Intercalation compounds of fluorinated graphite with camphor

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The title compounds of the composition $C_{2.22}FHal_y \cdot zC_{10}H_{16}O$ ($y = 0.1$ and 0.02 for Hal = Cl and Br, respectively) have been prepared and found to be the compounds of stage at $z = 0.14$.

The synthesis methods for intercalation compounds of fluorinated graphite (ICFG) with different organic compounds exhibiting mutual solubility are well known.[1,2] These methods are based on the following exchange reactions:

$$C_nHalF_m + Me_2CO \rightarrow C_xFHal_y \cdot z_1Me_2CO + R_1 \rightarrow C_xFHal_y \cdot z_2R_1 + z_1Me_2CO, \quad (1)$$

$$C_xFHal_y \cdot z_2R_1 + R_2 \rightarrow C_xFHal_y \cdot z_3R_2 + z_2R_1, \quad (2)$$

where $x \approx 2$. ICFG with ClF_3 or BrF_3, which were obtained according to procedures described in refs. 3 and 4 were used as the initial C_nHalF_m.

However, there is no publications on the methods providing intercalation of solids from solutions into fluorinated graphite using reactions (1) and (2). Methods based on the intercalation of solids from their solutions are widely used to synthesise intercalated graphite compounds.[5,6] Because of this, the development of the intercalation of solids from their solutions into fluorinated graphite is topical.

We studied the intercalation of camphor from acetone, ethanol and acetic acid solutions into fluorinated graphite. The solvents are able to form ICFG,[1,2] *i.e.*, to penetrate into the interstitial space of fluorinated graphite according to reactions (1) and (2). For this reason, the solutions of camphor as a model substance to be intercalated were examined in this study.

The synthesis of ICFG is described below. A weighed portion of C_nHalF_m (1–2 g) was placed in a Teflon vessel, acetone (20 ml) was added, and the mixture was kept at room temperature for 3 days. The solid phase was filtered off through a glass filter, washed two or three times with 5% camphor solutions in appropriate solvents, and kept in these solutions for 5 days. Next, the solid product was placed onto a filter and washed with the corresponding solvent to remove solid camphor impurities. Finally, the product was dried in a nitrogen flow to a constant mass. The absence of solid camphor in the resulting ICFG was checked by X-ray diffraction analysis.

^{1}H NMR spectra were recorded on a pulse Bruker SXP-4-100 spectrometer at a frequency of 90.01 MHz. IR spectra were recorded on a Specord 75-IR spectrometer. The samples of mass 3–3.5 mg were prepared as pellets with KBr. The composition of the ICFG was studied by elemental analysis for C, F, H and Cl (or Br). X-ray diffraction patterns were recorded on a DRON-3 diffractometer using filtered CuKα radiation (Ni filter). The patterns of samples under a layer of the liquid phase were recorded using a special Teflon cell covered with a Teflon film 5 μm in thickness. The patterns of dried samples were recorded using a quartz cell with applied vacuum grease.

^{1}H NMR spectra of dried ICFG with camphor at 298 K contained a single (within the range 0–25 kHz) rather narrow signal ($\Delta H_{1/2} \approx 2.151$ kHz), which is characteristic of the intercalated substances. This is the evidence of high mobility of camphor in the interstitial space of fluorinated graphite, which is typical of monomolecular layers of intercalated substances in layered compounds.[7,8]

Table 1 X-Ray diffraction data for ICFG.[a]

Intercalated compound	Under liquid solvent		After drying in air	
	$J_c = d_{001}$/Å	$d_i^a = J_c - 6$/Å	J_c/Å (experiment)	$J_c^b = d_{001} + 6$/Å (calculation)
Acetone	9.6	3.6	15.4	15.6
Ethanol	—	—	15.6	—
Acetic acid	9.3	3.3	15.6	15.3
5% camphor solution in:				
Acetone	11.5	5.5	11.5	17.5
Ethanol	11.6	5.6	11.6	17.6
Acetic acid	11.6	5.6	11.6	17.6

[a] d_i^a denotes the calculated data of the 'thickness' of intercalated monomolecular layers; J_c^b denotes the calculated data of the identity period for the stage 2 ICFG. Initial compound is ICFS with BrF_3.

X-ray diffraction patterns of dry samples exhibit (i) the retention of stage 1 in the ICFG with camphor, (ii) the transition of stage 1 into stage 2 for the ICFG with acetone, ethanol and acetic acid. The latter case is a common feature of the ICFG formed according to reactions (1) and (2) with volatile intercalants.[1,2]

Interlayer distances in fluorinated graphite containing no intercalants (in the initial ICFG with BF_3) are 6 Å.[9] This allows us to estimate the 'thickness' of intercalated monolayers of intercalants in the stage 1 ICFG as $d_i^a = J_c - 6$ Å and the identity period for stage 2 ICFG as $J_c^b = J_c + 6$ Å. X-ray data (Table 1) suggest that J_c for the stage 1 ICFG synthesised using 5% camphor solutions is ~11.6 Å and does not depend on the nature of solvent, *i.e.*, it is determined by the size and orientation of intercalated camphor molecules.

Figure 1 shows the IR spectra of the initial camphor, ICFG with acetone and ICFG obtained using a 5% camphor solution in acetone. The IR spectra of ICFG exhibit bands in the C–F bond absorption region (1100–1200 cm^{-1}), which are characteristic of the initial C_nHalF_m compounds and ICFG with liquid intercalants obtained from these compounds. The absorption bands characteristic of individual camphor (1020, 1050, 1385, 1410, 1450, 1740, 2840 and 2950 cm^{-1}) are observed in the IR spectrum of ICFG with camphor, similarly to the spectrum of the initial camphor, but the absorption bands corresponding to acetone (530, 1220, 1360, 1420, 1715, 2920 and 3000 cm^{-1}) are absent in this case (while they are observed in ICFG with acetone). The IR spectra of dry ICFG obtained from the solutions

Table 2 Composition of ICFG with camphor after drying in air.[a]

Experiment	Elemental analysis, found (calculated) (%)			Calculated (%)			Empirical formula
	C	F	Br	C_m	C_c	R	
1	64.56 (62.85)	27.89 (28.27)	2.00 (2.64)	39.12	25.44	32.27	$C_{2.22}FBr_{002} \cdot 0.144R$
2	64.22 (63.21)	28.13 (27.63)	2.30 (2.58)	39.42	24.80	31.46	$C_{2.22}FBr_{002} \cdot 0.140R$
3	61.49 (63.25)	26.82 (27.56)	2.40 (2.56)	37.62	23.87	30.29	$C_{2.22}FBr_{002} \cdot 0.141R$
4	61.47 (63.33)	26.62 (28.43)	2.10 (2.57)	37.32	24.15	30.64	$C_{2.22}FBr_{002} \cdot 0.143R$

[a] ICFG were prepared using a 5% camphor solution in ethanol (experiment nos. 1 and 2) or a 5% camphor solution in acetone (experiment nos. 3 and 4).

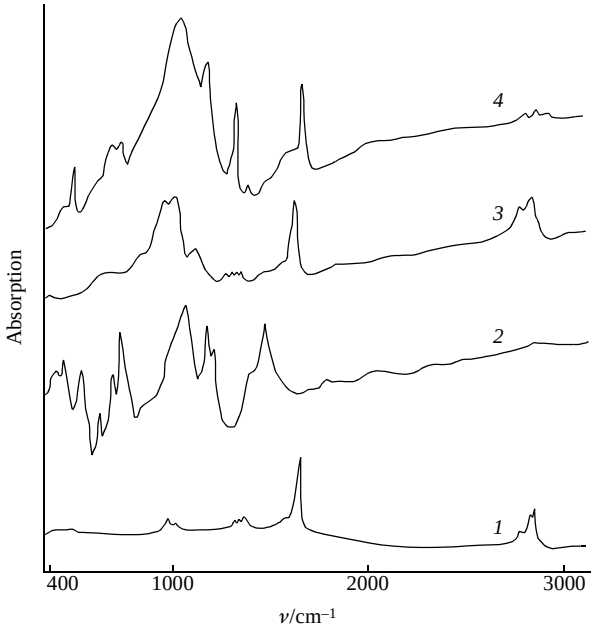

Figure 1 IR spectra of (*1*) camphor and (*2*)–(*4*) ICFG: (*2*) C_nBrF_m, (*3*) ICFG with a 5% camphor solution in acetone and (*4*) ICFG with acetone.

of camphor in ethanol and acetic acid are similar to the above spectra. These data allow us to assume that the solvents are absent from dry ICFG with camphor.

Based on this assumption and on the elemental analysis data (Table 2), the empirical formulae of dry ICFG with camphor (R) were calculated. In the absence of solvents in these ICFG, the total carbon (C) content of the ICFG described as $C_xFHal_y{\cdot}zC_{10}H_{16}O$ is evidently determined by the carbon of the matrix (C_m) and the carbon of camphor (C_c), or $C = C_m + C_c$. C_m was calculated using the atomic ratio of carbon to fluorine (C_m/F) in ICFG formed in reactions (1) and (2). It is known[10] that this ratio is close to 2.22 when C_nBrF_m is used. C_c was calculated as the difference $C - C_m$. This allowed us to calculate the empirical formulae of the obtained ICFG with camphor.

The data in Table 2 are the evidence of good reproducibility of the syntheses and show that the calculated camphor content of the dry ICFG is practically independent of the nature of solvent. This confirms the assumption that the solvents are absent from dry ICFG, which was based on the IR-spectral data. Table 2 shows that the empirical formula of dry ICFG obtained according to reactions (1) and (2) using C_nBrF_m and 5% camphor solutions in acetone, ethanol and acetic acid is close to $C_{2.22}FBr_{0.02}{\cdot}zC_{10}H_{16}O$, where $z \sim 0.14$.

Similar experiments and calculations showed that the composition of dry ICFG with camphor obtained using C_nClF_m is close to $C_{2.23}FCl_{0.1}{\cdot}zC_{10}H_{16}O$, where $z \sim 0.14$.

Thus, reactions (1) and (2) can be used to synthesise ICFG with solids. The decomposition of stage 1 ICFG in air, which was described in ref. 10 is not a common feature of ICFG. The stage 1 ICFG stable in air can be prepared when solids are intercalated from their solutions by reactions (1) and (2). Of course, the kinetic stability of these compounds is implied.

References

1 N. F. Yudanov, A. S. Nazarov and I. I. Yakovlev, *Tezisy dokladov VI Vsesoyuznogo simpoziuma po khimii neorganicheskikh ftoridov* (*Proceedings of VI All-Union Symposium on Chemistry of Inorganic Fluorides*), Novosibirsk, 1981, p. 94 (in Russian).

2 V. G. Makotchenko, A. S. Nazarov, G. C. Yur'ev and I. I. Yakovlev, *Zh. Neorg. Khim*., 1991, **36**, 1950 (*Russ. J. Inorg. Chem.*, 1991, **36**, 1110).

3 A. S. Nazarov, V. G. Makotchenko and I. I. Yakovlev, *Zh. Neorg. Khim.*, 1978, **23**, 1680 (*Russ. J. Inorg. Chem.*, 1978, **23**, 925).

4 Y. I. Nikonorov and L. L. Gornostaev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978, **9**, 55 (in Russian).

5 E. Stumpp, *Mater. Sci. Eng*., 1977, **31**, 53.

6 R. Vangelisti and A. Herold, *Mater. Sci. Eng.*, 1977, **31**, 67.

7 A. M. Panich, A. M. Danilenko, S. P. Gabuda and I. I. Yakovlev, *Zh. Strukt. Khim.*, 1988, **29** (2), 55 [*J. Struct. Chem*. (*Engl. Transl.*), 1988, **29**, 211].

8 A. M. Panich and N. F. Yudanov, *Zh. Strukt. Khim.*, 1991, **32** (2), 79 [*J. Struct. Chem*. (*Engl. Transl*.), 1991, **32**, 220].

9 N. F. Yudanov and L. T. Chernyavski, *Zh. Strukt. Khim.*, 1988, **29** (3), 78 [*J. Struct. Chem*. (*Engl. Transl.*), 1988, **29**, 412].

10 N. F. Yudanov and L. T. Chernyavski, *Zh. Strukt. Khim.*, 1987, **28** (4), 86 [*J. Struct. Chem*. (*Engl. Transl.*), 1987, **28**, 534].

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