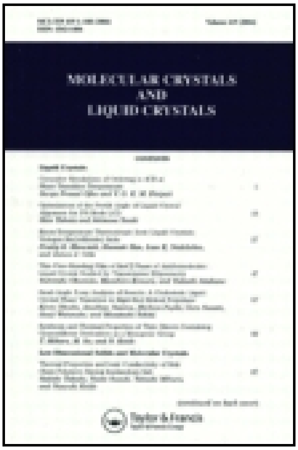

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Andre Hamwi [a], Gilles Dondainas [a] & Jacques Dupuis [b]

[a] Laboratoire de Chimie des Solides, URA, 444CNRS

[b] Laboratoire d'Electronique et de Résonance Magnétique Université, B. Pascal-Clermont-Fd, 63177, Aubière, France

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C_{60} COMPOUNDS WITH ACCEPTORS

ANDRE HAMWI*, GILLES DONDAINAS* AND JACQUES DUPUIS**
* Laboratoire de Chimie des Solides, URA 444 CNRS
**Laboratoire d'Electronique et de Résonance Magnétique
Université B. Pascal-Clermont-Fd, 63177 Aubière,France.

Abstract Intercalation compounds of C_{60} with MoF_6 were studied by means of X-ray diffraction, ^{19}F NMR, FTIR, EPR, and Li solid cell electrochemical discharge. They indicate the predominant presence of MoF_5 species suggesting an oxidative process of C_{60}.

INTRODUCTION

It has been demonstrated that solid C_{60} can be readily intercalated with electron donor substances such as alkali metals to give compounds with different dopant concentrations[1]. This involves electron transfer from alkali metal atoms to C_{60} molecules and suggests a large electron affinity of C_{60}. However, its oxidative intercalation by an acceptor remains, up to now, unknown. Although new compounds with Cl_2[2], Br_2[3], and I_2[4] were obtained, there is no electron transfer between C_{60} and the intercalate. As far as the fluorine is concerned, it forms compounds in which the ionic character of the C-F bond could not be confirmed[5]. In addition, it seems that fluorine reacts rapidly with a C_{60}/C_{70} mixture at room temperature but very slowly with pure C_{60}, resulting in both cases in highly fluorinated compounds and indicating the high reactivity of fullerene towards fluorine gas. This suggests a study of C_{60} behaviour with inorganic fluorides which are considered as strong Lewis acids. In this paper we report the first example, at present, of a fullerene intercalation compound with MoF_6 as the electron acceptor.

EXPERIMENTAL

A C_{60}/C_{70} mixture (about 80% of C_{60}) and pure C_{60} (>99.5%) samples, obtained from MGP-ISAR (France), were used. MoF_6 vapour reactions with C_{60} (about 50 mg) were carried out at room temperature or at 60°C, for several days, in monel reactors. After reaction, the excess of MoF_6 was evacuated using a dry nitrogen flow. Products were removed from the reactor in a dry glove box under argon atmosphere and then different physico-chemical measurements were carried out (for apparatus see reference 5). X-ray diffraction patterns were recorded using the Debye-Scherrer's method.

Results and discussion

Several compounds with different $C_{60}(MoF_6)_x$ compositions, depending on the reaction temperature, were prepared. At room temperature, for 4 to 6 days, using C_{60}/C_{70} mixture, compounds with $x = 2.6$ and $x = 3.5$ were obtained, while a temperature of 60 °C led to others with $x = 6$. Under these last conditions pure C_{60} gives an $x = 3$ compound. A higher MoF_6/C_{60} ratio was also obtained: $x = 9$ with C_{60}/C_{70} mixture when the reaction was carried out at 60°C for 2 days and further kept at room temperature for 2 more days. For all compounds, x values were determined by mass uptake.

X-ray diffraction shows patterns which depend on the x value. The $x < 4$ patterns are surprisingly similar to that of starting C_{60}. As the MoF_6 rate increases, peak intensities slightly change but no subsequent reflections appear for $x < 4$ samples although the sample volumes become higher. Formation of a mixture of an amorphous phase and unreacted C_{60} may explain this result. Intercalated molybdenum fluoride species may not occupy the octahedral and tetrahedral sites without significantly disturbing the C_{60} lattice, since the average MoF_6 Van der Waals radius is about 2.7 Å, while vacant octahedral and tetrahedral sites have radii of about 2.1 Å and 1.1 Å, respectively. Both $x = 6$ and $x = 9$ samples exhibit similar X-ray diffraction patterns which are very different from that of C_{60}, with nevertheless narrower and more intense reflections for the last sample, owing to a higher degree of crystallization. Data could perfectly be indexed on the basis of a hexagonal cell with constants a = 18.167 Å and c = 18.284 Å.

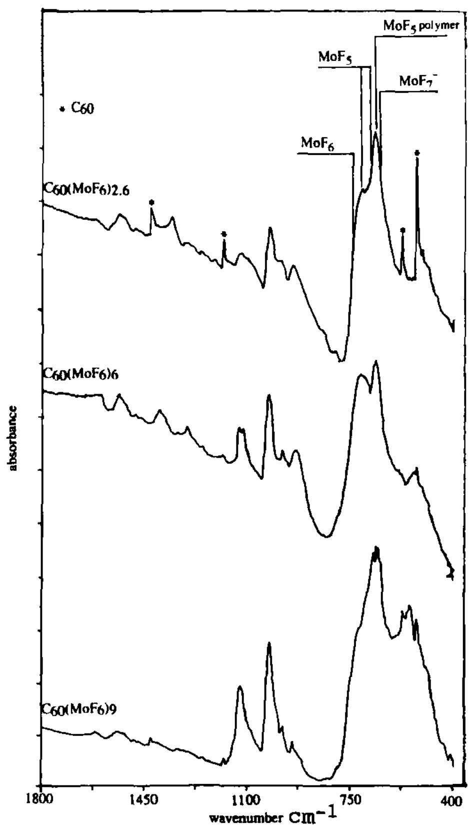
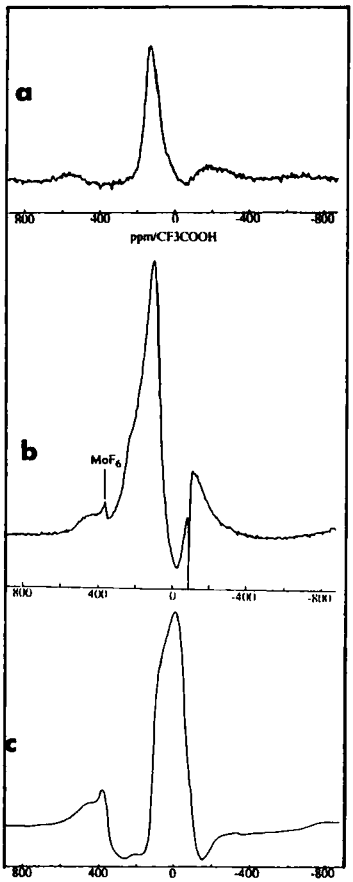


FIGURE 1 FTIR absorption spectra of different x samples

The FTIR spectra of some samples (4 mg diluted in 200 mg of KBr plate) are given in Figure 1. All show a main strong broad band in the 600-800 cm^{-1} region enclosing various vibrational modes of Mo-F bonds observed in different molybdenum fluoride species, such as MoF_6 vapour (742 cm^{-1}), monomeric MoF_5 (683, 713 cm^{-1}), tetrameric MoF_5 (660 cm^{-1}), and MoF_7^- (645 cm^{-1}). However, two smaller bands appear at

1125 and 1028 cm^{-1}, increasing as the MoF_6/C_{60} ratio increases, suggesting a partial fluorination of compounds since both may be related to semi-ionic and ionic C-F bonds[6] (covalent C-F stretching usually appears at 1250 cm^{-1}). In addition, it can be noticed that bands characteristic of C_{60} remain present whatever the MoF_6/C_{60} ratio, although it is much more evident for weaker MoF_6 contents.



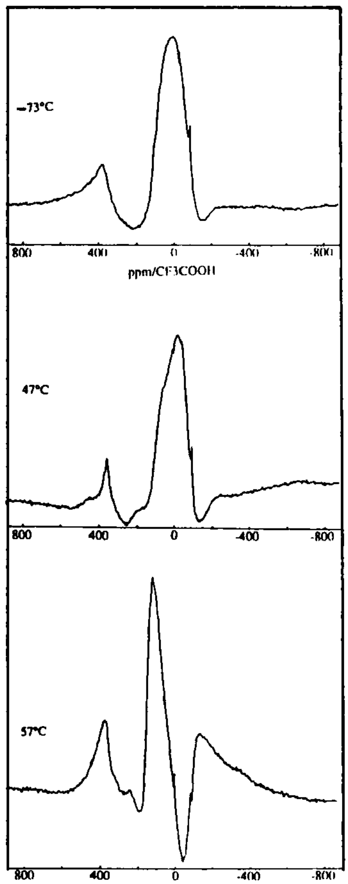


FIGURE 2 Room temperature ^{19}F NMR spectra of different samples: a) x = 3 (pure C_{60}), b) x = 6, c) x = 9

FIGURE 3 ^{19}F NMR spectra of x = 9 sample as a function of temperature.

Thermogravimetric analysis (TGA) of the x = 9 sample showed an initial weight loss at about 100 °C. Up to 350 °C the residual compound was found to be C_{60} by X-ray diffraction and IR measurements.

Room temperature ^{19}F NMR spectra of different x samples are given in Figure 2, whereas Figure 3 shows the temperature dependence of the x = 9 sample spectra. All exhibit a similar spectrum which is dominated by a broad peak, the position of which varies slightly as a function of x. This may be related to the concentration effect of different paramagnetic species. Moreover, a quite similar spectrum to those of Figure 2 was recorded for a pure solid MoF_5 sample.

The EPR signal with g = 2.72 and 2.56 obtained for x = 6 and x = 3 (pure C_{60}) samples, respectively, are similar to that of pure solid MoF_5. However, a very weak signal, recorded in the case of the x = 3 pure C_{60} sample with g = 2.003, could be identified.

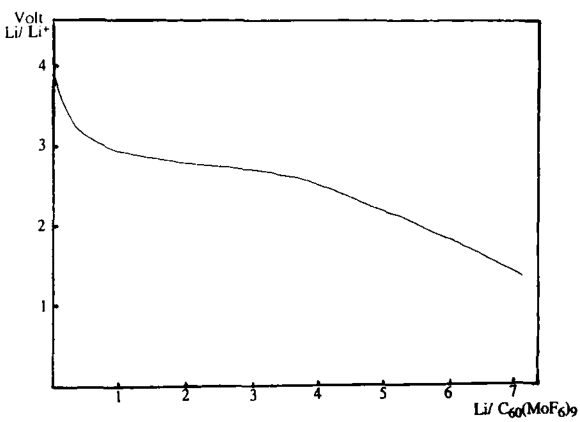


FIGURE 4 Galvanostatic discharge curve of Li / $P(EO)_8$, $LiClO_4$ / $C_{60}(MoF_6)_9$ polymer solid electrolyte cell under 7 $\mu A.cm^{-2}$.

The electrochemical reduction study was carried out using a Li / $P(EO)_8$, $LiClO_4$ / $C_{60}(MoF_6)_9$ polymer solid electrolyte lithium cell working at 80°C (PEO = polyethylene oxide). The discharge curve is presented in Figure 4. It shows a plateau potential at about 2.85 V vs Li/Li^+ corresponding to a 3 intercalated Li^+/C_{60}, and then a regular potential decrease occurs up to 8 Li^+/C_{60} intercalation. The first step could well be compared to that of graphite fluoride CF_x discharge-like cell[7].

In conclusion, MoF_5 appears as the predominant intercalated species suggesting the oxidation of solid C_{60} by MoF_6. At the moment, the number of charge transfer cannot be evaluated. Although the electrochemical discharge put forward at least a three electron transfer per C_{60} molecule at a constant potential, the nature of reduced species could not be distinguished and more characterization measurements are required. Finally, this example is considered as a first step on the route to the exploration of the properties of this novel type of C_{60} intercalation compounds.

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