered. When M^{II} and M^{III} are different elements, this ordering mechanism by electron transfer cannot of course operate and the cubic pyrochlore structure is generally preserved. In this sense the cubic compounds are frozen high-temperature modifications. This is in accordance with their high molar volume, which is often higher than the molar volume sum of the binary components.

The existence of a clear-cut radius/lattice constant relation for the cubic pyrochlores $CsM^{II}M^{III}F_6$ has already been mentioned.[67] It should be noted that isostructural oxides $CsM^{V}M^{VI}O_6$ and all intermediate compositions of oxide fluorides CsM_2X_6 (X = O, F) are also known.[194]

2. Anisotropically Linked [MF$_6$] Groups

When not all the corners of octahedra are linked in the same way or when edges or faces are shared between

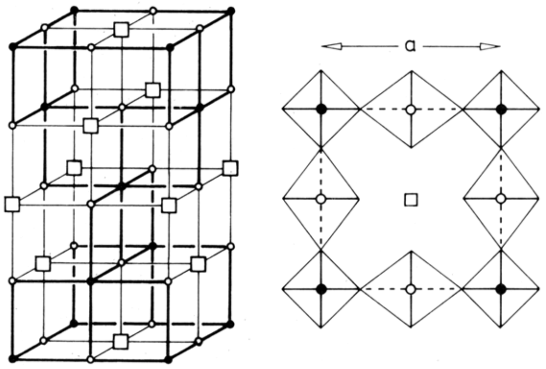


Figure 3. Order of octahedral vacancies in the framework structure of the cation-deficient perovskites $K_4Mn_3F_{12}$[164] and $Cs_2Ba_2Cu_3F_{12}$[179] and the chiolite-like arrangement of Jahn–Teller-elongated octahedra in its basal plane.

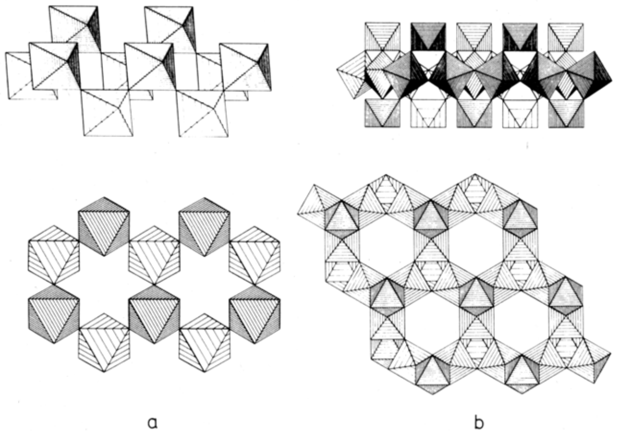


Figure 4. (a) Puckered layer structure of $CsBa_2Ni_2F_9$,[126] a cation-deficient hexagonal perovskite (rhombohedral 9L structure). (b) Triple-layer structure of $Cs_4CoCr_4F_{18}$, deriving from the pyrochlore framework. In both layer types, a and b, each shown in different projections, the octahedra have three fac-terminal ligands at the sheets' surfaces.

the octahedra, the bonding, structure, and physical properties become more or less anisotropic. This is often indicated by the formation of chain and layer structures, which according to Tables IV and VI vary widely depending on geometry-related factors like composition and relative ionic sizes. In addition, anisotropy may be introduced through electronic and electrostatic effects. Examples are the d^4 and d^9 configurations or other Jahn–Teller systems, or heterobimetallic compounds containing transition-metal ions of different charges. Some relevant principles will be shown in the following.

a. Single Bridges: Corner-Sharing Only. In the compositional F:M range between 3 and 4 the double- and triple-layer structures of $K_3Zn_2F_7$[147] and $Cs_4CoCr_4F_{18}$[153] are found, deriving from the perovskite and pyrochlore structure, respectively (cf. Figure 4b). The largest group in this range, however, is that of the weberites $A_2M^{II}M^{III}F_7$ (A = Na, Ag),[10,195] which form framework structures. At least two structural variants exist,[176–180] but in all of them it is the higher charged cation M^{III} which retains two of its ligands unshared (cf. Figure 14). The difference involves the position, cis or trans, of these terminal ligands. It depends on the chain directions of the M^{II} ions, which form 60° rotated or parallel rows of trans corner-sharing octahedra, interconnected by the M^{III} ions.