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On the Stabilization of Fullerenes by Caged Atoms: Singly and Multiply Charged $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$ Ions

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We have measured the kinetic energy release distributions for unimolecular C_2 loss from singly and multiply charged $Sc_3N@C_{78}^{z+}$ ($z = 1, 2$) and $Sc_3N@C_{80}^{z+}$ ($z = 1, 2, 3$). Using finite heat bath theory, we deduce the dissociation energies of these endohedral ions toward loss of C_2. The data show that the complexation energies (i.e., the adiabatic binding energies between Sc_3N and the fullerene cage C_n^{z+}) are, for a given charge state and within the experimental uncertainty, identical for $n = 76$, 78, and 80.

Introduction

The fascinating possibility of caging atoms in fullerenes was noticed immediately by Kroto et al. when they proposed the hollow icosahedral structure of C_{60}.[1] Very soon, endohedral fullerenes were formed in the gas phase by laser vaporization of metal-impregnated graphite[2] or by energetic collisions between empty fullerenes and atoms.[3] The field exploded soon after the macroscopic synthesis of fullerenes was developed by Krätschmer et al.;[4] nowadays, a large variety of fullerenes with caged metallic and nonmetallic elements have been synthesized and purified (see refs 5 and 6 for recent reviews).

The kinetic stability of metallofullerenes under ambient conditions had originally presented some puzzles. Until 2000, all attempts to isolate C_{60}-based metallofullerenes proved futile[5,7] except for $Li@C_{60}$, which could be generated by Li ion implantation into C_{60} films.[8] It has been realized[9] that chemically unreactive metallofullerenes often employ chemically reactive fullerene isomers; electron transfer from the caged metal to the fullerene may even stabilize species that violate the isolated-pentagon rule, such as $Sc_3N@C_{68}$.[10]

While chemical stability is essential for the successful isolation and possible application of endohedrals, it says little about the thermodynamic stability of the complex. A measure of the thermodynamic stability is the complexation energy, also termed stabilization or embedding energy; it is usually defined as

$$M + C_n \rightarrow M@C_n - E_{\mathrm{cmplx}}(M@C_n) \qquad (1)$$

where M is an atom or complex of atoms. E_{cmplx} will be negative if reaction 1 is exothermic.

E_{cmplx} has been computed by many groups, especially for C_{60}. For inert gas atoms, stabilization increases continuously from $E_{\mathrm{cmplx}} = -0.01$ eV for He to ≈ -0.4 eV for Kr; it decreases again for Xe due to steric repulsion.[11] For C_{70}, the trend is similar.[12] For Li and Na cations caged in C_{60}, the computed values range from about -0.5 to -1.5 eV.[13,14] Steric effects were also observed in a study of alkali cations and halides: small ions (Li^+, Na^+, F^-, Cl^-) stabilize while larger ions (Rb^+, Br^-, I^-) destabilize the cage.[13] However, size is not the only criterion. N, P,[15] O, F,[16] and even H [17] are found to destabilize C_{60} by as much as 1 eV whereas As is surprisingly stabilizing by -0.4 eV.[18]

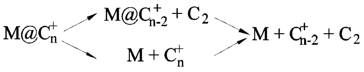
How do these calculated values compare with experimental data? There are none to compare with. The only experimental approach that provides an *indirect* clue to the stabilization has been explored by Lifshitz and co-workers.[19−22] They have measured the kinetic energy release (KER) for unimolecular dissociation of endohedral fullerene ions which, with the exception of $N@C_{60}^+$ that loses the caged nitrogen,[21] proceeds by loss of C_2:

$$M@C_n^+ \rightarrow M@C_{n-2}^+ + C_2 - D(M@C_n^+) \qquad (2)$$

From these data, one can derive using finite heat bath theory[23] the dissociation energies $D(M@C_n^+)$.[24,25] For some systems, especially for $Kr@C_{60}^+$, $La@C_{82}^+$, and $Tb@C_{82}^+$, the dissociation energies were found to exceed those of the corresponding empty fullerene ions

$$C_n^+ \rightarrow C_{n-2}^+ + C_2 - D(C_n^+) \qquad (3)$$

by several eV.[22] The result was interpreted as a stabilization of the cage upon introduction of the endohedral complex.[22,25] However, this kind of stabilization does *not* necessarily imply a high complexation energy, as is easily seen from the thermodynamic cycle:



(4)

from which follows the relation:

$$D(M@C_n^+) - D(C_n^+) = -E_{\mathrm{cmplx}}(M@C_n^+) + E_{\mathrm{cmplx}}(M@C_{n-2}^+) = -\Delta E_{\mathrm{cmplx}}(M@C_n^+) \qquad (5)$$

provided all quantities in eq 5 are adiabatic.

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Thus, a measurement of dissociation energies provides the *differential* complexation energy ($\Delta E_{\mathrm{cmplx}}$) as defined in eq 5. The large negative values of $\Delta E_{\mathrm{cmplx}}$ reported for $Kr@C_{60}^{+}$ [20], for example, could either mean that Kr strongly *stabilizes* C_{60}^{+} or that it *destabilizes* C_{58}^{+}. Unfortunately, no theoretical values are available for the stabilization energy of $Kr@C_{58}$ or its ions; therefore, we cannot tell which of these alternative explanations is the correct one.

There seems to be only one endohedral system for which complexation energies have been computed for adjacent sizes, namely, for $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$.[26] These metallofullerenes can be synthesized and purified with a yield that even exceeds that of empty C_{84};[27] their discovery has prompted several experimental[28] and theoretical[26,29−31] investigations. More recently, other trimetallic nitride endohedrals have been purified where one or more Sc atoms are replaced by Y, La, Lu, Er, or some other rare-earth element.[32]

Here we report on the kinetic energy released in reactions 2 and 3 for triscandium nitride endohedrals. From the combination of these data, the differential complexation energies for $Sc_3N@C_{78}^{z+}$ in charge states $z = 1$ and 2 and for $Sc_3N@C_{80}^{z+}$ in charge states $z = 1$, 2, and 3 can be derived. The effect of z on $\Delta E_{\mathrm{cmplx}}$ is of interest because theoretical investigations indicate that charge transfer within the strongly bound Sc_3N core and between the core and the fullerene cage is essential for the huge stabilization (order of 10 eV) of these complexes.[26,30] So far, the only experimental data for trimetallic nitride endohedrals have been reported by Lifshitz and coworkers for singly charged $Sc_3N@C_{80}$.[22] Surprisingly, for all charge states and for $n = 78$ as well as $n = 80$, we obtain values for $\Delta E_{\mathrm{cmplx}}$ that are consistent with zero, within the experimental uncertainty of $\approx$0.6 eV. This implies that the complexation energies of $Sc_3N@C_n^{z+}$ do not depend on size for $n = 76$, 78, 80.

Experimental Section

The apparatus consists of a high-resolution double-focusing mass spectrometer (Varian MAT CH5-DF) of reversed Nier-Johnson type BE1 geometry combined with a second electrostatic analyzer E2.[33] Either $Sc_3N@C_{80}$ (obtained from Luna nanoMaterials) or a mix of higher fullerenes containing mainly C_{76}, C_{78}, C_{84}, and C_{92} (MER Corporation) were, without further treatment, evaporated into a vacuum of about 10^{-7} Torr from a temperature-controlled oven operating at 450−700 °C. The effusive beam is intersected by an electron beam of 120 eV energy and a current of 1 mA. The resulting ions are extracted perpendicular to the fullerene and electron beams and accelerated into the mass spectrometer with 3 kV. Ions pass through the first field free region, are momentum-analyzed by a magnetic sector field B, enter a second field-free region (ff2), pass through a 90° electric sector field (E1), enter a third field free region (ff3, length 92 cm), pass through another electrostatic sector field (E2), and are detected by an electron multiplier. Referenced to the time of their formation, C_{60}^{+} parent ions traverse ff3 during the time interval $75 \leq t \leq 91\ \mu$s. The corresponding times for other ions of mass m (in atomic units) and charge state z are obtained by multiplying with $\sqrt{m/720z}$.

Mass-analyzed ion kinetic energy (MIKE) spectra of ions that undergo spontaneous decay in ff3 are analyzed by tuning the magnet and first electric sector field to transmit the parent ion (mass m_{p}) and by scanning the sector field voltage of E2. In this mode, B and E1 constitute a double-focusing high-resolution mass spectrometer, and E2 will transmit fragment ions (mass m_{f}) formed in ff3 if the sector field voltage (U_{f}) is set to

$$U_{\mathrm{f}} = \frac{m_{\mathrm{f}}}{m_{\mathrm{p}}} U_{\mathrm{p}} \tag{6}$$

This relation also holds for multiply charged parent ions provided the charge state of the fragment ions equals that of the parent ions. These MIKE spectra, together with a scan of the parent ion around voltage U_{p}, provide the experimental raw data from which the kinetic energy release and the dissociation energies will be derived.

Data Analysis

Experimental MIKE peaks are usually converted to kinetic energy release (KER) distributions $f(\epsilon)$ by removing statistical noise, deconvoluting with the smoothed parent ion peak, differentiating the resulting spectrum, and converting the sector-field voltage to kinetic energies.[25,34] We have inverted the procedure in order to avoid errors that may arise from data smoothing and deconvolution; details have been described elsewhere.[35] In the present work $f(\epsilon)$ is that distribution which, with proper parametrization, provides a best fit between a synthetic MIKE spectrum computed from $f(\epsilon)$ and convoluted with the parent ion peak and the observed MIKE spectrum.

$f(\epsilon)$ reveals the transition state temperature $T^{\dagger}$ of the evaporative ensemble of decaying cluster ions[36]:

$$f(\epsilon) \propto \epsilon\sigma(\epsilon) \exp\left[\frac{-\epsilon}{k_{\mathrm{B}}T^{\dagger}}\right] \tag{7}$$

where $\sigma(\epsilon)$ is the capture cross section for the reverse of reactions 2 or 3. For unimolecular decay of C_{56}^{+}, C_{58}^{+}, C_{60}^{+},[35] and some other atomic cluster ions,[37] the capture cross section agrees with the Langevin cross section, $\sigma(\epsilon) \propto 1/\sqrt{\epsilon}$ although, on physical grounds, one would expect that $\sigma(\epsilon)$ reflects the hard-sphere cross section of the fullerene and therefore deviates from the Langevin cross section, especially at low energies. However, as discussed in an earlier publication, high-quality MIKE spectra show no evidence for this expected deviation.[35] As a result, the transition state temperature is related to the average KER:

$$1.5k_{\mathrm{B}}T^{\dagger} = \bar{\epsilon} \tag{8}$$

According to Klots's finite heat-bath theory,[23] one derives from $T^{\dagger}$ the isokinetic temperature T_{b} of a canonical ensemble that would have the same rate as the evaporative ensemble:

$$T_{\mathrm{b}} = T^{\dagger}\frac{\exp[\gamma/(C-1)] - 1}{\gamma/(C-1)} \tag{9}$$

where $k_{\mathrm{B}}C$ is the vibrational heat capacity of the parent ion. We assume the value given by the equipartition theorem, $C = 3p - 6$ where p is the number of atoms in the cluster. γ is the Gspann factor defined as[38]

$$\gamma = \ln\frac{A}{k} = \frac{D}{k_{\mathrm{B}}T_{\mathrm{b}}} \tag{10}$$

where D is the activation energy of the reaction, k is its rate coefficient, and A is the preexponential in the Arrhenius relation that is assumed here for $k(T_{\mathrm{b}})$. If an evaporative ensemble of cluster ions is sampled at time t after excitation and if competing cooling channels can be neglected, then the most likely decay rate will be characterized by[39]

$$k = 1/t \tag{11}$$

The A-factor is usually assumed to be independent of cluster size n. In the present work we use $A = 2 \times 10^{19}$ s^{-1} for all species. This value is identical to, or very close to, the value used in several other recent studies of unimolecular dissociation of fullerene ions.[24,40−42] This value may appear to be unrealistically large, but it includes too large factors, namely, the reaction path degeneracy and the rotational partition function of the C_2 fragments.[43] Lifshitz[41] has estimated an upper limit of $A = 8 \times 10^{20}$ for C_{60}.

To compare our results with related measurements by Lifshitz and co-workers,[20,22] we have to reanalyze their data because those authors had used a constant value of $\gamma = 33$ which implies, from eqs 10 and 11, size-dependent A-factors. We start from their published $T^{\dagger}$ values and use $A = 2 \times 10^{19}$ s^{-1}. As for the rate k, we note that Lifshitz and co-workers consistently assume $k = 10^5$ s^{-1} for MIKE scans of fullerene ions in their VG-ZAB-2F instrument. However, an examination of the published geometric design of that instrument[44] reveals that the transit time between the region where the ions are fully accelerated to 8 keV and the second field free region averages ≈ 25 μs for C_{60}^{+}. Hence we use $k = 4 \times 10^4 \sqrt{720/m}$ s^{-1} where m is the mass of the parent ion in atomic mass units.

We also noticed that the values for the average KER and the transition state temperatures that were reported in refs 20 and 22 are inconsistent with eq 8. They are also inconsistent with the more general relation $\bar{\epsilon} = (\ell + 1)k_B T^{\dagger}$(where the parameter ℓ is obtained from a fit to the KER distribution) that applies to the "model-free" analysis[23] chosen by the authors. Not knowing the source of this inconsistency, we decided to use their published values of $T^{\dagger}$ rather than $\bar{\epsilon}$ because $T^{\dagger}$ is more directly connected to the dissociation energy (D) that we wish to extract.

From the preceding paragraphs it may appear that our results for the dissociation energies will depend on various assumptions made in the analysis. However, most assumptions have a very small effect on the results. For example, assuming a constant (size-independent) value for the Gspann factor instead of a constant A-factor changes the differential complexation energy (eq 5) by less than 0.01 eV. Applying the concept of microcanonical temperatures[45] instead of the "finite heat-bath theory" will not change the results at all provided both theories are applied to the same order of approximation. If the concept of microcanonical temperatures is applied to first order, then the dissociation energies will increase by 0.02 eV, but the differential complexation energies will remain virtually unchanged. The largest uncertainty lies in the value of A. Changing its value by an order of magnitude will change the dissociation energies by 7%.

Finally, in our analysis we have ignored the effect of radiative cooling. As discussed elsewhere,[46] this will result in dissociation energies that are too low by about 4% for the fullerene sizes discussed here. At any rate, the effect of the corrections discussed above on the *differential* complexation energies will be rather small unless the A factor, or the radiative cooling, of endohedral fullerenes strongly differs from that of empty ones. This seems unlikely.

Results and Discussion

Effect of Isotopomers on MIKE Spectra. Of particular concern in the present study was the effect that isotopomers may have on the shape of the MIKE peaks and, therefore, on the values that are derived for the average KER and dissociation energies. While scandium has only one naturally occurring isotope (^{45}Sc) and nitrogen is nearly (99.6% ^{14}N) isotopically pure, the large number of carbon atoms makes it quite likely that fullerenes contain one or more ^{13}C isotope (natural abundance 1.108%). The mass spectrum of $Sc_3N@C_{80}$ in Figure 1, recorded with two different resolution settings, illustrates this. The isotopically pure molecule at mass 1109 u is the most abundant, but it constitutes only 41% of the total ion signal.

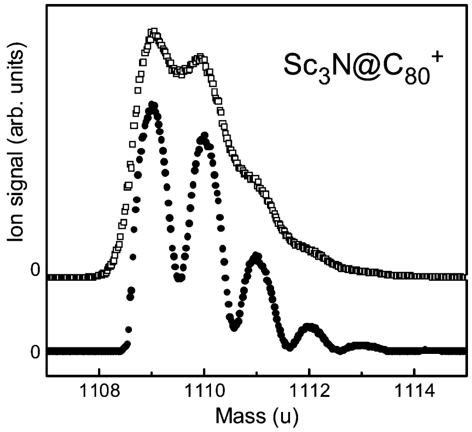

Figure 1. Mass spectra of $Sc_3N@C_{80}^{+}$ ions recorded by scanning the magnetic sector with the slits fairly wide open (upper spectrum, open squares) and nearly closed (lower spectrum, full circles). The peak at 1109 u is isotopically pure ^{12}C; peaks at higher masses contain one or more ^{13}C isotopes.

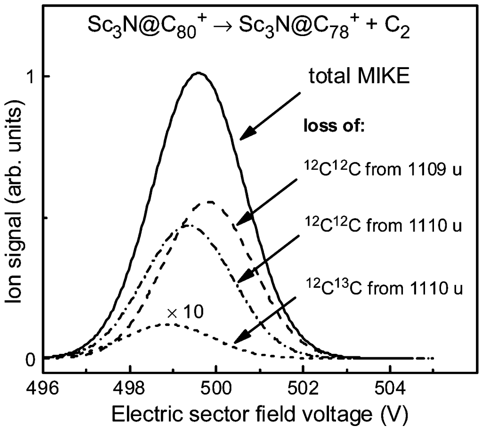

Figure 2. Computer-generated MIKE peaks for unimolecular loss of C_2 from $Sc_3N@C_{80}^{+}$ showing the broadening that arises from the presence of ^{13}C isotopes, see text for details. Only the two most abundant isotopomers of the parent ion, at mass 1109 u (containing no ^{13}C isotope) and 1110 u (one ^{13}C) are considered. Either $^{12}C^{12}C$ or $^{12}C^{13}C$ may be lost from $m = 1110$ u.

The mass spectra shown in Figure 1 were recorded with our double-focusing mass spectrometer equipped with an additional electrostatic analyzer (BEE geometry). An instrument with BE geometry can equally well resolve the different isotopomers,[22] but its resolution is deceiving because the electric sector field voltage is fixed during a regular mass scan. In contrast, during a MIKE scan the parent ions are selected only with the magnetic sector field, and "wrong" parent ions of slightly different mass will also contribute to the MIKE spectrum. For an illustration of these problems and how they are solved if an instrument with BEE geometry is used, see ref 47.

As an illustration, we show in Figure 2 a computer-generated MIKE peak for the reaction

$$Sc_3N@C_{80}^{+} \rightarrow Sc_3N@C_{78}^{+} + C_2 \tag{12}$$

TABLE 1. Average Kinetic Energy Release ($\bar{\epsilon}$), Transition State Temperature ($T^{\dagger}$), and Activation Energy (D) for C_2 Loss Calculated from Our Data Using Finite Heat Bath Theory and Arrhenius Preexponential of 2×10^{19} s^{-1} [a]

parent ion	$\bar{\epsilon}$ (meV)[b]	$T^{\dagger}$ (K)[b]	D (eV)[b]	$T^{\dagger}$ (K)[c,d]	D (eV)
$C_{60}{}^{+}$	394 ± 3	3030	10.25	3300,[c] 3600[d]	10.63, 11.6
$C_{78}{}^{+}$	355 ± 13	2747	9.00		
$C_{78}{}^{2+}$	352 ± 32	2724	8.83		
$C_{78}{}^{3+}$	348 ± 15	2693	8.68		
$Sc_3N@C_{78}{}^{+}$	362 ± 20	2802	9.17		
$Sc_3N@C_{78}{}^{2+}$	342 ± 20	2647	8.57		
$C_{80}{}^{+}$	367 ± 15	2840	9.26	3500[d]	11.04
$C_{80}{}^{2+}$	371 ± 23	2871	9.30		
$C_{80}{}^{3+}$	357 ± 15	2762	8.89		
$Sc_3N@C_{80}{}^{+}$	378 ± 15	2925	9.56	3470[d]	10.93
$Sc_3N@C_{80}{}^{2+}$	374 ± 15	2894	9.36		
$Sc_3N@C_{80}{}^{3+}$	372 ± 20	2879	9.25		
$C_{82}{}^{+}$	332 ± 17	2569	8.39	2860[c]	9.0

[a] Values in the last column have been calculated by us (see Data Analysis section) from transition-state temperatures reported by Lifshitz and co-workers.[20,22] [b] This work. [c] Ref 20. [d] Ref 22.

For the sake of clarity, we only consider the two most abundant isotopomers of mass 1109 u (containing no ^{13}C isotopes) and 1110 u (one ^{13}C), with the relative probabilities computed from the natural abundance of ^{13}C. We assume that the 1109 u parent passes at an electric sector field voltage of 510.86 V (eq 5). Therefore, after loss of C_2 (mass 24 u) the fragment ion will appear at 499.8 V. The width of this peak (after proper correction for other broadening mechanisms) depends on the square of the average KER. In Figure 2, we chose a width as determined in the present experiments. However, in a BE instrument metastable fragment ions from the parent ion of mass 1110 u will also contribute. In the MIKE spectrum they will appear at 499.35 V if a $^{12}C^{12}C$ dimer is lost or at 498.89 V in the less likely case that a mixed $^{12}C^{13}C$ dimer is lost.

The solid curve in Figure 2 is the summed contribution of these three channels. It is very nearly Gaussian, but its width (root-mean-square standard deviation) is 2.7% larger than that of the individual components. This would suggest a KER that is too large by 5.4%. The error will increase to 11% if decay of all other parent isotopomers and their possible fragment ions (having lost a mass of 24, 25, or 26 u) is taken into account. The actual error in the experiment will depend on the KER and on the degree of discrimination against parents that have the wrong mass.

In the present work, all metastable reactions were measured in ff3. In this situation, parent ions are selected for a MIKE scan by the magnetic as well as the first electrostatic sector field (i.e., their resolution is as good as the resolution of a regular mass spectrum recorded with a BE instrument). As a result, wrong parent ions that contain ^{13}C isotopes cannot enter ff3. However, this technique requires narrow slits and comes at the cost of low count rate. Alternatively, for the measurements involving weak parent ion beams where we had to use wider slits, we corrected the results for contamination by other isotopomers based on detailed test experiments combined with theoretical modeling of those spectra.[48]

In some situations it is practically impossible to select isotopically pure parent ions. For example, the most abundant isotopomer of $Kr@C_{60}$ has a mass of 804 u. However, ions at this mass will not only be comprised of $^{84}Kr@(^{12}C)_{60}$, but they may contain as many as six ^{13}C isotopes because the lightest naturally occurring isotope of krypton is ^{78}Kr. As a result, the MIKE peak from this parent ion will be tailed toward lower electric sector field voltages because loss of C_2 implies loss of 24, 25, or even 26 u. A tail has indeed been reported for the $Kr@C_{60}{}^{+}$ MIKE peak,[20] but the authors attributed it solely to collision-induced dissociation. To extract the correct, intrinsic width of this MIKE peak one would have to apply comprehensive quantitative modeling as illustrated in ref 47.

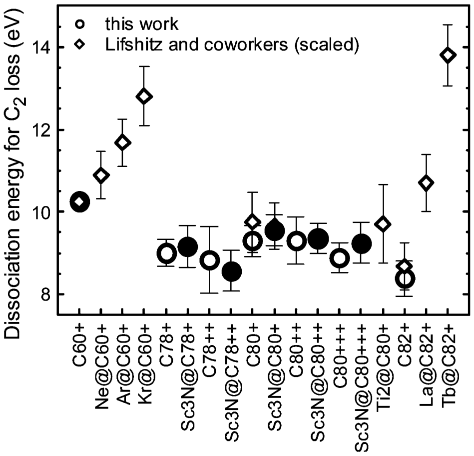

Figure 3. Empty and filled circles: Dissociation energies for C_2 loss from singly and multiply charged fullerene ions measured in this work for empty and filled fullerenes, respectively. Diamonds: Dissociation energies derived from transition state temperatures reported by Lifshitz and co-workers,[20,22] scaled to match our value for $C_{60}{}^{+}$.

Dissociation and Complexation Energies. In Table 1 we list the average kinetic energies, the corresponding transition state temperatures, and the dissociation energies for C_2 loss from singly and multiply charged trimetallic nitride fullerene ions and some empty fullerene ions. The dissociation energies are graphed in Figure 3 as circles. Error bars were computed from the uncertainties of the average KER listed in Table 1. The kinetic energy release distributions indicate that dissociation proceeds without reverse activation barrier; therefore, our dissociation energies are adiabatic values, as assumed in eq 5. Recent experimental[49] and theoretical studies[50] indicate that C_2 attachment to neutral or charged C_{60} and other fullerenes features a complex reaction path, but again, there is no evidence for a net reaction barrier.

Also listed are transition state temperatures that Lifshitz and co-workers[20,22] reported for the reactions considered here, based on the "model-free" analysis of their KER distributions. In the last column we show the dissociation energies that we calculate from their $T^{\dagger}$ values (see Data Analysis section for details). They are significantly higher than ours, and their values for two separate measurements of $C_{60}{}^{+}$ differ by 9%. This problem had already been noticed by the authors;[22] they chose to scale all their dissociation energies such that the currently accepted dissociation energy of $D(C_{60}{}^{+})$ was reproduced. We adopt the same procedure (i.e., all dissociation energies shown in the last column of Table 1 are multiplied by 10.25/10.63 and 10.25/11.6 for data published in refs 20 and 22, respectively). The results are shown in Figure 3 as open diamonds. We also include dissociation energies for $Rg@C_{60}{}^{+}$ (Rg = Ne, Ar, Kr) and a few other metallofullerenes. They are derived similarly from transition state temperatures reported by Lifshitz and co-workers;[20,22] uncertainties are taken from their published dissociation energies, and scaled.

Several features in Figure 3 are noteworthy:

(1) The dissociation energies of $Sc_3N@C_{78}{}^{z+}$ and $Sc_3N@C_{80}{}^{z+}$ do not, within the experimental error, depend on the charge state z. This also holds for the empty fullerenes ions C_{78} and C_{80}, in agreement with previous studies of singly, doubly, and triply charged C_{58}, C_{60}, and C_{70} ions.[24,42]

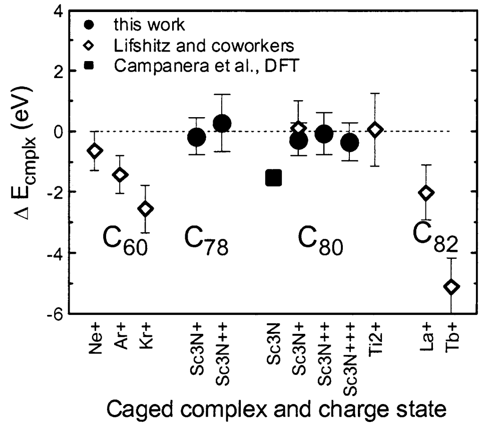

Figure 4. Differential complexation energy (see eq 5 for a definition). The caging fullerene is indicated in the figure; the caged complex M and the charge state of M@C_n^{z+} are indicated below the abscissa. A negative value implies that C_n^{z+} is stabilized by M more strongly than C_{n-2}^{z+}. Filled circles and open diamonds are experimental values derived from the data shown in Figure 3. The full square is from density functional calculations.[26,51]

(2) The dissociation energies for $Sc_3N@C_n^{z+}$ (n = 78, 80) agree, within the experimental error, with the corresponding energies of the empty, singly charged fullerene ions.

(3) The agreement between our values and the scaled values that we derive from measurements by Lifshitz and co-workers is quite good.

From eq 5, we compute the differential complexation energies, $\Delta E_{cmplx}(M@C_n^{z+})$. To compute $\Delta E_{cmplx}(M@C_n^{+})$ for the metallofullerenes analyzed by Lifshitz and co-workers, we chose their values for the dissociation energies of C_{80}^{+} and C_{82}^{+} (open diamonds in Figure 3), not ours. This procedure increases the likelihood that any systematic errors will cancel.

The differential complexation energies are summarized in Figure 4. For $Sc_3N@C_{78}^{z+}$ and $Sc_3N@C_{80}^{z+}$, they are zero within the experimental error. This means that the caged complex stabilizes the fullerene ion (C_{78}^{z+} or C_{80}^{z+}) as much as the next smaller fullerene ion (C_{76}^{z+} or C_{78}^{z+}) for all charge states investigated. Therefore, the complexation energies are identical within the experimental error of about 0.6 eV:

$$E_{cmplx}(M@C_{80}^{\ z+}) \approx E_{cmplx}(M@C_{78}^{\ z+}) \approx E_{cmplx}(M@C_{76}^{\ z+}) \tag{13}$$

for z = 1 and 2 (and z = 3 for the first part of the equation). Note, however, that we cannot determine the dependence of the complexation energy on the charge state z (see eq 5).

The result that $Sc_3N@C_{80}^{z+}$ and $Sc_3N@C_{78}^{z+}$ have identical thermodynamic stabilities is perhaps not too surprising because (neutral) $Sc_3N@C_{80}$ as well as $Sc_3N@C_{78}$ are both known to be very stable; they can be isolated in remarkably high yields.[27] Formally, six electrons are transferred from the Sc_3N core to the fullerene, thus filling three low-lying orbitals in C_{78} and completely filling the HOMO in C_{80} (I_h).[26] Furthermore, this charge-transfer amplifies the strength of the ionic interaction within the encapsulated Sc_3N cluster because the negative charge of the central N atom and the positive charges on the surrounding Sc atoms increase upon caging.[26,29]

For neutral $Sc_3N@C_{80}$, complexation energies of −10.72 eV [30] and −11.60 eV [26] have been calculated with density functional methods for the most stable endohedral isomer (I_h symmetry, isomer 7). Of particular interest is the work by Poblet and co-workers[26] because they have also computed E_{cmplx} for $Sc_3N@C_{78}$; the value for the most stable endohedral isomer ($D_{3h'}$, isomer 5) is −9.70 eV. However, the most stable isomers of empty fullerenes are D_{5d} (isomer 1) and $C_{2v'}$ (isomer 3) for C_{80} and C_{78}, respectively. We obtain the adiabatic complexation energies relative to these isomers by adding the computed energy differences[51] between the corresponding isomers of empty fullerenes, namely, $E(I_h, 7) - E(D_{5d}, 1) = 0.50$ eV for C_{80}, and $E(D_{3h'}, 5) - E(C_{2v'}, 3) = 0.13$ eV for C_{78}. This results in a differential complexation energy of $\Delta E_{cmplx}(Sc_3N@C_{80}) = -11.1 + 9.57$ eV $= -1.53$ eV. This value is included in Figure 4.

The theoretical result does not agree well with the experimental values, which range from −0.3 to +0.1 eV for singly through triply charged species, with estimated uncertainties ±0.6 eV. The theoretical complexation energies listed above refer to neutral systems, but the computed complexation energies[51] of neutral and singly charged $Sc_3N@C_{80}$ in I_h symmetry differ by a mere 0.04 eV, with the ion value being more negative than the neutral. However, the large complexation energy computed[52] for the much smaller $Sc_3N@C_{68}$ (see below) suggests that the experimental result is entirely reasonable.

The next smaller species, $Sc_3N@C_{76}$, has not yet been synthesized. Is it not stabilized as efficiently by the caged complex? This conclusion would be at variance with our experimental result (eq 13). However, although a large (negative) complexation energy favors a large yield in the production of metallofullerenes, isolation also requires kinetic stability which strongly depends on the electronic structure and, in particular, the HOMO−LUMO gap. That is, “missing” metallofullerenes do not necessarily have low thermodynamic stability. Furthermore, the successful purification of the much smaller metallofullerene $Sc_3N@C_{68}$[10] indicates that steric effects do not limit the thermodynamic stability of Sc_3N based metallofullerenes for $n \geq 68$. In fact, a very recent quantum chemical study[52] shows that the complexation energy of $Sc_3N@C_{68}$ is as large as that of $Sc_3N@C_{80}$. Specifically, referenced to the most stable isomers of C_{68} (D_3) and Sc_3N (D_{3h}), a complexation energy of −12.08 eV is obtained at the B3LYP/6-31G* level of theory.

Conclusions

From a measurement of the distribution of the kinetic energy released upon C_2 loss from $Sc_3N@C_n^{z+}$ (n = 78 and 80), we have deduced the differential complexation energies of these metallofullerene ions. The values are zero within the estimated experimental uncertainty of 0.6 eV. This implies that the thermodynamic stabilization of C_{76}^{z+}, C_{78}^{z+}, and C_{80}^{z+} upon encapsulation of Sc_3N does not depend on the size of the fullerene. The result is unexpected because $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$ are known to be dramatically stabilized by the caged complex; they can be synthesized and isolated with high yield and purity, whereas isolation of $Sc_3N@C_{76}$ has not been reported so far. However, the importance of kinetic stability for the purification of metallofullerenes should be kept in mind. Future measurements of differential complexation energies of smaller endohedral fullerenes will make it possible to determine the size at which the large thermodynamic stability of trimetallic nitride fullerenes collapses due to electronic or steric effects.

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References and Notes

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) (a) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779. (b) Guo, T.; Smalley, R. E.; Scuseria, G. E. *J. Chem. Phys.* **1993**, *99*, 352.

(3) (a) Schwarz, H.; Weiske, T.; Böhme, D. K.; Hrusak, J. In *Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH Publishers: New York, 1993; p 257. (b) Wan, Z.; Christian, J. F.; Basir, Y.; Anderson, S. L. *J. Chem. Phys.* **1993**, *99*, 5858.

(4) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, W. K.; Huffman, D. R. *Nature* **1990**, 347, 354.

(5) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843.

(6) Akasaka, T.; Nagase, S., *Endofullerenes*: *A New Family of Carbon Clusters*; Kluwer Academic: Dordrecht, 2002.

(7) Kubozono, Y. In *Endofullerenes*: *A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic: Dordrecht, 2002; p 253.

(8) Kusch, C.; Krawez, N.; Tellgmann, R.; Winter, B.; Campbell, E. E. B. *Appl. Phys. A* **1998**, *66*, 293.

(9) Aihara, J. *J. Phys. Chem. A* **2002**, *106*, 11371.

(10) Stevenson, S.; Fowler, P. W.; Heine, T.; Duchamp, J. C.; Rice, G.; Glass, T.; Harich, K.; Hajdu, E.; Bible, R.; et al. *Nature* **2000**, *408*, 427.

(11) (a) Bühl, M.; Patchkovskii, S.; Thiel, W. *Chem. Phys. Lett.* **1997**, *275*, 14. (b) Darzynkiewicz, R. B.; Scuseria, G. E. *J. Phys. Chem. A* **1997**, *101*, 7141. (c) Darzynkiewicz, R. B.; Scuseria, G. E. *J. Phys. Chem.* **1998**, *102*, 3458.

(12) Sung, Y. K.; Son, M. S.; Jhon, M. S. *Inorg. Chim. Acta* **1998**, *272*, 33.

(13) Proft, F. D.; Alsenov, C. V.; Geerlings, P. *J. Phys. Chem.* **1996**, *100*, 7440.

(14) (a) Hira, A. S.; Ray, A. K. *Phys. Rev. A* **1995**, *52*, 141. (b) Liu, J. N.; Wata, S.; Gu, B. L. *Phys. Rev. B* **1994**, *50*, 5552. (c) Cioslowski, J., *Electronic Structure Calculations on Fullerenes and Their Derivations*; Oxford University Press: Oxford, 1995. (d) Bernshtein, V.; Oref, I. *J. Chem. Phys.* **1998**, *109*, 9811. (e) Varganov, S. A.; Avramov, P. V.; Ovchinnikov, S. G. *Phys. Solid State* **2000**, *42*, 388.

(15) Larsson, J. A.; Greer, J. C.; Harneit, W.; Weidinger, A. *J. Chem. Phys.* **2002**, *116*, 7849.

(16) Lu, J.; Zhang, X. W.; Zhao, X. G. *Chem. Phys. Lett.* **1999**, *312*, 85.

(17) Smith, R.; Beardmore, K.; Belbruno, J. *J. Chem. Phys.* **1999**, *111*, 9227.

(18) BelBruno, J. J. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2002**, *10*, 23.

(19) Laskin, J.; Jimenez-Vazquez, H. A.; Shimshi, R.; Saunders: M.; DeVries, M. S.; Lifshitz, C. *Chem. Phys. Lett.* **1995**, *242*, 249.

(20) Laskin, J.; Peres, T.; Khong, A.; Jimenez-Vazquez, H. A.; Cross, R. J.; Saunders: M.; Bethune, D. S.; DeVries, M. S.; Lifshitz, C. *Int. J. Mass Spectrom.* **1999**, *185*/*186*/*187*, 61.

(21) Cao, B. P.; Peres, T.; Cross, R. J.; Saunders: M.; Lifshitz, C. *J. Phys. Chem. A* **2001**, *105*, 2142.

(22) Peres, T.; Cao, B. P.; Shinohara, H.; Lifshitz, C. *Int. J. Mass Spectrom.* **2003**, *228*, 181.

(23) Klots, C. E. *Z. Phys. D* **1991**, *21*, 335.

(24) Matt, S.; Sonderegger, M.; David, R.; Echt, O.; Scheier, P.; Laskin, J.; Lifshitz, C.; Märk, T. D. *Chem. Phys. Lett.* **1999**, *303*, 379.

(25) Laskin, J.; Lifshitz, C. *J. Mass Spectrom.* **2001**, *36*, 459.

(26) Campanera, J. M.; Bo, C.; Olmstead, M. M.; Balch, A. L.; Poblet, J. M. *J. Phys. Chem. A* **2002**, *106*, 12356.

(27) (a) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; et al. *Nature* **1999**, *401*, 55. (b) Olmstead, M. H.; de Bettencourt-Dias, A.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem.* **2001**, *40*, 1223.

(28) (a) Macfarlane, R. M.; Bethune, D. S.; Stevenson, S.; Dorn, H. C. *Chem. Phys. Lett.* **2001**, *343*, 229. (b) Ioffe, I. N.; Ievlev, A. S.; Boltalina, O. V.; Sidorov, L. N.; Dorn, H. C.; Stevenson, S.; Rice, G. *Int. J. Mass Spectrom.* **2002**, *213*, 183. (c) Iezzi, E. B.; Duchamp, J. C.; Harich, K.; Glass, T. E.; Lee, H. M.; Olmstead, M. M.; Balch, A. L.; Dorn, H. C. *J. Am. Chem. Soc.* **2002**, *124*, 524.

(29) Krause, M.; Kuzmany, H.; Georgi, P.; Dunsch, L.; Vietze, K.; Seifert, G. *J. Chem. Phys.* **2001**, *115*, 6596.

(30) Kobayashi, K.; Sano, Y.; Nagase, S. *J. Comput. Chem.* **2001**, *22*, 1353.

(31) Kobayashi, K.; Nagase, S. In *Endofullerenes*: *A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic: Dordrecht, 2002; p 99.

(32) (a) Iezzi, E. B.; Duchamp, J. C.; Fletcher, K. R.; Glass, T. E.; Dorn, H. C. *Nano Lett.* **2002**, *2*, 1187. (b) Dorn, H. C.; Iezzi, E. B.; Stevenson, S.; Balch, A. L.; Dunchamp, J. C. In *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic: Dordrecht, 2002; p 121.

(33) Gluch, K.; Fedor, J.; Matt-Leubner, S.; Echt, O.; Stamatovic, A.; Probst, M.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **2003**, *118*, 3090.

(34) (a) Matt, S.; Sonderegger, M.; David, R.; Echt, O.; Scheier, P.; Laskin, J.; Lifshitz, C.; Märk, T. D. *Int. J. Mass Spectrom.* **1999**, *187*, 813. (b) Holmes, J. L.; Osborne, A. D. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 189. (c) Vekey, K.; Szilagyi, Z. *Int. J. Mass Spectrom. Ion Proc.* **1997**, *165*, 1.

(35) Gluch, K.; Matt-Leubner, S.; Echt, O.; Deng, R.; Andersen, J. U.; Scheier, P.; Märk, T. D. *Chem. Phys. Lett.* **2004**, *385*, 449.

(36) (a) Weisskopf, V. *Phys. Rev.* **1937**, *52*, 295. (b) Klots, C. E. *J. Chem. Phys.* **1994**, *100*, 1035. (c) Hansen, K.; Näher, U. *Phys. Rev. A* **1999**, *60*, 1240.

(37) Hansen, K. *Chem. Phys. Lett.* **2004**, *383*, 270.

(38) Klots, C. E. *J. Phys. Chem.* **1988**, *92*, 5864.

(39) (a) Klots, C. E. *J. Chem. Phys.* **1993**, *98*, 1110. (b) Hansen, K.; Andersen, J. U.; Hvelplund, P.; Möller, S. P.; Pedersen, U. V.; Petrunin, V. V. *Phys. Rev. Lett.* **2001**, *87*, 123401.

(40) (a) Matt, S.; Echt, O.; Scheier, P.; Märk, T. D. *Chem. Phys. Lett.* **2001**, *348*, 194. (b) Matt, S.; Parajuli, R.; Stamatovic, A.; Scheier, P.; Märk, T. D.; Laskin, J.; Lifshitz, C. *Eur. Mass Spectrom.* **1999**, *5*, 477. (c) Peres, T.; Cao, B. P.; Cui, W. D.; Khong, A.; Cross, R. J.; Saunders: M.; Lifshitz, C. *Int. J. Mass Spectrom.* **2001**, 210, 241. (d) Deng, R.; Echt, O. *Chem. Phys. Lett.* **2002**, *353*, 11.

(41) Lifshitz, C. *Int. J. Mass Spectrom.* **2000**, *198*, 1.

(42) Tomita, S.; Andersen, J. U.; Gottrup, C.; Hvelplund, P.; Pedersen, U. V. *Phys. Rev. Lett.* **2001**, *87*, 073401.

(43) Hansen, K.; Echt, O. *Phys. Rev. Lett.* **1998**, *82*, 460.

(44) Morgan, R. P.; Beynon, J. H.; Bateman, R. H.; Green, B. N. *Int. J. Mass Spectrom.* **1978**, *28*, 171.

(45) (a) Andersen, J. U.; Bonderup, E.; Hansen, K. *J. Chem. Phys.* **2001**, *114*, 6518. (b) Andersen, J. U.; Bonderup, E.; Hansen, K.; Hvelplund, P.; Liu, B.; Pedersen, U. V.; Tomita, S. *Eur. Phys. J. D* **2003**, *24*, 191.

(46) Gluch, K.; Matt-Leubner, S.; Echt, O.; Concina, B.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **2004**, *121*, 2137.

(47) Gluch, K.; Matt-Leubner, S.; Michalak, L.; Echt, O.; Stamatovic, A.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **2004**, *120*, 2686.

(48) Gluch, K. Physics Doctoral thesis, Universität Innsbruck, 2003.

(49) (a) Shvartsburg, A. A.; Hudgins, R. R.; Dugourd, P.; Gutierrez, R.; Frauenheim, T.; Jarrold, M. F. *Phys. Rev. Lett.* **2000**, *84*, 2421. (b) Budyka, M. F.; Zyubina, T. S.; Ryabenko, A. G.; Muradyan, V. E.; Esipov, S. E.; Cherepanova, N. I. *Chem. Phys. Lett.* **2002**, *354*, 93.

(50) (a) Xia, Y. Y.; Mu, Y. G.; Xing, Y. L.; Wang, R. J.; Tan, C. Y.; Mei, L. M. *Phys. Rev. B* **1998**, *57*, 14950. (b) Budyka, M. F.; Zyubina, T. S.; Ryabenko, A. G. *Int. J. Quantum Chem.* **2002**, *88*, 652.

(51) Poblet, J. M. Personal communication.

(52) Hagelberg, F. Personal communication.