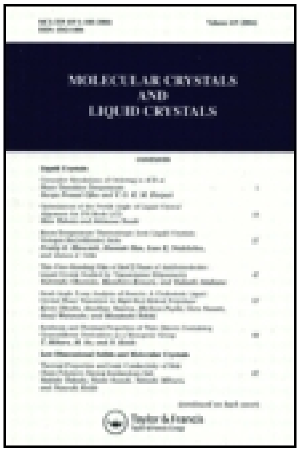

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Upon the Conversion of C_{60} Fullerene with Interhalogen Compounds

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Upon the Conversion of C_{60} Fullerene with Interhalogen Compounds

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C_{60} fullerene was converted with IBr as well as ICl. Two methods of preparation were used: Either the molten interhalogen compound was mixed up with C_{60}, or C_{60} was exposed to the vapour phase of the interhalogen compounds. After removing excess IBr or ICl respectively by gentle warming, the reaction products were ascertained to have the compositions $C_{60}(IBr)_{2.6}$ and $C_{60}(ICl)_{3.2}$. X-ray diffraction and Raman spectroscopy proved these compounds to be intercalation compounds. However besides intercalation, part of the C_{60} balls were found to undergo halogenization or dimerization. EPR spectra show two singlet lines corresponding to the C_{60}^{+} radical cation and a paramagnetic partially negatively charged interhalogen species. The C_{60}^{+} signal is comparatively broad, indicating a strong coupling between paramagnetic centers.

Keywords: fullerene, C_{60}, interhalogen compounds, IBr, ICl

INTRODUCTION

Since the discovery of C_{60} in 1985 by Kroto et al. and the elaboration of an efficient preparation method in 1990 by Krätschmer et al., a variety of studies on fullerenes chemical and physical properties have been performed. Among a multitude of derivatives, the intercalation compounds with alkali metals as K or Rb attract particular interest due to the appearence of superconductivity[1]. Unfortunately alkali metal doped fullerenes are very unstable in air, loosing their superconducting properties within minutes. Therefore various attempts have been made to prepare superconducting fullerene derivatives on the basis of other dopants. The similarity of the ionization potentials of C_{60} and several aromatic hydrocarbons, which are known as donors in charge-transfer-complexes[2], suggested to convert C_{60} with electron acceptors as I_2, Br_2, or Cl_2[3]. However the occurrence of superconductivity in these derivatives has not been found, not even in $C_{60}(I_2)_{1-2}$, which turned out to be an intercalation compound. In contrast, the conversion of C_{60} with ICl leads to the formation of a superconducting phase[4]. In this paper we present some results concerning the structure of C_{60}-IBr and C_{60}-ICl compounds.

EXPERIMENTAL

All substances used were of reagent grade and were used without further purification.

C_{60} was prepared as reported elsewhere[5].

IBr and ICl were prepared from the elements at 45°C, 5 h in the case of IBr and 22°C, 24 h in the case of ICl. Purification was performed by manifold crystallization.

For chemical analysis the C_{60} derivatives were disintegrated in boiling 20% NaOH solution containing 2% Na_2SO_3. The residue, consisting of C_{60}, was rinsed with water and subsequently dried and weighed. In the solution I^-, Br^-, and/or Cl^- were determined by titration with 0.1 M $AgNO_3$ using potentiometric indication.

Raman spectra were recorded at room temperature using a Bruker IFS 66 spectrometer attached to a Bruker FRA 106 Raman unit (Nd:YAG-laser, 1064 nm, 0-300 mW, resolution 1 cm^{-1}).

EPR spectra were recorded at room temperature with a Bruker ER 420 spectrometer at 9.8 GHz.

Thermal decomposition reactions in N_2 atmosphere were studied in a Sartorius 7092 magnetic suspension thermobalance.

X-ray powder diffraction patterns were obtained with a goniometer MZ 3, Röntgen-Seifert, Ahrensburg, using CuK_α radiation.

RESULTS AND DISCUSSION

C_{60} was converted with molten IBr at 50-60°C for 1-3 weeks. After 1 week the reaction proved not to be complete, whereas after 3 weeks only small brominated C_{60} fragments could be detected. Therefore for further experiments the reaction time was chosen to be 2 weeks. The raw product contained various amounts of excess IBr, which could be removed by passing over N_2 at room temperature. The composition of the final product was ascertained to be $C_{60}(IBr)_{2.6}$. A similar product was obtained by exposing C_{60} to IBr vapour at 60°C for 2 weeks in a sealed glass ampoule. The conversion of C_{60} with ICl under the same reaction conditions gave a compound with the stoichiometry $C_{60}(ICl)_{3.2}$.

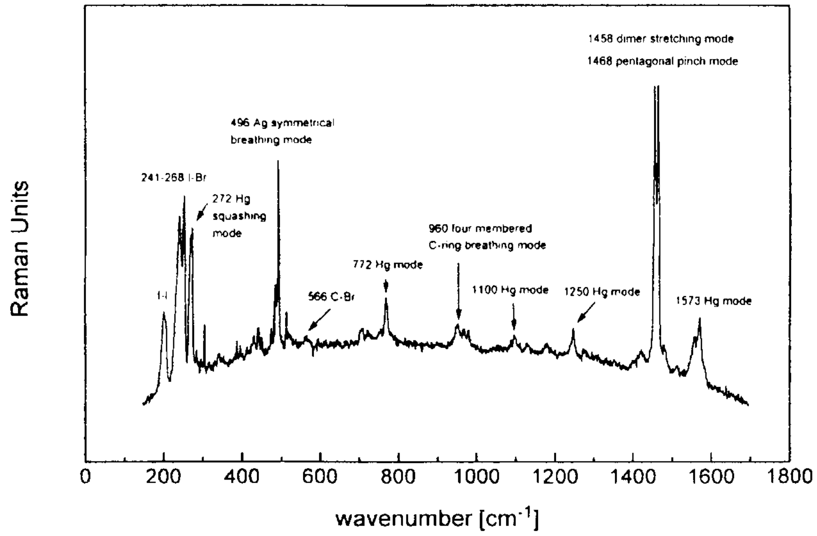

FIGURE 1: Raman spectrum of $C_{60}(IBr)_{2.6}$.

In the Raman spectra of $C_{60}(IBr)_{2.6}$ (Fig. 1) and $C_{60}(ICl)_{3.2}$ all fundamental vibrations of pure C_{60} can be detected. Furthermore the Raman bands of IBr or ICl respectively, as well as of I_2 are present. In addition C-Br or C-Cl vibrational bands can be observed. These results are consistent with the existence of intercalation compounds. However, upon intercalation a small portion of the respective interhalogen compound will attack the C_{60} ball causing bromination or chlorination. As a result, elementary iodine is found in the compounds. In the case of $C_{60}(IBr)_{2.6}$ two additional Raman bands, corresponding to the stretching and the breathing mode of a four membered carbon ring, occur. This four membered ring is formed between two C_{60} balls upon dimerization. This result is in accordance with the discovery that C_{60} tends to form oligomers upon the conversion with strong oxidizers.
The EPR spectra reveal two singlet lines, indicating an electron transfer from C_{60} to the interhalogen compound. The C_{60}^{+} signal is unusually broadened due to a strong coupling between the paramagnetic centers.
From the X-ray powder patterns it can be concluded that both C_{60} interhalogen compounds crystallize in orthorhombic cells with a=18.29 Å, b=16.69 Å, c=12.53 Å for $C_{60}(IBr)_{2.6}$ and a=10.23 Å, b=22.67 Å, c=14.81 Å for $C_{60}(ICl)_{3.2}$.
In Fig. 2 the thermogravimetric curve of $C_{60}(IBr)_{2.6}$ is displayed. As can be seen the main mass loss occurs at temperatures far below the decomposition temperature of covalently bonded $C_{60}Br_x$, which is an additional proof of the existence of an intercalation compound. However the mass loss above 175°C can be attributed to a small portion of Br covalently bonded to C_{60}. Equivalent results were obtained with $C_{60}(ICl)_{3.2}$. Attempts to grow single crystals of $C_{60}(IBr)_{2.6}$ and $C_{60}(ICl)_{3.2}$ in order to obtain a complete structural characterization by single crystal X-ray diffractometry are going on.

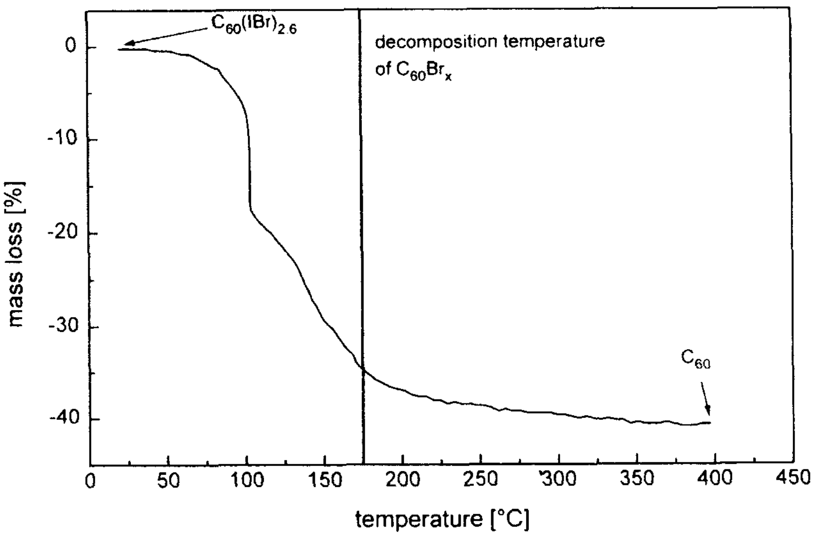

FIGURE 2: Thermogramm of $C_{60}(IBr)_{2.6}$.

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