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Study of the reactivity of chalcogen hexafluorides with graphite

A. Hamwi*, D. Claves, A. Senhaji

Laboratoire des Matériaux Inorganiques — CNRS UMR 6002, Université Blaise Pascal — Clermont-Ferrand, 63177 Aubière Cedex, France

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Abstract

The intercalation reaction of chalcogen hexafluorides, EF_6 (E = S, Se, Te), with graphite was investigated. It occured only under a fluorine atmosphere and first stage intercalation compounds were obtained with TeF_6 or SeF_6, as well as a partial graphite fluorination. SF_6 did not intercalate but catalyzed the complete fluorination of graphite. All compounds were characterized by X-ray diffraction, thermogravimetric analysis, infrared and ^{19}F NMR spectroscopies. Entities, such as TeF_6 and SeF_6 were identified. Others, such as EF_7^-, EF_8^{2-}, ..., and possible SeF_n polymeric forms could exist. In all cases, the presence of fluorinated graphite was found. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Graphite intercalation compounds; Chalcogen fluorides; Graphite fluorides; Fluorine

1. Introduction

Extensive studies have been carried out on graphite intercalation compounds (GICs), particularly with alkali metals and transition-metal chlorides [1]. Because of their low volatility and their low oxidation power, most transition-metal fluorides do not intercalate into graphite. Only volatile high valency metal fluorides or non-metal fluorides give intercalation compounds with graphite [2]. The great interest in fluoride–graphite derivatives is illustrated by numerous reviews concerning their electrochemical and lubricant properties [3].

Interhalogen and particularly halogen fluorides GICs have been reported. In these earlier compounds, an excess of fluorine atoms was found, indicating the carbon network fluorination [4], whereas main group V non-metal higher fluorides (AsF_5 and SbF_5, for instance) easily intercalate without carbon fluorination [5].

The intercalation of main group VI non-metal (S, Se, and Te) fluorides has not yet been studied, though previously mentioned by us some years ago [6]. In this paper, we will report the detailed synthesis and characterization of different compounds obtained by the reaction of chalcogen hexafluorides with graphite.

Whilst some fluorides (MoF_6, IrF_6, PtF_6, TcF_6, ReF_6, ...) [7–9] will intercalate into graphite in their pure state, others (WF_6, NbF_5, TaF_5, TiF_4, IF_5, BF_3, ...) will require the presence of an oxidizing atmosphere, such as chlorine or fluorine [2]. Because of their physico-chemical properties and their very low chemical reactivity, the intercalation of chalcogen hexafluorides appears very difficult. Indeed, these fluorides are almost inert, even towards air or moisture, except TeF_6 which is slowly but completely hydrolyzed by water. This may be the reason why the intercalation of these fluorides has not been studied.

2. Results and discussion

The high similarity in the physical and chemical properties of chalcogen hexafluorides leads us to suggest that their intercalation into graphite should occur under the same conditions. Indeed, all attempts to obtain a graphite mass increase by direct reaction of those hexafluorides (without fluorine), between −70°C and RT, for 10–24 h, failed. X-ray diffractograms showed no reflections other than those of graphite. On the other hand, under a fluorine atmosphere, a graphite mass increase was obtained in 10 h. A maximum weight uptake was obtained when the reaction time was prolonged to 24 h. This maximum corresponds to the formation of a first stage intercalation compound in the case of TeF_6 and SeF_6. As we will show below, SF_6 did not intercalate into graphite, whatever the reaction conditions. Therefore, the graphite mass increase obtained in this case is due to fluorine intercalation.

Generally, under the same conditions, graphite flakes need a longer reaction time than graphite powder to form

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* Corresponding author. Tel.: +33-473-407103; fax: +33-473-407108.
E-mail address: hamwi@chimtp.univ-bpclermont.fr (A. Hamwi).

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Table 1
Formula and d_1 (c parameter) value for first stage TeF_6 and SeF_6-graphite intercalation compounds

Fluoride	TeF_6		SeF_6	
	Composition	$d_1 \pm 0.03$ (Å)	Composition	$d_1 \pm 0.03$ (Å)
Flakes	$C_{19.02}TeF_{7.09}$	8.18	$C_{16.71}SeF_{7.35}$	8.16
Powder	$C_{19.17}TeF_{7.21}$	8.19	$C_{15.05}SeF_{7.60}$	8.20

intercalation compounds of given stage. Typical results are compiled in Tables 1 and 2, where only dark-blue first stage TeF_6 and SeF_6 GICs characteristics are presented. Fig. 1 shows the X-ray diffraction patterns of these compounds. In all cases, partial fluorination was systematically obtained when the reaction time was prolonged until the first stage formation. Compounds of high stage were obtained in shorter reaction time without partial fluorination (for example, third stage $C_{32.50}TeF_{6.10}$, $I_c = 15.20$ Å, was characterized and no Bragg reflections from graphite fluoride were observed).

It is well known that there are two distinct kinds of graphite fluorides [10]. The one prepared at high temperature (>300°C) under a fluorine atmosphere involves highly covalent C–F bond, and consequently, the planarity of carbon layers is lost [11,12]. The other form can be obtained at room temperature under F_2 in the presence of liquid or gaseous HF [11,13,14], gaseous mixture of HF-fluorides [15], or even in the presence of a very small amount of gaseous fluorides, such as HF, AsF_5, IF_5, OsF_6 [16], WF_6, or SbF_5 [3]. It has been suggested that the planarity of the graphene layers is preserved in such cases and that the C–F bonds have a semi-ionic character. According to these latest considerations, compounds obtained using SF_6 exclusively correspond to semi-ionic fluorinated graphite and have formulae $C_{6.0}F_{1.34}(SF_6)_{0.01}$ and $C_{7.0}F_{1.03}(SF_6)_{0.01}$ for graphite powder and flakes, respectively. Indeed, X-ray diffractograms show only ($h\,k\,l$) peaks characteristic of first stage CF_x (graphite fluoride), with $I_c = 5.25{-}5.50$ Å, in agreement with those of semi-ionic graphite fluorides [14]. This is also confirmed by IR spectroscopy, since IR spectra of these compounds (Fig. 2) exhibit a strong band in the 1020–1150 cm^{-1} range, which could be assigned to

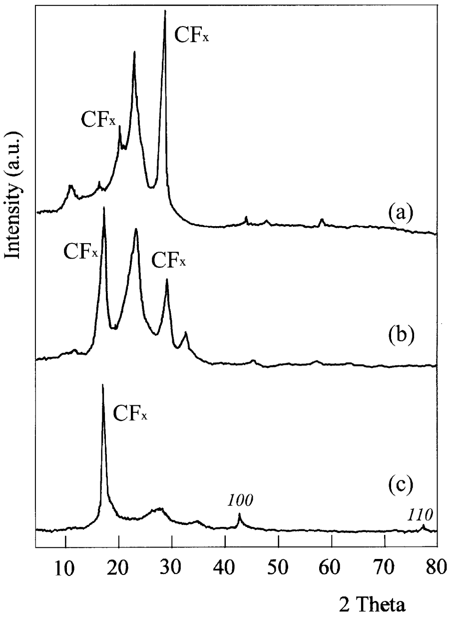

Fig. 1. X-ray diffraction patterns of compounds obtained by reaction of (a) TeF_6; (b) SeF_6; and (c) SF_6 on graphite flakes under a F_2 atmosphere.

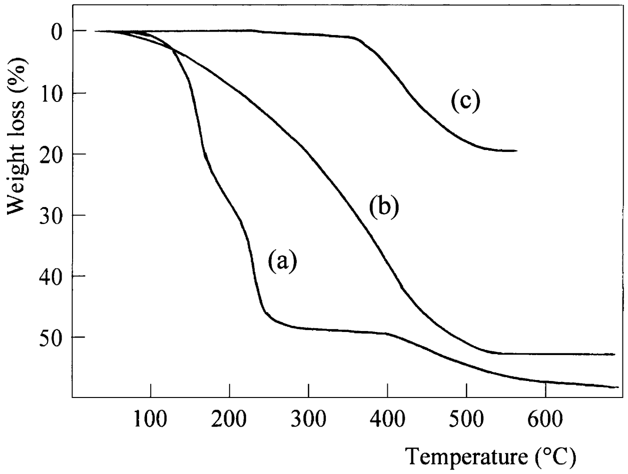

Fig. 2. FT-IR spectra of (a) TeF_6; (b) SeF_6; and (c) SF_6-graphite compounds.

Table 2
Experimental and calculated X-ray diffraction data for first stage TeF_6 and SeF_6–GICs[a]

$C_{19.02}TeF_{7.09}$; flakes; $d_1 = 8.18 \pm 0.03$ (Å)				$C_{16.71}SeF_{7.35}$; flakes; $d_1 = 8.16 \pm 0.03$ (Å)			
($0\,0\,l$)	d	$I/I_{0,\mathrm{exp}}$	$I/I_{0,\mathrm{cal}}$	($0\,0\,l$)	d	$I/I_{0,\mathrm{exp}}$	$I/I_{0,\mathrm{cal}}$
(0 0 1)	8.18	7	6.1	(0 0 1)	8.14	1	2
(0 0 2)	4.083	100	100	(0 0 2)	4.062	100	100
(0 0 4)	2.060	1.5	5.1	(0 0 3)	2.743	10	8.5
(0 0 5)	1.625	2	0.8	(0 0 4)	2.053	1.7	3.2
(0 0 6)	1.361		1.5	(0 0 5)	1.620	2.5	1

[a] I/I_0 calculated from isolated TeF_6 octahedrons and edge-sharing SeF_6 octahedrons, located at half distance from the graphene layers. Taking into account the existence of a fluorinated graphite phase, the E/F and E/C ratios were refined and gave compositions in the vicinity of the experimental ones.

semi-ionic C–F bond stretching. Concerning TeF_6 and SeF_6–GICs, other bands could be ascribed to Te–F and Se–F bonds in some specific species like TeF_6 (727 cm^{-1}), TeF_7^- (620 cm^{-1}) and SeF_6 (728 cm^{-1}) (near those reported in the literature: 752 cm^{-1} for TeF_6 [17], 620 or 625 cm^{-1} for TeF_7^- [18,19] and 780 cm^{-1} for SeF_6 [17]). The presence of SeF_7^- and SeF_8^{2-} species in these compounds cannot be directly established, since no infrared data are available. Some work [18,19] has already shown the existence of TeF_7^- in compounds, such as CsF–TeF_6 and $[N(Me)_4]TeF_7$ (main IR absorption bands are situated at 620–625 cm^{-1}) and the existence of TeF_8^{2-} in compounds, such as 2RbF–TeF_6 and $[N(Me)_4]_2TeF_8$ (main IR absorption bands are situated at 558 or 645 and 587 cm^{-1}, respectively). It should also be noted that, as observed in the present cases, the M–F ($M = W$, Mo, ...) absorption bands of the most similar species MF_7^- and MF_8^{2-} are generally situated in the range of 400–800 cm^{-1} [2]. Moreover, it seems that the Se–F band shifting of SeF_6 towards low frequencies (from 780 to 728 cm^{-1}) should be due to polymeric forms of intercalated SeF_n ($n < 6$), formed through the dissociation of intercalated species, after warming to room temperature following the synthesis process. It is well known that solid SeF_4 is polymeric (SeF_6 octahedral linked by Se–F–Se fluorine bridges) and Se–F band absorption is situated at 702 cm^{-1} [20]. Relative intensities (I/I_0) calculations of (0 0 l) X-ray diffraction peaks (Table 2) suggested the presence of fluorine atoms in the middle plane between two successive graphene layers, which is in agreement with the polymerization hypothesis (Se–F–Se fluorine bridges).

Fig. 3 shows the weight loss curves for the TeF_6, SeF_6, and SF_6-graphite samples, as a function of temperature. As generally known for GICs, the thermal decomposition of the TeF_6-graphite compound occurs in steps (Fig. 3a), forming several stable intermediates (second stage, third stage, ...). The SeF_6-graphite sample decomposes continuously (Fig. 3b), which seems to confirm the polymeric state of some intercalated species. The decomposition of the SF_6 based compound, which is thermally stable up to 380°C, almost corresponds to that of graphite fluorides already reported in the literature [15]. The end of the two previous decomposition curves can be compared to the latter, thus, confirming the presence of fluorinated graphite phases in these compounds. In all cases, after complete decomposition (fluoride and/or fluorine deintercalation) at about 500°C the remaining products were characteristic of pure graphite.

Fig. 4 shows room temperature ^{19}F NMR spectra of the EF_6-graphite based samples. Two kinds of line can be distinguished in the TeF_6 and SeF_6-graphite spectra. First, a narrow line is centered at +29 or +112 ppm, which is assigned unambiguously to TeF_6 or SeF_6 species, respectively (the chemical shifts δ of pure TeF_6 and SeF_6 are +20.6 and +128 ppm, respectively [21]). No more information is available concerning other forms of fluorinated chalcogens except for TeF_7^- ($\delta_{CFCl_3} = 16.1$ [19] or 17 ppm [22], extrapolated to the CF_3COOH reference: $\delta_{CF_3COOH} = +96$ or +96.9 ppm, respectively). No corresponding line was observed near +96 ppm because, at room temperature, a rapid exchange between the different fluorinated species may possibly occur, leading to a single averaged NMR line,

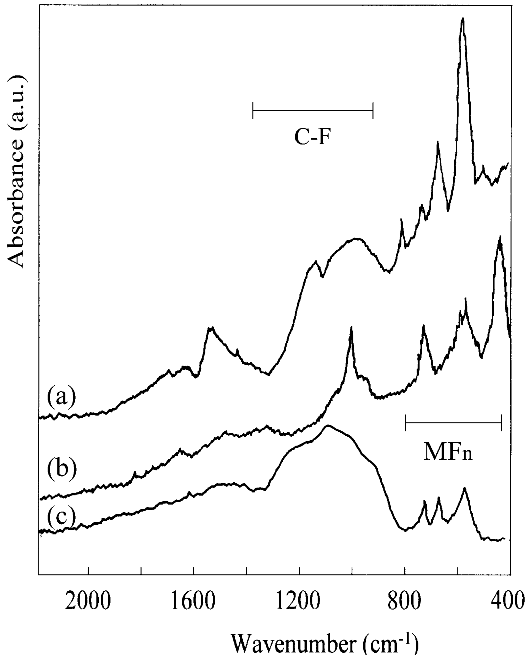

Fig. 3. TGA curves of powder samples: (a) $C_{19.17}TeF_{7.21}$; (b) $C_{16.71}SeF_{7.35}$; and (c) $C_{6.0}F_{1.34}(SF_6)_{0.01}$.

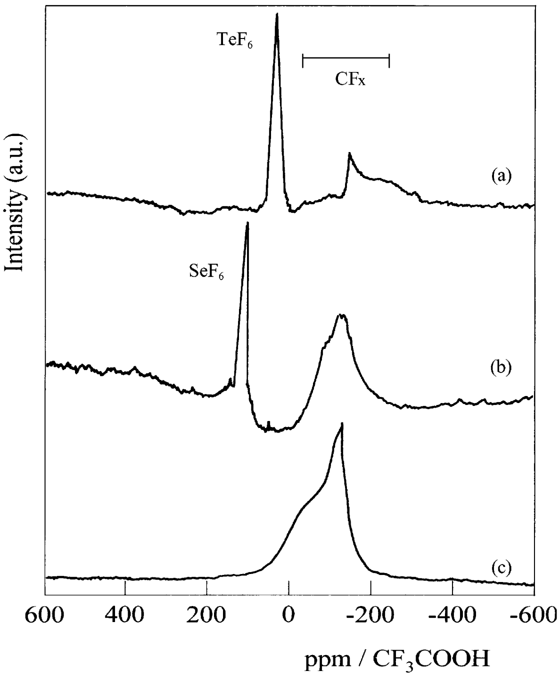

Fig. 4. ^{19}F NMR spectra of (a) TeF_6; (b) SeF_6; and (c) SF_6-graphite compounds.

close to the TeF_6 one which appeared as the main species. Secondly, one broad and asymmetrical line is displayed from 0 to -270 ppm for all compounds, which could be split into at least two components. By comparing these spectra with others reported for CF_x [23], it seems reasonable to assign these lines to the fluorine atoms directly bonded to the graphene layers. Different C–F bondings were characterized in this chemical shift range as covalent, semi-ionic or even ionic (F^- is shifted to -50 ppm [21] and F in covalent graphite fluoride is shifted to -120 ppm [23]). No line corresponding to SF_6 species was observed on the SF_6-graphite based compound NMR spectrum $\delta_{SF_6} = +127$ ppm [21]. This confirms that only graphite fluorination takes place in the presence of SF_6 and F_2, in good agreement with the above chemical analysis and IR results.

3. Conclusions

In spite of the high similarity in their physical and chemical properties, chalcogen hexafluorides do not behave in the same manner towards graphite. At low temperature, besides the formation of fluorinated graphite phases in the presence of F_2, TeF_6 and SeF_6 could be intercalated into graphite. SF_6 gave only fluorinated graphite compounds. The fluorination level of the carbon network increased in the order Te < Se < S. Besides intercalated TeF_6 and SeF_6, the presence of other intercalated species ($EF_7{}^-$, $EF_8{}^{2-}$, ...) could be considered. In addition, as known for some selenium fluorides, some polymeric forms should exist between graphene layers.

4. Experimental

Chalcogen hexafluorides EF_6 (E = S, Se, Te) were prepared by the reaction of elemental fluorine F_2 (Comurhex, purity 99.98%) with elemental chalcogen (10^{-2} mol, Aldrich, purity 99.8%), at room temperature, in a horizontal nickel reactor. EF_6 formed were then condensed in a vertical nickel reactor containing Madagascar natural graphite (3×10^{-2} mol, powder: ∅ #100 μm, or flakes: 1 mm in size). The graphite containing part of the reactor was maintained at a temperature between -30 and -40°C (slightly above the fluorides' sublimation points) and the reactor was then isolated under fluorine (1 atm). After 1 day, the reactor was heated to room temperature and the gas excess ($F_2 + EF_6$) was evacuated using a dry nitrogen flow. Graphite–fluoride products were removed from the reactor and handled in a dry glove box under pure argon atmosphere. Their chemical compositions were determined by elemental analysis (Service Central d'Analyse CNRS, Lyon, France) and were confirmed by mass uptake measurements. Samples were then characterized by X-ray diffraction (Cu Kα), NMR measurements, infrared spectroscopy (Nicolet FTIR 5SX spectrometer, KBr disks, 4000–400 cm^{-1} — only spectra between 2200 and 400 cm^{-1} are presented here as no band appears between 4000 and 2200 cm^{-1}), and thermogravimetric analysis. ^{19}F NMR spectra were measured on a Bruker MSL 300 spectrometer operating at 282.49 MHz for ^{19}F. Chemical shifts are expressed in ppm downfield from external CF_3COOH standard as positive values. All chemical shifts are given with a precision of ±5 ppm.

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