Graphite Compounds with Chlorine Trifluoride

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Herrn Prof. Dr. E. Stumpp zum 60. Geburtstag gewidmet
Z. Naturforsch. 44b, 755–760 (1989); received March 7, 1989

Chlorine Trifluoride, Graphite Compounds, Graphite Fluoride, Graphite Intercalation Compounds

Graphite intercalation compounds of the acceptor type are formed with CIF₃ only at low temperatures near 0 °C. Different compounds are obtained in the absence or in the presence of HF. Thermal decomposition near room temperature or preparation at 20–50 °C lead to green or yellow-green graphite compounds of the covalent type, which differ, however, in their X-ray diffraction patterns and IR spectra from the graphite fluorides prepared at high temperatures.

Introduction

Many element fluorides and chlorides are intercalated in graphite [1]. Acceptor compounds are formed in the reaction, that means that electrons are transferred from the carbon layers of graphite — also called graphene layers [2] — to the intercalated substance. Either discrete anions are intercalated or the electrons are more or less delocalized in the intercalated layers as e.g. in FeCl₃-graphite.

Stage 1 acceptor compounds in which every interlayer space is filled with intercalate frequently have the general formula Cₓ⁺ₓEXₓ⁻⁻·mY with Y being either free element halide or solvent molecules; x has usually a value between 24 and 27. Such compounds present a steel-blue, metallic appearance due to the position of the Drude plasma edge. Higher stage compounds with a smaller proportion of filled interlayers between the graphene layers are shiny black.

Often, in the case of very reactive fluorides, the carbon layers will be more or less strongly fluorinated with formation of covalent C–F bonds. Surface fluorination has been observed even with SbF₅ after relatively long reaction times [3].

The intercalation of CIF₃ in graphite has been described in the literature but the reports disagree on the appearance and composition of the reaction products. Selig et al. [4] described a compound of the approximate formula Cₓ₁₆FClₓ₈ which did not differ markedly in its appearance from the original graphite. CIF₃ was formed as a by-product in the reaction. A green, hydrophobic product of the composition Cₓ₁₄Hₓ₂Fₓ₃ CIFₓ₂HFₓ⁻⁻ ( = Cₓ₁₄CIFₓ₃Hₓ) was obtained from a CIF₃ solution in anhydrous hydrogen fluoride at 22 °C [5]. Other authors found a compound Cₓ₁₄ₓxFₓ₅ₓ·1.5HF ( = Cₓ₁₄ₓCIFₓ₃Hₓ₁.₅) [6]. Pale-yellow, transparent platelets with the composition CₓF·0.46CIF₃ ( = Cₓ₊₂CIFₓ₃) were formed after 15–20 days at 0 °C with a solution of CsF in CIF₃ [7, 8]. The appearance and a very low electrical conductivity are indications that this compound is not an acceptor intercalation compound but a covalent compound related to graphite fluoride, (CFₓ)ₓ. It was concluded from the infrared and ¹⁹F NMR spectra that mobile CIF₃ molecules are intercalated between fluorinated carbon layers, no C–Cl bonds could be detected [8, 9]. In contrast, considerable electrical conductivity at 293–346 K was found by Nikonorov et al. [10]. Very recently it has been reported that no carbon fluorination occurs in the absence of HF [11]. With CIF₃, HF and F₂ black CClₐ₀.₀₆F₀.₅₂ ( = Cₓ₁₆ₓCIFₓ₅ₓ) and green CClₛ₀₁₀.₀₆F₀.₆₅ ( = Cₓ₂₀ₓCIFₓ₁₅ₓ) were obtained. Both compounds produced quite similar X-ray diffraction patterns.

With BrF₅, similar to CIF₃, the observations are also contradictory: a green compound has been described [12] whilst other authors [13] claimed that the appearance of the reaction product, Cₓ₈BrFₓ₃ was similar to that of graphite, apart from an increase in volume. Also compositions between Cₓ₈BrFₓ₁₂ [14] and Cₓ₁₆ₓBrFₓ₉ₓ [15] have been found for the reaction product of graphite with liquid BrF₅, indicating heavy carbon fluorination. According to Selig et al. the reaction product of graphite with BrF₅ of the approximate composition Cₓ₅BrFₓ₁₃ is very similar to the dark green material obtained with BrF₅ [4].
These discrepancies in the descriptions of the reaction products led us to study the reaction of graphite with CIF₃ in more detail. The green color seemed to indicate an electronic structure different from that in the usual acceptor compounds. We succeeded in preparing blue intercalation compounds at low temperature.

Experimental

Natural graphites of better than 99.5% purity were used: S 40 flakes with a particle diameter of 0.2—1 mm, and AF powder (1—10 μm) were from Kropfmühl, Bavaria; Madagascar flakes (ca. 1 mm) were also used. Authentic white graphite fluoride (CF₁₂)₉ was provided by the Ozark-Mahoning Co. (USA).

CIF₃ (98%) from Matheson Comp., and HF from Linde were used. The gases were first condensed at −60 °C into a Monel cylinder until the level of the liquid reached an electrode introduced through a screwed-in PTFE plug, producing an electrical contact between the electrode and the cylinder. Usually, 6 ml were thus condensed. The liquids, first HF, then CIF₃ were distilled into a second Monel cylinder containing between 1 and 5 g of the graphite. The temperature of this cylinder was thermostated (±0.5 °C) between 0 and 50 °C. After reaction times between 1 and 5 days, the excess reagent was blown out in an N₂ stream (for reaction temperatures of 20 °C or higher) and passed over crushed silicon for destruction of the CIF₃, or it was vacuum-distilled into a cold trap (−75 °C). The samples were finally dried in an N₂ stream. The apparatus, consisting of Monel and copper, was checked for leaks before each experiment. In a dry glove-box the samples were transferred to Schlenk tubes for further handling.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Starting material</th>
<th>Reaction temp.</th>
<th>Reaction time</th>
<th>Color</th>
<th>CI [%]</th>
<th>F [%]</th>
<th>Approx. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>S 40</td>
<td>0 °C</td>
<td>3d</td>
<td>blue-black</td>
<td>9.8</td>
<td>28.9</td>
<td>C₅₉IF₁₃</td>
</tr>
<tr>
<td>10</td>
<td>Mad.</td>
<td>0 °C</td>
<td>3d</td>
<td>dark blue, shiny</td>
<td>12.2²</td>
<td>37.3³</td>
<td>C₃₁IF₁₅</td>
</tr>
<tr>
<td>11</td>
<td>Mad.</td>
<td>5 °C</td>
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<td>blue-black</td>
<td>16.1</td>
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<tr>
<td>12</td>
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<td>5 °C</td>
<td>3d³</td>
<td>grey-black, shiny</td>
<td>10.6</td>
<td>44.4</td>
<td>C₁₂IF₁₅</td>
</tr>
<tr>
<td>9</td>
<td>AF</td>
<td>20 °C</td>
<td>2d</td>
<td>light blue, dull</td>
<td>10.7</td>
<td>31.9</td>
<td>C₁₆IF₁₅</td>
</tr>
<tr>
<td>4</td>
<td>S 40</td>
<td>20 °C</td>
<td>5d</td>
<td>blue-green, exfoliated</td>
<td>11.2</td>
<td>54.6</td>
<td>C₆IF₁₅</td>
</tr>
<tr>
<td>6</td>
<td>AF</td>
<td>30 °C</td>
<td>1d</td>
<td>olive green</td>
<td>14.5</td>
<td>34.5</td>
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For chemical analysis, parts of the samples were treated in a Parr bomb with a fused Na₂O₂/NaOH mixture (addition of a little diethyleneglycol-diethyther facilitated ignition on heating). Chloride was determined by potentiometric titration with 0.001 M AgNO₃, and fluoride by titration with 0.033 M La(NO₃)₃ at pH 5.5 with use of a fluoride-sensitive electrode (Orion). For Debye-Scherrer X-ray analysis the samples were filled into capillaries of Lindemann glass. Infrared spectra were taken by the KBr pellet technique.

Discussion

Table I presents the analytical data for a selection of typical preparations. At first sight, one sees that the color of most of the samples is the lighter, going from black to dark blue to green, and to yellowish-green, the higher the temperature of preparation was. An exception was sample no. 2 prepared at 12 °C which had the lightest color and a relatively high fluorine content. However, this sample was exfoliated indicating that there might have been a thermal excursion due to an exothermic reaction. Sample no. 4 which was also exfoliated had a similarly high fluorine content. The F/C ratio in the exfoliated samples was slightly above 1.00. On microscopic inspection such samples appeared inhomogeneous in color.

The green samples did not have a metallic luster and did quite obviously not belong to the group of metallic acceptor compounds. They were practically electrical insulators. The samples were hydrophobic, and most of them were stable in air or in contact with water. Fluoride and chloride could be detected in water only with samples prepared below 10 °C. The glass vessels showed traces of HF etching only after several days.

Table I. Preparation conditions and chemical composition of the reaction products of graphite with HF + CIF₃.

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² After spontaneous decomposition, see text; ³ reaction with CIF₁ only, no HF added.
The shiny, dark blue compound no. 10, however, began to decompose exothermally shortly after transfer to the Schlenk tube. Cl$_2$ or CIF was evolved and the glass was heavily etched, yet the flakes were barely exfoliated. The color of the material changed to blue-green within 10 hours. The analytical data, the diffractogram and the infrared spectrum could only be obtained from the decomposed sample.

The ratio of fluorine to chlorine was in most cases near to 5 ± 0.5, and higher in the samples which showed the lightest coloring. Nazarov et al. [8] had observed in their preparation a similar ratio of 5.17, although their pale-yellow material was richer in (Cl + F) than our compounds.

In a second set of experiments the graphite was treated with the vapor over a 1:1 (by volume) mixture of CIF$_3$ and HF. The liquid mixture and the graphite were maintained at the same, constant temperature. As shown in Table II, in this case the ratio F/C increased drastically with the temperature (the vapor pressure of pure CIF$_3$ increases from 0 °C to 12 °C only from $6 \cdot 10^4$ Pa to $9.7 \cdot 10^5$ Pa); there was also a marked decrease in the F/Cl ratio. The samples no. 13–15 contained free graphite and remained black. Only the freshly prepared sample no. 16 showed a distinct blue color, which changed to black after several days storage at −20 °C. Analyses and X-ray patterns were determined immediately after preparation in this case.

It has been claimed that carbon fluorination occurs only in the presence of HF [8, 11]. We found, however, that our sample no. 12 which was prepared without HF addition had a much higher F/Cl ratio than the material prepared at the same temperature with HF present. This sample differed from the other samples not only in appearance but also in its X-ray diffraction pattern. In this case a neat (00l) series with $l = 1$ to 4 was found whilst the other samples gave relatively broad reflections as listed in Table III. The (100) and (110) reflections were always present in addition, indicating no significant increase in the a-axis relative to graphite. With most

$$ \begin{array}{|c|c|c|c|c|c|}
\hline
\text{Sample} & \text{Starting} & \text{Reaction} & \text{Reaction} & \text{Cl [%]} & \text{F [%]} & \text{Composition} \\
\text{no.} & \text{material} & \text{temp.} & \text{time} & & & \\
\hline
13 & AF & 0 °C & 4 d & 0.89 & 7.7 & C_{30}\text{CIF}_{16} \\
14 & S 40 & 5 °C & 10 d & 1.40 & 9.4 & C_{30}\text{CIF}_{26} \\
15 & S 40 & 8 °C & 10 d & 2.46 & 11.9 & C_{30}\text{CIF}_{40} \\
16 & S 40 & 12 °C & 10 d & 7.66 & 19.6 & C_{30}\text{CIF}_{48} \\
\hline
\end{array} $$

Table III. X-ray diffraction patterns.

$$ \begin{array}{|c|c|c|c|c|c|}
\hline
\text{Sample} & \text{Observed reflections* [pm]} \\
\text{no.} & \\
\hline
12 & Four (00l) reflections for d$_l = 7.00$ pm \\
16 & 790 s \\
17 & 740 s \\
10 & 745 vs \\
11 & 745 vs \\
9 & 745 vs \\
4 & 760 vs \\
6 & 760 vs \\
5 & 760 vs \\
2 & 745 vs \\
C_{12}\text{CIF}_{3} \text{H}_6 \text{[5]} & 664 vs \\
C_{6}\text{CIF}_{2} \text{[8]} & 750 vs \\
\text{CF}_{3}\text{F}_{19} & 577 s \\
\text{C}_{2}F_{23} \text{[23]} & \approx 815 vs \\
\hline
\end{array} $$

* (100) and (110) of the graphene layers were always observed (=213 and =123 pm). In most samples also weak reflections fitting the pattern for NiSiF$_6$·6 H$_2$O were observed.
samples there were faint sharp lines corresponding to the most intense lines of NiSiF$_6$·6H$_2$O (ASTM index 8–8). One sample showed these lines in higher intensity allowing identification. Other transition metal hexafluorosilicates give similar diffraction patterns. Presumably, the ClF$_3$ was contaminated with SiF$_4$. The samples had been exposed to moist air during filling of the capillaries; very likely this is the source of the water of hydration. On thermal decomposition of the samples small concentrations of SiF$_4$ could be detected in the gaseous products together with ClF$_3$ and ClF.

The layer spacing of 700 pm of sample no. 12 excludes double-layers of chlorine atoms in the intercalated layers as in AlCl$_3$-graphite ($d_1 = 954$ pm). The value of 700 pm would fit well, however, for a single layer of Cl atoms, as in AuCl$_3$-graphite ($d_1 = 680$ pm [16]), implying that the T-shaped ClF$_3$ molecules are intercalated in a flat position.

For graphite with intercalated hydrogen fluoride (oxidation with F$_2$) spacings larger than 750 pm or smaller than 670 pm have been reported [17].

The d values for the X-ray reflections are summarized in Table III. For comparison, the diffraction patterns described in the literature for the reaction products of graphite with ClF$_3$, are included in the table as well as those of CF$_{112}$ and C$_2$F. In the case of carbon monofluoride, CF$_{112}$, the layer spacing increases with decreasing F content [18].

There were only a few, relatively broad diffraction lines observed with the samples prepared in the presence of HF. Some of these can be indexed as second order reflections but there was no extended (00l) series as is usually observed with acceptor compounds. In the case of sample no. 16, the lines at 790, 385, 246 and 182 pm could be tentatively indexed as a (00l) series with $d_1 = 740$–770 pm. The strong peaks at 750 ± 10 and 530–550 pm seem to be both (00l) reflections as can be deduced from the analogy of the spot patterns of the lines in the case of large-flake preparations which show preferred orientation in the X-ray capillaries. There is no simple relationship between these spacings, they must arise from different phases. A clear interpretation of the diffraction patterns is not possible. Spacings of ca. 750 and 670–640 pm have also been observed for graphite chemically or electrochemically oxidized in anhydrous HF [17]. The general formula C$_x$F$_y$ (HF), suggests that these are acceptor-type compounds, however.

Infrared spectroscopy was used in attempts to elucidate the nature of the intercalated species. Fig. 1 shows a few typical spectra. Many of our spectra looked generally similar, with variations in the details. The spectrum of the decomposed compound no. 10 was similar to the spectra shown by Nazarov et al. [7, 8] for C$_{8,7}$ClF$_{5,2}$, but it is much better resolved. However, in their sample the peak near 1100 cm$^{-1}$ was much more intense than that at ca. 1220 cm$^{-1}$. There is general agreement that the absorptions at 1050–1100 cm$^{-1}$ and ca. 1220 cm$^{-1}$ arise from C–F bonds. The latter peak coincides with the main absorption of (CF$_{112}$)$_n$. Poly(tetrafluoroethylene) produces two bands at 1155 and 1225 cm$^{-1}$.

The samples no. 4 and 5 showed the absorption peaks of HF$_2^-$, but it cannot be ruled out that this
species was formed in the KBr pellet by hydrolysis (KBr contains always some moisture).

The peaks near 650 and 740 cm\(^{-1}\) have been ascribed to C\(_1\)F\(_2\) + [5]. Apart from the implausibility of the existence of such a species in the compounds, it follows from Fig. 1 that both peaks vary in their relative intensity, and hence cannot arise from the same species. The presence of C\(_1\)F\(_3\)\(^+\), which has been assumed by Nazarov et al. [7], can also be ruled out since this ion absorbs strongly in the range 400–600 cm\(^{-1}\) [19]. These authors ascribed the strong peak at 750 cm\(^{-1}\) to C\(_1\)F\(_3\). However, this compound produces weak absorptions at 760 and 742 cm\(^{-1}\), and a strong peak at 702 cm\(^{-1}\) [20]. Therefore, taking into account the shift to lower wave numbers by 30–50 cm\(^{-1}\) in the adsorbed state, one could associate the strong peak at 645 cm\(^{-1}\) with \(v_2\) of C\(_1\)F\(_3\). The peak at 320 cm\(^{-1}\) would fit with \(v_3\) of C\(_1\)F\(_3\) (328 cm\(^{-1}\)). However, \(v_3\) at 442 cm\(^{-1}\) is also intense for free C\(_1\)F\(_3\), and there are only weak peaks in our spectra near this wave number.

The sharp peak at 482 cm\(^{-1}\) with sample no. 4 could arise from SiF\(_6\)\(^{2-}\), with the second, somewhat larger band at 741 cm\(^{-1}\) [21] contributing to the relatively high peak near 745 cm\(^{-1}\). Contributions by CIF to this band (758 and 786 cm\(^{-1}\) [22]) appear possible, but this could be only a minor constituent. The peak at 745 cm\(^{-1}\) may also be caused by C–Cl bonds. The relatively weak absorption at 1585 cm\(^{-1}\) which also appears in some of our spectra has been attributed to C=Cl double bonds [7].

No IR spectra could be measured with the samples no. 11–17 because of their strong absorption.

**Conclusions**

True intercalation compounds of the acceptor type can be obtained with C\(_1\)F\(_3\) only at low temperatures, near 0 °C. In the absence of hydrogen fluoride a stage 1 compound with an interlayer spacing of 700 pm was found. However, in contrast to literature reports, heavy carbon fluorination occurred as well. Also in the presence of HF, metallic, blue first-stage compounds were formed, which are very unstable and decompose at room temperature to covalent graphite compounds. The intercalated species could not be determined but the presence of C\(_1\)F\(_3\) can be inferred from the instability and from the fact that some C\(_1\)F\(_3\) was evolved on heating. Graphite hydrogenfluorides are stable at room temperature.

During decomposition, or on preparation at slightly higher temperatures, the color of the preparations evolves from metallic blue to dull blue, green, and finally yellow. Possibly the green color results from the encapsulation of small blue particles in a yellow matrix. The hydrophobic, electrically insulating materials appear to be covalent graphite compounds. Their X-ray diffraction patterns are similar to those observed with other graphite-fluorine compounds. The infrared spectra show however, that the samples differ considerably from graphite monofluoride, (CF)\(_n\), Substoichiometric covalent (CF\(_{1-x}\))\(_n\) compounds, and also (C\(_2\)F\(_3\))\(_n\), are grey to black and show larger interlayer spacings.

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

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