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TIMS AND MALDI TOF OF ENDOHEDRAL $^{99m}\text{Tc}@C_{60}$ METALLOFULLERENE

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Abstract

Mass spectral studies (both TIMS – thermal ionization and MALDI TOF – matrix-assisted laser desorption time-of-flight mass spectrometry) of the endohedral metallofullerenes, $^{99m}\text{Tc}@C_{60}$ and $^{99m}\text{Tc}@C_{70}$, provided detailed structural and reactivity information about these unusual species. MS experiment revealed that both fullerenes and endohedral metallofullerenes fragment by multiple C2 loss. However, a difference in the terminal fragmentation products was observed for metallofullerene relative to C_{60} , suggesting that the encapsulation metal strongly impacts the fragmentation product. Singly charged cations of the metallofullerenes ($M@C_n^+$) were completely unreactive in the gas phase with oxygenated compounds such as ethylene oxide: however, the corresponding neutral species appear to react readily with oxygenated species. Collisional dissociation of the ionized endohedral fullerenes listed above revealed multiple C2 loss (either as sequential C2 loss or larger C_{2n} eliminations) to generate similar terminal fragmentation products, which might be predicted due to the similar ionic radii of the encapsulated metals. The observed ionization energies of endohedral molecules were, 5.1 ± 0.1 eV and 5.3 ± 0.1 eV, respectively.

Introduction

During the last few years, considerable progress has been made in the exploration of metallofullerene chemistry especially that endohedral [1-3]. As is well known, fullerenes have a unique type of inner empty space with their unusual cage-like structures. A wide variety of metal atoms may reside in this space and form endohedral metallofullerenes. These new series of materials with novel physical and chemical properties are very important for their potential application as new types of superconductors, organic ferromagnets, nonlinear optical materials, functional molecular devices, magnetic resonance imaging agents, biological tracing agents, etc., which will have great influence over electronics, optics, electromagnetics and medicine. Up to now, many metals including Group 3 metals (Sc, Y, La), Group 2 metals (Ca, Sr, Ba), alkali metals (Li, Na, K, Cs) and some tetravalent metals (U, Zr, Hf) have been successfully encapsulated into a fullerene cage to form mono-, di-, and trimetallofullerenes. Especially, the important progress has been marked by the successful isolation and purification of many metallofullerenes, which has led to further investigation of their molecular structures, physical and chemical properties as well as electronic states by a variety of experiment means, particularly that of spectroscopy. Subsequently, an active search for new of the selective synthesis of individual metallofullerenes was performed *in situ* in a mass spectrometer with the aim of exercising mass spectrometric

monitoring of gas phase reaction products. In favourable cases, small amounts of TIMS reaction products could be collected directly from the mass spectrometer on a cold plate for additional MALDI TOF characterization, even before macroscopic amounts were available.

Results

Tc@C₆₀, and TcC₇₀: Tc carbonyl was the first Tc reagent used successfully for the *in situ* thermal ionization incorporation ^{99m}Tc into C₆₀ and C₇₀ in a mass spectrometer. A series of experiments performed at 400-800 °C with various C₆₀ or C₇₀/Tc carbonyl ratios showed that endohedral fullerenes were the main products (Figures 1 and 2) without impurities. Observed ionization energies for Tc@C₆₀ and Tc@C₇₀ were 5.1 eV and 5.3 eV respectively. The following crucial information about behaviour of these species were: (a) they are thermally stable, since vacuum resublimation did not result in a change in composition of the mixture. Subsequent MALDI TOF mass spectral analysis of the powdered material collected from the cold parts of the ion source after completion of the reaction precisely reproduced the results obtained during the *in situ* experiments. Singly charged cations of the metallofullerenes (M@C_n⁺) were completely unreactive in the gas phase with oxygenated compounds such as ethylene oxide: however, the corresponding neutral species appear to react readily with oxygenated species. Collisional dissociation of the ionized endohedral fullerenes listed above revealed multiple C2 loss (either as sequential C2 loss or larger C2n eliminations) to generate similar terminal fragmentation products, which might be predicted due to the similar ionic radii of the encapsulated metals. Electron impact fragmentation of Tc@C₆₀ is showed in Figure 3.

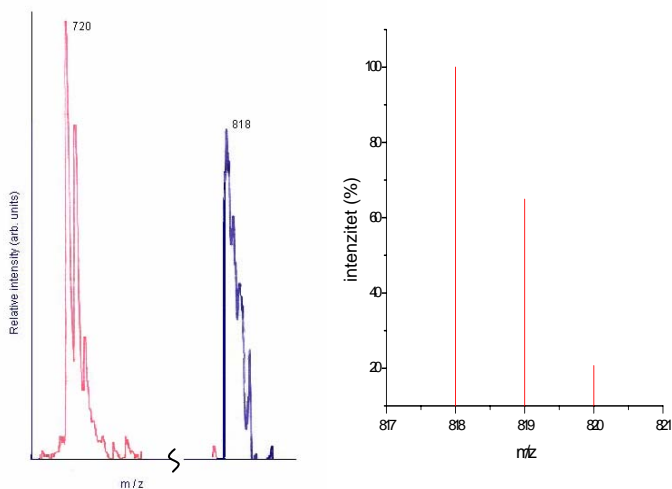


Fig. 1.

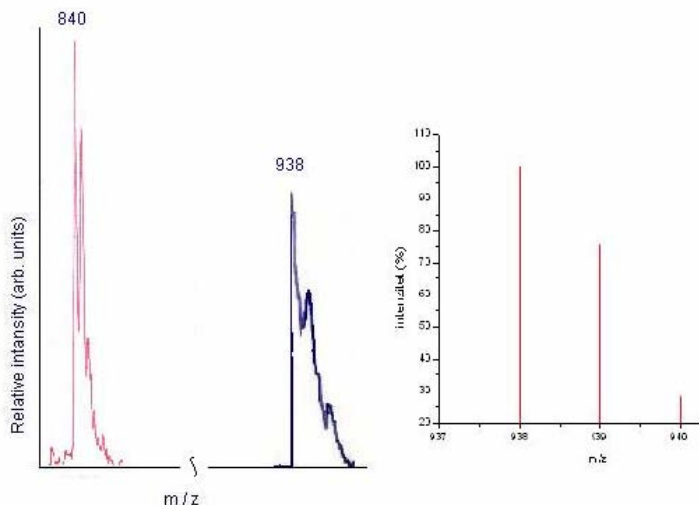


Fig. 2.

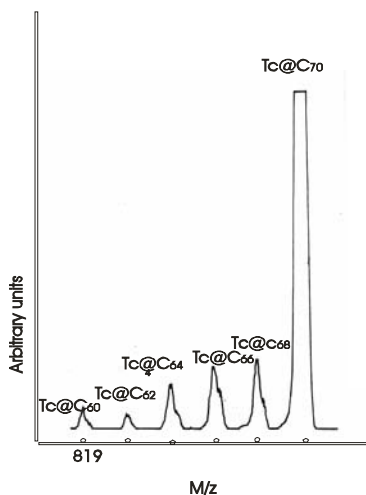


Fig. 3.

Fig. 1 and 2. Mass spectrum for an endohedral ^{99m}Tc C_{60} and C_{70} . experimental and theoretical spectrum.. In addition, one observes the isotopic composition of C_{60} and C_{70} .

Fig. 3. Electron impact fragmentation mass spectrum of $^{99m}\text{Tc}@C_{70}$.

Acknowledgments

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