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NOVEL GRAPHITE SALTS AND THEIR ELECTRICAL CONDUCTIVITIES

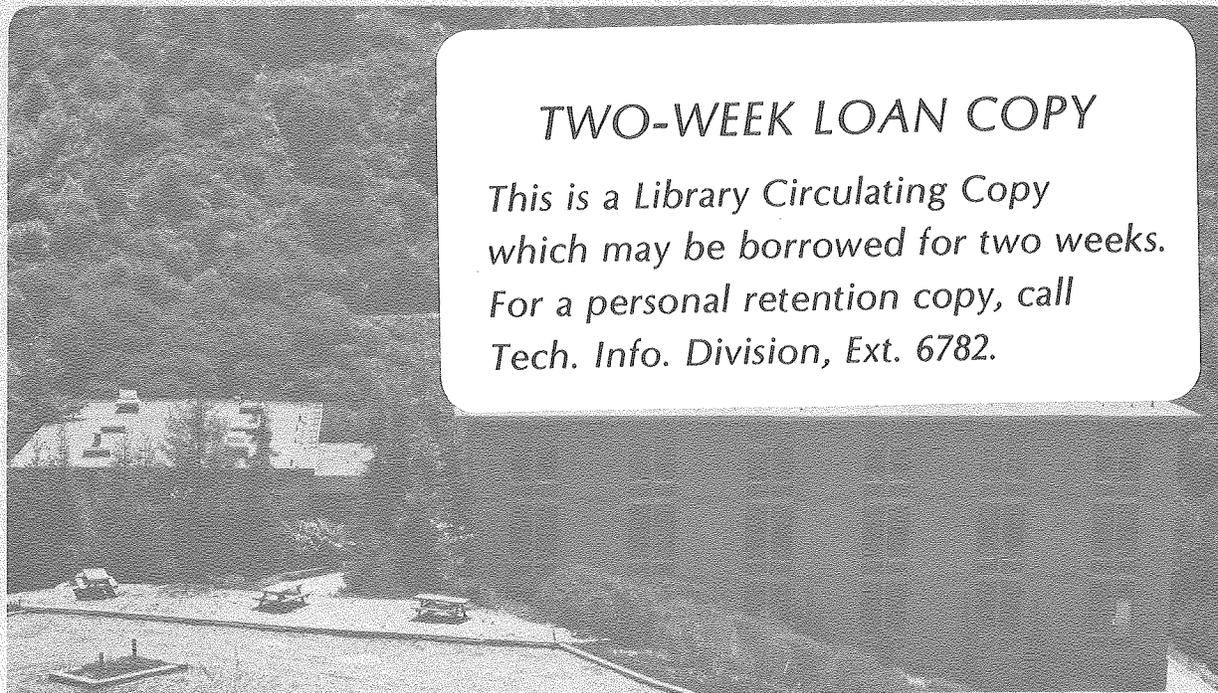
N. Bartlett, E. M. McCarron, B. W. McQuillan
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NOVEL GRAPHITE SALTS AND THEIR ELECTRICAL CONDUCTIVITIES

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ABSTRACT

A set of novel first stage graphite salts of general formula $C_8^+MF_6^-$ has been prepared ($M = Os, Ir, As$). Single crystal X-ray diffraction studies indicate that these salts are hexagonal with $a \approx 4.9$ and $c \approx 8.1 \text{ \AA}$. The unit cell volume indicates that the anions are closely packed in the galleries. Platinum hexafluoride, which is the most powerful oxidizer of the third transition series, forms a first stage compound, which analytical, structural and magnetic studies establish as $C_{12}^{2+}PtF_6^{2-}$. In this salt the anions are not close packed, but the electron withdrawal from the graphite planes is greater than for the $C_8^+MF_6^-$ series. The variation in the electrical conductivity (in the ab plane), as a function of composition, has been investigated 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 $C_{24}MF_6$ (second stage); the conductivity being an order of magnitude greater than that of the parent HOPG. Intercalation beyond $C_{24}MF_6$ leads to a marked decrease in conductivity. C_8MF_6 is comparable in conductivity to the parent graphite. This behavior contrasts with the graphite/ AsF_5 system in which a steady increase in conductivity 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 prepared¹ 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, $S_2O_6F_2$.^{2,3} Previous work⁴ 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.^{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,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 ($< 1^\circ$) 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.⁸ 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 5×5 (ab) $\times 1$ mm were cleaved and abraided 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 PtF_6 , 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 PtF_6 experiments, weighed powdered graphite was exposed overnight to PtF_6 , or to $\text{O}_2^+\text{PtF}_6^-$, 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 $\sim 25^\circ$. Excess hexafluoride was removed under vacuum at $\sim 25^\circ$ 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 CF_4 formation. On the basis of the good approximation, that the "nitrogen" was CF_4 , the carbon analyses were corrected. The results are given in Table 1. WF_6 or ReF_6 did not spontaneously intercalate graphite but mixtures of each hexafluoride with fluorine were observed to react.⁹

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 $\text{Hg}(\text{Co}(\text{SCN})_4)_2$ was used as a standard.¹⁰ The results for C_8OsF_6 and C_8IrF_6 , are compared with data for $\text{SF}_3^+\text{OsF}_6^-$ and $\text{H}_3\text{O}^+\text{IrF}_6^-$ (ref. 11) in Figures 1 and 2. The platinum material, $\text{C}_{12}\text{PtF}_6$ was essentially non-magnetic, the diamagnetic term approximately cancelling a Pauli-type paramagnetism.

Single-Crystal Precession Photograph Data for C_8OsF_6 :

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 $a = 2.46(1)$, $c = 6.70(2)$ 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 $a = 4.92(2)$ 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 $\Delta V = K (\text{area})^2 \underline{t} \cdot \underline{\sigma}$, where ΔV represents a voltage change, \underline{t} the thickness of the sample, $\underline{\sigma}$ the specific conductivity, 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) containing 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 $\sim 25^\circ$. 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 $\sim 25\%$ first and 75% of the second stage at this point of maximum conductivity. The occasional X-ray diffraction evidence also supports this. At this position of maximum conductivity there was a marked slowing in the rate of intercalation of MF_6 and an increase in pressure (to > 200 torr) of the intercalant 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, occasionally 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 $C_{20}MF_6$, for MF_6 incorporation richer than $C_{20}MF_6$, (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 $C_{13}MF_6$ the conductivity would continue to decrease significantly over a period of several hours. No such conductivity maximum was noted for the intercalation of AsF_5 . The conductivity per plane of graphite was observed to increase smoothly up to the first-stage limiting composition of $\sim C_8AsF_5$. Conversion of C_8AsF_5 to C_8AsF_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 $C_{16}AsF_6$, prepared by treating the graphite with a AsF_5/F_2 mixture, exhibited a graphite plane conductivity close to the maximum value observed in the OsF_6 and 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 (OsF_6^- , 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 OsF_6 and 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 monochromator. 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 MF_7^- or MF_8^{2-} ions are probably formed) neither WF_6 nor ReF_6 is incorporated massively into graphite. The more powerful oxidizers OsF_6 and IrF_6 each intercalate easily up to a limiting composition C_8MF_6 . The most

powerful oxidizer, PtF_6 , is readily intercalated by powdered graphite but to a limiting composition of $\text{C}_{12}\text{PtF}_6$. This anomaly is explained by the magnetic data.

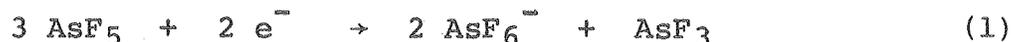
These data for C_8OsF_6 and C_8IrF_6 , which are presented in Figures 1 and 2, show that in each case the dominant guest species has to be the MF_6^- ion. For each salt the appropriate formula is $\text{C}_8^+\text{MF}_6^-$. Moreover, since the volume of the hexagonal C_8MF_6 unit cell, which is $170.9(1) \text{ \AA}^3$, is essentially the sum of the volume of eight carbon atoms, as in hexagonal graphite¹³ ($= 70.00 \text{ \AA}^3$) and the volume of a hexafluoride⁷ ($= \sim 105 \text{ \AA}^3$), 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_8OsF_6 and C_8IrF_6 , but it does appear to be important in the PtF_6 case. The diamagnetism of $\text{C}_{12}\text{PtF}_6$ confirms that the guest is PtF_6^{2-} . This means that the graphite is more highly oxidized in $\text{C}_{12}\text{PtF}_6$ than in the C_8IrF_6 or C_8OsF_6 cases. It is probable that the incomplete filling of the galleries in $\text{C}_{12}\text{PtF}_6$ 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 ($5 \times 5 \times 0.5 \text{ mm}$) 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 $C_{12}PtF_6$, as the findings given in Table 2 indicate.

Single-crystal precession photographs of C_8OsF_6 show that the salt is primitive hexagonal, the a_0 value of $4.92(2) \text{ \AA}$ being twice that of hexagonal graphite.¹³ The c_0 value of $8.10(3) \text{ \AA}$ is consistent with the OsF_6^- being oriented with a threefold axis parallel to c_0 . With this orientation the effective height¹⁴ of OsF_6^- is $\sim 4.7 \text{ \AA}$. Since the effective thickness of a graphite sheet¹³ is 3.35 \AA the anticipated c_0 value for the primitive unit cell is the sum of these values i. e. $\sim 8 \text{ \AA}$. This suggests the unit cell in Figure 5. However, over 1-2 days, at $\sim 20^\circ C$, the diffraction became less sharp, the hk -indexed spots eventually spreading to rings. More OsF_6 failed to restore long-range order. Powder photographs of C_8IrF_6 , OOl data for HOPG C_8IrF_6 , and single-crystal precession data for C_8AsF_6 show that the same unit cell is appropriate for all.

Although HOPG samples of the first stage PtF_6^{2-} salt have not been obtained, powder data for $C_{12}PtF_6$ and 2nd and 3rd stage HOPG/ PtF_6 OOl reflections, indicate that the PtF_6^{2-} -occupied gallery height is $\sim 7.54 \text{ \AA}$. 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 C_8IrF_6 ; where $c_0 = 8.06 \text{ \AA}$. Indeed other observations also indicate that the gallery height is somewhat sensitive to the charging. The results given in Table 3, for first stage $C_xAsF_6^-$ salts, show that as the concentration of AsF_6^- in the graphite galleries increases (as x decreases) the c_0 value (obtained from 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 equation⁶:



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 C_{8.4}AsF₅ to that in C_{13.1}AsF₆⁷ 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. $t/t_0 \sim 1.7$). 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 OsF_6 and the IrF_6 systems the conductivity dropped catastrophically with MF_6 uptake beyond C_{20}MF_6 . Indeed, for MF_6^- salts, formation of first-stage material appears to be associated with decreased conductivity. With PtF_6^{2-} salts however, even second stage $\text{C}_{24}^{2+}\text{PtF}_6^{2-}$ 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 MF_6^{2-} ion is more likely to localize high positive charge at a carbon atom than a single MF_6^- . 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 C_8MF_6 , 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 C_8MF_6 . A structural change, involving distortion of the graphite sheets and slow relocation of the MF_6^- 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/ AsF_5 with the graphite/ AsF_6^- 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 C_{12.7}AsF₅ was converted to C_{12.7}AsF₆. 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,⁶ 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

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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 $\{2 \times 1.82/\sqrt{3}\} + \{2 \times \text{van der Waals radii of the F ligands (which is taken to be } \sim 1.3 \text{ Å)}\}$.

Table 1. Maximum intercalation of HOPG graphite by metal hexafluorides

Hexafluoride	Form of Graphite	Gravimetry	Analyses	Stage, c_0 (Å) ±0.03
WF ₆		does not intercalate		
ReF ₆		does not intercalate		
OsF ₆	powder	{(a) C ₉ OsF ₆ (b) C _{7.72} OsF ₆	{(a) C _{8.13} OsF ₆ (b) C _{7.81} OsF ₆	1st, 8.10
	HOPG (5 × 5 × 1 mm)	{(a) C _{9.9} OsF ₆ * (b) C _{11.6} OsF ₆ *		1st, 8.10
IrF ₆	powder	{(a) C _{8.01} IrF ₆ (b) C _{8.01} IrF ₆	{(a) C _{7.98} IrF ₆ (b) C _{8.05} IrF ₆	1st, 8.05
	HOPG (5 × 5 × 1 mm)	{(a) C _{8.3} IrF ₆ * (b) C _{10.8} IrF ₆ * (c) C _{10.6} IrF ₆		1st, 8.06
PtF ₆	powder	{(a) ---- (b) C _{12.0} PtF ₆ (c) C _{11.0} PtF ₆	{(a) C _{12.4} PtF ₆ (b) C _{12.0} PtF ₆ (c) C _{12.4} PtF ₆	1st, 7.56

* experiment terminated prior to achieving a limiting composition

Table 2. Composition and Electrical Conductivity Data for HOPG/MF₆ and HOPG/AsF₅/F₂ Intercalates

Sample	Composition (Gravimetric)	$\frac{\sigma}{\sigma_G}$ †	$\frac{t}{t_0}$ §	$\frac{k}{k_G}$ **	Comments
1	C _x OsF ₆	8.0	-----	13.7	conductivity maximum
	C _{9.9} OsF ₆	1.0	2.48	2.4	deep blue
2	C _{19.3} OsF ₆	8.2	2.00	14.0	deep blue
	C _{11.6} OsF ₆	1.3	2.45	3.1*	deep blue
3	C _x IrF ₆	6.2	-----	10.6	conductivity maximum
	C _{8.0} IrF ₆	1.2	2.41	2.9	deep blue
4	C _{21.0} IrF ₆	8.0	1.81	13.7	deep blue
	C _{8.1} IrF ₆	0.6	2.68	1.5*	deep blue
5	C _{8.1} IrF ₆	0.4	2.45	1.0*	deep blue
6	C _{10.6} IrF ₆	0.6	2.41	1.4*	deep blue
7	C _{~30} PtF ₆	1.0	1.68	2.4	green-blue
8	C _{~24} PtF ₆	0.8	2.00	1.3	green-blue
9	C _{16.0} AsF ₅	11.7	1.96	20.0	steel blue
	C _{12.7} AsF ₅	11.3	2.41	28.2	steel blue
	C _{12.7} AsF ₆	0.5	2.41	1.2*	fluorinated deep blue
10	C ₂₀ AsF ₅	9.7	1.85	16.6	
	C ₁₁ AsF ₆	2.2	2.48	5.2*	addition of AsF ₅ + F ₂
	C _{7.8} AsF ₆	1.5	2.48	3.7*	"

* 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.

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

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

** 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

Sample	00 l Features	\bar{c} (Å) * (± 0.03 Å)
C _{8.1} OsF ₆	1st stage	8.10
C _{8.1} IrF ₆	1st stage	8.06
C _{~30} PtF ₆	2nd stage	10.88 [†]
	3rd stage	14.25
C _{8.1} AsF ₆	1st stage	7.86
C _{9.7} AsF ₆	1st stage	8.00
C _{13.1} AsF ₆	1st stage	8.04
C _{8.4} AsF ₅	1st stage	8.02
C _{13.1} AsF ₅	1st stage	8.00
	2nd stage	11.34
C _{16.5} AsF ₅	2nd stage	11.35

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

* The true unit cell \bar{c} may, in some cases be a simple multiple of this value, which derives from the simplest indexing of 00 l data.

Table 4. Third Transition Series Hexafluorides: The Non-Bonding Electron Configurations, Molecular Volumes and Electron Affinities

	WF ₆	ReF ₆	OsF ₆	IrF ₆	PtF ₆
dt _{2g} ⁿ	n = 0	1	2	3	4
Molecular volume (Å ³) orthorhombic phase (a)	108.5	106.5	105.7	105.4	104.6
E (eV)	3.5 (b)	5 (d)	6.5 (d)	8 (d)	9.2 (c)

(a) S. Siegel and D. A. Northrop, *Inorg. Chem.*, 5, 2187 (1966).

(b) P. M. George and J. L. Beauchamp, *Chem. Phys.*, 36, 345, (1979).

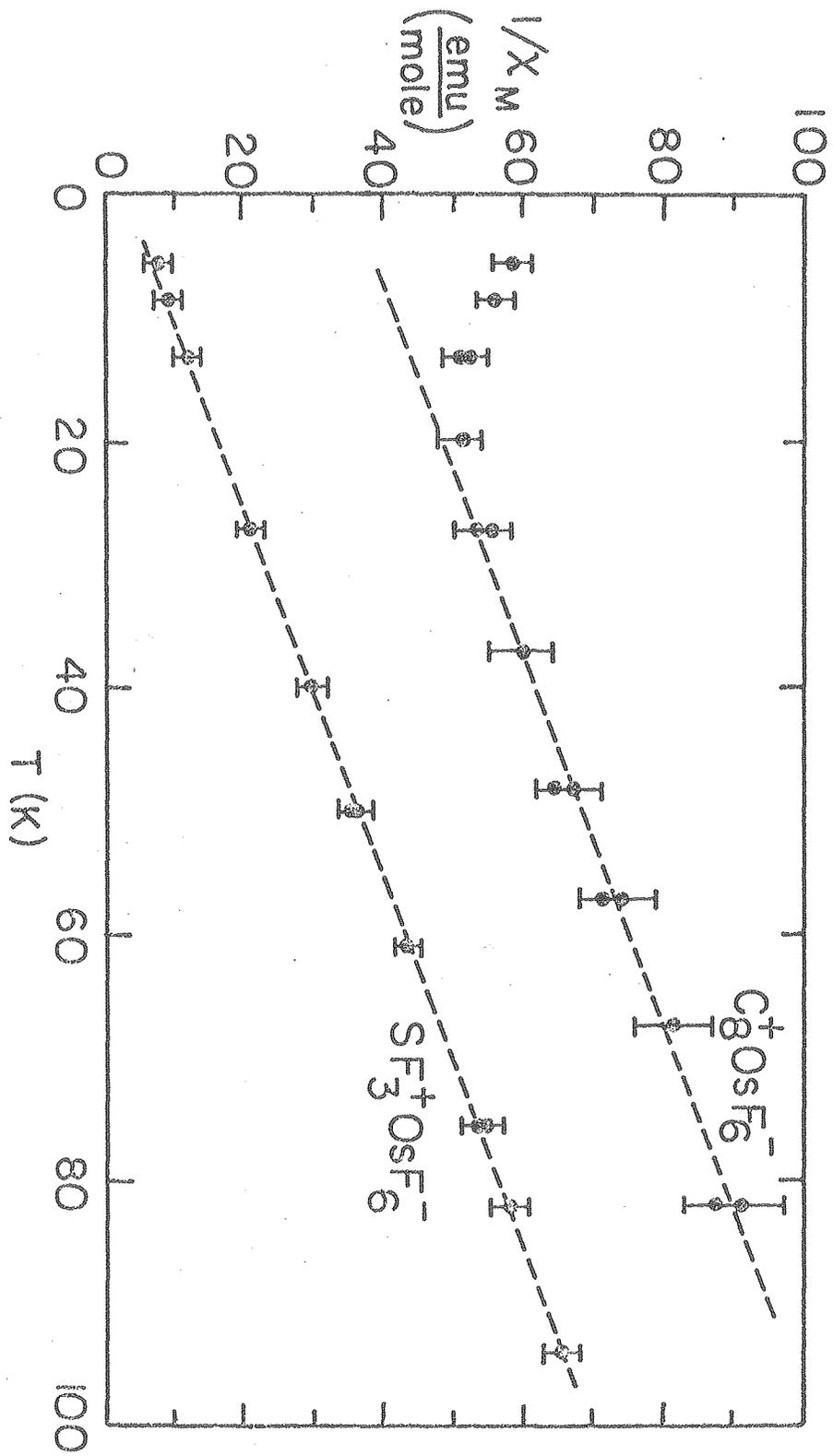
(c) P. Barberi and N. Bartlett, unpublished results based on $\Delta H_f \{O_2PtF_6 \text{ (cryst.) from } O_2 \text{ (g) and } PtF_6 \text{ (g)}\} = -60 \text{ kcal mol}^{-1}$.

(d) Estimated values.

Figure Captions

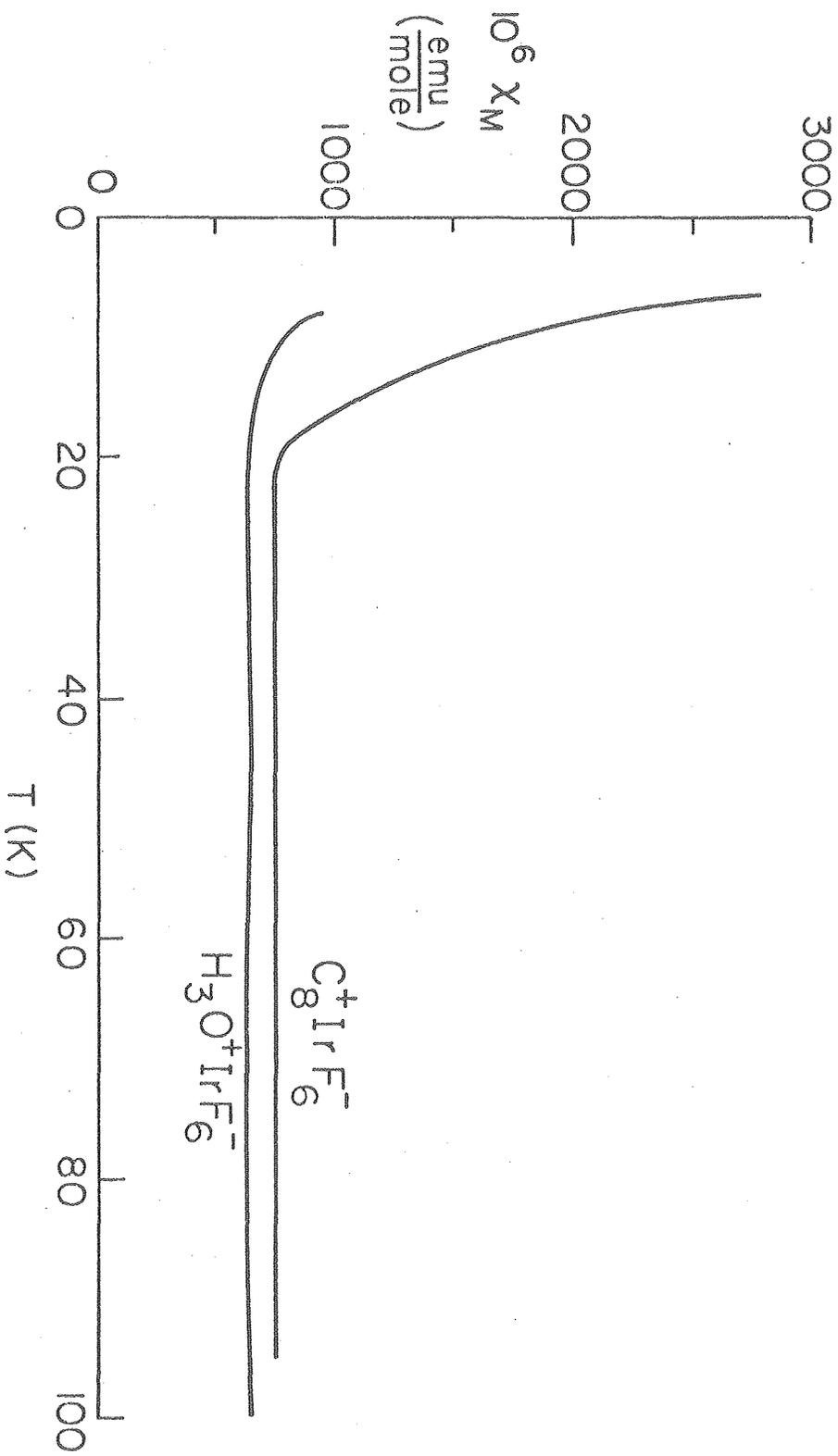
1. Magnetic susceptibility -- temperature relationships for $C_8^+OsF_6^-$ and $SF_3^+OsF_6^-$.
2. Magnetic susceptibility -- temperature relationships for $C_8^+IrF_6^-$ and $H_3O^+IrF_6^-$.
3. Apparatus for conductivity measurements on HOPG and HOPG-intercalates.
4. Response of conductivity of HOPG-IrF₆ intercalates as a function of IrF₆ uptake.
5. Projection of the C_8MF_6 (M = Os, Ir, As) unit cell in relation to the graphite lattice.

Figure 1. Magnetic susceptibility -- temperature relationships for $\text{Cg}^+\text{OsF}_6^-$ and $\text{SF}_3^+\text{OsF}_6^-$.



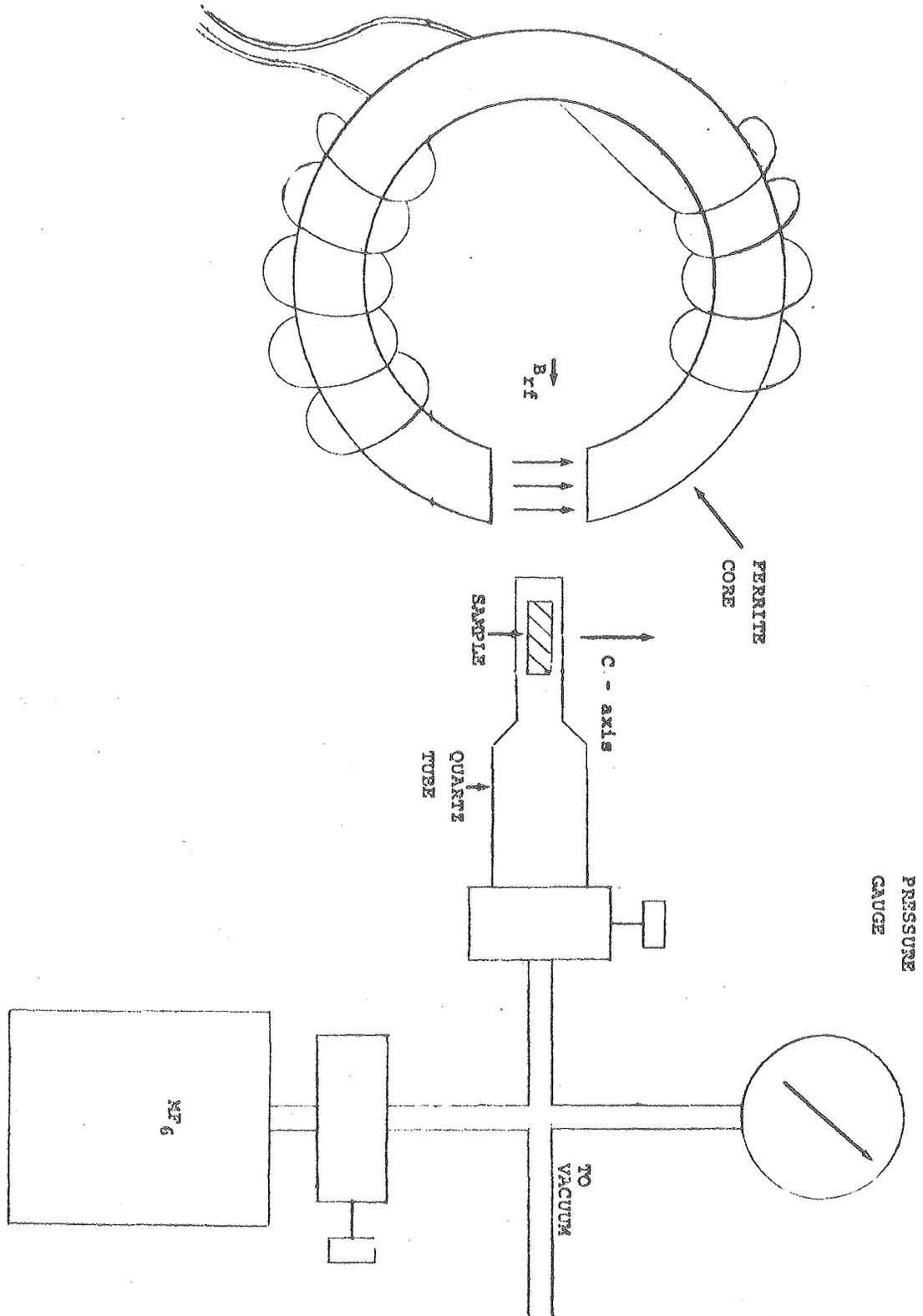
XBL788-5512

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



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

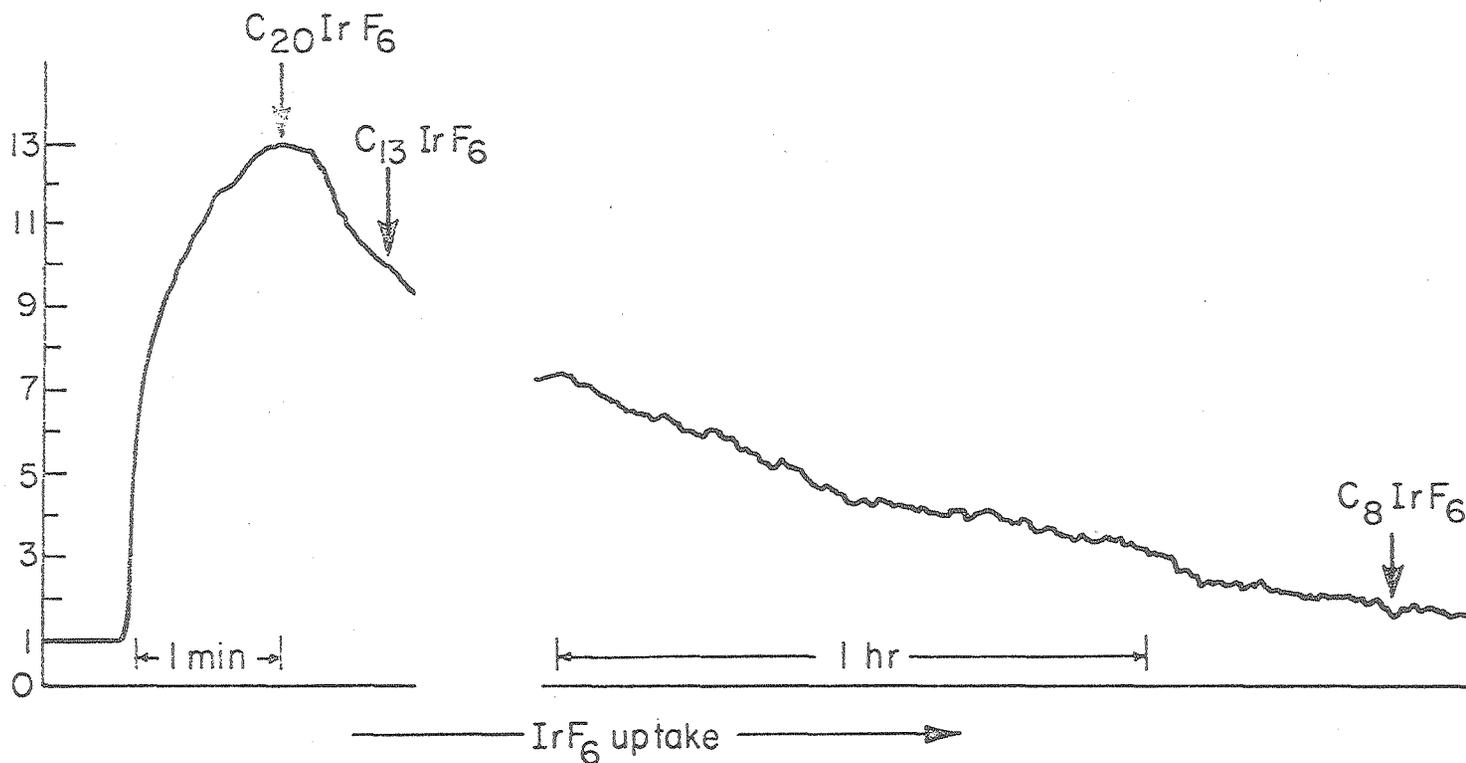


XBL 796-10128

Figure 4. Response of conductivity of HOPG-IrF₆ intercalates as a function of IrF₆ uptake.

Ratio of electrical conductivity in a graphite
plane in intercalate to that in parent graphite

28



XBL 795-6323

Effect of IrF_6 intercalation on the conductivity of highly oriented pyrolytic graphite.

Figure 5. Projection of the C_8MF_6 ($M = Os, Ir, As$) unit cell in relation to the graphite lattice.

