Lawrence Berkeley National Laboratory

Title
NOVEL GRAPHITE SALTS AND THEIR ELECTRICAL CONDUCTIVITIES

Permalink
https://escholarship.org/uc/item/0jc6c39q

Author
Bartlett, N.

Publication Date
2012-01-10
NOVEL GRAPHITE SALTS AND THEIR ELECTRICAL CONDUCTIVITIES

N. Bartlett, E. M. McCarron, B. W. McQuillan and T. E. Thompson

February 1980
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
NOVEL GRAPHITE SALTS AND THEIR ELECTRICAL CONDUCTIVITIES

N. Bartlett, E. M. McCarron and B. W. McQuillan
Department of Chemistry, University of California and the
Materials and Molecular Research Division, Lawrence Berkeley
Laboratory, Berkeley, California 94720 (U.S.A.)

T. E. Thompson
SRI International, Menlo Park, California 94025 (U.S.A.)

ABSTRACT

A set of novel first stage graphite salts of general formula \( \text{C}_8^+ \text{MF}_6^- \) has been prepared (M = Os, Ir, As). Single crystal
X-ray diffraction studies indicate that these salts are hexagona-
with \( a \approx 4.9 \) and \( c \approx 8.1 \ \text{Å} \). The unit cell volume indicates that
the anions are closely packed in the galleries. Platinum hexa-
fluoride, which is the most powerful oxidizer of the third
transition series, forms a first stage compound, which analy-
tical, structural and magnetic studies establish as \( \text{C}_{12}^2^+ \text{PtF}_6^2^- \).
In this salt the anions are not close packed, but the electron
withdrawal from the graphite planes is greater than for the
\( \text{C}_8^+ \text{MF}_6^- \) series. The variation in the electrical conductivity
(in the ab plane), as a function of composition, has been investi-
gated with the OsF\(_6\), IrF\(_6\), PtF\(_6\) and AsF\(_5\) intercalates. For
OsF\(_6\) and IrF\(_6\), the conductivity, per plane of graphite, is
found to be a maximum at approximately \( \text{C}_{24} \text{MF}_6 \) (second stage);
the conductivity being an order of magnitude greater than that
of the parent HOPG. Intercalation beyond \( \text{C}_{24} \text{MF}_6 \) leads to a
marked decrease in conductivity. \( \text{CsMF}_6 \) is comparable in con-
ductivity to the parent graphite. This behavior contrasts with
the graphite/AsF\(_5\) system in which a steady increase in con-
ductivity per graphite plane, with increasing AsF\(_5\) content, is
observed. For the PtF\(_6\) system, the second as well as the first
stage materials are poorly conducting.
Introduction

In earlier studies we prepared\textsuperscript{1} the salt $C_8^+SO_3F^-$ from pyrolytic graphite and the first salt of layer boron nitride, by exploiting the powerfully oxidizing fluorosulfate radical, which derives from peroxydisulfuryldifluoride, $S_2O_6F_2$.\textsuperscript{2,3} Previous work\textsuperscript{4} in these laboratories had established that iridium hexafluoride will, oxidatively, displace $SO_3F$ from fluorosulfates. It was also evident that $O_2^+$ salts would be superior oxidizers to $SO_3F$ radical. Reports on the oxidation of graphite by $O_2^+AsF_6^-$ and a comparison with the $AsF_5$ intercalate have been given previously.\textsuperscript{5,6} In this report we will emphasize the oxidation of graphite by the third-transition-series metal hexafluorides. The aim has been to establish the nature of the guest species in the graphite galleries, the degree of oxidation of the graphite, and the dependence of the electrical conductivity upon the stage and the extent of electron withdrawal from the graphite sheets.

The third-transition-series metal hexafluorides are excellent for this purpose in that they constitute a set, well graded in oxidizing power,\textsuperscript{7} yet almost isodimensional; moreover, as gases they may be readily transported and applied and their activity controlled, to some extent, by pressure regulation.

Experimental

Materials: Graphite used in the conductivity studies was highly oriented pyrolytic graphite (HOPG) with small (< 1°) c-axis spread. Single crystal studies were carried out using
natural crystals obtained from a calcite marble of the Santa Lucia formation by dissolution of the marble in concentrated hydrochloric acid. The crystals were washed with water, dried and selected by X-ray precession photography. Rhenium, osmium, iridium, and platinum hexafluorides were prepared and handled as previously described. Tungsten hexafluoride was used as obtained from B and A division of Allied Chemical. Arsenic pentafluoride, supplied by Ozark-Mahoning, was purified by a brief pumping at -78°C and was shown by its infrared spectrum to contain no impurities. Fluorine was used as obtained from Matheson Gas Co. Inc.

Sample Preparation: Blocks of HOPG approximately 5 x 5 (ab) x 1 mm were cleaved and abraded from larger sheets. Such pieces were used in the conductivity studies. Powdered graphite was obtained from the HOPG by sawing with several hacksaw blades clamped together. Except for the work with PtF₆, it was usual for the intercalation to be carried out in a quartz tube with a Monel Whitey valve provided with Swagelock compression fittings with teflon ferrules. Weighing of this assembly before and after the intercalation gave a composition, but in the first experiments in each series the gravimetric composition was always checked by elemental analysis. In the PtF₆ experiments, weighed powdered graphite was exposed overnight to PtF₆, or to O₂⁺PtF₆⁻, in a Monel can provided with a teflon-gasketed lid. Since all of the intercalates were unstable in moist air they were all handled in the dry atmosphere of a vacuum Atmospheres Corporation Drilab.
Maximum Intercalation: In order to determine the limiting composition, powdered graphite was exposed to an excess of the hexafluoride. The hexafluoride was transferred under vacuum to the well dried material and was left in contact with the graphite overnight at ~25°. Excess hexafluoride was removed under vacuum at ~25° to constant weight. Analysis: The samples were also submitted to conventional carbon and hydrogen analysis, but since it was found, by infrared spectroscopy, that this procedure resulted in the formation of small quantities of carbon tetrafluoride and other fluorocarbons, it was customary to carry out a "nitrogen" analysis, which provided a measure of the CF₄ formation. On the basis of the good approximation, that the "nitrogen" was CF₄, the carbon analyses were corrected. The results are given in Table 1. WF₆ or ReF₆ did not spontaneously intercalate graphite but mixtures of each hexafluoride with fluorine were observed to react.

Magnetic Susceptibility Measurements: Powdered samples, encapsulated in plug-capped Kel-F containers were studied using a vibrating sample magnetometer (Princeton Applied Research Corpn.). Measurements were made in the range 4.2 - 100°K and Hg(Co(SCN)₄)₂ was used as a standard. The results for C₈OsF₆ and C₈IrF₆, are compared with data for SF₃⁺OsF₆⁻ and H₃O⁺IrF₆⁻ (ref. 11) in Figures 1 and 2. The platinum material, C₁₂PtF₆ was essentially non-magnetic, the diamagnetic term approximately cancelling a Pauli-type paramagnetism.

Single-Crystal Precession Photograph Data for C₈OsF₆: Zero-layer precession photographs of graphite single crystals
(< 1 mm in any dimension) obtained from Santa Lucia marble, established the graphite to be hexagonal with \( a = 2.46(1) \) Å, \( c = 6.70(2) \) Å. Such a crystal in a quartz 'wool' suspension within a thin-walled quartz capillary (0.5 mm diam.) was intercalated with OsF\(_6\). This was done by attaching the capillary to a Teflon FEP tube connected to the vacuum system and OsF\(_6\) supply. The crystal was dried under vacuum prior to exposure to the OsF\(_6\) vapor, which had been put on NaF to remove hydrogen fluoride. The crystal was maintained in the vapor (at 250-300 torr) for 3-6 hours. No evidence of any decomposition of OsF\(_6\) (to OsF\(_5\)) was seen. Zero layer precession photographs indicated a first stage product of hexagonal symmetry with \( a = 4.92(2) \) Å and \( c = 8.10(3) \) Å.

**Electrical Conductivity Measurements:** Measurement of basal plane electrical conductivities was made by the contactless radio frequency inductive technique recently described by Zeller, Denenstein and Foley,\(^{12}\) and illustrated in Figure 3. For this purpose HOPG was cut into pieces each roughly square, approximately of 5 mm edge and 0.5 mm thickness (along the \( c \) axis). The graphite was compared with a calibrated copper standard of nearly the same size. The induced eddy current was sensed in a secondary circuit and the conductivity was derived from the empirically evaluated relationship \( \Delta V = K \text{(area)}^2 t \cdot \sigma \), where \( \Delta V \) represents a voltage change, \( t \) the thickness of the sample, \( \sigma \) the specific conductivity, \( \text{area} \) the \( ab \) plane area, and \( K \) the proportionality constant. With the arrangement represented in Figure 3 it was possible to monitor the conductivity of a sample
in the course of intercalation. It was also possible, by
detaching and weighing the tube (complete with valve) contain-
ing the sample, to check the composition gravimetrically.
Moreover, a travelling microscope (with the sample in place)
or a micrometer (with the sample in the Drilab) were used to
determine the thickness of the sample. Occasionally a sample
was subjected to an X-ray diffraction scan to determine which
stage or stages were present.

The vacuum dried graphite (HOPG pieces), in its quartz
container was exposed to either OsF$_6$ or IrF$_6$ vapor (at 15 and
11 torr respectively) at ~25°. In each case, the conductivity
increased rapidly with MF$_6$ uptake as represented in Figure 4
and attained a maximum value somewhat above the MF$_6$ content
appropriate for a second stage material (i.e. C$_{24}$MF$_6$). The
ratio of the thickness of the sample to that of the original
graphite, and the gravimetry, are consistent with a mixed phase
which is ~25% first and 75% of the second stage at this point
of maximum conductivity. The occasional X-ray diffraction evi-
dence also supports this. At this position of maximum conduc-
tivity there was a marked slowing in the rate of intercalation
of MF$_6$ and an increase in pressure (to > 200 torr) of the inter-
calant was required to bring about renewal of MF$_6$ uptake. This
renewed MF$_6$ uptake appears to be coincident with the development
of a first stage material. There was detectable exothermicity,
ocasionally the sample, which had remained intact to this point,
cleaved. The most dramatic effect, however, was the decrease
in conductivity, which became progressively lower, with MF$_6$.
uptake, beyond this point. It was also observed that whereas a steady value for the conductivity was quickly obtained (usually within one minute or so) at all compositions up to \( \text{C}_{20}\text{MF}_6 \), for \( \text{MF}_6 \) incorporation richer than \( \text{C}_{20}\text{MF}_6 \), (and in association with the catastrophic conductivity decrease) the conductivity value became markedly time dependent. Data are given in Table 2. Thus for a composition \( \text{C}_{13}\text{MF}_6 \) the conductivity would continue to decrease significantly over a period of several hours. No such conductivity maximum was noted for the intercalation of \( \text{AsF}_5 \). The conductivity per plane of graphite was observed to increase smoothly up to the first-stage limiting composition of \( \sim \text{C}_8\text{AsF}_5 \). Conversion of \( \text{C}_8\text{AsF}_5 \) to \( \text{C}_8\text{AsF}_6 \) by treatment of the former with fluorine gas at \( \sim 25^\circ \) (2 atmospheres pressure) until the sample no longer consumed it, led to a marked drop in conductivity as shown by the data given in Table 2. On the other hand, a sample of HOPG of composition \( \text{C}_{16}\text{AsF}_6 \), prepared by treating the graphite with a \( \text{AsF}_5/\text{F}_2 \) mixture, exhibited a graphite plane conductivity close to the maximum value observed in the \( \text{OsF}_6 \) and \( \text{IrF}_6 \) systems.

Electrical Conductivity Measurements, HOPG/PtF\(_6\): The conductivity work for Graphite/PtF\(_6\) was hampered by two factors. First, the highly reactive nature of PtF\(_6\) complicated the gravimetric work and although X-ray data provided a convenient check on the stage produced, it was not possible to determine the extent of the gallery occupancy. Secondly, the reaction of PtF\(_6\) with HOPG is extremely slow. This is probably a consequence of the double-charged PtF\(_6\)\(^{2-}\) anion having a low
mobility relative to singly charged species \((\text{OsF}_6^-, \text{IrF}_6^-)\).

An HOPG/PtF\(_6\) sample with the composition \(\text{C}_{12}\text{PtF}_6\) has not yet been prepared, this limit having been achieved with graphite powder. Yet even in second stage \((\text{C}_{24}\text{PtF}_6)\) material, low \((ab\ plane)\) conductivities have been observed. This is in contrast with the \(\text{OsF}_6\) and \(\text{IrF}_6\) results.

**X-ray Diffraction Studies on HOPG Intercalation Compounds:**

Diffraction tracings of the HOPG intercalation compounds used in the conductivity measurements were obtained on a Phillips - Norelco powder diffractometer equipped with a graphite monochrometer. Because of moisture sensitivity, the samples were loaded into a sample holder in the Drilab, and covered with a thin plastic wrap, which was then sealed with an o-ring compression fitting. Samples were placed in the holder each with its c-axis perpendicular to the powder plane. Observable reflections were limited to \(00l\). Representative results are listed in Table 3.

**Results and Discussion**

The ease of incorporation of the third-transition-series hexafluorides into graphite and the stability of the resultant salt, appears to depend simply upon the electron affinity of the hexafluoride as shown in Table 4. Thus except in the presence of fluorine gas (when \(\text{MF}_7^-\) or \(\text{MF}_8^{2-}\) ions are probably formed) neither \(\text{WF}_6\) nor \(\text{ReF}_6\) is incorporated massively into graphite. The more powerful oxidizers \(\text{OsF}_6\) and \(\text{IrF}_6\) each intercalate easily up to a limiting composition \(\text{C}_8\text{MF}_6\). The most
powerful oxidizer, PtF$_6$, is readily intercalated by powdered graphite but to a limiting composition of C$_{12}$PtF$_6$. This anomaly is explained by the magnetic data.

These data for C$_8$OsF$_6$ and C$_8$IrF$_6$, which are presented in Figures 1 and 2, show that in each case the dominant guest species has to be the MF$_6^-$ ion. For each salt the appropriate formula is C$_8^+$MF$_6^-$. Moreover, since the volume of the hexagonal C$_8$MF$_6$ unit cell, which is 170.9(1) Å, is essentially the sum of the volume of eight carbon atoms, as in hexagonal graphite$^{13}$ (= 70.00 Å$^3$) and the volume of a hexafluoride$^7$ (= ∼ 105 Å$^3$), it is evident that the MF$_6^-$ species must be close packed in the graphite galleries. It seems therefore that the degree of oxidation of the graphite is not the composition-limiting factor for C$_8$OsF$_6$ and C$_8$IrF$_6$, but it does appear to be important in the PtF$_6$ case. The diamagnetism of C$_{12}$PtF$_6$ confirms that the guest is PtF$_6^{2-}$. This means that the graphite is more highly oxidized in C$_{12}$PtF$_6$ than in the C$_8$IrF$_6$ or C$_8$OsF$_6$ cases. It is probable that the incomplete filling of the galleries in C$_{12}$PtF$_6$ is a consequence of the much greater energy needed to yield the average carbon atom charge of +1/6 relative to +1/8. There is a possibility that the true intercalation limit for PtF$_6$ has not been reached in this work. It is difficult to intercalate HOPG pieces (5 × 5 × 0.5 mm) to produce uniform first stage samples. Evidently the intercalated PtF$_6^{2-}$ is not very mobile with the consequence that each HOPG sample is invariably concave at the center. The finely powdered samples do intercalate quickly to an impressively constant composition
close to $\text{C}_{12}\text{PtF}_6$, as the findings given in Table 2 indicate.

Single-crystal precession photographs of $\text{C}_8\text{OsF}_6$ show that the salt is primitive hexagonal, the $a_0$ value of 4.92(2) Å being twice that of hexagonal graphite. The $c_0$ value of 8.10(3) Å is consistent with the $\text{OsF}_6^-$ being oriented with a threefold axis parallel to $c_0$. With this orientation the effective height of $\text{OsF}_6^-$ is $\sim$ 4.7 Å. Since the effective thickness of a graphite sheet is 3.35 Å the anticipated $c_0$ value for the primitive unit cell is the sum of these values i.e. $\sim$ 8 Å. This suggests the unit cell in Figure 5. However, over 1-2 days, at $\sim$ 20°C, the diffraction became less sharp, the $hk$-indexed spots eventually spreading to rings. More $\text{OsF}_6$ failed to restore long-range order. Powder photographs of $\text{C}_8\text{IrF}_6$, $\text{OOL}$ data for HOPG $\text{C}_8\text{IrF}_6$, and single-crystal precession data for $\text{C}_8\text{AsF}_6$ show that the same unit cell is appropriate for all.

Although HOPG samples of the first stage $\text{PtF}_6^2-$ salt have not been obtained, powder data for $\text{C}_{12}\text{PtF}_6$ and 2nd and 3rd stage HOPG/$\text{PtF}_6$ $\text{OOL}$ reflections, indicate that the $\text{PtF}_6^2-$-occupied gallery height is $\sim$ 7.54 Å. Evidently the greater Coulomb attraction between graphite sheet and guest, consequent upon the higher positive charge of the former and the double negative charge of the latter, is responsible for the appreciable contraction when compared with $\text{C}_8\text{IrF}_6$: where $c_0 = 8.06$ Å. Indeed other observations also indicate that the gallery height is somewhat sensitive to the charging. The results given in Table 3, for first stage $\text{C}_x\text{AsF}_6^-$ salts, show that as the concentration of $\text{AsF}_6^-$ in the graphite galleries increases (as $x$ decreases) the $c_0$ value (obtained from $\text{OOL}$ reflections from
HOPG samples) decreases. It is also evident, from the data in Table 3, that the graphite/AsF₅ materials show a larger gallery spacing than the AsF₆⁻ salts of comparable arsenic content. If the AsF₅ incorporation into graphite is followed by complete conversion into AsF₆⁻ and AsF₃ according to the equation:

\[
3 \text{AsF}_5 + 2 \text{e}^- \rightarrow 2 \text{AsF}_6^- + \text{AsF}_3
\]  

(1)

the charges both on the guests and the graphite sheets can at most be two thirds the charges in the related AsF₆⁻ material. The data are not very precise, therefore it is necessary to be somewhat cautious, but the similarity of the gallery height in C₈.₄AsF₅ to that in C₁₃.₁AsF₆⁷ is consistent with extensive conversion according to equation (1).

The ab plane electrical conductivity data are presented in Table 2. The conductivity per plane of graphite relative to the conductivity of a plane of the parent graphite, as a function of iridium hexafluoride uptake, is shown in Figure 4 (the behavior for OsF₆ intercalation is essentially the same). With the pressures of OsF₆ and IrF₆ used in this work, all HOPG tablets quickly, and with proper MF₆ uptake, assumed the thickness appropriate for a second stage (i.e. t/t₀ ≈ 1.7). The uptake of MF₆ was smooth and rapid up to a composition of approximately C₂₄MF₆ but slowed significantly after the second stage composition (C₂₄MF₆) was attained. Up to this point (see Figure 4) the conductivity per plane increased. Note from Table 2 that the conductivity is approximately the same for the IrF₆ and OsF₆ systems close to C₂₀MF₆. To carry the intercalation towards
the first stage it was necessary to increase the pressure of the intercalant. This had to be done with caution since the change to a first stage material, once initiated, proved to be a highly exothermic process and extensive cleavage could then occur. For both the OsF₆ and the IrF₆ systems the conductivity dropped catastrophically with MF₆ uptake beyond C₂₀MF₆. Indeed, for MF₆⁻ salts, formation of first-stage material appears to be associated with decreased conductivity. With PtF₆²⁻ salts however, even second stage C₂₄²⁺PtF₆²⁻ is a poor conductor. Therefore, poor conductivity is associated with high positive charge in the graphite sheets. No doubt the cooperative effect of two anions (one on each side of the graphite sheet) or the double charge of an MF₆²⁻ ion is more likely to localize high positive charge at a carbon atom than a single MF₆⁻. Positively charged carbon atoms will tend to be boron-atom like and will make more bonds than the neutral atoms and this probably leads to distortion from the regular trigonal graphite net. Thus the structure for C₈MF₆, shown in Figure 5 may not be the stable one. Indeed this may account for the loss of long-range order observed in single crystals of C₈MF₆. A structural change, involving distortion of the graphite sheets and slow relocation of the MF₆⁻ species, would also account for the observation that the conductivity of first-stage materials, at constant composition, decreased steadily over a period of several hours. This fits in with the time scale of the apparent loss of long-range order in the single-crystal diffraction studies already alluded to.

The comparison of the graphite/AsF₅ with the graphite/AsF₆⁻ system is particularly interesting. We have found that it is possible to convert incompletely-intercalated first-stage
graphite/AsF₅ to its AsF₆⁻ counterpart, by treating the former with fluorine gas. In this way a sample of composition C₁₂.₇AsF₅ was converted to C₁₂.₇AsF₆. The excellent conductivity of the former was replaced by a conductivity more like that of the first stage OsF₆⁻ and IrF₆⁻ salts and not very different from that of graphite itself. This could mean that the conversion represented by equation (1) is not extensive and that the continuous increase in conductivity per plane of graphite on intercalation, up to and including the first stage, is simply a consequence of the concentration of charged guests never being high enough to produce large charge localization effects. In the face of other evidence, however, another explanation may apply. The coexistence of AsF₃ with AsF₆⁻ (and even some AsF₅) within the galleries is more likely to result in a less ordered and less periodic charge distribution than in the MF₆⁻ cases. Thus it may be that the guest species in graphite/AsF₅ are never in commensurate register with the graphite lattice. Indeed it may even be that the MF₆⁻ anions in second-stage C₂₄MF₆ are not commensurate with the graphite sheet either.

Reliable structural information is urgently needed for C₈MF₆, C₂₄MF₆ and C₈AsF₅ to provide a basis for response to the questions raised by the conductivity studies.
Acknowledgments

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract No. W-7405-Eng-48. We also thank Dr. Arthur Moore of Parma Technical Center, Union Carbide Corp., for his generosity in supplying some of the HOPG graphite used in this work. We also gratefully acknowledge partial financial support from a grant from the Exxon Education Foundation for institutional support.
References


4. C. Salentine and N. Bartlett, unpublished work.


9. N. Bartlett and E. M. McCarron, to be published.


14. Since in OsF$_6^-$ the M-F internuclear distance is approximately 1.82 Å [M. A. Hepworth, K. H. Jack and G. J. Westland, J. Inorg. Nucl. Chem., 2, 79 (1956).], the effective packing length (along c) should be \(2 \times \frac{1.82}{\sqrt{3}} + \{2 \times \text{van der Waals radii of the F ligands (which is taken to be } \sim 1.3 \text{ Å)}\).
<table>
<thead>
<tr>
<th>Hexafluoride</th>
<th>Form of Graphite</th>
<th>Gravimetry</th>
<th>Analyses</th>
<th>Stage, $c_0$ (Å) ±0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>WF$_6$</td>
<td>does not intercalate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReF$_6$</td>
<td>does not intercalate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsF$_6$</td>
<td>powder</td>
<td>[(a) C$_9$OsF$_6$]</td>
<td>(a) C$_{8.13}$OsF$_6$</td>
<td>1st, 8.10</td>
</tr>
<tr>
<td></td>
<td>HOPG (5 × 5 × 1 mm)</td>
<td>[(b) C$_{7.72}$OsF$_6$]</td>
<td>(b) C$_{7.81}$OsF$_6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(a) C$_9.9$OsF$_6$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(b) C$_{11.6}$OsF$_6$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrF$_6$</td>
<td>powder</td>
<td>[(a) C$_8.01$IrF$_6$]</td>
<td>(a) C$_{7.98}$IrF$_6$</td>
<td>1st, 8.05</td>
</tr>
<tr>
<td></td>
<td>HOPG (5 × 5 × 1 mm)</td>
<td>[(b) C$_{8.01}$IrF$_6$]</td>
<td>(b) C$_{8.05}$IrF$_6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(a) C$_{8.3}$IrF$_6$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(b) C$_{10.8}$IrF$_6$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(c) C$_{10.6}$IrF$_6$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtF$_6$</td>
<td>powder</td>
<td>[(a) ----]</td>
<td>(a) C$_{12.4}$PtF$_6$</td>
<td>1st, 7.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(b) C$_{12.0}$PtF$_6$]</td>
<td>(b) C$_{12.0}$PtF$_6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[(c) C$_{11.0}$PtF$_6$]</td>
<td>(c) C$_{12.4}$PtF$_6$</td>
<td></td>
</tr>
</tbody>
</table>

* experiment terminated prior to achieving a limiting composition
Table 2. Composition and Electrical Conductivity Data for HOPG/MF$_6$ and HOPG/AsF$_5$/F$_2$ Intercalates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (Gravimetric)</th>
<th>$\frac{\sigma}{\sigma_G}$</th>
<th>$\frac{t}{t_0}$</th>
<th>$\frac{k}{k_G}$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_x$OsF$_6$</td>
<td>8.0</td>
<td>----</td>
<td>13.7</td>
<td>conductivity maximum</td>
</tr>
<tr>
<td></td>
<td>C$_{9.9}$OsF$_6$</td>
<td>1.0</td>
<td>2.48</td>
<td>2.4</td>
<td>deep blue</td>
</tr>
<tr>
<td>2</td>
<td>C$_{19.3}$OsF$_6$</td>
<td>8.2</td>
<td>2.00</td>
<td>14.0</td>
<td>deep blue</td>
</tr>
<tr>
<td></td>
<td>C$_{11.6}$OsF$_6$</td>
<td>1.3</td>
<td>2.45</td>
<td>3.1*</td>
<td>deep blue</td>
</tr>
<tr>
<td>3</td>
<td>C$_x$IrF$_6$</td>
<td>6.2</td>
<td>----</td>
<td>10.6</td>
<td>conductivity maximum</td>
</tr>
<tr>
<td></td>
<td>C$_{8.0}$IrF$_6$</td>
<td>1.2</td>
<td>2.41</td>
<td>2.9</td>
<td>deep blue</td>
</tr>
<tr>
<td>4</td>
<td>C$_{21.0}$IrF$_6$</td>
<td>8.0</td>
<td>1.81</td>
<td>13.7</td>
<td>deep blue</td>
</tr>
<tr>
<td></td>
<td>C$_{8.1}$IrF$_6$</td>
<td>0.6</td>
<td>2.68</td>
<td>1.5*</td>
<td>deep blue</td>
</tr>
<tr>
<td>5</td>
<td>C$_{8.1}$IrF$_6$</td>
<td>0.4</td>
<td>2.45</td>
<td>1.0*</td>
<td>deep blue</td>
</tr>
<tr>
<td>6</td>
<td>C$_{10.6}$IrF$_6$</td>
<td>0.6</td>
<td>2.41</td>
<td>1.4*</td>
<td>deep blue</td>
</tr>
<tr>
<td>7</td>
<td>C$_{30}$PtF$_6$</td>
<td>1.0</td>
<td>1.68</td>
<td>2.4</td>
<td>green-blue</td>
</tr>
<tr>
<td>8</td>
<td>C$_{24}$PtF$_6$</td>
<td>0.8</td>
<td>2.00</td>
<td>1.3</td>
<td>green-blue</td>
</tr>
<tr>
<td>9</td>
<td>C$_{16.0}$AsF$_5$</td>
<td>11.7</td>
<td>1.96</td>
<td>20.0</td>
<td>steel blue</td>
</tr>
<tr>
<td></td>
<td>C$_{12.7}$AsF$_5$</td>
<td>11.3</td>
<td>2.41</td>
<td>28.2</td>
<td>steel blue</td>
</tr>
<tr>
<td></td>
<td>C$_{12.7}$AsF$_6$</td>
<td>0.5</td>
<td>2.41</td>
<td>1.2*</td>
<td>fluorinated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>deep blue</td>
</tr>
<tr>
<td>10</td>
<td>C$_{20}$AsF$_5$</td>
<td>9.7</td>
<td>1.85</td>
<td>16.6</td>
<td>addition of</td>
</tr>
</tbody>
</table>

* denotes time dependent values. Samples 5 + 6 are representative of $t = \infty$ values for conductivity (~3 weeks). Multiple entry samples are approx. time = 12 hrs.

$\sigma_G = (26 \pm 3) \times 10^3 \Omega^{-1} \text{cm}^{-1}$.

$\frac{t}{t_0}$ represents the thickness of sample and $t_0$ the thickness of the HOPG piece from which it was derived; 1st stage $t/t_0 \approx 2.4$, and 2nd stage $t/t_0 \approx 1.7$.

** Specific conductivity normalized per plane of graphite, simply $(\frac{\sigma}{\sigma_G} \times \frac{t}{t_0}) = \frac{k}{k_G} = \frac{\Delta V_{\text{sample}}}{\Delta V_{\text{graphite}}}$.
Table 3. X-ray Diffraction Data for Some HOPG Intercalation Compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>O02 Features</th>
<th>c (Å) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8.1OsF6</td>
<td>1st stage</td>
<td>8.10</td>
</tr>
<tr>
<td>C8.1IrF6</td>
<td>1st stage</td>
<td>8.06</td>
</tr>
<tr>
<td>C8.30PtF6</td>
<td>2nd stage</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3rd stage</td>
<td>10.88†</td>
</tr>
<tr>
<td>C8.1AsF6</td>
<td>1st stage</td>
<td>7.86</td>
</tr>
<tr>
<td>C9.7AsF6</td>
<td>1st stage</td>
<td>8.00</td>
</tr>
<tr>
<td>C13.1AsF6</td>
<td>1st stage</td>
<td>8.04</td>
</tr>
<tr>
<td>C8.4AsF5</td>
<td>1st stage</td>
<td>8.02</td>
</tr>
<tr>
<td>C13.1AsF5</td>
<td>1st stage</td>
<td>8.00</td>
</tr>
<tr>
<td>C16.5AsF5</td>
<td>2nd stage</td>
<td>11.34</td>
</tr>
</tbody>
</table>

† Implies a 1st stage spacing of ~7.54 Å.

* The true unit cell c may, in some cases be a simple multiple of this value, which derives from the simplest indexing of O02 data.
Table 4. Third Transition Series Hexafluorides: The Non-Bonding Electron Configurations, Molecular Volumes and Electron Affinities

<table>
<thead>
<tr>
<th></th>
<th>WF₆</th>
<th>ReF₆</th>
<th>OsF₆</th>
<th>IrF₆</th>
<th>PtF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>dt₂g^n</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Molecular volume (Å³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>orthorhombic phase (a)</td>
<td>108.5</td>
<td>106.5</td>
<td>105.7</td>
<td>105.4</td>
<td>104.6</td>
</tr>
<tr>
<td>E (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>P. Barberi and N. Bartlett, unpublished results based on ΔHᶠ[O₂PtF₆ (cryst.) from O₂ (g) and PtF₆ (g)] = -60 kcal mol⁻¹.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>Estimated values.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure Captions

1. Magnetic susceptibility -- temperature relationships for C$_8^{+}$OsF$_6^{-}$ and SF$_3^{+}$OsF$_6^{-}$.

2. Magnetic susceptibility -- temperature relationships for C$_8^{+}$IrF$_6^{-}$ and H$_3^{0+}$IrF$_6^{-}$.

3. Apparatus for conductivity measurements on HOPG and HOPG-intercalates.

4. Response of conductivity of HOPG-IrF$_6$ intercalates as a function of IrF$_6$ uptake.

5. Projection of the C$_9$MF$_6$ (M = Os, Ir, As) unit cell in relation to the graphite lattice.
Figure 1. Magnetic susceptibility -- temperature relationships for $\text{C}_8^+\text{OsF}_6^-$ and $\text{SF}_3^+\text{OsF}_6^-$. 
Figure 2. Magnetic susceptibility -- temperature relationships for $\text{Ca}^+\text{IrF}_6^-$ and $\text{H}_3\text{O}^+\text{IrF}_6^-$. 
Figure 3. Apparatus for conductivity measurements on HOPG and HOPG-intercalates.
Figure 4. Response of conductivity of HOPG-IrF$_6$ intercalates as a function of IrF$_6$ uptake.
Effect of IrF₆ intercalation on the conductivity of highly oriented pyrolytic graphite
Figure 5. Projection of the C$_8$M$\text{F}_6$ ($M = \text{Os, Ir, As}$) unit cell in relation to the graphite lattice.