Chemically Induced Spin Transfer to an Encased Molecular Cluster: an EPR Study of $Sc_3N@C_{80}$ Radical Anions

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Since the preparation of macroscopic quantities of endohedral fullerenes (EF),[1] a large number of investigations have been performed to elucidate the topology and the electronic structure of these new species. There was general consensus that the inner surface of the carbon cage should be quite inert against attack from an encased atom or ion and that covalent binding should be rather weak. As consequence, ionic structures were proposed for group III elements, and zero charge transfer was indeed observed for group V elements.[2] Clearly, such models are oversimplified, and more recent investigations have revealed that for the most abundant species such as $La@C_{82}$ substantial covalency is observed, which can be envisaged as strong coupling of atomic and molecular wave functions.[3]

It was therefore tempting to study whether a variation of the total charge of the compound by reduction or oxidation could effect the charge distribution between cage and encapsulate. It was even speculated that single-electron reduction might lead to a one-step valency change of the encapsulated ion.[4] Such a drastic change in charge and spin distribution should have major effects in the EPR spectrum of the compound. First experiments performed on lanthanide EF were rather inconclusive, however, as no change in the EPR spectrum was detected. A simple explanation may be given by the fact that these systems are spin doublets in their uncharged ground state, and addition or removal of only one electron could lead to an EPR silent singlet state, or a paramagnetic triplet state. Even if a triplet electron spin state would be formed, contributions from zero-field-splitting (ZFS) to spin relaxation would probably broaden the EPR signal beyond detectablitiy. In both cases, reduction could probably only be sensed by a loss in EPR intensity of the unreduced neutral compound which would be difficult to quantify in the presence of a large background signal.

Formation of an EPR silent electron spin singlet ground state is consistent with the assumption of a weakly coupled ionic system, in which three electrons are already transferred to the cage in the uncharged compound, forming a singly occupied nondegenerate HOMO. Further charge accumulation by one-step reduction was assumed to be restricted to the molecular orbitals of the cage. Recently it was demonstrated by a NMR study that under one-step reduction of $La@C_{82}$ indeed a diamagnetic closed shell spin system is formed.[5] As dianions of group III MEF apparently are not stable enough for an EPR study, no spectra of such odd-electron systems were reported, and as result the proposed model of reduction-induced valency change of the encased ion lacks experimental verification.

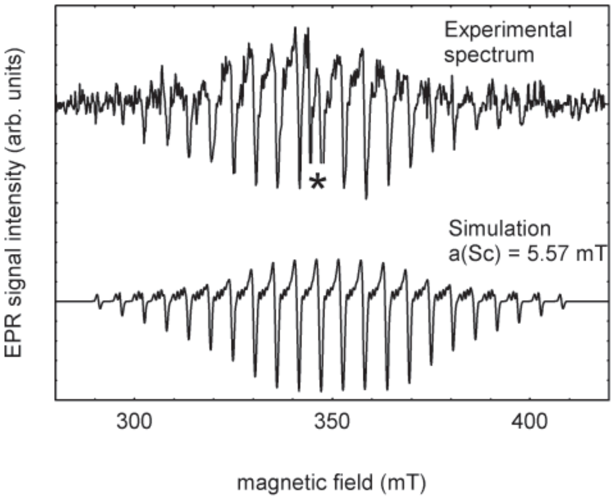

Figure 1. Experimental and simulated X-band EPR spectra of monoanions of $Sc_3N@C_{80}$. The spectrum was measured at room temperature. The asterix denotes a narrow impurity signal close to the spectral center at $g = 1.9984(2)$.

It therefore seemed attractive to start with an even-electron EPR silent singlet spin system and to try to study monoanions or monocations. Because of the notorious instability of for instance group II compounds, no data have yet been reported for these systems. As alternative we have chosen the stable $Sc_3N@C_{80}$ molecule for a study.[6] This compound can be obtained in macroscopic quantities, and has an $S = 0$ electron spin ground state as was proven by ^{45}Sc NMR.[6] If, as anticipated, reduction-induced spin transfer to the encased cluster would occur, this effect could be detected by measuring hyperfine interaction (hfi) with scandium ($I = {}^7/_2$) and nitrogen ($I = 1$) nuclear spins of the encased cluster. Furthermore, direct comparison of these values with data from previously measured $Sc_3@C_{82}$[7] and $Sc@C_{82}$[8] compounds is possible.

HPLC-pure samples of $Sc_3N@C_{80}$ were purchased from Luna Innovations, Inc., and used without further purification. Sealed samples of approximately 10^{-4} M concentration were prepared using carefully de-oxygenated tetrahydrofuran (THF). Reduction was performed by preparing first a solution of solvated electrons using a Na/K alloy. Subsequently, this solution was transferred to a thin film of $Sc_3N@C_{80}$ molecules, prepared by solvent evaporation. Concentration and reduction status were controlled by repeated contact with the solvated electron solution and addition of additional solvent. All of these manipulations were performed in the sealed sample tube. EPR spectra were measured with a standard continuous wave X-band EPR spectrometer (BRUKER ESP 300E). Upon reduction at room temperature, the solvent turned yellow, and an EPR signal could be detected. In Figure 1, the experimental spectrum, which extends over a range of 150 mT is depicted. At least 15 regularly spaced groups of lines separated by 5.56 mT can be identified, which according to the simulation originate from hfi with three equivalent scandium nuclei. Because of the rather large hfi constant, second-order splittings of the order of 0.5 to 5 mT (!) lead to a multitude of

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Table 1. Scandium Isotropic hfi Coupling Constants and Line Widths of Different EF Measured at Room Temperature

compound	a_{iso}(Sc) (mT)	line width (mT)
Sc@C$_{82}$	0.380	0.005
Sc$_3$@C$_{82}$	0.625	0.078
Sc$_3$N@C$_{80}$	5.56	0.5

transitions, resulting in a characteristic asymmetric line shape if—as in our case—individual lines cannot be resolved. Within experimental accuracy, no nitrogen hfi could be detected. The line shape function used for spectrum simulation was 0.5 mT, setting an upper limit for the "missing" nitrogen hfi. The observed line width of 0.5 mT is surprisingly large. At the moment we can only speculate about its origin. Comparing the intensity variation with nuclear spin quantum number M_I in the experimental and simulated spectra, no significant linear or quadratic M_I dependence is seen within the limited signal-to-noise ratio. Such a dependence would be expected if modulation of the isotropic scandium hfi by hopping between nonequivalent sites or modulation of the anisotropic part of the hfi by either internal or external molecular tumbling would dominate spin relaxation. This would be reasonable to assume because of the large size scandium hfi. Modulation of the electric field gradient at the scandium site would also be M_I-dependent.[9] It could also be speculated that the large line width originates from a dynamic Jahn—Teller effect, because a two-fold degenerate HOMO compatible with C_{3v} symmetry could be lowered to C_s, thus giving rise to two different Sc hfcc. Such symmetry-lowering has, in fact, been observed when optimizing the structure of the compound. Still, in the apparent absence of nuclear spin-dependent relaxation mechanisms, we are left with possible contributions from g-matrix anisotropy and spin rotational interaction as dominating mechanisms. Spin-exchange processes can also not be excluded at the moment. Further studies are in progress to determine the dominant interactions leading to spin relaxation.

The situation is similar with respect to line broadening seen in the neutral spin doublet Sc$_3$@C$_{82}$. Published spectra do not give any indication of a second-order splitting.[10] Differentiated EPR lines are symmetric to a high degree, indicating that the homogeneous line width is significantly larger than the second-order splitting which results in a multitude of lines separated by ca. 0.01 mT and displaced by up to 0.05 mT. It was speculated that modulation of the isotropic hyperfine coupling constant (hfcc) is dominating spin dephasing at lower temperatures, but no quantitative analysis could be performed probably because individual lines could not be resolved.[11] In particular, the reason for a M_I-independent relaxation mechanism rendering the width of the individual hfi components much larger than the widths of EPR transitions of a single encased scandium (Sc@C$_{82}$) (see Table 1) is still unknown.

In Table 1, experimental values of isotropic scandium hfi coupling constants of three EF are compiled, showing an order of magnitude increase in Sc hfi for Sc$_3$N@C$_{80}$ anions compared to previously studied neutral compounds. Their small hfi was rationalized by assuming transfer of three electrons to the cage, thus forming a diamagnetic encapsulate with predicted small Sc hfi. No calculated values have been reported for the two neutral EF, presumably because only recently cage topology, i.e., its symmetry, and binding position for Sc@C$_{82}$ have been determined,[12] and in case of the cluster-type EF, calculations are impeded by the apparent fast mobility of the encased clusters. As a first approach for an hfi estimate of the anion we have chosen a fixed cluster orientation leading to the highest possible total symmetry of the compound. This is obtained by placing the planar Sc$_3$N cluster of D_{3h} symmetry with its C_3 axis along one of the C_3 symmetry axes of the C$_{80}$ cage, resulting in the point group C_{3v} for the entire compound. DFT and HF calculations on a basis set level of 3-21G* resulted in hfi constants and charge distributions compiled in Table 2. Increasing the basis set to 6-31G* for the cluster did not change the values significantly. A strong dependence of the Fermi contact hfi on the total charge is predicted.

Table 2. Charge Distribution and Isotropic hfcc Calculated for a Fixed Geometry of C_{3v} Symmetry

	ROB3LYP/3-21G*	ROHF/3-21G*	
anion	+ 4.47	+4.86	cluster charge
uncharged	+4.59	+4.99	
cation	+4.78	+5.27	
anion	+1.78	+1.99	Sc charge
uncharged	+1.82	+2.04	
cation	+1.88	+2.14	
anion	−0.85	−1.11	N charge
uncharged	−0.87	−1.13	
cation	−0.86	−1.15	
anion	20 MHz	40 MHz	Sc Fermi contact hfi
cation	125 MHz	190 MHz	
anion	0	0	N Fermi contact hfi
cation	1 MHz	9 MHz	

Comparison of predicted values for the cation, anion, and neutral compound shows that at this computational level the charge of the cluster seems to be rather insensitive to reduction or oxidation. In contrast, the experimental finding of an unusual large Sc hfcc in the anion indicates that charge (and spin) transfer from the cage to the freely suspended cluster occurs under reduction. May be this is not so much remarkable because the four-fold degenerate G_g HOMO of empty C$_{80}$ already "hosts" two electrons in its neutral state and is "closed" under transfer of six electrons from the encased cluster. Under reduction, a higher cage orbital would have to be involved, a situation the compound avoids by transferring additional charge to the internal cluster instead. The situation is completely different for Sc@C$_{82}$ and Sc$_3$@C$_{82}$, in which the open-shell state is formed by the cage orbitals and Sc contact hfi results from spin polarization.

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