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Neil Bartlett

March 1981

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ELECTRON-OXIDATION OF AROMATIC MOLECULES, LAYER-FORM BORON NITRIDE AND GRAPHITE

By Neil Bartlett

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INTRODUCTION

This paper reviews that work at Berkeley, over the past eight years, which has been devoted to the electron-oxidation of aromatic molecules and polycyclic, electron-delocalized systems. Graphite is the infinite-sheet relative of such molecules and its electron-oxidation has been our major interest recently. The first salt of electron-oxidized layer-form boron nitride has resulted from these studies, and a greater understanding has been achieved of the factors which are important for intercalation of graphite by oxidizers. The polycyclic hydrocarbon salts and the boron nitride and graphite salts are good electrical conductors and some of the last may have value as electrode materials.

PERFLUOROAROMATIC

The relatively high ionization potential of hexafluorobenzene (10.0 eV) requires an extraordinary oxidizer such as the dioxygenyl cation, $O_2^+$:

Proofs to Professor N. Bartlett, FRS.,

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and this reagent is also effective for the electron-oxidation of per-fluorotoluene and perfluoropyridine. Since the salt, C₆F₆⁺AsF₆⁻, is thermodynamically unstable, has a half-life of only an hour or so at room temperatures, and yields volatile products:

\[ 2 \text{C}_6\text{F}_6\text{AsF}_6 \rightarrow \text{C}_6\text{F}_6 + 1,4\text{-C}_6\text{F}_8 + 2 \text{AsF}_5, \]

it is the reagent of choice for the electron-oxidation of the highest fluoroaromatics, e.g.:

\[ \text{SO}_2\text{ClF} \]

These highly coloured salts (C₆F₆⁺, yellow; C₁₀F₈⁺, dark green; C₅F₅N⁺, deep blue) are simple paramagnets. This is consistent with structural evidence. The salt C₆F₆⁺AsF₆⁺ has a rhombohedral unit cell containing one formula unit (a = 6.60(1)Å; α = 106.0(1)° V = 246.1Å³) in which each ion is surrounded by eight ions of the other kind, in a rhombohedral variant of the CsC₁₂ structure. The structure of C₁₀F₈⁺AsF₆⁻ is less certain, but the X-ray powder data has been indexed on the basis of a tetragonal cell (a = 8.24(1); c = 18.44(9); V = 1252 Å³, Z = 4) the dimensions and symmetry of which indicate a simple ionic lattice.

The rhombohedral, unimolecular, unit cell of C₆F₆⁺AsF₆⁻ was unexpected since a Jahn-Teller distortion was anticipated for the cation. Evidently the distortion is too subtle to be manifest at temperatures down
to $-130^\circ$, since single crystals remain rhombohedral down to that temperature.

Undoubtedly the synthetic approaches for the smaller perfluoroaromatics will be applicable to the synthesis of salts of the perfluoropolycyclic carbon species, but it appears that the polycyclic hydrocarbons can also be successfully electron oxidized to yield salts. The larger polycyclic cations provide for the possibility of enforced overlap of cation with cation, since the effective thickness of an anion such as $\text{AsF}_6^-$ (See Figure 1) is approximately 4.7Å, whereas that of a polycyclic hydrocarbon or aromatic molecule is $\sim 3.4$Å. It was the possibility of such overlap and the impact that such overlap could have upon the electrical conductivity of the salts, which encouraged the attempts to synthesize them.

**ELECTRON-OXIDATION OF POLYCYCLIC HYDROCARBONS AND BENZENE**

Oxidants such as $\text{O}_2^+\text{AsF}_6^-$ or $\text{C}_6\text{F}_6^+\text{AsF}_6^-$ can be used in the oxidatively robust solvent $\text{SO}_2\text{CIF}$, if the temperature is kept below $-20^\circ$, but it is then a poor solvent for the polycyclic hydrocarbons. Interaction of hydrocarbons such as anthracene, phenanthrene, or coronene with these oxidizers, in that solvent, yields deeply coloured solids (with deep blue or purple hue). These solids are amorphous to X-rays. The packed finely divided solids conduct electricity and the conductivity appears to be at least as good as that of graphite. Unfortunately the absence of crystalline material has prevented structural work and meaningful
conductivity studies.

Interaction of benzene with $O_2\overset{+}{AsF_6}^-$ or $C_6F_6\overset{+}{AsF_6}^-$ always yielded a mixture of two solids, one a colorless solid, soluble in anhydrous hydrogen fluoride, and the other a blue-black electrically conducting, insoluble solid. The former has proved to be the salt $(C_6H_5)_2\overset{+}{AsF_2}^+AsF_6^-$ which can be made quantitatively by the interaction:

$$2C_6H_6 + 2AsF_5 \xrightarrow{\text{in SO}_2ClF} \text{or HF, } 0^\circ C \rightarrow (C_6H_5)_2\overset{+}{AsF_2}^+AsF_6^-.$$

The latter is a salt of poly(paraphenylene), $(C_6H_4)_x\overset{+}{AsF_6}^-$. Values of $x$ have been observed between 1.8 to 4.4. It depends upon the relative quantities of benzene and oxidant and upon the reaction conditions. It seems that electron-oxidation of benzene is a first-step to this polymer salt and a plausible reaction sequence is:

$$2C_6H_6\overset{+}{AsF_6}^- \rightarrow C_6H_6 + C_6H_6F_2 + 2AsF_5$$

$$xC_6H_6F_2 \rightarrow (C_6H_4)_x + 2xHF$$

$$(C_6H_4)_x + 0_2(C_6F_6^+) \rightarrow (C_6H_4)_x^+ + O_2(C_6F_6).$$

BORON NITRIDE OR GRAPHITE WITH $S_2O_6F_2$

Salts derived by electron oxidation of graphite have long been known but such materials gained a new significance with the demonstration by Ubbelohde and his coworkers that they were electrical conductors (in the ab plane) comparable with or, in some cases, superior to aluminium.
metal. Graphite itself is a semimetal, the conductivity being due to a small overlap of the valence band (fully occupied at 0°K) and the conduction band (empty at 0°K). The electron-oxidation of the graphite which occurs on formation of salts such as the first stage bisulfate, $C_{24}^+H_2SO_4^-\cdot2H_2SO_4$, removes electrons from the valence band and thus increases the number of electron-hole carriers. This provides the basis for the order of magnitude increase in conductivity which accompanies the oxidation of the graphite. 7

The fluorosulfate radical, $SO_3F^-$, first discovered by Dudley and Cady 8 and conveniently preparable 9 in high purity by decomposition of xenon bisfluorosulfate, $Xe(SO_3F)_2$:

$$XeF_2 + 2HSO_3F \rightarrow Xe(SO_3F)_2 + 2HF;$$
$$Xe(SO_3F)_2 \rightarrow Xe + S_2O_6F_2; S_2O_6F_2 \rightarrow 2SO_3F^-$$

offered the prospect of being able to prepare an analogue of the bisulfate, $C_{24}^+H_2SO_4^-\cdot2H_2SO_4$, in which a much higher positive charge in the carbon layers could be achieved, viz: $C_{24}^{3+}3SO_3F^-$. Indeed treatment of graphite with $S_2O_6F_2$ yields fluorosulfates 10 for which the limiting composition is approximately $C_7SO_3F$. This is a blue solid which is vacuum stable at room temperature and, as an electrical conductor, is superior to graphite in the $ab$ plane.
If graphite is partially intercalated by $\text{SO}_3\text{F}$ and then treated with fluorosulfonic acid first-stage material of approximate composition $C_7(\text{SO}_3\text{F})_x(\text{HSO}_3\text{F})_{1-x}$ is formed. Samples have been prepared where $x$ is as small as one third and even lower values may be attainable. Such acid-rich materials have higher ab plane electrical conductivities than the fully oxidized material. This is not understood. X-ray powder photography also shows that the acid containing material is always more crystalline than that devoid of acid. This indicates that $C_7(\text{SO}_3\text{F})_x(\text{HSO}_3\text{F})_{1-x}$ has a more ordered structure than $C_7\text{SO}_3\text{F}$. The higher order in the acid-rich material could be a consequence of hydrogen bonding between guest species but it may also signify that the carbon layers in the $C_7(\text{SO}_3\text{F})_x(\text{HSO}_3\text{F})_{1-x}$ material are more regular than in $C_7\text{SO}_3\text{F}$. Certainly there is a correspondence here (see below) with the instability of single crystals of the $C_8\text{MF}_6$ salts, such as $C_8\text{AsF}_6$ (which degenerate to ab plane-disordered slabs) whereas single crystals of $C_8\text{AsF}_5$ retain their crystallinity over long periods.

Each of the materials $C_7\text{SO}_3\text{F}$ and $C_7(\text{SO}_3\text{F})_x(\text{HSO}_3\text{F})_{1-x}$ is metallic and they will interact when mixed to yield a material of an intermediate composition which is determined merely by the molar ratio of the reactants. The data for the $c$ and $a$ axis parameters given in Figure 2 indicate that the $c$ parameter is essentially linearly dependent upon the composition. Of course the interaction involves simply the transfer of protons and electrons between the reactants. Even between the dry mixed solids this appears to be facile.
Although layer-form boron nitride is an electrical insulator because of the more than 3 eV gap between the valence and conduction bands, the close structural relationship to graphite, illustrated in Figure 3, suggested that oxidative intercalation of the nitride might be achieved by SO$_3$F. This proved to be so. The first stage blue salt has a composition close to (BN)$_{3.7}$SO$_3$F. The c axis is larger than in the graphite case (8.0(1) and 7.7(1)Å respectively). This may mean that the SO$_3$F$^-$ groups are oriented with their threefold axes parallel to c, the negative end of the dipole being pointed at the more positive B atoms and away from the N atoms. Unfortunately the poor crystallinity of the (BN)$_{3.7}$SO$_3$F and its instability (it slowly generates BF$_3$) have frustrated structural studies. Crude electrical conductance studies show that the powdered boron nitride salt is at least comparable with graphite powder. Oxidation of boron nitride with S$_2$O$_6$F$_2$ in the presence of HSO$_3$F suggests that acid salts comparable with the graphite analogues can be prepared. Unfortunately the instability$^{12}$ of boron nitride with respect to hydrogen fluoride and to fluorine have limited the range of oxidizers to be applied to it.
HEXAFLUOROMETALLATES OF GRAPHITE

The steady increase in oxidizing capability with atomic number of the transition metal, in the hexafluorides of the third transition series, has provided insight into factors which are important for the intercalation of such molecules into graphite. Relevant properties of the hexafluorides and the established formulations for the fully intercalated graphite salts are given in Table 1. The almost constant size of the hexafluorides means that for a given formulation $C_x^{+}MF_6^-$, as may be appreciated from consideration of Figure 4, the enthalpy of formation is determined mainly by the electron affinity. Since neither WF$_6$ nor ReF$_6$ will alone oxidize and intercalate into graphite, whereas the stronger oxidizers OsF$_6$ and IrF$_6$ each do so spontaneously at room temperatures, to yield first-stage materials of limiting composition $C_8^{+}MF_6^-$, it appears that an electron affinity superior to that of ReF$_6$ but less than or equal to OsF$_6$ is essential for the oxidative intercalation. Since the minimum value possible for the electron affinity of ReF$_6$ is 107 kcal mole$^{-1}$, this sets a lower limit for the electron affinity for any hexafluoride oxidizer.

Complete intercalation of single crystals of graphite by either OsF$_6$ or IrF$_6$ preserves the single crystal character for a short time. A $C_8^{+}MF_6^-$ composition is characterized by a hexagonal unit cell with $a_0 = 4.92(2)\text{Å}; c_0 = 8.10(3)\text{Å}; V = 170\text{Å}^3$, $Z = 1$. This represents a close packing of the guest species since, as may be seen from Table 1,
the effective volume of a hexafluoride molecule is \( >100\text{Å}^3 \) and the volume occupied by eight C atoms in rhombohedral graphite\(^{14}\) is \( 70\text{Å}^3 \). Indeed it is observed that graphite floated on liquid tungsten hexafluoride, and intercalated by OsF\(_6\) or IrF\(_6\), sinks as the intercalation process comes to an end. Rough structural studies from X-ray diffraction data\(^{11}\) indicate that the MF\(_6^-\) ions are, for the most part, oriented with a three fold axis parallel to the \( c_0 \) axis of the graphite as represented in Figure 4. The disposition of the MF\(_6\) species with respect to the C atoms of the graphite grid is not established, but the model in Figure 5(a) is compatible with the data for the crystalline material.

The graphite salt of composition C\(_8\)AsF\(_6\) can be prepared by oxidizing graphite with excess \( O_2^+ \text{AsF}_6^- \) (or more conveniently excess C\(_6\)F\(_6\)AsF\(_6\)), using SO\(_2\)ClF as the solvent. The oxidation of single crystals yields, initially, material which is isomorphous with C\(_8\)OsF\(_6\) and C\(_8\)IrF\(_6\). All three of these materials lose all \( ab \) plane order when kept at room temperature for several days. There appears to be no change in composition. This loss of crystallinity seems to correlate with a marked decrease in \( ab \) plane electrical conductivity, observed\(^{13}\) in first stage materials prepared from large pieces (5 x 5 mm x 0.5 mm) of highly oriented pyrolytic graphite (HOPG). This loss of crystallinity and decrease in conductivity could signify transfer of fluorine from MF\(_6^-\) to the carbon, but there is also the possibility that the high positive charge on the carbon layers and cooperative localization of that charge,
by anions on each side of the layer (a situation peculiar to first-stage materials) may induce a distortion in the graphite layer.

The second and higher stage graphite MF$_6$ compounds are better behaved. The staging formula for these systems is $\text{C}_{12n}\text{MF}_6$, where $n$ is the stage. Indeed only in the first stage does the gallery become filled with close-packed guests as shown in Figure 5(a). The first stage is unique in having a compositional range: $\text{C}_{12}\text{MF}_6$ to $\text{C}_8\text{MF}_6$. Obviously if we have an ordered distribution of guests in the galleries of first-stage $\text{C}_{12}\text{MF}_6$, or its higher stage relatives $\text{C}_{12n}\text{MF}_6$, that arrangement will be as shown in Figure 5(b). Note that the close-packed arrangement for $\text{C}_8\text{MF}_6$ places each ion in close contact with six similar ions, whereas the $\text{C}_{12n}\text{MF}_6$ gallery packing results in each ion having only three such neighbours. Clearly, the $\text{C}_12\text{MF}_6$ gallery packing will be energetically preferable as long as there are galleries available for occupancy. The MF$_6^-$ salts, of second stage or higher, all appear to be good electrical conductors with specific conductivities ($ab$ plane) approximately an order of magnitude better than the pristine graphite for $n = 2$. On the other hand the second stage PtF$_6^{2-}$ salt, $\text{C}_{24}^{2+}\text{PtF}_6^{2-}$ is a relatively poor conductor, barely distinguishable from graphite itself. Again this poor conductivity may be a consequence of carbon-layer structural changes induced by the highly charged guest species.
THE INTERACTION OF ARSENIC PENTAFLUORIDE WITH GRAPHITE

The report by Vogel and his coworkers\textsuperscript{15} of \textit{ab} plane conductivities comparable with copper in the graphite/AsF\textsubscript{5} intercalation compounds (first described by Selig and his coworkers\textsuperscript{16}) attracted much attention. These materials were all the more interesting to Bartlett and his co-workers for two reasons: (1) because of their possible relationship to the C\textsubscript{x}\textsuperscript{+} AsF\textsubscript{6}\textsuperscript{-} salts and (2) because PF\textsubscript{5}, although physically similar to AsF\textsubscript{5}, was unable, alone, to form graphite intercalation compounds.

It seemed to Bartlett that this difference in behaviour of AsF\textsubscript{5} and PF\textsubscript{5} was attributable to the superior electron oxidizing capability of the former. This relative capability can be expressed in terms of the enthalpies for the generalised reaction (the data for which are set out in Table 2):

\[ 2e^- + 3EF_5(g) \rightarrow 2EF_6(g) + EF_3(g) \]

Since the EF\textsubscript{6}\textsuperscript{-} are biggest it is they which determine the carbon layer separation and lattice energy (see Figure 4) hence such an oxidation ought to be comparable with the oxidative intercalation of graphite by the transition metal hexafluorides. It is therefore satisfying to note that the estimated enthalpy per oxidizing equivalent of AsF\textsubscript{5} is more exothermic than the enthalpy for the one-electron reduction of ReF\textsubscript{6}. On the other hand PF\textsubscript{5} is seen to be a poorer electron oxidizer than
WF₆. Significantly however PF₅ intercalated in the presence of fluorine¹⁷ to yield a salt of limiting composition C₈⁺PF₆⁻.

Indeed the evidence for the conversion to AsF₆⁻ and AsF₃ on intercalation of AsF₅ into graphite is now overwhelming. The first clear support for the conversion came from arsenic-absorption-edge synchrotron-radiation spectra illustrated in Figure 6. These spectra represent a true bulk property of each substance. The absorption feature which is illustrated arises from excitation of an arsenic atom 1s (core) electron to a molecular orbital of predominantly 4p character, and as seen, there is an appreciable chemical shift from one arsenic species to another. Evidently the graphite/AsF₅ material contains AsF₆⁻ and AsF₃⁻. Such synchrotron radiation surveys have been carried out on three separate occasions on fresh samples and the findings have always been qualitatively the same. Yet there has been much reluctance to accept this simple interpretation.¹⁹ The reason for the disagreement appears to lie in the failure of others to recognise the dynamical nature of the processes involved in the intercalation of graphite by AsF₅.

If graphite is intercalated by an appropriate molar quantity of AsF₅, in a container with small dead space (so as to generate the limiting composition material C₈AsF₅) the arsenic absorption edge spectrum clearly shows²⁰ the 1s → 4p type transitions characteristic of AsF₃ and AsF₆⁻. When a vacuum is applied to this material, some AsF₅ is removed at least initially, but the bulk of the volatiles proves to be AsF₃. The residual material has a
composition close to $C_{14}AsF_6$ and the absorption-edge spectrum then indicates that the only As-containing species is $AsF_6^-$. Moreover an excellent strategy for the preparation of an almost pure first stage material of composition $C_{12}AsF_6$ is to expose graphite to several cycles (five is adequate) of arsenic pentafluoride gas, followed by a dynamic vacuum, to constant weight. Clearly one has a dynamic equilibrium, which lies largely to the right:

$$xC + 3AsF_5 \rightleftharpoons C_{x}^{2+}2AsF_6^-:AsF_3$$

The molecular species $AsF_5$ and $AsF_3$ are each removed under vacuum, but as the average charge per carbon atom decreases the concentration of $AsF_5$ becomes smaller.

The conversion of $AsF_5$ to $AsF_6^-$ and $AsF_3$ also accounts for the difference in the staging formulae for $C_xAsF_5$ and $C_xAsF_6$. Except for the first stage $AsF_6^-$ salt, which has a compositional range $C_8AsF_6$ to $C_{12}AsF_6$, the staging formula is $C_{12n}AsF_6$ ($n$ being the stage). For graphite/$AsF_5$, the formula $^{21}$ is $C_8AsF_5$. If the $AsF_5$ is entirely converted to $AsF_6^-$ and $AsF_3$, then each stage could be represented by the formula $C_{12n}AsF_6^{1-}AsF_3$. One can view the ideal arrangement of the guest species as an anion assembly conforming to that of Figure 5(b), the neutral $AsF_3$ molecules then residing in the vacant sites (those occupied by $AsF_6^-$ in $C_8AsF_6$). Such an arrangement provides each charged species with only three nearest neighbours and hence a favourable Coulomb energy.
A series of electrical conductance measurements and composition/stage studies,\textsuperscript{22} carried out on HOPG slabs, has established that, for second and higher stages, there is no significant difference in the conductivity of $C_{12n}\text{AsF}_6 \cdot \frac{1}{2}\text{AsF}_3$ (i.e. $C_{8n}\text{AsF}_5$) and $C_{12n}\text{AsF}_6$. Addition of $\text{AsF}_3$ to $C_{12n}\text{AsF}_6$, to yield $C_{8n}\text{AsF}_5$, neither changes the stage nor the conductivity. The reverse also holds true.

The fluorination of the $C_{8n}\text{AsF}_5$ materials, as a route to $C_{12n}\text{AsF}_6$ salts, led to a surprising discovery. For second and higher stage materials the fluorine consumption was consistently that required by the equation:

$$C_x\text{AsF}_5 + F_2 \rightarrow C_x\text{AsF}_6 \cdot F$$

The half mole of fluorine, over and above that required to form $\text{AsF}_6^-$, is not removed in a dynamic vacuum and the magnetic properties of $C_x\text{AsF}_6 \cdot F$ are not significantly different from those of $C_x\text{AsF}_6$. Thus odd species such as $F_2^-$ can be discounted. The extra fluorine can however be titrated by arsenic trifluoride.\textsuperscript{20,22} Thus a $C_{12n}\text{AsF}_6$ salt can be prepared by the route:

$$3C_{4x}\text{AsF}_6 \cdot F + \text{AsF}_3 \rightarrow 4C_{3x}\text{AsF}_6$$

but treatment with excess $\text{AsF}_3$ leads to the generation of a material indistinguishable from that prepared from graphite and $\text{AsF}_5$:

$$C_{2x}\text{AsF}_6 \cdot F + \text{AsF}_3 \rightarrow 2C_x\text{AsF}_5$$
The appropriate formulation for the fluorine rich materials is $\text{C}_{12n}^{2+} \text{AsF}_6^{-} \cdot \text{F}^-$. This requires that each of the vacant sites of the $\text{C}_{12n} \text{AsF}_6$ guest array, must contain $2\text{F}^-$, each at the poles of a hole in the $\text{AsF}_6^-$ array (which hole is large enough to accomodate $\text{AsF}_6^-$ itself). The puzzle is that fluorine should enter the occupied galleries of $\text{C}_{12n} \text{AsF}_6$ and not the unoccupied ones. This problem is of course related to the long standing one associated with the failure of fluorine gas to intercalate graphite.\(^{23}\)

It seems that the non-entry of fluorine into unoccupied galleries may simply be associated with the inability of the small $\text{F}^-$ ion to move forward into the gallery. This ion is comparable in diameter ($\sim 2.7\text{Å}$) to the dimensions of a carbon-atom hexagon of the graphite layers ($2.84\text{Å}$ across the hexagon). Thus $\text{F}^-$ located above such a hexagon of carbon atoms will concentrate positive charge at those atoms and will, as a consequence, lie in a deep potential well. On the other hand a $\text{F}^-$ ion entering an occupied gallery can be imagined as forming (fleetingly) a relatively large jelly-fish species such as $\text{AsF}_7^{2-}$, which can shed an $\text{F}^-$ ion on a side opposite to that of $\text{F}^-$ entry. Thus ready migration of $\text{F}^-$ into the body of the occupied gallery could readily occur.

Clearly materials such as $\text{C}_{8n} \text{AsF}_5$, $\text{C}_{12n} \text{AsF}_6$ and $\text{C}_{12n} \text{AsF}_6 \cdot \text{F}$ provide the possibility for electrochemical interconversion and preliminary experiments indicate that such experiments are highly reversible.\(^{24}\) A major
point of interest is the high oxidizing potential of $\text{C}_{24}\text{AsF}_{6}\cdot\text{F}$, which, although not a good conductor, is no worse than graphite. Such materials should be excellent for electrochemical fluorination. They themselves have marked resistance to oxidation. Because the carbon layers maintain the form of the material and serve as the source and sink for electrons, such materials can in principle be cycled indefinitely through redox cycles and are therefore of prime interest as a basis for energy storage systems.

CONCLUSION

Although powerful oxidizers such as transition metal hexafluorides, $\text{O}_2^{+}$ salts, and Lewis fluoroacids in combination with fluorine can be successfully applied to the electron oxidation of a wide variety of electron delocalized systems, it is in the oxidation of the mundane polymeric material graphite where the most surprising, intellectually satisfying, and potentially most important findings have been made. But there is a sense of just being at the beginning of an important enterprise.

ACKNOWLEDGEMENTS

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2. Richardson, T. J., Tanzella, F. L., and Bartlett, N., to be published.


1. Some properties of the third transition series hexafluorides and the formulations of their graphite salts at the intercalation limit.

2. Enthalpy changes for electron-oxidation by AsF$_5$ or PF$_5$. 
TABLE 1. Some properties of the third transition series hexafluorides and formulations of their graphite salts at the intercalation limit.

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<tr>
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<th>WF$_6$</th>
<th>ReF$_6$</th>
<th>OsF$_6$</th>
<th>IrF$_6$</th>
<th>PtF$_6$</th>
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<td>no</td>
<td>$C_8^+\text{OsF}_6^-$</td>
<td>$C_8^+\text{IrF}_6^-$</td>
<td>$C_2^+\text{PtF}_6^{2-}$</td>
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<tr>
<td>Intercalation</td>
<td>Intercalation</td>
<td></td>
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</table>

(c) Barberi, P. and Bartlett, N., unpublished results based on

$$\Delta H_f\{O_2\text{PtF}_6\text{ (cryst.) from } O_2(g) \text{ and PtF}_6(g)\} = -60 \text{ kcal mol}^{-1}.$$  
(d) Estimated values.
(e) Ref. 13. This is composition at intercalation limit.
Table 2. Enthalpy changes for electron-oxidation by gaseous AsF$_5$ or PF$_5$
(all values in kcal mole$^{-1}$)

\[
\begin{align*}
MF_5(g) + F_2 + e^- & \rightarrow MF_6(g) \quad \leq -158^{a,b} \quad \leq -170^a \\
(2MF_5(g) + F_2 + 2e^- & \rightarrow 2MF_6^- \quad \leq -316 \quad \leq -340) \\
MF_5(g) & \rightarrow MF_3(g) + F_2(g) \quad 152^c \quad 98^d \\
3MF_5(g) + 2e^- & \rightarrow 2MF_6(g) + MF_3(g) \quad \leq -164 \quad \leq -242 \\
\end{align*}
\]

Electron affinity \((3/2MF_5(g) + e^- \rightarrow MF_6(g) + MF_3(g)) \geq 82 \geq 121

FIGURES

1. A possible structural model for AsF$_6^{-}$ salts of polycyclic hydrocarbon cations.

2. Lattice parameters as a function of composition for $C_7(SO_3F)_x(HSO_3F)_{1-x}$.

3. Comparison of the structures of graphite and layer-form boron nitride.

4. A Born-Haber cycle for hexafluorometallate salts of graphite, $C_x^+MF_6^{-}$.

5. Models for the ordered packing of the guest species in (a) $C_8MF_6$ and (b) $C_{12}MF_6$.

6. X-ray absorption near the As-atom absorption edge involving $1s \rightarrow 4p$ type transitions for a variety of arsenic compounds.
Figure 2

Triangles indicate duplicate run of a given composition.
3.354 Å

Graphite

Figure 3

2.464 Å

Boron Nitride

3.330 Å

XBL 8010-6013
**MF₆⁻ in a Graphite Gallery**

- **carbon**
  - F F F
  - M
  - F F F

- **carbon**
  - 1.33 Å
  - 2 x M-F / √3 ≈ 2 Å
  - 1.33 Å

- C ≈ 8.0 Å

**Figure 4**

- Ionization work

- Expansion work

- Electron affinity

- $\Delta H < 0$ (ΔS < 0)

- Graphite + MF₆

- $\Delta G$ -ve, $\Delta H$ must be exothermic

- Lattice energy

- $n^+$

- $n^+$

- $MF_6^-$

- $MF_6^-$

- $MF_6^-$

- $MF_6^-$

XBL 818-11358
proposed $C_8MF_6$ structure

proposed $C_{12}MF_6$ structure

$C_8MF_6$ guest packing

ordered $C_{12}MF_6$ guest packing

Figure 5

XBL819-1791
Figure 6 XBL 798-10982
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