GRAPHITE INTERCALATION COMPOUNDS WITH ReF$_6$ AND TcF$_6$:
ELECTRONIC AND MAGNETIC PROPERTIES

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ABSTRACT

   Magnetic, structural and electronic properties of new graphite compounds with
ReF$_6$ and TcF$_6$ are presented. Together with previous data, these provide evidence
for the existence of a correlation between the layer spacing, the charge trans-
fer and electron affinities of the transition metal hexafluorides.

INTRODUCTION

   The intercalation of transition metal hexafluorides (MF$_6$) into graphite is of
interest, because these hexafluorides comprise a unique group of isostructural
and nearly isodimensional intercalants differing mainly in their electronic con-
figurations and oxidizing properties [1-5]. The intercalation reaction may gen-
erally be written as

$$nC + MF_6 \rightarrow C_n^{+x}(MF_6^-)_x(MF_6)_{1-x} \tag{1}$$
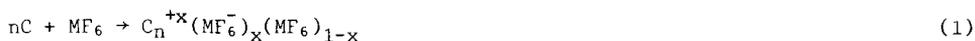
where x denotes the degree of charge transfer. Recently [4,5], we demonstrated
that in some cases x can be extracted from simultaneous ESR and susceptibility
studies of the magnetic intercalate species. Particularly, for OsF$_6$ we confirm an
earlier suggestion by Bartlett [3] that x = 1. Similar measurements on graphite
compounds with MoF$_6$ lead to a charge transfer, x = 0.2 [5].
   We report the intercalation of highly oriented pyrolytic graphite (HOPG) with
the hexafluorides ReF$_6$ and TcF$_6$ for the first time.

EXPERIMENTAL

Materials

The graphite used was HOPG in the form of blocks approximately 3 x 7 x 0.2 mm. Rhenium and technetium hexafluorides were prepared by fluorination of the metal powders - the former in the presence of excess metal, the latter with excess fluorine.

Sample preparation

Intercalated samples were obtained by exposing the HOPG to the MF_6 at room temperature. Reaction rates were controlled by maintaining the MF_6 reservoirs at suitably low temperatures. The intercalation of ReF_6 works best by immersing the HOPG in liquid ReF_6 (m.p. 18.5°C). Even then stage I is reached only after about three weeks. Appropriate precautions were taken with the radioactive TcF_6 ($T_\frac{1}{2}$ = 2 x 10 years). Stoichiometries were determined by weight uptake. Stages were characterized by (ool) diffractograms using Cu Kα radiation through Mylar covered samples. These were handled in an inert atmosphere Drilab.

Magnetic measurements

ESR measurements were carried out in the X band over the temperature range between 2K and 300K. Susceptibility measurements were performed on a supercon- ducting quantum interference device (SQUID) down to 4K.

Electrical conductivity measurements

Basal plane electrical conductivities were measured by the contactless in- ductive rf technique [3]. The specific conductivity normalized per graphite plane was monitored continuously by a motor driven ferrite core and the sample in/out difference, ΔV, recorded as a function of time.

RESULTS AND DISCUSSION

Contrary to earlier reports, ReF_6 intercalates into HOPG, albeit extremely slowly. In this sense it resembles the intercalation of MoF_6 [5]. During the course of the intercalation the electrical conductivity increases smoothly reaching an asymptotic value of σ/σ_g = 6.5 at stage I (σ_g is the basal plane conductivity of pure HOPG). Stage I of HOPG/ReF_6 has a filled layer spacing of d = 8.35 Å; i.e. close to that of C_8MoF_6 which ranges between 8.35 - 8.45 Å. Magnetic susceptibility measurements on $C_{10}ReF_6$ (stage I) indicate a Curie law with an effective magnetic moment of μ = 1.25 BM. This moment is between that of neutral ReF_6 (μ = 0.25 BM) [6] and that of ReF_6^- in the alkali hexafluoro- rhenates (μ = 1.5 to 2.1 BM) [7]. No ESR signal associated with ReF_6^- ($5d^2$ con- figuration) could be observed down to T = 2K. This is not surprising as to the best of our knowledge no resonance associated with a localized spin d^2

configuration has ever been observed in any metallic environment. The lower stage HOPG/ReF$_6$ compounds are unstable. In the absence of excess ReF$_6$, they deintercalate slowly reaching a stable stage IV compound (d = 18.33A) after about 16 hours.

The intercalation of technetium hexafluoride (TcF$_6$) into HOPG resembles that of OsF$_6$. When HOPG is exposed to TcF$_6$ vapor ($\sim$10 torr), the conductivity rises rapidly, reaching a maximum ($\sigma/\sigma_g \simeq 7$) at approximately stage II (d = 11.46 Å). Upon further exposure, stage I is reached (d = 8.12 Å) for which the conductivity ratio $\sigma/\sigma_g \leq 1$. Changes in the c-axis thickness, t, confirm the values calculated from the X-ray diffraction: i.e. for stage I, the thickness ratio with respect to that of HOPG:t/t_o = 2.4 (the calculated value based on X-rays is 2.42); for stage II, t/t_o = 1.77 (calculated 1.71). The magnetic susceptibility of C$_{10}$TcF$_6$ (stage I) follows Curie behavior down to 4K with an effective magnetic moment $\mu \simeq 0.7$ BM. This falls between the moments of neutral TcF$_6$ (μ = 0.45 BM) [6] and those of TcF$_6^-$ in the alkali hexafluorotechnetates (μ = 2.25 to 2.51 BM) [8]. ESR studies of stage I and II HOPG/TcF$_6$ samples indicate clear ten-line hyperfine resolved spectra associated with ^{99}Tc nuclei (I = 9/2, 100% abundance) in the liquid helium temperature range. These spectra can be interpreted using a spin Hamiltonian with S = 1/2, g = 2 and isotropic hyperfine interaction. The large hyperfine interaction ^{99}A = 330±15 G is in agreement with previous estimates for ^{99}Tc in a d^1 configuration [9].

For the case of HOPG/ReF$_6$, the magnetic properties are consistent with the oxidizing power of ReF$_6$. Assuming that the effective magnetic moment of the intercalated ReF$_6^-$ is similar to that in KReF$_6$ (i.e. 2.1 BM) and that the magnetic properties of C$_n$ReF$_6$ are due to the presence of both neutral ReF$_6$ and charged ReF$_6^-$, we calculate the degree of charge transfer to be x $\simeq$ 0.35. This incomplete charge transfer is correlated with the light blue color of the final product and the very long intercalation process with the relatively high final σ as has been observed with MoF$_6$. The situation is more complicated in the case of TcF$_6$. The known chemistry of TcF$_6$ [10] indicates that it falls between OsF$_6$ and IrF$_6$ in oxidizing power, but probably nearer the former (see Figs 1 and 2 for the electron affinities of the MF$_6$ compounds). Thus, the degree of charge transfer is expected to be about one charge per TcF$_6$. Indeed, the dark blue color of the TcF$_6$/ HOPG, the relatively fast intercalation, and low final σ, strongly support significant charge transfer as expected for the TcF$_6$ oxidizing power. However, the magnetic properties seem to be in conflict with such a conclusion. The relatively small (average) magnetic moment of HOPG/TcF$_6$ seems to indicate that most of the intercalant species are in the form of TcF$_6$ molecules. This is consistent with the ESR result, as the ESR spectra can be interpreted in terms of a 5d^1 (g=2, S=$\frac{1}{2}$) electronic configuration corresponding to neutral TcF$_6$. The magnetic properties of HOPG/TcF$_6$ are not understood at the present time. However,
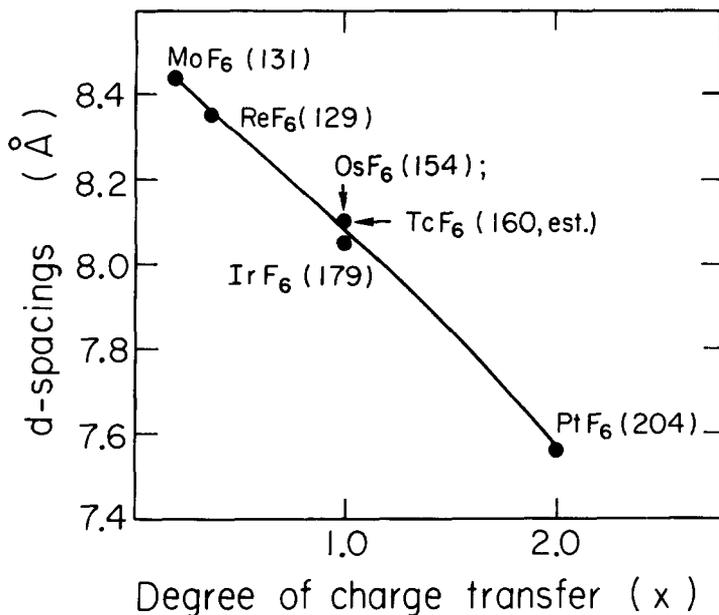
Fig. 1. C-axis d-spacings vs. Degree of Charge Transfer (x). Numbers in paren-
theses are estimated electron affinities of MF_6. The value of PtF_6 is from
$C_{12}PtF_6$ assuming the intercalated species is PtF_6^{-2} (reference 3).

the d-spacing of $C_{10}TcF_6$ is in consonance with the known oxidizing properties of
TcF_6.

The most striking feature of our experimental results is the existence of a
correlation between the layer spacing and the charge transfer for the hexafluo-
ride series (Fig. 1). The charge transfer was determined from the magnetic prop-
erties in the case of MoF_6, ReF_6, OsF_6, and PtF_6. For TcF_6 and IrF_6 the oxidiz-
ing properties suggest x = 1, and this is indicated in the figure. The plot
shows that the layer spacing decreases smoothly with increasing charge transfer
(or electron affinity). This can be understood by a simple classical model
involving a balance between coulombic attractive and elastic repulsive inter-
actions. The results in Fig. 1 provide evidence that the degree of charge
transfer is directly reflected by the lattice spacing in the hexafluoride series
The relationship between oxidizing powers and electron affinity (E.A.) of the
transition metal hexafluorides has already been pointed out [11]. For the 5d
series, the E.A. were estimated by interpolation between the measured value for
WF_6 (104 kcal-mole^{-1}) and one calculated for PtF_6 from a Born-Haber cycle for
$O_2^+PtF_6^-$.

As seen from Fig. 2, the present work puts these values on a firmer basis. It
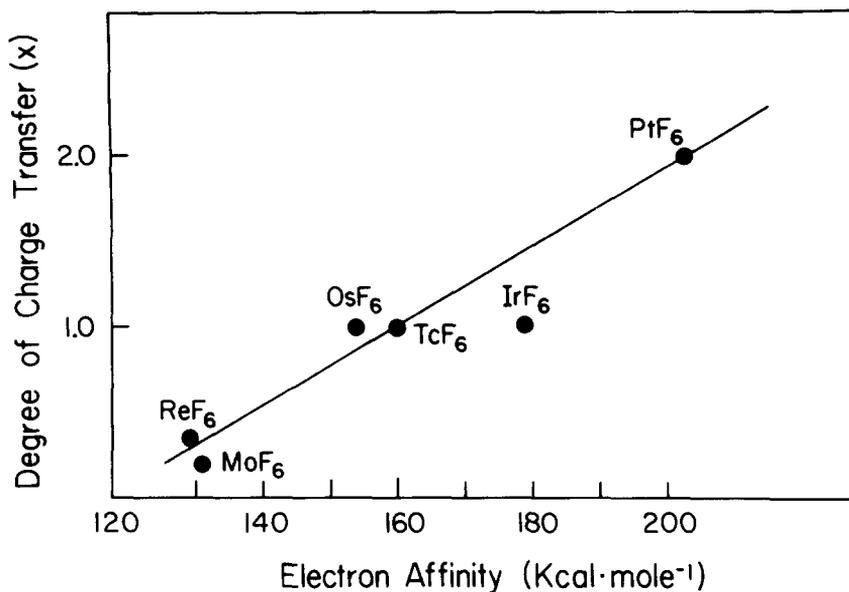moreover indicates that the E.A. given previously for IrF_6 is overestimated and/

Fig. 2. Degree of Charge Transfer per MF_6(x) vs. E.A.

or that IrF_6 is partially reduced to IrF_6^{-2} upon intercalation, and thus x > 1. The slightly shorter d-spacing for C_8IrF_6 supports this. Indeed preliminary magnetic susceptibility measurements on HOPG/IrF_6 show a slight Curie component superimposed on the large temperature independent paramagnetism reported earlier [3].

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