Fluorogermanium(IV) Salts of Graphite. A System in Equilibrium with Elemental Fluorine

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Summary Pyrolytic graphite is not intercalated by GeF_4 alone but is intercalated by GeF_4–F_2 mixtures to yield, at the intercalation limit, at 20 °C, a first-stage material, $C_{12}GeF_{5-6}$, which is in equilibrium with gaseous fluorine

Germanium tetrafluoride is a superior fluoride ion acceptor since it can stabilize the O_2^+ ion and the NF_4^+ ion in salts [1] It is this superior fluoride-ion acceptor capability which must account for our observation that pyrolytic graphite readily intercalates GeF_4 in the presence of fluorine, but does not do so, even with high pressures of GeF_4, if fluorine is absent Similar experiments, in which SiF_4 was substituted for GeF_4, failed to bring about any silicon fluoride intercalation It has long been known[2] that GeF_4 is a superior fluoride ion acceptor to SiF_4 since, with SF_4, the former yields the salt $(SF_3^+)_2GeF_6^{2-}$, whereas the silicon analogue is not stable at ordinary temperatures and pressures (in spite of the lattice energy of the silicon analogue being slightly more favourable by virtue of the smaller size of SiF_6^{2-})

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Treatment of either powder or pieces of highly oriented pyrolytic graphite (HOPG), with GeF_4–F_2 mixtures, results in a GeF_4 uptake which is dependent upon the quantity of F_2 available. The quantity of F_2 determines the stage, *n*. A given $C_{12n}GeF_5$ stage takes up GeF_4 to reach a limiting composition $C_{12n}GeF_5 \cdot 1/2\ GeF_4$. In a dynamic vacuum this material loses GeF_4, but not fluorine.‡ When the F_2–GeF_4 ratio is 1 : 1 (at a total pressure of 2 atmospheres) the limiting composition of the graphite intercalate is $C_{12}GeF_6$. Also, if a first-stage material, which is richer in germanium than $C_{12}GeF_5$, is fluorinated, GeF_4 is eliminated and fluorine consumed to again yield $C_{12}GeF_6$: $C_{12}GeF_5 \cdot xGeF_4 + 1/2\ F_2 \rightarrow C_{12}GeF_6 + xGeF_4$.

The first-stage material $C_{12}GeF_6$, at 20 °C, loses F_2 in a dynamic vacuum, but not GeF_4, to yield $C_{12}GeF_5$. The change is reversed by applying a pressure (2 atm) of fluorine at 20 °C, the consumption (by tensimetry) being appropriate for the conversion expressed in equation (1).

$$C_{12}GeF_5(c) + 1/2\ F_2(g) \rightleftharpoons C_{12}GeF_6(c) \qquad (1)$$

These observations imply that the free-energy change for equation (1), at *ca.* 20 °C, is close to zero.

It is probable that the formulations for the graphite compounds are $C_{12}^{2+}GeF_6^{2-}$ and $C_{12}^{+}GeF_5^{-}$. *X*-Ray data, from mixed 1st/2nd stage HOPG pieces, show that the gallery height, '*c*' (*i.e.*, the graphite-network to next graphite-network spacing) $\leqslant$ 7·80 Å for $C_{12}GeF_6$ and $\geqslant$ 8·23 Å for $C_{12}GeF_5$, which is consistent with marked increase in the Coulombic attraction between guest and host for C_{12}^{2+}-GeF_6^{2-} compared with $C_{12}^{+}GeF_5^{-}$. The $C_{12}^{2+}GeF_6^{2-}$ formulation is related to that proposed for the limiting composition[3] of the PtF_6 intercalate, $C_{12}PtF_6$. The platinum salt, being diamagnetic, must be $C_{12}^{2+}PtF_6^{2-}$, which contrasts with the iridium hexafluoride limiting-composition salt which is $C_8^{+}IrF_6^{-}$.[3] The ordered structure for $C_{12}GeF_6$ is probably as indicated in the Figure.

The equilibrium (1), must be a consequence of a close balancing of the fluoride ion affinities of GeF_4, the lattice energies of $C_{12}^{2+}GeF_6^{2-}$ and $C_{12}^{+}GeF_5^{-}$, and the work functions of the graphite. There is no such equilibrium for $C_{12}PtF_6$, undoubtedly because of much higher stability of PtF_6^{2-}, compared with GeF_6^{2-}. Even PF_5, which is a poorer F^- acceptor than AsF_5, intercalates in graphite, in the presence of fluorine,[4] to yield at the limit C_8PF_6, but this, like its arsenic and transition metal analogues, is vacuum stable at *ca.* 20 °C.

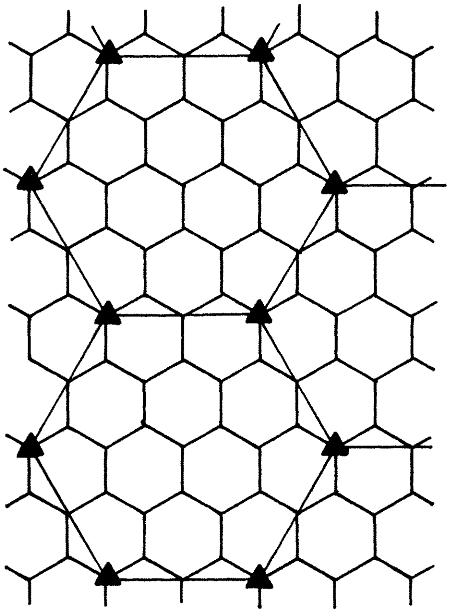

FIGURE. Structural model for $C_{12}MF_6$.

Clearly $C_{12}GeF_6$ is a solid which must have an oxidizing and fluorinating capability close to that of elemental fluorine itself.

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‡ $C_{12n}GeF_5$ also takes up either SiF_4 or SF_6 reversibly. For SiF_4 the limiting composition is $C_{12n}GeF_5 \cdot \frac{1}{2}SiF_4$. SF_6 (1 atm) yields $C_{12n}GeF_5 \cdot$ *ca.* $\frac{1}{6}SF_6$.

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[2] N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 1961, **3417** and unpublished observations.

[3] N. Bartlett, E. M. McCarron, B. W. McQuillan, and T. E. Thompson, *Synthetic Metals*, 1980, **1**, 221.

[4] E. M. McCarron and N. Bartlett, to be published.