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THE REACTION OF ARSENIC PENTAFLUORIDE WITH GRAPHITE FLUOROSULFATE

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SUMMARY

The reaction of graphite fluorosulfate with an excess of arsenic(V) fluoride produces the new intercalation compound  $C_{14}^+ [AsF_5(SO_3F)]^-$ . Identification as a first stage compound rests on the observed interlayer separation of 7.92 Å and the position of  $\nu_{E2g}$  at  $1636\text{ cm}^{-1}$  in the Raman spectrum. Evidence for  $[AsF_5(SO_3F)]^-$  as intercalant is based on  $^{19}F$  NMR spectra of the solid material.  $C_{14}^+ [AsF_5(SO_3F)]^-$  is found to exhibit high electrical conductivities in the basal plane.

INTRODUCTION

The intercalation of arsenic pentafluoride,  $AsF_5$ , into graphite, first reported by Selig and coworkers [1], has been in the past extensively studied for two major reasons:

- (i) The unusually high electrical conductivity reported for the resulting graphite intercalation compounds has aroused much interest in these materials [2], and
- (ii) while the composition for stages 1 to 3 is given by the general formula  $C_{8n}AsF_5$ , where n is the stage [3], the oxidation state of the intercalant and the extent of charge transfer have produced much discussion [4] in the past.

The equilibrium:



first proposed by Bartlett and coworkers, [5]-[7] appears to have been generally accepted, but its exact position and hence the precise degree of charge transfer in the acceptor intercalation compounds is still subject to much debate [8].

A somewhat clearer picture should be expected for the graphite hexafluoroarsenates(V), because only As(V) in the form of the  $\text{AsF}_6^-$  should be present, with the stoichiometry indicating the extent of charge transfer. Subsequently two different structural types have been reported: Cyclic pumping on  $\text{C}_{8n}\text{AsF}_5$  to remove  $\text{AsF}_3$  and  $\text{AsF}_5$ , followed by further interaction with more  $\text{AsF}_5$  leads to a material with a staging formula  $\text{C}_{12n}\text{AsF}_6$  [6][10]. More recently [6a] the composition proposed has been amended to  $\text{C}_{14}\text{AsF}_6$  with an interlayer separation of 7.6 Å reported. Fluorination of 1st stage  $\text{C}_8\text{AsF}_5$  with elemental fluorine [6], or oxidative graphite intercalation with  $\text{O}_2^+\text{AsF}_6^-$  [5] had been claimed to lead to  $\text{C}_8\text{AsF}_6$  as the limiting composition.

The simultaneous intercalation of  $\text{F}^-$  during the direct fluorination of higher stage  $\text{C}_{8n}\text{AsF}_5$  [6][9][11] or even the formation of covalent C-F bonds on fluorination [12] and the cointercalation of solvent, eg. nitromethane [12a] are some of the complications encountered en route to graphite hexafluoroarsenates. It appears then, that formation of simple binary graphite hexafluoroarsenates is by no means simple, that some existing formulations such as  $\text{C}_8^+\text{AsF}_6^-$  may have to be revised and that this aspect of graphite-arsenicfluorides is as controversial as the graphite -  $\text{AsF}_5$  system itself.

The graphite-arsenic pentafluoride intercalation compounds and the graphite hexafluoroarsenates differ in their basal plane electrical conductance. For  $\text{C}_{8n}\text{AsF}_5$  rather high, 'metallic', stage dependant conductivities are reported [9], [13]-[15]. Even though initial claims [16] of specific

conductivities higher than found for copper, could not be confirmed, graphite -  $\text{AsF}_5$  materials are the most highly conducting graphite intercalation compounds.

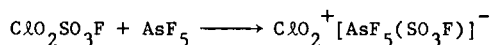
Noticeably lower basal plane conductivities are observed for graphite hexafluoroarsenates [9], [17], in particular for first stage compounds or materials, where direct fluorination with  $\text{F}_2$ , has produced  $\text{F}^-$  in lattice positions. A greater charge localization or the formation of covalent C-F bonds in these materials have been cited [12][17] as the principal reasons for this feature. In contrast higher stage graphite hexafluoroarsenates are again rather highly conducting [17].

We have been interested for some time in exploring new synthetic routes to graphite intercalation compounds, with graphite fluorosulfate as a convenient starting material. This compound, with a limiting composition of about  $\text{C}_7\text{SO}_3\text{F}$ , is easily obtained by the oxidative intercalation of bis(fluoro-sulfonyl) peroxide,  $\text{S}_2\text{O}_6\text{F}_2$  into various forms of graphite [7], [18] and [19] according to:



with  $n$  as low as about 7.

Solvolysis reactions of this material, best viewed as  $\text{C}_7^+\text{SO}_3\text{F}^-$ , in trifluoromethyl sulfuric acid,  $\text{HSO}_3\text{CF}_3$  [18] and in antimony pentafluoride,  $\text{SbF}_5$  [20], have resulted in a complete intercalant exchange and produced  $\text{C}_{12}\text{SO}_3\text{CF}_3$  and  $\text{C}_8\text{SbF}_6$  respectively. In particular the  $\text{SbF}_5$  reaction strongly suggests a possible extension to  $\text{AsF}_5$  as a suitable reactant. A precedent may be seen in the reaction of  $\text{AsF}_5$  with chloryl fluorosulfate,  $\text{ClO}_2\text{SO}_3\text{F}$  [21]:



The  $[\text{AsF}_5(\text{SO}_3\text{F})]^-$  ion has also been identified in solution in liquid  $\text{SO}_2$  by  $^{19}\text{F}$  NMR spectroscopy [22]. The previously mentioned high electrical conductivities of  $\text{AsF}_5$  containing graphite intercalation compounds supplies a good incentive for this study and preliminary results [23] have yielded an impure but highly conducting product.

We now report the synthesis and characterisation of a new first stage graphite intercalation compound of composition  $C_{14.3} [AsF_5(SO_3F)]$ , and results of electrical conductivity measurements in the system  $C_nSO_3F/AsF_5$ .

## EXPERIMENTAL

### Chemicals

Graphite powder (SPI-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 [24]. Arsenic pentafluoride was obtained from Ozark Mahoning Company and purified by repeated distillation in a metal vacuum line.

### 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 [25]. 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. Infrared spectra were obtained on a Perkin-Elmer 598 grating spectrophotometer. Gaseous samples were contained in a Monel metal cell of 8 cm path length, fitted with  $AgCl$  windows and a Whitey 1KS4-316 valve. 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 [26]. The ferrite core system was operated at an induction frequency of 16.8 kHz. This frequency was chosen after several trials to achieve a good signal to noise ratio while still avoiding skin depth problems [34]. Samples of low thickness (0.2 to 0.4 mm) were used both for calibration as well as for conductivity measurements. The electrical conductivity  $\sigma$  was evaluated from the relationship  $\Delta V = Kts^2\sigma$ , with  $\Delta V$  = voltage change observed in the sensory coil, measured with a Keithley 148 nanovolt 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 arsenic, sulfur 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 Carlo 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 [27].

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. The oxidative intercalation of  $S_2O_6F_2$  was performed in a Pyrex reaction vial fitted with Teflon stem valves (Kontes Glassware). The reaction was followed by recording weight changes. Intercalation of  $AsF_5$  was performed in a monel metal reactor of ~150 ml volume, fitted with a detachable lid with Teflon gaskets and a Whitey LKS4-316 valve.

Synthetic reaction

In a typical preparation 0.3380 g of  $C_{7.2}SO_3F$ , synthesised from graphite (SP1) and bis(fluorosulfonyl)peroxide [18], were transferred into a Monel metal reactor in the dry box. After evacuation of the reactor,  $AsF_5$  was transferred in vacuo, with the reactor at  $-198^\circ C$ . The amount of  $AsF_5$  was monitored by pressure changes in the vacuum system and calculated to give a pressure of approximately 5 atmospheres at room temperature inside the reactor. The reactor was allowed to warm up to room temperature and to stand for 48 hours, with occasional shaking to ensure that the solid particles were exposed to  $AsF_5$ . Volatile products were removed in vacuo with the reactor at  $-50^\circ C$ , collected and analysed by IR spectroscopy. With only a very slight residual pressure remaining, the reactor was allowed to warm to room temperature and opened inside the dry box. The reaction product was found to be an extremely moisture sensitive, dark blue powder. The material could be stored in a dry atmosphere without noticeable deintercalation.

Samples for conductivity measurements were prepared from HOPG plates in a similar manner. The predominant stage of the sample was determined by gravimetry and changes in sample thickness.

## Chemical analysis:

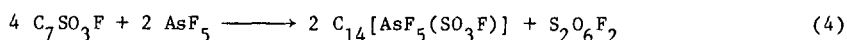
	C	As	S	F
Calculated for $C_{14.2}AsF_5SO_3F$ %:	38.80	17.05	7.29	25.94
Found %:	39.30	17.29	7.47	26.14

Ratio: As:S:F = 1:1.01:5.96

Interlayer separation:  $I_c = 7.92 \pm 0.03 \text{ \AA}$

## RESULTS AND DISCUSSION

The reaction of graphite fluorosulfate,  $C_7SO_3F$ , with arsenic(V) fluoride,  $AsF_5$ , results in the partial extrusion of fluorosulfate and the intercalation of  $AsF_5$  to form the intercalated anion  $[AsF_5(SO_3F)]^-$ . The following approximate reaction equation is suggested:



in analogy to the previously reported reaction of  $AsF_5$  with  $ClO_2SO_3F$  [21].

Supporting evidence regarding this reaction will now be discussed.

The reaction of  $AsF_5$  with  $C_7SO_3F$  should be performed in a metal reactor, with  $AsF_5$  purified by trap to trap distillation and contact with glass should be avoided. The metal reactor dried and conditioned prior to use permits the safe handling of  $AsF_5$  at pressures of about 5 atmospheres and avoids the formation of  $SiF_4$  as a byproduct. Initial attempts in glass vials, similar to the ones employed in the conversion of  $C_7SO_3F$  into  $C_8SbF_6$  by solvolysis in liquid  $SbF_5$  [20], had resulted in the formation of  $SiF_4$ , detectable in the volatile fraction by infrared spectroscopy. In addition the  $^{19}F$  NMR spectrum of the solid reaction product showed an additional signal at -176 ppm. Assignment of this line to  $SiF_4$  is based on a published precedent [28]. Since there has been a recent report on a graphite intercalation compound of the composition  $C_{24}SiF_5$  [29], some  $SiF_4$  may also be intercalated resulting in impure products.

The resulting graphite intercalation compound  $C_{14}[AsF_5(SO_3F)]$  has limited thermal stability. Gas evolution in vacuo starts at 40°C, with  $AsF_5$  initially the sole gaseous product as detected by its infrared spectrum [30]. At 60 to 70°C deintercalation of  $SO_3F$  as  $S_2O_6F_2$  is noted, again identified by its infrared spectrum [31]. Initial release of  $AsF_5$  on heating and a similar limited thermal stability are also reported for  $ClO_2[AsF_5(SO_3F)]$  [21]. Evidence for the formation of  $AsF_3$  during the thermal decomposition is not obtained.

The limited thermal stability of  $C_{14}[AsF_5(SO_3F)]$ , as well as its high sensitivity towards moisture affect the microanalysis for carbon adversely. During sample manipulation and weighing prior to combustion slight fuming and weight loss are noted. Subsequently values for carbon content are slightly higher than expected, an unusual occurrence for fluorine containing graphite intercalation compounds, where incomplete combustion due to some  $CF_4$  formation results commonly in a lower carbon content than indicated by gravimetry. It appears that partial deintercalation, perhaps promoted by the presence of moisture results in erroneously high carbon values. The analytical data for As, S and F obtained on the sample allow an indirect determination of the carbon content, by calculating first the  $AsF_5(SO_3F)$  content (61.98%) with the remainder, 38.02% assumed to be carbon. This would suggest a composition of  $C_{13.7}[AsF_5(SO_3F)]$ . For simplicity formulation as  $C_{14}[AsF_5(SO_3F)]$  is maintained throughout this discussion.

It appears that  $C_{14}[AsF_5(SO_3F)]$  represents the limiting composition for this intercalation compound. The 1st stage nature of this material is evidenced by the observed interlayer separation  $I_c$  of  $7.92 \pm 0.03 \text{ \AA}$  and the position of the Raman active lattice vibration  $\nu_{E2g}$  at  $1636 \text{ cm}^{-1}$ . The interlayer separation has slightly increased from  $7.81 \text{ \AA}$  for  $C_7SO_3F$  [18] upon reaction with  $AsF_5$ , but falls below a value of  $8.10 \text{ \AA}$  reported for  $C_8AsF_5$  [3].

A good case for  $C_{14}[AsF_5(SO_3F)]$  as a new, unique intercalation compound rather than a mixture of  $C_8AsF_5$  and  $C_7SO_3F$  can be made along three general lines.

- i The composition  $C_{14}[AsF_5(SO_3F)]$  discussed above is different from an average composition of  $\sim C_{15}[AsF_5(SO_3F)]$ , expected for a 1:1 mixture of  $C_7SO_3F$  and  $C_8AsF_5$ .
- ii Microanalysis on several samples obtained under different conditions but always with  $AsF_5$  in a large excess has reproducibly



indicated a As:S ratio of very close to 1.0. This finding argues against a gradual replacement of  $\text{SO}_3\text{F}$  by  $\text{AsF}_5$  which may ultimately lead to  $\text{C}_8\text{AsF}_5$ , and would definitely result in variable As to S ratios, depending on reaction times and conditions.

iii The  $^{19}\text{F}$  NMR spectrum of  $\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$  is inconsistent with the presence of a mere mixture. The chemical shift data obtained together with relevant literature data are summarized in Table 1.

The  $^{19}\text{F}$  NMR spectrum of solid  $\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$  shows two single, well separated resonances. An intense, sharp signal at  $-54.0$  ppm rel. to  $\text{CFC}\ell_3$  is attributed to the  $\text{AsF}_5$  group, while a weaker line at  $+4.0$  ppm appears to be due to F in a  $\text{SO}_3\text{F}$  group.

TABLE 1

$^{19}\text{F}$  NMR data for  $\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$  and related compounds

Compound	$\delta(\text{As-F})$ ppm*	$\delta(\text{S-F})$ ppm*	Ref
$\text{C}_{14}\text{SO}_3\text{F}$	-	14.8	33
$\text{C}_8\text{AsF}_5$	-49.0	-	35
$\text{C}\ell\text{O}_2[\text{AsF}_5(\text{SO}_3\text{F})]$	-49.1	40.3	32
$\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$	-54.0	4.0	This work

\*  $\delta$  AsF and  $\delta$  SF rel. to  $\text{CFC}\ell_3$

The  $\text{SO}_3\text{F}$  resonance is shifted strongly upfield, relative to the corresponding line in the high resolution spectrum of  $\text{C}\ell\text{O}_2[\text{AsF}_5(\text{SO}_3\text{F})]$  dissolved in  $\text{HSO}_3\text{F}$  [32]. Upfield shifts on intercalation are commonly found in  $\text{SO}_3\text{F}$  containing graphite intercalation compounds. Graphite fluoro-sulfates,  $\text{C}_n\text{SO}_3\text{F}$ , with n ranging from 7-12, exhibit a single resonance in the range of 10 to 15 ppm depending on n [33], significantly different from the signal at  $+4.0$  ppm for  $\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$ .

The  $\text{AsF}_5$  resonance is shifted only moderately upfield relative to the corresponding high resolution values [21], [32]. Expected fine structure due to fluorine-fluorine coupling in the  $\text{AsF}_5$  group is apparently unresolved in the solid state spectrum.

Similarly no resolution of fine structure for the  $\text{AsF}_5$ -group is reported for solutions of  $\text{C}_{10}\text{O}_2[\text{AsF}_5(\text{SO}_3\text{F})]$  in  $\text{HSO}_3\text{F}$  [21], however for the  $[\text{AsF}_5(\text{SO}_3\text{F})]^-$  ion in liquid  $\text{SO}_2$  at  $-70^\circ\text{C}$ , two multiplets at  $-47.5$  and  $-69.6$  ppm respectively are observed [22].

It seems then, a distinct, albeit thermally rather labile  $[\text{AsF}_5(\text{SO}_3\text{F})]^-$  ion is present and formulation as  $\text{C}_{14}^+[\text{AsF}_5(\text{SO}_3\text{F})]^-$  is indicated. Greater charge delocalisation in the complex anion allows tighter packing compared to  $\text{C}_7^+\text{SO}_3\text{F}^-$ , on account of reduced anion repulsion. In contrast to the direct intercalation of  $\text{AsF}_5$  into graphite to give  $\text{C}_8\text{AsF}_5$  [1], [2], the reaction of  $\text{AsF}_5$  with  $\text{C}_7^+\text{SO}_3\text{F}^-$  to give  $\text{C}_{14}^+[\text{AsF}_5(\text{SO}_3\text{F})]^-$  represents an overall reduction of graphite rather than an oxidation and formation of  $\text{AsF}_3$  during this reaction is neither expected nor observed.

Not unexpectedly, considering the reduction in positive charge on graphite during the conversion reaction,  $\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$  shows rather high specific electrical conductance values. The results of our measurements are summarized in Table 2 on the following page.

While 1st stage graphite fluorosulfate is a rather poor electrical conductor with  $\sigma/\sigma_g = 2.1$ , its reaction with  $\text{AsF}_5$  results in a substantial enhancement of the specific conductivity, and the  $k/k_g$  values, representing the conductivity enhancement factor normalized for each carbon plane reach values of about 23. These high conductivity values, measured on first stage compounds, compare well to corresponding values for  $\text{C}_8\text{AsF}_5$  [10], [13], [14] and [34], and a similar carrier density is suggested for both  $\text{C}_8\text{AsF}_5$  and  $\text{C}_{14}[\text{AsF}_5(\text{SO}_3\text{F})]$ .

TABLE 2

Electrical Conductivities of  $C_{14}[AsF_5(SO_3F)]$  and related compounds

Sample (approx. stage)	$\sigma \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$	$\sigma/\sigma_g^*$	$k/k_g^{**}$	$t/t_o$
1 $C_{7.2}SO_3F/AsF_5$ (I) <sup>a</sup>	22.0	9.5	22.42 <sup>@</sup>	2.36
2 $C_{8.3}SO_3F/AsF_5$ (I)	21.1	9.1	22.61	2.50
3 $C_{14}SO_3F/AsF_5$ (II)	23.4	10.1	17.85	1.82
4 $C_{15.8}SO_3F/AsF_5$ (II)	26.9	11.6	18.40	1.56
5 $C_{20.5}SO_3F/AsF_5$ (III)	25.3	10.9	19.83	1.76
6 $C_{20}AsF_5$ (II)+(III)	37.0	16.0	24.16 <sup>@</sup>	1.51
7 $C_8AsF_5$ (I)+(II)	25.0	10.8	21.71 <sup>@</sup>	2.01
8 $C_{7.2}SO_3F$ (I)	4.8	2.1	5.81	2.60

\*  $\sigma/\sigma_g = 2.32 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ ,  $\sigma$  was evaluated as described in instrumentation section.

\*\*  $k/k_g$  denotes specific conductivity normalized per plane of graphite,  

$$k/k_g = \frac{\Delta V}{\Delta V_g}$$

@ Due to uncertainty in the value of  $\Delta V_g$ ,  $k/k_g$  was calculated according to:

$$k/k_g = \frac{\sigma}{\sigma_g} \times \frac{t}{t_o}$$

a The predominant stage of the material is given in brackets. Sample 6 may be a mixture of stage II and III as indicated by its  $t/t_o$  value, same argument holds for sample 7 as well.

Very similar high electrical conductivities are also obtained when higher stage graphite fluorosulfates are reacted with  $AsF_5$  inside the conductivity cell (samples 3 to 5). However these data must be viewed with some caution for the following reasons:

- i We have shown recently [34] that higher stage graphite fluorosulfates exhibit rather high specific conductivities already and enhancement effects upon reaction with  $AsF_5$  are rather small;

- ii It is not entirely clear whether  $[\text{AsF}_5(\text{SO}_3\text{F})]^-$  formation occurs in these higher stage materials. Thickness measurements still suggest the presence of higher stage materials even after exposure to  $\text{AsF}_5$ , but these measurements are of limited accuracy, and
- iii There could have been interaction between  $\text{AsF}_5$  and the glass system.

Nevertheless the conversion of  $\text{C}_7\text{SO}_3\text{F}$  into  $\text{C}_{14}\text{AsF}_5\text{SO}_3\text{F}$  provides an easy avenue to highly conducting materials which may prove useful for other graphite intercalation compounds.

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