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THE RELATIONSHIP OF GRAPHITE/AsF_5 INTERCALATION COMPOUNDS TO $C_x^+AsF_6^-$ SALTS

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Graphite intercalated by AsF_5 has been reported to give compounds of formula $C_{8n}AsF_5$ where n is the stage. It is doubtful however if materials of exact composition $C_{8n}AsF_5$ have ever been obtained. The intercalation of graphite by AsF_5 is associated with electron oxidation of the graphite according to the equation: $3AsF_5 + 2e^- \rightarrow 2AsF_6^- + AsF_3$. Because of the easy removal or displacement of AsF_3 the As:F ratio is readily increased beyond 5. By treating graphite with excess AsF_5, removing volatiles under vacuum and repeating the cycle seven times a first stage salt $C_{10}^+AsF_6^-$ ($C_O \approx 7.96\text{Å}$) is made. Interaction of graphite with AsF_5 in the molar ratio 8:1, within a small volume reactor, yields a material of approximate composition C_8AsF_5. The major component of the volatiles at the onset of their removal is AsF_5, but, at a composition close to $C_{10}AsF_5$, is AsF_3. 'Graphite AsF_5' can be prepared by adding AsF_3 to C_xAsF_6 salts. The electrical conductivities of 'AsF_5' and AsF_6 relatives will be compared and discussed.

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FLUOROSULFATE CONTAINING INTERCALATION COMPOUNDS

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Direct oxidative intercalation of bis(fluorosulfuryl)peroxide, $S_2O_6F_2$ into graphite has been reported (1) to yield a binary graphite salt of the composition C_8SO_3F. We report on reactions of this compound. Solvolysis in HSO_3CF_3 yields quantitatively $C_{12}SO_3CF_3$ while with SbF_5, C_8SbF_6 is formed. The intercalation of $BrSO_3F$ and $ClSO_3F$ is studied as well. In the first case $C_{12}BrSO_3F$ is formed. Subsequent reaction with $S_2O_6F_2$ yields $C_{16}Br(SO_3F)_3$. With $ClSO_3F$ no stable chlorine containing intercalates form and materials of the composition $C_{10}SO_3F$ result instead. The results of Raman, IR, X-ray diffraction and ^{19}F-nmr are discussed.

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