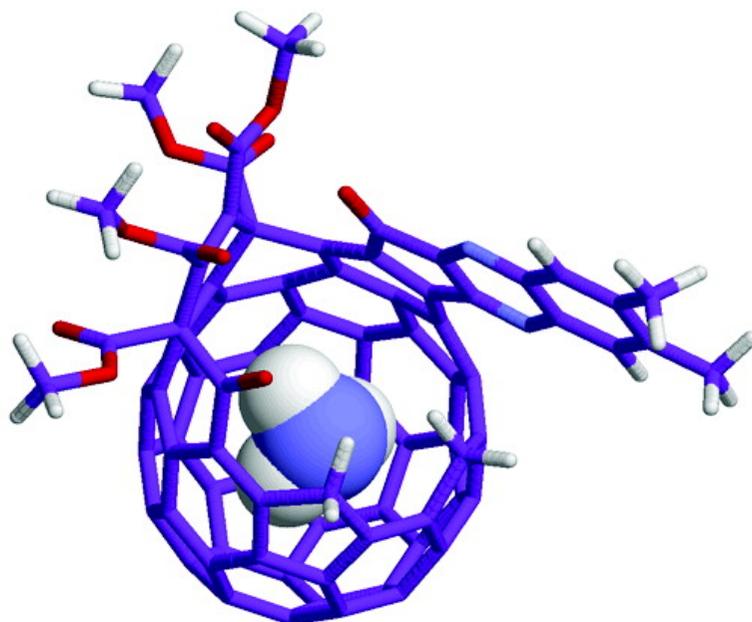


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Putting Ammonia into a Chemically Opened Fullerene

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Abstract: We put ammonia into an open-cage fullerene with a 20-membered ring (1) as the orifice and examined the properties of the complex using NMR and MALDI-TOF mass spectroscopy. The proton NMR shows a broad resonance corresponding to endohedral NH₃ at $\delta_{\text{H}} = -12.3$ ppm relative to TMS. This resonance was seen to narrow when a ¹⁴N decoupling frequency was applied. MALDI spectroscopy confirmed the presence of both 1 ($m/z = 1172$) and 1 + NH₃ ($m/z = 1189$), and integrated intensities of MALDI peak trains and NMR resonances indicate an incorporation fraction of 35–50% under our experimental conditions. NMR observations showed a diminished incorporation fraction after 6 months of storage at -10 °C, which indicates that ammonia slowly escapes from the open-cage fullerene.

Introduction

Ever since the discovery of fullerenes in 1985,¹ it was realized that the space inside could hold atoms and even small molecules. Several methods have been developed for producing endohedrally doped fullerenes, including ion bombardment and high-pressure/high-temperature techniques.^{2–9} The main drawbacks of these methods are low yield (<1%) and the need for extreme reaction conditions. A relatively new approach to producing endohedral fullerenes has been the “molecular surgery” method, whereby a hole is chemically opened on the surface of the fullerene cage, and a gas molecule is inserted reversibly through the orifice.^{10–24} This method avoids the drawbacks of the others because the orifice in the fullerene considerably lowers the

activation barrier for insertion of the dopant molecule. A high incorporation fraction of small molecules into the fullerene can thus be achieved under relatively mild reaction conditions. Komatsu et al. added groups to C₆₀ to create a 13-membered ring in the carbon cage.¹⁴ This is large enough to permit H₂ and He to enter.^{15,16} They then devised a sequence of reactions that closed the hole, trapping H₂ inside to produce H₂@C₆₀ in high yield.¹⁷

Several synthetic groups have been working to produce novel open-cage fullerene derivatives with various orifice sizes.^{12,13,16,19–22} In particular, Iwamatsu et al.^{20,21} have succeeded in synthesizing a fullerene with a 20-membered ring as the orifice (1), the largest opening synthesized on a fullerene to date; see Figure 1.

The size of this orifice is such that a water molecule spontaneously incorporates into the fullerene cage at room temperature.²¹ Furthermore, it has been shown that, under suitable reaction conditions, CO can be incorporated into 1.²³ We report here the synthesis of a new endohedral fullerene,

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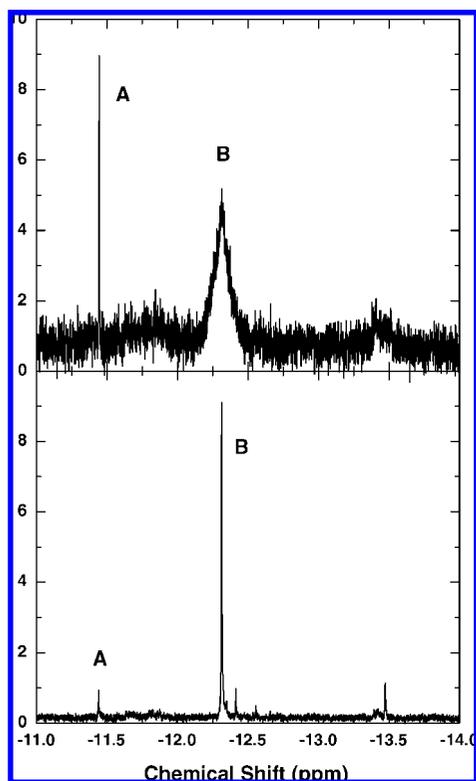


Figure 3. Upfield region of the proton NMR of $\text{NH}_3@1$. Top panel: Undecoupled spectrum. Bottom panel: With ^{14}N decoupling applied. Peak A is due to $\text{H}_2\text{O}@1$, and peak B is due to $\text{NH}_3@1$. Note: Spectra have been rescaled (see text).

ammonia dissolved in CDCl_3 ($\delta_{\text{H}} = 0.465$ ppm) is characteristic of endohedral molecules inside fullerenes, as the ring currents induced by the external static magnetic field produce an opposing field inside the fullerene, which shields the nuclei inside. This effect has been predicted theoretically and observed experimentally in a number of other endohedral fullerenes.^{16,20,25–33} Two potential causes were hypothesized for the significant broadening of the observed proton resonance. First, the broadening could be due to the coupling with the nuclear spin of the nitrogen. Because ^{14}N has a nuclear spin of $I = 1$, the proton peak should be split into a 1:1:1 triplet. However, ^{14}N has a large electric quadrupole moment, and, in an asymmetric environment, the tumbling of the molecule causes rapid enough relaxation of the ^{14}N spin to broaden the three proton peaks to give a single broad line. This effect is common in protons bonded to nitrogen. Second, the umbrella inversion of ammonia inside the open-cage fullerene might be slow on the NMR time scale, leading to a broadening of the line as the protons spend more time in unequal chemical environments.

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Table 1. Chemical Shifts

	NH_3	$\text{NH}_3@1$	$\Delta\delta$
^1H	0.465	−12.3	−12.8
^{14}N	−66.7	−87.8	−21.1

The first hypothesis was tested by decoupling the ^{14}N nucleus from the surrounding protons. An rf pulse at the ^{14}N resonant frequency causes rapid transitions among the three m states in ^{14}N . The pulse sequence was tested on tetraethylammonium chloride salt dissolved in D_2O . Here, the tetrahedral symmetry around the ^{14}N means that the electric field gradient at the nucleus is zero, and the quadrupolar relaxation is not present. The characteristic 1 Hz N–H j -coupling in the methyl protons of the salt disappeared when the rf was set to the salt's ^{14}N resonant frequency. Gaussian 03³⁴ GIAO calculations at the B3LYP/6-311G++(2p,2d) level indicated that the ^{14}N frequencies of the ammonium salt and the endohedral ammonia were separated by ~ 100 ppm. A ^{14}N decoupling frequency of $\delta_{\text{N}} = -87.75$ ppm (relative to the ammonium salt) collapsed the large ammonia proton line at $\delta_{\text{H}} = -12.3$ ppm from 45 to 2 Hz fwhm, as seen in the bottom panel of Figure 3. This observation indicates that the extreme broadening of the line is caused mainly by rapid quadrupolar relaxation of the ^{14}N nucleus, which, in turn, relaxes the protons bound to it. It should be noted that the measured intensities of the water peak (peak A) in the two panels are the same; the ordinate has been rescaled on the bottom panel.

We measured the upfield shifts for both protons and ^{14}N caused by putting ammonia into **1** (Table 1). The proton NMR of free ammonia showed a single narrow peak at 0.465 ppm. The peak is narrow and not split by ^{14}N because the protons rapidly exchange with trace amounts of water in the solvent. This difference is yet another proof that the ammonia that we are studying is inside **1** and protected from exchange. The upfield shift due to the incorporation is then 12.8 ppm. As stated above, we find the ^{14}N resonance in $\text{NH}_3@1$ is at -87.75 ppm relative to tetraethylammonium ion. Using ^{14}N NMR, we found the resonance for NH_3 is at -66.67 ppm relative to tetraethylammonium ion. This gives an upfield shift for the nitrogen of 21.1 ppm. The difference between the effects on protons and ^{14}N is due to the different positions in the open-cage fullerene cage and to the different effects of the solvent for the dissolved ammonia.

To test the second hypothesis, the sample was cooled to -80 °C without the decoupling field. There are two orientations of the ammonia molecule in the cage: with the hydrogens pointed toward or away from the mouth. If the interconversion is sufficiently slow, the proton peak will broaden. If the temperature is decreased, the interconversion slows still further, and the NMR spectrum would show two peaks. The ammonia proton fwhm decreased from 45 to 13 Hz, probably due to the decreased quadrupole relaxation of the ^{14}N , but did not split into two lines. Also, several other lines too broad to be distinguished from the noise appeared to be sharpened as well, although not as much as when decoupled. When the spectrum was decoupled at -80 °C, no additional effects beyond those reported in the room-temperature decoupling experiment relating to peak height or area were seen. This suggests that the small extra resonances observed at low temperatures are not additional

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conformations of NH_3 inside **1**, but rather NH_3 inside chemically modified derivatives of **1**, likely byproducts of the reaction of ammonia with the external scaffolding around the orifice of **1**.

After more than 6 months of storage under N_2 at $-10\text{ }^\circ\text{C}$, the resonance at $\delta_{\text{H}} = -12.3\text{ ppm}$ was still observed in the ^1H NMR spectrum of our sample, but at greatly reduced intensity. The small resonance due to $\text{H}_2\text{O}@1$, however, remained at roughly the original intensity. These results indicate that the incorporation of ammonia into the open-cage fullerene is reversible and that the incorporated gas leaks out of the cage over a long period of time. Water apparently has a low barrier for going into or out of **1**. Therefore, $\text{H}_2\text{O}@1$ rapidly equilibrates with the trace water in the NMR solvent. Ammonia that escapes from **1** diffuses out of the NMR tube and is lost.

Summary

We have demonstrated the incorporation of NH_3 into the open-cage fullerene **1**. NMR and MALDI spectroscopy indicate the formation of $\text{NH}_3@1$ where the ammonia is highly shielded by the fullerene cage and the protons undergo rapid relaxation in the presence of the ^{14}N electric quadrupole moment. The gas is observed to slowly escape over time, reverting to the original empty open-cage fullerene.

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Supporting Information Available: Complete ref 34. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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