# $La_2@C_{72}$: Metal-Mediated Stabilization of a Carbon Cage

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In this study, we report production, isolation, and characterization for the relatively small endohedral metallofullerene, $La_2@C_{72}$. As described, $La_2@C_{72}$ is readily isolated from conventional electric-arc-generated carbon/metal soot. This new species was purified by HPLC chromatography and characterized by laser desorption mass spectrometry and UV−vis spectroscopy. The mass spectrum also demonstrates the presence of the monometal species, $La@C_{72}$, but the absence of empty-cage $C_{72}$. Since empty-cage $C_{72}$ has not been successfully isolated to date, the results of the present study are in agreement with the argument for metal-mediated stabilization of the $C_{72}$ carbon cage by lanthanum ions. The chromatographic retention data suggest that the electronic structure of $La_2@C_{72}$ is consistent with a $(La^{3+})_2@C_{72}{}^{6-}$ species and the prediction of a relatively small dipole moment.

## Introduction

The recent discovery and isolation of metal-encapsulated fullerenes ($A_m@C_{2n}$, $m = 1-3$, $n = 30-70$) represents a unique class of new compounds. These endohedral metallofullerenes[1−28] are of special interest because of their unique structural arrangement and potential applications.[2,3,29] For example, predicted applications already include possible uses as nonlinear optical devices,[3] catalysts,[3] superconductors,[2,29] lasers,[2] and ferroelectric materials.[2,3] Although most endohedral metallofullerenes isolated to date have cages of 80 carbons or greater ($Sc_2@C_{74}$,[17,18] $Sc_2@C_{84}$,[3,17,18,24,26] $Sc_3@C_{82}$,[22,23,25−27] $Y@C_{82}$,[12,13,26] $Y_2@C_{90}$,[21] $La@C_{82}$,[14−16,19−21] $La_2@C_{80}$,[19,21] $Gd@C_{82}$,[16,26,28] $Gd_2@C_{90}$,[21] $Er_2@C_{82}$,[27] and $Pr@C_{82}$[26]), a notable exception is the smaller cages (e.g., $C_{70}-C_{74}$) which have only a limited number of isolated pentagon rule (IPR) satisfying cage isomers. Most of the endohedrals isolated to date are mono- or dimetallofullerenes (MMF and DMF). For the $C_{72}$ empty cage, only one IPR allowed isomer is predicted ($D_{6d}$) which leads to a limied number of anticipated encapsulated endohedral metallofullerene isomers, $A_m@C_{72}$ (Figure 1). In similar fashion, the empty-cage $C_{74}$ fullerene has only one IPR-allowed structure ($D_{3h}$).[17,18] In experimental agreement, $Sc_2@C_{74}$ has also been purified,[32] but without concomitant isolation of the corresponding empty-cage $C_{74}$ fullerene. Thus, there is a paucity of examples for those endohedrals with the smaller $C_{72}-C_{74}$ type cage structures apparently stabilized by the presence of encapsulated metal atoms.

In this paper, we report the production, separation, and characterization of a unique dimetal metallofullerene (DMF) species, $La_2@C_{72}$. As previously noted, there is only one possible $C_{72}$ empty-cage structure[33] ($D_{6d}$ symmetry) that satisfies the isolated pentagon rule.[32−34] In this regard, it should be noted that the computer-generated structure for $La_2@C_{72}$ (Figure 1) with the metal atoms along the $D_6$ symmetry axis is one of only a few possible isomers and shown only for illustrative purposes.

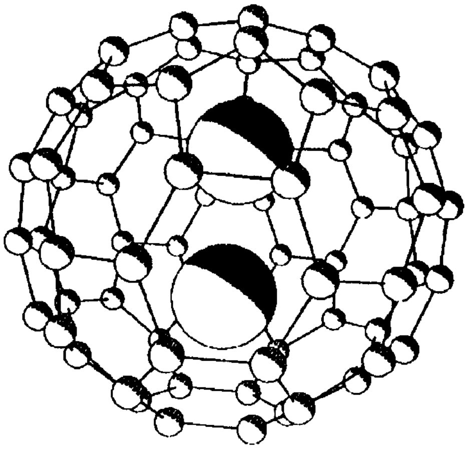

**Figure 1.** Computer-generated structure for $La_2@C_{72}$ ($C_{72}$ $D_{6d}$ cage symmetry). The metal atoms are placed along the $D_{6d}$ symmetry axis.

## Experimental Section

The production method used here to obtain metallofullerenes is very similar to the original Krätschmer−Huffman[35] arc-burning method. Cored rods packed with a mixture of graphite and either pure lanthanum, $La_2O_3$, or lanthanum carbide were arc-burned in a fullerene generator under a dynamic He atmosphere.[27] During this process metallofullerene and fullerene-rich soot formed which deposits on the cooled chamber walls. In addition, a carbide-like deposit formed on the counter electrode, and optimum results were obtained by also repeatedly back-burning the deposit on the anode. The rod preparation parameters utilized graphite rods (diameter of 6 mm, cored to 4 mm) filled with a $La_2O_3$/graphite mixture with a metal concentration doping of 0.5−5 atomic %. Typical electric-arc

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operating production parameters consist of 20−25 V, 95−115 A, and 180−220 Torr of helium. It is noteworthy that the relative abundances of mono-, di-, and trimetallofullerenes can be controlled to some extent by choosing an appropriate metal concentration. For low metal concentrations (1%) the monometallofullerenes were, as expected, found to be the most abundant, whereas for high metal loading (>2%) the dimetal species were more abundant. In this manner, a higher metal loading was utilized to optimize yields for $La_2@C_{72}$ and other dilanthanum metallofullerenes. The fullerenes and metallofullerenes were extracted by dissolving them in toluene, $CS_2$, or 1,2-dichlorobenzene immediately after collection of the soot. The facile extraction is clearly important for certain metallofullerenes (e.g., $La@C_{82}$) which are unstable in aerobic environments.[37,38] For extraction of the $La_m@C_{2n}$ species from the electric-arc-generated soot, both $CS_2$ and 1,2-dichlorobenzene were found to be good solvents.

Following this extraction protocol, the initial $La_m@C_{2n}$ raw extract was filtered over a plug of glass wool. The initial chromatographic separations of metallofullerene fractions incorporated two Perkin-Elmer polystyrene columns connected in series. Specifically, a polystyrene column of dimensions 25 cm × 10 mm PL gel, 10 $\mu$m, 1000 Å, was followed by a 25 cm × 10 mm PL gel, 5 $\mu$m, 500 Å polystyrene column. As a mobile phase, a $N_2$-degassed, 80% toluene/20% decalin (v/v) solvent system was selected for most chromatographic separations. Conditions for these polystyrene separations were 1.0 mL/min of mobile phase with UV detection at 340 nm. In the second and final stage, a highly selective semipreparative Trident-Tri-DNP (dinitrophenyl) column (Buckyclutcher, 25 cm × 10 mm i.d., Regis Chemical, Morton Grove, IL) was utilized for isolation of $La_2@C_{72}$. The chromatographic retention behavior of $La_2@C_{72}$ on a pentabromobenzyl column (PBB, 25 cm × 10 mm i.d., Phenomenex Co., Torrance, CA) was also investigated. For the PBB column, carbon disulfide was selected as the mobile phase.

Further details on HPLC instrumentation, on-line EPR detection, and negative-ion mass spectrometry for this study have been previously published.[22,37] For the mass spectra obtained from the laser desorption time-of-flight (LD-TOF) method, the wavelength of the ionizing photons used was 193 nm. This mass spectrometry technique enhances the metallofullerene/fullerene ratio since at this wavelength it takes two photons to ionize empty-cage fullerenes, whereas the ionization of the metallofullerenes occurs through only single-photon processes. The UV−vis spectrum of $La_2@C_{72}$ was obtained with a Perkin-Elmer Lambda-6 spectrophotometer equipped with a 190−900 nm scanning range. A quartz cuvette with a path length of 1 mm and cell volume of 300 $\mu$L was utilized. All optical measurements were obtained under ambient conditions with decalin as the solvent.

## Results and Discussion

It is clear that a rich array of MMF and DMF endohedrals are produced as illustrated (Figure 2) by the laser desorption mass spectrum of the $La_m@C_{2n}$ extract obtained by the experimental procedure described vide supra, $La_2O_3$/graphite mixture (metal concentration, 4 atom %). Apart from the empty-cage fullerenes—dominated by $C_{60}$ and $C_{70}$ (not shown)—at the lower mass region, one observes strong peaks corresponding to $La@C_{82}$ and $La_2@C_{72}$. The relatively high abundance of the latter species suggests optimized production of $La_2@C_{72}$ and other DMF endohedral species. This is not the case for the MMF species, $La@C_{82}$, which is usually one of the more abundant endohedrals present in electric-arc preparations. It is interesting to note that the DMF species extend to much larger carbon cages (at least $La_2@C_{140}$). A limited study of the yield dependence of the cored rod preparation (pure metal versus metal oxide) suggests only small changes in the total yield (10−20%); however, slightly better results were obtained with the metal oxide ($La_2O_3$).

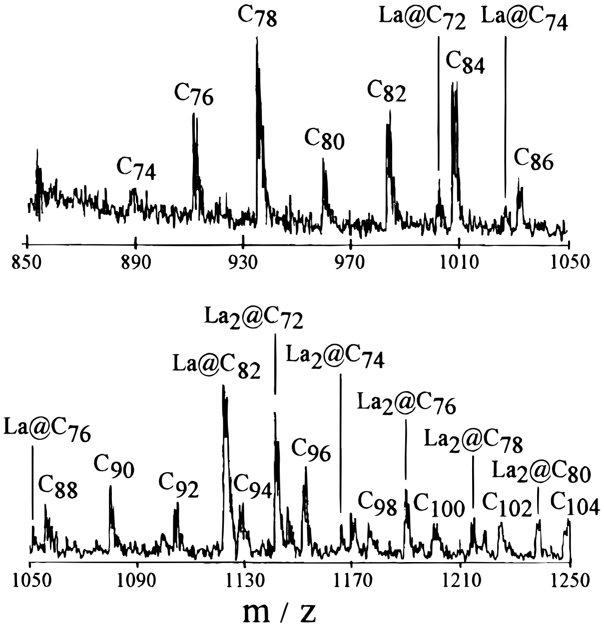

**Figure 2.** Laser desorption time-of-flight (LD-TOF) mass spectrum of $La_m@C_{2n}$ stock.

The MMF, $La@C_{72}$ species is also produced and extracted from the soot. Furthermore, there is mass spectral evidence of a monometal series ($La@C_{72}$, $La@C_{74}$, $La@C_{76}$, etc.) and the corresponding DMF series ($La_2@C_{72}$, $La_2@C_{74}$, $La_2@C_{76}$, etc.) for this extract. However, there is no mass spectral evidence for the empty-cage $C_{72}$ and only a trace of $C_{74}$ (Figure 2). In contrast, the $La_2@C_{74}$ and $La_2@C_{76}$ species are present in reduced preponderance in comparison with their corresponding empty-cage analogues. These results suggest that the $C_{72}$ cage is stabilized in some fashion by electron donation from the lanthanum metal atom(s). This interpretation is supported by a recent gas-phase study[43] which describes the importance of electron donation to stabilize both the $C_{72}$ and $C_{74}$ empty-cage systems. Another significant feature of this sample is the apparent absence of $La_m@C_{60}$ and $La_m@C_{70}$ species. Although $C_{60}$ and $C_{70}$ dominate the mass spectrum, the production of endohedral metallofullerenes with these cage structures has not been observed with the present solvent used in the isolation protocol.

A stock solution of $La_m@C_{2n}$ extract (3 mg/mL) was prepared with $N_2$-degassed toluene/decalin solvent (4:1, v/v). To remove the lower mass empty-cage fullerenes (e.g., $C_{60}$, $C_{70}$, and $C_{84}$), this solution was injected into two polystyrene columns that were connected in series. To obtain the metallofullerene fraction, on-line electron paramagnetic resonance (EPR) detection was implemented as previously described.[22] As previously demonstrated, the EPR-active metallofullerenes ($A_m@C_{2n}$, $m$ = 1 or 3) nicely serve as "markers" for the overall coelution of the metallofullerene fraction.[22,37] The separation on this polystyrene chromatographic phase was subsequently performed at ambient temperature with a flow rate of 1 mL/min. With these conditions, an EPR-active fraction containing $La@C_{82}$ and $La_2@C_{72}$ was obtained from 28 to 35 min as indicated in Figure

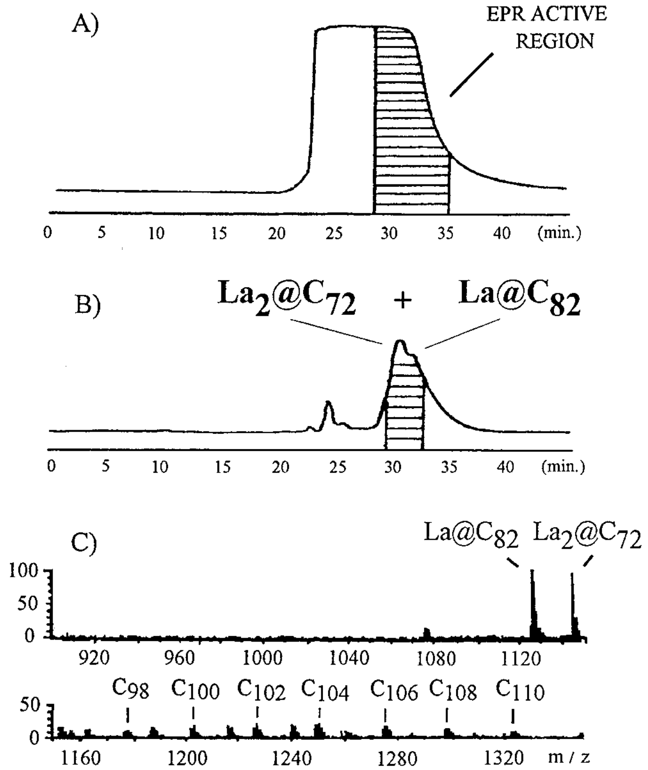

**Figure 3.** (a) HPLC−UV trace for the first polystyrene injection of $La_m@C_{2n}$ starting stock material, 1.0 mL/min, 80:20 toluene/decalin, and 340 nm detection. The EPR active region of 28−37 min corresponds to $La@C_{82}$—the marker for the overall metallofullerene fraction. (b) HPLC−UV trace following five recovery and reinjections into the polystyrene column. (c) Negative-ion desorption chemical ionization (NI-DCI) mass spectrum of (b).

3a. For comparison, the empty-cage $C_{60}$−$C_{84}$ fullerenes possess earlier retention times of 23−28 min. Due to high sample loading (poor chromatographic resolution), several recovery and reinjection steps were necessary to satisfactorily remove these abundant empty-cage fullerenes. Specifically, a total of five reinjections of this EPR-active fraction was necessary in order to obtain a sample dominant in endohedral metallofullerenes (Figure 3b). To determine the composition of this final polystyrene fraction, a mass spectrum was obtained as presented in Figure 3c. This mass spectral data clearly indicate a sample dominant in $La@C_{82}$ and $La_2@C_{72}$. At this stage, a small amount of contaminate higher empty-cage fullerenes ($C_{96}$−$C_{112}$) was also present. This separation protocol is consistent with previous results in which $C_{60}$, $C_{70}$, and $C_{84}$ were removed utilizing polystyrene columns as an initial cleanup procedure.[22,39]

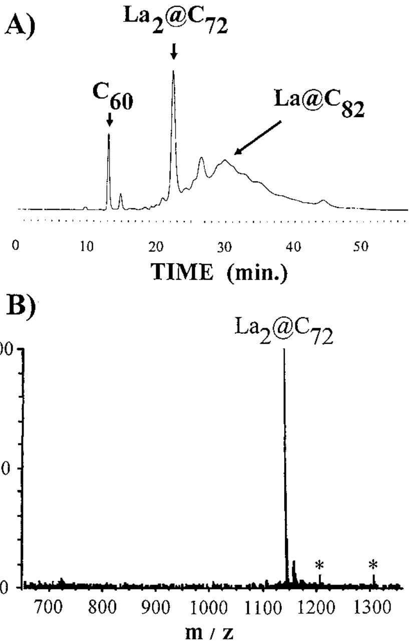

**Figure 4.** (a) HPLC−UV trace of the $La_2@C_{72}$/$La@C_{82}$ fifth polystyrene pass, EPR-active fraction with the Buckyclutcher column, 1.1 mL/min, 80:20 toluene/decalin, and 340 nm detection. (b) Negative-ion desorption chemical ionization (NI-DCI) mass spectrum for isolated $La_2@C_{72}$. The asterisk represents the standard Ultramark 1621 used for mass calibration.

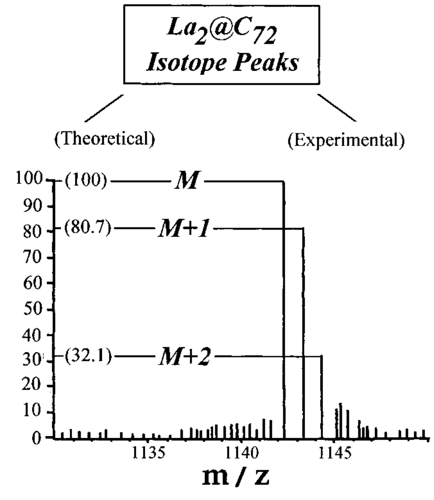

**Figure 5.** NI-DCI mass spectrum following a high-resolution isotope peak mass analysis which compares the experimental and theoretical predictions.

A more selective chromatographic phase was necessary for the final purification stages. Specifically, the more selective Buckyclutcher column was utilized based on previous studies which indicate that this tridentate, dinitrophenyl stationary phase[38] is very useful in both fullerene and metallofullerene separations. The chromatogram for an initial cleanup injection with the Buckyclutcher column is presented in Figure 4a. The dominant peak at 22.4 min was then collected and characterized by both negative-ion desorption chemical ionization (NI-DCI) and laser desorption time-of-flight (LD-TOF) mass spectrometry. The negative-ion mass spectrum for purified $La_2@C_{72}$ is presented in Figure 4b. To further support the assignment of $La_2@C_{72}$, a high-resolution mass spectrometric isotope peak analysis (Figure 5) was performed and is consistent with the formula $La_2@C_{72}$. The estimated weight of the final $La_2@C_{72}$ sample was only 10−100 $\mu$g (from 50 mg of soluble lanthanum extract). However, a weak UV−vis absorption spectrum was obtained (Figure 6) for the faintly purple sample. The spectral features for $La_2@C_{72}$ included absorptions at 339, 522, and 631 nm with a stronger broad absorption centered at 808 nm. For comparison, results for a purified $La_2@C_{80}$ sample reported by Kikuchi and co-workers[21] exhibited prominent UV−vis absorption peaks at approximately 336, 366, 421, 465, and 549 nm. In addition, they reported a very weak absorption centered at around 678 nm followed by a weak, broad absorption ranging from 800 to 900 nm. Although there are obvious differences in the $La_2@C_{72}$ and $La_2@C_{80}$ spectra due to different cage structures and electronic environments, there are, nevertheless, certain similarities between these two species. For example, the following absorptions of $La_2@C_{72}$ (versus $La_2@C_{80}$) are observed: 339 nm (366 nm), 522 nm (549 nm), 631 nm (678 nm), and 808 nm (800−900 nm) suggest that the absorptions

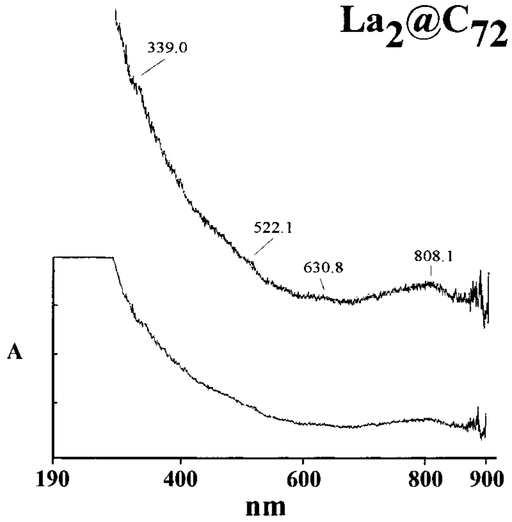

**Figure 6.** UV−vis absorption spectrum for isolated $La_2@C_{72}$ in decalin.

of $La_2@C_{72}$ occur in similar regions as the $La_2@C_{80}$ species but with a small shift toward longer wavelengths. This red shift of $La_2@C_{80}$ relative to $La_2@C_{72}$ is in good agreement with an earlier study[39] of UV−vis trends for empty-cage fullerenes. In the latter study, it was established that increases in the carbon cage sizes generally result in absorption shifts toward longer wavelengths. Thus, it is not surprising that the $C_{80}$ cage structure in $La_2@C_{80}$ exhibits an overall slight red shift relative to the smaller $C_{72}$ cage structure for $La_2@C_{72}$.

In addition to UV−vis characterization, the chromatographic behavior of $La_2@C_{72}$ provides insight regarding the charge distribution and dipole moment for this species. In a recent paper, Fuchs and co-workers[44] have used chromatographic retention data to predict the dipole moment for several MMF's. In this approach, it is now recognized that strong dipole−dipole interactions dominate the retention mechanism between the fullerene (or MF) solute and Buckyclutcher, tripodal dinitrophenyl chromatographic phase, whereas other less polar stationary phases, such as PYE (pyrenylethyl) and PBB (pentabromobenzyl) phases, exhibit weaker induced dipole−dipole interactions and dispersion forces. As argued by Fuchs, the latter dispersion forces depend on the polarizability of the fullerenes (or MMF's) and the stationary phase. Furthermore, numerous earlier studies have clearly demonstrated a linear relationship between the chromatographic retention parameter, capacity factor ($k'$), and the empty-cage fullerene carbon cage number ($N$) for a number of different chromatographic phases (see Figure 7). Thus, this chromatographic parameter is proportional to the polarizability and number of $\pi$ electrons on the fullerene cage surface (Figure 7). For empty-cage fullerene isomers, only minor deviations from this linear dependence are usually observed because of subtle differences in the symmetry for the same cage size.

The retention time data (e.g., log $k'$, $k'$ = capacity factor) for $La_2@C_{72}$ were obtained for both the Buckyclutcher and PBB columns (Figure 7). With the PBB stationary phase, $La_2@C_{72}$ (log $k' = -0.149$) eluted in the region corresponding to empty-cage $C_{77}$−$C_{78}$ (Figure 7a). This result is consistent with isoelectronic data for a $(La^{3+})_2@C_{72}{}^{6-}$ species and assumes no significant induced dipole−dipole interactions for the $La_2@C_{72}$/PBB stationary phase system. Previous studies[10,14,40−42] on $La@C_{82}$ have suggested that the charge on the La atom was in the +3 oxidation state. However, the charge per metal atom of lanthanum DMF's (e.g., $La_2@C_{80}$) has not been established.

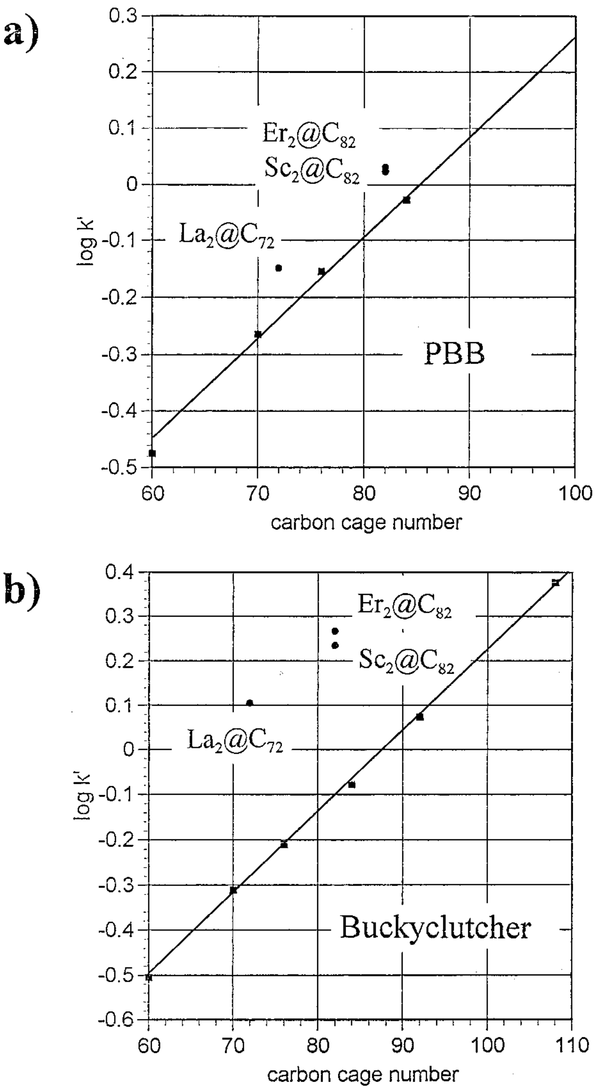

**Figure 7.** Log of the chromatography capacity factor, $k'$, versus carbon cage number for the (a) pentabromobenzyl, PBB, column, $CS_2$ mobile phase and (b) Buckyclutcher column, 80/20 toluene/decalin mobile phase.

This result is also consistent with a number of other DMF endohedrals (e.g., $Er_2@C_{82}$) which exhibit capacity factors close to empty-cage, $C_{88}$. In this latter case, a fluorescence study[45] of $Er_2@C_{82}$ also supports a +3 oxidation state for this species. For short-range interactions, the two diametrically opposed metal atoms oriented in a symmetric cage lead to the prediction that these DMF's should be nonpolar and exhibit relatively small dipole moments. This suggests that DMF polarizability (and corresponding number of $\pi$ electrons) dominates the chromatographic separation with the PBB phase and nonpolar solvents (carbon disulfide). This leads to a prediction of a vanishing small dipole moment and predicts a $(La^{3+})_2@C_{72}{}^{6-}$ electronic structure for this species. However, it is important to emphasize that other retention mechanisms (including induced dipole−dipole) undoubtedly also contribute to the observed capacity factors for this DMF with the PBB stationary phase.

For the tripodal dinitrophenyl chromatographic phase, it is now recognized that strong dipole−dipole interactions dominate the retention mechanism between the fullerene (or MF) solute and this Buckyclutcher phase. For example, with the Buckyclutcher column, $La_2@C_{72}$ (log $k' = 0.102$) exhibits an elution time slightly beyond empty-cage $C_{92}$. Note that the isoelectronic analogues of $(La^{2+})_2@C_{72}{}^{4-}$ and $(La^{3+})_2@C_{72}{}^{6-}$ would be $C_{76}$

and C$_{78}$ and possess log $k'$ values of only $-0.210$ and $-0.173$, respectively. As expected, the elution time of La$_2$@C$_{72}$ near C$_{92}$ suggests a stronger retention mechanism for all MMF's and DMF's with the Buckyclutcher stationary phase. It is also possible that La$_2$@C$_{72}$ possesses a significant dipole moment that contributes to its retention mechanism and corresponding elution time. However, the chromatographic data also suggest that the dipole moments for La$_2$@C$_{72}$, Sc$_2$@C$_{82}$, and Er$_2$@C$_{82}$ are similar. The deviation from the empty-cage slope is 20$-$22 carbon atoms for each of these DMF's and suggests that La$_2$@C$_{72}$ has a similar charge and dipole moment as Sc$_2$@C$_{82}$ and Er$_2$@C$_{82}$. Thus, these DMF's are expected to have small dipole moments based on previous arguments (vide supra). On the other hand, MMF's are expected to have a significant dipole moment, and this is supported by the observation that Sc@C$_{82}$ (log $k' = 0.355$) coelutes significantly later with C$_{106}$$-$C$_{108}$.

## Conclusion

In this paper we have described the isolation and preliminary characterization of La$_2$@C$_{72}$. Surprisingly, the La$_2$@C$_{72}$ species is readily produced and extracted from lanthanometallofullerene soot. Isolation of this molecule represents an important initial step in understanding the mechanistic features for endohedral production and structural features of smaller metal-stabilized cages. The mass spectral results also demonstrate the presence of La$_2$@C$_{74}$ but the absence of empty-cage and C$_{72}$ and C$_{74}$. Since empty-cage C$_{72}$ and C$_{74}$ have not been isolated to date, the results are in general agreement with the argument for metal-mediated stabilization of these small cages by lanthanum ions. The chromatographic retention data are consistent with $(\mathrm{La}^{3+})_2@\mathrm{C}_{72}{}^{6-}$ for the electronic structure of this species. In addition, comparative retention behavior between La$_2$@C$_{72}$ with Sc$_2$@C$_{82}$ and Er$_2$@C$_{82}$ leads to the prediction of a relatively small dipole moment for the latter species.

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