

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

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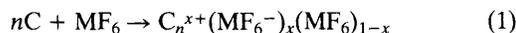
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Magnetic and structural properties of new graphite compounds with ReF₆ and TcF₆, together with previous data, provide evidence for the existence of a correlation between the layer spacing and the charge transfer for the metal hexafluorides.

The intercalation of transition metal hexafluorides (MF₆) 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 (WF₆) to 1.830 Å (IrF₆),^{6,7} while for MoF₆, Mo–F is 1.820 Å.⁸ Thus, the MF₆ molecules are also nearly isodimensional. Furthermore, the M–F distance in OsF₆[–] 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 OsF₆ we confirm an earlier suggestion by Bartlett³ that $x = 1$. Similar measurements on graphite compounds with MoF₆ lead to a charge transfer, $x \sim 0.2$.⁵



We report the intercalation of highly oriented pyrolytic graphite (HOPG) with the hexafluorides ReF₆ and TcF₆ for the first time.

Contrary to earlier reports, ReF₆ intercalates into HOPG, albeit extremely slowly. The intercalation works best by contacting the HOPG with liquid ReF₆ (m.p. 18.5 °C). Even then, stage I is reached only after about three weeks. In this sense it resembles the intercalation with MoF₆.⁵ 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–ReF₆ has a filled layer spacing of $d = 8.35$ Å; *i.e.*, similar to that of C₈MoF₆ which ranges between 8.35 and 8.45 Å. Magnetic susceptibility measurements of C₁₀ReF₆

(stage I) indicate a Curie law with an effective magnetic moment of $\mu = 1.25 \mu_B$. This moment is between that of neutral ReF₆ (0.25 μ_B)¹⁰ and that of ReF₆[–] in the alkali hexafluororhenates (1.5–2.1 μ_B).¹¹ No e.s.r. signal associated with ReF₆[–] (5d² 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 d² configuration has ever been observed in any metallic environment.

The intercalation of technetium hexafluoride (TcF₆) into HOPG resembles that of OsF₆. When HOPG is exposed to TcF₆ 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 C₁₀TcF₆ (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 TcF₆ (0.45 μ_B)¹⁰ and those of TcF₆[–] in the alkali hexafluorotechnetates (2.25–2.51 μ_B).¹² E.s.r. studies of stages I and II HOPG–TcF₆ samples indicate clear ten-line hyperfine resolved spectra associated with ⁹⁹Tc 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 A (⁹⁹Tc) = 330 ± 15 G† is in agreement with previous estimates for ⁹⁹Tc in a d¹ configuration.¹³

For the case of HOPG–ReF₆, the magnetic properties are

† 1 G = 10^{–4} T.

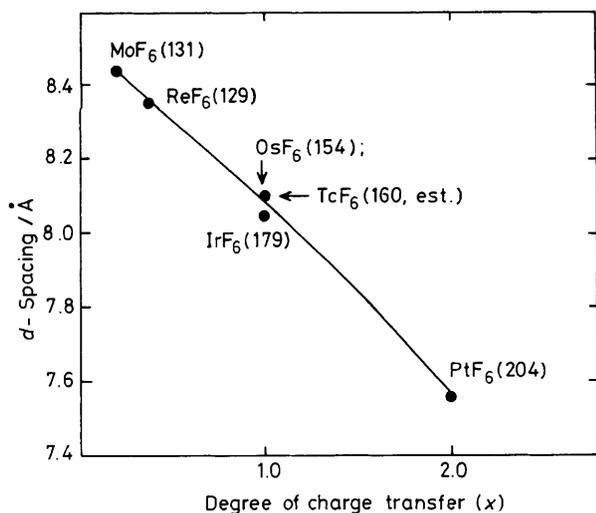


Figure 1. *c* Axis *d* spacing vs. degree of charge transfer (*x*). Numbers in parentheses are estimated electron affinities of MF₆. The value for PtF₆ is from C₁₂PtF₆ assuming the intercalated species is PtF₆²⁻ as inferred from magnetic susceptibility measurements (ref. 3).

consistent with the oxidizing power of ReF₆. Assuming that the effective magnetic moment of the intercalated ReF₆⁻ is similar to that in KReF₆ (*i.e.*, 2.1 μ_B) and that the magnetic properties in C₁₀ReF₆ are due to the presence of both neutral ReF₆ and charged ReF₆⁻, 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 MoF₆. The situation is more complicated in the case of TcF₆. The known chemistry of TcF₆ indicates that it falls between OsF₆ and IrF₆ in oxidizing power, but probably nearer the former (see Figure 1 for the electron affinities of the MF₆ compounds). Thus, the degree of charge transfer is expected to be about one charge per TcF₆. Indeed, the dark blue colour of the TcF₆-HOPG, the relatively fast intercalation, and low final σ, strongly support significant charge transfer as expected for the TcF₆ 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 TcF₆ while the TcF₆⁻ (d²) in analogy to ReF₆⁻ would

not give rise to a signal. However, the relatively small magnetic moment of HOPG-TcF₆ is in conflict with the presence of large amounts of TcF₆⁻. The magnetic properties of HOPG-TcF₆ are thus not understood at the present time. However, the *d* spacing of C₁₀TcF₆ is in consonance with the known oxidizing properties of TcF₆.

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 MoF₆, ReF₆, and PtF₆. For TcF₆ and IrF₆ 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.

We gratefully acknowledge the supply of HOPG from Dr. W. A. Moore of the Union Carbide Co. and financial support from the Volkswagen Foundation.

Received, 29th April 1985; Com. 565

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