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Some Advances in High Oxidation-State Fluorine Chemistry of the Past Forty Years

N. Bartlett

February 1993

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Some Advances in High Oxidation-State Fluorine Chemistry of the Past Forty Years

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What follows is an abbreviated version of the Bonner Chemiepreis Lecture given 19 October 1992 in the Chemische Institute der Rheinischen Friedrich-Wilhelms-Universität, Bonn, Germany, by Professor Neil Bartlett, Department of Chemistry, The University of California at Berkeley, CA.

"Some Advances in High Oxidation-State Fluorine Chemistry of the Past Forty Years"

Meine Damen und Herren,

Es ist mir eine groβe Ehre, als erster mit dem Bonner Chemiepreis ausgezeichnet zu werden. Die gute Tradition des berühmten Chemikers Kekulé wird von den Chemikern der Bonner Universität bis zum heutigen Tage würdig fortgeführt.

Meine besondere Freude über den Preis rührt daher, daβ er mir von Kollegen zuerkannt wurde, deren Arbeiten ich sehr bewundere. Es gibt noch einen weiteren Grund, weshalb ich heute besonders gerne hier bin. Vor einer Reihe von Jahren hat Herr Appel mich zu einem Vortrag nach Bonn eingeladen. Ich habe damals versprochen zu kommen, konnte mein Versprechen jedoch nicht mehr vor seiner Emeritierung einlösen. Mit dem heutigen Tage kann ich also auch diese lange bestehende Zusage erfüllen.

Leider ist meine Kenntnis der Sprache Goethes so gering und meine Aussprache so seltsam, daβ ich besser in Englisch fortfahre, damit ich überhaupt verstanden werde.

In 1956 after starting on my postgraduate work in fluorine chemistry in the laboratories of Professor P.L. Robinson of King's College in the University of Durham[1] England, I became interested in the possibility of synthesizing platinum difluoride. To make it, I planned to use sulfur tetrafluoride, to reduce platinum tetrafluoride, PtF_4, which was the only established fluoride of platinum at that time. I prepared PtF_4, by the method given by A.G. Sharpe[2]. Sharpe had pointed out that PtF_4 made in his way was always contaminated by bromine. I decided that I would remove this bromine by fluorinating the PtF_4, by heating it in a stream of fluorine gas. I expected the bromine to be converted to the volatile fluoride, bromine pentafluoride. The fluorination was carried out with the PtF_4 contained in a nickel boat, within a glass tube. As I warmed the PtF_4 in the fluorine gas stream, I was surprised to see a red vapor above the solid PtF_4. When I heated more strongly, the red vapor increased greatly. Simultaneously, as was evident from the etching of the glass, the fluorine was also attacking it (to release oxygen and silicon tetrafluoride). A red solid was rapidly deposited on the cooler tube walls downstream, and soon no solid remained in the nickel boat. I immediately concluded that this somewhat volatile red solid must be a new, high oxidation-state platinum fluoride or oxyfluoride, but its identity was not settled until late in 1961, when D.H. Lohmann and I proved it[3] to be the salt, $O_2^+PtF_6^-$. This was the decisive discovery which led to the oxidation of xenon, and to the initiation of noble-gas chemistry.

In the meantime PtF_6 had been discovered[4] by Dr. Bernard Weinstock and his coworkers at the Argonne National Laboratory, U.S.A. After the $O_2^+PtF_6^-$ formulation had been settled, it was clear that PtF_6 should oxidize O_2 spontaneously to give that salt. I made PtF_6 (by Weinstock's method) and mixed it with O_2. The $O_2^+PtF_6^-$ salt immediately was produced. This confirmed the formulation and demonstrated, unequivocally, that PtF_6 was an oxidizer of remarkable power. This is roughly quantified by the Born Haber Cycle, given in Figure 1. I was forced to conclude, from such considerations, that the electron affinity of the PtF_6 molecule must be at least twice that of a fluorine atom.

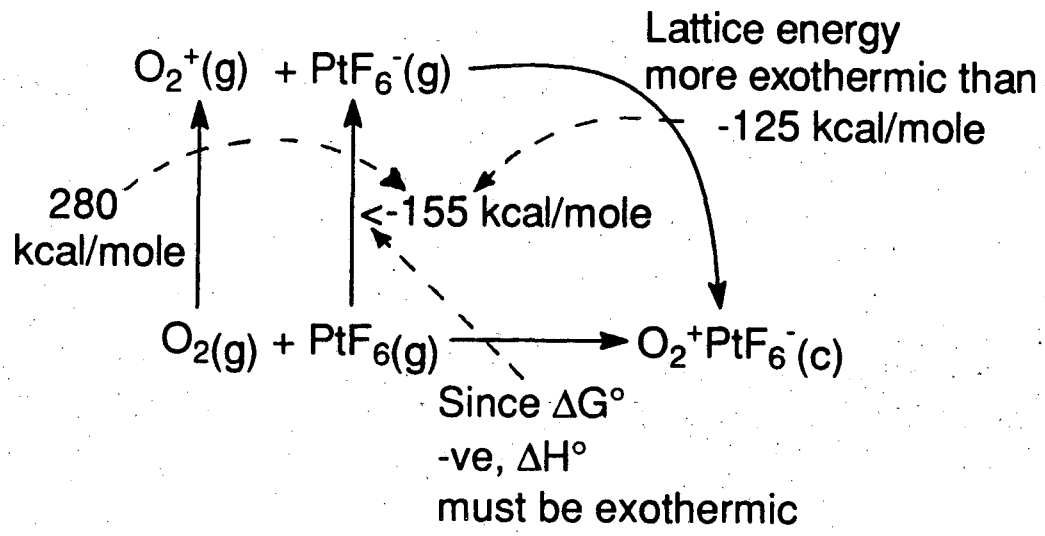


Figure 1. A Born-Haber cycle for $O_2^+PtF_6^-$

In early February 1962, as I was preparing a lecture, I noticed in a textbook, the familiar plot of first ionization potential as a function of atomic number (Figure 2). This

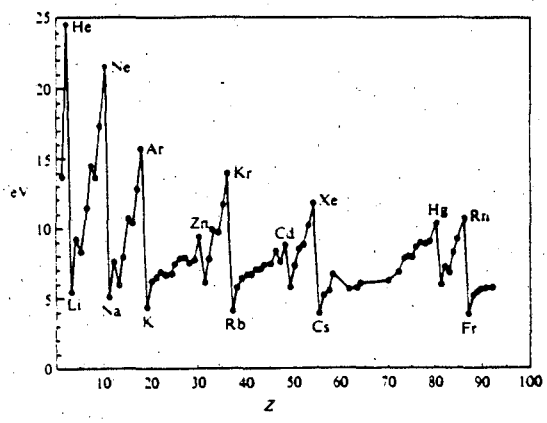


Figure 2. Variation of the first ionization potential with atomic number

immediately suggested a new test for the oxidizing power of PtF_6. The plot reminded me that the effective nuclear charge of an atom decreases markedly with increasing atomic number, down any group in the Periodic Table. I immediately checked the values for the heavier

noble gases, and saw that the ionization potential of xenon was essentially the same as that of O_2, radon being even lower. Because the anion in such a salt as $O_2^+PtF_6^-$, or the speculated Xe^+PtF_6, is relatively large, the small increase in cation size associated with the latter formulation would, I estimated, only lower the lattice energy by about 10 kj mol^{-1}. Since work with radon was out of the question for me, I immediately ordered xenon and prepared some PtF_6.

The first experiment was carried out in dry glass and quartz apparatus as shown in Figure 3. A small sample of PtF_6 was transferred to the quartz sickle gauge, and was allowed to vaporize in the gauge, closed by the metal valve[1]. Following pressure measurement the PtF_6 was transferred to (b) via the break-seal by-pass which was then sealed at X. Xenon was admitted to the gauge to the same pressure as the PtF_6 sample. The sample of Xe from the gauge was condensed in (a) at -196°C and valves 2 and 1 closed to ensure a small volume. Both the Xe and PtF_6 were vaporized, then the break-seal separating them was broken with nickel balls, moved within the system by means of an external magnet. The interaction of the gases, to produce an orange solid, was immediate and the gauge showed that the residual pressure in the system was low.

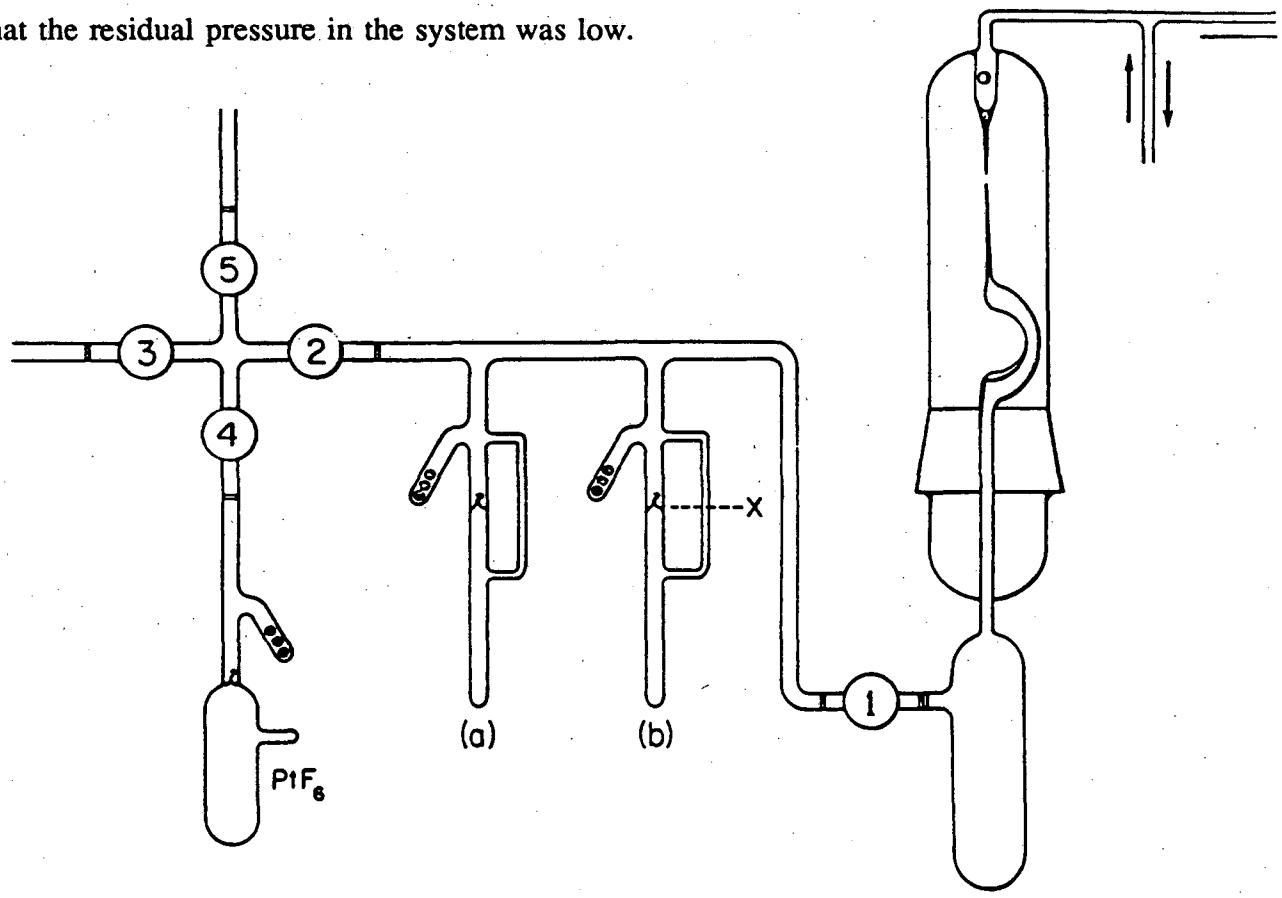


Figure 3. The Xe + PtF_6 Experiment

At that time (March 23, 1962) I had no coworkers experienced enough to help me with the experimental work. The experiment therefore was not ready until about 7pm on that Friday. When I broke the seal between the red PtF_6 gas and the colorless xenon gas, there was an immediate interaction, to precipitate an orange solid. At once, I tried to find someone with whom to share the exciting finding, but everyone, it appeared, had left for dinner!

This launched xenon chemistry[5,6] but the reaction itself proved to be more complex than initially contemplated. It took several years to show[7] that there are two reactions occurring when the gases (PtF_6 and Xe) are mixed in comparable proportions. In such circumstances the composition of the solid product is between $XePtF_6$ and $Xe(PtF_6)_2$. The two reactions are:

$$Xe_{(g)} + PtF_{6\,(g)} \rightarrow Xe^+\ PtF_6^-$$

$$Xe^+\ PtF_6^- + PtF_{6\,(g)} \rightarrow XeF^+\ PtF_6^- + PtF_5$$

By diluting the PtF_6 with the inert molecule SF_6, and using a large stoichiometric excess of xenon, the composition can be brought very close[6,7,8] to that of $XePtF_6$. This, yellow-orange solid, unlike $XeF^+PtF_6^-$, gives no X-ray diffraction pattern, but its chemical reactions and its magnetic behavior indicate that it is a Pt(V) compound. Since the magnetic susceptibility of the $XePtF_6$ (see Fig. 4) is almost temperature independent[8], and the structure must surely

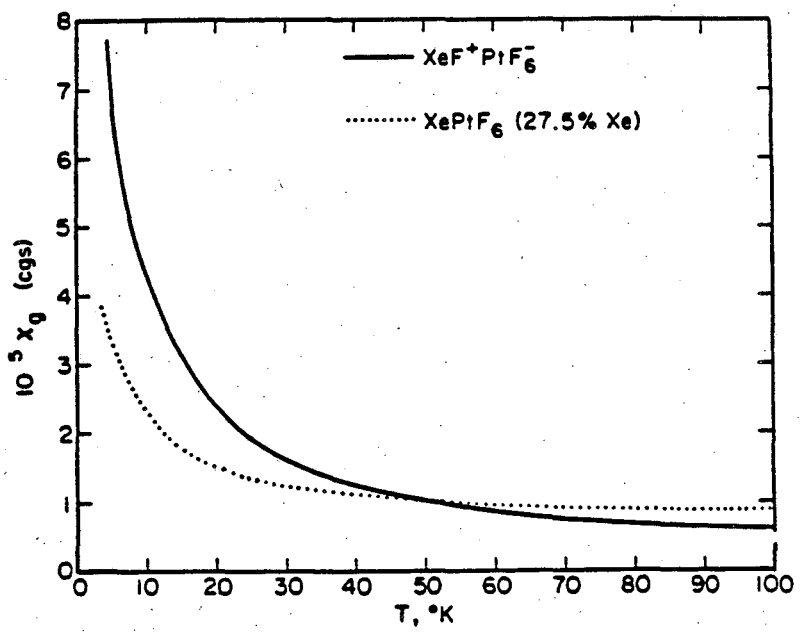
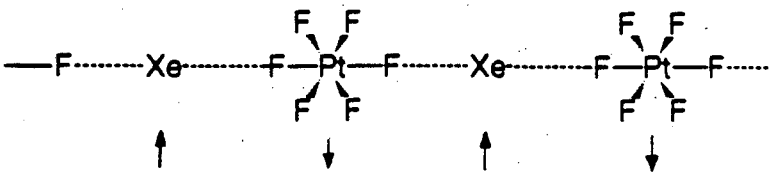


Figure 4. $10^5\ \chi g$ vs T plot for $XeF^+PtF_6^-$ and $XePtF_6$ (27.5% Xe).

contain Pt(V) octahedrally coordinated by F ligands, it is probable that the material is a xenon bridged polymer as represented in Figure 5. Because the magnetic susceptibility is almost temperature independent (except for a low-temperature Curie tail) the solid could be a one dimensional metal.



Xe^{I} & Pt^{V} are probably of comparable electronegativity

Figure 5. The possible atomic & magnetic structure in $Xe^{I}Pt^{V}F_6$

It was found[6,7] that when $Xe^{+}PtF_6^{-}$ and $XeF^{+}PtF_6^{-}$ were heated to ~ 160°C, each evolved XeF_4:

$$4\ XePtF_6 \rightarrow 2XePt_2F_{10} + Xe + XeF_4$$

$$2\ XeFPtF_6 \rightarrow XePt_2F_{10} + XeF_4$$

and at 430°C XeF_2 was evolved:

$$XePt_2F_{10} \rightarrow XeF_2 + 2PtF_4$$

but before these preparations had been discovered, the difluoride[9,10] and tetrafluoride[11] had already been described.

The difluoride of xenon is much easier to make than that of krypton.[12,13,14] So even a xenon/fluorine mixture, in a Pyrex glass bulb exposed to sunlight, is a convenient way to make rather good quality XeF_2 in multigram quantities[15,16]. To prepare KrF_2 however, it is necessary to trap the product at low temperature (from a fluorine-atom/krypton reaction mixture), since the molecule is thermodynamically unstable[17] with respect to Kr and F_2. This can be understood when we recognize that the bonding of the noble gas atom G to the F atoms is dependent on the removal of one electron to the <u>two</u> F ligands, these ligands being single-electron bonded to the xenon, F • G • F, the charge distribution being approximately $^{-1/2}FG^{+1}F^{-1/2}$. But as we see from Figure 6 the ionization potential of Kr is approximately 2 eV

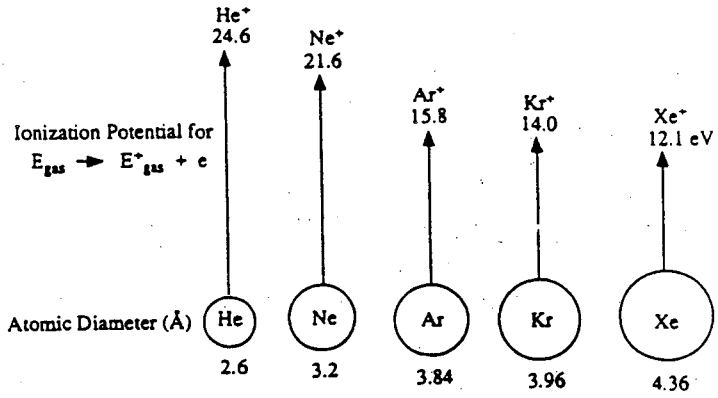


Figure 6. Ionization potentials and atomic diameters for the noble-gas atoms

higher than that of Xe. This accounts for the total bond dissociation energy of XeF_2 being approximately that much higher than the total bond dissociation energy of KrF_2. We can therefore appreciate from Figure 7, (since the ionization potential of argon is about 2eV

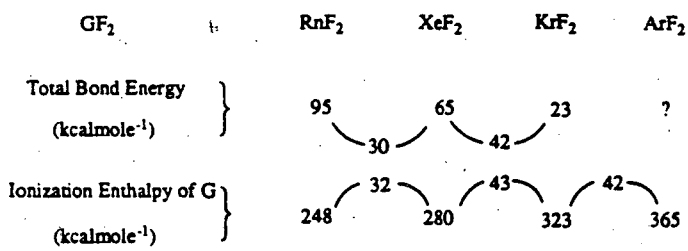


Figure 7. Total bond energy of GF_2 and ionization potentials of G

higher than that of krypton) that ArF_2 cannot be bound. But experimental work by Berkowitz and his coworkers[18] and high level calculations by Frenking et al[19] show that the cation $(ArF)^+$, which is isoelectronic with the classical molecule ClF, is bound by ~ 50 k cal $mole^{-1}$. This then raises the question of the possible existence of $(ArF)^+$ salts.

As may be appreciated from Figure 8, the stabilization of an $(ArF)^+$ salt makes

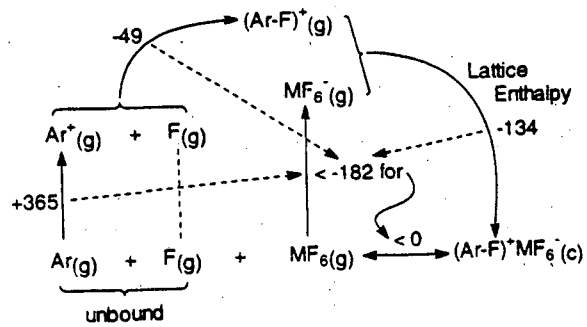
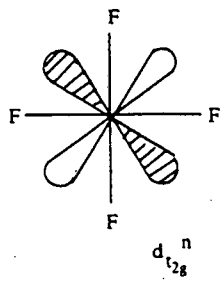


Figure 8. Concerning the stability of $(Ar\text{-}F)^+MF_6^-$
(enthalpies in kcal $mole^{-1}$)

extraordinary demands. A small anion is needed for high lattice energy. This anion, however, must have a very high ionization potential, and the only candidate meeting both these criteria is an MF_6^- anion. But which MF_6^- could serve? In Figure 9 we see that the electron affinity of each of the third transition series hexafluorides is increased by



	WF_6	ReF_6	OsF_6	IrF_6	PtF_6	AuF_6
n=	0	1	2	3	4	5
E(rounded) ($kcalmole^{-1}$)	80	105	130	155	180	205

Figure 9. Electron Configurations (t_{2g}^n) for the 3rd transition series hexafluorides and estimated electron affinities

approximately 1eV for each unit increase in atomic number of the metal atom[20]. As the

atomic number increases, so does the electron population of the approximately non-bonding t_{2g}^* molecular orbitals, which are filled only in the (so far unknown) molecule HgF_6. We might then expect AuF_6, which so far is also unknown, to have an electron affinity ~ 1eV higher than that of PtF_6^- i.e. ~ 9.0eV. We believe that AuF_6^- could possibly stabilize ArF^+. In the early 1970's we made many efforts to prepare that molecule, but did not succeed. We did however make[21] the first AuF_6^- salts and, as expected, these stabilize high oxidation state cations such as KrF^+ and O_2^+. In the attempts to prepare AuF_6 we did find a way to make single crystals of AuF_3 and that provided a basis for the work on AgF_3 and its derivatives that have brought us to a new set of extraordinary oxidizers.

Christie's chemical preparation of fluorine[22] by interaction of liquid antimony pentafluoride with K_2MnF_6 (so liberating the thermally unstable MnF_4) caused me to ponder on the possibility of using strong fluoroacids in anhydrous hydrogen fluoride solution to capture F^- from anions, and so free the parent binary fluoride. This was first done in collaboration with my colleague Professor B. Žemva and his coworkers, of the Institute Jožef Stefan, in the summer of 1987. One of the experiments used AgF_4^- to generate AgF_3.[23] Salts of AgF_4^- had already been prepared by Professor Hoppe and his coworkers in the 1950's.[24,25] The reason for the late discovery[26] of AgF_3, is its thermodynamic instability. An anion, because it is relatively electron rich, stabilizes a high oxidation state best. The electronegativity of Ag(III) in AgF_3 is higher than that of Ag(III) in the anion. Abstraction of F^- from AgF_4^- in anhydrous hydrogen fluoride, (AHF), gave[26] the parent binary fluoride:

$$AgF_4^- + BF_3 \xrightarrow[0°C]{AHF} AgF_3 + BF_4^-$$

This is of high purity only if the BF_4^- salt, dissolved in AHF, is removed at low temperatures and the AHF itself is removed quickly.

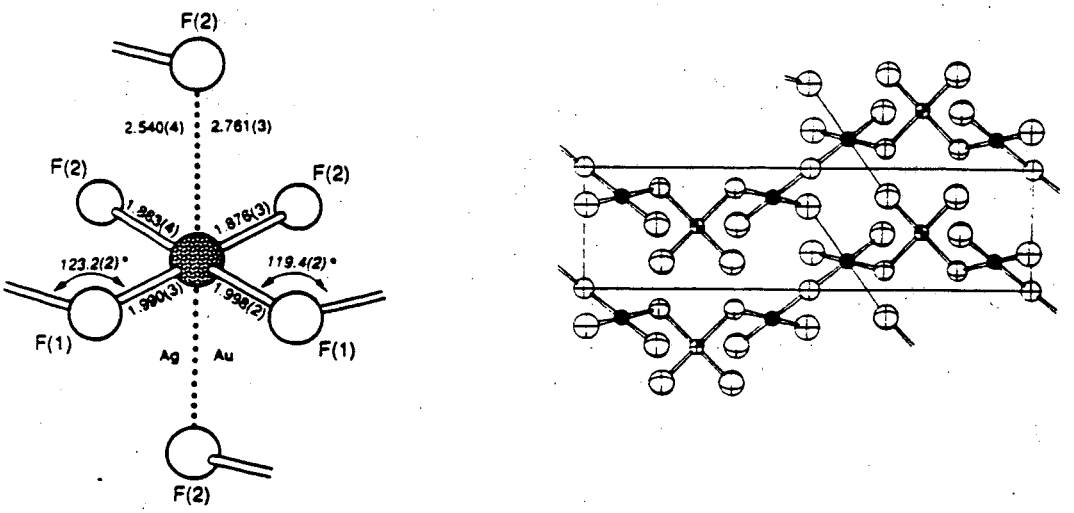


Figure 10. Structural features of AgF_3 and AuF_3

The structure of AgF_3 is similar to that of AuF_3 as shown in Fig 10, each metal atom being close-coordinated by four F ligands in an approximately square arrangement. If this is designated the *xy* plane, we see that the *z* axis distances, to the next nearest F ligands, for each of the metal atoms, are much shorter for silver than for gold. This is consistent with the d_z^2 valence-electron pair of the silver atom being much more tightly bound, and hence smaller in effective volume, than its counterpart on gold. This is in considerable measure due to the large relativistic effect in the gold atom[26]. When free of HF, the AgF_3 is kinetically stable at ordinary temperatures, but its loss of fluorine in AHF demonstrates its thermodynamic instability:

$$3\ AgF_3 \underset{20°C}{\overset{AHF}{\rightarrow}} Ag^{2+}[AgF_4]^-_2 + 1/2\ F_2$$

The solid product of this decomposition is identical with the material described previously[27,28] as AgF_3.

From what has already been said, it will be appreciated that we were very interested in the possibility of removing a fluoride ion from AgF_3 to generate a cationic species AgF_2^+. Clearly such a species should have Ag(III) in a more electronegative condition than Ag(III) in AgF_3, and therefore be a very potent oxidizer. We noted that the fluoroacid AsF_5 in AHF did

dissolve AgF_3, but elemental fluorine was slowly produced, along with a blue solution of solvated Ag^{2+}. Removal of AHF yielded the known $AgF^+AsF_6^-$ salt[29]: $AgF_3 + AsF_5 \rightarrow [AgF_2^+ AsF_6^-] \rightarrow AgF^+AsF_6^- + 1/2\ F_2$. In an effort to detect the possible intermediate, $[AgF_2]^+$, we introduced Xe as a mild reducing agent, anticipating that the $[AgF_2]^+$ species, if present, would oxidize Xe to a xenon fluoride[30]. Xenon was immediately consumed, but we were surprised to find that the Ag(III) was reduced to Ag(I)! This caused us to investigate the oxidizing properties of cationic Ag(II) in AHF.

A convenient route to cationic Ag(II) salts is to treat[30] AgF_2 with BF_3 in AHF, but the best procedure[31], which can be easily regulated to generate single crystals, is to fluorinate $AgBF_4$:

$$AgF_2 + BF_3 \xrightarrow{AHF} AgFBF_4 \text{ or } AgBF_4 + 1/2F_2 \xrightarrow{AHF} AgFBF_4$$

The $AgFBF_4$ interacts with xenon in the presence of additional BF_3 to give XeF_2 at room temperature:

$$2\ AgF^+\ BF_4^- + Xe + BF_3 \xrightarrow{AHF} 2\ AgBF_4 + XeF_2 + BF_3$$

The reaction does not proceed without the addition of BF_3, which is needed to produce the AHF solvated Ag^{2+} ion. The oxidizing power of this ion is also illustrated by its interaction with certain perfluoro-organic molecules[32]. Such reactions are best done using $AgFAsF_6$ with an additional mole of AsF_5.

The interaction of the blue Ag^{2+}/AHF solution with hexafluorobenzene at -65°C, immediately precipates orange-yellow $C_6F_6^+AsF_6^-$, which we had prepared previously[33].

$$Ag^{2+} + 2AsF_6^- + C_6F_6 \xrightarrow{AHF} AgAsF_6 + C_6F_6^+AsF_6$$

This shows that the Ag^{2+}/AHF is acting as a potent one-electron oxidizer. This is in harmony with the high second ionization potential of silver which, as may be seen from Figure 11, is higher than those of either copper or gold, and even xenon! Indeed that of silver is the highest second ionization potential of any metal, except the alkali metals (where, of course, the second ionization potential involves removal of a core, noble-gas electron). Additionally, the d^9 electron configuration of Ag(II) is an antibonding one, therefore the solvation of Ag^{2+} by AHF involves essentially only s and p functions in the bonding. Such bonds must be relatively weak.

	eV	(kcal mole^{-1})
Cu^{2+}	20.29	(467.9)
Ag^{2+}	21.49	(495.6)
Au^{2+}	20.50	(472.8)
Xe^{2+}	21.21	(489.1)

Figure 11. The electron affinities of divalent cations

The interaction of the Ag^{2+}/AHF with perfluoropropene proceeds quantitatively below -65°C to perfluoropropane!

$$CF_3.\ CF = CF_2 + 2\ Ag^{2+} + 2HF \rightarrow CF_3.CF_2.CF_3 + 2Ag^{+} + 2H^{+}$$

This probably involves a sequence of one-electron oxidation and F^- addition reactions, as indicated in Figure 12.

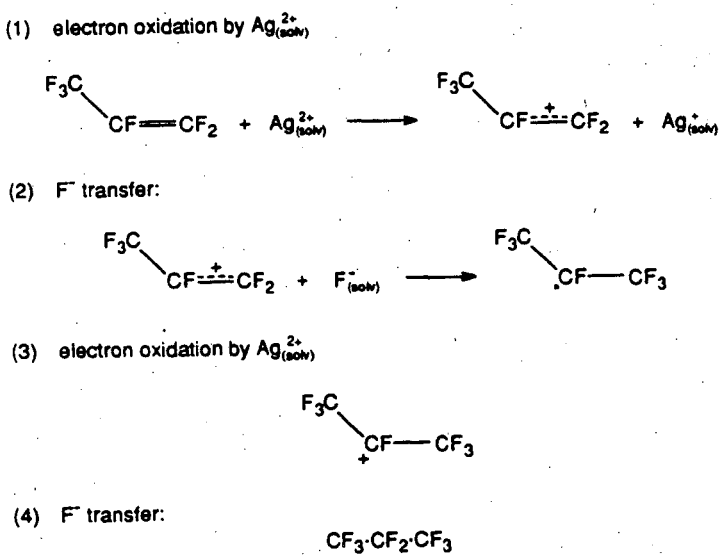


Figure 12. Probable mechanism of $Ag_{(solv)}{}^{2+}$/AHF Fluorination of $CF_3 \cdot CF{=}CF_2$

A further reaction, that with O_2, indicates that Ag^{2+}/AHF at least approaches PtF_6 in oxidizing power. A blue solution of Ag^{2+} (with 2 AsF_6^-) at -75°C will combine with oxygen to generate $O_2^+AsF_6^-$, the mixture becoming colorless, but on warming to -65°C the blue color of Ag^{2+} is again apparent and, at room temperature, the uptake of O_2 is barely detectable:

$$O_2 + Ag^{2+} + 2\ AsF_6^- \underset{\geq -65°C}{\overset{-75°C}{\rightleftharpoons}} AgAsF_6 + O_2^+AsF_6^-$$

The oxidation of O_2 is much more decisive with cationic Ag(III). When AgF_3 is treated with AsF_5 in AHF in the presence of O_2 there is an essentially quantitative uptake of O_2 to make $O_2^+AsF_6^-$, according to the equation:

$$AgF_3 + 3AsF_5 + O_2 \underset{20°C}{\overset{AHF}{\rightarrow}} AgF^+AsF_6^- + O_2^+AsF_6^-$$

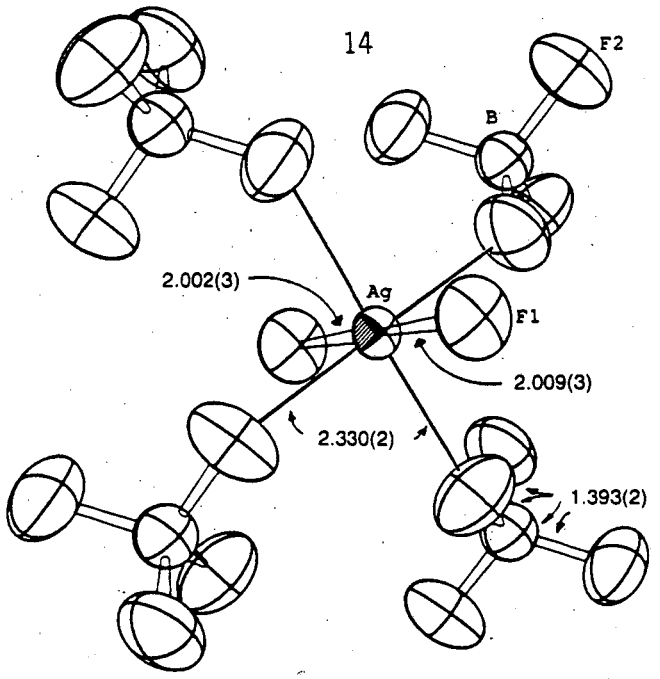


Figure 13a. The tetragonally-distorted octahedra F environment of the Ag(II) in $AgFBF_4$ (90% probability ellipsoids).

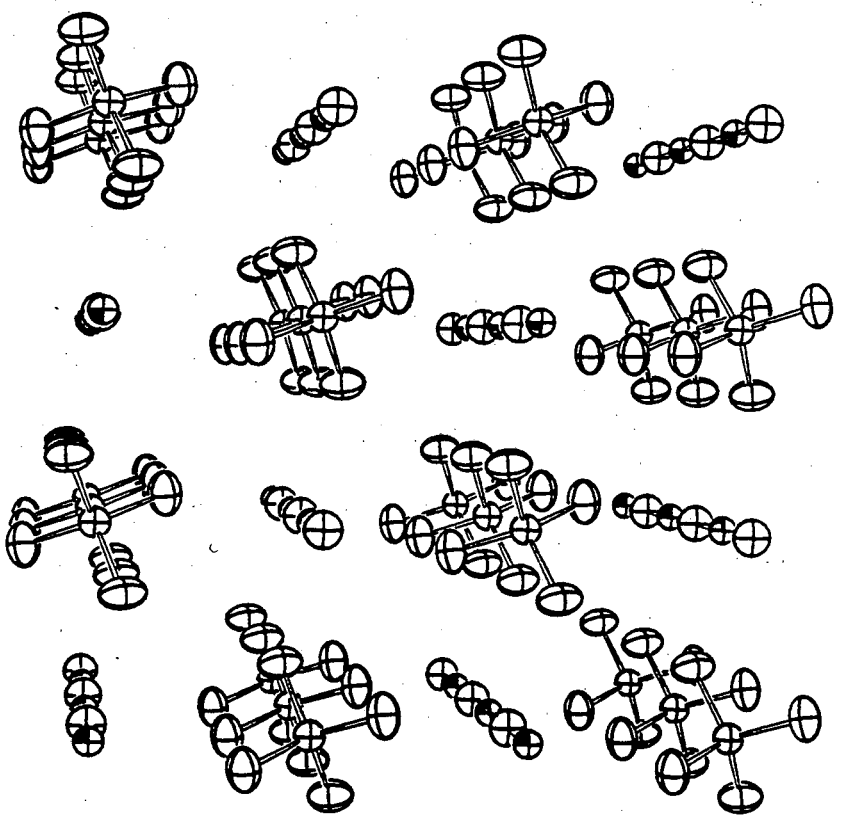


Figure 13b. The $AgFBF_4$ extended structure (50% probability ellipsoids).

At -30°C the $Ag(AsF)_2$ is very soluble in the AHF and the O_2AsF_6 only slightly so. Therefore the two salts are readily separated and purified. This oxidation of O_2 to O_2^+ by Ag(III) shows that it rivals PtF_6 in oxidizing power.[34]

As we have seen, cationic Ag(II) and Ag(III) are highly electronegative. They must be close to the F atom in electronegativity. This makes the AgF^+ salts interesting also from a solid-state chemistry viewpoint. Figure 13 shows the crystal structure[31] of $AgF^+BF_4^-$. Here we see linear chains of alternating silver and fluorine atoms in the poly-cation. The two F ligands for each silver atom are symmetrically placed (within the 3σ criterion of the structure determination, which is of good precision). There is therefore no evidence for a Peierls distortion[35]. In addition the magnetic susceptibility (shown in Figure 14) and the optical properties are consistent with the $(AgF)^{n+}_n$ chain being a one dimensional metal[31]. Indeed, with the Ag(II) and F ligand orbitals likely to have similar energies, a metallic band system is not unexpected. But of course this also reminds us of the superconducting copper oxide situation and one has therefore, in addition, to countenance the possibility of there being superconducting fluorides, in the Ag(II) or Ag(II)/(III) fluoride systems. Because of this possibility we have undertaken to attempt to prepare two or three dimensional (2D or 3D) silver fluoride chain systems. We have succeeded in making 3D examples.

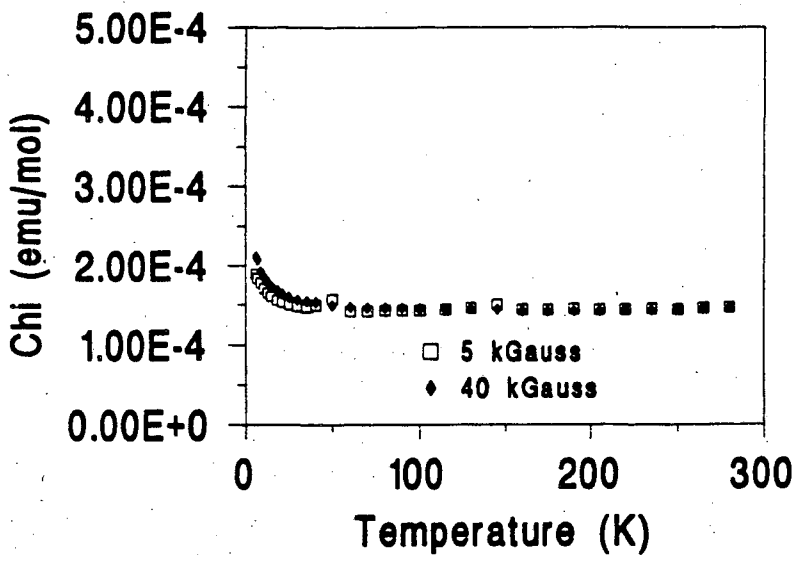


Figure 14. Evidence for the metallic nature of $AgFBF_4$

When AgF_2 (or better $AgF^+BF_4^-$) in AHF is treated[36] with $O_2^+MF_6^-$ salts (M = As, Au, Pt, Ru) salts of composition $(AgF_2)_3^+MF_6^-$ are produced. These all have the structure (which is not yet known in detail) illustrated in Figure 15. It is a pseudo-trifluoride structure, related

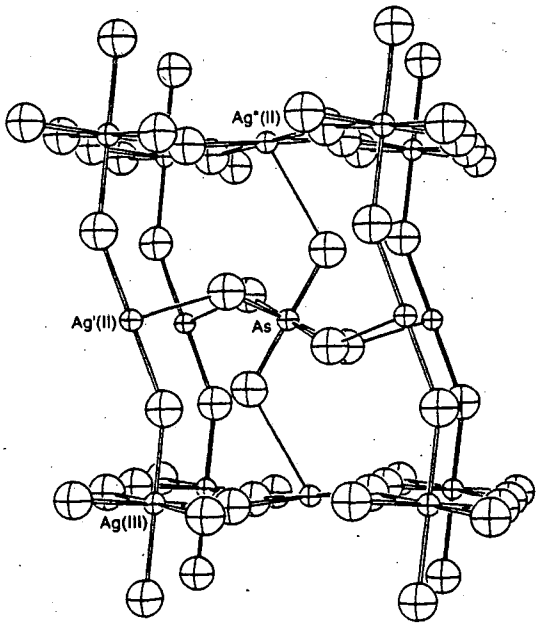


Figure 15. The probable structure of $(AgF_2)_3AsF_6$

to that of pervoskite. Here the M-F-M bridges are puckered (~ 140°), whereas in perovskite they are linear. Note that there are three different Ag environments. The MF_6^- anion M-F distances must, in all cases, be close to 1.8Å. This means that those F ligands must all be long bonded to the Ag atoms, to which they bridge. Therefore we have an approximately linearly coordinated silver (Ag'(II)), an approximately square coordinated silver (Ag''(II)), and an octahedrally coordinated silver atom, which we identify as Ag(III). Again the magnetic susceptibility (see Figure 16) shows that we have approximately temperature independent paramagnetism (except for the Curie tail at low temperatures) and this is consistent with metallic behavior. With redox manipulation it may indeed prove possible to

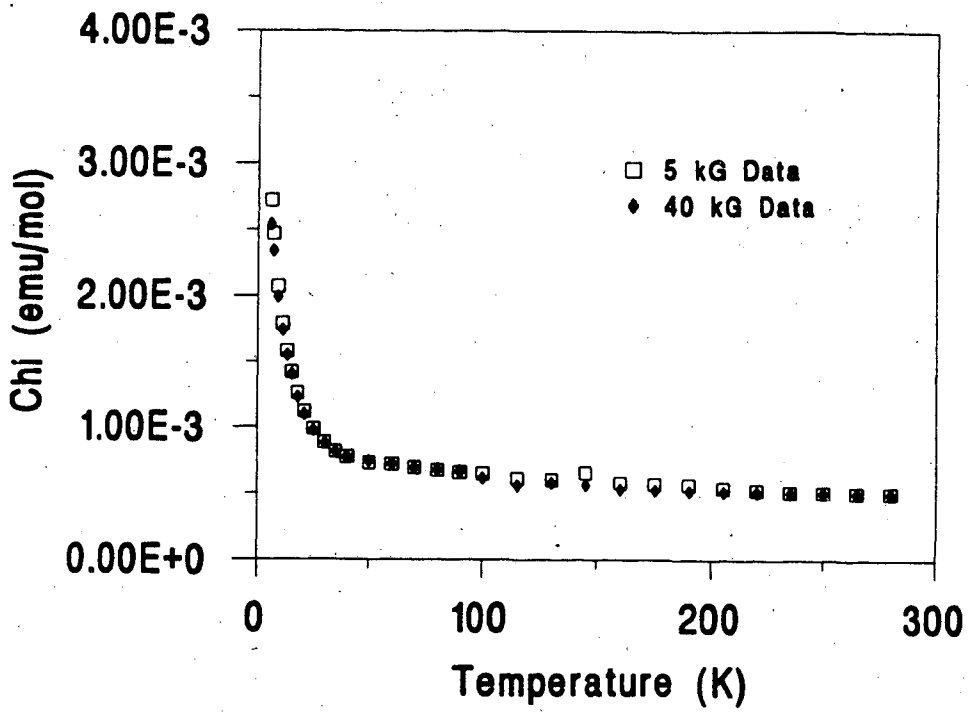


Figure 16. The dependence of the magnetic susceptibility of $(AgF_2)_3AsF_6$ on temperature.

derive superconducting relatives of these salts. Certainly the $(AgF_2)^+_3$ cage is highly electron withdrawing, since it oxidizes the IrF_6^- ion {$E(MF_6)$ = ~ 7.0 eV} to IrF_6. Only ions of higher ionization potential than IrF_6^- will stabilize that cation.

So, we see that in AHF, high oxidation-state cations, of Ag(II) or Ag(III) have remarkable oxidizing capability, already rivaling {and in the Ag(III) case surpassing} PtF_6. With many other high oxidation state cations yet to be investigated, this again raises the hope that eventually even the $(ArF)^+$ species can be made. That, however, is a very hard task!

It has been a great pleasure to be here in Bonn and to give this lecture. Thank you for listening so attentively.

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