Layer Spacing as a Probe for Charge Transfer in Graphite Intercalation Compounds with Transition Metal Hexafluorides

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Magnetic and structural properties of new graphite compounds with ReF_6 and TcF_6, together with previous data, provide evidence for the existence of a correlation between the layer spacing and the charge transfer for the metal hexafluorides.

The intercalation of transition metal hexafluorides (MF_6) into graphite is of particular interest, because these hexafluorides comprise a unique group of isostructural intercalants differing mainly in their electronic configurations and oxidizing properties.[1—5] In the 5d series, the M–F distances range from 1.833 Å (WF_6) to 1.830 Å (IrF_6),[6,7] while for MoF_6, Mo–F is 1.820 Å.[8] Thus, the MF_6 molecules are also nearly isodimensional. Furthermore, the M–F distance in OsF_6^- is nearly the same (~1.82 Å).[9]

The intercalation reaction may generally be written as in equation (1), where x denotes the degree of charge transfer. Recently,[4,5] we have demonstrated that x can be extracted from simultaneous e.s.r. 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, $x \sim 0.2$.[5]

$$nC + MF_6 \rightarrow C_n^{x+}(MF_6^-)_x(MF_6)_{1-x} \qquad (1)$$

We report the intercalation of highly oriented pyrolytic graphite (HOPG) with the hexafluorides ReF_6 and TcF_6 for the first time.

Contrary to earlier reports, ReF_6 intercalates into HOPG, albeit extremely slowly. The intercalation works best by contacting the HOPG with liquid ReF_6 (m.p. 18.5 °C). Even then, stage I is reached only after about three weeks. In this sense it resembles the intercalation with MoF_6.[5] During the course of the intercalation, the basal plane conductivity, σ, increases smoothly, reaching an asymptotic value of $\sigma/\sigma_g \sim 6.5$ 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.*, similar to that of C_8MoF_6 which ranges between 8.35 and 8.45 Å. Magnetic susceptibility measurements of $C_{10}ReF_6$ (stage I) indicate a Curie law with an effective magnetic moment of $\mu = 1.25\ \mu_B$. This moment is between that of neutral ReF_6 ($0.25\ \mu_B$)[10] and that of ReF_6^- in the alkali hexafluororhenates (1.5—2.1 μ_B).[11] No e.s.r. signal associated with ReF_6^- ($5d^2$ configuration) could be observed down to $T = 2$ K. This is not surprising, as to the best of our knowledge no resonance associated with a d^2 configuration has ever been observed in any metallic environment.

The intercalation of technetium hexafluoride (TcF_6) into HOPG resembles that of OsF_6. When HOPG is exposed to TcF_6 vapour, the conductivity rises rapidly, reaching a maximum ($\sigma/\sigma_g \sim 7$) 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 $t/t_0 = 2.4$ (the calculated value based on X-ray data is 2.42); for stage II, $t/t_0 = 1.77$ (calc. 1.71). The magnetic susceptibility of $C_{10}TcF_6$ (stage I) follows Curie behaviour down to 4 K with an effective magnetic moment $\mu \sim 0.7\ \mu_B$. This falls between the moments of neutral TcF_6 ($0.45\ \mu_B$)[10] and those of TcF_6^- in the alkali hexafluorotechnetates (2.25—2.51 μ_B).[12] E.s.r. studies of stages 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 $S = ½$, $g = 2$, and isotropic hyperfine interaction. The large hyperfine interaction A (^{99}Tc) = 330 ± 15 G† is in agreement with previous estimates for ^{99}Tc in a d^1 configuration.[13]

For the case of HOPG–ReF_6, the magnetic properties are

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† $1\ G = 10^{-4}\ T$.

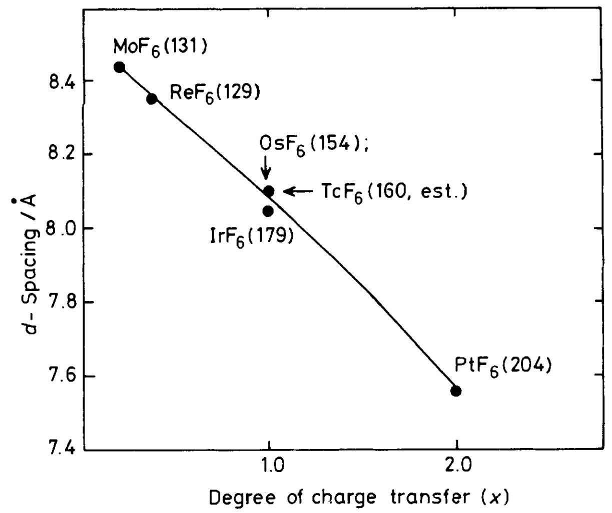

Figure 1. *c* Axis *d* spacing *vs.* degree of charge transfer (x). Numbers in parentheses are estimated electron affinities of MF_6. The value for PtF_6 is from $C_{12}PtF_6$ assuming the intercalated species is PtF_6^{2-} as inferred from magnetic susceptibility measurements (ref. 3).

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 μ_B) and that the magnetic properties in $C_{10}ReF_6$ are due to the presence of both neutral ReF_6 and charged ReF_6^-, we calculate the degree of charge transfer, x, to be ~0.35. This incomplete charge transfer is consistent with the pale blue colour 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 indicates that it falls between OsF_6 and IrF_6 in oxidizing power, but probably nearer the former (see Figure 1 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 colour 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 observed e.s.r. signal could possibly arise from relatively small concentrations of neutral TcF_6 while the TcF_6^- (d^2) in analogy to ReF_6^- would not give rise to a signal. However, the relatively small magnetic moment of HOPG–TcF_6 is in conflict with the presence of large amounts of $Tc^VF_6^-$. The magnetic properties of HOPG–TcF_6 are thus not understood at the present time. However, 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 hexafluoride series (Figure 1). The charge transfer was determined from the magnetic properties in the case of MoF_6, ReF_6, and PtF_6. For TcF_6 and IrF_6 the oxidizing properties suggest x ~1, and this is indicated in Figure 1. 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 interactions. The results in Figure 1 provide evidence that the degree of charge transfer is directly reflected by the lattice spacing in the hexafluoride series.

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