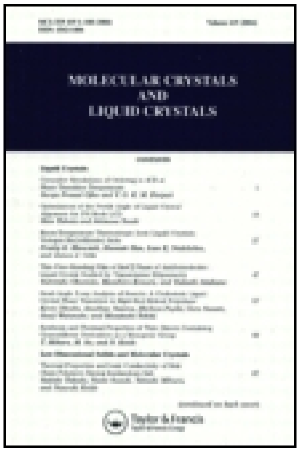

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Inorganic Fluorides - Fullerenes Compounds

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Inorganic Fluorides - Fullerenes Compounds

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Syntheses of new inorganic fluorides - fullerenes compounds with IrF_6, NbF_5 and TaF_5 were investigated. X-ray diffraction, IR and NMR measurements revealed the presence of anionic and reduced fluoride species. Some reactions with NbF_5, TaF_5, TiF_4 were performed under chlorine atmosphere as a result of which chlorinated compounds were obtained.

Keywords : fullerenes; inorganic fluorides; chlorination

INTRODUCTION

Because of its high ionization potential, insertion of electron acceptors in C_{60} is not a straightforward process. However, in a few studies the reactions of fullerenes with Lewis acids in liquid solution media are reported[1-3]. Particularly, the reaction of AsF_5 in a SO_2 solution has been investigated[2]. Meanwhile, we have reported the solid-gas reaction of C_{60} with MoF_6[4] whereby compounds having up to 9 MoF_6 per C_{60} were obained. We also studied the reaction with some inorganic fluorides such as NbF_5, TaF_5, TiF_4, ..., but the reaction ratios never reached the high MoF_6:C_{60} ones[5]. In addition, formation of reduced fluorides was observed.

We report here reactions of C_{60} with IrF_6, and the syntheses of compounds with higher NbF_5:C_{60} and TaF_5:C_{60} ratios. We also report on the influence of an oxidative chlorine atmosphere on the syntheses for some of these fluorides.

EXPERIMENTAL

Pure C_{60} (> 99.5 %) samples have been used. Reactions with solid fluorides were carried out using the same methods as previously described[5]. Gaseous IrF_6 was condensed onto C_{60} in a highly dehydrated Pyrex-glass tube. Reactions under chlorine atmosphere were carried out either in a Monel reactor or in sealed Pyrex-glass tubes containing C_{60}, metallic fluoride, and 2 to 5 atm of Cl_2. MF_n:C_{60} ratios were determined from C_{60} mass uptake.

X-ray diffraction, FTIR and solid state ^{19}F NMR spectroscopy were used for characterization. Thermogravimetric analyses (TGA) have been performed under dry argon with a heating rate of 4°C/min from 20 to 600°C. More details on the preparation and the characterization can be found in a previous publication[5].

RESULTS AND DISCUSSION

Reaction temperatures between 45 and 100°C during 5 to 11 days led to four different C_{60}-IrF_6 compounds with IrF_6:C_{60} ratios of 2, 6, 14, and 19. For IrF_6:C_{60} = 2, the X-ray diffraction pattern showed the presence of the fullerene lattice, as already observed for weak MoF_6:C_{60} ratios in C_{60}-MoF_6[4]. This was also confirmed by FTIR spectra on which the C_{60} characteristic bands were still present. For higher IrF_6:C_{60} ratios, the low crystallinity of the compounds did not permit X-ray diffraction studies. For all compounds, the various vibration modes of the Ir-F bonds in the 400-700 cm^{-1} region were observed (in literature data, IrF_4 : 691, 688, 545 cm^{-1};IrF_5 : 715-

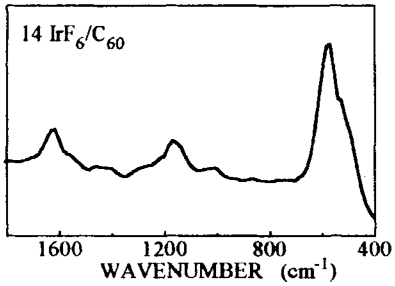

FIGURE 1 Infrared spectrum

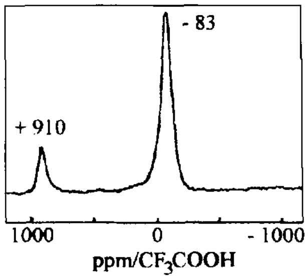

FIGURE 2 ^{19}F NMR spectrum

642, 533 cm^{-1}; IrF_6 : 719 cm^{-1}). The absorption in the 1125-1024 cm^{-1} region is characteristic of the C-F bond vibration (Fig. 1). The ^{19}F NMR spectrum of the 14 IrF_6:C_{60} (Fig. 2) showed two lines related to different IrF_x species centered at -83 and +910 ppm (CF_3COOH was used as external reference). This is different from the spectrum of pure IrF_6 which exhibits only one broad line at -126.5 ppm. The broad line at -83 ppm could be partially attributed to fluorinated fullerenes[6]. TGA analyses confirmed the presence of $C_{60}F_x$: a weight loss occured from 240 to 310°C[6]. A second weight loss beginning at 400°C probably shows the IrF_4 disproportion into IrF_3 and volatile IrF_5, as mentioned in the literature and observed by infrared spectroscopy.

We have already reported on the reactivity of fullerenes towards niobium and tantalum pentafluorides[5]. However, the MF_5:C_{60} ratios did not exceed 2. Using shorter reaction times, we succeeded to synthesize compounds with MF_5:C_{60} ratios as high as 6 and 10 (with M = Ta and Nb, respectively). These high ratios were obtained for the following specific reaction conditions : 210°C during 24 hours for TaF_5 and 150°C during 15 hours for NbF_5. X-ray diffraction patterns evidenced new isostructural phases for both fluorides (Fig. 3). These phases were observed even with low MF_5:C_{60} ratio compounds, in which C_{60} and MF_3 reflections predominate. As the diffraction patterns of these new phases turned out to be very complex, it was not possible to propose any structure up to now. Infrared spectra showed intense bands in the 400-700 cm^{-1} region (Fig. 4) assigned to reduced and anionic fluoride species such as MF_3, MF_6^-, MF_7^{2-} [5]. As already observed[4], the C_{60} characteristic bands intensities decreased as the MF_5:C_{60} ratio increased, and they completely disappeared for higher ratios (MF_5:C_{60} > 6). The presence of MF_6^-

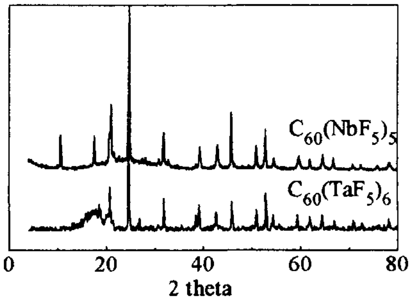

FIGURE 3 X-ray diffraction (Cu K_α radiation)

and MF_7^{2-} species was confirmed by ^{19}F NMR measurements. TGA analyses of high MF_5:C_{60} ratio compounds showed one weight loss for both fluorides corresponding to anionic MF_x species loss. C_{60}-TaF_5 compounds (decomposition at 310°C) appeared to be more stable than C_{60}-NbF_5 (decomposition at 210°C). Infrared and X-ray analysis of the residues showed the presence of MF_3 species, but no C_{60} could be detected.

Under 2 atm Cl_2 pressure, using the same reaction conditions as described above, high MF_5:C_{60} ratios have also been obtained, however, a partial chlorination of the fullerenes occured. X-ray diffraction patterns of compounds with weak mass uptake showed C_{60} and MF_3 phases, whereas in the case of great mass uptake the samples exhibited a low crystallinity. Infrared spectra were similar to those of C_{60}-MF_5 compounds (Fig. 4), but an additional broad band appeared at 850 cm^{-1} corresponding to C-Cl vibrations[7-9]. For higher C_{60} mass uptake, fluoride bands were the most intense ones (Fig. 4 : C_{60}-TaF_5-Cl_2). It is interesting to note that under the same conditions, pure chlorine did not react directly with fullerene material. The interpretation of ^{19}F NMR spectra of C_{60}-MF_5-Cl_2 compounds is more complex compared to those of C_{60}-MF_5. For example, C_{60}-NbF_5-Cl_2 spectra revealed a broad line between 0 and +300 ppm (Fig. 5) decomposed in three lines splitted at +146/+176 (assigned to bridged fluorines Nb-F-Nb : note that liquid and solid MF_5 phases are in polymeric form), +210 (assigned to NbF_6^-) and +252 ppm. The latter line may be attibuted to chlorinated fluorides such as NbF_5Cl^- species, considering that the NMR CF_4 line is shifted downfield with chlorine substitution. C_{60}-TaF_5-Cl_2 compounds generally revealed two broad

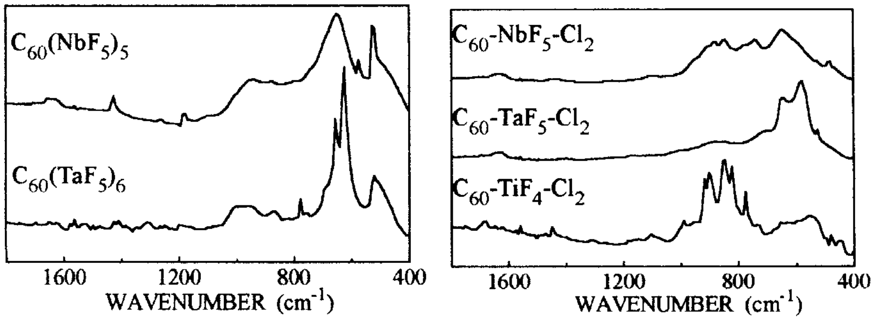

FIGURE 4 Infrared spectra

lines centered at +100/+150 and -100/-120 ppm (Fig. 5). Two narrow lines could be distinguished in the downfield broad line : +170/+180 ppm (assigned to TaF_5Cl^-) and +100/+110 ppm (assigned to TaF_6^-). The line at -120 ppm is very similar to that previously reported[5] and is probably due to Ta-F-Ta vibrations. The remaining compounds after TGA analysis showed C_{60} and reduced TaF_x species, but no C-Cl bond vibration was present.

In the case of the reaction of C_{60} with TiF_4, whatever the experimental conditions, no additional results were obtained compared to those previously published[5] (TiF_4:C_{60} ratios remained < 1). However, weak fullerene fluorination was observed at higher temperatures (350-450°C). Syntheses under chlorine atmosphere (0.5-5 atm) and at 300°C during few hours often produced orange compounds characteristic of highly chlorinated fullerenes[7-9]. The infrared spectra showed, as expected, the C-Cl vibration modes in the 800-900 cm^{-1} region, and a broad weak band in the 500-600 cm^{-1} region (Fig. 4) which should be assigned to metallic fluorides. The presence of fluoride species has been confirmed by ^{19}F NMR measurements. Depending on the Cl_2 pressure, two types of spectra were recorded (Fig. 5). For the higher pressure, a single narrow line was observed at -31 ppm, which was temperature independent. It probably corresponds to TiF_xCl_y species. For lower pressure, spectra revealed two broad lines at +142

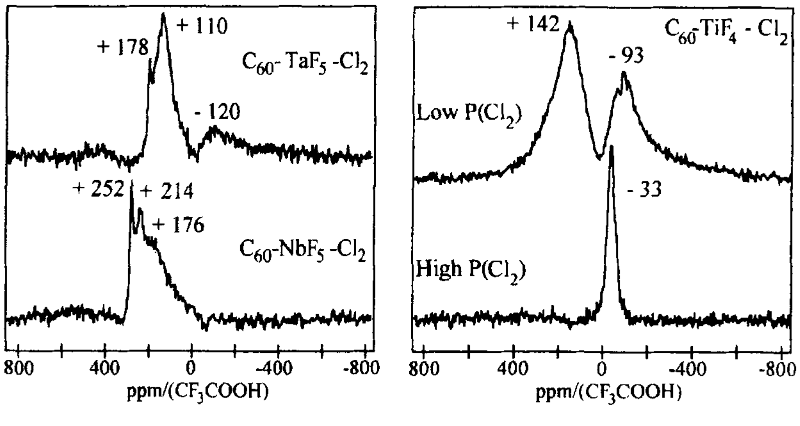

Figure 5 Solid state ^{19}F NMR spectra

and -100/-135 ppm. The first line may be assigned to TiF_6^- (TiF_6^- : +165 ppm), and also to $TiF_{4-x}Cl_x$ species. The second line is very similar to that of titanium tetrafluoride and therefore may be assigned to polymeric species.

CONCLUSION

Due to its high volatility, IrF_6 reacts readily with C_{60} to give amorphous compounds having considerable IrF_6:C_{60} ratio. Because of the vigorous fluorinating properties, the fullerenes underwent a partial fluorination and consequently reduced fluorides were formed.

High MF_5:C_{60} ratio compounds with good crystallinity could be prepared, but it seems that the MF_5:C_{60} ratio decreased with increasing reaction time. These new phases are still under investigation. As already observed, anionic MF_x species have been indentified. Their presence may suggest a fullerene oxidation process. In spite of the chlorine atmosphere, reduced metal fluorides oxidation did not occur, chlorine reacted more readily with MF_x-C_{60} to form MF_xCl_y-C_{60} compounds.

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