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LETTERS

Electron Affinity of Some Endohedral Lanthanide Fullerenes

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We report the first electron affinity measurements for some endohedral gadolinium metallofullerenes. Knudsen cell mass spectrometry has been used for the study of the gas-phase composition over the KF−Gd@C_n system. Both neutral and negatively charged species C_{60}, C_{70+2n} (n = 0, 1, ..., 10), Gd@C_{74}, Gd@C_{76}, Gd@C_{78}, Gd@C_{80}, and Gd@C_{82} were detected at 931−960 K, which permitted determination of equilibrium constants of electron exchange reactions. The electron affinities of gadolinium metallofullerenes were found to be greater than those of the parent fullerenes. In contrast to the empty fullerenes, endohedral metallofullerenes revealed no strong dependence of their electron-accepting ability on the size of the fullerene cage.

Introduction

Endohedral metallofullerenes were first observed in 1985 in the mass spectra of the products of laser vaporization of a graphite target soaked in a water solution of $LaCl_3$.[1] Later they were found in the soot prepared by arc vaporization of La_2O_3-graphite rods;[2] now the encaged metal atoms include many lanthanide and transition metals.[3] Electronic properties of endohedral metallofullerenes have been of particular interest, the most frequently discussed question being the charge transfer from the metal atom to the fullerene cage. On the basis of the experimental methods that allow characterization of the encaged metal state (magnetic momentum measurements, UV spectroscopy, etc.), it has been suggested that the charge on any lanthanide atom (including Gd) inside the C_{82} cage is close to +3.[4,5] However, the theoretical investigations predict that in Gd@C_{82} the effective charge on the Gd-atom is close to +2 ($4f^75d^1$) due to the lanthanide contraction.[6]

Electron affinity (EA) is an important characteristic of the electronic structure of a molecule. The theory predicts that the EA values of the endohedral lanthanide metallofullerenes M@C_{82} (M = La, Ce, Eu, Gd) are close to 3.2 eV[6] while the EA values for C_{60} and C_{82} calculated by the same authors are 2.57 and 3.37 eV, respectively.[7] This shows that despite the high negative charge on the fullerene cage, the EA values for the lanthanide metallofullerenes can be even greater than for some empty fullerenes. These predictions were confirmed by the voltammometric data that demonstrated lower reduction potentials for M@C_{82} (M = Y, La, Ce, Gd) than for C_{60}.[8] The 0.02 eV difference between the calculated EA values of $La^{3+}@C_{82}^{3-}$ and $Gd^{2+}@C_{82}^{2-}$ may be explained if one applies the model of electron donation from the metal atom to LUMO and LUMO+1 of C_{82}. LUMO+1 remains unoccupied (Gd^{2+}) or becomes semioccupied (La^{3+}) and is responsible for the electron attachment, while the metal atom does not affect this process. Nevertheless, the model of a point charge on a La-atom that has a particular location inside the C_{82} cage gives EA values of 3.45 and 3.66 eV when the La-atom is charged 2+ and 3+, respectively.[7] More experimental data are necessary in order to find out to what extent the entrapped metal atom effects the electronic structure of the endohedral molecules and what the actual charge on the Gd-atom is. It can be very useful to compare the experimental electron affinities for Gd@C_n, and for the other metallofullerenes, in which the charge on the metal atom is predicted to be +2 (or +3) by both theoretical and experimental researchers; for example, lanthanide

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metallofullerenes $La^{3+}@C_n^{3-}$, $Ce^{2+}@C_n^{2-}$ and nonlanthanide $Y^{3+}@C_n^{3-}$.

The experimental data on the electron affinities of metallofullerenes are very scarce. Compton et al. estimated the electron affinity of the $La@C_n$ molecules ($n = 60, 70-84$) by means of ICR-FT mass spectrometry using the bracketing technique.[9] Their estimation (2.7 eV < EA < 3.3 eV) agrees with the theoretical predictions.[6] In our earlier paper, the EA value of $Gd@C_{60}$ determined from the ion-molecular equilibria measurements was found to be 2.9 ± 0.2 eV[10]—higher than the EA value of C_{60} (2.66 eV).[11] In this Letter we report the EA values for the $Gd@C_n$ molecules (n=74−82) and a new estimation of the EA value for $La@C_{74}$, which were determined by means of Knudsen cell mass spectrometry (KCMS) from the ion-molecular equilibria involving metallofullerenes $Gd@C_n$, $La@C_{74}$, and C_{74} (or C_{76}).

Experimental Section

Gadolinium- and lanthanum-containing fullerene samples prepared by the arc vaporization of M_2O_3-graphite rods with the subsequent in situ extraction of the fullerenes and metallofullerenes by sublimation were purchased from the TDA Research Inc. The sample was placed into a platinum Knudsen effusion cell along with potassium fluoride, the latter being added to increase the concentration of the fullerene and metallofullerene anions in the gas phase. The neutral component of the beam evaporating from the cell was ionized by electron impact (EI) (75 eV) and analyzed by the magnetic sector mass spectrometer MI-1201V.[12] The negatively charged component was evacuated from the cell by the electric field (2 kV) and mass analyzed. Measurements of the intensities of both neutral and negatively charged gadolinium metallofullerene molecules were performed at two temperatures: 931 and 960 K. To measure accurately the signal-to-noise ratio in the EI mode, a movable shutter placed in front of the effusion cell was used; mass spectra in the negative mode were virtually background free in the mass range of interest (700−1200 amu).

The neutral $La@C_{74}$ molecule was not detected by our instrument; we have measured the intensity of anion $La@C_{74}^-$ at 900 K and estimated the $La@C_{74}^+$ intensity from the detection limit of our instrument in order to determine the lower limit to the EA value of $La@C_{74}$.

The equilibrium constants for the electron exchange reactions between the gadolinium metallofullerene $Gd@C_n$ (or $La@C_{74}$) and C_{74} (or C_{76}) neutral molecules and their anions were studied:

$$M@C_n + C_m^- = M@C_n^- + C_m \qquad (1)$$

The equation that relates the equilibrium constants of isomolecular reactions 1 and measured ion intensities is as follows

$$K_p = (I_{M@C_n^-}/I_{C_m^-})[(I_{C_m}/I_{M@C_n})/(\sigma_{C_m}/\sigma_{M@C_n})] \qquad (2)$$

where σ is the ionization cross section of the corresponding molecule. No experimental data on the ionization cross sections of endohedral compounds are available, to our knowledge. Therefore, the ratio between the ionization cross sections of C_m and $M@C_n$ molecules was taken as the ratio between the number of carbon atoms in their fullerene cages; this has been found a good approximation for the empty fullerenes C_{60} and C_{70}.[13] Suggesting that the differences in the entropy and enthalpy between the fullerene molecules and their anions and between the metallofullerene molecules and their anions are nearly equal, we have

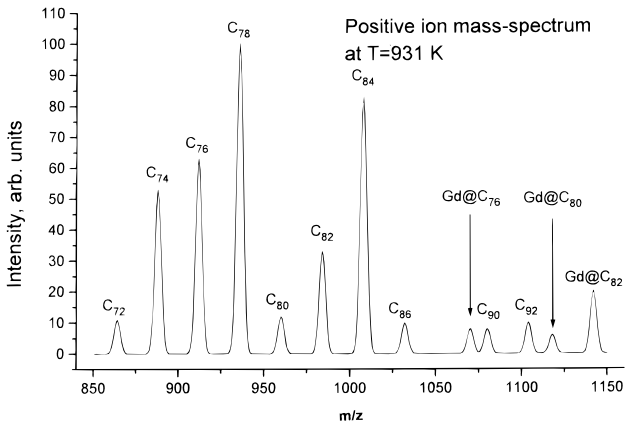

Figure 1. Electron impact positive ion mass spectrum of the KF−$Gd@C_n$ system at 931 K in the mass range 850−1150 *m*/*z*.

$$RT \ln K_p(1) = -\Delta G^0_T(1) \cong -\Delta H^0_0(1) = EA(M@C_n) - EA(C_m) \qquad (3)$$

The equilibrium constants obtained were averaged (T = const), the uncertainty being estimated as a factor of 2; then, using eq 3 and EA values for C_{74} and C_{76} from our earlier work,[12] the EAs of metallofullerenes were calculated.

Results and Discussion

Figures 1 and 2 show the representative positive (electron impact (EI)) and negative ion (thermal ionization (TI)) mass spectra of the gas phase over the $Gd@C_n$−KF system at T = 931 K. The EI mass spectrum demonstrates that the maximal abundance among the metallofullerenes occurs for $Gd@C_{82}$ while the C_{82} intensity is lower than that of C_{76} and C_{78}; this fact is in agreement with the observation made by Sun et al.[14] However, the relatively high abundance of C_{74} in the metallofullerene-containing soot is surprising and needs further investigation. Notably, C_{74} is one of the few higher fullerenes ($C_{n<100}$) that has not been isolated by the Soxhlet extraction−HPLC separation method. Comparison of Figures 1 and 2 shows that relative intensities of negative ions of metallofullerenes are higher than of their parents, thus giving an indication of their larger EA. The obtained experimental results are presented in Table 1.

The EA value of C_{84} was calculated in order to examine whether equilibrium in the effusion cell was attained. Our experimental value (3.16 eV) is rather close to 3.14 eV,[12] so one can suggest that the experiment was carried out under the equilibrium conditions. In Table 2 the obtained EA data are presented together with the EA values for the empty fullerenes.[12]

It is remarkable that presence of the Gd-atom inside the fullerene cage brings about an increase in its electron affinity. Another interesting result is that no strong dependence of the EA values on n for $Gd@C_n$ (n = 74−82) was found—the EA values fall within a narrow interval (3.2−3.3 eV)—while for the C_n molecules maximum at C_{74} and minimum at C_{76} is quite prominent as well as the previously established general trend of increasing EA with the fullerene size.[12] This observation implies that the pecularities of the electronic structure of the parent fullerenes do not significantly affect EA of their endohedral derivatives while the state of the inner metal ion is rather important for the description of the endohedral metallofullerenes' electronic properties. This result agrees with the linear dependence between the third ionization potentials of the lanthanide metal atoms and the first reduction potential of their endohedral C_{82} derivatives in solution.[15] The explanation of

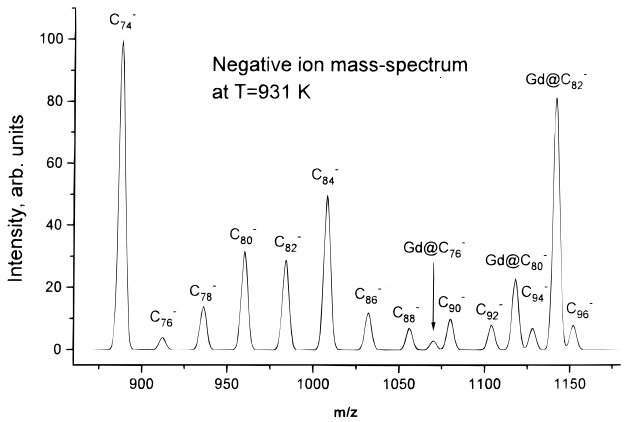

Figure 2. Thermal negative ion mass spectrum of the KF−Gd@C_n system at 931 K in the mass range 850−1150 *m*/*z*.

TABLE 1: Equilibrium Constants of Reactions C_{74}^- + Gd@C_n = C_{74} + Gd@C_n^- and C_{74}^- + C_{84} = C_{74} + C_{84}^-

	T = 931 K			T = 960 K		
	positive ion intensity, arb. units	negative ion intensity, arb.units	K_p	positive ion intensity, arb. units	negative ion intensity, arb. units	K_p
Gd@C_{74}				4	3	0.59
Gd@C_{76}	2.5	2	0.23	3	2	0.58
Gd@C_{78}				2	2	0.75
Gd@C_{80}	1.5	14	2.5	0.5	1	1.5
Gd@C_{82}	6	49	2.2	4	6.5	1.2
C_{74}	16	61		15	21	
C_{84}	25	30	9.7	75	29.5	11.1

TABLE 2: Electron Affinities of C_n and Gd@C_n

n	EA(Gd@C_n), eV[a]	EA(C_n), eV[b]
74	3.24[c]	3.28 ± 0.07
76	3.2 ± 0.1	2.89 ± 0.05
78	3.26[c]	3.10 ± 0.06
80	3.3 ± 0.1	3.17 ± 0.06
82	3.3 ± 0.1	3.14 ± 0.06

[a] The uncertainty (±0.1) includes experimental error in k_p and uncertainty in EA(C_{74}). [b] Data are taken from ref 12. [c] Estimation from a single measurement.

the similar correlation between the ionic radii of the M^{3+} ions and the first reduction potentials is that the highest electron density on SOMO (semioccupied orbital, responsible for the electron attachment) occurs on the nearest to the metal atom area on the cage that causes the dependence between the electron attachment energy and the distance from the metal atom to the cage, the latter being the function of the ionic radii of the encaged metal ions.[8] This suggestion is contradictory to the model of a point charge inside the negatively charged fullerene cage. So far we do not have sufficient experimental data to prefer any of these models, and the final choice is to be done after investigation of the other metallofullerenes. If one applies the point charge model, our results fit better to the $Gd^{2+}@C_n^{2-}$ model. The model calculation gives a small overestimation (3.45 eV)[7] in comparison with our experimental data, similar to the difference in the calculated (3.37 eV)[7] and experimental EA values of C_{82}.[12]

The new estimation of the lower limit to EA of La@C_{74} was found to be 2.9 eV; this agrees with the result reported by Compton et al.[9]

Conclusion

In conclusion, we have obtained the first experimental values of the electron affinity for a number of gadolinium metallofullerenes and estimated the EA value for La@C_{74}. Derivatization of a fullerene molecule from inside, i.e., trapping the Gd-atom in the fullerene cage, gives rise to an increase in its electron affinity; the size of the fullerene cage itself does not considerably affect the EA value for these molecules. The obtained EA values for gadolinium metallofullerenes are better described by the pointed charge model in which the metal bears two positive charges ($Gd^{2+}@C_n^{2-}$).

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