



# PHYSICAL CHEMISTRY 2004

## *Proceedings*

*of the 7<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry*

*Volume I and II*

September 21-23, 2004  
Belgrade, Serbia and Montenegro



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Editors

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ISBN 86-82457-12-x  
Title: Physical Chemistry 2004. (Proceedings)  
Editors A. Antić-Jovanović and S. Anić  
Published by: The Society of Physical Chemists of Serbia, Student-  
ski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia  
and Montenegro  
Publisher: Society of Physical Chemists of Serbia  
Printed by: "Jovan" Printing and Published Comp;  
300 Copies; Number of Pages: x + 906; Format B5;  
Printing finished in September 2004.  
Text and Layout: Aleksandar Nikolić

*300 – copy printing*

## TIMS AND MALDI TOF OF ENDOHEDRAL METALLOFULLERENES

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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,  $\text{Li}@C_{60}$ ,  $\text{Li}_2C_{70}$  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  $5.9 \pm 0.1$  eV,  $5.3 \pm 0.1$  eV and  $5.7 \pm 0.1$  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

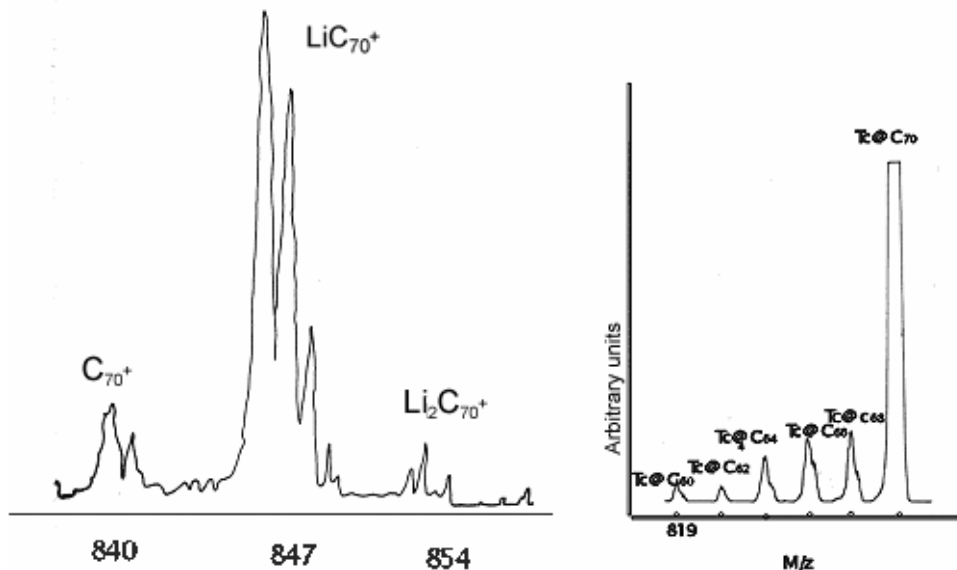
TIMS reaction products could be collected directly from the mass spectrometer on a cold plate for additional MALDI TOF characterization, even before macroscopic amounts were available.

## Experimental

The mass spectrometers used in this investigation were a 12-inch radius,  $90^\circ$  sector, magnetic instrument of local design and MALDI TOF Voyager De Pro (AB Applied Biosystem, UK). Thermal ionization instrument was equipped with a combined electron impact Nier-type and surface ionization source. The beam of the molecules to be investigated was produced by heating the  $C_{70}$ , LiI sample in a Re canoe in the vicinity of a Re ionizing filament, where a certain fraction of the neutrals are ionized (for  $Li_2@C_{70}$ ,  $C_{60}$  and LiI for  $Li@C_{60}$  and carbonyl Tc and  $C_{70}$  for  $^{99m}Tc@C_{70}$ ). The biological behaviour of fullerene derivatives shows their considerable potential for medical applications. We have produced, characterized and purified (in milligram quantities) endofullerenes containing Li or gamma-ray emitting  $^{99m}Tc$  by the metal ion implantation technique (by introducing negatively charged  $C_{60}$  or  $C_{70}$  into a low-temperature Tc plasma column by a strong axial magnetic field). Identification of and  $^{99m}Tc@C_{70}$  has been accomplished by application of ultra-low level radiation detection methods and mass spectrometry. Appropriately derivatized endofullerenes could be used as a pharmaceutical for medical imaging. Such encapsulation of Li and radionuclides in a carbon cage could facilitate their inert transport through biological systems and await further studies.

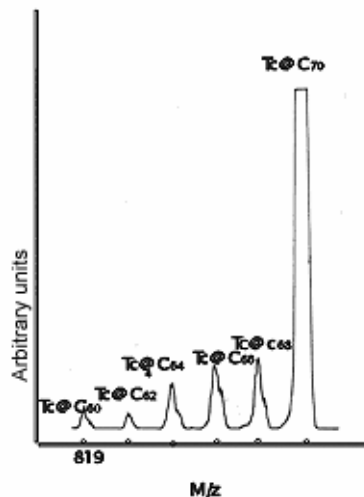
## Results

$Li@C_{60}$ , and  $Li_2C_{70}$ : LiI was the first Li reagent used successfully for the *in situ* thermal ionization incorporation Li into  $C_{60}$  and  $C_{70}$  in a mass spectrometer [4]. A series of experiments performed at 400-800°C with various  $C_{60}$  or  $C_{70}$ /LiI ratios showed that endohedral fullerenes were the main products (Figure 1) without impurities. Observed ionization energies for  $Li@C_{60}$  and  $Li_2@C_{70}$  were 5.9 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 (Figure 3). 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 (Figure 2).



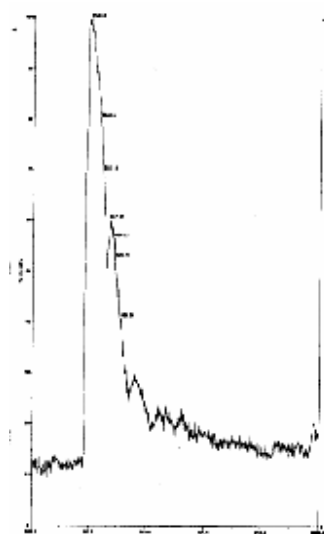
**Figure 1.** Mass spectrum for a  $C_{70}$ /LiI sample containing  $C_{70}^+$ ,  $Li@C_{70}^+$  and  $Li_2@C_{70}^+$  species.

The ratio of the filled to the empty fullerene is seen to be about 1.5: 8: 1. In addition, one observes the isotopic composition of Li and C.



**Figure 2.** Electron impact fragmentation mass spectrum of  $^{99m}Tc@C_{70}$ .

**Figure 3.** MALDI mass spectra (linear mode) of  $Li_2@C_{70}$ .



### Acknowledgments

This work was financially supported by the Ministry of Science and Environmental Protection, Republic of Serbia, under Project No. 1995.

### References

- [1] D.S. Bethune, R.D. Johnson, J.R. Salem, M.S. de Vries, S.C. Yannoni, *Nature*, 1993, 36, 123.
- [2] S. Nagase, K. Kobayashi, T. Akasaka, *Bull. Shem. Soc. Jpn.*, 1996, 69, 2131.
- [3] S. Nagase, K. Kobayashi, T. Akasaka, *J. Mol. Struc. Theochem.*, 1997, 398-399, 221.
- [4] A. Djeric, M. Veljkovic, O. Neskovic, M. Miletic and K. Zmbov, *Full. Sci. Tech.*, 2000, 8(6), 461.