X-Ray crystallographic and EPR spectroscopic characterization of a pyrrolidine adduct of $Y_3N@C_{80}$

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Crystallographic data for the pyrrolidine adduct $Y_3N@C_{80}C_4H_9N\cdot 2.5CS_2$ reveals a slightly pyramidalized Y_3N unit with idealized mirror symmetry that straddles the site of addition but does not directly interact with the addend.

The discovery that the yields of endohedral fullerenes could be increased by the addition of nitrogen to the Krätschmer–Huffman electric arc process for fullerene generation has made the $M_3N@C_{80}$ family of endohedrals available in quantities suitable for research on potential applications.[1] The ability to encapsulate a series of lanthanide ions inside these cages confers a multitude of useful magnetic and spectroscopic properties on these endohedrals,[2,3] while the external functionalization of these endohedral fullerenes offers a means to modify their chemical and physical properties. Functionalization of the I_h isomer of $Sc_3N@C_{80}$ has been accomplished using both a Diels–Alder reaction and an azomethine ylide addition.[4–6] These cases led to the formation of adducts at the 5:6 ring junction of the cage. In contrast, azomethine ylide addition to $Y_3N@C_{80}$ produced an adduct in which the addition occurred initially at the 6:6 ring junction.[7] Thus the internal metal ions appear to exert control over the site of addition. We have recently found that the pyrrolidine adduct of $Y_3N@C_{80}$ thermally isomerizes from the 6:6 to the 5:6 isomer.[8] This was also the case for the *N*-ethyl azomethine ylide monoadduct on $Er_3N@C_{80}$.[8] In order to probe the effect of the internal metal on the addition product, we report here the structure of the neutral molecule and the electronic structure of the LUMO of a 5:6 azomethine ylide adduct of $Y_3N@C_{80}$. As far as we know this is the first crystal structure of an endohedral trimetallic nitride containing yttrium and the first structure of an endohedral pyrrolidinofullerene derived from a trimetallic nitride compound.

The synthesis of the 5:6 *N*-ethyl pyrrolidine monoadduct of $Y_3N@C_{80}$ involved the thermal rearrangement of the 6:6 isomer, which was prepared as previously described.[7,8] In a typical rearrangement reaction, 2 mg of the 6:6 regioisomer was heated at 160 °C in 2 mL of *o*-dichlorobenzene under argon and the isomerization was followed to completion by thin layer chromatography to produce the 5:6 regioisomer in a quantitative yield. Characterization of the 5:6 regioisomer consisted of ^1H NMR, MALDI-TOF, HPLC (Cosmosil Buckyprep-M), and electrochemistry.

Black plates of $Y_3N@C_{80}C_4H_9N\cdot 2.5CS_2$ suitable for X-ray crystallography were obtained by carefully layering a 0.5 mL portion of benzene over a saturated carbon disulfide solution of the complex and adding a second 0.5 mL portion of methanol on top of the first two layers.† Two orthogonal views of the structure of the adduct are shown in Fig. 1. The fullerene cage is fully ordered, while there is minor disorder in the positions of the yttrium ions inside the cage. The position of the major form with 0.89 occupancy for the Y_3N group is shown in Fig. 1. There are also two distinctly minor orientations of the Y_3N group, one with 0.07 occupancy, the other with 0.04 fractional occupancy which are not shown in the figure. Since these two forms are such minor contributors to the overall structure only the major form will be considered here. However, the presence of these minor forms suggests that the Y_3N group is somewhat free to move about inside the carbon cage. An alternative possibility, disorder of the entire molecule, is not reasonable because there is not enough space in the crystal to accommodate the bulky addend in different locations.

The Y–N distances (Y1–N1, 2.067(5); Y2–N1, 2.051(5); Y3–N1, 2.022(4)) show some variations as is common for such endohedral species. As expected, the Y–N distances are generally longer than the Sc–N distances (2.032(3), 2.020(3), and 2.029(3) Å) in the functionalized adduct, $Sc_3N@C_{80}C_{10}H_{12}O_2$[4] but shorter than the Gd–N distances (2.038(8), 2.085(4), 2.117(5)) in $Gd_3N@C_{80}$.[9] The Y_3N unit in the major orientation is slightly pyramidalized as shown in Fig. 2, which shows the Y_3N unit seen edge on to emphasize the out-of-plane displacement (0.13 Å) of the nitrogen atom. This out-of-plane displacement can be attributed to the size of the yttrium ions. Y^{3+} (ionic radius 1.01 Å) is larger than either Sc^{3+} (ionic radius 0.87 Å) or Lu^{3+} (ionic radius 1.00 Å) but smaller than Gd^{3+} (ionic radius 1.05 Å).[10] Thus, the M_3N units in $Sc_3N@C_{80}$ and $Lu_3N@C_{80}$ are planar,[11] while the Gd_3N unit in $Gd_3N@C_{80}$ is more highly pyramidalized (N out-of-plane displacement, 0.52)[9] than is the Y_3N unit in $Y_3N@C_{80}C_4H_9N$.

The Y_3N group is positioned so that Y1 and Y2 occupy similar positions and straddle the site of addition. They are each situated over 5:6 ring junctions of the cage with the following distances: Y1–C29, 2.375(6); Y1–C11, 2.379(6); Y2–C39, 2.354(6); Y2–C19, 2.383(6) Å. In contrast Y3 is positioned so that it is closest to a single carbon atom of the cage with a Y3–C80 distance of 2.312(6) Å.

Consideration of the pyramidalization angles θ_p,[12] (θ_p for graphite = 0°; θ_p for C_{60} = 11.6°) for the individual fullerene carbons of the cage reveals that the yttrium ions push the closest carbon atoms out from the surface as the data in Fig. 3 show. The

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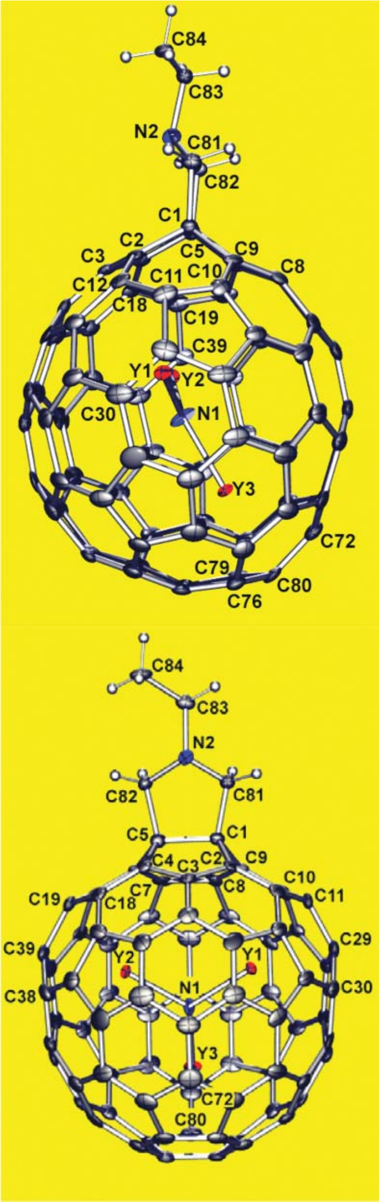

Fig. 1 Two orthogonal views of the structure of the endohedral adduct in $Y_3N@C_{80}C_4H_9N \cdot 2.5CS_2$ with 30% thermal contours. Only the major site (0.89 occupancy) for the Y_3 group is shown.

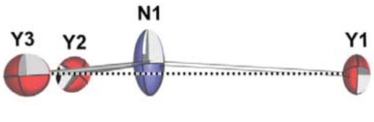

Fig. 2 A view of the Y_3N portion at the major site (0.89 occupancy) showing the small out-of-plane displacement (0.13 Å) of the nitrogen atom.

carbon atoms nearest the site of addition show a wide range of pyramidalizations. For carbon atoms further from the addition site, those at the junction of two hexagons and a pentagon are more pyramidalized than the carbon atoms at the junction of three hexagons. A similar situation was observed in $Sc_3N@C_{80}C_{10}H_{12}O_2$ previously.[4]

The addition has occurred at a 5:6 ring junction as prior spectroscopic data suggested.[7,8] As a result of adduct formation, the C1–C5 bond of the endohedral has lengthened to 1.654(8) Å. For comparison, the average 5:6 bond length in I_h C_{80} is 1.44 Å. When a similar reaction occurs with C_{60}, addition involves a 6:6 ring junction and results in an elongation of that bond from 1.38 to 1.604(5) Å.[13] Recently the structure of a pyrrolidine adduct of $La_2@C_{80}$ has been reported, but in this case the addition involved a 6:6 ring junction.[14]

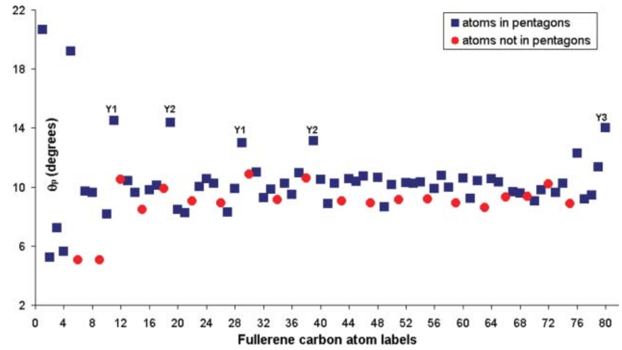

Fig. 3 A plot of the pyramidalization angles (θ_p) for the fullerene carbon atoms in $Y_3N@C_{80}C_4H_9N \cdot 2.5CS_2$. The sixty carbon atoms that reside at the junction of a pentagon and two hexagons are shown as squares while the twenty others that reside at the junction of three hexagons are shown as circles. The carbon atoms that are closest to yttrium atoms are labeled Y1, Y2, or Y3.

Electron paramagnetic resonance (EPR) experiments of the mono-anion of $Y_3N@C_{80}C_4H_9N$ were conducted in a vacuum-sealed two compartment cell having an attached EPR tube. X-Band spectra were recorded at room temperature using a Bruker EMX spectrometer. The compound was dissolved in dry THF and reduced upon repeated contact with K metal. Initially the sample of the starting adduct showed no EPR spectrum. Upon contact with the potassium the experimental spectrum shown in Fig. 4 developed. Fig. 4 also shows the simulated spectrum. The spectrum shown in Fig. 4 disappeared upon further contact with K metal, presumably due to the formation of a dianion with a different spin-state.

The first-order simulation of the EPR spectrum of the mono-anion of $Y_3N@C_{80}C_4H_9N$ resulted in an excellent fit within 0.05 G

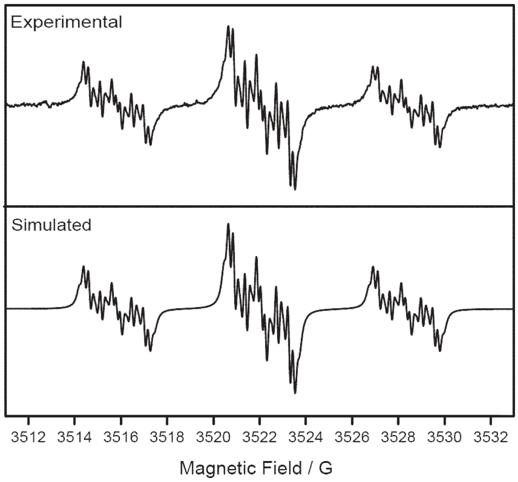

Fig. 4 Experimental and simulated EPR spectra of the K metal-reduced mono-anion of $Y_3N@C_{80}C_4H_9N$ in THF at 298 K.

uncertainty, see Fig. 4. The simulation is perfectly consistent with the symmetry observed for the neutral compound as deduced from the crystal structure. Two equivalent Y nuclei having the largest hyperfine coupling constants (6.26 G) and a unique Y center (1.35 G) are consistent with an Y_3N cluster with idealized mirror symmetry, as shown in the crystal structure. Some unpaired spin density is localized on the cluster nitrogen as evidenced by a coupling constant of 0.51 G. Two pairs of equivalent hydrogen atoms with slightly different hyperfine splittings (0.21 and 0.19 G) provide evidence that the LUMO of $Y_3N@C_{80}C_4H_9N$ is not exclusively confined to the internal cluster. Previous ESR results for $M_3N@C_{80}$ were limited to the anion radical of the unfunctionalized compound with M = Sc, which showed exclusive spin localization in the cluster, with three equivalent Sc hyperfine nuclei of 55.6 G.[15] The present results indicate similar spin localization in the cluster but the N nucleus hyperfine is now detectable. The presence of hydrogen hyperfine structure indicates that the most probable orientation of the internal cluster of the fullerene mono-anion is very similar to that of the neutral molecule since the highest unpaired spin density resides on the two Y nuclei closest to the pyrrolidine addend. The EPR spectral linewidths are very narrow (0.16 G), and the g-value of 1.998915 is somewhat lower than the typical values observed for carbon-centered radicals, indicating significant metal-based unpaired spin.

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Notes and references

† *Crystal data*. Needles of $C_{84}H_9N_2Y_3 \cdot 2.5CS_2$, $M = 1502.99$, tetragonal, space group $P4_12_12$, $a = b = 14.949(2)$ Å, $c = 41.966(8)$ Å, $V = 9378(3)$ Å^3 at 90(2) K, μ(Mo-Kα) = 3.975 mm^{-1}, $Z = 8$. Refinement of 13176 reflections, 928 parameters, and 1 restraint yielded $wR2 = 0.151$ for all data and a conventional $R1 = 0.057$ based on 10805 reflections with $I > 2\sigma(I)$. CCDC 602149. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604011j

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