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Chapter 8

TRANSITION METAL FLUORIDES

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Introduction

The years since the pioneering work of Moissan, Ruff and Klemm have seen a steady growth in transition metal fluoride chemistry which is now a mature research area. The number of compounds characterised is enormous; some idea of the scope of transition metal fluoride chemistry can be obtained by browsing through the review literature. Recent examples include solid-state structures of binary fluorides [1], preparations and reactions of oxofluorides [2], hexavalent transuranium fluorides [3], chromium, molybdenum and tungsten fluorides [4], and platinum metal fluorides [5]. In this chapter it has been necessary to be selective and for this reason developments reported during the past 10 years have been concentrated upon.

Uses

From a technological standpoint, UF_6 and UF_4 are pre-eminent due to their key positions in the nuclear fuel industry [6]. The importance of UF_6 as a candidate for laser isotope separation processes is no doubt one of the reasons why its vibrational [7] and electronic [8] spectra have received intense study. A similar comment can be made about PuF_6 [9]. Arising from such work is the recognition that UF_5 is a primary product from UV photolysis of UF_6 [10]. The behaviour of PuF_6 may be similar, but here it appears that PuF_5 has only transient existence under the reaction conditions used [11].

Oxidative fluorination of organic compounds by cobalt(III) fluoride is a well-established route to fluorocarbon species, and selectivity is considerably enhanced if tetrafluorocobaltates(III), usually the K^+ or Cs^+ salts, are used [12]. Very recently, VF_5 has been used to perform similar reactions [13], and the use of UF_6 as a selective oxidant for organics (oxidation sometimes being achieved without concomitant fluorination) has been advocated [14]. MoF_6 [15] and WF_6 [16] have both been used to fluorinate carbonyl groups in organic molecules, formation of strong metal–oxygen bonds contributing to the driving force for the reaction. However, transition metal fluorides are still relatively unpopular as reagents in organic chemistry,

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possibly because their manipulation is considered to be rather difficult, and is certainly unfamiliar to most organic chemists.

Tantalum pentafluoride has played a useful role in the development of hydrocarbon chemistry in super-acid media. Electrochemical [17] and Hammett acidity function [18] measurements both indicate that the acidity of anhydrous HF is enhanced by the addition of TaF_5. Although it is a weaker acid in anhydrous HF than SbF_5, it is not reduced by hydrocarbon solutes and catalytic reactions are therefore more likely. Reactions that have been studied in HF/TaF_5 include the alkylation of alkanes by larger alkanes [19] or ethene [20]. It is not clear whether these super-acid reactions will compete economically with heterogeneous catalysis in the petroleum field, but the involvement of oil companies in research work is apparent. TaF_5 is also a catalyst for the liquid-phase addition of HF to polychlorinated ethenes [21].

Further details on commercially important transition metal fluorides are given by Meshri in Chapter 10.

Preparation of fluorides

Binary high oxidation state fluorides

Oxidative fluorination

Elementary fluorine is still the most widely used reagent for the preparation of binary fluorides. Although flow techniques can be used to prepare fluorides of many of the early d-block elements [22], fluorination under static conditions, with rapid cooling of thermally unstable fluorides, is preferred for platinum metal hexafluorides [23]. A simple metal reactor has been designed for the synthesis of RuF_6 [24] using the latter approach, and this has also been used for the synthesis of PuF_6 [25].

High-pressure fluorination of CrO_3 at 443 K leads to CrF_6 as one product, the compound being characterised partly by its matrix-isolated IR spectrum [26]. This is one of several recent papers which deal with chromium(VI) and -(V) fluorides. Others include the synthesis of several CrF_6^- salts, for example $[NF_4][CrF_6]$ [27], and of $CrOF_3$, which is prepared by the fluorination of CrO_3 with ClF or BrF_3 followed by cautious fluorination with F_2 [28]. A good example of a photochemical fluorination using F_2 is the oxidation of UF_4 to UF_6 below room temperature [29], while F_2, activated by a high-voltage electrical discharge, reacts with heated palladium metal to give what is claimed to be PdF_6 [30]. The product is still incompletely characterised, but the reaction is of interest since the thermodynamic stability of PdF_6 at ambient temperature should be marginal [23].

Noble gas fluorides have played a part in developing the fluorine chemistry of gold and silver, a pleasing development in view of the role played by PtF_6 in the discovery of xenon fluorides. Fluorination of AuF_3 in the presence of XeF_6 leads to $[Xe_2F_{11}][AuF_6]$ [31], and KrF_2 reacts with Au metal in anhydrous HF giving $[KrF][AuF_6]$. Pyrolysis of the latter compound at 333 K leads to orange, diamagnetic AuF_5 [32]. The pentafluoride is also formed by the thermal decomposition of $[O_2][AuF_6]$ *in vacuo* [33], the dioxygenyl salt being prepared by the high-temperature, high-pressure reaction of Au metal with an O_2/F_2 mixture [34]. A red-brown, paramagnetic solid, whose stoichiometry corresponds to AgF_3, results from the oxidation of Ag metal, AgF or AgF_2 by KrF_2 in anhydrous HF. Its magnetic properties suggest that the formulation $Ag^{II}[Ag^{IV}F_6]$ is a possibility [35].

KrF_2 has also been used to prepare tetravalent lanthanide fluorides, LnF_4, where Ln = Ce, Pr and Tb [36], and to oxidise PuF_3 to PuF_4 [37]. In the latter reaction, the hoped-for PuF_5 was not observed. PuF_4 is rapidly oxidised by O_2F_2 at low temperatures giving PuF_6. This and similar reactions can be followed by FT-IR spectroscopy [38].

Reductive syntheses

When the hexafluoride of an element is accessible, the corresponding pentafluoride can often be obtained in a pure state by reduction. A well-established route, which has its origin in the 1960s, is to use I_2 in IF_5 as the reducing agent, and OsF_5 [39], TcF_5 [40] and NpF_5 [37] can be prepared in this way. More recent alternatives are to use H_2 gas or Si in anhydrous HF as the solvent. Pentafluorides of Mo, Re, Os and Ir have been prepared by these means in high yields; longer reaction times with appropriate stoichiometries result in the tetrafluorides [41].

All of these routes have been utilised for the preparation of β-UF_5, interest in this compound having greatly increased in recent years, partly due to the recognition that uranium(V) is stable with respect to disproportionation in many organic solvents. UV irradiation or HF as catalyst are necessary if H_2 is used as the reductant [42], and the I_2^+ cation is an intermediate when the I_2 route is used [43]. Other reducing agents that have been used to perform the reduction $UF_6 \rightarrow \beta\text{-}UF_5$ are HBr in anhydrous HF [44], CO under photolytic conditions [45] and PF_3 [46]. Conditions for multi-gram syntheses have been described using the last two reagents [45, 46], and α-NpF_5 can also be prepared by PF_3 reduction of NpF_6 in HF [47]. α-UF_5 is prepared by reduction of UF_6 with SO_2 at 433 K [48].

Oxotetrafluorides and H_3O^+ salts: controlled hydrolysis of hexafluorides

Hydrolysis reactions, so often a nuisance in fluorine chemistry, have been turned to good account for the preparation of oxotetrafluorides and H_3O^+ fluorometallates. The secret is to perform the reactions in anhydrous HF. Water is either added directly, with careful control of the addition, or is produced *in situ* from quartz wool. Oxotetrafluorides so prepared include those of Re [49], Os [50], U [51, 52], Np [53] and Pu [54]. The synthesis of UF_4O was particularly important since the compound was previously unknown. An alternative, general route to MF_4O compounds from MF_6 uses B_2O_3 as the oxygen source. It is applicable where M = Mo, W, U, Re and Os

[55]. The preparations and properties of individual oxofluorides are discussed in detail elsewhere [2].

When the high oxidation state fluoride is a good Lewis acid, for example a pentafluoride, or is a strong oxidising agent, for example IrF_6, PtF_6 or RuF_6, the product isolated from reaction of H_2O in HF is an H_3O^+ fluorometallate salt. This is a very convenient route to such compounds, and those now known include $[H_3O][MF_6]$, where M = U [56], Nb or Ta [57], $[H_3O][TiF_5]$ [58], $[H_3O][WF_5O]$ [57], $[H_3O][MF_6]$, where M = Ir, Pt or Ru, and $[H_3O]_2[PtF_6]$ [50].

Chalcogen fluorides

Compounds of this type are still relatively rare, and at the present time appear to be limited to tungsten(VI), molybdenum (VI), rhenium(V), -(VI) and -(VII), yttrium and lanthanum, the chalcogen usually being sulphur but sometimes selenium. WF_4X (X = S or Se) compounds and their derivatives have been examined in greatest detail, both in the solid state and in acetonitrile [59]. Preparations of MF_4X compounds generally involve reactions between MF_6, M = W, Mo or Re, and Sb_2X_3 [59, 60, 61], B_2S_3 [61] or elemental sulphur or selenium [62].

Complex fluorides

The ability of fluorine to stabilise oxidation states of 3d elements that are regarded as 'unusual' by coordination chemists has long been recognised. Thus nickel(IV) fluorine compounds, for example, were known and studied for many years before nickel(IV) macrocycle derivatives. Thermal decomposition of a ternary Ni(IV) fluoride has been used for the production of very pure F_2 [63], and NF_4^+ salts of NiF_6^{2-} and MnF_6^{2-} have attracted interest in view of their high active fluorine contents, coupled with their good thermal stability [64].

Experimental techniques for high-pressure (kbar range), high-temperature reactions involving F_2 [65, 66] have been developed to the point where, if not routine, they are relatively common. The emphases have been to obtain accurate structural data, ideally by single crystal studies [65], and to study the relationships between structure and physical properties, e.g. magnetic properties [66]. Some of the compounds which illustrate current interests are described below.

Carmine-red, monoclinic Na_2NiF_6 has been prepared in a pure state for the first time [67] and the series of $A_2[NiF_6]$, A = Na - Cs inclusive, compounds is now complete. Further work on the compounds $A_2[MnF_6]$, A = K, Rb and Cs, indicates that they are air-stable. The previously reported ready decomposition behaviour is therefore ascribed to trace impurities [68]. Single crystal X-ray work on K_2MnF_6 has shown that the Mn–F distance is 1.79 Å, much shorter than that previously estimated [69]. New, complex fluorides of tetravalent lanthanides include A_3LnF_7 (A = alkali metal; Ln = Ce, Pr or Tb), which have the $(NH_4)_3ZrF_7$ structure [70]. The Cs_2AgF_6 phase, prepared by high-pressure fluorination of a 2:1 CsF/AgF_2

mixture, is formulated as an Ag^{III},Ag^{V} compound on the basis of its magnetic behaviour [71], *cf.* AgF_3 which has been described above [35]. A number of copper(III) complex fluorides have been prepared; most are paramagnetic [72], but $Cs[CuF_4]$ appears to contain square-planar Cu^{III} and is diamagnetic [73]. Finally, one of the most interesting recent reports has concerned the stabilisation of Pd^{III} in $Na[PdF_4]$ and in the elpasolites $A_2B[PdF_6]$ (A, B = alkali metal) [66, 74]. EPR studies indicate a low spin $t_{2g}{}^6e_g{}^1$ configuration for Pd^{III} with a significant Jahn–Teller effect.

As for binary fluorides, noble gas fluorides are sometimes alternatives to F_2 for the preparation of ternary compounds. Tetravalent lanthanide compounds, Cs_3LnF_7, have been prepared by this means [36], *cf.* ref. 70, as has $(NH_4)_4UF_{10}$ [75]. The latter compound results from the oxidation of $(NH_4)_4UF_8$ with XeF_2, and the coordination number of uranium is believed to be >8. What may be related complexes are A_3UF_9, A = K or Rb, which are prepared from high-temperature reactions between A_3UF_7 and F_2 [76].

Structural work

Solid-state structures of binary fluorides

The structures of solid, binary fluorides of the d-block are conveniently described in terms of the close-packing of fluorine atoms, the metal atoms occupying octahedral holes [1]. Such descriptions, of course, do not allow any conclusions to be drawn regarding the nature of the metal–fluorine bonding involved, the close-packing model applying equally well to solid, molecular hexafluorides as to ionic difluorides [1]. Although structural information is now available for the majority of binary d-block fluorides, and has been authoritatively reviewed recently [1], hexa- and penta-fluorides have been investigated in greatest detail.

Hexafluorides of the d-block are dimorphic with orthorhombic and cubic, plastic, high-temperature forms. Detailed studies have been made of MoF_6 and WF_6 by neutron powder diffraction, and comparison of the results with analogous work on UF_6 indicates that MoF_6 and WF_6 exist as more compact and spherically-shaped molecules than UF_6. The molecular librations are therefore greater for the d-block compounds since the tendency of their molecules to interlock is smaller. For this reason, UF_6 has no cubic, plastic phase [77].

For d-block pentafluorides there is a change from cubic close-packing to hexagonal close-packing of fluorine atoms from left to right across the block [1]. Three structural types have been established, the NbF_5 structure, also found for Ta, Mo and W, the VF_5 structure, adopted by Cr, Re and Tc, and the RhF_5 type found for Ru, Os, Ir, Pt and possibly Au [1]. Diagrammatic representations of these units are given in Fig. 8.1.

The propensity for fluorine bridging in d-block pentafluorides is reflected in their derivative chemistry and physical properties. For example, magnetic susceptibility data for solid MoF_5 [78], RuF_5 and OsF_5 [79] have

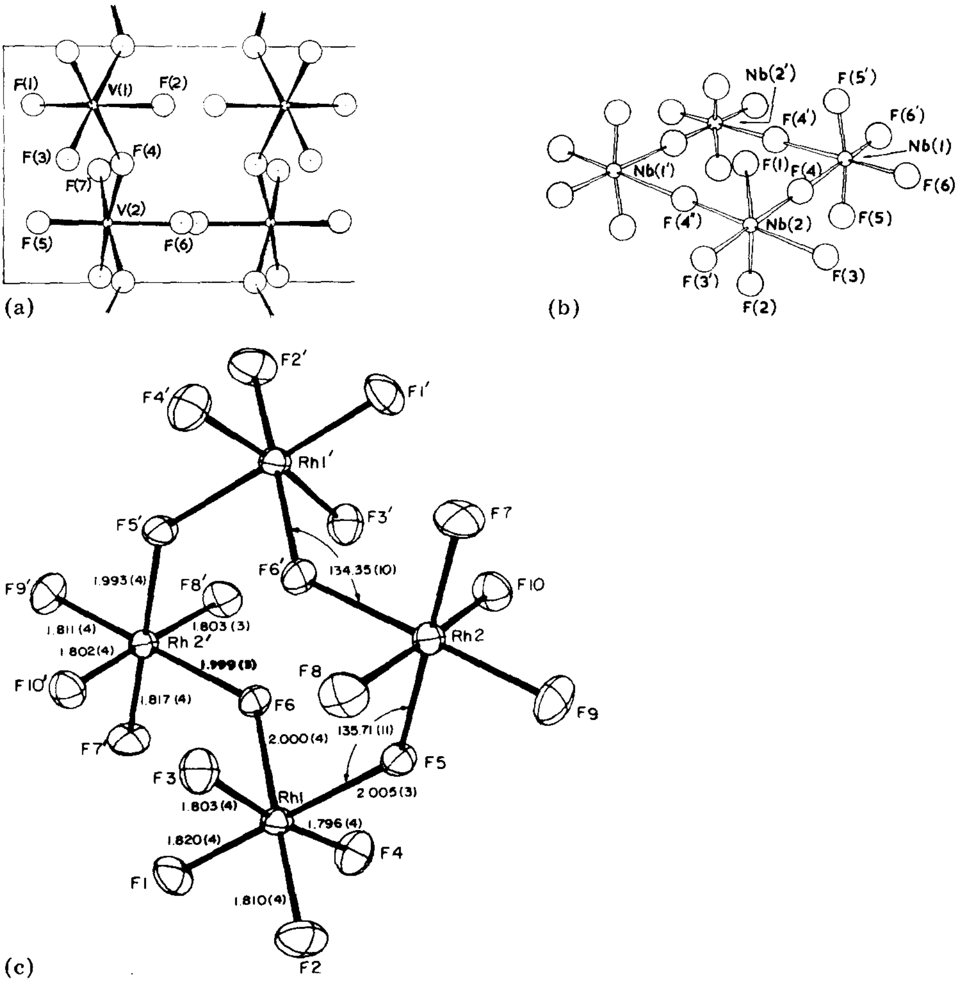


Fig. 8.1. The molecular units in the three types of d-block pentafluoride structures. (a) VF_5 (reproduced by permission from *J. Chem. Soc. (A)*, (1969) 1651); (b) NbF_5 (reproduced by permission from *J. Chem. Soc.*, (1964) 3714); (c) RhF_5 (reproduced by permission from *Inorg. Chem.*, *12* (1973) 2640).

been accounted for on the basis of M_4F_{20} clusters, although for MoF_5 it is possible that a small concentration of $(MoF_5)_3$ is also present [78]. Extensive crystallographic work on d-block oxotetrafluorides indicates that they are closely related structurally to pentafluorides. Oxygen ligands are invariably terminal [2].

Crystallographic studies of lower fluorides appearing prior to 1982 are reviewed elsewhere [1]. Three compounds investigated since that date are α-ZrF_4, the high-temperature form in which triangular dodecahedra are present [80], a modification of FeF_3 with a tungsten bronze type of structure [81] and LaF_3. The latter fluoride characteristically forms twinned

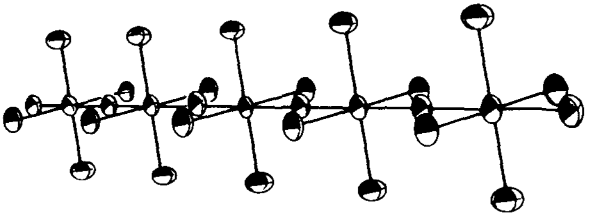


Fig. 8.2. The chain structure in α-UF_5 (reproduced by permission from *Inorg. Chim. Acta*, *37* (1979) 129).

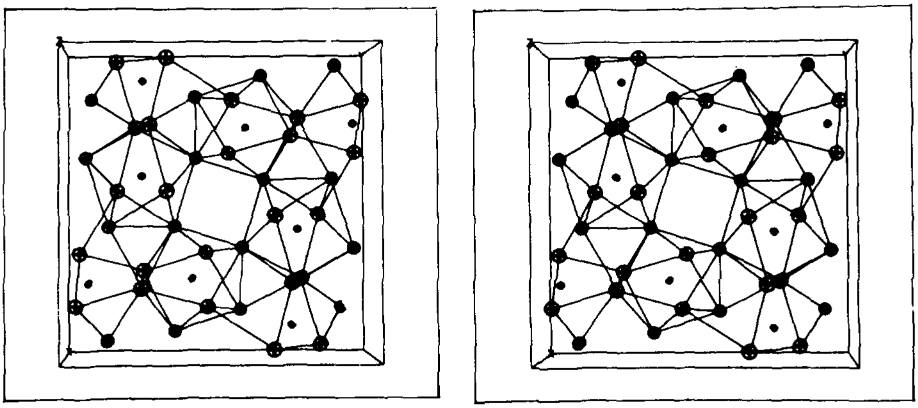


Fig. 8.3. A stereoview of the β-UF_5 unit cell structure (reproduced by permission from *Acta Crystallogr.*, *B32* (1976) 3311).

crystals, and its structure has been a matter of controversy. However, the latest X-ray and neutron diffraction work appears to have ended the controversy [82].

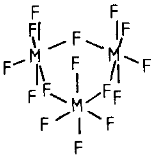
The α-, high-temperature and β-forms of UF_5 have very similar standard formation enthalpies at 298 K [83], but rather different structures (Figs. 8.2 and 8.3).

Uranium is eight-coordinate, $[UF_{6/2}F_2]_\infty$, in β-UF_5. The UF_8 polyhedron is intermediate between a dodecahedron and a square antiprism, although the latter results in a better fit with the observed atomic positions [84]. In α-UF_5 six-fold coordination of U^V occurs, but the structural unit is *trans*-$[UF_2F_{4/2}]_\infty$ rather than the *cis* form [48, 85]. Uranium is seven-coordinate in both α- and β-UF_4O. In each case U^{VI} has pentagonal bipyramidal geometry, the two modifications resulting from different spatial arrangements of the O and F atoms [52, 86, 87].

Vapour-state structures of d-block pentafluorides and related molecules

Since d-block pentafluorides are quite volatile at ambient temperatures or just above, there has been great interest in determining the relationships between the solid and vapour states. Molecular beam mass spectrometry provided the first definitive evidence for the existence of polymeric species in pentafluoride vapours [88], prompting a reappraisal of much of the earlier vibrational spectroscopic work. Molecular beam deflection experiments in inhomogeneous electric fields gave information regarding the polarity, or lack of it, of the vapour species [88]. All the pentafluorides exhibit non-polar behaviour except for VF_5 and CrF_5 where temperature-dependent polarity was observed. Subsequent work on VF_5 is consistent with its polar behaviour. A gas electron-diffraction study [89] and the analysis of its low frequency Raman spectrum [90] both suggest that there are very small deviations from D_{3h} symmetry in the monomer, although not all aspects of its molecular motion can be accounted for. The situation for CrF_5 is less clear-cut. A gas electron-diffraction study has been interpreted on the basis of a C_{2v} structure, consistent with the Jahn–Teller prediction [91], but very recently it has been claimed that vaporisation of CrF_5 leads to CrF_4 and CrF_6 [26]. Further investigation would appear to be indicated.

Vapour pressure measurements [92] on Nb and Ta pentafluorides indicate the importance of $(MF_5)_3$ (M = Nb or Ta) species, and this conclusion has been confirmed by subsequent electron-diffraction studies [93, 94]. The trimeric species has D_{3h} symmetry (1), and this has also been found for $(MoF_5)_3$, again by electron diffraction [95].



(1)

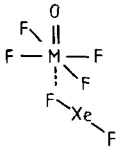
All of these electron-diffraction studies employed relatively low nozzle temperatures (318 - 333 K). In contrast, the composition of AuF_5 at *ca.* 493 K, as determined by electron diffraction, appears to be predominantly $(AuF_5)_2$ of D_{2h} symmetry, with some $(AuF_5)_3$ [96].

Structural studies of d-block oxotetrafluoride vapours, whether by electron diffraction [2] or by matrix isolation spectroscopy, of which a recent example is that of CrF_4O [97], all indicate that the important vapour species is a distorted square-pyramidal monomer. Oxygen occupies the apical position. A similar geometry is found for WF_4S and WF_4Se, the chalcogen atoms being apical [98].

The liquid state and solution

These situations are the most difficult from which to extract unambiguous structural information, and the experimental methods used are distinctly 'sporting'. Vibrational spectroscopy has been used to make suggestions regarding the structure of liquid pentafluorides, for example CrF_5 [99]. The presence of fluorine bridges are inferred from the observation of bands(s) in the region 450 - 500 cm^{-1}. Unfortunately, from an experimental point of view, such bands are strong in the IR spectrum, but are usually weak in the Raman. Although ^{19}F NMR spectroscopy has been widely used to examine diamagnetic transition metal fluoride derivatives, e.g. many of the substituted derivatives and Lewis acid–base complexes described subsequently were identified by this means, it has only been rarely used to study the parent fluorides. One example is VF_5 in SO_2ClF, whose ^{19}F NMR spectrum has been analysed on the basis of short, *cis*-fluorine-bridged chains [100].

It is highly desirable that NMR studies should include nuclei additional to ^{19}F, since the chance of unambiguous structural identification is greatly increased. Thus a combination of ^{19}F and ^{51}V NMR spectroscopy has been used to identify *trans*-$[VF_4O_2]^{3-}$ in aqueous solution [101] and $[VCl_{4-n}F_nO]^-$, $n = 1$ - 4 inclusive, in organic solvents [102]. Using a similar approach, ^{19}F and ^{125}Xe NMR spectroscopy has been used to study adducts formed between MF_4O, M = Mo or W, and XeF_2 in BrF_5 and SO_2ClF solution, the species (2) and (3) being identified [103]. A third example is the identification of the anions (4) and (5) in MeCN solution by a combination of ^{19}F and ^{14}N NMR spectroscopy [104]. Tungsten(VI) fluorides are particularly suitable for study by NMR spectroscopy, since important structural information can be obtained from the ^{183}W satellite spectra.



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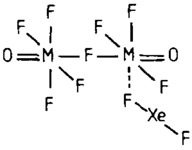
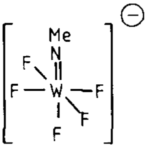


(3)

M = Mo,W



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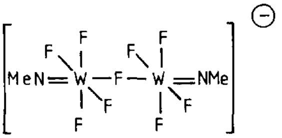


(5)

Reactions of high oxidation state fluorides

Formation of substituted derivatives

The general route for the replacement of fluorine by another ligand (X) involves bond cleavage of B—X or Si—X bonds, for example in BX_3 or Me_3SiX, by a hexa- or penta-fluoride. Providing the moiety X is not susceptible to oxidation by the fluoride to be substituted, such reactions are straightforward. Careful control of stoichiometry and temperature enables the intermediate products in the stepwise substitution process to be identified. Recent examples of this type of behaviour are the series $UF_{6-n}(OMe)_n$ [105] and $UF_{6-n}(OTeF_5)_n$ [106] identified from reactions of UF_6 with Me_3SiOMe and $B(OTeF_5)_3$, respectively. Halogen-exchange reactions involving UF_5 proceed at near-ambient temperatures without a change in oxidation state [107]; however, analogous reactions of UF_6 result in U^V products unless very low temperatures are used. Uranium(VI) chloride fluorides decompose above *ca.* 213 K [108], but have been positively identified by IR spectroscopy in liquid Xe [109], and by ^{19}F NMR spectroscopy in chlorofluoromethanes below 213 K [110].

The combination of halogen exchange and redox behaviour shown by the more oxidising hexafluorides can be turned to good account in synthesis, e.g. one of the best routes to $OsCl_5$ is the reaction of OsF_6 with excess BCl_3 below room temperature [111]. Mixed halides, for example $Os_2Br_4F_5$ and $Ir_2Cl_6F_3$, have been prepared by similar routes [112]. A related observation is that uranium(V) fluoride fluorosulphates are produced from the insertion of SO_3 into U^{VI}—F bonds [113].

Some of the most interesting substituted derivatives recently prepared involve nitrogen-containing ligands. WF_6 is a sufficiently weak oxidising agent to react with Me_3SiN_3 to give monomeric WF_5N_3. Structural and estimated bond-energy data for this compound are both consistent with the presence of a W—N single bond. The compound decomposes explosively at 336 K [114]. ReF_6 and Me_3SiN_3 react to give ReF_4N which reacts with ClF_3 at 273 K to give purple $ReF_5(NF)$ and orange $ReF_5(NCl)$ [115]. X-ray crystallographic work shows that in both cases the ReNX (X = F or Cl) moieties are nearly linear, and thermochemical measurements on $ReF_5(NCl)$ indicate a strong Re—N bond, far greater than the W—N bond energy in WF_5N_3. Although the bond order is formally two, it seems possible that it is actually greater than this. The solid-state structure of $ReF_5(NCl)$ is shown in Fig. 8.4.

The study of F-for-F substitution reactions in metal fluorides requires the use either of dynamic ^{19}F NMR spectroscopy, or of an isotopic tracer. The latter technique has been used to examine exchange reactions between Me_3SiF, labelled with radioactive fluorine-18 (half-life 110 min), and WF_6, $WF_{6-n}(OMe)_n$ ($n = 1 - 4$) [116], UF_6 and UF_5 [117]. In all cases there is a close similarity between ^{18}F exchange involving $Me_3Si^{18}F$ and the analogous

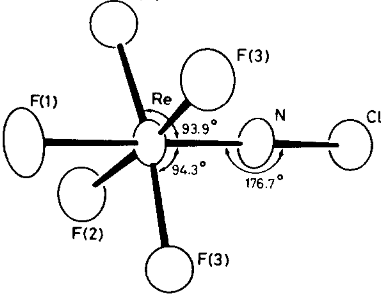


Fig. 8.4. Molecular structure of $ReF_5(NCl)$ (reproduced by permission from *J. Chem. Soc., Chem. Commun.*, (1982) 958).

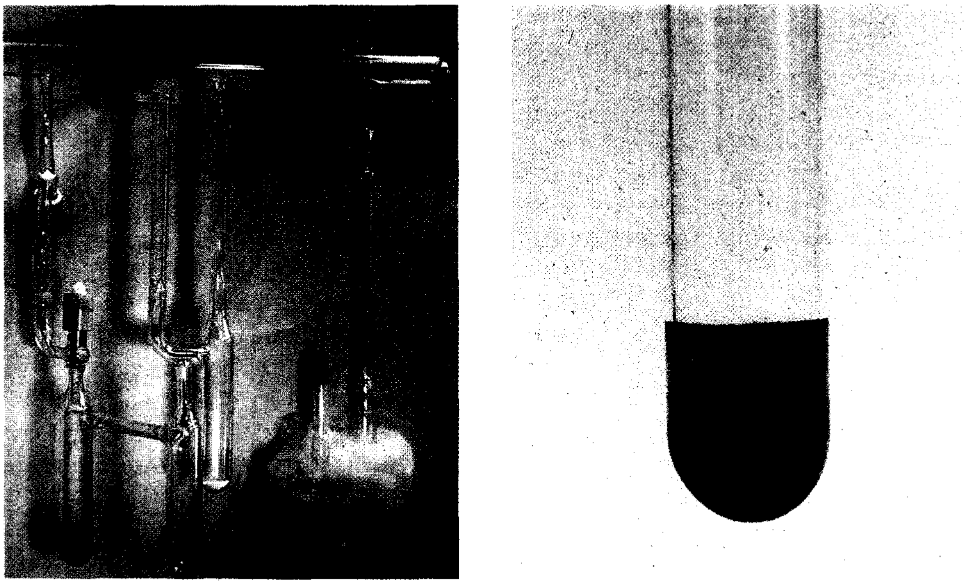
Me_3SiOMe substitution reaction. W^{VI}—F bonds are kinetically less labile than U^{VI}—F or U^{V}—F bonds, and associative mechanisms have been proposed for reactions in the $WF_{6-n}(OMe)_n$ series.

Redox reactions of hexafluorides

The oxidising abilities of d-block hexafluorides in the absence of a solvent increase from left to right across a row in the Periodic Table, 4d hexafluorides being stronger oxidising agents than their 5d analogues. These relationships were first established from reaction chemistry with simple one-electron reductants, e.g. NO and O_2 [118], and they have been reinforced by later work in which the reactions are more complex [119]. A similar approach has enabled f- and d-block hexafluorides to be compared, e.g. the oxidising abilities increase in the order $WF_6 < MoF_6 < UF_6$ and $OsF_6 < PuF_6 < RuF_6$ [3, 25]. Interest in redox properties has been stimulated by recognition that hexafluorides of Mo, U, Os, Ir and Pt oxidise graphite with concomitant intercalation of hexafluorometallate anions [120], similarly polyacetylene is doped to the metallic regime by several hexafluorides, including WF_6 and ReF_6, which do not oxidise graphite [121]. Recent determinations of the electron affinities of WF_6 (338 [122] and 324 kJ mol^{-1} [123]) and of UF_6 (538 [124] and 556 kJ mol^{-1} [125]), together with estimated values for other d-block hexafluorides, have enabled hexafluoride–graphite chemistry to be placed on a rational thermodynamic basis [120].

Reversible oxidation–reduction waves due to the couples MF_6/MF_6^- (M = Mo or W) have been characterised both in anhydrous HF [126] and in rigorously purified MeCN [127] by cyclic voltammetry. In both solvents MoF_6 is the stronger oxidising agent by *ca.* 1 V, suggesting fortuitous cancellation of solvation energies. The data in MeCN were obtained as part of a larger study of the couples MF_6^z/MF_6^{z-1}, where $z = 0, -1, -2$ and M = Ta, Nb, W, Mo, Re, Os and Ru. The linear progressions observed, with the couples become more oxidising in going from left to right across a given row, and less oxidising in going from the 4d to the 5d series, have been related to the nuclear and electronic structure of the central atom (d^0 - d^3). Deviations are observed for $d^3 \rightarrow d^4$ and subsequent couples due to spin-pairing [127].

WF_6, MoF_6 and UF_6 in MeCN are capable of oxidising a variety of transition and post-transition metals to give solvated metal cation salts of the appropriate MF_6^- anion [128, 129]. In some cases the oxidation state of the metal cation obtained depends on the hexafluoride used, thus Tl metal is oxidised to Tl^{III} by MoF_6 or UF_6, but to Tl^{I} by WF_6. The order of oxidising ability in MeCN, determined by a combination of cyclic voltammetry and redox chemistry, is $UF_6 > MoF_6 > NO^+ > Cu^{2+} \geqslant WF_6$ [130]. In this solvent WF_6 is differentiated from UF_6 and MoF_6, both by its weaker oxidising power and by its ability to accept an F^- ion from WF_6^- to form WF_7^- [130, 131]. Molecular iodine is oxidised by MoF_6 or UF_6, but not by WF_6, in MeCN to give isolable $[I(NCMe)_2][MF_6]$ (M = Mo or U) salts [132] (Fig. 8.5). This behaviour is in contrast to that observed in IF_5 solution



(a) (b)

Fig. 8.5. Preparation of [I(NCMe)$_2$][MoF$_6$] from $I_2 + MoF_6$ in MeCN. (a) The apparatus; (b) the reaction in progress. (From the author's laboratory, photographs taken by L. McGhee and R. Munro.)

[43], where I_2 is oxidised to I_2^+ by UF_6 but not by MoF_6, and emphasises the importance of the solvent in redox behaviour.

Acid–base reactions

Formation of fluorometallates

The most obvious demonstration of hexa- and penta-fluoride Lewis acidity is the formation of fluorometallate(VI or V) salts by reactions with suitable donors of the F^- ion. Hexafluorometallates(V), formally derived from essentially all of the known d- and f-block pentafluorides, have been characterised in the solid state, but the formation of hepta- and octa-fluorometallates(V or VI) is limited to elements towards the left of the 4d, 5d and 5f series. NO^+ is a favourite counter-cation, since FNO is a good F^- ion donor, and many MF_6^- salts are accessible by oxidation of NO with MF_6 [118, 133, 134]. In one of the relatively few solution studies to be reported, FNO has been used to generate oxofluorometallates(VI) derived from MoF_4O and WF_4O in anhydrous HF [135]. In the same solvent, MF_6^- (M = Nb, Mo, W and Os) anions react with the strong Lewis acid SbF_5 to generate the appropriate pentafluoride [136].

The vibrational spectra of solid heptafluorometallates [134, 137 - 140] and octafluorometallates [134, 138 - 140], usually with NO^+ or alkali-metal counter-cations, are of some interest since, in principle, decisions regarding an anion's shape can be made from a full vibrational analysis. This is not a trivial problem however, since interconversions among different spatial arrangements are facile. Spectra obtained are very often temperature- and cation-dependent, hence information from X-ray and neutron diffraction, and from ^{19}F NMR spectroscopy [137, 139 - 141] is very desirable. Although room-temperature vibrational spectra can be assigned on the basis of a non-rigid pentagonal bipyramid (D_{5h}) for MF_7^{2-} (M = Nb, Ta [134, 137]) and for MF_7^- (M = Mo, W [134, 138], Re [138] and U [139, 140]), the symmetry of UF_7^- is no higher than C_{2v} at low temperatures [139 - 141], and from the most recent study of K_2TaF_7 [137] it has been concluded that TaF_7^{2-} ions have no symmetry in the crystal state. Similarly, assignments in D_{4h} symmetry have been made for MF_8^{2-} (M = Mo, W or Re [134, 138]) and in O_h symmetry for UF_8^{2-} [139, 140]. Low-temperature spectra of the latter indicate that the symmetry is no higher than D_{2d} [140].

Heterogeneous Lewis acid–base reactions between anhydrous CuF_2 or TlF and WF_6 in MeCN lead to soluble Cu^{II} or Tl^{I} heptafluorotungstates(VI) [142], and a similar type of reaction has been used to prepare copper(II) TaF_6^- [143] and UF_6^- [144] salts. The WF_7^- anion undergoes rapid intermolecular exchange with WF_6 in MeCN solution [142], and the behaviour of $[WF_6(N_3)]^-$ in SO_2 and $[WF_6(CN)]^-$ in CH_2Cl_2 towards WF_6 is similar [145]. In the latter two cases, exchange is believed to occur via a displacement mechanism involving free and complexed WF_6. Reactions between $[NF_4][HF_2 \cdot nHF]$ and WF_6, UF_6 [146], CrF_5 [27], WF_4O [147] or UF_4O [148] in anhydrous HF result in the corresponding NF_4^+ fluorometallate or oxofluorometallate salts.

Fluorine-bridged complexes

Adducts between p-block fluorides and d-block pentafluorides are well known. X-ray crystallographic study of such adducts indicates transfer of an F^- ion from p- to d-block fluoride, but often substantial secondary fluorine bridging links anion to cation. Good examples of this phenomenon are $[SeF_3][Nb_2F_{11}]$ and $[SeF_3][MF_6]$, M = Nb or Ta. To a good approximation these are ionic solids, but the fluorine environments about Se^{IV} are more complex than is implied by the formulation SeF_3^+ [149]. Other examples are $[XeF_5][RuF_6]$, $[XeF][RuF_6]$ [150] and a tetrafluoride derivative, $[XeF_5]_2[PdF_6]$ [151].

On the basis of their crystal structures, the adducts $NbF_5 \cdot SbF_5$ [152], $UF_5 \cdot 2SbF_5$ [153], $UF_4O \cdot 2SbF_5$ [154], $MoF_4O \cdot SbF_5$ and $ReF_4O \cdot SbF_5$ [155] make a contribution to the overall interaction from the ionic formulation in which the transition metal fluoride or oxofluoride moiety acts as the donor, for example $[NbF_4][SbF_6]$. These structures, therefore, provide further evidence of the very strong Lewis acidity of SbF_5. Similar structural suggestions have been made for the adducts $VF_5 \cdot SbF_5$ [156], $UF_5 \cdot 2MF_5$ (M = Nb or Ta), $1.5UF_5 \cdot AsF_5$ [157], $UF_5 \cdot AsF_5$ [158], $UF_4O \cdot 3MF_5$ (M = Nb or Ta) and $UF_4O \cdot 2BiF_5$ [159] on the basis of vibrational spectroscopic work. In each case the first-named moiety is considered to be the fluorine donor. The ability of ReF_7 to behave as a Lewis base has been demonstrated, for example, by the formation of $[ReF_6][SbF_6]$ [160], $[ReF_6][Sb_2F_{11}]$ [160, 161] and $[ReF_6][Sb_3F_{11}]$ [161]. Thermodynamic arguments suggest that ReF_7 is a slightly weaker Lewis base than IF_7, and this is consistent with the observed displacement of ReF_7 from $[ReF_6][AuF_6]$ by IF_7 [162].

Transition metal carbonyl fluorides

This chapter concludes with a brief description of carbonyl fluorides of some d-block metals. This is a field that presents a great synthetic challenge to combine oxidising and reducing ligands on the same metal atom. It also illustrates many of the topics that have been dealt with earlier in this chapter. The breakthrough in the field came with the determination of several crystal structures, which have enabled the subject to be placed on a sound basis. They also emphasise the usefulness of the 18-electron rule [163].

One of the simplest carbonyl fluorides is $Re(CO)_5F$, which can be prepared by halogen exchange from $Re(CO)_5Cl$ in anhydrous HF [164, 165], or from $Re(CO)_5Br$ and AgF in fluorobenzene [166]. It is also found as a component of the fluorine-bridged adduct $Re(CO)_5F \cdot ReF_5$. This species is the product of the oxidation of $Re_2(CO)_{10}$ by XeF_2 in CCl_2FCClF_2 or anhydrous HF [165], and is one of the products isolated from the $Re_2(CO)_{10}/ReF_6$ reaction in anhydrous HF at room temperature [167]. Its X-ray crystal structure [168] indicates that the $Re^{I}—F—Re^{V}$ bridge is non-linear (141°), and suggests that the C_{4v} units, $Re(CO)_5^+$ and ReF_5, compete equally for F^-. This is one of several $Re(CO)_5F$ adducts known [163]. Thermal decomposition of $Re(CO)_5F$ in refluxing C_6H_5F results in the formation of $[Re(CO)_3F]_4 \cdot 4H_2O$, which has a cubane structure [166]. The monomeric $Re^{I}(CO)_3F$ unit can be obtained, however, in the presence of other ligands, e.g. *fac*-$Re(CO)_3(tmen)F$, where tmen = tetramethylethylenediamine [169].

Other carbonyl fluorides that have been characterised structurally include $[Re(CO)_6][Re_2F_{11}]$, isolated from the $Re_2(CO)_{10}/ReF_6$/anhydrous HF system [167], $[Ru(CO)_3F_2]_4$ and $[Ru(CO)_3F_2 \cdot RuF_5]_2$ [170]. The ruthenium compounds are prepared by the oxidation of $Ru_3(CO)_{12}$ with XeF_2 and by the reduction of RuF_5 with CO under flow conditions, respectively. Both are fluorine-bridged tetramers, closely related structurally to $(RuF_5)_4$.

Prognosis

To a great extent transition metal fluorine chemistry has developed as an entity separate from the mainstream chemistry of transition metals. It is to be hoped that in the future the subject will keep its coherence, but that there will be more points of contact (carbonyl fluoride chemistry and the use of metal hexafluorides as reagents are recent examples) so that cross-fertilisation of ideas and experimental techniques can occur. Only then will fluorine cease to be regarded as a 'peculiar' ligand by the transition metal chemical community.

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