

Recent Developments in the Chemistry of Some Electronegative Elements

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In 1962 a frontier of chemistry was opened by the discovery of noble gas compounds.¹ Since then this field has experienced vast development, and many reviews cover the first ten hectic years of work.²

Soon it became obvious that noble gas chemistry had to be seen in close relationship to halogen chemistry and to the chemistry of fluorides and oxyfluorides of certain other, heavier nonmetal elements such as selenium, tellurium, and antimony, especially in their higher oxidation states. Although the total number of original papers dealing with the chemistry and structure of nonmetal fluorides and related species exceeds several thousand, there is still no review available that covers the complete literature. But the structural principles of those compounds are now well-known, especially if the coordination number six is not exceeded.³

Xenon hexafluoride is one of the molecules with a formally higher coordination number, if one counts the nonbonding electron pair. Thus, its structure has caused much confusion; the most recent theory, based on physical measurements, is presented here. A more chemical way of solving such a problem would be to prepare other hexavalent xenon compounds like XeL_6 and to investigate their structures. Out of many choices of suitable ligands L, only $-OTeF_5$ and perhaps $-OSeF_5$ have been found to be appropriate. Fluorine stabilizes high oxidation states (PtF_6 , XeF_6 , IF_7 , ReF_7) for several reasons: its small size and strong electron withdrawal produce a strong, partly ionic bond. This effect can be achieved by the ligand $-OTeF_5$ as well. And fluorine is not likely to be eliminated as F_2 , since the dissociation energy of F_2 is very small. On the other hand, the ligand dimers $F_5TeOOTeF_5$, $F_5SeOOSeF_5$, FSO_2OOS-O_2F , and others are readily formed, as the peroxide bonds are quite strong. Thus it was to be expected that no ligand would be better than fluorine, but research in this direction has produced much new information.

The Xenon Hexafluoride Structure Problem

It is now well established that XeF_6 is the highest fluoride of xenon.^{4,5} In contrast to XeF_2 and XeF_4 , its structure has prompted 15 years of discussion, but is now almost clear. The fundamental problem must be separated into several parts, as the structure differs in all three physical states. This behavior is different from that of other known hexafluorides, 15 altogether, which are plainly octahedral.⁶

In the gaseous state XeF_6 is monomeric⁷ but not octahedral, though the deviation from octahedral

symmetry is smaller than predicted by the VSEPR model.⁸ The structure is best described in terms of a mobile electron pair that moves over the faces and edges of the octahedron and thus distorts it in a dynamic manner.⁹ From its vapor pressure it can be concluded that XeF_6 is associated in the condensed phase. The association in nonpolar solvents like F_5SOSF_5 , $n-C_5F_{12}$, CF_2Cl_2 , and SO_2ClF has been verified by ^{19}F and ^{129}Xe nuclear magnetic resonance. The latter NMR method was first used only recently, but is now the best analytical probe for any kind of xenon chemistry in solution. ^{129}Xe has a natural abundance of 26.4% (xenon enriched up to 60% is commercially available), a nuclear spin of $1/2$, and a gyromagnetic factor very close to that of ^{13}C . The ^{129}Xe NMR spectra of many xenon compounds have now been observed.¹⁰⁻¹⁴ The results of XeF_6 in solution¹¹ at temperatures below $-100^\circ C$ have caused much skepticism; however, repetition of the measurements has not allowed any conclusions other than those derived from the first NMR spectra.^{12,13}

These spectra (Figure 1) have to be interpreted in terms of a tetramerization of XeF_6 in which both the xenon and the fluorine atoms are magnetically equivalent. Each xenon atom couples to 24 equivalent fluorine atoms and each fluorine atom to 4 equivalent xenon atoms. Thus, the fluorine atoms in the cluster Xe_4F_{24} are bound in a nonrigid manner and are equilibrated by a scrambling mechanism that is best named a cogwheel mechanism (Figure 2). Attempts to freeze out the fluorine migration have been made but could not be confirmed.^{12,14}

Undoubtedly this cluster has the largest known number of nonrigid bonded ligands, namely 24. The low-temperature configuration of Xe_4F_{24} is somewhat like the high-temperature form of $Rh_4(CO)_{12}$.^{15,16} In

(1) N. Bartlett, *Proc. Chem. Soc. London*, 218 (1962).

(2) See, e.g., N. Bartlett and F. O. Sladky, "The Chemistry of Krypton, Xenon and Radon", in "Comprehensive Inorganic Chemistry", Vol. 1, Pergamon Press, Oxford-New York, 1976 p 213.

(3) K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 18, 181 (1979).

(4) B. Weinstock, E. E. Weaver, and C. P. Knop, *Inorg. Chem.*, 5, 2189 (1966).

(5) One can estimate that a xenon octafluoride would be thermodynamically unstable toward loss of fluorine atoms. This would indicate kinetic instability, except at cryogenic temperatures.

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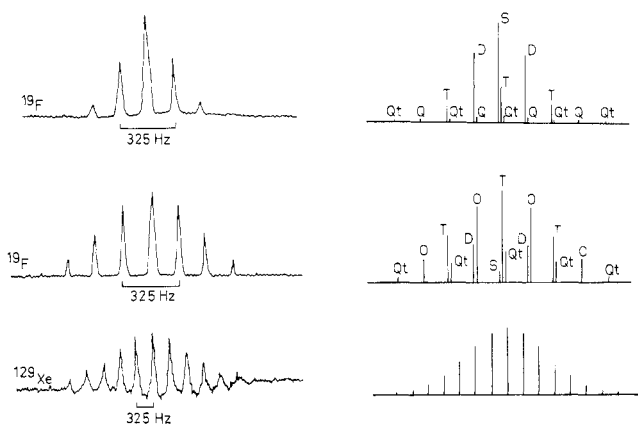


Figure 1. (Above) ^{19}F NMR spectrum of XeF_6 in CF_3Cl at -130°C (natural isotopic abundance, $^{129}\text{Xe} = 26.4\%$). (Middle) ^{19}F NMR spectrum of XeF_6 in CF_3Cl at -130°C with an enriched sample of ^{129}Xe (62.5%). (Bottom) ^{129}Xe NMR spectrum in CF_2Cl_2 at -120°C . The interpretation of these spectra is shown on the right-hand side. Under the assumption of a tetramerization to Xe_4F_{24} and the equivalency of four xenon and 24 fluorine atoms, five different species are in solution: $^{129}\text{Xe}_4\text{F}_{24}$, $^{129}\text{Xe}_3\text{XeF}_{24}$, $^{129}\text{Xe}_2\text{Xe}_2\text{F}_{24}$, $^{129}\text{XeXe}_3\text{F}_{24}$, and Xe_4F_{24} . As only ^{129}Xe has a nuclear spin of $1/2$, the first species shows in the ^{19}F NMR a 1:4:6:4:1 quintet (Qt), the second a 1:3:3:1 quartet (Q), the third a 1:2:1 triplet (T), the fourth a 1:1 doublet (D), and the fifth a singlet (S). Many of those lines overlap within the line width, and the intensity of the resulting nine lines depends upon the ^{129}Xe concentration. In the case of 62.5% the line intensities are (calculated) 3.8:18.8:49.8:84.5:100:85.5:49.8:18.3:3.8 and (observed) 3.1:18.1:48.8:83.2:100:83.4:50.1:17.8:2.9. The ^{129}Xe spectrum shows a binomial function of 24th order: (calculated down from the center line) 100:92:72.5:48.3:27.2:12.8:4.9:1.6...; (observed) 100:93.3:68.8:45.8:29.1:14.5:4.1... The fit between experimental and calculated lines is striking. As cannot be shown here, no other kind of multiplicity can explain these spectra.

the dynamic rhodium carbonyl there are no problems concerning the binding forces of such a cluster, as there are bonds between the metal atoms, in addition to mobile carbonyl bridges. In Xe_4F_{24} , however, the mobile fluorine bridges alone are responsible for the existence of the cluster. While any xenon-xenon interaction is highly speculative,¹⁷ one can, just by counting, find enough orbitals and electrons to form four three-center two-electron bonds, each on one plane. A comparable bonding model is that of B_4Cl_4 . Certainly the general chemistry of xenon does not call for electron-deficient bonds, though the charge of the xenon in XeF_6 is found indeed to be some 1.5 positive units.¹⁸ Attempts have failed to measure the Xe-Xe distances in the cluster in solution, mainly because of experimental difficulties.

It is interesting to compare the structure of the cluster in solution with the solid-state structure of XeF_6 . The cubic modification is the only one (out of four) that has been fully analyzed.¹⁹ The unit cell contains 24 tetrahedral $(\text{XeF}_5^+\text{F}^-)_4$ and 8 octahedral $(\text{XeF}_5^+\text{F}^-)_6$ units. The tetrahedras are comparable to the dynamic cluster in the dissolved state. However, the Xe-Xe distances are quite large (4.2 Å) here and do not favor

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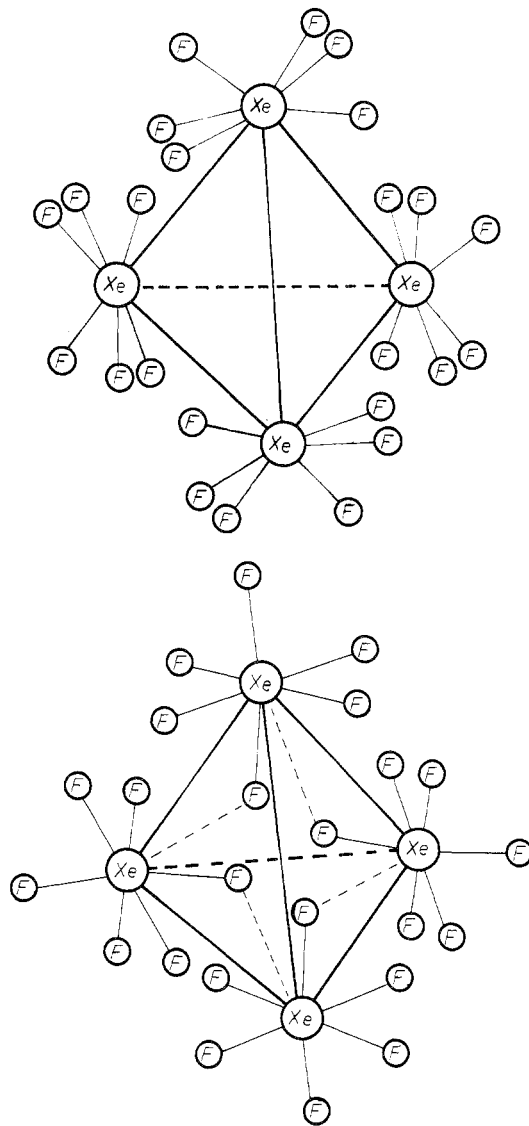


Figure 2. The cluster Xe_4F_{24} in two of its configurations. In the first configuration each xenon holds six fluorine atoms, and in the second four F atoms bind the Xe atoms by Xe-F-Xe bridges. The latter picture resembles very much the $(\text{XeF}_5^+\text{F}^-)_4$ tetramer in the solid state.¹⁹ All fluorine atoms take part in this dynamic process, which is best explained as a cogwheel mechanism. (Reprinted with permission from ref 10, 11, and 13. Copyright 1974, Johann Ambrosius Barth.)

the speculative bonding model in solution. On the other hand, in the crystal the fluorine atoms are in fixed positions.

For a simple, binary compound the structural behavior of XeF_6 is without parallel. The species chemically most similar in behavior is SeF_4 , because it has (including one electron pair) an odd number of ligands, is highly associated in the liquid phase, and easily forms SeF_3^+ and SeF_5^- ions, just as XeF_6 forms XeF_5^+ , XeF_8^{2-} , and XeF_7^- . However, even at -140°C SeF_4 is monomeric in solution, and a freezing-out effect occurs in the fluorine NMR spectrum.²⁰

$\text{Xe}(\text{OSeF}_5)_2$, $\text{Xe}(\text{OTeF}_5)_2$, $\text{Xe}(\text{OTeF}_5)_4$, $\text{O}=\text{Xe}(\text{OTeF}_5)_4$, $\text{Xe}(\text{OTeF}_5)_6$

There has been hope that ligands other than fluorine could form single covalent bonds to xenon. Indeed, the

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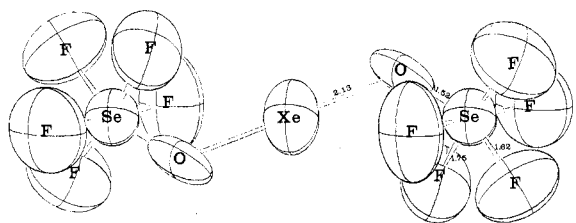
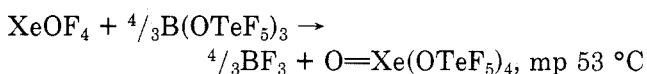
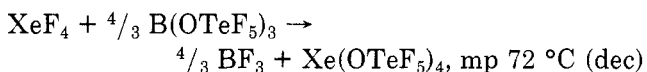
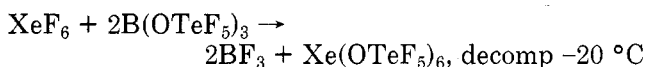


Figure 3. Crystal structure of $\text{Xe}(\text{OSeF}_5)_2$. This structure determination is complicated by a threefold disorder along the Se-Xe-Se axis.

first ligand of this type was fluorosulfate.²¹ However, the compounds FXeOSO_2F and $\text{Xe}(\text{OSO}_2\text{F})_2$ decompose at room temperature or slightly above, and the fluorosulfate of XeF_6 turned out to be ionic: $\text{XeF}_5^+\text{SO}_3\text{F}^-$.²² The situation changed when the substances $\text{Xe}(\text{OTeF}_5)_2$ and $\text{Xe}(\text{OSeF}_5)_2$ were made.^{23,24} These do not decompose below 100 °C, and their covalent character is well established by their ^{129}Xe NMR spectra¹⁰ and their crystal structures²⁵ (Figure 3). Once it was shown that the ligands $-\text{OSeF}_5$ and $-\text{OTeF}_5$ have the capacity of stabilizing high oxidation states, almost like fluorine, a large amount of their chemistry was studied (see below). The process of getting higher valent xenon linked to these ligands turned out to be very difficult and was successful only in the case of the $-\text{OTeF}_5$ ligand. Only recently $\text{Xe}(\text{OTeF}_5)_4$, $\text{Xe}(\text{OTeF}_5)_6$, and $\text{O}=\text{Xe}(\text{OTeF}_5)_4$ as stable, oxygen single-bonded xenon(IV) and xenon(VI) compounds have been made for the first time.²⁶



The ^{129}Xe NMR of $\text{O}=\text{Xe}(\text{OTeF}_5)_4$ is shown in Figure 4. It gives a full structural description of the molecule by the coupling to axial and equatorial fluorine atoms and to the ^{125}Te isotopes.

The most interesting species, $\text{Xe}(\text{OTeF}_5)_6$, is a dark red, almost violet crystalline solid. The deep color indicates that the molecule is monomeric, like the yellow XeF_6 . The color has to do with the nonbonding electron pair on xenon, as $\text{Te}(\text{OTeF}_5)_6$ lacks this electron pair and is colorless.²⁷ Due to the sensitivity of $\text{Xe}(\text{OTeF}_5)_6$ to light and elevated temperatures, structural investigations are difficult but are in progress.

The ligands $-\text{OSeF}_5$ and $-\text{OTeF}_5$ were not found to form stable compounds with krypton. KrF_2 could not

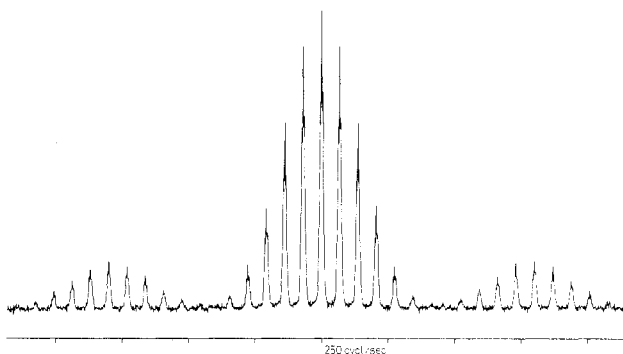


Figure 4. ^{129}Xe NMR spectrum of $\text{O}=\text{Xe}(\text{OTeF}_5)_4$, solution in $\text{C}_2\text{F}_4\text{Cl}_2$, 55.33 MHz. The chemical shift of $\delta = -5121$ against atomic xenon is typical for six-valent xenon. The splitting into quintets ($J_{\text{Xe-F}} = 4$ Hz), 13 lines out of a multiplet of 17 ($J_{\text{Xe-F}} = 55$ Hz), and the satellites ($J_{\text{Xe-}^{125}\text{Te}} = 1281$ Hz) give an almost complete structure description. (Reprinted with permission from ref 26. Copyright 1978, Verlag Chemie GMBH.)

be converted into $\text{Kr}(\text{OTeF}_5)_2$. Only the decomposition products Kr and $\text{F}_5\text{TeO}(\text{OTeF}_5)$ ($\text{F}_5\text{SeO}(\text{OSeF}_5)$) were observed, indicating the intermediate formation of an oxygen-bonded krypton compound, as these peroxides are the typical decomposition products of all xenon compounds as well. Thus KrF_2 and its ionic derivatives KrF^+ and Kr_2F_3^+ remain the only krypton compounds known.²⁸ On the other hand, xenon is known to bind even to nitrogen in $\text{FXeN}(\text{SO}_2\text{F})_2$.²⁹ XeCl_2 can be made only at cryogenic temperatures.³⁰ Despite many attempts, a xenon-carbon bond has not yet been achieved.

Group Electronegativity of the $-\text{OSeF}_5$ and $-\text{OTeF}_5$ Groups

The reason why the $-\text{OSeF}_5$ and $-\text{OTeF}_5$ groups form the most stable xenon compounds after the simple fluorides has not been fully answered. One may define group electronegativities for these ligands. Certainly electronegativity has no clear meaning, as there are several definitions. The concept becomes even more confusing if electronegativity is extended to whole groups. Even so, a qualitative argument is possible with the valence shell electron pair repulsion model.⁸ This predicts that in a trigonal bipyramid the two axial positions are occupied by the more electronegative atom or ligand, whereas in the case of a square pyramid of the IF_5 type, the equatorial positions are occupied by the more electronegative ligands. There are numerous examples for this substitutional behavior in case of the trigonal bipyramid. A substitution with $-\text{OSeF}_5$ or $-\text{OTeF}_5$ on a trigonal bipyramid has not yet been achieved. However, we have replaced fluorine atoms of IF_5 with those ligands. All other groups like $-\text{OCH}_3$ or $-\text{CF}_3$ on IF_5 indeed prefer the axial position,³¹⁻³³ as

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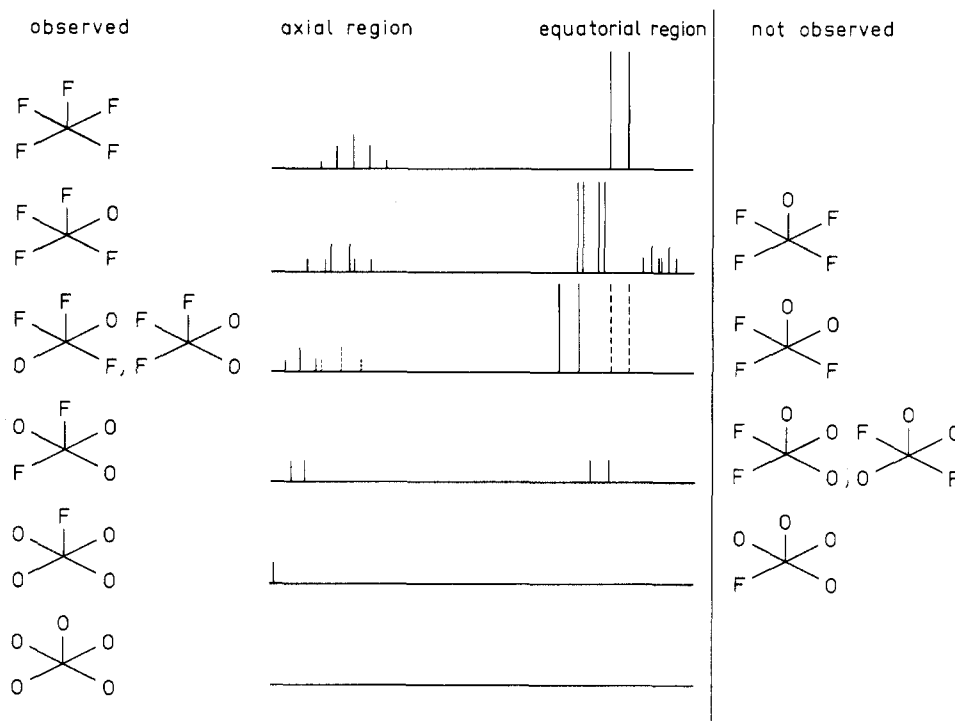
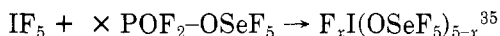
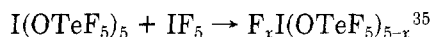
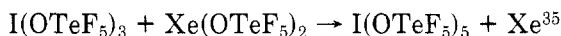
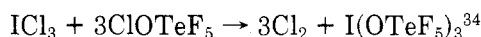


Figure 5. ^{19}F NMR spectra of $\text{F}_x\text{I}(\text{OTeF}_5)_{5-x}$ and $\text{F}_x\text{I}(\text{OSeF}_5)_{5-x}$, schematically with the tellurium and selenium bonded fluorine atoms omitted. The assignment is easily made by the appearance of the axial-bonded fluorine atom in a downfield area. The ligands $-\text{OTeF}_5$ and $-\text{OSeF}_5$, as indicated by O, do not go into the axial position, where normally the less electronegative ligands have to go. (Reprinted with permission from ref 35. Copyright 1978, Verlag Chemie GMBH.)

predicted. The surprise is that in the compounds $\text{F}_x\text{I}(\text{OTeF}_5)_{5-x}$ and $\text{F}_x\text{I}(\text{OSeF}_5)_{5-x}$ the substitutional behavior is inverted.

These species were made according to the equations:



The conformational analysis of the mixed substituted molecules was done by the ^{19}F NMR of the iodine-bonded fluorine atoms, as shown in Figure 5. Fluorine keeps the *axial* position, meaning that in the sense of the VSEPR model the ligands $-\text{OTeF}_5$ and $-\text{OSeF}_5$ are more electronegative than fluorine. Kinetic factors cannot explain this abnormal substitutional behavior, as prolonged reaction time and heating do not change the results. Nor can it be a steric effect: there is no reason why $\text{F}_4\text{I-OTeF}_5(\text{eq})$ should be sterically favored over $\text{F}_4\text{I-OTeF}_5(\text{ax})$, and X-ray structures of the closely related compounds *trans*- $\text{F}_2\text{Te}(\text{OTeF}_5)_4$ ³⁶ and $\text{Te}(\text{OTeF}_5)_6$ ²⁷ show that there is no important steric hindrance between the quite bulky ligands (Figure 6).

The high formal electronegativities of those groups are certainly a result of the inductive effect of five fluorine atoms, possibly enhanced by some $(\text{pd})_\pi$ backbonding between oxygen and selenium or tellurium. The latter effect is supported by the structural investigation of F_5SOSF_5 , $\text{F}_5\text{SeOSeF}_5$, and $\text{F}_5\text{TeOTeF}_5$.

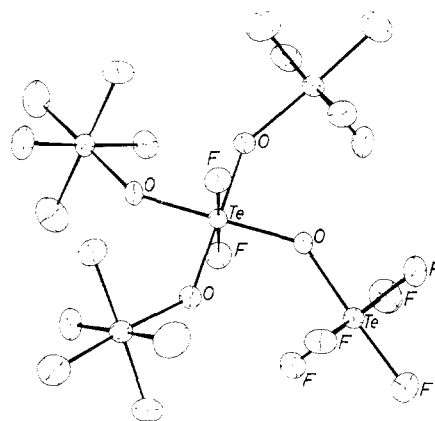


Figure 6. Molecular structure of $\text{Te}_5\text{O}_4\text{F}_{22}$. Most tellurium(VI) oxyfluorides have the general formula $\text{Te}_n\text{O}_{n-1}\text{F}_{4n+2}$. Here the species is best formulated as *trans*- $\text{F}_2\text{Te}(\text{OTeF}_5)_4$. The environment around the tellurium atoms is always octahedral. (Reprinted from ref 36).

Here indeed a sterically unfavorable eclipsed configuration is maintained, probably by some $(\text{pd})_\pi$ double bonding.³⁷ Once the high electronegativity of these groups was established, it became clear that the chemistry of those ligands could become as extensive as that of fluorine (Table I^{23,26,34,38-46}). Only helium,

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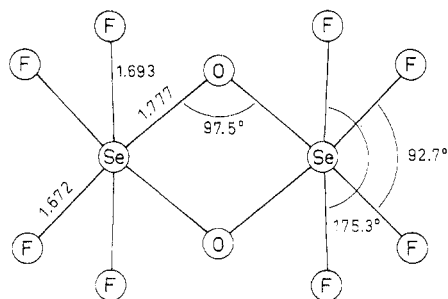
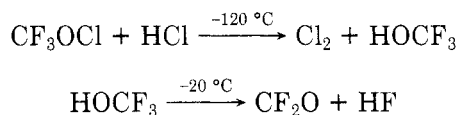
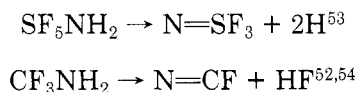


Figure 8. Molecular structure of $\text{Se}_2\text{O}_2\text{F}_8$, as determined by electron diffraction. The structure of $\text{Te}_2\text{O}_2\text{F}_8$ is almost identical. The Se-Se or Te-Te distances are surprisingly short. (Reprinted with permission from ref 59. Copyright 1974, Verlag Chemie GMBH.)

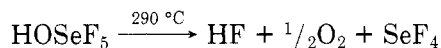
decrease on sulfur by formation of a sulfur-oxygen double bond. This reaction is very similar to the decomposition of trifluoromethanol, which was made very recently.^{51,52}



In general, the SF_5 group closely resembles the CF_3 group.



HOSeF_5 , however, is stable to 290 °C and then decomposes in a quite different way:



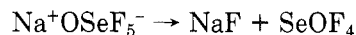
The oxidation state +6 for selenium is less favored than in the two neighboring elements S and Te (see below). This effect is certainly a result of the incomplete shielding of the nuclear charge by the first filled d shell (transition-metal contraction) and can be seen as related to the late discovery of the perbromates⁵⁵ and AsCl_5 ,⁵⁶ about 150 years after corresponding compounds of their neighbors in the periodic system. Thus HOSeF_5 is a highly oxidative, aggressive fluorinating agent and is preferably handled in materials like Kel-F and Teflon FEP. Only in the absolute absence of HF does it fail to attack stainless steel. (HOTeF_5 even exceeds the stability of HOSeF_5 and is by far a weaker oxidizer.) The anhydrofluoride of HOSeF_5 , SeOF_4 , was very difficult to synthesize. Absolutely pure $\text{Na}^+\text{OSeF}_5^-$ decomposes in vacuo at 200 °C.⁵⁷

(51) K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **16**, 322 (1977).

(52) G. Klöter and K. Seppelt, *J. Am. Chem. Soc.*, **101**, 347 (1979).

(53) A. F. Clifford and L. C. Duncon, *Inorg. Chem.*, **5**, 692 (1966).

(54) G. Klöter, W. Lutz, K. Seppelt, and W. Sundermeyer, *Angew. Chem., Int. Ed. Engl.*, **16**, 707 (1977).



SeOF_4 probably has the same structure as SOF_4 —trigonal bipyramidal with the double-bonded oxygen in the plane. The unusual coordination number 5 can be considered the driving force for its dimerization to $\text{Se}_2\text{O}_2\text{F}_8$, a molecule with a four-membered ring unit^{57,58} (Figure 8).

The analogous compound of tellurium, $\text{Te}_2\text{O}_2\text{F}_8$, was prepared by pyrolysis of $\text{Li}^+\text{OTeF}_5^-$ or $\text{B}(\text{OTeF}_5)_3$ and studied by electron diffraction as well.⁵⁷⁻⁵⁹ The four-membered-ring unit seems to be a general building principle for the heavier nonmetal elements. Ions like $\text{Te}_2\text{O}_8(\text{OH})_2^{6-}$ or $\text{I}_2\text{O}_8(\text{OH}_2)_4^{4-}$, as well as $\text{As}_2\text{O}_2\text{F}_8^{2-}$, all exhibit a four-membered-ring unit.⁶⁰⁻⁶² The recently determined crystal structure of IO_2F_3 shows it to be a dimer, $\text{I}_2\text{O}_4\text{F}_6$, with a four-membered ring.⁶³ Such a structure maintains the high coordination number 6 and avoids double-bonded oxygen.

The monomer TeOF_4 has not yet been detected. Here the necessity of the coordination number 6 is strict. Generally, double bonds on Te(VI) are not known, as arithmetically they would lead to lower coordination numbers. It is unnecessary to use orbital theory to explain this effect. In IOF_5 a double bond is possible while the CN of 6 is retained. All other tellurium(VI) oxide fluorides have octahedrally coordinated tellurium²⁷ (Figure 6). (The more extensively discussed problems of double bonds on silicon can be explained similarly: any silicon double-bonded species would have CN 3, and the latter seems to be impossible in stable compounds under normal conditions. If the favored CN 4 is retained, as in POF_3 or SO_2F_2 , double-bonded species are present.)

Conclusion

My intention has been to show that in the classical field of the electronegative elements there has been some exciting progress, despite the fact that this field has largely been neglected in recent years in favor of transition-metal chemistry. I regret that many other significant discoveries in this field, such as the development of the halogen fluorides and oxyfluorides, could not be mentioned in the limited space of this Account.

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(56) AsCl_5 is made from AsCl_3 and Cl_2 at -100°C by UV irradiation. It decomposes at -30°C . The oxydechloride AsOCl_3 is more stable. K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **15**, 377 (1976); **15**, 766 (1976); *Z. Anorg. Allg. Chem.*, **434**, 5 (1977); **439**, 5 (1978).

(57) K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **13**, 91 (1974); *Z. Anorg. Allg. Chem.*, **406**, 287 (1974).

(58) H. Oberhammer and K. Seppelt, *Inorg. Chem.*, in press.

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