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THE RELATIONSHIP OF GRAPHITE/AsF₅ INTERCALATION COMPOUNDS TO C_x⁺AsF₆⁻ SALTS

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Graphite intercalated by AsF₅ has been reported to give compounds of formula C_{8n}AsF₅ where n is the stage. It is doubtful however if materials of exact composition C_{8n}AsF₅ have ever been obtained. The intercalation of graphite by AsF₅ is associated with electron oxidation of the graphite according to the equation: $3\text{AsF}_5 + 2\text{e}^- \rightarrow 2\text{AsF}_6^- + \text{AsF}_3$. Because of the easy removal or displacement of AsF₃, the As:F ratio is readily increased beyond 5. By treating graphite with excess AsF₅, removing volatiles under vacuum and repeating the cycle seven times a first stage salt C₁₀⁺AsF₆⁻ (C₀ = 7.96Å) is made. Interaction of graphite with AsF₅ in the molar ratio 8:1, within a small volume reactor, yields a material of approximate composition C₈AsF₅. The major component of the volatiles at the onset of their removal is AsF₃, but, at a composition close to C₁₀AsF₅, is AsF₃. 'Graphite AsF₅' can be prepared by adding AsF₃ to C_xAsF₆ salts. The electrical conductivities of 'AsF₅' and AsF₆ relatives will be compared and discussed.

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FLUOROSULFATE CONTAINING INTERCALATION COMPOUNDS

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Direct oxidative intercalation of bis(fluorosulfonyl)peroxide, S₂O₆F₂ into graphite has been reported (1) to yield a binary graphite salt of the composition C₆SO₃F. We report on reactions of this compound. Solvolysis in HSO₃CF₃ yields quantitatively C₁₂SO₃CF₃ while with SbF₅, C₈SbF₆ is formed. The intercalation of BrSO₃F and ClSO₃F is studied as well. In the first case C₁₂BrSO₃F is formed. Subsequent reaction with S₂O₆F₂ yields C₁₆Br(SO₃F)₃. With ClSO₃F no stable chlorine containing intercalates form and materials of the composition C₁₀SO₃F result instead. The results of Raman, IR, X-ray diffraction and ¹⁹F-nmr are discussed.

1 N. Bartlett, R.N. Biagioni, B.W. McQuillan, A.S. Robertson and A.C. Thompson, J. Chem. Soc. Chem. Commun., 200 (1978).