

# NANO-SPACES AND ADSORPTION PROPERTIES OF THE NESTLED GRAPHITE INTERCALATION COMPOUND $C_{14}AsF_6$

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## Introduction

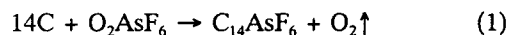
The ideal compositions for the nestling of  $AsF_6^-$  in the stage-1  $C_xAsF_6$  graphite intercalation compounds (GICs) have been determined to be  $C_{14}AsF_6$  at room temperature [1] and  $C_{16}AsF_6$  below 170 K [2], where the fluoride ligands of  $AsF_6^-$  are nestled in contiguous three-fold sets of carbon hexagons of the graphite. The exact ratios of C:As:F=14(16):1:6, however, are difficult to attain owing to the high reactivity of  $AsF_5/F_2$ . In the course of the study on nested  $C_xAsF_6$  [1], it was found that the direct solid-solid reaction of  $O_2AsF_6$  with graphite yields  $C_xAsF_6$ . We have recently found that this reaction is much faster than it had been thought at the time; the reaction proceeds essentially within a matter of 10 seconds when an effective mixing of the solids is applied. This reaction scheme was extended to graphite/ $O_2SbF_6$  system and GICs of hexafluoro-antimonate are synthesized for the first time. Adsorption isotherms of nitrogen at 77 K for  $C_xAsF_6$  and  $C_xSbF_6$  were measured. The nested  $C_{14}AsF_6$  adsorbs  $N_2$  up to the composition  $C_{14}AsF_6 \cdot \frac{1}{2}N_2$ , whereas the adsorption capacity of un-nestled compounds  $C_xAsF_6$  ( $x < 10$ ) is about 1/10 of that of the nested  $C_{14}AsF_6$ . This is attributed to the low in-plane density of guest species in the nested  $C_{14}AsF_6$ .

## Experimental

$AsF_5$  was prepared by the reaction of fluorine with As at above 200°C. It was purified by trap to trap distillation.  $SbF_5$  was purchased from Aldrich.  $O_2MF_6$  (M=As, Sb) was prepared by exposing a mixture of  $O_2$ ,  $F_2$  and  $MF_5$  to UV light [3]. A T-shaped reaction cell, whose branches consisted of a valve and two FEP tubes, was used for the preparation of GICs. Reactions were carried out as follows: SP-1 graphite powder (30–100 mg; Union Carbide) and  $O_2MF_6$  were weighed separately in an FEP tube, and after attaching the pressure gauge to the cell *via* the valve,  $O_2MF_6$  was transferred onto the graphite, and the mixture was shaken by directly hitting the end of the elastic FEP tube by fins of a small fan.

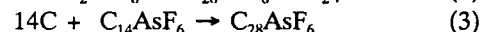
## Results and Discussion

Fig. 1 shows the reaction progress for the formation of nested  $C_{14}AsF_6$  monitored by pressure increase. The pressure rises according to the following equation:



Initially the cell was filled with nitrogen and the pressure was measured every second. At  $t \approx 40$  s  $O_2AsF_6$  was transferred onto graphite (*ca.* 100 mg). The reaction immediately started as the mixture was perturbed in an effort to transfer  $O_2AsF_6$  thoroughly. When a violent shaking started at  $t \approx 200$  s, the pressure increased drastically but stopped increasing within 10 s, indicating a very fast solid phase reaction.

Quite recently it was found that the stage-2 nested  $C_{28}AsF_6$  can be obtained according to either of the following two equations:



The reaction of eq. (3) was carried out by mixing graphite and  $C_{14}AsF_6$  in the same manner as for graphite and  $O_2AsF_6$ . It is to be noted that this reaction proceeds easily at room temperature indicating a high mobility of  $AsF_6^-$  anions within the graphite gallery and across the crystallites interfaces.

The reaction of graphite and  $O_2SbF_6$  yielded  $C_{12n}SbF_6$  with  $I_c = 8.21 + 3.35(n-1)$  Å where  $n$  is the stage. XRD patterns of  $C_xSbF_6$  do not indicate the nestling of  $SbF_6^-$  probably because of its larger size compared with  $AsF_6^-$ .

Adsorption isotherms of nitrogen at 77 K for nested and un-nestled  $C_xAsF_6$  are shown Fig. 2. Sample (b)  $C_{9.8}AsF_6$ , was made with  $AsF_5/F_2$ , and the other  $C_xAsF_6$  were made with  $O_2AsF_6$ . Samples (b)  $C_{9.8}AsF_6$  and (c)  $C_{11.9}AsF_6$  are un-nestled, whereas samples (d)  $C_{13.6}AsF_6$  and (e)  $C_{15.1}AsF_6$  are nested. Fig. 3 shows adsorption isotherms of nitrogen at 77 K for  $C_xSbF_6$ . As can be seen from the figures, the amounts of  $N_2$  adsorbed by the nested  $C_xAsF_6$  are significantly larger than those by the un-nestled  $C_xAsF_6$ ,  $C_xSbF_6$  and pristine graphite. The amount of  $N_2$  adsorbed by the nested  $C_{15.1}AsF_6$  corresponds to the formula  $C_{15.1}AsF_6 \cdot \frac{1}{2}N_2$ . This is because that in the nested  $C_{14}AsF_6$  the in-plane density of the  $AsF_6^-$  is low as shown in Fig. 4 [1]. This value of 14 is to be compared with 8 in  $C_{8n}AsF_5$  [4], 6–6.5 in  $C_{6-6.5n}SbF_5$  [5] and 12 in  $C_{12n}SbF_6$  where  $n$  is the stage. Without nestling,  $C_{14}AsF_{5-6}$  would be a mixture of stages-1 and -2 with higher in-plane density of guest species, which would hinder the incorporation of  $N_2$ .

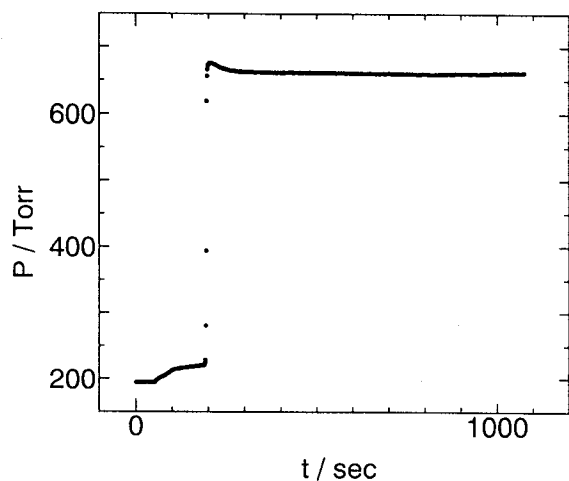


Fig. 1 Progress of the reaction of graphite with  $O_2AsF_6$  for the formation of nested  $C_{14}AsF_6$  monitored by pressure increase.

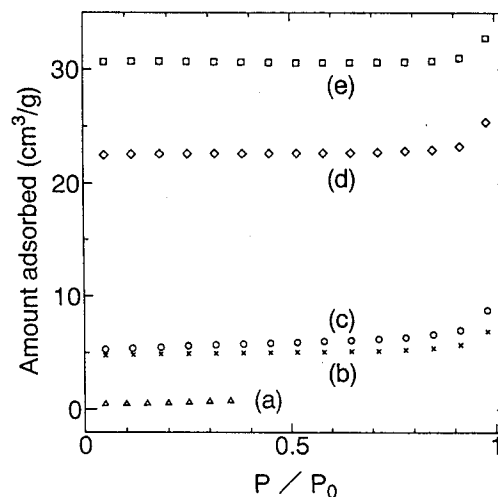


Fig. 2 Adsorption isotherms of nitrogen at 77 K for (a) graphite, (b)  $C_{9.8}AsF_6$ , (c)  $C_{11.9}AsF_6$ , (d) nested  $C_{13.6}AsF_6$ , and (e) nested  $C_{15.1}AsF_6$ .

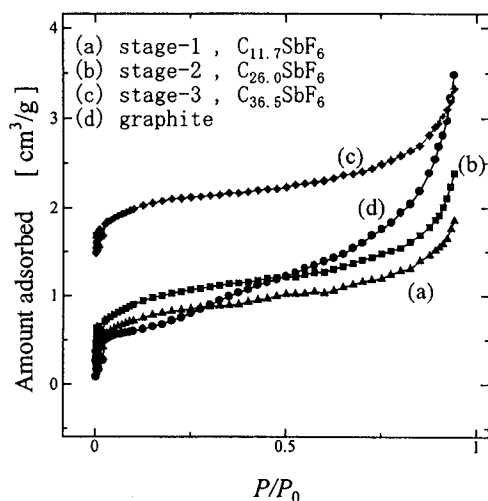


Fig. 3 Adsorption isotherms of nitrogen at 77 K for (a) stage-1  $C_{11.7}SbF_6$ , (b) stage-2  $C_{26.0}SbF_6$ , (c) stage-3  $C_{36.5}SbF_6$ , (d) graphite.

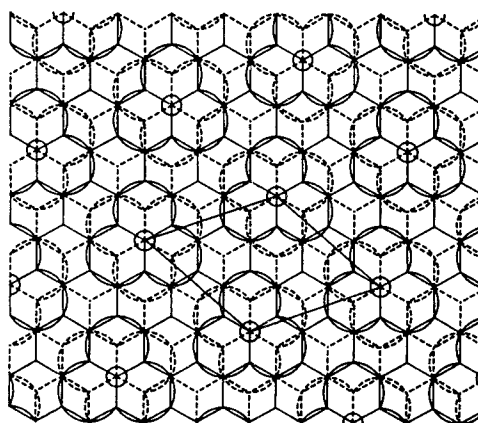


Fig. 4 In-plane  $\sqrt{7}\times\sqrt{7}$  arrangement of  $AsF_6^-$  for  $C_{14}AsF_6$ .

## Acknowledgments

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## References

[1] Okino F, Bartlett N. Hexafluoroarsenates of graphite from its interaction with  $AsF_5$ ,  $AsF_5+F_2$ , and  $O_2AsF_6$ , and the structure of  $C_{14}AsF_6$ . *J Chem Soc, Dalton Trans* 1993; 2081-2090.

[2] Okino F, Sugiura Y, Touhara H, Simon A. The order-disorder transition of stage-1 graphite fluoroarsenate intercalation compound: the structure of  $C_{16}AsF_6$  below 170 K. *J Chem Soc, Chem Commun* 1993;562-564.

[3] Shamir J, Binenboym J. Photochemical synthesis of dioxygenyl salts. *Inorg Chim Acta* 1968;2:37-38.

[4] Falardeau ER, Hanlon LR, Thompson TE. Direct synthesis of stage 1-3 intercalation compounds of arsenic pentafluoride in graphite. *Inorg Chem* 1978;17:301-303.

[5] Thompson TE, Falardeau ER, Hanlon LR. The electrical conductivity and optical reflectance of graphite- $SbF_5$  compounds. *Carbon* 1977;15:39-43.