Endohedral Complexation of Helium Atoms by Derivatised Fullerenes

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Tandem mass spectrometry experiments reveal the first examples of helium encapsulation by derivatised fullerenes with retention of the fullerene substituents; this has been observed for both aminated C_{60} and C_{70} adducts.

While studies of the physical properties and chemical nature of the fullerenes, *i.e.* the characteristics of their carbon skeleton, have continued apace since their discovery, another area of interest has been concerned with the inner space of the molecules and the ability of these closed cage species to form endohedral complexes with both inert gas and metal atoms.

Early experiments carried out on the fullerenes resulted in the formation of so-called metallofullerenes[1] by the laser ablation of metal-doped graphite samples. Although initially there was a possibility that the metals might be bonded to the outside of the fullerene cage,[2] it has now been shown unequivocally that the metal atoms are encapsulated within the cage structure of the fullerene.[3–6] Such species are described by the notation M@C_x, which denotes that the metal, M, is incorporated within the fullerene C_x.[4] Recently, it has also been shown[7] that formation of helium encapsulated fullerenes also occurs during the Krätschmer–Huffman fullerene production process[8] of evaporating graphite electrodes under a helium atmosphere.

Formation of such endohedral complexes, either by laser ablation or by using the Krätschmer–Huffman process, requires that the 'prisoner' atom be 'folded in' to the fullerene cage as it is forming. An alternative method of encapsulating atoms of inert gases within fullerenes was discovered by Schwarz *et al.*[9] The encapsulation occurs when the fullerenes undergo collisional induced dissociation (CID) during tandem mass spectrometry experiments. Whereas normally the CID process results only in fragmentation of molecules, in the case of the fullerenes it is also possible to witness incorporation of the collision gas into the preformed fullerene cage.

This technique provides evidence that the mass spectrometry fragmentation products are caged species,[9] and it also provides clues to the structural arrangement of the species formed.[10] However, so far it has only been possible to witness incorporation of metal or inert gas atoms into the basic, underivatised fullerene cages. Attempts have been made by Weiske *et al.*[11] to incorporate helium into derivatised C_{60}, *e.g.* $C_{60}H^+$, $C_{60}D^+$ or $C_{60}(H)CH_3^{\cdot +}$; however, penetration of the cage by the helium always resulted in complete dissociation of the substituents from the fullerene surface. In the communication we present details of the first examples of the incorporation of helium into the cages of both substituted C_{60} and C_{70} fullerenes with retention of the adduct functionalities together with the formation of a stable, substituted C_{60} endohedral species.

A tandem mass spectrometry (MS–MS) study was performed on the species $C_{70}H_x(NMe_2)_x$ where x = 1 to 8, the products of the reaction between a mixture of C_{60} and C_{70} and dimethylamine at 0 °C.[12] The mass spectra were recorded on a Kratos Concept IIHH four-sector (Manchester, UK) tandem mass spectrometer operating under fast atom bombardment (FAB) ionisation conditions with xenon atoms of 8 keV energy *m*-Nitrobenzyl alcohol (*m*NBA) was the matrix of choice. MS1 was used to obtain the double focused mass spectrum and CID was employed using helium as the collision gas, such that 70% of the precursor ion beam was attenuated with the collision cell floated at 4 kV. Mass resolution is in excess of 1000, sufficient to eliminate ^{13}C isotopes; therefore all mass selected ions in the MS–MS spectra correspond to purely ^{12}C species. Array detection was employed after MS2 and all data were obtained in the positive ion mode.

As expected it was possible to see helium atom encapsulation by the C_{70} that results from fragmentation of the amine adducts, together with the smaller fullerenes formed by breakdown of the C_{70}. Furthermore, MS–MS on the peaks at *m*/*z* 884 (Fig. 1) and 1060 (Fig. 2) both revealed the existence of peaks corresponding to M + 4. The peak at *m*/*z* 884 corresponds to the species $[(C_{70}H{\cdot}NMe_2) + H - H_2]^+$, whereas the peak at *m*/*z* 1060 represents $[(C_{70}(H{\cdot}NMe_2)_5) + H - 3H_2]^+$. The M + 4 peaks which accompany each of these species can be considered as arising from insertion of helium atoms inside the substituted fullerene, without loss of the amine functionality. A semi-empirical minimised structure of the lowest energy isomer for the encapsulated species at *m*/*z* 888 is shown in Fig. 4.

In addition to these two examples, each of the eight amine adducts undergo fragmentation to produce two breakdown products of *m*/*z* 752 and 736. Similar ions have previously been

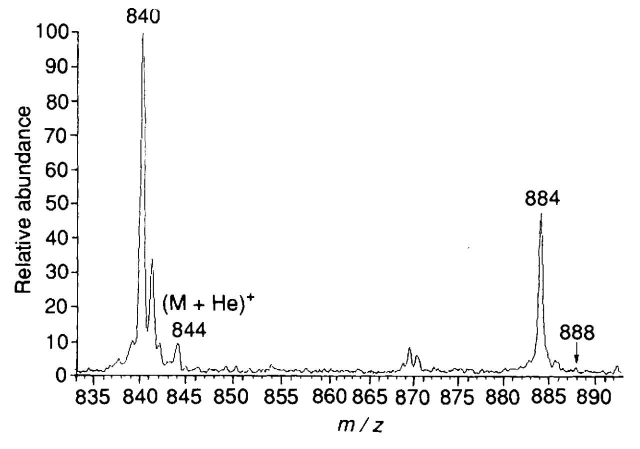

Fig. 1 Endohedral helium encapsulation by *m*/*z* 884 ion in fragment ion scan of *m*/*z* 1060. Other peaks visible are *m*/*z* 885 $[M + H]^+$, 844 $[He@C_{70}]^+$, 842 $[C_{70}H_2]^+$, 841 $[C_{70}H]^+$ where M represents the fragmentation ion *m*/*z* 884.

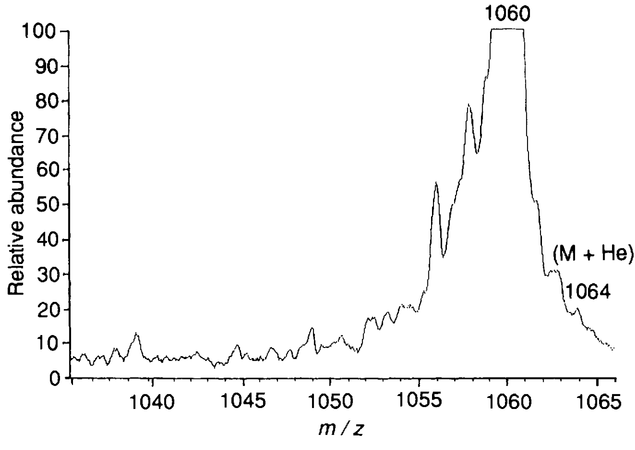

Fig. 2 Endohedral complexation by *m*/*z* 1060 ion. Other peaks visible are *m*/*z* 1062 $[(He@M) - H_2]^+$, 1061 $[(He@M) - H_2 - H]^+$, 1059 $[M - H]^+$, 1056 $[M - 2H_2]^+$ where M represents the mass selected ion *m*/*z* 1060.

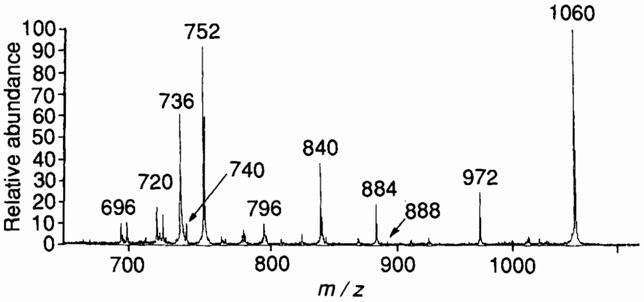

Fig. 3 Fragmentation of *m/z* 1060 showing production of *m/z* 736 $[(C_{60}NH_2)^+]$ and its endohedral helium complex $(He@C_{60}NH_2)^+$ (*m/z* 740)

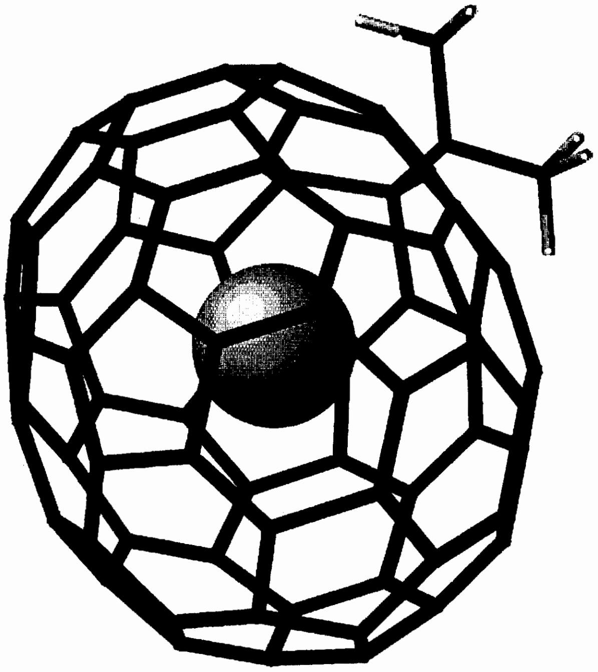

Fig. 4 Semi-empirical minimised structure of the lowest energy isomer of $(He@C_{70}NMe_2)^+$ (*m/z* 888). Calculations were carried out on a Tektronix CAChe workstation using MOPAC 6.0. The helium atom is displayed at 99% van der Waals radius.

witnessed by Stry *et al.*[13] MS–MS studies reveal that the *m/z* 736 species undergoes two losses of 1 unit (*i.e.* two losses of H) and further fragments to C_{60} and $He@C_{60}$. It can therefore be assumed that this species is the stable fragmentation product $(C_{60}NH_2)^+$ for which the encapsulation product $(He@C_{60}NH_2)^+$ is also witnessed under CID conditions (Fig. 3). Similar analysis of *m/z* 752 has not revealed any endohedral complexation.

In conclusion, we have shown for the first time that it is possible to incorporate helium atoms into the cages of substituted C_{70} compounds without fragmentation of the adduct species. Furthermore, these amine adducts all fragment to produce the same stable, helium-incorporated, aminated C_{60} species, $(He@C_{60}NH_2)^+$. This process is not necessarily a major one, as it varies with collision energy.[9] However, it is interesting to note that the smaller the fullerene cage fragment ion, the larger the relative intensity of the encapsulated product. For example, the relative intensities of C_{58} and $He@C_{58}$ are almost equal (Fig. 3). At present we are extending our study to examine further examples of endohedral atom encapsulation of other C_{60} and C_{70} derivatives.

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