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LETTERS

Pyramidal Structures of Lanthanide−C_{60} Clusters ($Ln_n(C_{60})_m$: Ln = Eu and Ho)

Satoshi Nagao, Yuichi Negishi, Akiko Kato, Yoshiaki Nakamura, and Atsushi Nakajima*

Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Koji Kaya

Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan, and Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

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Novel lanthanide organometallic clusters, $Ln_n(C_{60})_m$, consisting of lanthanide atoms (Ln; Ln = Eu and Ho) and C_{60} molecules were produced in gas phase by a two-laser vaporization method. The $Ln_n(C_{60})_m$ clusters were produced predominantly at compositions of $(n, m) = (n, n + 3)$ [$n = 1-4$]. These stoichiometries showed no chemisorption reactivity toward CCl_4 and O_2 reactants. The cluster having (1, 4) composition is proposed to form a tetrahedral structure, in which a Ln atom is surrounded by four C_{60} molecules. In larger clusters with $(n, n + 3)$ composition, each Ln atom is found in a local (1, 4) group. Together with the results of sequential chemisorption of Cl atoms on cluster cations, photoelectron spectroscopy of cluster anions leads us to conclude that $Ln_1(C_{60})_m$ clusters are charge-transfer complexes expressed as $Ln_1^{x+}(C_{60})_m^{x-}$, and that Eu and Ho atoms exist as Eu^{2+} and Ho^{3+} ions, respectively.

1. Introduction

The successful synthesis of the C_{60} molecule has opened a way to create modified fullerenes.[1] An important discovery in this respect was that of superconductivity at rather high temperatures in the alkaline−C_{60} solids.[2,3] There has been intensive research activity in the field of chemically modified fullerenes, specifically fullerenes containing encapsulated atoms.[4−17] C_{60}-based charge-transfer clusters are one of the promising candidates for the synthesis of novel compounds with tailored properties, which include superconducting and optical properties. Since it has been expected that donor elements of the groups 1, 2, and 13 as well as lanthanides and actinides can form stable charge-transfer complexes with the fullerenes, there have been a number of experiments on the formation and the characterization of their metallofullerides.

For lanthanide fullerides, a report of the superconducting $Yb_{2.5}C_{60}$ phase provides incentive for synthesizing other lanthanide C_{60} fullerides.[18] The lanthanide donor atoms are ionized, resulting in the release of electrons to form negatively charged fullerenes. In the ytterbium fulleride, moreover, there is evidence for short-range, covalent interactions, which suggests that lanthanides do not react with the fullerenes according to a simple intercalation reaction, but react to form covalently bound lanthanide fullerides where the lanthanide ion interacts strongly with the fullerene. To obtain materials with better-defined structures, it is worthwhile to investigate the interaction of fullerenes with lanthanides in a controlled way. Making lanthanide fullerides in the gas phase may allow us to prepare well-defined deposited materials. There is much more fullerene

* Corresponding author.

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chemistry to be explored, and the investigation of rare-earth fullerides may open up a new field of organolanthanide chemistry.

The application of laser vaporization to the gas-phase synthesis of organometallic compounds enables us to prepare the constituents without the interfering effects of solvents, aggregation phenomena, and counterions. In this letter, we present results on the gas-phase synthesis of lanthanide fullerides for Eu and Ho. Mass spectrometry, photoelectron spectroscopy, and chemical probe techniques have been applied to reveal information on their geometric and electronic structures, especially the oxidation states of the lanthanide atom. We find donor elements of lanthanides to form stable charge-transfer clusters along with superstructures composed of multi-lanthanide atoms and multi-C_{60} molecules, where Eu and Ho can work as divalent and trivalent atoms, respectively.

2. Experimental Section

Details of the experimental setup were previously described elsewhere.[19,20] Briefly, lanthanide (Ln; Ln = Eu or Ho)−C_{60} binary clusters were produced in the gas phase by laser vaporization using the second harmonic of two pulsed Nd^{3+}:YAG lasers (wavelength = 532 nm). Each laser was focused onto a rotating and translating rod; one was a lanthanide metal rod, and the other was a C_{60} rod. The energy of the vaporization laser was 10−15 mJ/pulse for the Ln metal rod and 70−100 μJ/pulse for the C_{60} rod. The laser vaporization of C_{60} was very sensitive to the laser energy. For example, a laser energy of more than 200 μJ/pulse resulted in noticeable fragmentation of C_{60} via "C_2 loss". Consequently, the laser vaporization of the C_{60} rod should occur downstream from that of the metal rod because the reverse order results in the fragmentation of C_{60} due to the high laser fluence for the metal rod. The hot vapors of Ln and C_{60} were quenched to room temperature by a pulsed He carrier gas (5−6 atm stagnation pressure), and Ln−C_{60} clusters were generated. After the cluster beam was skimmed, the neutral clusters were ionized in a static electric field by an ArF excimer laser (6.42 eV), whereas the positive or negative ions were accelerated with a pulsed electric potential to 4 kV without photoionization. The ions were mass-analyzed by a time-of-flight (TOF) mass spectrometer with a reflectron. To detect heavy cluster ions efficiently, an ion detector known as an "Even-cup" was used.[21]

Chemical probe measurements were made using a conventional flow-tube reactor.[22] Inside the flow-tube reactor, O_2 or CCl_4 seeded in He was injected in synchronization with the flow of the clusters, and the adducts of Ln−C_{60} clusters were also mass-analyzed.

The PES spectra of the target anions were measured using an apparatus equipped with a magnetic bottle TOF photoelectron spectrometer.[23] The Ln−C_{60} clusters were similarly generated by the two-laser vaporization, and only the cluster anions were accelerated to 900 eV. After being selected by a mass gate, the target anions were decelerated and photodetached with the fourth harmonic (266 nm; 4.66 eV) of a Nd^{3+}:YAG laser. The photoelectron signal was typically accumulated to 15000−30000 shots. The obtained energy resolution was about 20 meV fwhm at 1 eV electron energy. The energy of the photoelectron was calibrated by measuring photoelectron spectra of Au^-. [24,25] The laser power for photodetachment was in the range of 3−5 mJ/cm^2, and no power-dependent processes for the spectrum shape were observed.

3. Results and Discussion

Figure 1 shows mass spectra of (a) $Eu_n(C_{60})_m^+$ and (b) $Ho_n(C_{60})_m^+$ cluster cations produced by the ablation of Ln (Ln = Eu or Ho) and C_{60} targets. Peaks of the cationic clusters are labeled according to the notation, $(n, m)^+$, denoting the number of Ln atoms (n) and C_{60} (m). Under the prevalent conditions, the contribution of Ln_n^+ cluster to $Ln_n(C_{60})_m^+$ formation was negligible because the abundance of the Ln_n^+ clusters ($n \geq 2$) was less than 1/1000 that of the Ln^+ atoms. Both mass spectra indicate a common pattern of prominent peaks (i.e., "magic number"). The prominent peaks in the mass spectra correspond to $(n, m) = (1, 1)^+$, $(1, 2)^+$, $(1, 3)^+$, and $(1, 4)^+$, $(2, 5)^+$, $(3, 6)^+$, and $(4, 7)^+$, which are expressed as $(1, m)^+$ [$m = 1-3$] and $(n, n + 3)^+$ [$n = 1-4$] have common structures. The mass distribution of the prominent clusters remained unchanged even when the concentration of Ln atoms was increased with higher laser fluence for the Ln rod. Moreover, we observed similar patterns in the mass spectra of anionic and neutral as well as the cationic Ho−C_{60} clusters. This implies that all of the cationic, anionic, and neutral Ln−C_{60} clusters composed of (1, m) [$m = 1-3$] and (n, $n + 3$) [$n = 1-4$] have common structures. The magic numbers for Ln−C_{60} cluster cations are different from those of the other organometallic clusters such as M_T−C_{60},[20] M_T−C_6H_6,[26] and Ln−C_8H_8.[27] Since the bonding in Ln−C_{60} clusters was expected to be ionic, we performed a chemical probe experiment using CCl_4 as reactant to deduce their geometric structures and charge distributions.

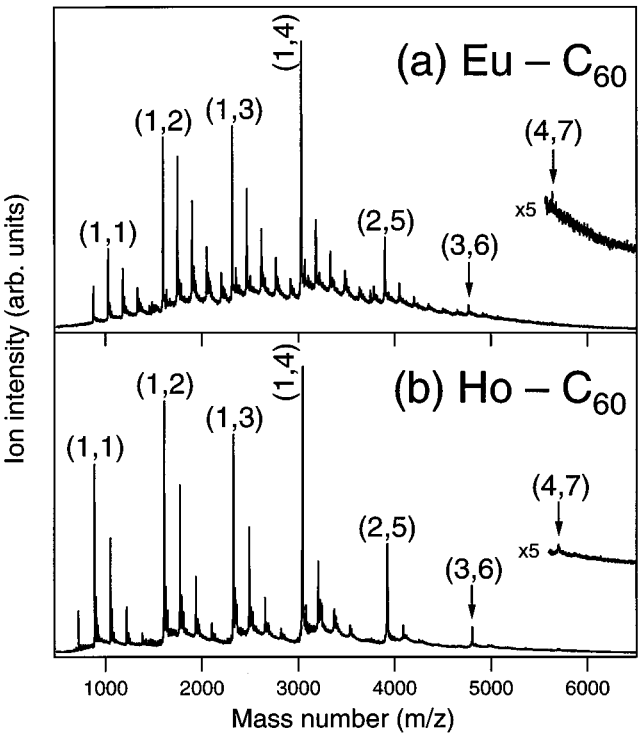

Figure 1. Time-of-flight mass spectra of (a) Eu−C_{60} and (b) Ho−C_{60} cluster cations. Peaks of the cluster cations are labeled according to the notation (n, m), denoting the number of metal atoms (n) and C_{60} molecules (m).

Figure 2 shows the mass spectra of Ho−C_{60} cluster cations (a) after and (b) before the reaction toward CCl_4 seeded in He gas. The clusters composed of $(n, n + 3)^+$ and C_{60}^+ itself were nonreactive toward CCl_4, while the others were reactive, resulting in the formation of Cl-atom adducts ($Ho_n(C_{60})_mCl_k^+$). Here, it is assumed that the Cl^- ion, generated through the dissociation of CCl_4, is concerned in the formation process. Dissociative electron attachment from the cluster might be most conceivable, where CCl_4 dissociates into Cl^- and CCl_3. It is reasonably presumed that an exterior Ho atom in $Ho_n(C_{60})_m^+$

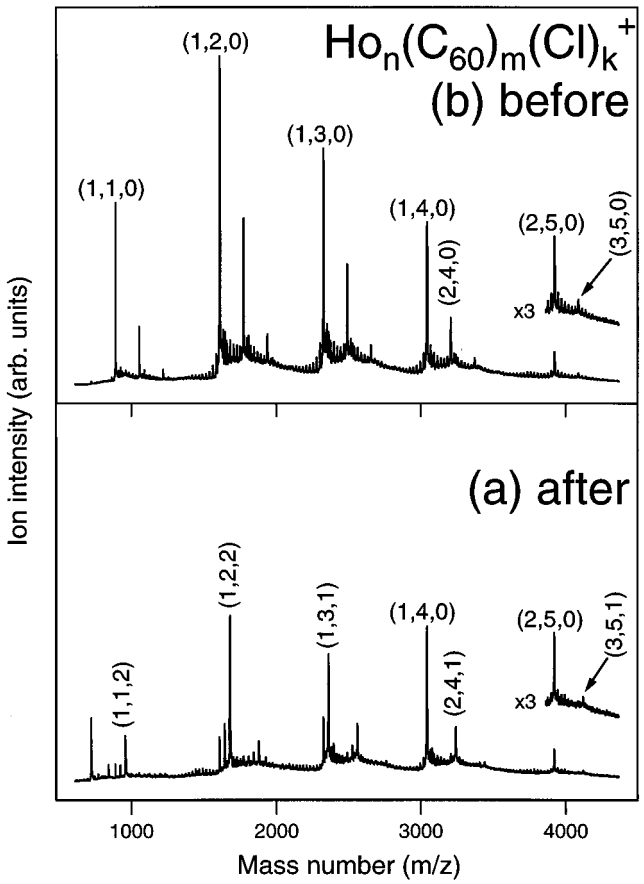

Figure 2. Time-of-flight mass spectra of Ho−C_{60}−Cl cluster cations (a) after and (b) before the reaction with CCl_4 reactant (m = 1−5). Peaks of the cluster cations are labeled according to the notation (n, m, k), denoting the numbers of Ho atoms (n), C_{60} molecules (m), and Cl atoms (k).

is the reaction site for the chloridization because C_{60}^+ itself does not show the chloridization reaction. Similarly, $Ho_n(C_{60})_{n+3}^+$ were also nonreactive toward an oxygen molecule (O_2). This lack of reactivity implies that $Ho_n(C_{60})_{n+3}^+$ should have no exterior Ho atoms. It is proposed that $Ho_1(C_{60})_4^+$ forms a tetrahedral methane-like structure, as shown in Figure 3c, where the Ho atom is geometrically blocked by the surrounding C_{60}s. Since it is reasonably presumed that $Ho_1(C_{60})_4^+$ is the smallest unit of $Ho_n(C_{60})_{n+3}^+$ species, plausible structures of the other $(n, n+3)^+$ follow as in Figure 3d−f. The addition of $Ho_1(C_{60})_1$ to $Ho_1(C_{60})_4^+$ gives $Ho_2(C_{60})_5^+$ (Figure 3d) consisting of two local $Ho_1(C_{60})_4$ groups, resulting in a tetracapped trigonal bipyramid. The successive addition of $Ho_1(C_{60})_1$ sequentially forms a local $Ho_1(C_{60})_4$ group. The composition of $Ho_n(C_{60})_{n+3}^+$ can be expressed as $Ho_{1+j}(C_{60})_{4+j}^+$ [j = 0−3], in which each Ho atom is favorably surrounded by four C_{60}s.

As described above, the anionic and neutral Ho−C_{60} clusters were also produced predominantly at the composition of $(n, n+3)^{-/0}$. They show the same behavior in mass distributions irrespective of different charging states, which indicates that all of the cationic, anionic, and neutral clusters of Ho−C_{60} form the common geometric structures constituting of $Ho_1(C_{60})_4$ units. As well as $Ho_n(C_{60})_m^+$, $Eu_n(C_{60})_m^+$ clusters show almost the same behavior; $Eu_n(C_{60})_{n+3}^+$ (n = 1−4) are produced abundantly and they are nonreactive toward CCl_4, suggesting that $Eu_n(C_{60})_{n+3}^+$ also consists of the tetrahedral unit of $Eu_1(C_{60})_4$. Correspondingly, stability of $(n, n+3)^+$ species is generally observed in the lanthanide−C_{60} clusters such as Ce−C_{60}, Nd−C_{60}, Yb−C_{60}, which indicates that the structural unit of (1, 4) is common among Ln−C_{60} clusters. While (1, 4) takes the tetrahedral structure, (1, 2) and (1, 3) should be regarded as precursors of (1, 4) and they should act as a reaction site toward a gas reactant, as shown in Figure 3, parts a and b. The chemical probe experiment can reveal their structure as described below.

In general, the lanthanide complexes are well-known as charge-transfer complexes where the Ln atoms are multiply-charged cations and the ligands are charged anions.[27] By analogy of the reported lanthanide complexes, it is conceivable that all of the Ln atoms take the oxidation state of +3 except that Eu and Yb atoms can also take that of +2. Since the C_{60} molecule has a lowest unoccupied molecular orbital (LUMO) which is triply degenerated, it is intriguing to estimate the amount of electrons transferred from the Ln atom to C_{60} molecules in Ln−C_{60} clusters. To deduce the electronic structure of Ln−C_{60} clusters, photoelectron spectroscopy of $Ln_1(C_{60})_m^-$ anions were performed. Figure 4 shows the photoelectron spectra of (a) $Eu_1(C_{60})_m^-$ and (b) $Ho_1(C_{60})_m^-$ at 266 nm (4.66 eV). In the spectra, the horizontal axis corresponds to the electron binding energy, E_b, defined as $E_b = h\nu - E_k$ where E_k is the kinetic energy of the photoelectron. Arrows indicate threshold energies (E_T), which correspond to the upper limit of the adiabatic electron affinity (AEA). The obtained AEAs of $Eu_1(C_{60})_m$ and $Ho_1(C_{60})_m$ species are tabulated in Table 1. For $Eu_1(C_{60})_3$ and $Ho_1(C_{60})_4$, no effective photodetachment occurs at 266 nm and only lower limits of their AEAs are obtained as 4.0 eV.

When the spectra of $Ln_1(C_{60})_m^-$ were compared as a function of the number of C_{60} molecules (m), it was found that the AEA of $Ho_1(C_{60})_3$ is almost the same to that of $Ho_1(C_{60})_2$, whereas the AEA of $Eu_1(C_{60})_3$ is higher than that of $Eu_1(C_{60})_2$. This difference between Eu−C_{60} and Ho−C_{60} can be explained by the preferred oxidation states of the Ln atoms. Assuming that Eu and Ho atoms become Eu^{2+} and Ho^{3+}, respectively, the allotment of valence electrons in $Ln_1(C_{60})_m^-$ anions are expected to be in accordance with the drawing in Figure 5. Here, it is reasonably assumed that the extra electron in the $Ln_1(C_{60})_m^-$ anions should be localized on C_{60}. In fact, the theoretical calculation by Nagase et al. indicates that the Ln atom is positively charged in endohedral metallofullerenes such as La@C_{82} and Ce@C_{82}, transferring valence electrons to the fullerene cage.[13]

According to the bonding scheme shown in Figure 5, for Ho−C_{60} the energy difference between the anion and the corresponding neutral, $EA(Ln_1(C_{60})_m)$, can simply be estimated by the following equations:

$$EA(Ho^{3+}C_{60}^{3-}) = EA(C_{60} \rightarrow C_{60}^{4-}) - EA(C_{60} \rightarrow C_{60}^{3-}) + \Delta \quad (1)$$

$$EA(Ho^{3+}(C_{60})_2^{3-}) = EA(C_{60} \rightarrow C_{60}^{2-}) - EA(C_{60} \rightarrow C_{60}^{-}) + \Delta \quad (2)$$

$$EA(Ho^{3+}(C_{60})_3^{3-}) = EA(C_{60} \rightarrow C_{60}^{2-}) - EA(C_{60} \rightarrow C_{60}^{-}) + \Delta \quad (3)$$

$$EA(Ho^{3+}(C_{60})_4^{3-}) = EA(C_{60} \rightarrow C_{60}^{-}) + \Delta \quad (4)$$

where Δ is Coulomb binding energy between Ho^{3+} and the charged C_{60}. Apparent from the equations, the EA of (1, 2) and (1, 3) for trivalent Ho is the same, which is consistent with the experimental finding. Furthermore, the increase of EA with the number of C_{60} can be realized by these equations. Recently density function calculations predict the EAs for the multiply

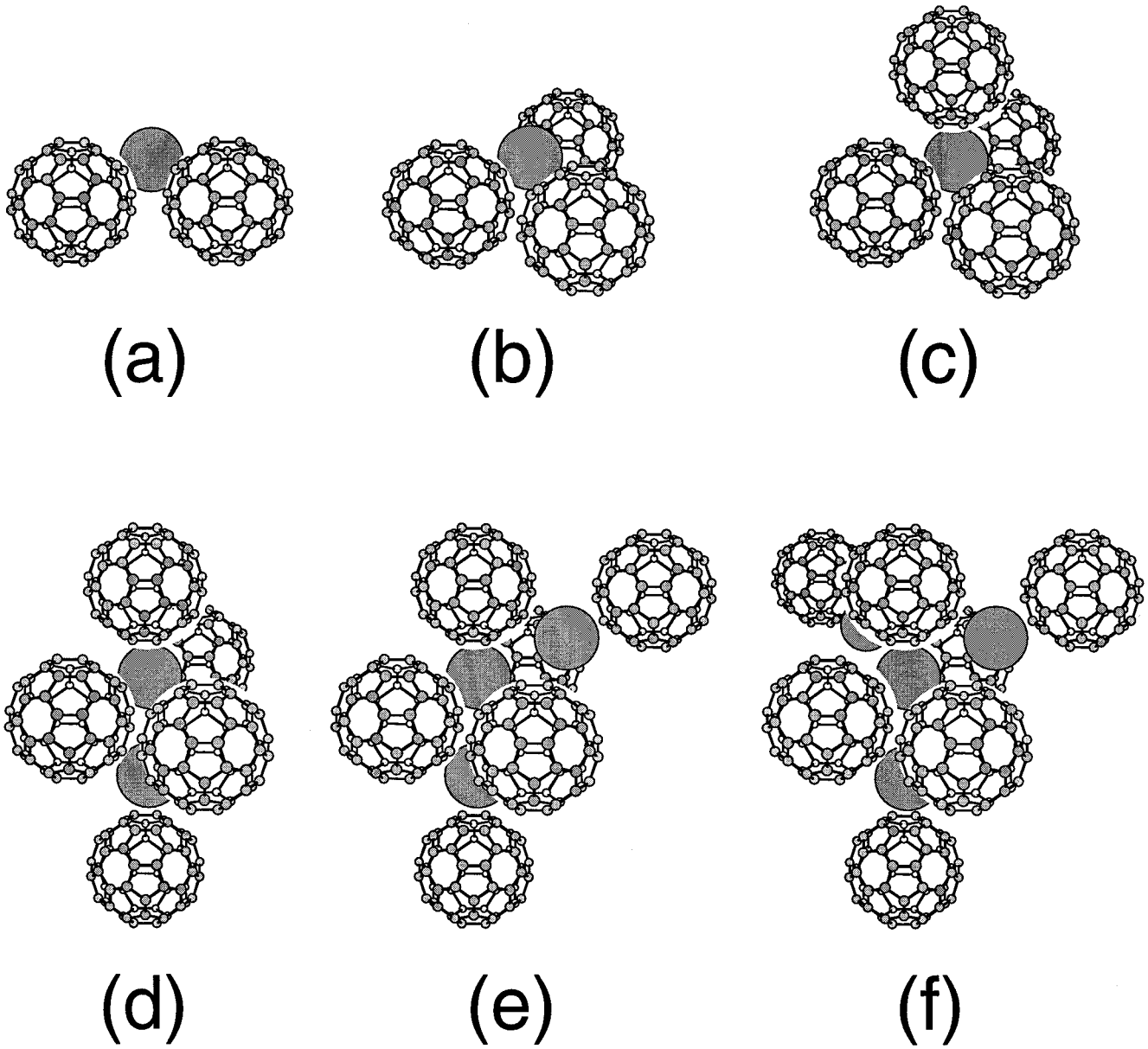

Figure 3. Proposed geometric structures; (a) $Ln_1(C_{60})_2$, (b) $Ln_1(C_{60})_3$, (c) $Ln_1(C_{60})_4$, (d) $Ln_2(C_{60})_5$, (e) $Ln_3(C_{60})_6$, and (f) $Ln_4(C_{60})_7$ (Ln = Eu and Ho).

charged C_{60}, C_{60}^{x-} ($x = 1-5$).[28] The experimental EA difference between (1, 1) and (1, 2) for Ho−C_{60} was obtained to be 0.68 eV, and the estimated value is 0.35 eV based on the predicted values. In this scheme, the EA of the (1, 4) is predicted to be more than 8 eV, which gives a reasonable explanation for there being no effective photodetachment from $(1, 4)^-$ with a photon energy of 4.66 eV. In $(1, 4)^-$, each C_{60}^- accepts one electron from the Ho atom and the excess charge, satisfying the charge distributions of Ho^{3+} and $4C_{60}^-$. In conclusion the Ln−C_{60} clusters are formed through ionic bonding, distributing the valence electrons into the ligand molecules of C_{60}.

For Eu−C_{60} (Figure 5a), on the other hand, the monotonic increase in EA can similarly be rationalized by the charge distribution with Eu^{2+}, because the detached electron is released from different charged C_{60}; C_{60}^{3-} for $(1, 1)^-$, C_{60}^{2-} for $(1, 2)^-$, and C_{60}^- for $(1, 3)^-$. This explanation successfully leads us to the conclusion that Eu and Ho atoms in $Ln_1(C_{60})_m$ clusters take +2 and +3 oxidation states, respectively. This conclusion on the net charges of $Ln_1(C_{60})_m$ is also consistent with the following results for the formation of $Ln_n(C_{60})_m(Cl)_k^+$.

For ionic clusters, it is anticipated that a chemical probe, such as the attachment of a halogen atom, can lead to insight into the charge distribution. Although the chemical method involves some ambiguity as to whether the charge distribution might result from the addition of the probing atom, the number of attached halogen atoms (k) should reflect the probable charge distribution, because a halogen atom acts as an acceptor of one electron. The maximum numbers of k (k_{max}) obtained under saturated chloridization conditions were investigated, and they are summarized in Table 2 for $Ln_n(C_{60})_m(Cl)_k^+$.

For both $m = 1$ and 2, k_{max} is 1 for $Eu_1(C_{60})_mCl_k^+$, while k_{max} is 2 for $Ho_1(C_{60})_mCl_k^+$. The results of the k_{max} for $Ln_1(C_{60})_mCl_k^+$ evidently indicate that Eu atoms take the oxidation state of +2, and Ho atom does that of +3, because their charge distribution can successfully be described as $Eu^{2+}{}_1(C_{60}{}^0)_m(Cl^{1-})_1$ and $Ho^{3+}{}_1(C_{60}{}^0)_m(Cl^{1-})_2$, having a neutral C_{60}. It suggests that a strong charge−charge-induced dipole interaction occurs between Eu^{2+}/Ho^{3+} ion and C_{60} molecule in $Ln_1(C_{60})_mCl_k^+$. In fact, the reported polarizability of C_{60} is very large ($\sim 80 \times 10^{-24}$ cm^3).[29,30] For Ln_1 $(C_{60})_3Cl_k^+(m = 3)$, however, k_{max} is 1

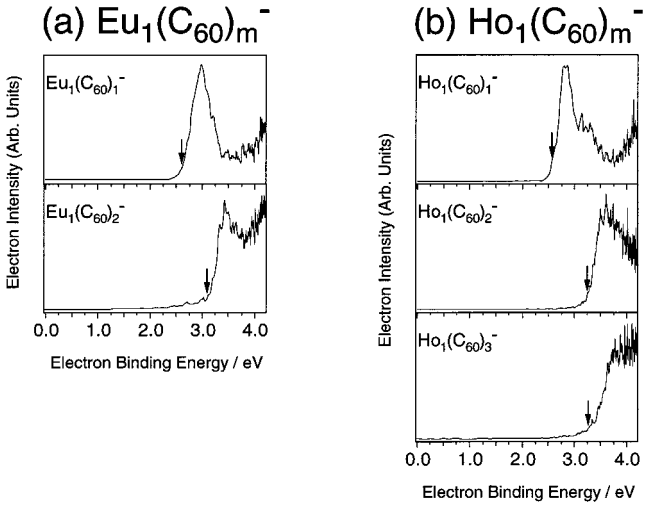

Figure 4. Photoelectron spectra of (a) $Eu_1(C_{60})_m^-$ ($m = 1$ and 2) and (b) $Ho_1(C_{60})_m^-$ ($m = 1-3$) measured at a photon energy of 4.66 eV (266 nm). The downward arrows indicate threshold energies, corresponding to adiabatic electron affinities (AEAs).

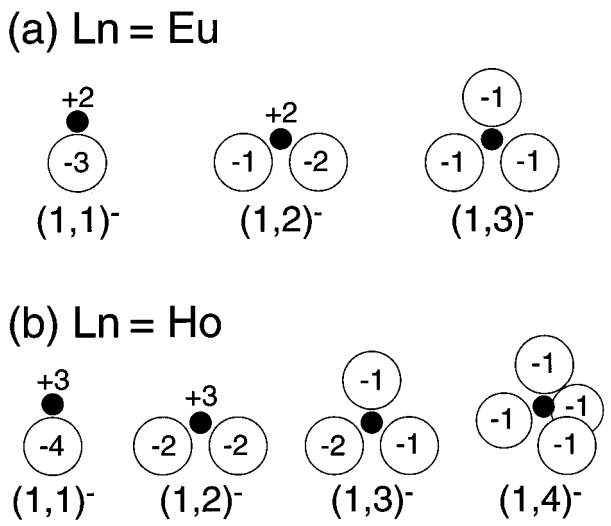

Figure 5. Allotment of valence electrons of $Ln_1(C_{60})_m^-$ are also shown schematically. These are based on the assumptions that the extra electron in $Ln_1(C_{60})_m^-$ anions is localized on C_{60}. The successful explanation for the size dependence of EAs and Cl-atom adducts indicates that Eu and Ho atoms take the oxidation states of +2 and +3, respectively.

TABLE 1: Adiabatic Electron Affinities of $Ln_1(C_{60})_m$ Clusters (Ln = Eu and Ho) in eV

cluster	Ln=Eu	Ln=Ho
$Ln_1(C_{60})_1$	2.61(12) [a]	2.56(12)
$Ln_1(C_{60})_2$	3.10(25)	3.24(19)
$Ln_1(C_{60})_3$	> 4.0	3.25(21)
$Ln_1(C_{60})_4$	–	> 4.0

[a] 2.61(12) represents 2.61 ± 0.12.

for both Ln = Eu and Ho. According to the charge distribution with Eu^{2+} and Ho^{3+}, $Ho_1(C_{60})_3$ should attract two Cl atoms, forming $Ho^{3+}{}_1(C_{60}{}^0)_3(Cl^{1-})_2$. This discrepancy is expected to be attributable to steric hindrance of $Ln_1(C_{60})_3$: the electronic repulsion Cl^- could prevent attaching the second Cl atom to $Ln_1(C_{60})_3Cl_1^+$.

For $Ln_n(C_{60})_4(Cl)_k^+$ and $Ln_n(C_{60})_5(Cl)_k^+$, moreover, a Cl atom can similarly be attached to them. $Ln_{n+1}(C_{60})_{n+3}^+$ and $Ln_{n+2}(C_{60})_{n+3}^+$ can attract one and two Cl atom(s) because they have one and two exterior Ln atom(s), respectively. The exterior Ln atom can act as a site for the Cl-atom addition and they satisfy the charge distribution of Ln^{2+}/Ln^{3+} with Cl^- ion(s).

TABLE 2: The Maximum Number of k_{max} for $Ln_n(C_{60})_m(Cl)_k^+$

species		k_{max}	
n	m	Ln=Eu	Ln=Ho
1	1	1	2
1	2	1	2
1	3	1	1
1	4	0	0
2	4	1	1
3	4	2	2
2	5	0	0
3	5	1	1
4	5	2	2

In summary, we have reported a new class of fullerene chemistry between C_{60} and rare-earth metal atoms of Eu and Ho. This experiment reveals a new form of exohedral metallofullerenes, and photoelectron spectroscopy of the mass-selected metallofullerenes provides the information on the charge distribution; Eu and Ho atoms in the $Ln-C_{60}$ clusters take the oxidation states of +2 and +3, respectively. This gas-phase preparation of metallofullerenes has the advantage that selected precursor components can lead to novel structures of deposited materials in a controlled fashion. Since the $Ln_n(C_{60})_{n+3}$ clusters are stable toward O_2, deposited $Ln-C_{60}$ materials might be promising to be developed even under exposure to air.

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