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PREPARATION AND CHARACTERISATION OF GRAPHITE HEXAFLUORO ANTIMONATE(V)

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SUMMARY

Solvolysis of graphite fluorosulfate, $C_8^+SO_3F^-$, in a large excess of antimony(V) fluoride results in the quantitative conversion to graphite hexafluoroantimonate, $C_8^+SbF_6^-$, as a first-stage intercalation compound with an interlayer separation of $8.19 \pm 0.03 \text{ \AA}$. The compound is characterised by microanalysis, ^{19}F nmr spectroscopy, and Raman spectroscopy and shows increased electrical basal plane conductance over that of graphite.

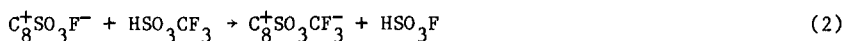
INTRODUCTION

Intercalation of antimony pentafluoride, SbF_5 , in graphite was first reported in 1973 [1]. The composition of the first stage compound as $C_{6.0-6.5}SbF_5$ with an interlayer separation of 8.46 \AA and the existence of higher stage intercalation compounds were subsequently confirmed [2] [3]. While SbF_5 -graphite intercalation compounds have found wide and varied uses [4], and have attracted much attention, the exact nature of these materials is still somewhat unclear. ^{121}Sb Mossbauer spectra [5] have suggested the presence of both Sb(III) and Sb(V), produced by the equilibrium:

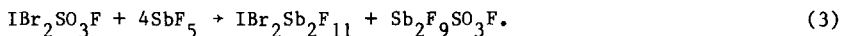


formulated in analogy to the equilibrium found for AsF_5 -graphite intercalation compounds [6]. However, the exact position of this equilibrium and hence the extent of charge transfer from graphite to the intercalant, as expressed in terms of the carrier density parameter f [7], is subject of much debate.

Such a parameter should be both stage and temperature dependent. According to a recent $^{19}\text{Fnmr}$ study [8] a previously reported value of 0.20 at room temperature [9], may still be too high and should perhaps be closer to 0.10 for a first-stage compound. In any event, f appears to be consistently lower than for corresponding AsF_5 -graphite intercalation compounds [8]. Our approach, aimed at a better understanding of the nature of these SbF_5 -graphite intercalation compounds, is to devise a feasible synthetic route to graphite salts with SbF_6^- as the only intercalant. A similar objective has been reached by Bartlett et al. [6] in the reaction of $\text{O}_2^+\text{AsF}_6^-$ with graphite. The solvolysis of $\text{C}_8^+\text{SO}_3\text{F}^-$ [10] in an excess of SbF_5 appears to provide a promising pathway for three reasons: (i) the potential starting material, $\text{C}_8^+\text{SO}_3\text{F}^-$, is easily obtained by the oxidative intercalation of bis(fluorosulfonyl)peroxide, $\text{S}_2\text{O}_6\text{F}_2$, into the graphite lattice [10] [11]. (ii) We have recently [11] reported on the quantitative replacement of the fluorosulfate by trifluoromethylsulfate group through solvolysis in an excess of HSO_3CF_3 according to:



(iii) There are precedents for the intended solvolysis in SbF_5 , [12] [13] as exemplified by the reaction of various interhalogenfluorosulfates [12], e.g.



Extension of reaction (3) to the solvolysis of $\text{C}_8^+\text{SO}_3\text{F}^-$ seemed therefore logical.

There have been previous attempts to obtain graphite hexafluoroantimonates. Two conflicting reports on the products of the reaction of graphite and NO_2SbF_6 in dry nitromethane are found. While in one case [14] the simultaneous intercalation of solvent, SbF_6^- and even NO_2SbF_6 was suggested, the other report [15] claims graphite hexafluoroantimonates corresponding to stages 1 to 8. However subsequently, after chemical analysis, this claim was revised [16], reporting now an 'ideal composition' of $\text{C}_{23n}\text{SbF}_6(\text{CH}_3\text{NO}_2)_{1.7}$, with n the stage number. Not unexpectedly the successive treatment of graphite first with AsF_5 and then with NO_2SbF_6 , again in CH_3NO_2 produced rather complex mixtures as indicated by their $^{19}\text{Fnmr}$ spectra [17]. All these reports illustrate both the pitfalls and urgent need of chemical analysis in this field.

EXPERIMENTAL

Chemicals

Graphite powder (SP1 - Union Carbide) and plates of HOPG (highly oriented pyrolytic graphite) were used in this study. All graphite samples were dried immediately before use by heating the sample in vacuo to 150°C for 24 hours.

Bis(fluorosulfonyl)peroxide, $S_2O_6F_2$ was prepared by catalytic (AgF_2) fluorination of sulfur trioxide [18]. Antimony pentafluoride was obtained from Ozark Mahoning Company and purified by repeated distillations, first at atmospheric pressure in a counter stream of dry nitrogen, and then in vacuo in an all-glass apparatus.

Instrumentation

Raman spectra were recorded with a Spex Ramalog 5 Spectrometer, equipped with an Ar^+ laser (Spectra Physics 164) with the 514.5 nm line used for excitation. A back scattering geometry was used similar to the one described in the literature [19]. The sample was contained in a Teflon sample holder, fitted with circular quartz windows. Spectra were recorded on low laser output power to prevent de-intercalation. X-ray powder photographs were obtained using a Phillips powder camera of 57 mm radius and a Cu source. Samples were sealed in 0.5 mm O.D. Lindemann glass capillaries.

Room temperature ^{19}F solid state NMR spectra were taken at 188 MHz with a Bruker CXP-200 Fourier Transform-NMR spectrometer using a high power ^{19}F probe. Samples were contained in NMR tubes of 30 mm length with a 5 mm O.D.

Electrical conductivity measurements were made at room temperature by contactless radio frequency induction [20]. The ferrite core system was operated at an induction frequency of 16.8 kHz. Samples of low thickness (0.2 to 0.4 mm) were used both for calibration as well as for conductivity measurements. The electrical conductivity σ was evaluated from the relationship $\Delta V = Kts^2\sigma$, with ΔV = voltage change observed in the sensory coil, measured with a Keithley 148 nano volt meter; t = sample thickness and s = sample area were measured with a toolmakers micrometer and a travelling microscope respectively; K , the instrument constant, was determined by calibration with Cu, Al, Brass and Pb.

Analysis and Sample Manipulation

Microanalysis for antimony and fluorine contents was performed by Analytische Laboratorien, Gummersbach, West Germany. Chemical analysis for carbon was carried out by Mr. P. Borda of this department. A Carbo Erba Model 1106 analyser employing a flash oxidation technique was used and CuO was added to samples. Details of the method were similar to those given in a recently published report [21].

Analytical data obtained suggest a composition $C_8^+SbF_6^-$

	C	Sb	F	Total	Sb/F ratio
Calculated for $C_8^+SbF_6^-$ [%]	28.94	36.70	34.36	100.00	6.0
Found [%]	28.57	36.96	34.21	99.74	5.89

Standard vacuum line techniques were used for the transfer of volatile materials. Solids were manipulated in a Vacuum Atmosphere Corp. "Dri Lab," Model HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train" Model No. He-93-B circulating unit. Reactions--oxidative intercalation as well as solvolysis--were performed in Pyrex reaction vials fitted with Teflon stem valves (Kontes Glassware). All reactions were followed by recording weight changes.

Synthesis of $C_8^+SbF_6^-$

In a typical reaction 0.2043 g of graphite powder (SP1) was reacted with a large excess (about 10.0 ml) of $S_2O_6F_2$ at room temperature for 24 hours. The excess of $S_2O_6F_2$ was removed in vacuo and a dynamic vacuum was maintained until no further weight loss occurred, at a composition $C_8^+SbF_6^-$ (gravimetric).

To this sample about 10 ml of SbF_5 were distilled in vacuo, the reaction mixture was warmed to 45°C to facilitate mixing of the reactants and maintained for 6 days at this temperature. The volatile reaction products were identified by their IR spectra as a mixture of SbF_5 and $Sb_2F_9SO_3F$ [12]. Complete removal of all volatiles in vacuo allowed isolation of a dark blue, powdery solid. A dynamic vacuum was maintained until constant weight was reached.

RESULTS AND DISCUSSION

The analytical data allow two important conclusions: (a) the fluorosulfate groups are quantitatively removed as $\text{Sb}_2\text{F}_9\text{SO}_3\text{F}$ in analogy to reported precedents [12], and (b) the new counter ion is SbF_6^- . The Sb/F ratio of 5.89 is slightly below expectations but this may be either due to analytical inaccuracies--one notices the carbon and fluorine values are commonly rather low, because interference from rather inert CF_4 is a complication--or very small amounts of polyanions e.g. $\text{Sb}_2\text{F}_{11}^-$ may be present. We have, however, found no evidence for this ion e.g. in the ^{19}F nmr spectrum. As a consequence of the composition, one positive charge for 8 carbon atoms is suggested. The composition $\text{C}_8^+\text{MF}_6^-$ is generally found where MF_6^- is the intercalant [6] [22], and a similar close packed structure is suggested for $\text{C}_8^+\text{SbF}_6^-$, than has been reported for these first stage compounds.

The replacement of SO_3F^- by SbF_6^- has also caused an increase in the inter-layer separation from $7.81 \pm 0.03 \text{ \AA}$ to $8.19 \pm 0.03 \text{ \AA}$. Similar values are found for $\text{C}_8^+\text{AsF}_6^-$ with 8.10 \AA [6] and other $\text{C}_8^+\text{MF}_6^-$ compounds [22]. Since for both $\text{C}_8^+\text{AsF}_6^-$ and $\text{C}_8^+\text{SbF}_6^-$ similar charge density distributions are likely in the graphite layers, the difference may be attributed to the slightly larger SbF_6^- ion. In isostructural salts with common cations - $\text{C}_5\text{H}_6\text{N}^+$ in this case - internuclear separations for M-F bonds of 1.77 and 1.87 \AA are reported for AsF_6^- and SbF_6^- respectively [23]. As found for $\text{C}_8^+\text{AsF}_6^-$ [6], a hexagonal unit cell with the AsF_6^- closely packed - C_3 axis of AsF_6^- parallel to the c axis of the intercalation compound - may be found in case of $\text{C}_8^+\text{SbF}_6^-$ as well. It may be recalled, that first stage intercalation compounds of the type $\text{C}_{6.0-6.5}\text{SbF}_5$ have larger interlayer separations, with 8.46 \AA generally reported [2] [3]. Both a tighter packing of the intercalant and also a lower charge distribution may be responsible here for the larger values.

The formulation of $\text{C}_8^+\text{SbF}_6^-$ as a first stage graphite intercalation compound is also reflected in a Raman band at $1636 - 1640 \text{ cm}^{-1}$, attributed to the E_{2g} mode of the expanded graphite lattice. The frequency shift from $1580 \pm 2 \text{ cm}^{-1}$ in graphite itself is typical for first stage compounds [24] [25]. There are no Raman bands due to the intercalant observable in the spectrum.

The ^{19}F nmr spectrum shows a single resonance at -121 ppm with respect to CFCl_3 as reference. Both SbF_5 and SbF_6^- have been reported to resonate in this area [8] [17].

Finally, electrical conductance measurements on intercalated HOPG plates give values of $1.65 \times 10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature and σ/σ graphite ratios of 7.11 for the composition $\text{C}_8^+\text{SbF}_6^-$. Not surprisingly higher conductance values are observed for graphite $-\text{SbF}_5$ intercalation compounds [26] where values between 2.7 and $3.4 \times 10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$ are reported. Details of our electrical conductance studies are to be published shortly.

CONCLUSION

As previously observed, solvolysis reactions of $\text{C}_8^+\text{SO}_3\text{F}^-$ open a novel route to well defined graphite salts. The only difference to previous solvolysis studies in SbF_5 by our group [12] [13] is the rather long reaction time required to effect complete substitution of the intercalant. This is doubtlessly a peculiarity of the layer structure of lamellar compounds.

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