A Novel Approach to the Synthesis of Endohedral Fullerenes as Demonstrated by Endohedral Barium Fullerenes

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A new route to endohedral fullerenes involving the evaporation of carbon and a metal at different positions, i.e. at different temperatures, in a radio-frequency furnace is described. For the first time, endohedral barium fullerenes within the composition range $Ba@C_{74}$ to $Ba@C_{136}$ have been produced in high yields as compared to hollow fullerenes, and have been extracted with CS_2. $Ba@C_{60}$ and $Ba@C_{70}$ are only soluble in CS_2 following sublimation. Furthermore, the first non-lanthanoid di-metallo fullerenes ranging in composition from $Ba_2@C_{88}$ to $Ba_2@C_{116}$ have been obtained. All endohedral barium fullerenes were characterized by mass spectrometry. Properties such as sublimation behaviour, solubility, and sensitivity to air have been studied.

Introduction

One of the most interesting topics in current chemistry is that of endohedral metal fullerenes. This new class of materials is highly promising with respect to chemical and physical properties. Moreover, if available in preparative amounts, endohedral metal fullerenes will open the way to a completely new, nanoscale, solid-state chemistry. The chemical properties of endohedral fullerenes will depend on the size of the carbon cage, as well as on the kind of element entrapped. To achieve a broad spectrum of properties, it is desirable to encage as many different elements as possible within as many different cages as possible. However, the basic requirement to be met, both for investigating the properties as well as for exploring the chemistry of endohedral metal fullerenes, is that they are available in preparative quantities. To date, this has only been achieved for the lanthanoid fullerenes, as well as for systems incorporating the related metals Sc and Y. By employing an arc-heating technique, mainly $RE@C_{60}$, $RE@C_{82}$, and $RE_2@C_{80}$ have been obtained (RE = rare earth). As a rule, rods of graphite containing the corresponding metallic oxides have been evaporated in an arc-discharge[1][2][3][4][5][6][7]. In the case of scandium, $Sc_2@C_n$ (n = 74, 82, 84) and $Sc_3@C_{82}$ have also been obtained[8][9]. All of these lanthanoid compounds are readily accessible by the same technique, since the metals used have some favourable thermal properties in relation to the temperature required to vaporize graphite: (i) Most of the lanthanoids, as well as Sc and Y, have very high boiling points (2000–3000 °C); (ii) the minimum reaction temperatures for the formation of the rare earth carbides from the metal oxides and graphite are within the same range, and (iii) both the boiling points and the decomposition temperatures of the rare earth carbides are far in excess of 2000 °C.

The quest for further elements with chemical and physical properties suitable for encaging them in fullerenes leads almost inevitably to the heavier alkaline earth metals. While extensive work has been carried out on endohedral lanthanoid fullerenes, there have been only a few publications on endohedral alkaline earth elements. Rose et al. investigated various endohedral mono-metal fullerene ions produced by laser irradiation of a mixture of Ca, Sr, and Ba salts with kerogen residues[10][11]. However, they did not obtain sufficient quantities for extraction or sublimation. At about the same time, Smalley and co-workers found $Ca@C_{60}$ upon laser vaporization of a calcium oxide/graphite mixture[12]. Kubozono et al. reported on the formation of $M@C_{60}$ (M = Ca, Sr, Ba) by arc-heating of MO/C rods[13][14][15]. However, no information on the yield of extractable material was given. Recently, Shinohara et al. published the synthesis, as well as the extraction and isolation by HPLC, of $Ca@C_n$ ($72 \leq n \leq 84$) using the same arc-heating method[16].

In our opinion, one reason for the rather limited degree of success, particularly in synthesizing endohedral strontium and barium fullerenes, lies in the thermodynamics of the carbides of these metals, as presented in Table 1.

Table 1. Thermodynamic data of Ca, Sr, and Ba and their compounds with O and C

	Ca	Sr	Ba
Boiling point M [°C]	1484	1384	1640
Melting point MO [°C]	2614	2430	1918
Reaction temperature [°C] $MO + 3\,C \rightarrow MC_2 + CO$	1700	<1772	1650
Melting point MC_2 [°C]	2300	$1772<T<2300$	1750 (dec.)

The difference between the sublimation temperature of graphite and the melting, boiling, or decomposition temperature of the respective metal carbides increases from the lanthanoid carbides through calcium carbide to barium carbide. The temperature in an arc-discharge experiment is in the range 5000–6000 °C, and there is no possibility of adjusting it to somewhat lower temperatures. This means, particularly in the case of barium, that most of the metal is vaporized before the graphite starts to sublime. Thus, the carbon and the metal vapor pressures are not well balanced.

Previously, we have reported on the syntheses of fullerenes and endohedral fullerenes using a radio-frequency furnace[17][18][19]. Our technique enables us to control the temperature, gas pressure, and flow rate of various cooling gases and gas mixtures precisely. We have been able to tailor this technique to the particularly sensitive task of simultaneously evaporating barium and carbon.

Results and Discussion

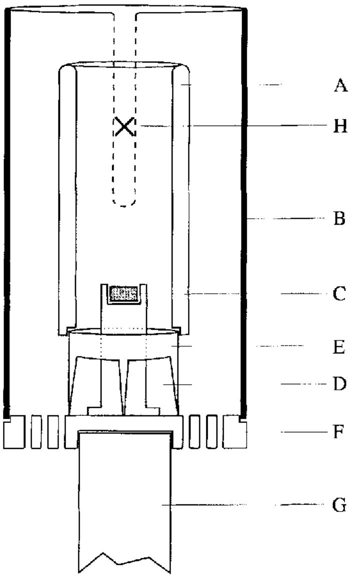
Using our approach we have been able to substantially increase both the amounts obtainable and the compositional variety of known endohedral barium fullerenes. Our crude material contains endohedral barium fullerenes and dibarium fullerenes in the composition ranges $Ba@C_{60}$ to $Ba@C_{136}$ and $Ba_2@C_{88}$ to $Ba_2@C_{116}$. The raw soot contains up to 20% by weight of extractable fullerenes and barium fullerenes, which is significantly better than the yields reported for comparable arc-discharge experiments[4][5][6]. This result was achieved by an independent evaporation of carbon and barium under optimized conditions. The conditions most conducive to the formation of endohedral barium fullerenes are to maintain a temperature of 2450 °C at the carbon source and to heat the barium to approximately 1800 °C in a helium atmosphere of 300 hPa, with a flow rate of 1400 l/h.

Apart from some slight modifications, the key features of our high-frequency furnace have been reported previously[17][18][19]. The experimental set-up allows for a spatial separation of the barium and carbon sources. A graphite cylinder is placed in the centre of the radio-frequency coil and the barium source is placed approximately 4 cm below the graphite. The two parts are separated from each other by carbon adapters and are surrounded by a tube of pyrolytical boron nitride that acts as thermal shielding. Figure 1 shows the described set-up. The whole assembly, including the carbon and barium sources, is isolated from air by a water-cooled quartz glass tube, and is connected to a tandem-arranged cooling trap. For further details, see the Experimental Section.

All endohedral barium fullerenes are sensitive to air, $Ba@C_{60/70}$ more so than the others. All can be sublimed from the raw soot and, with the exception of $Ba@C_{60/70}$, can be directly extracted from the raw soot with CS_2 or toluene.

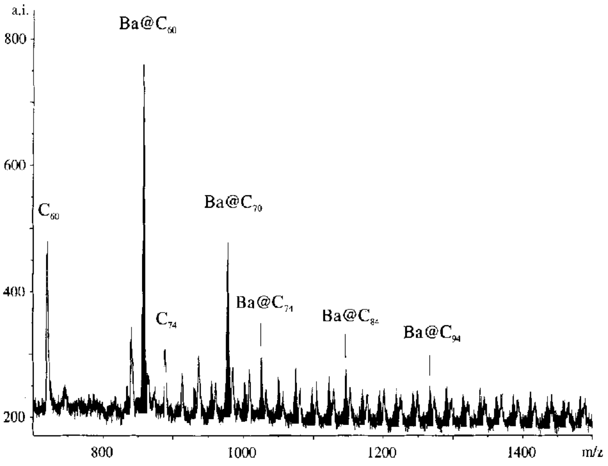
According to the results of mass spectrometry $Ba@C_{60}$ and $Ba@C_{70}$ appear to be the main products in the raw soot collected (Figure 2). They can be sublimed at 500 °C. We have observed that freshly sublimed $Ba@C_{60/70}$, separated from its soot matrix, is in fact soluble in CS_2. This is in contrast to earlier findings, that $M@C_{60/70}$ species are only soluble in aniline or pyridine, and not in the usual solvents for fullerenes[13][14][15]. Rather strong interactions between $Ba@C_{60/70}$ and the soot itself might explain their insolubility in CS_2 prior to sublimation. In solution, $Ba@C_{60/70}$ are oxidized within a few days if exposed to air. An oxygen uptake up to the composition $Ba@C_{60}O_2$ has been determined by mass spectrometry. On the other hand, solid $Ba@C_{60/70}$ is quite stable in air. Only a slight decrease of the MS peak intensity is observed after storage of the samples in air for months, as compared to the situation with hollow C_{60}. Both in solution and in the solid state, the oxidation of $Ba@C_{60}$ proceeds more rapidly than that of $Ba@C_{70}$. Thus, $Ba@C_{60}$ seems to be the least stable endohedral barium fullerene if exposed to air. It undergoes very facile fragmentation in a laser desorption mass spectrometer with successive loss of C_2 fragments. The combination of the properties sublimability, high stability in air as a solid and the solubility in the completely apolar solvent CS_2 are giving strong evidence for the endohedral character of $Ba@C_{60/70}$.

Figure 1. Detailed set-up of the elements in the hot zone. Graphite cylinder for evaporation (A), PBN cylinder, half-slit (B), Ba/C or BaB_6/C sample (C), graphite cone (D), graphite "crown" adapter, with slits (E), graphite platform with slits for cooling gas (F), water-cooled brass base or BN rod (G), measuring point for the pyrometer (H)



The endohedral barium fullerenes $Ba@C_n$ ($72 \leq n \leq 136$) are the first endohedral alkaline earth fullerenes to have been prepared in larger quantities other than $Ca@C_n$ ($72 \leq n \leq 84$)[16]. As in the case of $Ba@C_{60/70}$ the same combination of properties is giving strong evidence for their endohedral character. Some of their properties are quite different from those of $Ba@C_{60}$ and $Ba@C_{70}$. $Ba@C_{72-136}$ can be easily separated from the raw soot by soxhlet extraction with CS_2, toluene or halogenated benzenes. We prefer CS_2, because of its greater volatility. Their sublimate is also soluble in CS_2. It is possible to enrich the endohedral barium fullerenes with respect to empty fullerenes by multistage sublimation. Figure 3a shows the mass spectrum of a fresh CS_2 solution of the final sublimation fraction col-

Figure 2. LD-TOF mass spectrum (positive ions) of the raw soot, sampled from the cooling trap. The peaks belonging to endohedral barium fullerenes are marked in black. Note the high peak intensity of Ba@C_{60} and Ba@C_{70} as compared to hollow C_{60} and C_{70}



lected at 800°C. The highest peaks are attributable to the endohedral species. They were found to be quite stable in air, both in solution and as solids. Figure 3b shows the mass spectrum of the same sample after exposure to air for one month. The high intensity of the peak for Ba@C_{84} is especially remarkable considering the preferred formation of RE@C_{82} when using lanthanoids. Other maxima in the yields are seen for Ba@C_{74}, Ba@C_{90}, and Ba@C_{94}. Ba@C_{72} is produced only in very small quantities, which is in contrast to the results obtained using calcium[16]. As in the case of Ba@$C_{60/70}$, within one month the peak intensities of Ba@C_{76} and Ba@C_{78} are seen to decrease. The stability of endohedral barium fullerenes in air, especially in the compositional range from Ba@C_{60} to Ba@C_{84}, seems to increase with increasing size of the carbon cage. In this respect, Ba@C_{74} is a remarkable exception, and very interesting in comparison with hollow C_{74}. Using the radio-frequency furnace, C_{74} has been produced in similar quantities as C_{60} and C_{70}, which might be explained by the mild reaction conditions. Some behaviour differing from that of other fullerenes (C_{74} cannot be extracted directly from the raw soot although it can be sublimed) has been reported elsewhere[3]. However, our observation is that hollow C_{74} is soluble in CS_2 like Ba@$C_{60/70}$, provided that it is freshly sublimed (see Figure 3a). In solution, it is oxidized very rapidly on exposure to air, whereas in the solid state it is oxidized only very slowly. The calculated electron affinity of C_{74} [20][21] is believed to be responsible for the particular properties observed.

For the first time, endohedral di-metallo fullerenes other than the known lanthanoid species have been obtained. As can be seen from Figure 4, Ba_2@C_n species ($88 \leq n \leq 116$) were produced. In contrast to the dilanthanoid fullerenes, we found no Ba_2@C_{80}; two barium atoms seem to need at least a C_{88} cage. In the mass spectrum, characteristic triplets can be seen (e.g. Ba_2@C_n/Ba@C_{n+12}/C_{n+24}). All endohedral dibarium fullerenes can be sublimed, or extracted with CS_2, directly from the raw soot.

Figure 3a. Mass spectrum (positive ions) of a CS_2 solution obtained from a fraction freshly sublimed at 800°C

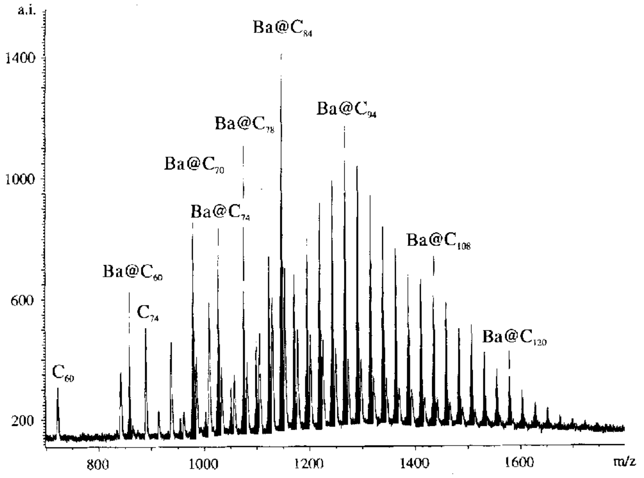


Figure 3b. Mass spectrum (positive ions) of the same CS_2 solution used to obtain Figure 3a after exposure to air for one month

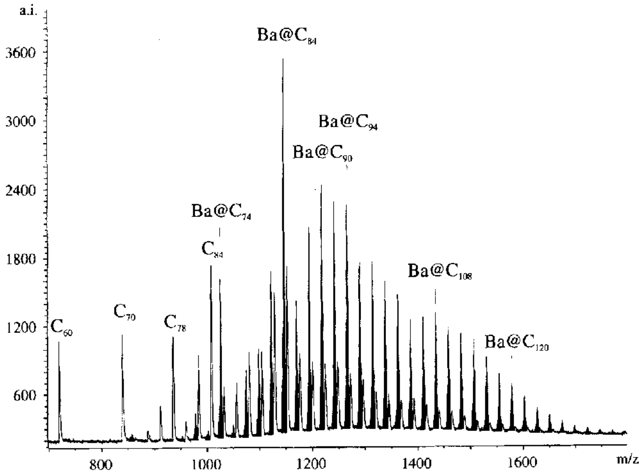
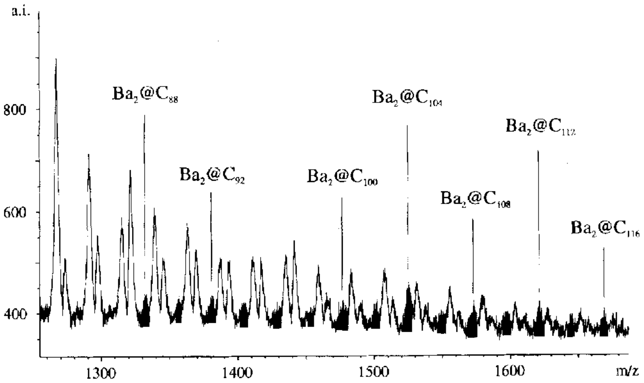


Figure 4. Mass spectrum (positive ions) of a CS_2 extract of the raw soot sampled from the cooling trap. The soot contains various Ba_2@C_n species ($88 \leq n \leq 116$). Maxima in peak intensity appear for Ba_2@C_{104} and Ba_2@C_{112}



Generally, three ways of adjusting the compositions of the endohedral fullerenes formed have been found: (i) Sampling of the soot deposited adjacent to the hot spot and of that collected from the cooling trap reveals a different composition of the products. Raw soot from the cooling trap has a higher content of endohedral and higher fullerenes since it is protected from the UV radiation of the reaction zone. UV radiation seems to lead to partial decomposition of these fullerenes; (ii) Spatial separation of the barium and carbon sources is crucial for the optimal formation of all the described barium fullerenes. When the barium source is too cold, the barium vapour pressure is too low and consequently an undesired low endohedral-to-hollow fullerene ratio results. Conversely, if the barium source gets too hot, an extremely high barium vapour pressure suppresses the formation of fullerenes in general. In the latter case, the endohedral barium fullerenes detected in low concentrations consist mainly of Ba@C_{60} and Ba@C_{70}; (iii) Furthermore, we observe a shift to Ba@$C_{60/70}$ in the barium fullerene composition of the raw soot if the central carbon construction is electrically earthed. Insulation by a mass of boron nitride in the form of a long rod leads to higher endohedral fullerenes.

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Experimental Section

Details of the radio-frequency furnace have been reported previously[17][18][19]. Here, the elements of the hot zone are described (see Figure 1). The carbon source consists of a graphite cylinder (height: 50 mm, outer diameter: 26 mm, wall thickness: 3 mm, rounded edges). Barium is placed in the top of a graphite cone, either as the metal (chips grated from a compact rod in a glove box) or as barium hexaboride. When barium metal is used, it is protected from oxidation by graphite powder and placed 4 cm below the hottest spot of the graphite cylinder. Barium hexaboride is placed only 3 cm below the hottest spot. The separation of the carbon and metal sources is fixed by carbon adapters. These have slits in order to prevent coupling to the radio-frequency field. Both parts are surrounded by a half-slit tube of pyrolytical boron nitride (diameter: 42 mm), which prevents the outer quartz glass tube from coming into contact with barium, and, at the same time, guides the barium vapour over the hot graphite cylinder. The whole assembly is placed either directly on top of a water-cooled brass base (earthed) or on an intervening 12 cm long boron nitride rod (insulated), with the carbon cylinder in the centre of the radio-frequency coil. The whole set-up is isolated from air by a water-cooled quartz glass tube. The installation is evacuated to 10^{-3} hPa. The carbon components were degassed in vacuo by heating them to 1000°C. Carbon was then heated to 2450°C (detected on the surface of the graphite cylinder by a pyrometer) in flowing helium (300 hPa, 1400 l/h). In this way, carbon and barium were evaporated simultaneously. The raw soot was collected under inert conditions from the upper water-cooled surfaces of the quartz glass tube and from the tandem-arranged trap, which was cooled with liquid nitrogen. The soot from the cooling trap was directly sublimed onto sample holders of a mass spectrometer. Sublimation occurred at 10^{-6} hPa and 500°C, 700°C and 800°C, respectively, with a heating rate of 2000°C/h. The color of the CS_2 solution of the first sublimate, consisting mainly of hollow fullerenes, was deep red, whereas that of the CS_2 solution of the final sublimate, consisting mainly of endohedral barium fullerenes, was dark amber. All the endohedral barium fullerenes were stored under argon since the larger ones are also less air-stable than hollow fullerenes.

The radio-frequency emitter was manufactured by Hüttinger, Freiburg (IG 30/400, high ohmic version, radio-frequency terminal output: 36 kW, input in graphite cylinder by optimal accommodation: 30 kW, output frequency: 400 kHz). – The pyrometer used for temperature control was from Maurer, Kohlenberg (TMRS 485-2). – Mass spectrometry was performed using a laser desorption time-of-flight mass spectrometer from Bruker-Franzen, Bremen (Biflex, nitrogen laser 337 nm). – Materials: Graphite rods, Reinstgraphit "EK96", were purchased from Kogo, Oberpleis, pyrolytical boron nitride "PBN" from Ringsdorff, Bonn. The cooling gas was helium 4.6 (99.996%) from Messer Griesheim. The remaining materials were barium rods 99%+ (Aldrich, Steinheim, 23/709-4), barium hexaboride, 100 mesh (Aldrich, Steinheim, 39/479-3), toluene p.a. (Riedel-de Haën, Seelze, 32249), and CS_2 p.a. (Merck-Schuchardt, Hohenbrunn, 8.22304).

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