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Reactions of Organic Compounds with Higher Fluorides of *f*- and *d*-Elements in Groups V and VI

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The interaction of higher fluorides of *f*- and *d*-elements in Groups V and VI of the Periodic System with alkanes, alkenes, aromatic compounds, and also hetero-organic derivatives containing silicon, nitrogen, phosphorus, oxygen, and sulphur is surveyed. The relative oxidising powers of the inorganic fluorides are assessed. Organic donors possessing lone pairs of electrons form with penta- and hexa-fluorides of low oxidising power relatively stable adducts, least stable with the hexa-fluorides. Highly active inorganic fluorides undergo with organic compounds redox and substitution reactions, yielding complicated mixtures of metal-containing and fluorinated organic substances. A list of 169 references is included.

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I. INTRODUCTION

Reaction between various classes of organic compounds and inorganic fluorides such as silver(II), cerium(IV), lead(IV), bismuth(III), manganese(III), and cobalt(III) fluorides, which are selective fluorinating agents, has formed the subject of reviews[1,2] and books[3-5], and use of several of these agents has been shown to be highly effective. Hitherto, however, no summary has appeared of results on the reaction of organic compounds with higher fluorides of actinides and *d*-elements in Groups V and VI of the Periodic System, which exhibit not so much fluorinating as strongly complexing properties. Inadequate study has been made of the chemistry of complex compounds of *d*- and *f*-elements having a high formal degree of oxidation of the central atom and with coordination numbers ≥ 6. The present Review represents an attempt to make certain generalisation on the basis of material published up to 1975 inclusive.

The terminology and the classification of Mulliken and Pearson[6] have been adopted in characterising donor–acceptor interactions and those of Ingold[7] and Tobe[8] for the reactions. The term "adduct" for compounds isolated individually and for those in solution is used in Cotton and Wilkinson's concept[9] as definition of a compound formed by two neutral molecules, one of which is a donor of electrons and the other an acceptor.

Towards most organic compounds not containing strongly electronegative substituents the higher fluorides of transition elements exhibit the properties of Lewis acids of various strengths (electrophilic reagents), defined by Mulliken[6] as *v*-type acceptors, having vacant orbitals on the central atom, which are able to accept the electrons of donors or abstract an electron from the reagent in the case of a redox step.

The present review discusses donors of various types[6]—σ-donors supplying electrons from a bonding orbital of a σ-bond, π-donors interacting with the acceptor by means of π-electrons of double bonds, and *n*-donors possessing lone pairs of electrons.

In order to analyse the laws governing the interaction of various classes of organic compounds with fluorides of *d*- and *f*-elements, the relative oxidising powers of the latter are assessed in Section II.

II. RELATIVE OXIDISING POWERS OF HIGHER FLUORIDES

After formation of bonds with fluorine in a higher state of oxidation Group V pentafluorides and Group VI hexafluorides have the respective structures $M^{5+}(d^0)F_5^-$ and $M^{6+}(d^0)F_6^-$:[10,11] i.e. no unpaired *d*-electrons remain in their outer orbitals. McDiarmid has found very good agreement between experimental ultraviolet absorption bands of molybdenum and tungsten hexafluorides and the bands to be expected from ligand field theory[11]. He estimates the splitting of the *d*-orbitals of molybdenum(VI) fluoride due to the ligand field as 40 000 cm^{-1}, which indicates a high stabilisation energy of the bonding t_{2g} orbitals. All six electronic transitions in the two hexafluorides are from σ- and π-orbitals of metal–fluorine bonds to $n(d)t_{2g}$ atomic orbitals of the metal. Pentafluorides of Group VI metals have one unpaired *d*-electron; the electronic structure of the outer shell of uranium(V), neptunium(V), and plutonium(V) fluorides is respectively $5f^0$, $5f^1$, and $5f^2$.

Molecules of the pentafluorides have a trigonal bipyramid structure[12,13] with D_{3h} point group symmetry, whereas molecules of the hexafluorides form a regular octahedron[10,13,14] with symmetry O_h. Distortion of the structure of fluoride molecules having unpaired electrons in *d*- and *f*-orbitals of the central atom (molybdenum(V), neptunium(VI), and plutonium(VI) fluorides)—the Jahn–Teller effect—is not observed, since for transition-metal complexes it is significant only when the antibonding e_g orbitals have different populations of electrons[15]. In most of the above fluorides only the t_{2g} orbitals are filled, for which this effect is considerably weaker and produces no appreciable distortion of the geometry of the complex[16].

In the solid state pentafluorides exist as partly ionised tetramers of various types[12]. In the gas phase the pentafluoride of vanadium is monomeric, but those of niobium, tantalum, and molybdenum are polymers with various proportions of tri-, di-, and mono-mers, among which an equilibrium determined by the temperature is established[12,17-19]. All the hexafluorides are highly volatile monomers in the gas phase[10], which can be explained by their greater coordination saturation than that of the pentafluorides.

The hexafluorides of actinides have been arranged[20] in the sequence—plutonium(VI) > neptunium(VI) > uranium(VI)—of diminishing oxidising power. The plutonium compound is a considerably stronger fluorinating agent than is the uranium derivative, and oxidises bromine trifluoride to the pentafluoride, whereas the trifluoride converts various uranium compounds, as well as metallic uranium, into uranium hexafluoride. Sulphur tetrafluoride does not react with uranium hexafluoride, but is converted into sulphur hexafluoride by plutonium hexafluoride. Finally, plutonium hexafluoride fluorinates uranium tetrafluoride and diuranium nonafluoride to the hexafluoride[21,22]. Plutonium(VI) fluoride reacts vigorously with several organic compounds[23,24] that are stable towards uranium hexafluoride.

Few data are available on the oxidising power of neptunium hexafluoride, merely[20] that it partly oxidises bromine trifluoride to the pentafluoride. In the gas phase uranium(VI) fluoride does not react with molecular bromine, whereas the neptunium compound is reduced to the tetrafluoride[25]. A method has been patented[26] for separating a mixture of uranium and neptunium hexafluorides by reducing the latter on cobalt(II) fluoride granules at 105–220°C to the tetrafluoride. These results indicate that neptunium occupies an intermediate position between plutonium and uranium with respect to the oxidising power of its hexafluoride.

A review[2] stated that vanadium pentafluoride was unable to substitute fluorine for hydrogen atoms in organic compounds, and only in certain cases able to add fluorine to double bonds. Such a description of the oxidising capabilities of the pentafluoride does not correspond to information from other sources. Clark and Emeléus showed[27] that vanadium(V) fluoride was a stronger fluorinating agent than bromine(III) and iodine(V) fluorides, and reacted quantitatively with tetrachloromethane at room temperature to form Freons of the methane series, including tetrafluoromethane. More severe conditions—in an autoclave at 220°C—are required for the reaction between tetrachloromethane and uranium hexafluoride[28–30]. O'Donnell et al., who studied[31–35] the reactivity of fluorides of *d*-elements in Groups V and VI, as well as uranium, in redox and exchange reactions, and later Reynes et al.[36] have shown that the reaction $UF_4 + 2VF_5 \rightarrow UF_6 + 2VF_4$ already occurs at 60°C. Thermodynamic calculation of the change in Gibbs free energy ΔG°_{298} of this reaction from the standard Gibbs free energies of formation G°_{f298}[37,38] shows that $\Delta G^\circ_{298} = -9$ kcal mole^{-1}: i.e. the reaction is thermodynamically possible. The results indicate that the oxidising power of vanadium pentafluoride is greater than that of uranium hexafluoride.

Uranium(VI) fluoride in turn converts tungsten(IV) and molybdenum(V) fluorides into the corresponding hexafluorides[32], and molybdenum hexafluoride oxidises[31] tungsten tetrafluoride to the hexafluoride. Furthermore, uranium hexafluoride is reduced vigorously by tetrachloroethylene[39], whereas molybdenum and tungsten hexafluorides do not react under these conditions[40]. Moreover, molybdenum hexafluoride reacts with tetrachloromethane and tetrachlorosilane, but tungsten hexafluoride does not react with these compounds right up to 220°C.[28,41] These results are consistent with conclusions reached by O'Donnell et al.[32], who arranged the hexafluorides in the reactivity sequence uranium > molybdenum > tungsten.

The oxidising power of molybdenum pentafluoride has not been studied, but the same type of structure as for niobium and tantalum pentafluorides[12] and the similar action of such reagents as ammonia[42], pyridine and its derivatives, and acetonitrile[43,44] indicate only a slight difference in chemical activity. Nevertheless, the molecule contains[5] an unpaired *d*-electron in the outer shell of the molybdenum ion, and is potentially more active. Fairbrother[45] mentions that niobium and tantalum pentafluorides, in contrast to the pentachlorides, exhibit no tendency to reduction and the elimination of halogen. Qualitative observations suggest[33,46] that niobium pentafluoride is rather more strongly oxidising than is tantalum pentafluoride. Brown[47] states that for the pentafluorides the strength of the Lewis acids decreases in the sequence tantalum > niobium > vanadium, i.e. in the reverse order to the decrease in oxidising power.

Thus on the basis of the above results the higher fluorides can be arranged in the sequence

$$PuF_6 > NpF_6 > VF_5 > UF_6 > MoF_6 > WF_6 > MoF_5 \geqslant NbF_5 \geqslant TaF_5$$

of diminishing oxidising power. This sequence is consistent with conclusions reached by Galkin and Tumanov[48] from a thermodynamic investigation of the dissociation of hexafluorides to tetrafluorides, who arranged the hexafluorides in the sequence

$$PuF_6 < NpF_6 < UF_6 < MoF_6 < WF_6,$$

of increasing thermodynamic stability. It is consistent also with an investigation[49] of the action of elementary iodine on uranium(VI) fluoride. The sequence suggests that the oxidising power of fluorides of *d*-elements in the same group becomes weaker with increase in the nuclear charge of the central ion, whereas for *f*-elements the oxidising power increases with the nuclear charge and the number of unpaired *f*-electrons in the outer orbitals.

Table 1. Force constants[50] of metal–fluoride bonds f_d, energies of rupture of bonds[51] E_{M-F}, and standard enthalpies of formation of fluorides $-\Delta H^\circ_{f,298}$.

Fluoride	PuF_6	NpF_6	VF_5	UF_6	MoF_6	WF_6	MoF_5	NbF_5	TaF_5
f_d, mdyn Å^{-1}	3.59	3.71	—	3.78	4.73	5.13	—	—	—
E_{M-F}, kcal mole^{-1}	—	—	114	108	105	121	—	142	—
$-\Delta H^\circ_{f,298}$, kcal mole^{-1}	407[52]	459[53]	341[38]	510[37]	372[54]	411[55]	347[56]	414[57]	435[58]

It is not without interest to compare the sequence of higher fluorides according to their oxidising power with certain molecular constants and thermodynamic functions of the compounds. Comparison of the data in Table 1 with the suggested reactivity sequence shows that increase in oxidising power is accompanied by a decrease in the metal–fluoride stretching force constants, in the energy of rupture of the bond, and by increase in the standard enthalpies of formation for the penta- and hexa-fluorides of *d*- and *f*-elements.

The higher chlorides of most of the elements considered are regarded by Hammond[59] as stronger acceptors than are the corresponding fluorides, owing to the great electronegativity of fluorine.

In actinide hexafluorides *f*-electrons are included in the bond with the fluorine atom. Bagnall[60] notes that the different spatial configuration of *f*-orbitals from *d*-orbitals may lead to different stereochemical consequences for the octahedral

symmetry inherent in hexafluorides. This would apparently have a definite influence on the chemical properties of the actinide hexafluorides.

The reaction of fluorides of *d*- and *f*-elements with members of various classes of organic compounds will be discussed in the following Sections.

III. ORGANIC σ-DONORS

1. Alkanes, Cycloalkanes, and Halogenated Alkanes

Research on the reaction between alkanes and higher fluorides of *d*- and *f*-elements was connected chronologically with the development of atomic technology, in particular with the manufacture of uranium hexafluoride, when it appeared necessary to produce organic compounds, used as greases and packing, that were resistant to the action of uranium hexafluoride, fluorine, and hydrogen fluoride[61-64].

Straight-chain alkanes right up to n-hexadecane react vigorously with uranium hexafluoride, with charring and the liberation of hydrogen fluoride, uranium tetrafluoride, and intermediate fluorides of uranium[63,64]. Reaction may or may not be accompanied by degradation of the carbon skeleton of the alkane depending on the conditions. A process has been patented[65] for fluorinating alkanes and chloroalkanes containing 1–12 carbon atoms with uranium hexafluoride at 70–600°C.

Colourless molybdenum and tungsten hexafluorides form yellow to orange solutions with n-hexane and cyclohexane. The rate of decomposition in the system formed by molybdenum hexafluoride with n-hexane is 1% h^{-1}.[66] Ultraviolet spectral measurements reveal the presence of weak equimolecular complexes (K_{ass} = 0.3–0.6 M).

Addition of vanadium pentafluoride and uranium hexafluoride to n-heptane and cyclohexane produces brown precipitates[67], indicating reduction of the fluorides, apparently to vanadium tetrafluoride and intermediate fluorides of uranium.

In connection with the use[68] of tetrachloromethane for the preparation of uranium tetrafluoride from the hexafluoride a study was made of the reaction of this hexafluoride and several related fluorides, e.g. molybdenum and tungsten hexafluorides, with chlorinated derivatives of methane, ethane, and propane[29,30,63,64,69,70]. It was found that at 25°C uranium hexafluoride was soluble in chloroform, tetrachloromethane, dichloroethylene, pentachloroethane, and perchloroethane[63,64]. A simple eutectic containing 6.5 mole % and melting at −28.9°C occurs in the uranium(VI) fluoride–tetrachloromethane system[71]. At room temperature a solution of the hexafluoride is stable for several weeks. Heating in an autoclave to 150°C leads to an exothermic reaction[63,68], the composition of the reaction products depending on the ratio of the reactants and the temperature. With an equimolecular mixture the products are UF_5, U_2F_9, U_4F_{17}, chlorine, and predominantly Freon 13. A threefold excess of tetrachloromethane yields uranium tetrafluoride, chlorine, and Freon 11. No detailed study of the reaction mechanism has been made; it is suggested that the reaction is catalysed by uranium tetrafluoride[68]. Under normal pressure this reaction occurs over the range 400–500°C.

Even at room temperature plutonium hexafluoride reacts vigorously with tetrachloromethane to form the tetrafluoride with Freons 12 and 13.[22] On reaction with tetrachloromethane at 20°C vanadium pentafluoride, which also possesses strong fluorinating properties, yields[27] a series of chlorofluoro-derivatives of methane up to tetrafluoromethane, with vanadium tetrachloride and trichloride. Molybdenum hexafluoride reacts with tetrachloromethane at 150–220°C to give $Mo(Cl, F)_5$, CCl_3F, CCl_2F_2, and traces of $CClF_3$. Tungsten(VI) fluoride is inert under these conditions.

Chloro-fluorinated alkanes are considerably more inert than the hydrocarbons and their chloro-derivatives. Thus difluorodichloromethane, chlorotrifluoromethane, and dichlorotetrafluoroethane do not react with plutonium hexafluoride at room temperature[72,73], although such reaction is thermodynamically possible for the first two compounds even with uranium hexafluoride[24]. However, while inert to pure uranium hexafluoride at 150°C, dichlorodifluoromethane partly reacts at this temperature even with uranium during the reduction of plutonium from a mixture of plutonium and uranium hexafluorides[72,73]. This indicates either that reduction by this reactant has a radical mechanism or that the process is catalysed by plutonium fluorides. Study of the binary liquid–liquid systems has shown[74,75] that uranium and molybdenum hexafluorides do not react with dichlorotetrafluoroethane.

Perfluoroalkanes are stable towards all the above fluorides, the most active of which—plutonium hexafluoride—gives a stable solution in n-perfluoroheptane[22]. Vanadium(V), molybdenum(VI), tungsten(VI), and uranium(VI) fluorides are stable in solution in perfluoroalkanes of various chain lengths[61,63,64] and in perfluorinated cyclohexane[64,66], methylcyclohexane[67], and dimethylcyclohexane[76,77]. In the systems formed by tungsten hexafluoride with perfluoro-n-pentane and perfluorocyclopentane the components are miscible in all proportions to form non-ideal solutions[78,79], which indicates the presence of intermolecular interactions. Niobium and tantalum pentafluorides are almost insoluble[67] in perfluoromethylcyclohexane, apparently because of their polymeric structure in the solid state.

According to Mulliken[6] the above alkanes, cycloalkanes, and their chlorinated derivatives are weak Lewis bases or σ-type donors with almost the same basicity (judging by the ionisation potentials) for alkanes and cycloalkanes having the same number of carbon atoms. On interaction of σ-donors and *v*-acceptors such as the higher fluorides of *d*- and *f*-elements, formation of stable complexes should not be observed[6], as is fully confirmed by the above examples. During irreversible oxidative fluorination the alkanes, chloroalkanes, and their cyclic derivatives will gradually become inert to all inorganic fluorides right up to plutonium hexafluoride as the hydrogen and chlorine atoms are successively replaced by fluorine.

2. Organosilicon Compounds

Vacant *d*-orbitals of the silicon atom, in contrast to carbon, are closely similar in energy characteristics to the outer *s*- and *p*-orbitals, which has a corresponding effect on the behaviour of silicon.

Tetrachlorosilane reacts[80] with vanadium pentafluoride at room temperature to form vanadium monochloride trifluoride, tetrafluorosilane, and chlorine; with uranium hexafluoride[32] it forms the tetrafluoride, tetrafluorosilane, and chlorine on being heated to 100°C; and with molybdenum hexafluoride it reacts only slightly[31] even above 100°C, giving the mixed compound $Mo_2Cl_3F_6$ and tetrafluorosilane in low yield. No reaction has been detected

in the binary systems formed by tetrachlorosilane with tungsten hexafluoride[31], and with niobium and tantalum pentafluorides[33].

In tetramethylsilane molybdenum and tungsten hexafluorides form red solutions that lose their colour on being frozen, which indicates that stable adducts are absent. Niobium pentafluoride is almost insoluble in this reagent[41].

The reaction of tungsten hexafluoride with methoxytrimethylsilane yields a series of derivatives $(CH_3O)_nWF_{6-n}$ ($n = 1-6$): i.e. it results in complete replacement of fluoride ions by methoxy-groups[81]. The reaction products included tungsten oxide tetrafluoride WOF_4 and unidentified compounds. With phenoxytrimethylsilane the products are phenoxytungsten pentafluoride and *cis*- and *trans*-diphenoxytungsten tetrafluoride[82]. The considerable bulk of phenyl in comparison with methyl groups apparently prevents the coordination of more than two around the tungsten atom. Reaction of molybdenum hexafluoride with dimethyldimethoxy-, methyltrimethoxy-, and tetramethoxy-silane yields[83] dimethylsilicon difluoride, methylsilicon trifluoride, and tetrafluorosilane respectively, as well as tetramethoxymolybdenum difluoride and pentamethoxymolybdenum fluoride. Noble and Winfield[84] described the preparation of a series of methoxy- and phenoxy-tungsten(VI) fluorides of general formula $(RO)_nWF_{6-n}$ (where $n = 1-4$ for the methoxy-group, and 1 or 2 for the phenoxy-group) by mixing tungsten hexafluoride with methyltrimethoxy-, dimethyldimethoxy-, and dimethyldiphenoxy-silane. At 80°C *cis*-dimethoxytungsten tetrafluoride decomposes with the formation of $WOF_4.(CH_3)_2O$. The action of various proportions of tetramethoxysilane on tungsten hexafluoride at 20°C yields[85] tetrafluorosilane, methoxytungsten pentafluoride, and *cis*-tetramethoxytungsten difluoride.

When a mixture of tungsten hexafluoride and trimethylsilyldiethylamine[82] is left at 20°C for 24 h, it is converted into bisdiethylaminetungsten tetrafluoride and then into tetrakisdiethylaminetungsten difluoride, the first of these compounds being a monomer and the second a polymer having fluoride bridges. A complex having the ligands in the proportions 3 : 3 was not observed.

Table 2. Products of the reactions of higher fluorides of *d*- and *f*-elements with organosilicon compounds.

Compound	Colour	M.p. (decomp.), °C	Ref.	Compound	Colour	M.p. (decomp.), °C	Ref.
$MoF(OMe)_5$	—	—	83	$WF_4(NEt_2)_2$	brown	—	82
$MoF_2(OMe)_4$	—	—	83	$WF_2(NEt_2)_4$	brown	—	82
$WF_5(OMe)$	white	(135), 80—85	81, 84, 85, 123, 144	$TaF_3(NEt_2)_2$	yellow	203	86
				$NbF_4(NEt)$	orange	150	86
cis-$WF_3(OMe)_3$	white	17—19	81	$NbF_3(NEt_2)_2$	pink	82	86
$WF_3(OMe)_3$	white	57—59	81	$NbF_4(NEt_2)_2 \cdot Py$	brown	56	86
cis-$WF_2(OMe)_4$	—	82	81, 85	$TaF_4(NEt_2)$	yellow	123	86
$WF(OMe)_5$	—	—	81	$TaF_4(NEt_2) \cdot Py$	yellow	115	86
$W(OMe)_6$	—	—	81	$TaF_3(NEt_2)_2 \cdot Py$	brown	51	86
$WF_5(OPh)$	red	80	82, 84, 123, 144	$TaF_4(NEt_2) \cdot 4MePy$	yellow	122	86
$WF_4(OPh)_2$	red	—	82, 84	$TaF_3(NEt_2)_2 \cdot 4MePy$	brown	20	86

The action of trimethylsilyldiethylamine on niobium and tantalum pentafluorides yields fluorotrimethylsilane and a series of compounds (Table 2) in which one or two fluoride ions have been replaced by a diethylamino-group[86]. On treatment with pyridine or 4-methylpyridine these compounds form adducts in which the coordination number has increased to 6. Replacement of >2 fluoride ions in the pentafluorides was considered to be disadvantageous for steric and electronic reasons, since dialkylamino-ligands, being good donors for *d*-elements, in this case form considerably weaker Lewis acids than the pentafluorides—the diethylamino-tetrafluoride and the bisdiethylamino-trifluoride—which are already incapable of reaction with a base (tetrakisdiethylaminotungsten difluoride can be obtained from tungsten hexafluoride).

It follows from the above account that tetrachlorosilane reacts only with fairly strongly oxidising fluorides such as those of vanadium(V), uranium(VI), and molybdenum(VI). Higher fluorides of niobium, tantalum, molybdenum, and tungsten readily undergo substitution with organosilicon compounds containing alkoxy-, phenoxy-, and dialkylamino-groups:

$$MF_6 + R_nSi(OR)_{4-n} \rightarrow MF_{2+n}(OR)_{4-n} + R_nSiF_{4-n},$$

or

$$MF_6 + n\,RO^- \rightarrow MF_{6-n}(OR)_n + n\,F^-,$$

i.e. the substrate molecule is attacked by the nucleophilic group RO^-, which is a stronger nucleophile than the fluoride ion, and for this reason displaces the latter from the coordination sphere of the central ion. Thus nucleophilic substitution of the S_N type occurs formally with penta- and hexa-fluorides of *d*-elements. Partial or complete substitution of fluoride ions in the electrophilic substrate molecule is observed depending on the conditions and on the steric characteristics of the entering group. Available data support rather an associative mechanism of nucleophilic substitution of the fluoride ion in pentafluorides and in tungsten and molybdenum hexafluorides. Thus exchange of fluorine is slowed down for *cis*-tetramethoxytungsten and tetrakisdialkylaminotungsten difluorides, which may indicate the formation of intermediate seven-coordinated compounds. Octahedral complexes having the electron confirguration d^0, d^1, d^2 and a partly covalent bond can be regarded[88] as coordinatively unsaturated compounds, capable under certain conditions of giving complexes of coordination number >6 by an S_N2 type of associative mechanism; on the other hand, an S_N1 dissociative mechanism of substitution is more typical of octahedral complexes having a large number of unpaired *d*-electrons. The definite effect of the nature of the entering group on the rate of substitution in the above reactions of pentafluorides and of tungsten and molybdenum hexafluorides with nucleophilic reagents can apparently be regarded as some confirmation of an associative mechanism.

It is of interest to examine the above reactions in terms of bond strengths and the electronic character of the reagents. The silicon–oxygen bond is thermodynamically more stable than the silicon–carbon bond (108 and 76 kcal $mole^{-1}$ respectively)[89], but the former is relatively easily cleaved by electrophilic reagents (such as the higher fluorides of *d*-elements in the present case), whereas the silicon–carbon bond is relatively inert in these reactions. Under electrophilic attack the silicon–chlorine bond (91 kcal $mole^{-1}$) is also more reactive than the less stable silicon–carbon and carbon–chlorine bonds (81 kcal $mole^{-1}$), judged by the action of tetrachlorosilane and tetrachloromethane on molybdenum(VI) fluoride[31,41]. It must be supposed that rupture of silicon–carbon bonds will be observed on attack by less electrophilic reagents than the higher fluorides of *d*-elements. Silicon–nitrogen and silicon–oxygen bonds show the same behaviour in the above reactions.

The organosilicon compounds studied are σ-donors in relation to the higher inorganic fluorides, and theoretically[6] are unable to form any stable complexes in a σ-donor–*v*-acceptor system, as is illustrated by the above results. With increase in donor strength towards the above fluorides of *d*-elements the organosilicon compounds can be arranged in the sequence

$$SiR_4 \leqslant SiCl_4 < R_3Si(OPh) < R_3Si(OR) < R_2Si(OR)_2 < RSi(OR)_3 < Si(OR)_4 < R_3Si(NEt_2),$$

which corresponds to increase in nucleophilicity of groups replacing the fluoride ion, in the sequence

$$R^- \leqslant Cl^- < PhO^- < RO^- < R_2N^-.$$

IV. π-DONORS

1. Alkenes and their Halogenated Derivatives

Ethylene and trichloroethylene were tried[64,68] as reductants for uranium(VI) fluoride, and expectedly proved more active than alkanes. The hexafluoride is reduced to uranium tetrafluoride even at −50°C by liquid trichloroethylene, which adds two fluorine atoms at the double bond. In the gas phase at 75–480°C this reaction also yielded the tetrafluoride, with hexachlorobenzene as one of the organic products[28]. In both cases the precipitated tetrafluoride was contaminated with organic compounds of unknown composition[28,90].

Reduction by tetrachloroethylene at 260–315°C yields[39] uranium tetrafluoride uncontaminated by any organic impurities. Analysis of the material balance in the patent[39] shows that the organic reaction product has the empirical formula C_2ClF_5. However, the appearance of Freons 114 and 116 is thermodynamically most probable[24] under these conditions; perhaps the reaction products comprise an equimolecular mixture thereof. Reddish-brown and yellow solutions respectively (stable in the absence of moisture) are formed in the binary liquid–vapour systems comprising tetrachloroethylene with molybdenum and tungsten hexafluorides. Calculation of excess free energies from published data[40] indicates the presence of approximately equimolecular adducts in the liquid phase. These compounds are unstable, since the hexafluorides can be removed from the solution when dry nitrogen is blown through.

The solubility of molybdenum pentafluoride and hexafluoride in hexachlorobuta-1,3-diene has been studied[91] between −25 and +120°C, red–violet solutions being obtained in all cases. Complete miscibility between the hexafluoride and the chlorocarbon is observed at 5–30°C. The liquid pentafluoride gives with this solvent a system comprising two liquids of limited miscibility with a consolute point at 105.3°C representing 0.635 mole fraction of molybdenum(V) fluoride. Neither the pentafluoride nor the hexafluoride was reduced under the experimental conditions.

As hydrogen and chlorine atoms in alkanes are replaced by fluorine, the sensitivity to electrophilic attack diminishes, while that to nucleophilic attack increases[92–94]. For this reason the above relatively weakly oxidising inorganic fluorides—at least those to the right of uranium hexafluoride—will apparently not react with fluoroalkenes.

Alkenes and chloroalkenes act as weak π-donors towards electrophilic reagents[6]. Unstable π-complexes are formed in these systems by means of π-electrons of the double bonds supplied to the acceptor.

Equimolecular π–*v* adducts, formed[40] by tetrachloroethylene with tungsten and molybdenum hexafluorides respectively, can apparently be regarded as intermediates in the reduction of the hexafluorides followed by addition of halogens at the double bond. The reduction of uranium hexafluoride to the tetrafluoride by chlorinated ethylenes[28,39,90] apparently takes place in two stages: addition of thorime atoms to the chloroethylenes is followed by substitution of chlorine by fluorine atoms in the chlorofluoroalkanes.

2. Aromatic Compounds

Benzene, toluene, and xylenes react with uranium hexafluoride at room temperature to form the tetrafluoride, hydrogen fluoride, and carbonaceous substances of unknown composition[64,95]. Nitrobenzene yields a turbid red solution[64]. Molybdenum hexafluoride is rapidly reduced in benzene and xylene to give a dark blue precipitate[95]. Binary systems of tungsten hexafluoride with benzene, toluene, and *p*- and *m*-xylenes have a red colour[41,95–97] and give equimolecular adducts. It was originally stated[98] that, in a bomb at 110°C, the hexafluoride is reduced by benzene to tungsten tetrafluoride. However, these results have not been confirmed[41], since heat-treatment of mixtures of the hexafluoride with benzene and toluene at 110°C or exposure to ultraviolet radiation has given a non-volatile, viscous dark brown liquid in which the ratio of fluorine to tungsten is ~4.7 and ~4.5 for the mixtures with benzene and with toluene respectively.

Addition of perfluorotoluene to a stable colourless solution of vanadium pentafluoride in perfluoromethylcyclohexane produces a red coloration, which then disappears. Similar changes have been observed in the absence of a diluent, as well as with hexafluorobenzene and perfluoro-*p*-xylene[67]. This indicates that the pentafluoride is reduced with preliminary formation of an unstable intermediate compound. Solutions of uranium hexafluoride in hexafluorobenzene, perfluorotoluene, and perfluoro-*p*-xylene have an orange colour[67,95,97], with those in the second solvent the most stable. A similar effect has been observed[95] with vanadium(V) and iodine(VII) fluorides. Molybdenum hexafluoride forms with hexafluorobenzene and octafluorotoluene orange-brown solutions, containing equimolecular adducts and stable for at least 24 h. The system with perfluoro-*p*-xylene is the least stable[95]. The pale yellow solutions of tungsten hexafluoride in perfluorinated benzene, toluene, and xylenes do not decompose[41,95,97] for a long time. Since niobium and tantalum pentafluorides are sparingly soluble in perfluoroarenes[67], no information is available on their behaviour in these solvents.

A recent paper[99] reports that the hydrogenation of benzene in the presence of an equimolecular mixture of hydrogen and tantalum(V) fluorides at 200°C gives high yields of toluene and ethylbenzene. Alkyl radicals are assumed[99] to be generated during the saturation of aromatic to alicyclic systems, after which ring cleavage occurs to give alkanes that interact with the radical-ions of benzene. It is noteworthy that the use of niobium and tantalum pentafluorides as Friedel–Crafts catalysts had been reported earlier[45].

Richardson and Bartlett have obtained[100] salts of the cation $C_6F_6^+$ by condensing hexafluorobenzene and tungsten hexafluoride on powdered AsO_2F_6, SbO_2F_6, and $Sb_2O_2F_{11}$ at −196°C, which are then allowed to warm up slowly to 0°C. The resulting salts have the composition $C_6F_6^+AsF_6^-$,

$C_6F_6^+SbF_6^-$, and $C_6F_6^+Sb_2F_{11}^-$, and gradually decompose at room temperature. The action of nitric oxide on the arsenic salt leads to quantitative formation of benzene and $AsNOF_6$.

The system comprising tungsten hexafluoride and a solution of naphthalene in tetrachloromethane has an orange–brown colour and equimolecular adducts[95]. In contrast, octafluoronaphthalene loses its colour when the supply of the hexafluoride ceases[82]. This is indirect evidence of the brief existence of adducts in this system. A product of the fluorination of dimethylnaphthalene, perfluoro-2-methylbicyclo[4,4,0]decane, forms stable colourless solutions with molybdenum, tungsten, and uranium hexafluorides[101].

The above results indicate that both aromatic hydrocarbons and their halogenated derivatives behave as weak π-donors towards the higher fluorides of the *d*- and *f*-elements considered, as also towards other halides, e.g. chlorides[6,102]. Interactions of such $\pi-v$ type are characteristically weak[6]. Hammond et al.[59,103], who undertook a systematic study based on spectrophotometric measurements of equilibrium constants, enthalpies, and thermochromism of systems formed by aromatic compounds and their halogenated derivatives with various halides of *f*- and *d*-elements in Groups IV–VI of the Periodic System, described all such interactions as "extraordinarily weak or almost contact". They attribute this[59] to unfavourable steric factors involved in contact between planar aromatic systems and the sperically symmetrical hexafluoride molecules, and to the slight overlap between the orbitals of the aromatic ligands and those of the halide molecules. Plane–plane interactions would have been sterically more favourable than the plane–sphere interactions.

Stronger interactions occur in the Menshutkin complexes (of antimony trichloride with arenes)[102], apparently owing to change in the geometry of the acceptor molecule and greater availability of its orbitals for displacing the electrons of the donors. Usanovich et al.[104] have investigated Menshutkin complexes by γ-resonance spectroscopy, and shown that complex formation is due to the transfer of π-electrons of the aromatic ring to p-orbitals of the antimony atom. In the fluorides under consideration here such a mechanism of electron transfer, it appears, will be weakened by the greater electronegativity of fluoride ions.

V. *n*-DONORS

1. Nitrogen-containing Compounds

It seens useful to begin with ammonia our consideration of the interaction of higher fluorides of *d*- and *f*-elements with nitrogen-containing organic compounds, since many of these are its derivatives. The reaction products are listed in Table 3.

Vanadium pentafluoride reacts with ammonia, ethylenediamine, tetramethylethylenediamine, and pyridine with reduction and the formation of $VF_4.L$, adducts of polymeric structure[12,105,106]. In ammoniacal uranium hexafluoride the pentafluoride is formed between −50 and −30°C, a mixture with NH_4UF_5 as the temperature rises to 0°C, and the latter compound at 100°C. 2-Fluoropyridine reacts[107] with uranium hexafluoride to give an adduct $UF_6.2NC_5H_4F$; in solution in dichloromethane the adduct is $UF_6.NC_5H_4F$.

A process has been patented[108] for separating a mixture of hydrogen and uranium(VI) fluorides by means of fluoroaliphatic and fluoroheterocyclic amines and diamines. The separation is based on the formation by these compounds of a stable adduct with hydrogen fluoride, while the hexafluoride is inert towards them.

At −130°C molybdenum hexafluoride is reduced by ammonia to the pentafluoride[109], which forms several ammines depending on the conditions. Keeping the

Table 3. Products of the reactions of higher fluorides of *d*- and *f*-elements with nitrogen-containing organic compounds.

Compound	Colour	M.p.(decomp.), °C	Ref.	Compound	Colour	M.p.(decomp.), °C	Ref.
$VF_4 \cdot NH_3$	orange	(250)	12,105	$WF_6 \cdot TMEn$	—	(95)	107
$VF_4 \cdot 3En$ *	—	—	105	$3WF_6 \cdot 2TMEn$	—	(155)	107
$VF_4 \cdot TMEn$ **	—	—	106	$WF_6 \cdot Me_2NCOH$	—	—	107
$VF_4 \cdot Py$	pinkish grey	(150)	12,105	$2WF_6 \cdot 3Py$	white	(115)	107,112
UF_4NH_4F	yellow-green	(400)	30	$WF_6 \cdot 2Py$	white	(146)	113
$UF_6 \cdot 2NC_5H_4F$-β	—	—	107	$WF_6 \cdot Py$	white	104	113
$UF_6 \cdot NC_5H_4F$-β	—	—	107	$Nb(Ta)F_5 \cdot 2NH_3$	—	—	42,105,114
$MoF_6 \cdot 2Py$	yellow	—	107	$Nb(Ta)F_5 \cdot Me_3N$	—	—	13,117
$MoF_6 \cdot 2CH_3CN$	—	—	111	$Nb(Ta)F_5 \cdot Et_3N$	red-brown	—	118,119
$MoF_5 \cdot NH_3$	red-brown	—	42,43,110	$Nb(Ta)F_5 \cdot 2EtNH_2$	green	—	118
$MoF_5 \cdot CH_3CN$	white	—	44	$Nb(Ta)F_5 \cdot Et_2NH$	red-brown	—	118
$MoF_5 \cdot 2CH_3CN$	white	—	43,111	$Nb(Ta)F_5 \cdot CH_3CN$	—	—	44,107
$MoF_5 \cdot CH_2ClCN$	white	—	44	$Nb(Ta)F_5 \cdot CH_2ClCN$	—	—	44,116
$MoF_5 \cdot Py$	—	—	40,43	$Nb(Ta)F_5 \cdot EtCN$	—	—	44,116
$MoF_5 \cdot 2Py$	pink	—	43	$NbF_5 \cdot 2Me_2NCOH$	—	—	120
$WF_6 \cdot 4NH_3$	brown	—	13,112	$NbF_5 \cdot 1,6En$	—	—	115
$WF_6 \cdot N_2H_4$	—	—	111	$Nb(Ta)F_5 \cdot 2Py$	—	—	44,114,115,120
$WF_6 \cdot 2N_2H_4$	—	—	107	$TaF_5 \cdot 2\text{-}Me\text{—}Py$	—	—	44
$WF_6 \cdot 3MeNH_2$	white	—	112	$TaF_5 \cdot 4\text{-}Me\text{—}Py$	—	—	44
$WF_6 \cdot Me_3N$	—	(150)	107,113				
$2WF_6 \cdot 3Me_3N$	—	(120)	107				

* En = tetraethylenediamine.

** TMEn = tetramethylethylenediamine.

pentafluoride in an atmosphere of ammonia for a long time yields a monoammine[42,43,110]. With pyridine[107] and acetonitrile[111] the hexafluoride gives adducts of composition $MoF_6.2L$.

Tungsten hexafluoride reacts with liquid ammonia[13,112] to give the tetrammine $WF_6.4NH_3$, and with hydrazine in acetonitrile[107,111] to yield 1 : 1 and 1 : 2 compounds, whereas molybdenum hexafluoride is reduced[111] by hydrazine with separation of the tetrafluoride, the complex $MoF_4.2NH_4F$, nitrogen, and ammonia. The reaction of tungsten hexafluoride with methylamine[112] gives $WF_6.3CH_3NH_2$, and with trimethylamine[107,113] $WF_6.(CH_3)_3N$ and $2WF_6.3(CH_3)_3N$ are formed; tetramethylethylenediamine[107] gives the complexes $WF_6.C_2H_4N_2(CH_3)_4$ and $3WF_6.2C_2H_4N_2(CH_3)_4$, dimethylformamide[107] $WF_6.DMF$, and pyridine $2WF_6.3C_5H_5N$,[107,112] $WF_6.2C_5H_5N$, and $WF_6C_5H_5N$.[113] The fluorine-19 nuclear magnetic resonance spectra of the first of these pyridine complexes show that one of the fluorine atoms is not equivalent to the other five, while the octahedral symmetry of the compound is preserved[107,112]. Conductivity measurements suggest[107] the structure $2[WF_5.C_5H_5N]^+F^-.C_5H_5N$.

Fluorides of quinquevalent niobium, tantalum, and molybdenum, in contrast to other pentahalides, e.g. the chlorides, do not undergo reduction on reaction with nitrogen based[114,115]. With ammonia they form adducts[42,105,114] of the types $Nb(Ta)F_5.2NH_3$ and $MoF_5.NH_3$; with acetonitrile, chloroacetonitrile, and propionitrile[44,116] equimolecular complexes are formed, but molybdenum pentafluoride forms also[43,111] $MoF_5.2CH_3CN$. With trimethylamine niobium and tantalum pentafluorides give[13,117] equimolecular complexes. Cryoscopic measurements enabled Buslaev et al.[118] to demonstrate the establishment of the equilibrium

$$2\{NbF_5 \cdot NEt_3\} \rightleftharpoons [NbF_6]^- + [NbF_4 \cdot 2NEt_3]^+$$

results which have since been confirmed by ebullioscopic and conductometric investigations on the system[119]. Treatment of molybdenum pentafluoride with pyridine yields[43] 1 : 1 and 1 : 2 adducts, whereas those of niobium and tantalum give 1 : 2 adducts[44,114,115]; the last two compounds are stable in air, but decompose when heated. Tantalum(V) fluoride forms equimolecular adducts with 2- and 4-methylpyridines, and perhaps also a 1 : 2 adduct with the latter. Investigation of the infrared spectra suggests that $MF_5.L$ adducts are monomeric, with symmetry lower than would correspond to the C_{4v} point group, whereas adducts of type $MF_5.2L$ may be ionised[44,114] $[MF_4L_4]^+[MF_6]^-$.

According to the first ionisation potentials[6] and the above experimental results the donor strength of nitrogen-containing organic compounds increases in the sequence

$$MeCN < EtCN < Py < NH_3 < MeNH_2 < EtNH_2 < Me_2NH < Et_2NH < Me_3N < Et_3N.$$

All these compounds have a lone pair of electrons on the nitrogen atom and are n-donors, strong Lewis bases. With the above fluorides of d- and f-elements nitrogenous compounds are able to form quite stable n-donor–v-acceptor adducts. The above sequence shows that the donor power increases on passing from heteroaromatic amines to primary, secondary, and tertiary aliphatic amines having small groups. It becomes weaker as hydrogen atoms in the alkyl groups are replaced by fluorine atoms, and in perfluoroalkylamines is almost completely absent[5]. Fluorine as a substituent has a similar effect on arylamines and heteroaromatic amines. This is supported by a patent[108] indicating that perfluorinated alkylamines, dialkylamines, peperidine, and pyrrolidine do not exhibit donor properties towards uranium hexafluoride.

Relatively strongly oxidising fluorides, such as those of vanadium(V), uranium(VI), and molybdenum(VI), are reduced by ammonia and, apparently, other organic compounds of greater basicity, and in the lower state of oxidation form quite stable adducts with excess of the organic reagent. In these complicated reactions not only does the state of oxidation of the central ion change but also the coordination number, with simultaneous substitution of ligands.

In reactions in which the inorganic fluorides do not undergo redox processes with nitrogen-containing organic compounds the coordination number increases by the addition of fresh organic ligands to the central atom. All these reactions can be included among nucleophilic additions of the Ad_N type. The most characteristic coordination numbers of the metals in these adducts are V^{IV} 5 and 6, M^V (M = Nb, Ta, Mo) 6 and 7, Mo^{VI} 8, W^{VI} 7–9, U^{IV} 5, and U^{VI} 7 and 8. The maximum coordination numbers are observed with ligands of small bulk—ammonia, primary alkylamines—whereas ligands having less favourable steric characteristics, e.g. tertiary amines, form complexes having lower coordination numbers. Pentafluorides of d-elements exhibit a clear tendency to acquire a six-coordinated structure. This indicates that the adducts have an octahedral structure, which is probably the most advantageous under these conditions.

Table 4. Products of the reaction of organophosphorus compounds with fluoride of d- and f-elements.

Compound	Colour	M.p. (decomp.), °C	Ref.	Compound	Colour	M.p. (decomp.) °C	Ref.
$WF_6 \cdot PPh_3$	—	(85)	107	$WF_6 \cdot \{OP(OPh)_3\}_n$	red	—	124
$WF_6 \cdot PMe_3$	orange	(80)	113	$WOF_4 \cdot OP(OMe)_3$	—	—	124
$[(MeO)_3PMe]^+[WOF_5]^-$	orange	(90)	123	$WOF_4 \cdot OP(Me)(MeO)_2$	—	—	124
$(MeO)_2MePO \cdot WOF_4$	—	—	123	$[W_2O_2F_9]^-[(MeO)_3PMe]^+$	—	—	124
$MeOWF_5 \cdot 1,3\,Py$	brown	—	123	$Nb(Ta)F_5 \cdot L$; L = $(PhO)_3PO$, $(BuO)_3PO$, Bu_3PO	—	—	135
$PhOWF_5 \cdot Me_3N$	red	—	123	Ph_3PO, $\{(CH_3)_2N\}_3PO$			

2. Phosphorus-containing Compounds

Tervalent phosphorus and nitrogen exhibit definite similarity in their chemistry, which is lost in states of higher oxidation. Table 4 lists products formed by several phosphorus-containing compounds with fluorides of d- and f-elements. Vanadium(V) fluoride is reduced by phosphorus trichloride[80] to vanadium chloride trifluoride, and by phosphorus trifluoride[35] to vanadium(IV) fluoride; in both cases phosphorus is oxidised to its pentafluoride. Phosphorus trichloride and trifluoride both convert uranium hexafluoride into the tetrafluoride[32,121], with temperatures of 150–300 °C regarded as optimum. Phosphorus trifluoride is used to convert molybdenum hexafluoride into the pentafluoride[31,122], and tungsten hexafluoride into the tetrafluoride[31]. Niobium and tantalum pentafluorides do not react with phosphorus trifluoride, but undergo exchange with the trichloride and tribromide, being converted ultimately into the corresponding pentabromides or pentachlorides and phosphorus trifluoride[33].

The ^{19}F-n.m.r. spectra of the adduct $WF_6.(CH_3)_3P$ in acetonitrile show that the tungsten is surrounded by six equivalent fluorine atoms[107,113]. It is suggested[113] that, as in the corresponding adduct with trimethylamine, a loose seven-coordinated structure is present in this compound.

At temperatures above 0°C tungsten hexafluoride reacts vigorously with trimethyl phosphite to give a dark orange liquid, whose composition depends on the reaction conditions[123], in particular on the ratio of the reactants. The reaction can in general be represented by the equations

$$(MeO)_3P + WF_6 \rightarrow (MeO)_2PF + MeOWF_5$$

$$(MeO)_3P + MeOWF_5 \rightarrow [(MeO)_3PMe]^+ \cdot [WOF_5]^-.$$

The formation of methyltrimethoxyphosphonium oxopentafluorotungstate shows that, in the presence of a suitable substrate, methoxytungsten pentafluoride develops a tendency to lose the methyl group as a methyl cation, which coordinates with the nucleophilic phosphorus atom or a fluoride ion:

$$MeOWF_5 \rightarrow [Me^+ + WOF_5^-] \rightarrow MeF + WOF_4.$$

This compound reacts with benzene to give toluene[123]:

$$MeOWF_5 + C_6H_6 \rightarrow C_6H_5Me + HF + WOF_4.$$

It is assumed that such reactions do not take place with phenoxytungsten pentafluoride. At 90°C the complex phosphonium salt decomposes:

$$[(MeO)_3PMe]^+ \cdot [WOF_5^-] \rightarrow WOF_4 \cdot OP(Me)(OMe)_2 + MeF.$$

Dimethyl methylphosphonate is formed from trimethyl phosphite by a Michaelis–Arbuzov rearrangement in the presence of the electrophilic catalyst tungsten hexafluoride, and gives the tungsten oxide fluoride an adduct in which the ligand occupies a *trans*-position with respect to the oxygen atom. Methoxytungsten and phenoxytungsten pentafluorides, like tungsten hexafluoride, are Lewis acids; the phenoxy-complex is converted on treatment with trimethylamine into a non-volatile red 1 : 1 adduct; methoxytungsten pentafluoride reacts with pyridine to give $CH_3OWF_5.1.3C_5H_5N$. The above results show that the reactions of tungsten hexafluoride with alkylphosphines, which contain only carbon–phosphorus bonds, are essentially additions similar to the reactions with amines. Attack by electrophilic reagents such as the hexafluoride on alkyl and aryl phosphites leads to rupture of a phosphorus–oxygen bond and replacement of an alkoxy-group by a fluorine atom.

Walker and Winfield[124] have investigated the reaction between tungsten hexafluoride and compounds containing a four-coordinated phosphorus atom. Even in benzene at 20°C triphenyl phosphate is converted into a red precipitate of undetermined composition. At 20°C trimethyl phosphate in proportions of 3–1 relative to tungsten hexafluoride gives after 2 h a mixture of phosphoryl and methyl fluorides, methoxytungsten pentafluoride, hexafluorophosphate and $W_2O_2F_9^-$ ions, and the equimolecular adduct of tungsten oxide tetrafluoride and trimethyl phosphate. It is assumed[124] that the hexafluorophosphate ion and methyl fluoride are formed from methoxytungsten pentafluoride and trimethyl phosphate. In the authors' opinion the presence of the hexafluorophosphate ion is due to the formation of trifluorodimethoxyphosphorane, present as tetramethoxyphosphonium hexafluorophosphate. At 20°C a mixture of tungsten hexafluoride, with dimethyl methylphosphonate passes into a mixture of methyldifluorophosphine oxide, methyl fluoride, the adduct $WOF_4.CH_3PO.(OCH_3)_2$, and the salt $[(CH_3O)_3PCH_3]^+[W_2O_2F_9]^-$. With dimethyl hydrogen phosphite at −80°C the hexafluoride gives phosphorus trifluoride and a non-volatile colourless deposit, which at 20°C rapidly becomes dark blue[124,125].

The above results indicate that alkyl phosphites and phosphates with tungsten hexafluoride undergo substitution at the site of rupture of a phosphorus–oxygen bond with subsequent exchange of alkoxy-groups and a fluoride ion. In view of the considerable difference in energy between bonds formed by phosphorus with carbon and with oxygen respectively (63 and 95 kcal mole^{-1}) it must be supposed that in organic derivatives of phosphorus the latter are considerably more subject than the former to the action of electrophilic reagents, and readily undergo exchange.

Table 5. Products of the reactions of higher fluorides of *d*- and *f*-elements with oxygen- and sulphur-containing compounds.

Compound	Colour	M.p.(decomp.), °C	Ref.	Compound	Colour	M.p. (decomp.), °C	Ref.
$MoF_6 \cdot Me_2O$	—	—	43	$WF_6 \cdot Me_2SO$	—	—	141
$MoF_6 \cdot Me_2S$	—	—	43	$WOF_4 \cdot (RO)_2SO$	—	—	123
$MoOF_4 \cdot (MeO)_2SO$	—	—	83	$[WOF_5]^-[(RO)_3S]^+$, R=Me; Et; Ph	—	—	123
$MoF_5 \cdot Me_2O$	white	(60)	43	$NbF_5 \cdot Me_2O$	red	31.5	117,120,136—138
$MoF_5 \cdot Me_2S$	yellow	(20)	43	$NbF_5 \cdot Me_2S$	white	76.2	44,136,137
$WF_6 \cdot Et_2O$	—	—	96,129,135	$NbF_5 \cdot Et_2O$	—	−7.8	13,123,136—138
$WF_5(OEt)$	—	—	123,144	$NbF_5 \cdot Et_2S$	—	85	13,123,136—138
cis-$WF_4(OEt)_2$	—	—	129	$NbF(OEt)_4$	yellow	35	133
$WOF_4 \cdot Et_2O$	—	(25)	129,135	$NbF_{5-n}(OEt)_n$, $n=1-3$	—	−20 ÷ −60	133
$WF_6 \cdot Et_2S$	yellow	(20)	115,135	$NbF_5 \cdot Me_2SO$	—	—	44,116,117
$WF_6 \cdot 2Et_2Se$	orange	(20)	115,135	$NbF_5 \cdot 2Me_2SO$	—	44	123,139,142,143
$WOF_4 \cdot EtOH$	—	—	129	$TaF_5 \cdot Me_2O$	red	80	117,123,136—138
$WSF_4 \cdot EtSH$	—	—	131	$TaF_5 \cdot 2Me_2O$	—	—	117
$WF_5(SEt)$	—	—	131	$TaF_5 \cdot Me_2S$	white	66,5	44,136,137
trans-$WF_4(SEt)_2$	—	—	131	$TaF_5 \cdot Et_2O$	—	−47.8	13,111,136,137
$WF_3S(SEt) \cdot EtSH$	—	—	131	$TaF_5 \cdot Et_2S$	—	—	13,111,136,137
$WF_5(OMe)$	white	85 (135)	123,144	$TaF(OEt)_4$	yellow	30	133
cis-$WF_4(OMe)_2$	white	18 (80)	81,84	$TaF_{5-n}(OEt)_n$, $n=1\div3$	—	−20 ÷ −60	133
trans-$WOF_4 \cdot Me_2O$	white	10 (20)	84,135	$TaF_5 \cdot Me_2SO$	—	—	44,116,117,139
$WF_5(OPh)$	red	80 (180)	82,84,123,144	$TaF_5 \cdot 2Me_2SO$	—	63,5	116,139
$WF_4(SPh)_2$	—	—	131				
$WSF_3(SPh) \cdot CH_3CN$	—	—	131				

In the case of triphenyl phosphate, however, cleavage of a phosphorus–oxygen bond is not observed, which may be attributable to a change in the character of the bond or in its accessibility to electrophilic attack resulting from the presence of an aromatic ring instead of an alkyl group.

The reaction of a trialkyl phosphate with tungsten hexafluoride can presumably be written

$$(RO)_3PO + 3WF_6 \rightarrow 3ROWF_5 + POF_3.$$

In the case of dialkyl alkylphosphonates the alkylphosphonic difluorides are formed, but not phosphoryl trifluoride, since the carbon–phosphorus bond is not involved in the reaction (at least at 20°C).

From theoretical considerations[126] and the above results it may be concluded that the donor power of tervalent phosphorus compounds towards the compounds surveyed here increases in the sequence

$$PF_3 < PCl_3 < PBr_3 < P(Ph)_3 < P(OMe)_3 < P(Me)_3.$$

The corresponding sequence for organic compounds of four-coordinated phosphorus is

$$(PhO)_3PO < (MeO)_3PO < (MeO)_2MePO.$$

Despite the absence of data for alkyl dialkylphosphinates and trialkylphosphine oxides in relation to tungsten hexafluoride, it may be supposed that the variation in their donor strength will be similar to that established[127] for uranyl and plutonium(VI) nitrates:

$$(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO.$$

A study[128] of the reaction of niobium and tantalum pentafluorides with tributylphosphine and triphenylphosphine oxides, tributyl phosphate, and hexamethylphosphoramide revealed in all cases the formation of adducts $MF_5.L$. Tributylphosphine oxide replaces fluorine in the MF_5 molecule to give *cis*- and *trans*-$[MF_4((CH_4H_9)_3PO)_2]^+.[MF_6]^-$. The donor power of the organophosphorus ligands increases in the sequence

$$(PhO)_3PO < (BuO)_3PO < Ph_3PO < [(CH_3)_2N]_3PO < Bu_3PO.$$

3. Oxygen- and Sulphur-containing Compounds

(*a*) Alcohols and thiols

Treatment of tungsten hexafluoride with ethanol produces a colourless solution[96], in which Buslaev et al.[129] established the presence of the anion WOF_5^-, indicating the considerable tendency of tungsten to form a multiple bond with oxygen. Other reaction products present are *cis*-diethoxytungsten tetrafluoride and $WOF_4.C_2H_5OH$ with a *trans*-arrangement of the oxygen atom and the alcohol molecule. Examination by the same workers of the stereospecificity of substitution in octahedral d^0 complexes[130] with ligands capable of forming multiple bonds with the central atom has established a *cis*-effect for a multiply bonded ligand, i.e. substitution primarily of a ligand in a *cis*-position relative to the multiply bonded ligand.

Treatment of a solution of ethanethiol in acetonitrile with tungsten hexafluoride yielded products analogous to those obtained with ethanol[131] (Table 5). A small excess of the thiol gives the unstable ethylthiotungsten pentafluoride, when then passes into the more stable *trans*-diethylthiotungsten tetrafluoride (with ethanol *cis*-diethoxytungsten tetrafluoride is obtained). With increase in the excess of ethanethiol adducts—$WSF_4.HSC_2H_5$ and $C_2H_5SWSF_3.HSC_2H_5$—are formed with the multiply bonded sulphur atom *trans* to the ligand molecule. Compounds of similar structure solvated by acetonitrile are present as intermediates. With benzenethiol the hexafluoride gives[131] the stable *trans*-diphenylthiotungsten tetrafluoride, which after a long time passes into the adduct $C_6H_5SWSF_3.CH_3CN$; no product having the composition $C_6H_5SWF_5$ has been observed.

In absolute ethanol niobium pentafluoride forms an electrically conducting dark red solution. The Nb-n.m.r. spectra[93] indicate the presence of the hexafluoroniobate anion, but no cation is detected[132]. Buslaev et al.[133] suggested that the complex anion is probably accompanied in this system by a cation that dissociates according to the scheme

$$[NbF_4(EtOH)_n]^+ \rightarrow NbF_4(OEt)\cdot EtOH + H^+ \rightarrow [NbF_4(OEt_2)]^- + 2H^+.$$

The latter workers studied the reaction of niobium[133] and tantalum[134] pentafluorides with the corresponding pentaethoxides $M(OC_2H_5)_5$, and obtained products $MF_{5-n}.(OC_2H_5)_n$ with $n = 1$–4 (Table 5). These compounds are oligomers containing on the average $m \simeq 2$ and 3.8 monomers for $n = 4$ and 1 respectively: i.e. the degree of polymerisation decreases with increase in the covalent character of the compound as metal–fluorine are replaced by metal–ethoxy bonds (in the solid state the pentafluorides exist as tetramers[12]).

The above results indicate that alcohols and thiols react with electrophilic fluorides—tungsten(VI), niobium(V), and tantalum(V)—by rupture of alkoxy–hydrogen (alkylthio–hydrogen) bonds with replacement of fluorine in the acceptor by an alkoxy-group under mild conditions (below 0°C). The scheme

$$WF_6 + RO{-}H \rightarrow ROWF_5 + HF$$

may be suggested. This stage apparently occurs, similarly to the reactions of organosilicon compounds[87], via formation of seven-coordinated compounds with the hexafluoride (six-coordinated for the pentafluorides) by an S_N2 mechanism with subsequent cleavage of a metal–fluorine bond and elimination of hydrogen fluoride. The relatively unstable[131] ethoxytungsten (or ethylthiotungsten) pentafluoride decomposes further according to the equation

$$EtOWF_5 \xrightarrow{t} WOF_4 + EtF,$$

or adds a second alkoxy-group

$$EtOWF_5 + EtO{-}H \rightarrow (EtO)_2WF_4 + HF.$$

The diethoxytungsten tetrafluoride is in turn converted into oxotungsten tetrafluoride:

$$(EtO)_2WF_4 \xrightarrow{t} WOF_4 + Et_2O$$

similarly to the dimethoxy-derivative (Ref. 85 and Table 2). The reaction mechanism with ethanethiol is apparently the same as that with ethanol[131], but the former exhibits greater donor strength, since, despite the larger bulk, three fluorine atoms in the tungsten hexafluoride molecule are replaced by an alkylthio-group, but only two by ethanol.

(*b*) Ethers and sulphides

Ethers, like alcohols, possess weakly basic properties: with Lewis acids, e.g. boron trifluoride, they form stable adducts by virtue of the presence of lone pairs of electrons on the oxygen. In contrast, uranium hexafluoride reacts vigorously with diethyl ether, to give uranyl and

hydrogen fluorides with a carbonaceous substance of unknown composition[64]. Hexa- and penta-fluorides of *d*-elements in Groups V and VI form with ethers the series of compounds shown in Table 5. When a 1 : 5 mixture of tungsten hexafluoride and dimethyl ether is kept in a steel bomb at 100–110°C for 5 h, the products are methyl fluoride, the adduct $WOF_4.(CH_3)_2O$, and a mixture of lower tungsten oxide fluorides and organic compounds[84,135]. Study of the volatility, infrared spectra, and ^{19}F-n.m.r. spectra suggests[84] that the adduct is a monomer of octahedral structure with the oxygen atom *trans* to the organic ligand. From an investigation of the reaction between tungsten hexafluoride and diethyl ether Buslaev et al. concluded[129] that the complex $WOF_4.(C_2H_5)_2O$ is obtained via an unstable intermediate compound $C_2H_5OWF_5$, owing to the tendency to form the more stable multiple bond W=O. It is pertinent to mention the observation by Noble et al.[123] that CH_3OWF_5 is able to lose the alkyl as the methyl cation.

Below room temperature the reaction of the hexafluorides with ethers and with dialkyl sulphides and selenides yields the adducts $MoF_6.(CH_3)_2O$, $MoF_6.(CH_3)_2S$,[43] $WF_6.(C_2H_5)_2O$,[96,129,135] $WF_6.(C_2H_5)_2S$, and $WF_6.2(C_2H_5)_2Se$.[115,135] The donor power towards the hexafluorides increases in the sequence $R_2O < R_2S < R_2Se$. It is assumed that tungsten hexafluoride is partly ionised in the adducts with sulphur and selenium derivatives[115,135]. Molybdenum pentafluoride forms equimolecular adducts with dimethyl ether and dimethyl sulphide, which readily eliminate the ligand molecules in a vacuum at 60 and 20°C respectively[43].

Niobium and tantalum pentafluorides form relatively stable compounds with dimethyl ether[117,120,136–138] and with dimethyl sulphide[44,136,137] (Table 5), which in a vacuum at the melting point distil without decomposition. Equimolecular adducts of these pentafluorides with diethyl ether and sulphide have not been isolated in the crystalline state, but information on them has been obtained from a study of their solutions[43,44,97,115]. It has been concluded from the ^{19}F-n.m.r. spectra that $NbF_5.(C_2H_5)_2O$, $NbF_5.(C_2H_5)_2S$,[116] and $TaF_5.(CH_3)_2O$ [117] are monomers with octahedral coordination. Conductivity measurements indicate a greater degree of association of adducts with sulphides than of those with ethers[139].

The above results show that under mild conditions ethers, dialkyl sulphides, and dialkyl selenides as *n*-donors[6] form with pentafluorides and hexafluorides of *d*-elements adducts that, like amines, act as nucleophilic reagents. These complexes have the structure of oxonium or sulphonium salts, as is confirmed by their conductivity. The most stable complexes are obtained with niobium, tantalum, and molybdenum pentafluorides, which are stronger Lewis acids than are the hexafluorides. Under more severe conditions (at elevated temperatures and pressures) ethers and apparently their sulphur and selenium analogues undergo cleavage by hexafluorides at the carbon–oxygen bond analogous to the cleavage of ethers by hydrohalic acids[140].

Muetterties noted[107] that the fluorine atoms are not entirely equivalent in the adducts, especially in $WF_6.R_2O$, and suggested an oxonium salt type of structure $[WF_5.R_2O]^+F^-$. If this hypothesis is correct, the course of the reaction is analogous to the cleavage of ethers:

$$1)\quad R\ddot{O}R + WF_6 \rightarrow [R{-}\underset{\underset{WF_6}{|}}{\ddot{O}}{-}R]^+ \cdot F^- \xrightarrow{t} ROWF_5 + RF.$$

Since $(RO)_2WF_4$ has been detected among the reaction products[129], an additional fluorine atom in $ROWF_5$ may be replaced:

$$2)\quad ROWF_5 + ROR \xrightarrow{t} (RO)_2WF_4 + RF.$$

The possible presence of hydrogen fluoride as an impurity in tungsten hexafluoride does not exclude the probability of another well known[140] reaction path, giving an alcohol, which then reacts more readily with the hexafluoride:

$$R_2O + HF \rightarrow [R\overset{H}{\ddot{O}}R]^+ \cdot F^- \rightarrow ROH + RF$$

$$ROH + WF_6 \rightarrow ROWF_5 + HF \text{ etc}$$

Hydrogen fluoride may thus act as a catalytic additive. On the basis of available data it is not possible to give preference to either mechanism.

Under the conditions investigated niobium, tantalum, and molybdenum pentafluorides do not undergo substitution with ethers, but form adducts usually of coordination number 6, sometimes 7. They are compounds of *n*–*v* type[6], in most cases relatively stable. Below room temperature molybdenum and tungsten hexafluorides give with ethers and sulphides less stable adducts of coordination number 7.

(*c*) Dimethyl sulphoxide, dialkyl sulphites, and diphenyl sulphite

As regards acetone all that is known[96] is that tungsten hexafluoride forms red solutions. Dimethyl sulphoxide differs from its oxygen analogue in having a non-planar molecule and in the presence of a p_π–d_π component of the S=O double bond. Hydrogen atoms in an α-position with respect to the sulphur or carbon atom in a sulphoxide or a ketone are capable of substitution by halogen[89].

A study of the interaction of tungsten hexafluoride and dimethyl sulphoxide based on infrared and ^{19}F-n.m.r. spectroscopy has established[141] that the main product, a viscous yellow oil, consists largely of two compounds—$WF_6.(CH_3)_2SO$ and WOF_4—accompanied by bisfluoromethyl ether, hydrogen fluoride, and $W_2O_2F_9^-$. This indicates a complicated reaction mechanism involving cleavage of S=O and C–S bonds with replacement of hydrogen by fluorine in the alkyl group.

Niobium and tantalum pentafluorides form 1 : 1 and 1 : 2 adducts with dimethyl sulphoxide[44,116,120,139,142]. On the basis of conductivity measurements and of infrared and ^{19}F-n.m.r. spectral data it has been suggested[139,142,143] that $NbF_5.2(CH_3)_2SO$ is ionised as $[NbF_4.L_4]^+[NbF_6]^-$. This is confirmed by the known ability of dimethyl sulphoxide to solvate primarily electrophilic species, cations[89,126]. The corresponding equimolecular compound does not contain the hexafluoroniobate anion[143]. The adduct $TaF_5.2(CH_3)_2SO$ has different ^{19}F-n.m.r. spectra from the analogous niobium compound, and is considerably more soluble in excess of the ligand. Establishment of the equilibria

$$2TaF_5 + 4L \rightleftharpoons TaF_6^- + TaF_4 \cdot L_4^+$$

$$2TaF_4 \cdot L_4^+ \rightleftharpoons TaF_6^- + TaF_2 \cdot L_n^{2+} + (8-n)\,L$$

was suggested[118].

The above results indicate that pentafluorides undergo addition reactions with dialkyl sulphoxides to form ionised complexes of coordination number 6 and 7, whereas tungsten hexafluoride, the least strongly oxidising among

hexafluorides, undergoes complicated substitution reactions, elucidation of whose mechanism requires further research.

Dimethyl sulphite converts molybdenum hexafluoride into $MoOF_4$, the organic reaction products being methyl fluoride and $CH_3O.SO.F$.[83] Apparently the mechanism is

$$MoF_6 + (RO)_2SO \rightarrow ROMoF_5 + ROS(O)F$$
$$ROMoF_5 \xrightarrow{t} MoOF_4 + RF .$$

Between −40 and +20°C dimethyl, diethyl, and diphenyl sulphites react similarly with tungsten hexafluoride[123,144]:

$$(RO)_2SO + WF_6 \rightarrow ROWF_5 + ROS(O)F .$$

Fluorosulphite esters give sulphur dioxide and the alkyl fluoride on thermal decomposition, and sulphur dioxide and hydrogen fluoride on hydrolysis. At moderate temperatures the compounds CH_3OWF_5 and $C_6H_5OWF_5$ are relatively stable monomers, which sublime readily in a vacuum and are soluble in benzene. At 135°C the former decomposes into WOF_4 and fluoromethane. The ^{19}F- and ^1H-n.m.r. spectra indicate[123] the presence of the adducts $WOF_4.(RO)_2SO$ and $[(RO)_3S]^+[WOF_5]^-$.

Thus dialkyl sulphites react with hexafluorides of *d*-elements with substitution of fluorine in the acceptor molecule by an alkoxy-group at the site of rupture of the sulphur–oxygen bond, by a mechanism presumably analogous to the cleavage of ethers.

4. Carboxylic Acids

The most characteristic reaction of carboxylic acids with halides, e.g. of phosphorus (Lewis acids), is the formation of acid halides. Molybdenum, tungsten, and uranium hexafluorides behave similarly towards acetic acid at 40–60°C,[145] giving acetyl fluoride and the corresponding oxide fluoride. The scheme

$$UF_6 + 2CH_3COOH \rightarrow UO_2F_2 + 2CH_3COF + 2HF$$
$$WF_6 + 2CH_3COOH \rightarrow WO_2F_2 + 2CH_3COF + 2HF$$
$$MoF_6 + CH_3COOH \rightarrow MoOF_4 + CH_3COF + HF$$

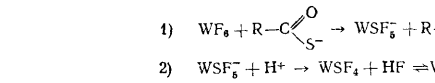
was suggested.

A study of the reaction of tungsten hexafluoride with acetic and thioacetic acids by ^{19}F-n.m.r. spectroscopy has shown[131] that sulphur and oxygen atoms are detached from the latter to give tungsten oxide and sulphide tetrafluorides:

$$2WF_6 + 2CH_3COSH \rightarrow WSF_4 + WOF_4 + 2CH_3COF + 2HF .$$

With increase in the ratio of thioacetic acid to the hexafluoride the tetrafluorides pass into the dimeric anions $W_2O_2F_9^-$ and $W_2S_2F_9^-$, and obviously into WSF_5^- (since WOF_5^- is present in the acetic acid system). It had been shown earlier[139] that the fluorine atom *trans* to the oxygen in WOF_5^-, and the bridging fluorine atom in the dimer $W_2O_2F_9^-$, carry a considerable proportion of the negative charge. It is significant[131,137] that both the carbonyl C=O and the C–O or C–S bonds are ruptured in the reaction in thioacetic acid—and it must be assumed in acetic acid (more correctly in their anions)—and also that the systems contain anions of the types WOF_5^-, as well as the compounds WOF_4 and hydrogen fluoride.

On the basis of experimental results[131] the interaction of tungsten hexafluoride with thioacetic acid can be written



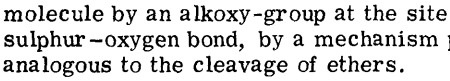
$$2)\quad WSF_5^- + H^+ \rightarrow WSF_4 + HF \rightleftharpoons W_2S_2F_9^- + H^+ .$$

In the second reaction the proton apparently coordinates with the fluorine atom of the substrate on which the negative charge is concentrated[139,146]. The appearance of WOF_4 together with WSF_4 as reaction product can be attributed to the existence of resonance structures of the acid anion[89], which leads to cleavage of the bonds attaching carbon to sulphur and to oxygen.

Trifluoroacetic acid, of similar strength to hydrochloric acid, reacts with uranium hexafluoride according to the equation[145,147]

$$2UF_6 + 2CF_3COOH \rightarrow 2HUF_6 + CF_3COF + CO_2 + COF_2$$

Hexafluorouranic acid is unstable, and decomposes[145] at 60°C into uranium(V) and hydrogen fluorides. In excess of the solvent the complex acid is converted into $2UF_5.CF_3COOH$. The diminished stability of trifluoroacetic acid (which undergoes degradation, whereas acetic acid is merely dehydrated) is attributed[145] to the proximity of fluorine atoms to the carbonyl group. Indeed, the presence of uranium(V) and carbon dioxide among the reaction products indicates decarboxylation, which is known to occur readily if a strongly electron-accepting group, in the present case trifluoromethyl, is attached to an α-carbon atom:



On the other hand, the presence of trifluoroacetyl fluoride indicates the progress in parallel of a reaction analogous to that occurring with acetic acid[131,145]. It is evident that the reaction is actually more complicated, and further research is necessary in order to refine the mechanism.

VI. COMPLEX FORMATION WITH ORGANIC LIGANDS

Although various compounds of *d*- and *f*-elements exhibit a strong tendency to form complexes[148], the fluorides are less strongly complex-forming than other compounds having ligands located to the left of fluorine in the spectrochemical series (e.g. chlorides, bromides). This is probably due to the greater electronegativity and the small size of fluoride ions, which form a compact screening shell diminishing the accessibility of vacant orbitals of the central atom in the fluorides for overlapping with the orbitals of organic ligands. This may explain why chlorides of *d*-elements are stronger Lewis acids than are the corresponding fluorides.

Fluorides of *d*-elements in the lower formal degrees of oxidation such as 3–5 have strong intermolecular coordinate bonds and, as Walton[149] has shown, form in the solid state lattices in which the metal is situated in an octahedral environment of six halide ions. The fall in the boiling point with increase in the number of ligands in the sequence of fluorides

$$MF_3 > MF_4 > MF_5 > MF_6$$

both for the same element and on moving from left to right along a series in the Periodic System, indicates an increase in coordination saturation and a decrease in the strength of intermolecular bonds. On the whole, hexafluorides possess a more covalent character than do tetra- and penta-fluorides. We shall examine the opportunities for inorganic fluorides in various states of oxidation to coordinate ligands containing lone pairs of electrons.

Trifluorides of *p*-elements—aluminium, gallium, indium—form[150] equimolecular adducts with diethylamine and tributylamine, and $MF_3.3NH_3$ with ammonia. Aluminium tribromide behaves similarly[151] towards dialkyl sulphides and selenides. Muetterties reported[107] that antimony and arsenic trifluorides give equimolecular adducts with dioxan and dimethylformamide, $2SbF_3.L$ is formed with pyridine and trimethylamine, and $SbF_3.2(CH_3)_2SO$ has been obtained with dimethyl sulphoxide. It may be supposed that interaction of trifluorides of *d*-elements with organic ligands will yield compounds of tetrahedral structure, since the considerable bulk of the ligands will prevent the appearance of adducts having higher coordination numbers.

Numerous examples of the preferential formation of $MF_4.2L$ adducts in reactions with amines, pyridine and its derivatives, dimethyl sulphoxide, and several other ligands have been demonstrated by Muetterties[107,152] for tetrafluorides of *d*-elements (titanium, zirconium, molybdenum) and *p*-elements (silicon, germanium, tin) and by Ennan[153] for silicon tetrafluoride. It was concluded[152] that octahedral coordination of the adducts with the metal tetrafluorides was preferred stoichiometrically. Smaller coordination numbers were observed probably because of steric hindrance in the case of bulky compounds having a metal–nitrogen bond, but this was almost completely absent from the metal–oxygen bond.

It follows from the above account that pentafluorides of *d*-elements form equimolecular adducts, considerably more rarely 1 : 2 compounds, with almost all organic ligands having lone pairs of electrons: i.e. a clear tendency to form complexes with octahedral coordination is evident in this case too.

Cotton and Wilkinson[148] point out that, in the ligand-field approximation for *d*-electrons, octahedral coordination contributes about double the energy separation of bonding t_{2g} and antibonding e_g orbitals in comparison with a tetrahedral field. This will obviously make octahedral coordination advantageous for complexes, including fluorides having a small number of unpaired *d*-electrons. The fluorides of *d*-elements discussed here are compounds of this type. Hence, under otherwise similar conditions, the energy of stabilisation of the ligand in an octahedral field should be the dominant factor. It is probably for this reason that tri-, tetra-, and penta-fluorides of *d*-elements undergo addition with *n*-donors possessing lone pairs of electrons, thereby acquiring a tetrahedral configuration with trifluorides (in the case of large ligands preventing a higher coordination number) and an octahedral configuration with tetra- and penta-fluorides.

Basolo and Johnson noted[154] that four-coordinated systems of *d*-elements react predominantly with the formation of new metal–ligand bonds, to which a high charge on the central ion makes a considerable contribution. Evidently there is every reason to apply this to pentafluorides. They add ligands more easily than do tri- and tetra-fluorides, in order to complete the octahedral coordination. This requires the formation of only one new metal–ligand bond, whereas in tri- and tetra-fluorides greater energy is necessary to break the considerable intermolecular forces in the condensed state and to create more than one new metal–ligand bond.

The situation is different with hexafluorides of *d*-elements, since they are structures having the energetically advantageous octahedral coordination. These hexafluorides differ greatly in oxidising and complexing properties. As shown above, the hexafluorides of *f*-elements surpass appreciably those of *d*-elements in oxidising power. This difference may be due to differences in the number of spatial configuration of *d*- and *f*-orbitals, which in turn presupposes different configurations and energies of formation of bonds. To the approximation of crystal field theory Bagnall[60] supposes that for *f*-orbitals an eight-coordinated structure is preferable, corresponding to a point group of symmetry D_{6h} (a regular hexagonal bipyramid) or the octahedral O_h (bonds directed from the centre towards the corners of a cube). Six-coordinated geometry of type O_h or D_{4h} is more favourable[148] for complexes of *d*-elements.

Matters are more complicated in the actual molecules of hexafluorides of *f*-elements, for *d*-electrons are also involved in bond formation (electronic structures—uranium $5f^36d7s^2$, neptunium $5f^46d7s^2$ or $5f^57s^2$, and plutonium $5f^67s^2$).[60] Nevertheless, available data indicate that in a six-coordinated structure hexafluorides of *f*-elements are less stable than are those of *d*-elements, and the stability of the compounds diminishes with increase in the number of *f*-electrons, an example being the decrease in stability in the sequence $UF_6 > NpF_6 > PuF_6$. For the reasons discussed above the hexafluorides of *d*- and *f*-elements will obviously differ also in complexing power, although no data are at present available providing unambiguous support for this hypothesis. It can be concluded from the work of Weinstock[10,155] that in general the stability of the hexafluorides diminishes with increase in the number of unpaired electrons—for the transition series

$$4d\text{—}MoF_6\,(d^0) > TcF_6\,(d^1) > RuF_6\,(d^2) > RhF_6\,(d^3)$$

$$5d\text{—}WF_6\,(d^0) > ReF_6\,(d^1) > OsF_6\,(d^2) > IrF_6\,(d^3) > PtF_6\,(d^4)$$

and for the actinides

$$5f\text{—}UF_6\,(5f^0) > NpF_6\,(5f^1) > PuF_6\,(5f^2).$$

The most intensive investigation has been made on the interaction of organic ligands with tungsten hexafluoride, which exhibits extremely weak oxidising properties and is more convenient for investigation than are other hexafluorides. In complexing power it is very close to the pentafluorides of *d*-elements. Jorgensen assumed[156] that the tungsten atom in the hexafluoride bore a formal charge of +5, whereas in molybdenum and rhenium hexafluorides the corresponding charge was +6. If this is in fact the case, the difference in oxidising power between molybdenum and tungsten hexafluorides is explicable: the latter is very similar to pentafluorides both in its comparatively weak oxidising power and in its tendency to form complexes, whereas molybdenum hexafluoride is a quite strong oxidant, and frequently undergoes complex formation only after reduction to the quinquevalent state.

Hexafluorides form the most stable complexes with *n*-donors having a relatively simple structure: e.g. nitric oxide gives $NO^+MoF_6^-$ and $NO^+UF_6^-$. The enthalpy of formation of the latter compound is −52 kcal mole^{-1}.[159] The formal state of oxidation of the metal in these compounds is +5. Tungsten hexafluoride does not react with nitric oxide.

Donors having a non-linear structure, such as nitrosyl and nitryl fluorides, give with uranium hexafluoride the compounds $NOUF_7$, NO_2UF_7, and $(NO_2)_2UF_8$,[160,161] with molybdenum hexafluoride $NOMoF_7$ and NO_2MoF_7,[161] and with tungsten hexafluoride $NOWF_7$ and NO_2WF_7.[162] The enthalpies of decomposition of $NOUF_7$ and NO_2UF_7 are respectively[161] 16.6 and 13.8 kcal mole^{-1}.

Uranium hexafluoride forms with alkali-metal fluorides a series of complexes varying in composition; with sodium fluoride, in particular, $NaUF_7$ [163] and Na_2UF_8 [164]

are obtained (having enthalpies of decomposition of 15.9 and 19.1 kcal mole^{-1} respectively—given by other workers[165] as 9.4 and 23.5 kcal mole^{-1}). The complexes Na_3UF_9 and $Na_3U_2F_{15}$ are also known[166]. Molybdenum and tungsten hexafluorides also form with sodium fluoride 1 : 1 and 1 : 2 complexes[163,167]. Neptunium and plutonium hexafluorides on treatment with sodium fluoride are reduced to the quinquevalent and quadrivalent states respectively, with liberation of elementary fluorine and formation of Na_3NpF_8 and Na_3PuF_7.[166]

The enthalpies of decomposition show that the complexes of hexafluorides with the above ligands are quite stable, except in the last two cases. The alkali-metal fluorides are ionic in character, their anions acting as donors with one lone electron in their ability to form stable bonds with υ-acceptors, in the present case halides of d- and f-elements. The nitric oxide, nitrosyl fluoride, and nitryl fluoride molecules possess a lone pair of electrons (they are n-donors) and a considerable capacity for polarisation, which also ensures relatively stable bonding with hexafluorides. The coordination numbers of the metals in these complexes are 7–9.

Among the classes of organic compounds considered, the following n-donors—amines, ethers, dialkyl sulphides, sulphoxides, and selenides, and pyridine and its derivatives—are able to form such bonds. The majority of published studies are concerned with the interactions of these donors with tungsten hexafluoride, in which it develops a coordination number 8, more rarely 7 or 9. In the case of the other hexafluorides only the adducts with pyridine and 2-fluoropyridine—$MoF_6.2C_5H_5N$, $UF_6.C_5H_4FN$, and $UF_6.2C_5H_4FN$—are known[107]. No investigations have yet been published on the structure of these compounds, their stability, or the effect of the nature and the geometrical dimensions of the ligand molecules on the properties of the adducts formed with hexafluorides.

It has been suggested in a recent publication[169] that compounds of d- and f-elements develop greater chemical differences in aqueous solution than as anhydrous halides and oxides. One might agree with this, since fluorine is located somewhat to the right of such anions as nitrate, chloride, etc. in the spectrochemical series, and theoretically have a greater levelling effect on the chemical individuality of the central ion in the adduct; on the other hand, water is situated to the right of fluorine in this series. It must also be borne in mind that the properties of halides of d- and f-elements have been studied considerably less fully in non-aqueous than in aqueous systems, so that there are as yet inadequate grounds for such a statement.

Investigation of the reactions of hexafluorides with organic n-donors necessitates a relatively complicated experimental technique, but the results may well make a definite contribution to the theory of complex formation by d- and f-elements and permit the use of organic donors as selective chemical reagents in fluorination, exchange, and addition reactions involving metal fluorides.

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