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SOLID-STATE STRUCTURES OF THE BINARY FLUORIDES OF THE TRANSITION METALS

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I. Introduction

There has been a great deal of interest in binary transition metal fluorides, over many years, both from the synthetic and structural points of view. Synthetically, this group of compounds has provided a challenge, ranging as it does from compounds that can be prepared from aqueous solution to those requiring either very sophisticated or very extreme techniques. Thus manganese difluoride can be separated from aqueous hydrofluoric acid solution (*1*), whereas the recently characterized gold pentafluoride (*2*) was synthesized through the intermediate formation of dioxygenyl hexafluoroaurate(V), which was decomposed thermally under controlled conditions. Chromium hexafluoride and osmium heptafluoride are formed (*3, 4*) only under conditions of high temperature and high excess pressure of fluorine, and can be isolated only by rapid quenching to liquid nitrogen temperatures.

On the structural side, the range of stoichiometries, virtually without the complication of nonstoichiometry, has led to well-defined structure types, again, in many cases, with a challenge in technique for the investigator. Some of the simpler structures have been known for

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many years, having been determined using the techniques of X-ray powder, or restricted-data, single-crystal, crystallography. Structurally, the atom positions in the compounds were defined by few parameters and single crystals easily obtained. Thus, the structure of disilver monofluoride (*5*) was elucidated in 1928 and the single positional parameter was determined from the relative intensities of a few single crystal reflections. A recent redetermination, using modern techniques (*6*), has led to little essential change in the accepted structure. The scope of structural work has broadened as the techniques both of manipulating compounds and of crystallography itself have improved. Particularly important has been the rapid automation of crystallography, with advances in computing. Much of the earlier powder work on simple compounds has now been supplemented by single-crystal studies, as high temperature methods for single crystal growth have been exploited. More recently, some of these compounds have been studied by neutron powder diffraction, using the sophisticated powder-profile technique (*7*) for refinement of structural parameters, where accuracy comparable with single-crystal X-ray results has been claimed.

In this technique, structural parameters are refined to fit the overall profile of the powder, neutron-diffraction pattern, which is assumed to consist of Gaussian-shaped peaks, centered at the Bragg-angle positions. The data consist of the point-intensity counts over the angular scan, and overlapping peaks are treated separately, using their contributions to the point intensities.

Although the structural chemistry of transition metal fluorides has been included in more general reviews (*8*), this article aims to collect the structural information now available, and to discuss the structural relationships within this group of compounds. The fluorides are considered in order of increasing number of fluorine atoms combined with the transition metal atom. This order emphasizes relationships within the transition metal series for a particular stoichiometry, although making a comparison of the different fluorides for a particular element more difficult. Fluorides of metals of the "end-groups" of the transition series (Sc, Y, La, Zn, Cd, and Hg) are sometimes included for comparison, although their structures are not discussed in detail.

II. Monofluorides

The only example of a monofluoride is that of silver, although such compounds might be expected for copper and gold, in the same triad. Silver fluoride has the simple rock-salt structure, and the most recent

report (*9*) gives a cubic unit-cell, $a = 4.936(1)$ Å, space-group $Fm3m$, resulting in an Ag—F separation of 2.468(1) Å. The effective, ionic charge (e^*/e) has been calculated (*9*) as ~0.9 and the compound is thus regarded as approximating closely to an ionic lattice.

The spectrum of the unstable diatomic CuF molecule has been observed at high temperatures, from the vapor above molten copper(II) fluoride (*10*), but no evidence for the solid material has been obtained, even after rapid quenching to room temperature. Lattice energy calculations, assuming that CuF would have the rock-salt structure, show that the disproportionation

$$2\ CuF \rightarrow Cu + CuF_2$$

is highly favored (*11*).

It is convenient here to consider the compound disilver monofluoride (or silver subfluoride). This was reported to have an anti-cadmium iodide structure in early work (*5*), and this has been confirmed more recently (*6*). From X-ray single-crystal results the unit cell is hexagonal, $a = 2.996$, $c = 5.691$ Å, space-group $C\bar{3}m$, and the Ag—F separation 2.451 Å, almost identical with that in silver monofluoride (2.468 Å). The structure consists of layers, with a plane of fluorine atoms sandwiched between two planes of silver atoms, giving the fluorine atom a coordination of six silver atoms, the same as in silver monofluoride. The silver atoms have separations of 2.996 and 2.814 Å, compared with 2.889 Å in the metal itself, and in line with the metallic conductivity of the compound.

III. Difluorides

Transition metal difluorides are known mainly for first transition series elements, with palladium and silver difluorides from the second series, and no examples from the third. All these compounds have either the rutile structure, or, for chromium, copper, and silver, a distorted variant, which can be correlated with a Jahn–Teller distortion of the octahedral coordination of the ions. This rutile structure type is associated with smaller cations and, for comparison, although zinc difluoride has the same rutile structure, cadmium and mercury difluorides have the cubic fluorite structure with eight coordination of the cations (*12*).

The difluorides of Mn, Fe, Co, Ni, and Zn were structurally characterized many years ago, but very accurate cell dimensions, and structural parameters, have been reported for melt-grown materials more

recently. Both powder (*13*) and single-crystal (*14*) techniques have been used, and cell dimensions are in good agreement. The detailed bond distances (Table I) show that the octahedral arrangement around the divalent metal has a slight, tetragonal compression with two bonds shorter than the other four. The distorted, octahedral coordination arises from the distortion in the rutile structure from a hexagonal close packing of anions. For idealized hexagonal close packing, the M—F—M angles would be at 90, 132, and 132°, rather than the planar, 130, 130, 100° arrangement found. This effect is more marked for FeF_2 where the difference in bond distance is 0.12 Å. Baur and Khan (*14*) have suggested from lattice energy calculations that only in zinc and manganese difluorides could ionic bonding be dominant, and that iron, and probably cobalt and nickel difluorides, must be at least partly nonionic. Vanadium difluoride is more difficult to prepare than the other first-series difluorides. It was reported to have the rutile structure by Stout and Boo (*15*), but only cell dimensions were given. Recently, more accurate cell dimensions were reported independently (*16*) and these have been confirmed by further reports from the original workers (*17, 18*). A nonstoichiometric phase, $VF_{2+\delta}$, has also been reported (*18*) but δ is very small, about 0.04, and cell dimensions are virtually identical with those of the pure difluoride. Palladium difluoride has the rutile structure (*19, 20*) despite the increased size of the palladium atom compared with the first-series metals.

Copper and chromium difluorides are isostructural, with monoclinc unit cells, which are a distorted variant of the tetragonal cell for the rutile structure. The detailed structure of the copper compound was originally derived from restricted single-crystal data (*21*), while that for chromium was based on an accurate X-ray powder-photographic determination (*22*) and an independent neutron powder study (*23*). The copper difluoride structure has been redetermined by two groups independently, using the neutron powder-profile technique (*24, 25*). Their results are in very good agreement. Fischer *et al.* (*24*) have reported the unit cell in space group $P2_1/c$, rather than the transformed $P2_1/n$, previously used to give a direct comparison with the rutile cell.

In the structure, the copper (or chromium) atom has a greatly distorted octahedral coordination, with two bond distances much longer than the other four (difference = 0.38 Å for Cu, 0.36 Å for Cr) and small, but significant differences between the pairs of short distances. The major distortion is correlated with the d^9, or high-spin d^4, electronic configuration of Cu(II) and Cr(II), respectively, giving an uneven occupation of the e_g orbitals—the Jahn–Teller effect. The differ-

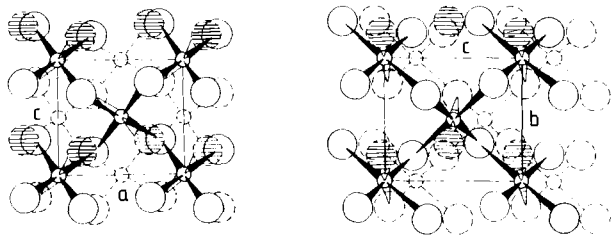
TABLE I

CRYSTALLOGRAPHIC DATA FOR TRANSITION METAL DIFLUORIDES

Compound	Space group (symmetry)[a]	a (Å)	b (Å)	c (Å)	β (degrees)	Bond distances (Å)	Formula unit volume (Å^3)	Reference
VF_2	$P4_2/mnm$ (T)	4.804(5)		3.236(5)		[2.087] × 4, [2.078] × 2	37.3	*17*
CrF_2	$P2_1/n$ (M)	4.732(2)	4.718(2)	3.505(2)	96.52(2)	[1.999, 2.036, 2.374] × 2	38.9	*14*
MnF_2	$P4_2/mnm$ (T)	4.8738(1)		3.3107(1)		[2.131] × 4, [2.104] × 2	39.3	*14*
FeF_2	$P4_2/mnm$ (T)	4.6945(4)		3.3097(1)		[2.118] × 4, [1.998] × 2	36.5	*14*
CoF_2	$P4_2/mnm$ (T)	4.6954(4)		3.1774(4)		[2.049] × 4, [2.027] × 2	35.0	*14*
NiF_2	$P4_2/mnm$ (T)	4.6498(3)		3.0838(1)		[2.022] × 4, [1.981] × 2	33.4	*14*
CuF_2[b]	$P2_1/n$ (M)	4.599(3)	4.546(3)	3.307(2)	96.57(3)	[1.913, 1.933, 2.307] × 2	34.4	*25*
ZnF_2	$P4_2/mnm$ (T)	4.7048(1)		3.1338(2)		[2.046] × 4, [2.012] × 2	34.7	*14*
PdF_2	$P4_2/mnm$ (T)	4.956(2)		3.389(2)		[2.155] × 4, [2.171] × 2	41.6	*19*
AgF_2	$Pbca$ (O)	5.813(3)	5.529(3)	5.073(3)		[2.07] × 4, [2.58] × 2	40.8	*26*
CdF_2	$Fm3m$ (C)	5.3880(5)				[2.333] × 8	39.1	*12*

[a] T, Tetragonal; M, monoclinic; O, orthorhombic; C, cubic.

[b] Alternative cell: $P2_1/c$, a = 3.309(3), b = 4.569(4), c = 5.362(5) Å, β = 121.11(3)° (*24*).



a b

FIG. 1. The puckered layers of $[MF_4]$ units in the structures of (a) silver and (b) copper difluorides. Single circles show atoms in one puckered layer and dashed circles those in the adjacent layer below. Those atoms from the adjacent layer above, which complete the distorted octahedral coordination, are shown hatched. (In silver difluoride they are directly above the dashed circles.)

ences between the short bonds are presumably a consequence of the packing, similar to that in the rutile structures. There is also a large angular distortion in the octahedron. The long metal-to-fluorine bond makes an angle of 12 or 15°, for copper or chromium, respectively, to the normal to the short-bonded, square plane.

In the silver difluoride structure there is a similar distorted octahedral coordination for the silver atom, although the symmetry is orthorhombic rather than monoclinic. The structure has been solved by neutron powder methods, by two independent groups, one using integrated-peak intensity data (*26*) and the other (*27*) powder-profile data. Their results are in excellent agreement. The most significant difference between the silver and copper coordination arrangements is the greater ratio of long to short bond distances, 1.248 for silver, compared with 1.177 for copper. The angular distortion is similar, with the long Ag—F distance making an angle of 16° with the normal to the square plane.

The change in symmetry from copper to silver is related to rather subtle structural differences. If only the four short M—F bonds are considered, then both structures consist of puckered layers formed by joining the square, $[MF_4]$ units through corners. These puckered layers lie directly over one another, related by a translation in copper difluoride, but are displaced alternately, related by a glide plane, in silver difluoride (*27*), (see Fig. 1). In both structures, the fluorine atoms are arranged in considerably distorted hexagonal close-packed arrays, the distortion being more marked for silver.

It has been suggested that the Jahn–Teller distortion is more marked in the silver than in the copper compound, and that this may

account for the structural difference (*27*). The increase in size alone does not appear to be a significant factor, since, correspondingly, nickel and palladium difluorides are isostructural.

The volume occupied by a formula unit is listed in Table I for each difluoride. This can be related to the change in size and electronic configuration along the first transition series. Thus, there is an increase from vanadium to manganese, a decrease from manganese to nickel and an increase from nickel to zinc, following the double curve, characteristic for the ligand-field stabilization effects. The three second-series compounds do not follow the same pattern, but show a steady decrease, with the volume for cadmium difluoride, with the fluorite structure, being less than that for manganese difluoride, with the rutile structure.

When subjected to high temperatures and pressures, polymorphs have been prepared for some of the difluorides. These all have distorted variants of the fluorite structure, with cubic, or pseudocubic, tetragonal cells. Manganese difluoride has been most studied (*28–30*) and similar polymorphism reported for cobalt and zinc difluorides (*30*). Recently, palladium and silver difluorides have been shown to behave in a similar way forming cubic metastable phases (*31*). In all cases there is a decrease in volume for the structure change.

IV. Trifluorides

In contrast with the difluorides, the distribution of trifluorides extends to the third series of the transition metals, where iridium and gold trifluorides are fully characterized. In the second series, trifluorides are known for the elements from niobium to rhodium, with the exception of technetium, and in the first series, from titanium to cobalt. All the trifluorides have been characterized structurally, with earlier reports based on X-ray powder-diffraction data, since the compounds were not prepared in single-crystal form until more recently, when high-temperature, crystal-growth techniques became available.

The early powder diffraction work has been verified in many cases but there has been some controversy and some modification of the early reports. Although this has only involved more accurate cell dimensions in some cases, in others, more accurate chemical analysis and synthesis has led to a reassignment of the identities of certain compounds. The presence of small amounts of oxide impurity is often crucial for the stability of particular structure types, or even compounds. This depends on the similar sizes of oxide and fluoride, and the

inability of X-ray methods to distinguish between them. Thus, there are early reports of cubic unit cells for the trifluorides of zirconium (*32*), niobium (*33*), tantalum (*34*), and molybdenum (*34*). All of these reports have now been queried, with confirmation of a cubic unit cell only for pure niobium trifluoride. It had been suggested that the stoichiometric trifluoride did not exist (*35*), and that all reports of the cubic compound referred to samples, NbO_xF_{3-x}, containing varying amounts of oxide impurity. However, the very careful work of Hagenmuller and his co-workers (*36*), involving the reduction of niobium pentafluoride with niobium metal, in a gold ampoule, with oxygen rigorously excluded, has confirmed both the existence and the cubic unit cell of the trifluoride.

Attempts to prepare zirconium trifluoride, by a similar direct reduction of the tetrafluoride with zirconium (*37*), have been unsuccessful, with no new phase formed. It was suggested that the earlier report was based on material which had either oxide or hydride impurity or which was, possibly, a metastable phase.

For molybdenum trifluoride, it has been established that the cubic material contains oxide impurity, and the pure compound has been prepared by the reduction of the pentafluoride (*38, 39*) or hexafluoride (*37*) with molybdenum metal and has a rhombohedral unit cell.

As a group, the trifluorides all have structures involving octahedral coordination of the metal atoms, although this is greatly distorted for manganese and for gold. By comparison, in the scandium triad, scandium has a similar structure, with six-coordination of the metal (*40*), but the two larger elements are different. Yttrium trifluoride has an eight-coordinate arrangement (*41*) and lanthanum trifluoride a coordination number of seven, nine, or eleven, depending on the distance selected as representing a bond (*42*). This is, presumably, a consequence of the larger sizes of the metal atoms.

The structures of the transition metal trifluorides can be considered either in terms of linking octahedra through all corners, thus achieving the required two-coordination for fluorine, or in terms of close-packed arrays of fluorine atoms, with metal atoms occupying a fraction of the octahedral holes. There are variations in detailed structure over the group and it has been classified into three structure types. These have been described in terms of changes in the packing of the anions, but attempts to correlate these changes with, for example, electron configuration, have been unsatisfactory.

The detailed structures of many trifluorides were reported by Jack and co-workers, from X-ray powder data, which gave very accurate integrated intensities. Although the results for cubic molybdenum and

tantalum trifluorides (*34*) have since been shown to refer to materials containing oxide, recent results from neutron powder-profile data for iron and chromium trifluorides (*43*) are in excellent agreement with the previous work (*44, 45*).

The simplest structure type corresponds to the rhenium trioxide structure, containing one formula unit per cubic unit cell. Scandium (*40*) and niobium (*36*) trifluorides have this arrangement which, therefore, appears to be favored for the larger cations. The M—F—M angle is 180° and the structure can be described either as a linking of octahedra, all in the same orientation, through all corners, or as a cubic close packing of anions, with a quarter of the anion sites vacant, and cations in a quarter of the octahedral holes. This leads to an open structure and the volumes per formula unit are the largest (apart from gold trifluoride) in the group (see Table II).

The rhombohedral unit cells for rhodium and iridium trifluorides (*44*) contain two formula units. The structure can be related to the first structure type by considering anion positions, which here correspond to a hexagonal, close-packed array. There are no vacant anion sites and the cations occupy one-third of the octahedral holes. This leads to M—F—M angles of 132°, characteristic for filling adjacent, octahedral holes in a hexagonal close-packed lattice. Alternatively, the structure can be described as a linking of octahedra through all corners, but the octahedra are now tilted with respect to each other.

The rhombohedral cells for the remaining trifluorides (*44–47*), excluding manganese and gold, are similar to those for the rhodium and iridium compounds (see Table II) but detailed structural analysis has shown that the anion packing for these compounds lies between cubic and hexagonal close packing, although it is closer to hexagonal. This leads to a characteristic M—F—M angle, which is close to 150° for most of the compounds, although for RuF_3 (*44*) it is 136°, and this compound is obviously very close to hexagonal close packing.

This structure type is an intermediate, and a range of structures can be envisaged, with the anion positions changing from cubic close-packed to hexagonal close-packed positions. Figure 2 illustrates the relationship between these two structure types. Only the rhombohedral pseudocell, containing one formula unit, is shown. The cell containing two units is obtained by adding layers of anions, in reverse order, to the pseudocell (*44*). The rhombohedral arrangement can be visualized as deriving from the cubic arrangement, by moving the anions closer together, with a consequent decrease of the M—F—M angle.

Although manganese trifluoride (*48*) has a monoclinic unit cell, the

TABLE II

CRYSTALLOGRAPHIC DATA FOR TRANSITION METAL TRIFLUORIDES

Compound	Space group (symmetry)[a]	a (Å)	b (Å)	c (Å)	$\alpha(R)$ or $\beta(M)$ (degrees)	Bond distances (Å)	M—F—M angle (degrees)	Formula unit volume (Å^3)	Reference
ScF_3	$Pm\bar{3}m$ (C)	4.0115				[2.006] × 6	180	65.0	*39*
TiF_3	$R\bar{3}c(R)$	5.519(2)			59.07(7)	[1.97] × 6	157	57.9	*45*
VF_3	$R\bar{3}c$ (R)	5.373(2)			57.52(3)	[1.95] × 6	147	51.7	*46*
CrF_3	$R\bar{3}c$ (R)	5.2643(3)			56.563(5)	[1.90] × 6	146	46.2	*43*
MnF_3	$C2/c$ (M)	8.904(3)	5.037(2)	13.448(5)	92.74(4)	[1.79, 1.91, 2.09] × 2	146[b]	50.2	*47*
FeF_3	$R\bar{3}c$ (R)	5.362(1)			57.99(1)	[1.92] × 6	153	52.0	*43*
CoF_3	$R\bar{3}c$ (R)	5.279(2)			56.97(2)	[1.89] × 6	149	48.4	*43*
NbF_3	$Pm\bar{3}m$ (C)	3.929(2)				[1.96] × 6	180	59.5	*35*
MoF_3	$R\bar{3}c$ (R)	5.666(1)			54.7(1)	[2.04] × 6	141	56.4	*37*
RuF_3	$R\bar{3}c$ (R)	5.408(1)			54.67(1)	[1.98] × 6	136	49.0	*43*
RhF_3	$R\bar{3}c$ (R)	5.330(1)			54.42(1)	[1.98] × 6	132	46.6	*43*
"PdF_3"	$R\bar{3}$ (R)	5.5234(5)			53.925(5)	[2.17] × 6, [1.90] × 6	133	51.1	*50*
IrF_3	$R\bar{3}c$ (R)	5.418(2)			54.13(3)	[2.01] × 6	132	48.5	*43*
AuF_3	$P6_122$ (H)	5.149		16.26		[1.91, 2.04, 2.69] × 2	116, 148	62.2	*48*

[a] C, Cubic; R, rhombohedral; M, monoclinic; H, hexagonal.

[b] Average angle.

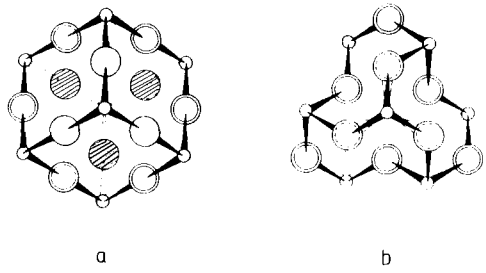


FIG. 2. The relationship between the idealized (a) cubic and (b) rhombohedral structures for transition metal trifluorides. In the close-packed arrangements single circles show atoms in the first layer and double circles those in the second layer. Atoms in the third layer are shown hatched for the cubic structure and dotted for the rhombohedral structure, where they lie directly under those in the first layer.

fluorine atoms conform to a packing arrangement of the intermediate type. The Mn—F—Mn angles average 146°, similar to the angles for the other trifluorides of this type. The distortion arises from the irregular coordination of the manganese atom. Like chromium in its difluoride, manganese here has a high-spin d^4 electron configuration, which confers the characteristic, Jahn–Teller distortion on its coordination arrangement. Thus there is a tetragonal elongation of the octahedron, with two long and four short manganese-to-fluorine distances. The significant, small difference between the pairs of short distances, and the difference between long and short distances (Δ = 0.24 Å), are very similar to those found in both chromium and copper difluorides.

The structural effect of electronic configuration is also seen for gold trifluoride (*49*). For this compound, in contrast to manganese trifluoride, which has a volume per formula unit in line with those for the other first transition series trifluorides, the volume per formula unit is the highest in the group, apart from scandium trifluoride, and the anion arrangement is not close packed. For Au(III), with a d^8 electronic configuration, a square-planar arrangement of ligands is usual. This is achieved in the trifluoride structure with two, cis-terminal, and two, cis-bridging, Au—F bonds, giving a slight distortion of the square plane. The bridging atoms link these square $[AuF_4]$ units into an infinite helical chain. In addition, there are weak interactions between the chains, through the terminal fluorine atoms, to complete a distorted octahedral coordination for gold, with two very long Au—F bonds of 2.69 Å. This gives a difference between long and short bonds of Δ = 0.72 Å, which is about twice the difference for the distorted environments of the metals of the first transition series.

This much greater tetragonal elongation of the octahedron has been

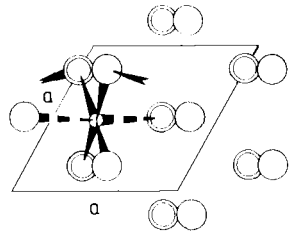


FIG. 3. The structure of gold trifluoride showing the arrangement of fluorine atoms in two adjacent planes, perpendicular to the sixfold axis. Double circles show atoms at $z = 0$ and single circles those at $z = \frac{1}{6}$.

ascribed (*49*) to the presence of two paired electrons in an orbital equivalent to the d_{z^2} orbital, compared with only one for Cr(II) or Mn(III) (or a difference from the $d_{x^2-y^2}$ orbital of one for Cu(II)).

This gross distortion of the coordination around the gold atom precludes a close packing of the fluorine atoms and this is reflected in the anomalously high volume per formula unit (Table II). Although the fluorine atoms lie in planes perpendicular to the sixfold axis of the cell (see Fig. 3), these planes are not arranged in a close-packed sequence.

Palladium trifluoride was originally included with the trifluorides of rhodium and iridium, as having a hexagonal close-packed structure (*44*). However, Bartlett and Rao (*50*) realized that the magnetic susceptibility of the compound was not compatible with the presence of Pd(III), and it was suggested that "PdF_3" was the salt $Pd^{2+}[PdF_6^{2-}]$, with palladium present in oxidation states II and IV. This satisfactorily explained the magnetic behavior, but the X-ray powder data were insufficient to allow a direct, structural verification. Accurate intensity data, from a neutron powder study, have allowed accurate parameters for the fluorine atoms to be derived (*51*), leading to Pd—F distances in alternate octahedra of 1.90 and 2.17 Å. These can be correlated with half the palladium atoms being in oxidation state IV, and half in oxidation state II, since the Pd—F distances are in excellent agreement with those of 1.95 in the tetrafluoride (*52*) and 2.155 and 2.171 Å in the difluoride (*19*).

A comparison of the volumes per formula unit for the trifluorides is more complicated than for the difluorides because of the changes in structure type. If these changes are ignored, then some correlation with electronic configuration is possible. For the first transition series the volume decreases from scandium to chromium, increases from chromium to iron, and decreases to cobalt. This is as expected for the characteristic ligand-field stabilization effects (*49*), comparable with those for the difluorides. In the second series, there is a decrease from

niobium to rhodium, where ruthenium and rhodium, unlike iron and cobalt, have low-spin configurations, and then an increase for palladium, which presumably reflects the presence of Pd(II), with two unpaired electrons in the antibonding e_g^* level (*49*).

In the third series iridium trifluoride has a volume which is slightly larger than that for rhodium trifluoride, in line with the small increase in size of the metal atom. The anomalously high volume for gold trifluoride has already been discussed.

It is convenient here to include fluorides with a metal-to-fluorine ratio of 1 : 2.5. There are three examples. The chromium (*53*) and manganese (*54*) compounds, which are not isostructural, can be considered of the type, MF_2,MF_3, containing di- and trivalent metals. The niobium compound (*35*) is the only example of a metal cluster fluoride reported as yet.

Although attempts have been made to prepare other fluorides with this stoichiometry, for example, by the interaction of the di- and trifluorides of iron and cobalt (*54*), these have been unsuccessful. For vanadium, the compound $VF_{2+\delta}$ presumably contains vanadium(III) but the structure remains that of rutile, with a maximum δ value of 0.04 (*18*).

Dichromium pentafluoride is an idealized formula, since the compound is reported (*55*) to have a composition in the range $CrF_{2.40-2.45}$. However, the structure derived using X-ray data, from a single crystal grown by high-temperature melt techniques, is based on the stoichiometric formula, with some vacant anion sites (*53*). The compound is monoclinic, $a = 7.773(5)$, $b = 7.540(5)$, $c = 7.440(5)$ Å, $\beta = 124.25(1)°$, space group $C2/c$.

In the structure the chromium atoms have octahedral coordination, virtually undistorted for half of them, assigned as Cr(III), and with the characteristic, tetragonal distortion for the remainder, assigned as Cr(II). The Cr—F distances average 1.89(1) Å around Cr(III), close to the value of 1.90 Å in chromium trifluoride (*45*). For Cr(II) there are two pairs of short distances of 1.955 and 2.010 Å, and two long distances of 2.572 Å, very similar to those in chromium difluoride (*23*), although with a larger distortion ($\Delta = 0.82$ Å). The long bond is again displaced from the normal to the square plane, in this case by 18°.

The structure can be divided into infinite chains of linked octahedra. Those for Cr(III), joined through opposite corners, with a Cr—F--Cr angle of 160°, have a very similar orientation to that in chromium trifluoride itself. Similarly, those for Cr(II), joined through opposite edges, have the same orientation as in the distorted rutile structure of the difluoride.

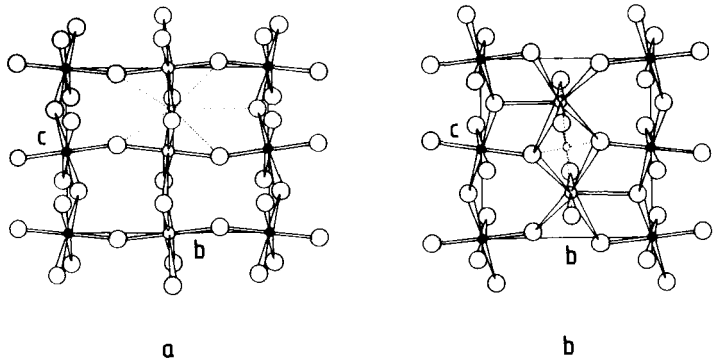


FIG. 4. A comparison of the structures of (a) Cr_2F_5 and (b) $MnCrF_5$. The metal ions are shown as small circles, with the trivalent ions shaded. Dotted circles and lines show the alternative metal atom sites in the two structures.

Dimanganese pentafluoride would not be expected to have the same structure as the chromium compound, since here Mn(III) has the d^4 configuration, leading to distortion, compared with Cr(II) as described above. The compound has been reported (*54*) to have an orthorhombic unit cell, $a = 15.44$, $b = 7.27$, $c = 6.17$ Å. This cell was established from X-ray powder data and no detailed structural analysis has been attempted. However, this cell is very close to that originally reported (*56*) for manganese(II) chromium(III) pentafluoride and a similar structure seems probable. The complete, single-crystal analysis for the mixed metal compound (*57*) has revealed a monoclinic unit cell, $a = 8.586(5)$, $b = 6.291(3)$, $c = 7.381(4)$ Å, $\beta = 115.46(7)°$, space group $C2/c$, with the reported orthorhombic symmetry arising from crystal twinning. The dimensions and arrangement of the octahedra containing Cr(III) are almost identical with those in the dichromium compound, with a F—Cr—F angle of 150°, but the Mn(II) coordination arrangement is a flattened pentagonal bipyramid.

Although there is a difference in the coordination of the divalent ions in the two structures, they are structurally related, since the pentagonal-bipyramidal and distorted-octahedral "holes" are alternative positions between the packed, zig-zag chains (see Fig. 4). The preference of Mn(II) for the seven-coordinate position may be related to its d^5 electronic configuration, with spherical symmetry, allowing a closer approach to an ionic bonding situation.

The volume per formula unit is the same for the two compounds, at 90 Å^3, and that for dimanganese pentafluoride is smaller at 86.6 Å^3. A decrease would be expected, and the dimanganese compound probably has a structure similar to the mixed metal compound, with a distortion

in the chains of octahedra to give Mn(III) the characteristic, coordination arrangement, with a tetragonal elongation of the octahedron.

The structure of the niobium compound is unique for fluorides. Metal atom clusters are common for lower halides, apart from fluorides, of niobium, tantalum, molybdenum, and tungsten. This structure has been established from X-ray powder and single-crystal data (*35*). The unit cell is cubic, $a = 8.19$ Å, space group $Im3m$, and contains clusters of six niobium atoms in an octahedral arrangement with Nb—Nb distances of 2.80 Å. Twelve fluorine atoms are associated with the cluster, with Nb—F distances of 2.05 Å, to give the usual $[M_6X_{12}]$ group. These groups are then linked into an infinite, three-dimensional array through six fluorine atoms, with Nb—F distances of 2.11 Å.

The structure has formally been related to that of sodium chloride (*35*). The fluorine atoms are in positions corresponding to cubic close packing, with vacant sites at the centers of the Nb_6 octahedra, and the niobium atoms then fill three-eighths of the octahedral holes.

V. Tetrafluorides

Although the number of tetrafluorides reported is as large as the number of di- and trifluorides (see Table III), this group of compounds is the least well characterized structurally of the transition metal fluorides. The synthesis of most of the expected tetrafluorides has been reported, with examples from titanium to manganese in the first, from zirconium to palladium (except for technetium) in the second, and from hafnium to platinum (except for tantalum) in the third series. Many of them have been little studied and, in general, they have not proved amenable to crystallographic structural analysis.

The only tetrafluoride for which a single crystal analysis has been reported is that of zirconium (*58*) which lies to the left of the series and exhibits eight, rather than the more characteristic six, coordination. The geometric arrangement around zirconium and, presumably, also around hafnium in the tetrafluoride (*59*), is a square antiprism, with each fluorine atom bridging a pair of zirconium atoms. The existence of a second crystalline form of the tetrafluorides (*59, 60*) has been reported. Although the unit cell for this α-form of hafnium tetrafluoride has been reported as tetragonal (*59*), from X-ray powder photographs, the corresponding α-zirconium tetrafluoride has been investigated, using both single-crystal and powder X-ray methods (*61*), and has a very large, monoclinic unit cell. No detailed structural analysis has been attempted.

TABLE III

CRYSTALLOGRAPHIC DATA FOR TRANSITION METAL TETRAFLUORIDES

Compound	Space group (symmetry)[a]	a (Å)	b (Å)	c (Å)	β (degrees)	Bond distances (Å)	Formula unit volume (Å^3)	Reference
TiF_4								
VF_4	(*O*)	5.33(1)	5.16(1)	9.35(2)			64.3	*68*
CrF_4								
MnF_4	$R3c$ or $R\bar{3}c$ (*Tr*)	19.53		12.59				*74*
ZrF_4	$I2/c$ (*M*)	9.57	9.89	7.66	94°28′	[2.10[b]] × 8	60.2	*58*
NbF_4	$I4/mmm$ (*T*)	4.081		8.162		[2.04] × 6	68.0	*66*
MoF_4								
RuF_4								
RhF_4	$Fdd2$ (*O*)	9.71(2)	9.05(2)	5.63(1)			61.8	*65*
PdF_4	$Fdd2$ (*O*)	9.339(5)	9.240(7)	5.828(3)		[1.95[b]] × 6	63.2	*52*
HfF_4	$I2/c$ (*M*)	9.48	9.86	7.63	94°29′		59.2	*58*
WF_4								
ReF_4	(*T*)	10.12		15.95				*80*
OsF_4								
IrF_4	$Fdd2$ (*O*)	9.64(2)	9.25(2)	5.67(1)		[1.95[b]] × 6	63.2	*64*
PtF_4	$Fdd2$ (*O*)	9.61(2)	9.28(2)	5.71(1)			63.7	*63*

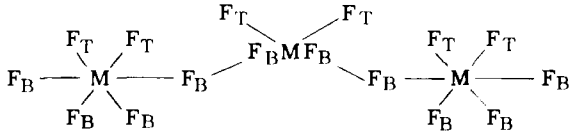
[a] *O*, Orthorhombic; *Tr*, trigonal; *M*, monoclinic; *T*, tetragonal.

[b] Average value.

The existence of polymorphs of these tetrafluorides has been questioned more recently (*62*) and it has been suggested that the reported structures depend on the presence of oxide. Such behavior would parallel that for some of the trifluorides discussed above.

The tetrafluorides of rhodium, iridium, palladium, and platinum have been studied by Bartlett and co-workers (*52*, *63–65*) using powder methods, since single crystals of these compounds have not yet been prepared. Using X-ray methods, platinum tetrafluoride (*63*) was initially reported to be monoclinic and, from the similarity of its unit cell to that of uranium tetrachloride, it was suggested that the compounds were isostructural, with an eight-coordinate arrangement. Later studies on iridium tetrafluoride (*64*) showed that the two tetrafluorides were isostructural, with orthorhombic unit cells, and the same structure was reported for the rhodium and palladium compounds (*65*). The metal atom positions were derived from X-ray powder intensities, and fluorine atom positions postulated to give a six-coordinate arrangement around the metal atoms.

The detailed atomic arrangement has now been confirmed (*52*) using the powder-profile method for neutron data, collected from palladium tetrafluoride. In the structure the palladium atoms have a slightly distorted octahedral coordination by fluorine, with two terminal and four bridging fluorine atoms, as required for the 1 : 4 stoichiometry. The fluorine atoms form an approximately hexagonal close-packed array, and the Pd—F—Pd angles are close to the theoretical 132°, for occupation of adjacent octahedral holes in such an array. The two terminal fluorine atoms are in cis positions in the octahedron, and the bridging fluorine atoms are coordinated to one metal atom trans to a terminal fluorine atom and to the other metal atom trans to a bridging fluorine atom.



Bartlett and co-workers (*65*) have pointed out the relationship of this structure to that of rutile. The MF_4 stoichiometry is achieved by an ordered removal of half the metal atoms from the MF_2 structure. Each fluorine atom is then either two- (for bridging atoms) or one-coordinate (for terminal atoms), rather than three-coordinate as in the rutile structure. In the rutile arrangement the anions are moved from hexagonal, close-packed positions to have a symmetric arrangement of three metal atom neighbors, with planar coordination. The tetra-

fluoride structure has the anions in positions much nearer to close packed, and achieves this by a change of M—F—M angle to 134° (close to the theoretical 132° for hexagonal close packing).

The only other established tetrafluoride structure is that for the niobium compound (*66, 35*). In this structure, like those of the platinum metal tetrafluorides, the niobium atom has an octahedral coordination, by two terminal and four bridging fluorine atoms. Here, however, the two terminal atoms are trans to one another and, with linear fluorine bridges, this leads to a very simple layer arrangement. The layers fit together to give fluorine atom positions corresponding approximately to a cubic close-packed array. On the basis of magnetic susceptibility and Mössbauer spectroscopy, tungsten tetrafluoride has been assigned a similar structure (*67*).

The third structure type for tetrafluorides has been inferred for vanadium tetrafluoride. Although the cell dimensions for this compound were established from single crystal X-ray data (*68*), no intensity data were obtained, because of difficulties in handling the crystals. However, the cell dimensions are very close to those for vanadium trifluoride oxide and chromium difluoride dioxide for which single crystal X-ray structure determinations have been achieved (*69*). The overall structure of the tetrafluoride can therefore be assumed to be very similar, if the effect of replacing oxide by fluoride is taken into account. The intensity data for X-ray powder photographs, reported by two groups independently (*68, 70*), are qualitatively in agreement with this assumption (*71*).

The vanadium atom has octahedral coordination by fluorine, with two cis terminal and four bridging atoms. Thus the environment of the metal is the same as for palladium tetrafluoride, but the mode of linking together of the octahedra is different. Pairs of octahedra are linked through cis bridges to give a double fluorine bridge, with M—F—M angle near to 90°. The remaining pair of cis bridging fluorine atoms then link to two other vanadium atoms. This leads to a close approach of pairs of vanadium atoms and can be correlated with the magnetic properties of the compound (*70*).

Although the linking through fluorine bridges is different from that in palladium tetrafluoride, the fluorine atom positions in vanadium tetrafluoride correspond approximately to a hexagonal close-packed array. The linking of octahedra leads to a complex layer structure, rather than the three-dimensional lattice of the palladium tetrafluoride arrangement.

There is a lack of structural information for the remaining tetrafluorides. In the first transition series titanium tetrafluoride is very

easy to synthesize directly, but there are no reports of structural data, even a powder photograph. Although Moss and Wright (*72*) mention obtaining crystals of the tetrafluoride from thermal decomposition of titanium difluoride oxide, no X-ray results are reported. Attempts to prepare crystals by sublimation of the tetrafluoride, through a thermal gradient, have only resulted in glassy droplets forming on the cooled surface (*71*). Chromium tetrafluoride is also relatively simple to synthesize, but again no structural data are available and sublimation gives a noncrystalline product (*71*, *73*).

Manganese tetrafluoride is considerably more difficult to prepare, but has recently been obtained in single crystal form by Hoppe (*74*) using a very elegant technique. The tetrafluoride was sublimed in a thermal gradient, under a high pressure of fluorine, mixed with oxygen. The sublimation was attributed to the intermediate formation of dioxygenyl pentafluoromanganate(IV). Although unit-cell dimensions have been reported (see Table IV) the compound is not isostructural with any other tetrafluoride, and the detailed atomic arrangement has not yet been reported. The very large rhombohedral cell presumably reflects a complex structural arrangement.

In the second and third transition series, there are no structural data for the tetrafluorides of molybdenum, ruthenium, tungsten, rhenium, and osmium; indeed the reports are virtually confined to synthetic details. Various reducing agents were used in the original preparations of these compounds, including iodine on ruthenium pentafluoride (*75*), tungsten hexacarbonyl on osmium hexafluoride (*76*), and benzene on tungsten hexafluoride (*77*). Molybdenum tetrafluoride was a product of the fluorination of molybdenum hexacarbonyl (*78*). Recent work by Paine and Asprey (*79*) has produced a more general method. Reduction in anhydrous hydrogen fluoride, using silicon or hydrogen, has given clean preparations of the molybdenum, rhenium, and osmium compounds.

However, all these syntheses have resulted in intractable powder samples, which were either poorly crystalline, or for which unit-cell dimensions were not obtained from the powder data. The tetragonal cell reported for rhenium tetrafluoride (*80*) is based on 20 powder lines and may not represent the correct crystal symmetry.

The volumes per formula unit for the tetrafluorides are not easily correlated, unlike those for the di- and trifluorides. This reflects the change from three-dimensional, network solids to either two-dimensional, or more loosely linked, networks. Significantly, the smallest volume is found for zirconium and hafnium tetrafluorides, although these metal atoms have the largest sizes. However, with an eight-

TABLE IV

CRYSTALLOGRAPHIC DATA FOR TRANSITION METAL PENTAFLUORIDES

Compound	Space group (symmetry)[a]	a (Å)	b (Å)	c (Å)	β (degrees)	Bond distances (Å)	Formula unit volume (Å^3)	Reference
VF_5	*Pmcn* (*O*)	5.40(1)	16.72(2)	7.53(1)		[1.69[b]] × 4, [1.97[b]] × 2	84.9	*81*
CrF_5	*Pmcn* (*O*)	5.5	16.3	7.4			82.9	*84*
NbF_5	*C*2/*m* (*M*)	9.62(1)	14.43(2)	5.12(1)	96.1(3)	[1.77[b]] × 4, [2.06[b]] × 2	88.3	*82*
MoF_5	*C*2/*m* (*M*)	9.61(1)	14.22(2)	5.16(1)	94.3(3)	[1.78[b]] × 4, [2.06[b]] × 2	87.8	*86*
TcF_5	*Pmcn* (*O*)	5.76(1)	17.01(2)	7.75(1)			94.9	*85*
RuF_5	$P2_1/a$ (*M*)	12.47(1)	10.01(1)	5.42(1)	99.8(5)	[1.91[b]] × 4, [2.06[b]] × 2	83.3	*88*
RhF_5	$P2_1/a$ (*M*)	12.3376(13)	9.9173(8)	5.5173(6)	100.42(2)	[1.808[b]] × 4, [1.999[b]] × 2	84.4	*83*
TaF_5	*C*2/*m* (*M*)	9.64(1)	14.45(2)	5.12(1)	96.3(3)	[1.77[b]] × 4, [2.06[b]] × 2	88.6	*82*
WF_5	*C*2/*m* (*M*)	9.61(2)	14.26(3)	5.23(2)	94.6(6)		89.3	*87*
ReF_5	*Pmcn* (*O*)	5.70(1)	17.23(2)	7.67(1)			94.1	*81*
OsF_5	$P2_1/a$ (*M*)	12.59(15)	9.91(10)	5.53(3)	99.5(3)	[1.84[b]] × 4, [2.03[b]] × 2	85.0	*89*
IrF_5	$P2_1/a$ (*M*)	12.267(3)	9.982(4)	5.431(2)	99.9(2)		81.9	*90*
PtF_5	$P2_1/a$ (*M*)	12.37(5)	9.84(4)	5.47(3)	99(1)		82.2	*90*
AuF_5								*2*

[a] *O*, Orthorhombic; *M*, monoclinic.

[b] Average value.

coordinate arrangement, they retain a three-dimensional structure. This leads to closer fluorine-to-fluorine contacts overall, despite the impossibility of anions forming a close-packed array.

The group of platinum–metal tetrafluorides has the next largest volume, with the third-series elements, iridium and platinum, showing the expected slight increase over rhodium and palladium. This is presumably a consequence both of the smaller metal atom sizes, and the close approach to hexagonal close packing for the anions. The largest volume is found for niobium tetrafluoride. The structure is described in terms of a cubic close packing of anions and the planar, sheet polymers do not appear to have increased the fluorine-to-fluorine separation for the nonbonded interactions. Thus, this large volume for a close-packed structure is in marked contrast to that of zirconium tetrafluoride, which is not close packed.

VI. Pentafluorides

Apart from that of the recently synthesized gold pentafluoride (*2*), which was reported to be amorphous, the structures of all the transition metal pentafluorides are known. For all the compounds, cell dimensions have been derived, either from X-ray powder photographs or from single-crystal data. For seven of them structural analyses, at various levels of accuracy, have been performed on single-crystal data, and the remainder have unit-cell dimensions closely similar to a compound of known structure (see Table V).

The structures fall into three groups, which are characterized by the pentafluorides of vanadium (*81*), niobium (*82*), and rhodium (*83*). From X-ray powder data, chromium (*84*) and rhenium (*81*) pentafluorides have the same structure as vanadium pentafluoride, for which a full single-crystal analysis has been reported (*81*). Technetium pentafluoride (*85*) is also in this group, with unit-cell dimensions derived from single-crystal measurements. Niobium (*82*), tantalum (*82*), and molybdenum (*86*) pentafluorides are isostructural and all three have been investigated, using restricted single-crystal data, which leads to less accurate molecular dimensions. Tungsten pentafluoride has been shown (*87*) to belong to this group from X-ray powder results.

Although the third structure type was established for ruthenium pentafluoride (*88*), the results were based on restricted single-crystal data, giving less accurate molecular dimensions. Full data were used for the structure analysis of the osmium compound (*89*) but the results were still unsatisfactory, because of the predominant scattering by the

TABLE V

CRYSTALLOGRAPHIC DATA FOR TRANSITION METAL HEXAFLUORIDES

Compound	Space group (symmetries)[a]	Measurement temperature (°C)	a (Å)	b (Å)	c (Å)	Bond distances (Å)	Transition temperature (°C)	Formula unit volume (Å^3)	Reference
CrF_6									*3*
MoF_6	*(C)*	−7	6.221(5)			[1.802] × 6	−9.6	120.4	*93*
	Pnma (O)	−80	9.559(9)	8.668(8)	5.015(5)	[1.81[b]] × 6		103.9	*96*
TcF_6	*(C)*	+10	6.16(3)				−5.3	116.8	*92*
	Pnma (O)	−19	9.55(2)	8.74(2)	5.02(2)			104.8	*92*
RuF_6	*(C)*	+25	6.11(1)				+2.5	114.0	*92*
	Pnma (O)	−30	9.44(2)	8.59(2)	4.98(2)			101.0	*92*
RhF_6	*(C)*	+25	6.13(2)				—	115.1	*92*
	Pnma (O)	−23	9.40(2)	8.54(2)	4.96(2)			99.5	*92*
WF_6	*(C)*	−5	6.30(1)			[1.829] × 6	−8.5	123.8	*94*
	Pnma (O)	−80	9.603(3)	8.713(4)	5.044(3)	[1.818[b]] × 6		105.5	*97*
ReF_6	*(C)*	+10	6.26(2)				−3.5	122.7	*92*
	Pnma (O)	−22	9.61(2)	8.76(2)	5.06(2)			106.4	*92*
OsF_6	*(C)*	+25	6.25(2)				+1.4	122.1	*92*
	Pnma (O)	−21	9.59(2)	8.75(2)	5.04(2)			105.7	*92*
IrF_6	*(C)*	+25	6.23(2)				−1.2	120.9	*92*
	Pnma (O)	−11	9.58(2)	8.73(2)	5.04(2)			105.4	*92*
PtF_6	*(C)*	+25	6.21(2)				+3.0	119.7	*92*
	Pnma (O)	−11	9.55(2)	8.71(2)	5.03(2)			104.6	*92*

[a] *C*, Cubic; *O*, orthorhombic.

[b] Average value.

osmium atom. A very accurate structure was then reported for rhodium pentafluoride (*83*), making it the best defined structurally of all the pentafluorides. Unit-cell dimensions for the isostructural iridium (*90*) and platinum (*90*) pentafluorides have been derived from single-crystal and powder studies, respectively. It seems likely that if crystalline gold pentafluoride is obtained, it will have the rhodium pentafluoride structure.

In the three structure types, the coordination of the metal atoms is the same, with a distorted octahedral arrangement of fluorine atoms. Two *cis*-fluorine atoms in the octahedron form bridges to two other metal atoms, and there are four terminal atoms. The distortion in the octahedron arises from the bridging fluorine atoms being further from the metal than the terminal fluorine atoms. The octahedral units are linked together to form either an infinite, zig-zag chain in the case of vanadium pentafluoride, or a closed tetramer in the other two cases. Thus, in comparison with the tetrafluorides, there is a change from a three- or two-dimensional, polymeric network to either a one-dimensional polymer, or to a small-polymer, molecular unit. The two tetramers are distinguished by the angle at the bridging fluorine atom. For niobium pentafluoride the Nb—F—Nb angle is close to 180°, giving linear bridges and a square arrangement of metal atoms. For rhodium pentafluoride the Rh—F—Rh angle is close to 135°, giving angular bridges and a rhombus of metal atoms. For comparison the V—F—V angle in vanadium pentafluoride is 150°.

Despite the molecular nature of the solid pentafluorides, the structures can be described in terms of close packing of fluorine atoms. Thus, the niobium pentafluoride tetramers pack together so that the fluorine atoms are in positions approximating to a cubic, close-packed array. The idealized structure can then be visualized as an ordered filling of one-fifth of the octahedral holes in such an array with niobium atoms. The theoretical Nb—F—Nb angle for filling adjacent octahedral holes is 180°. Similarly, the rhodium pentafluoride structure has fluorine atoms in positions approximating a hexagonal, close-packed array. Again an ordered filling of one-fifth of the octahedral holes in such an array will give the idealized structure, with a theoretical Rh—F—Rh angle of 132°. Idealized structures are shown in Fig. 5.

The V—F—V angle of 150° in the vanadium pentafluoride structure lies between those for the niobium and rhodium compounds. Thus, the structure cannot be described in terms of either of the close-packed arrangements. Although in the structure some approach toward close-packed planes of fluorine atoms can be seen, a comparison of volume per formula unit for the pentafluorides shows that for the second and

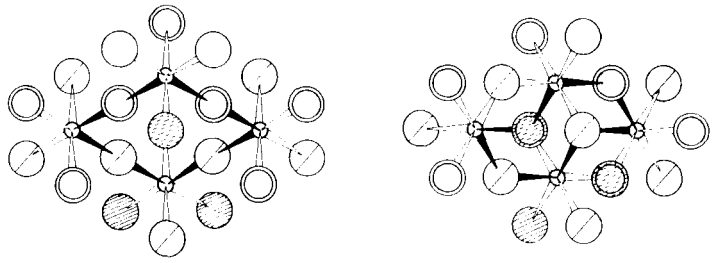


FIG. 5. Idealized, close-packed structures for (a) niobium and (b) rhodium pentafluorides. Atoms in the first, second, third, and fourth layers are shown as single, double, crossed, and hatched circles, respectively. The symbols for overlapped atoms are shown dashed. The bridge bonds are shaded.

third transition series, where a comparison can be made, those of technetium and rhenium are anomalously high. The vanadium pentafluoride structure, therefore, leads to inefficient packing together of the structural units.

If allowance is made for these anomalies, the volume per formula unit tends to decrease along each series, as would be expected for the decrease in size of the metal atom (see Table IV). The small variations, for example, for the tantalum and tungsten compounds, may reflect inaccuracies in some of the reported unit-cell dimensions.

It has been suggested (*79*) that polymorphism may occur for transition metal pentafluorides as it does for oxide tetrafluorides (*91*). X-Ray powder photographs of products from the reduction of hexafluorides in anhydrous hydrogen fluoride (*79*) showed that the samples of rhenium and osmium pentafluorides had different structures from those previously reported, but no unit-cell dimensions could be derived.

The formation of dimolybdenum nonafluoride, formally MoF_4, MoF_5, has been reported (*78*), but no structural data were obtained.

VII. Hexafluorides

Chromium is the only metal of the first transition series to form a hexafluoride (*3*). The compound is so unstable that no solid-state characteristics have been recorded. The metals of the second and third transition series form hexafluorides which, structurally as a group, are the most closely related of all the transition metal fluorides. These compounds are molecular species, with an essentially regular, octahedral arrangement of fluorine atoms around the metal atom. This leads

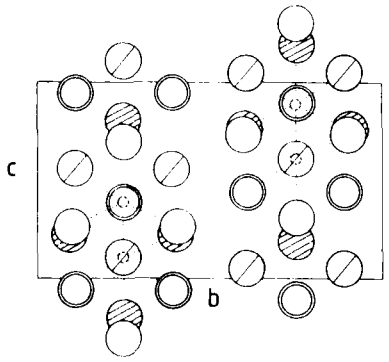


FIG. 6. The structure of tungsten hexafluoride showing the approximate double-hexagonal close packing of fluorine atoms. Hatched circles show atoms at $x = 0$, double circles those at $x = \frac{1}{4}$, single circles those at $x = \frac{1}{2}$, and crossed circles those at $x = \frac{3}{4}$, corresponding to the sequence ABAC. Metal atoms are shown as small, dasbed circles.

to an approximately spherical shape for the molecules, which can, therefore, pack together easily in the solid state.

All of these hexafluorides are dimorphic, with a high-temperature, cubic form and an orthorhombic form, stable below the transition temperature (*92*). The cubic form corresponds to a body-centered arrangement of the spherical units, with very high thermal disorder of the molecules in the lattice, leading to a better approximation to a sphere. Recently, the structures of the cubic forms of molybdenum (*93*) and tungsten (*94*) hexafluorides have been studied using neutron powder data, with the profile-refinement method and Kubic Harmonic analysis. In both compounds the "fluorine density" is nonuniformly distributed in a spherical shell of radius equal to the M—F distance. Thus, rotation is not completely free, and there is some preferential orientation of fluorine atoms along the axial directions. The M—F distances are the same as in the gas phase and in the orthorhombic form.

The orthorhombic form of the hexafluorides corresponds to an ordered arrangement of the octahedra, with the fluorine atoms interlocking efficiently. This gives an arrangement for the fluorine atoms, corresponding, approximately, to double hexagonal close packing, as shown in Fig. 6. The details of this structure were first reported from single-crystal studies of uranium hexafluoride (*95*), and the structures of the transition metal compounds were assumed to be the same for the very similar unit-cells, derived from X-ray powder data. For molybdenum (*96*) and tungsten (*97*) hexafluorides, Levy *et al.* (*97*) have used profile refinement of neutron powder data to derive atomic parameters. Thus,

the detailed packing arrangement has been confirmed and metal-to-fluorine distances reported.

The volumes per formula unit for the cubic forms of the hexafluorides show a marked increase compared with those for the corresponding orthorhombic forms (see Table V). This corresponds to the decrease in efficiency of packing when the molecular units "unlock" at the phase transition. The volumes decrease along the second and third transition series for both forms, as would be expected for the decrease in size of the metal atoms.

The related compounds, dimolybdenum undecafluoride and tetramolybdenum tricosafluoride, formally MoF_5,MoF_6 and MoF_5,$3MoF_6$, respectively, have been reported (*98*) but no structural studies have been attempted.

VIII. Heptafluorides

Only two transition metal heptafluorides are known. Rhenium heptafluoride is stable, but osmium heptafluoride is so unstable that no structural results for the solid compound have been reported (*4*). The rhenium compound is cubic (*92*) at room temperature, with unit-cell dimension $a = 6.26(2)$ Å, which is the same as that for rhenium hexafluoride (Table V). This cubic form is stable to $-90°C$, when a transition occurs to a form of lower symmetry, for which unit-cell dimensions are unknown (*92*).

Iodine heptafluoride exhibits a very similar dimorphism (*99*), with a high-temperature cubic form, unit-cell dimension $a = 6.28$ Å, at $-110°C$, and a transition below $-120°C$ to an orthorhombic form with $a = 8.74$, $b = 8.87$, and $c = 6.14$ Å, measured at $-145°C$. A single-crystal study of the low-temperature phase was reported to show a configuration for the heptafluoride distorted from the expected pentagonal bipyramid (*100*). There has been some controversy over the interpretation of the X-ray results but the experimental work is very difficult and the distorted model appears valid for the data available. The unit-cell similarity for the high-temperature form, and the low-temperature transition, suggests that rhenium heptafluoride is isostructural with the iodine compound.

There has been a recent report (*101*) that ruthenium octafluoride is formed in small amounts in the direct fluorination of the metal, or the dioxide. In view of the instability of osmium heptafluoride, and the nonformation of the octafluoride under forcing conditions (*4*), this report is surprising and further work appears necessary.

IX. Conclusion

Details of the solid-state structures of transition metal fluorides are now known for most of the compounds. Only for the tetrafluorides are there still a number of compounds to be characterized crystallographically.

Some generalizations can be made concerning the structures. Transition metal atoms are almost always coordinated by six fluorine atoms, and this leads to a description of the structures in terms of close packing of fluorine atoms, with metal atoms in octahedral holes. This is useful for *description,* without any implication that it has underlying significance in terms of bonding. Thus a close-packing description has been seen to be appropriate from silver monofluoride, with its predominantly ionic bonding, to tungsten hexafluoride, a molecular solid.

For trifluorides, tetrafluorides and pentafluorides, there is a change from cubic close packing to hexagonal close packing, on passing from the left- to the right-hand side of the transition series. For niobium, this leads to a cubic close-packed description, with linear Nb—F—Nb bridges, for all three fluorides, but for molybdenum there is a change from hexagonal close packing for the trifluoride, to cubic close packing for the pentafluoride. Unfortunately the tetrafluoride structure is still unknown. The reason for this change is not understood, although it has been suggested by Canterford and Colton (*8*) that weak π-bonding may account for the changes observed in the pentafluoride series.

The volume of space occupied, per fluorine atom, has often been quoted as about 18 Å^3. For the transition metal fluorides this is approximately so, although there is considerable variation, and the values are more often lower. For a particular metal, the variation in volume occupied with change in oxidation state is not simple. Thus for vanadium the volumes are VF_2, 19.5; VF_3, 17.2; VF_4, 16.1; VF_5, 16.1 Å^3, whereas for rhodium the values are RhF_3, 15.5; RhF_4, 15.5; RhF_5, 16.9; RhF_6, 16.7 Å^3.

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