An EXAFS Study of the Metallofullerene $Y_{C_{62}}$: Is the Yttrium Inside the Cage?

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A sample, determined by time-of-flight mass spectroscopy (TOFMS) to consist of $Y_{C_{62}}$ as the major metal– fullerene complex, was analyzed by X-ray absorption spectroscopy. The Y is found to have 7 ± 1 near-neighbor C atoms at 2.35 ± 0.02 Å and an Y neighbor at 4.05 ± 0.05 Å. The unequivocal observation of an Y–Y interaction is unexpected, since the mass spectral data show no indication of $Y_{C_{2}}$ as a major component of the sample. We believe that the combined TOFMS and extended X-ray absorption fine structure (EXAFS) results are not consistent with models that place the metal ion inside the fullerene cage. Instead, we propose that our data can be explained with a dimer of the form $Cs_{2}Y-X-YC_{62}$, where –X– is a bridging carbon or oxygen species. The short Y–C near-neighbor distance indicates a strong, bonding interaction between the metal ion and the fullerene cage.

Introduction

It has been suggested that the cavity created inside the “soccer-ball-like” structure of the $C_{60}$ fullerene clusters could trap metal ions to form endohedral complexes with interesting electron properties. Evidence for the formation of LaC$_{60}$ made by laser vaporization of a low-density graphite source impregnated with LaCl$_{3}$ was obtained by time-of-flight mass spectroscopy (TOFMS).$^{1}$ TOF peaks attributable to LaC$_{60}$ or LaC$_{n}^{+}$ were identified, where $n$ ranged from 44 to greater than 76. There was no evidence of clusters associated with more than one La ion; therefore, it was inferred that there is only one uniquely-stable binding site per $C_{60}$ and that this site is inside the $C_{60}$ cage. Photodissociation of metal–carbon clusters involves the successive loss of C$_{2}$ fragments, in a pattern similar to that obtained from photodissociation of the bare clusters.$^{2}$ The loss of C$_{2}$ rather than M$_{2}$ has been used to argue that the metal ion is sterically trapped inside the fullerene cage. This suggestion gains further support from the apparent stability of these metal complex= to reaction with either oxygen or moist air.$^{3}$ In particular, LaC$_{60}$ is found to be the only lanthanum fullerene to the description of the complex in terms of a $C_{60}$ cage? The latter interpretation is more consistent with the complexes LanCsCh inside the cage framework itself, each La ion replacing two carbon atoms, rather than being trapped inside the cage structure.$^{6}$ Recently, yttrium (Y) has been reported to be incorporated into the fullerene cages with even greater facility than La.$^{5}$ The metallofullerenes $Y_{C_{60}}$ and $Y_{C_{n}}$ are reported, with $Y_{C_{62}}$ appearing to be the most abundant dimeric compound.

Whether the metal ions are trapped inside or are outside the fullerene cage, or are incorporated into the cage structure itself, is difficult to determine because of both the small sample sizes and the variety of $C_{60}$ impurities present in the samples. We have chosen to use X-ray absorption spectroscopy (XAS) to provide direct information about the environment of the Y ion in these samples. XAS is a particularly suitable technique to study this problem because it is a single ion probe, and therefore by tuning the energy to the absorption edge of interest, it is possible to determine electronic and environmental information about a specific ion in a complex matrix.

Experiments

Sample Preparation and Characterization. The metallofullerene samples were prepared in our carbon plasma generator.$^{7}$ A 4.3-mm-diameter hole was drilled into a carbon rod of 6.3-μm thickness at a length of 38 mm. This rod was filled with a mixture of $Y_{2}O_{3}$ and graphite of equal volume quantities. The mixture was pressed into the tube, but no binder was used. This rod was inserted in the fullerene generator, carefully pumped down to 10$^{-2}$ Torr, and burned under our usual experimental conditions for fullerene production.$^{7}$ The soot obtained was collected with no special precautions to prevent air exposure. The soot was sonicated in toluene and centrifuged. The solution was decanted from the residue and dried. A mass spectrum of the material obtained by this procedure is shown in Figure 1a. The synthesis yielded the well-known distribution of all-carbon molecules, the fullerences $C_{60}$, $C_{70}$, ..., $C_{72}$, up to very high masses ($>3000$ amu). Other peaks are observed in the mass spectrum between the fullerene molecules, which are identified as series of $YC_{60}$ and $Y_{2}C_{62}$ molecules. The identified $YC_{6}$ molecules are present and larger $YC_{6}$ entities, with $n$ up to 100 and more. The most abundant molecules of this series are $YC_{50}$, $YC_{70}$, and $YC_{52}$ at $m/z = 929$, $977$, $1001$, and $1073$ amu, respectively. The smallest molecule observed of the $Y_{2}C_{62}$ series is $Y_{2}C_{74}$, and...
collected simultaneously. Si (31 1) crystals were used with 2-mm
with the all-carbon fullerenes (Figure 1b). The other metallo-
analysis.
X-ray absorption data were obtained on beamline X23-A2 at
600 700 800 900 1000 1100 1200 1300 1400
m/z
Figure 1. Time-of-flight mass spectra of positive ions, directly desorbed
by pulsed 266-nm laser irradiation: (a) toluene extract of soot containing
the all-carbon fullerenes C, and metallofullerenes YC, and YC, (b)
toluene extract of soot containing the all-carbon fullerenes C, and only
the metallofullerenes YC, and YC, at m/z = 1001 and 1073 amu,
respectively.
increased abundance in this series is found for YC33, YC32, YC31, and YC30
at m/z = 1114, 1162, 1234, and 1306 amu, respectively. Performing a milder extraction at room temperature
mainly dissolves YCE2 and a little YC, (less than 20%), together
with the all-carbon fullerenes (Figure 1b). The other metallo-
fullerenes remain in the residue after centrifuging and decanting
the solvent. Although the total amount of YC32 in the sample
depicted in Figure 1b is very small, it is used for X-ray absorption
analysis.
X-ray Absorption Spectroscopy. Yttrium K-edge (17 038 eV)
X-ray absorption data were obtained on beamline X23-A2 at
NSLS. Approximately 2-mg total weight of sample was used,
which ultimately limited the data quality. The data on the metal
fullerenes samples were obtained in the electron yield and
fluorescence mode using a Lytle detector, with the beat detection
slits in order to maximize flux on sample.
Extended X-ray absorption fine structure (EXAFS) is described
by scattering theory5-10 as
\[
\chi(k) = \sum_j N_j S_j(k) \exp(-2r_j^2/k^2) \exp(-2r_j/|k\lambda_j(k)|) \times
\sin (2kr_j + \phi_j(k)) (kr_j)^{-1}
\]
where k is the scattering wavevector, and the sum is over the j
coordination shells. Nj are the number of atoms in the jth
coordination shell with the Fj(k) backscattering amplitude. The
first exponential term accounts for thermal motion and static
disorder, and the second exponential represents the inelastic losses
that arise during the scattering processes. Sj(k) is an amplitude
reduction factor representing many-body effects, and \phi_j(k) is
the total phase shift experienced by the photoelectron. The back-
scattering amplitude and phase factors are abstracted from data
obtained on well-characterized standards, and the Debye–Waller
and disorder parameters obtained from the fitting procedures are
relative to the standards. The errors reported for the fitted
parameters are determined by combining errors from repeatedly
fitting the data, from fitting comparable compounds, and from
testing transferability on model materials.
Results
XANES. A comparison of several Y near-edge spectra is shown in
Figure 2. The total, normalized step height of the electron
yield spectra of the YC32 sample is about 0.015, reflecting both
the small total sample size (about 2 mg) and the low concentration
of the Y-containing phase in the sample. This step height can
be compared to a normalized step height of about 1, determined
from transmission mode spectra, found for samples which contain
approximately 100 mg Y/cm².
The edge obtained from the YC32 sample occurs at a slightly
higher energy than Y metal, or the other standards used here for
comparison. Since the absorption edge is known to shift to higher
energy with increasing charge at the central ion, the Y in our
sample is shown to have a relatively low electron density, consistent
with trivalent Y.
EXAFS. The background-subtracted EXAFS data, obtained
from the YC32 sample shown in Figure 1b, are shown in Figure
3a, and the Fourier transform of these data are shown in Figure
3b. Other samples, which contain the variety of Y,Cn species
The EXAFS data reveal an Y–C distance of $2.35 \pm 0.02$ Å. This distance is considerably shorter than the Y–C distances of $\approx 2.45$ Å in YC<sub>2</sub>, the Y–N distance of 2.438 Å in YN, and the 2.580 (3) Å extrapolated for the π-bonded compound Y(Bu<sub>3</sub>C<sub>6</sub>H<sub>12</sub>)<sub>2</sub>. The short Y–C distance indicates a strong interaction between the metal ion and the fullerene. This strong interaction is consistent with the apparent instability of our sample to reaction with moist air.

The interaction between the fullerene cage and the metal ion is further clarified by the determination of $7 \pm 1$ C atoms coordinated to the Y. The number of near neighbors, together with the Y–C distances, rules out the possibility that the Y ion sits at the center of the fullerene cage. This result also appears inconsistent with the suggestion that the Y ion could be incorporated into the C network that forms the cage structure, because the Y would be expected to have no more than four near-neighbor C atoms. In contrast, this result suggests that the Y ion is strongly bonded to the fullerene and is located over one of the five- or six-membered rings associated with the cage. The coordination determined here is different from that observed for osmylated C<sub>60</sub>, in which the O–Os–O unit has added across a six–six ring fusion. The geometry determined for the Y–C interaction, although our Y–C distance is considerably shorter than those observed for other Y–π-bonded systems. Although π-bonding is not commonly observed for rare-earth ions, there are structures reported for R (π-Bu<sub>3</sub>C<sub>6</sub>H<sub>12</sub>)<sub>2</sub> and R–(C<sub>6</sub>H<sub>12</sub>)<sub>2</sub>, where R = rare earth (including Sc and Y). Details of the metal–arene ring bonding are not currently understood but are discussed in general terms elsewhere.

The peak observed in the Fourier transformed data labeled peak II in Figure 3b arises from a Y–Y interaction at 4.05 ± 0.05 Å, considerably longer than the Y–Y distance of 3.556 Å found in the metal or the 3.66 Å found in the dicarbide. The relative intensities of peaks I and II in the EXAFS data are used to estimate that at least 70% of the Y contributing to peak I (attributed to Y–C scattering) is also contributing to peak II (the peak arising from Y–Y scattering). In other words, the Y–Y peak does not arise from a small impurity phase, relative to the YC<sub>2</sub> phase, but is instead related to the major, Y-containing phase in the sample.

The determination of about seven equidistant C atom near neighbors, together with the presence of an Y–Y interaction at about 4.05 Å, further supports the understanding of the structure of the metal–fullerene species in our sample. There are three possibilities to consider: (1) the Y ions are inside the fullerene cage, (2) one Y is inside and another is outside the cage, or (3) the metal ions are outside the cage. These possibilities are each discussed in turn.

From a geometric perspective, an Y–Y dimer would fit inside the fullerene cage. The sum of the two ring centroid–Y distances of 2.00 Å and the Y–Y distance of 4.05 Å is 6.05 Å. While the C<sub>2y</sub> is assumed to be elliptical, with the Y–Y bond aligned parallel to the major ellipse axis, and if the fullerene is slightly expanded, there may be adequate space inside the cage. However, there are several problems associated with this structural model. If the Y–Y bond is aligned along the elliptical axis of the fullerene cage, it is estimated that there should be at least 12 other C atoms at distances of about 2.5 Å that would contribute to the EXAFS spectra. Backscattering from these other C atoms is ruled out by our data. Another problem is the charge associated with the single fullerene cage. The data presented here, as well as independent XPS<sup>5</sup> and EPR<sup>4</sup> data on either La or Y samples, confirm that the metal ion is trivalent. If there are two Y<sup>3+</sup> ions not associated inside one fullerene, then both the Coulombic repulsion between the two charges and the −6 charge associated with the cage structure would be expected to significantly destabilize the cluster. However, there is experimental evidence that both C<sub>60</sub> and C<sub>70</sub> observed for selected shells in both NiO<sub>11</sub> and YN.<sup>12</sup> It should be stressed that whatever the cause of the phase shift at low k, the reasonable values of N and $\sigma^2$ uniquely establish the Y–Y interaction at 4.05 Å.

Discussion

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can accept six more electrons in solution.21 It should be noted that the Y–Y distance is too short to arise from two Y ions inside adjacent fullerene cages.

Perhaps our most significant problem with a structure in which both Y are inside the cage is the absence of any evidence of an Y3C2 species in our mass spectral data for this EXAFS sample. Our work on other samples convinces us that we can detect YC2 by our TOFMS experimental procedure. Furthermore, samples with multiple YCn components, as detected by TOFMS, produce EXAFS spectra too complex for us to analyze. A structural model involving Y or an Y–Y dimer inside the fullerene cage is difficult to reconcile with the TOFMS and EXAFS data obtained from our sample.

Instead of the Y–Y inside the fullerene cage, it is possible that one Y is inside and the other outside the cage. This structure would be consistent with the TOFMS if it is assumed that the outside Y ion is only weakly bound and is easily lost in the ionization process. However, the C6 cage would still necessarily assume a –6 charge. Furthermore, the Y–Y and Y–C distances are not consistent with two Y bonding across the cage. The ring centroid–Y distance is 2.2 Å, a distance that would require the two Y to be 4.4 Å apart, but the experimentally determined Y–Y distance is only 4.05 Å. Therefore, we believe that our data are not consistent with this interpretation.

The third possibility is that both Y ions are outside the fullerene cage. We believe that this model is most consistent with our data. We propose a structure in which the two Y ions are each associated with a different fullerene cage and the two YCn moieties are weakly associated, with a Y–Y distance of 4.05 Å. It is unlikely that two Y3+ would be directly bonded, since Coulombic repulsion would make this interaction unstable. Instead, we suggest a carbon- or oxygen-based bridge (–X–) between the two Y, to form C2Y–X–YC2 (I). We know from the analysis of peak I that the Y–X distance is about 2.35 Å, and we also know that the Y–Y distance is 4.05 Å. From these distances, we determine that the Y–X–Y angle is 150°, which is consistent with the forward focusing and subsequent complex phase shift observed in our Y–Y EXAFS. Furthermore, if the –X– bridging species could accept two electrons (one from each C2Y–), then our overall structure could also be used to reconcile the expectation that the cage accepts two electrons with the observation of Y3+. An (–X–)2 could be easily understood if the –X– bridge is oxygen, the presence of which has been reported in some metallofullerene samples.56 The EXAFS results presented here cannot distinguish between oxygen and carbon atoms as near neighbors.

In order to explain the TOFMS data, it is necessary to assume that dimer I either is not stable enough to be directly observed or does not itself form ions, but instead fragments into the observed C2Y ions. Furthermore, the C2Y– bonding would have to be strong enough to survive the ionization. The short Y–C distance observed experimentally is consistent with a strong bond, although metallofullerene bonding is generally not energetically stable for C6 and C24 conjugated systems, which are known to be air and moisture sensitive, although they are thermally stable.13 However, it may be misleading to extrapolate these smaller systems to the molecules under discussion here because the much larger π-system provided by the fullerene may well afford increased stability from both electronic and steric considerations.

Whichever of these metallofullerene structures proves correct, it must necessarily be consistent with the results presented here. Our data unequivocally show that (1) Y is trivalent, (2) Y has about seven near-neighbor C atoms, and (3) there is an Y–Y interaction at a distance of 4.05 Å, which is representative of the bulk of the Y in the sample. Clearly, further experimentation is required before the structure and bonding of the metal–fullerene are well understood.

Conclusions

The analysis of our XAS data leads us to conclude that the Y ions in our sample are trivalent and may not be inside the fullerene cage. They are strongly bonded over a five- or six-membered ring component of the cage. Our data suggest to us a model in which C2Y moieties couple through a bridging carbon or oxygen species to form a dimer. The existence of the molecule C2Y–X–YC2 is consistent with all of our data on this Y2C2 sample.

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References and Notes

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