Synthesis and Characterization of the Europium Fullerides Eu_xC_{60} ($x = 1-6$)

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Europium fullerides Eu_xC_{60} ($x = 1-6$) were prepared by metal ammonia solution synthesis. The products were investigated by X-ray powder diffraction, optical spectroscopy, FTIR, mass spectrometry, and magnetic susceptibility. All products were amorphous by powder X-ray diffraction and were free of ammonia as determined by mass spectrometry. Products prepared with $x = 1, 2, 3$ showed the presence of unreacted C_{60} in the optical spectra, FTIR spectra, and the powder diffraction pattern. FTIR spectra of the Eu_xC_{60} prepared with $x = 3$ show red-shifted frequencies of $F_{1u}(4)$ at 1399 and 1352 (1411) cm^{-1}, suggesting the presence of C_{60}^- and C_{60}^{6-}. FTIR spectra of Eu_xC_{60} samples prepared with $x = 4, 5, 6$ also show red-shifted frequencies and are discussed in detail. Magnetic susceptibility measurements show Curie−Weiss behavior above 50 K with experimental magnetic moments of 6.6 (1), 6.9 (1), and 5.9 (1) μ_B/Eu for $x = 3, 4, 5$ samples, respectively.

Introduction

Although a wide variety of fullerides have been prepared by the reaction of alkaline- and alkaline-earth[1−6] metals with C_{60}, little is known about rare-earth fullerides. In particular, the suggestion of superconductivity in a lanthanide C_{60} fulleride[7] along with a report of the superconducting $Yb_{2.75}C_{60}$ phase[8] provides incentive for synthesizing other lanthanide C_{60} fullerides. Alkali-metal and alkaline-earth-metal C_{60} salts are typically prepared by heating stoichiometric amounts of the metal with C_{60} in a sealed evacuated tube. In the case of the alkaline earth metals, the reaction mixture must be heated to fairly high temperatures (540−740 °C) with elaborate heating cycles in order to obtain a superconducting phase.[1−4] Calcium intercalates into the C_{60} face-centered-cubic lattice (fcc) to form a solid solution for Ca_xC_{60} ($0 \le x < 5$). The compound Ca_5C_{60} crystallizes in a simple cubic structure that is superconducting with a transition temperature, $T_c = 8.4$ K.[2] The strontium intercalated compounds, Sr_xC_{60}, show a solid solution range for $0 \le x \le 3$. In the vicinity of $x = 3$, a body-centered-cubic (bcc) A15 phase coexists with the fcc phase.[3] Sr_6C_{60} crystallizes in a bcc structure and is superconducting with transition temperature $T_c = 4$ K.[3] Ba_3C_{60} crystallizes in the bcc A15 structure,[4] and Ba_6C_{60} crystallizes in a bcc structure. Similar to Sr_6C_{60}, Ba_6C_{60} is also a superconductor with a transition temperature of 7 K.[1] Synchrotron radiation photoemission studies[9] show that Sr_xC_{60} and Ba_xC_{60} fullerides are metallic and that Mg_xC_{60} is semiconducting.

Aside from the alkali- and alkaline-earth metals, only the rare-earth metals, europium and ytterbium have been reported as fullerides with $Yb_{2.75}C_{60}$ being a superconductor.[8,10,11] Many of the transition metals react with C_{60} to give carbides or show clustering of the metal around the C_{60} and do not form intercalation compounds.[12−14] In addition, there are also polymeric C_{60} metal phases.[15−20]

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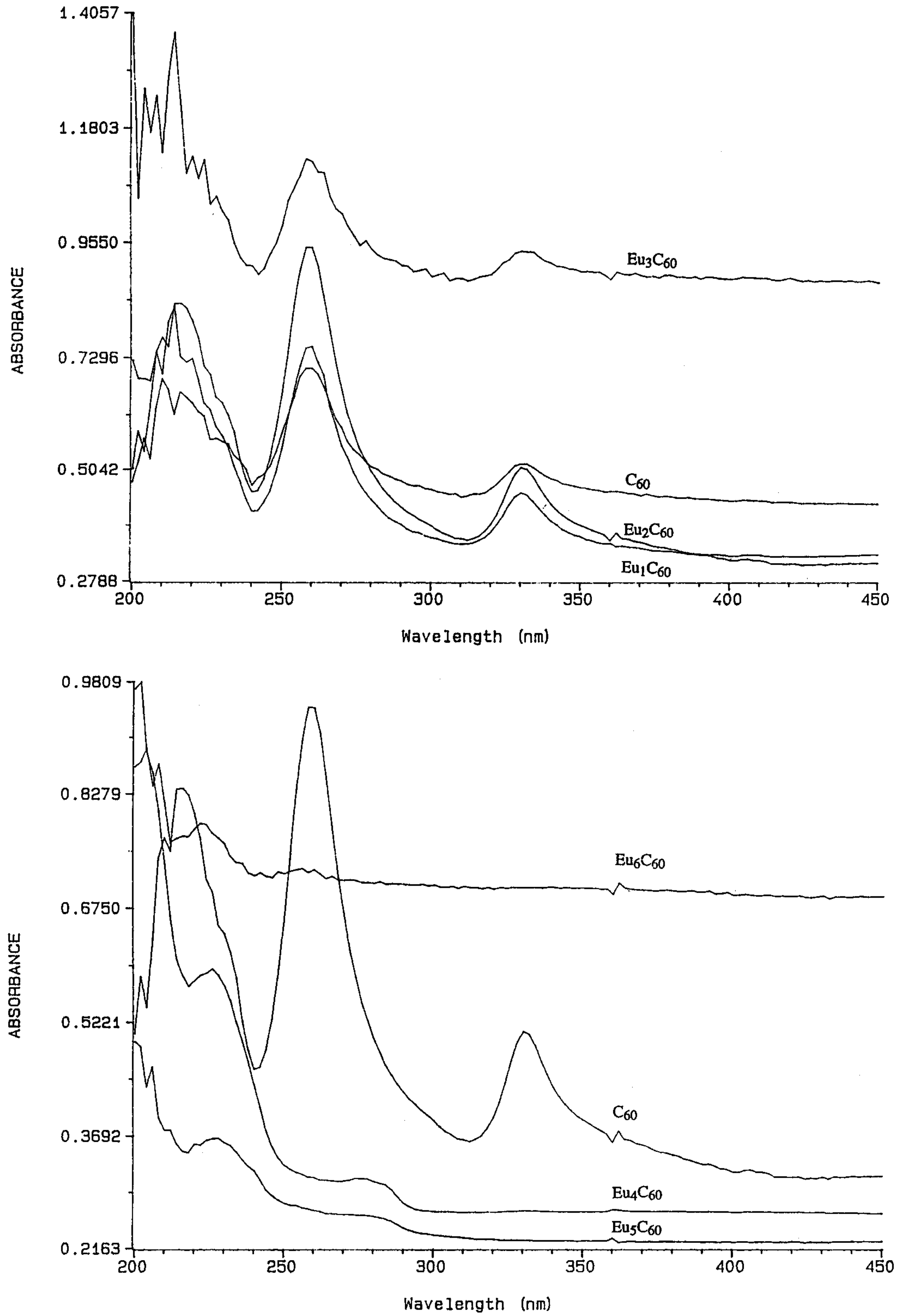

Figure 1. UV−vis spectra of (a, top) C_{60}, Eu_1C_{60}, Eu_2C_{60}, and Eu_3C_{60} and (b, bottom) C_{60}, Eu_4C_{60}, Eu_5C_{60}, and Eu_6C_{60} recorded as a mull in Nujol.

The metal ammonia route to alkali-metal C_{60} compounds has recently been developed.[21] Although this synthetic technique had been explored previously, it had been reported to yield an amorphous product that was not superconducting.[5,6] Buffinger et al. found that annealing a Rb_3C_{60} sample at 375 °C for 1−2 days provided a crystalline product with a large superconducting fraction. This technique is applicable to the preparation of compounds containing metals that are soluble in liquid ammonia. In particular, Eu and Yb intercalation compounds have been synthesized.[22,23] The synthesis and characterization of Eu_1C_{60} and Yb_xC_{60} by the metal ammonia route have been reported.[10,11] Although data for the ytterbium samples were reported, very little information was provided concerning the Eu_1C_{60} sample.[10] The ytterbium samples are complicated by the presence of NH_3,[10,11] and the europium

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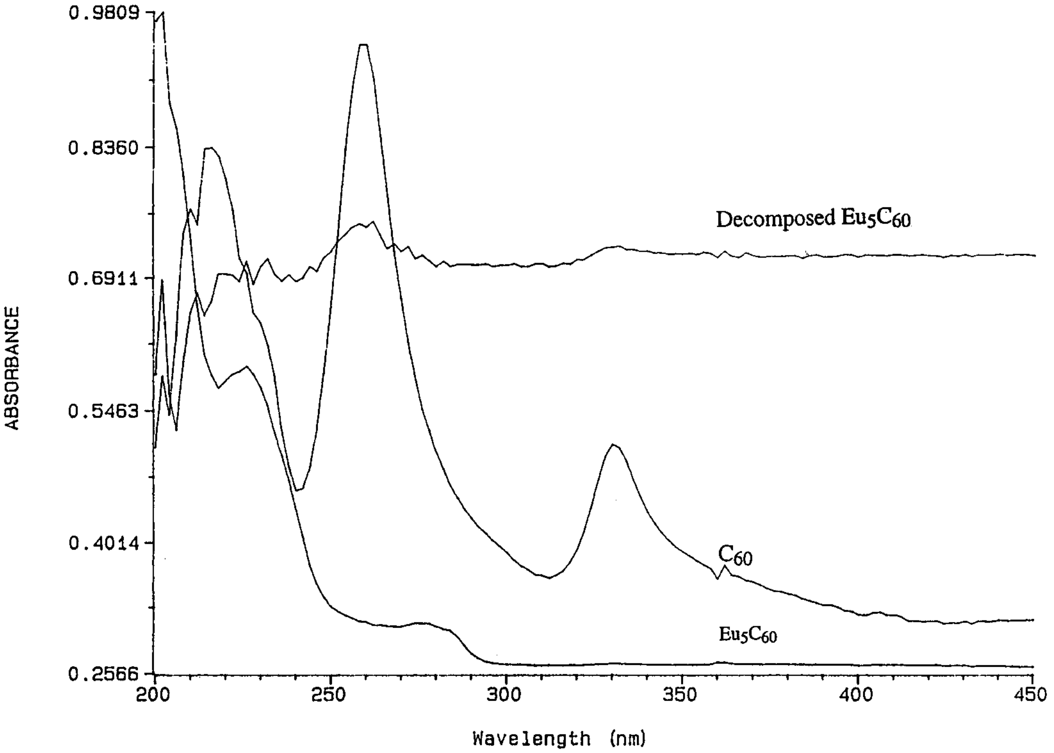

Figure 2. UV–vis spectra of C_{60}, Eu_5C_{60}, and the decomposed Eu_5C_{60} recorded as a mull in Nujol.

samples may provide additional insight into the structure and properties of these compounds. EPR and magnetic susceptibility data are reported for Eu_1C_{60} and it is suggested that europium is present in the mixed valent +2/+3 oxidation states.[10]

In this paper the investigation of Eu_xC_{60} ($x = 1-6$), will be presented. The europium fullerides are prepared by reacting the rare-earth metal with C_{60} in liquid NH_3 and are characterized by X-ray powder diffraction, optical and infrared spectroscopy, mass spectrometry, and temperature-dependent magnetic susceptibility.

Experimental Section

Materials and Synthesis. C_{60} was purchased from MER Corp. (>99.9%). Europium obtained from Ames Lab was used as received. All manipulations of europium and the europium–fullerene compounds were carried out under vacuum or inert atmosphere conditions.

The fullerides, Eu_xC_{60} ($x = 1-6$), were prepared by condensing approximately 15 mL of dried NH_3 onto stoichiometric amounts of C_{60} and Eu metal. C_{60} and Eu metal were weighed into a three-neck round-bottom flask. Liquid NH_3 was dried over Na and condensed onto the C_{60} and Eu metal. The temperature was maintained at −68 °C until the liquid NH_3 solution turned from a blue to a brown and finally to a colorless solution. Typical reaction times for the solution to turn colorless were $^1/_4$ h for $x = 1$ and 2, $^1/_2$ h for $x = 3$, 2 h for $x = 4$, $2^1/_2$ h for $x = 5$, and 6 h for $x = 6$. Once the solution turned colorless, the NH_3 was slowly distilled off. The flask was then gently heated (<80 °C) under vacuum to remove any residual ammonia. Samples were annealed under vacuum (pressed into a pellet), at 375 °C for 1−3 days. C, H, N content were analyzed for one sample, Eu_6C_{60}, which showed only trace amounts of N.[24] In an attempt to recrystallize the product, various polar solvents including CH_3OH, DMSO, DMF, acetone, and acetonitrile were investigated. The solvents were dried and distilled, and the product was handled under inert conditions. The products were insoluble in all polar organic solvents. The products were highly air sensitive. They decomposed in the drybox over a period of a week and also slowly decomposed in sealed, evacuated tubes after a period of about a week. Measurements were performed immediately after preparation and all samples were handled in nitrogen-filled dryboxes.

The reaction of Eu with C_{70} in liquid ammonia was also investigated. The fullerides, Eu_xC_{70} ($x = 1-6$), were prepared in the same fashion as described for Eu_xC_{60}. Typical reaction times for the solution to turn colorless were $<^1/_4$ h for $x = 1$ and 2, $<^1/_2$ h for $x = 3$, 1 h for $x = 4$, $1^1/_2$ h for $x = 5$, and $2^1/_2$ h for $x = 6$. These products were also very air sensitive and would decompose in the drybox over a period of several weeks.

X-ray Powder Diffraction. Diffraction patterns of C_{60} and Eu_xC_{60} were obtained with an Enraf Nonius Guinier powder camera (monochromatic Cu Kα_1 radiation) at room temperature. The air-sensitive sample was placed between two pieces of cellophane tape, and the camera was maintained under dynamic vacuum. In addition, several samples were sealed in quartz capillary tubes for measurement.

Mass Spectrometry. Deintercalated gaseous species for Eu_xC_{60} compounds were detected using a Trio-2 mass spectrometer (VG Masslab, Altrincham, UK) operated at 70 eV electron ionization. The compounds were heated from room temperature to 750 °C at a linear heating rate of 50 °C/min under vacuum (10^{-6} mbar). Profiles of specific ion abundance were plotted to analyze the evolution of individual gaseous species as a function of temperature.

Optical Spectroscopy. The spectra were recorded on a HP 8452A Spectrophotometer in the range 200−800 nm. A mull was prepared with the Eu_xC_{60} compound and mineral oil and placed between two optical plates. The sample was prepared in the drybox, and the measurement was performed immediately after the sample was taken out of the drybox. The mineral oil was found to provide sufficient protection from air. Optical spectra were also taken after the samples were exposed to air.

Infrared Spectroscopy. IR data were recorded on a Galaxy Series FTIR 3000 system in the range 400−4000 cm^{-1} with a resolution of 2 cm^{-1} using KBr pellets. The sample preparation and measurement were performed under N_2 gas.

Magnetic Susceptibility. Temperature-dependent magnetic susceptibilities were measured on a SQUID magnetometer.[25] Small pieces of sample pellet were placed into a

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[24] Midwest Microlab, Indianapolis, IN 46250.

[25] Quantum Design, Inc., San Diego, CA.

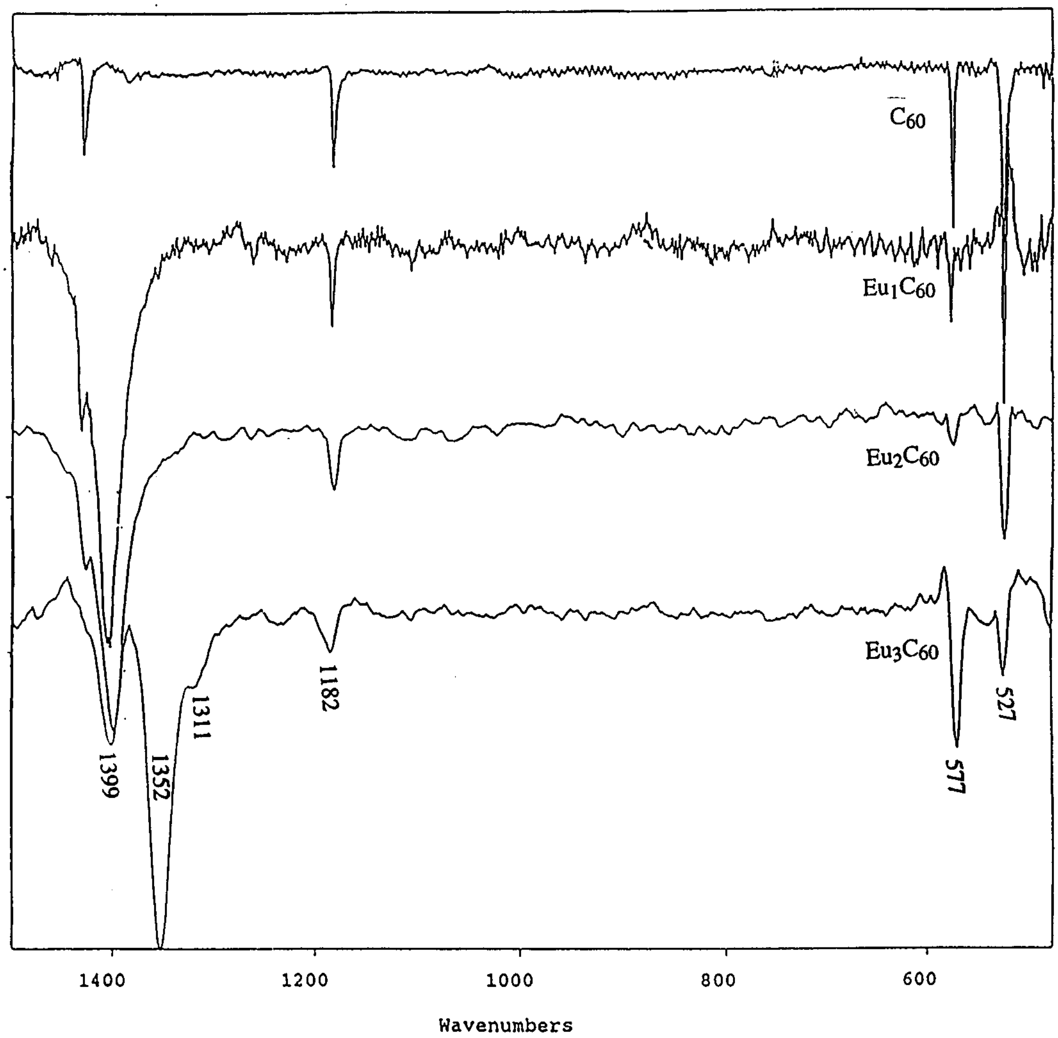

Figure 3. FTIR spectra of C_{60}, Eu_1C_{60}, Eu_2C_{60}, and Eu_3C_{60} recorded in KBr.

fused silica sample holder designed to provide near zero background which was then sealed under dried and purified He. Magnetization versus field was measured at 5 or 10 K. The magnetic susceptibility data were collected between 10 and 300 K.

Results and Discussion

Synthesis. The reaction of C_{60} with Eu in liquid ammonia occurs fairly rapidly. C_{60} is not soluble in liquid ammonia and by itself does not react under the reaction conditions.[26] Unlike what has been observed in alkali metal reactions with C_{60},[21] the liquid ammonia solution is blue upon initial condensation and appears to remain blue until the reaction is complete and the solution turns colorless. Evaporation of the ammonia leaves a black, highly air-sensitive, amorphous powder. Upon reaction with air, the samples turned a red-brown color immediately. The products also decompose in a drybox over a period of approximately 1 week, suggesting that they may also be light sensitive. The products were treated with dried and distilled toluene in order to determine if there was any unreacted C_{60} present. Compositions given are as-prepared and not analytically determined stoichiometries. In addition, the products will be referred to by their as-prepared compositions which is not meant to imply the actual fulleride phase or phases. Eu_1C_{60}, Eu_2C_{60}, and Eu_3C_{60} showed unreacted C_{60}, as determined by the UV−vis absorption spectrum of the solution. Annealed Eu_1C_{60}, Eu_2C_{60} and Eu_3C_{60} samples (in sealed, evacuated tubes at 375 °C for 1−3 days) showed unreacted C_{60} in the powder diffraction pattern. In addition, mulls of these samples showed peaks for C_{60} in the optical spectra. Annealing Eu_4C_{60}, Eu_5C_{60}, and Eu_6C_{60} at 375 °C for 1−3 days under vacuum or in a sealed tube did not improve the crystallinity, and the X-ray diffraction showed no observable peaks. Eu_4C_{60} was also annealed at 600 and 800 °C under vacuum, and the samples did not show any diffraction pattern. Attempts to recrystallize the product in a variety of solvents were unsuccessful. No NH_3(g) was observed by mass spectrometry, suggesting that NH_3 is not co-intercalated. It is possible that upon heating, one forms $Eu(NH_2)_2$ and perhaps EuNH as well, which has been suggested for Eu intercalated into graphite.[23] However, elemental analysis on one sample, Eu_6C_{60}, showed only trace amounts of N, suggesting that any ammonia that may co-intercalate is easily removed.

The reaction of C_{70} with Eu in liquid ammonia occurs in almost half the time as compared to that of the reaction of C_{60} with Eu. Evaporation of ammonia leaves a black, highly air-sensitive, amorphous powder. Since these C_{70} fullerides were also amorphous as determined by powder X-ray diffraction, no further characterization was carried out on these compounds.

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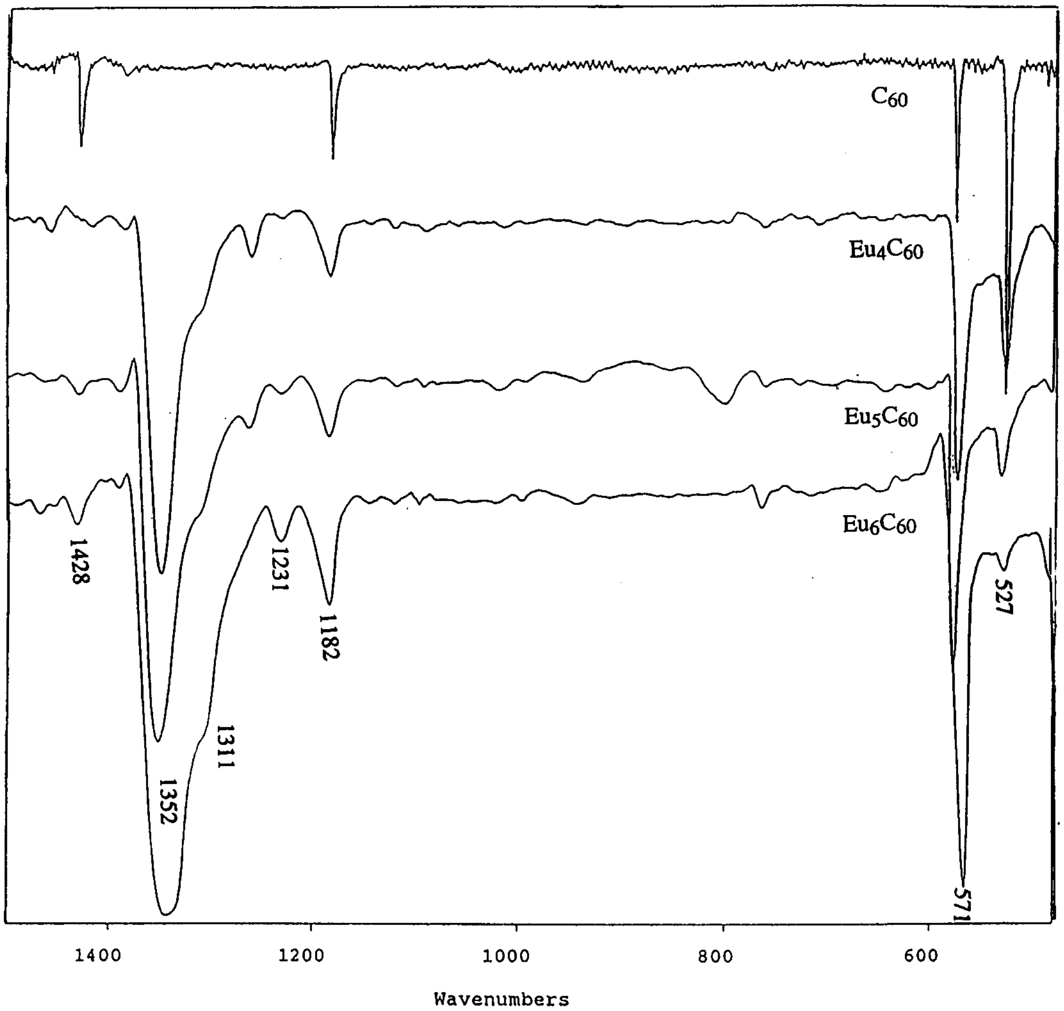

Figure 4. FTIR spectra of C_{60}, Eu_4C_{60}, Eu_5C_{60}, and Eu_6C_{60} recorded in KBr.

UV−Vis Spectroscopy. Figure 1 shows the UV−vis spectra for C_{60}, Eu_xC_{60}, $x = 1-3$, prepared as mulls. The spectra of Eu_xC_{60}, $x = 1-3$, are very similar to the UV−vis spectrum of pristine C_{60}. Figure 1 also shows the UV−vis spectra of C_{60}, Eu_4C_{60}, Eu_5C_{60}, and Eu_6C_{60}, prepared as mulls. The spectrum for C_{60} shows its characteristic absorptions at 329, 257, and 213 nm.[27] Eu_4C_{60} shows a very small absorption at 329 nm, an absorption at about 257 nm with a shoulder at 288 nm and an absorption at 225 nm. Eu_5C_{60} shows an absorption centered at about 280 nm and an absorption at 255 nm. Eu_6C_{60} shows a similar spectrum to Eu_5C_{60}. Although it is difficult to assign the features in the optical spectra, they indicate that Eu_4C_{60}, Eu_5C_{60}, and Eu_6C_{60} do not contain neutral C_{60} and might constitute several phases of varying x (Eu_xC_{60}). As mentioned earlier, these samples are highly air sensitive, and upon exposure to air turn to a red-brown color immediately. Synder and co-workers have reported on the decomposition of alkali-metal fullerides.[28] They were able to show that upon exposure to oxygen, A_6C_{60} (A = K, Rb) decomposes to A_4C_{60} and A_2CO_3. The A_4C_{60} upon further oxidation goes to C_{60} and A_2CO_3. We analyzed our Eu_5C_{60} sample by UV−vis spectroscopy after it had been exposed to air. Figure 2 shows the UV−vis absorption spectra of C_{60}, Eu_5C_{60} and decomposed Eu_5C_{60}. In the decomposed Eu_5C_{60} sample, an absorption at 329 nm which is absent in the undecomposed sample appears. This band at 329 nm is characteristic of C_{60}. Treating the decomposed sample with dry and distilled toluene gives a magenta solution with an electronic spectrum identical with that of C_{60}.

FTIR Spectroscopy. Figures 3 and 4 show the FTIR spectra of C_{60} and Eu_xC_{60}. C_{60} has four IR-active intramolecular vibrational modes with F_{1u} symmetry. These modes have been observed at 527, 577, 1182, and 1428 cm^{-1}.[29] The 527 cm^{-1} mode is primarily radial motion of carbon atoms, and the 1428 cm^{-1} mode is an almost pure tangential motion.[30] The IR spectroscopy of alkali metal fullerides A_xC_{60} ($x = 1, 3, 4, 6$) is well studied.[31,32] In addition to the bands assigned to C_{60}, Eu_1C_{60} shows a strong band at 1399 cm^{-1}, and the 1428 cm^{-1} band becomes a shoulder of the peak at 1399 cm^{-1}. The 1399 cm^{-1} band is attributed to the C_{60}^- anion.[31] Eu_2C_{60} has a spectrum very similar to that of Eu_1C_{60}. Eu_3C_{60}, however, displays a new broad band at 1352 cm^{-1} as well as a shoulder at 1311 cm^{-1} in addition to

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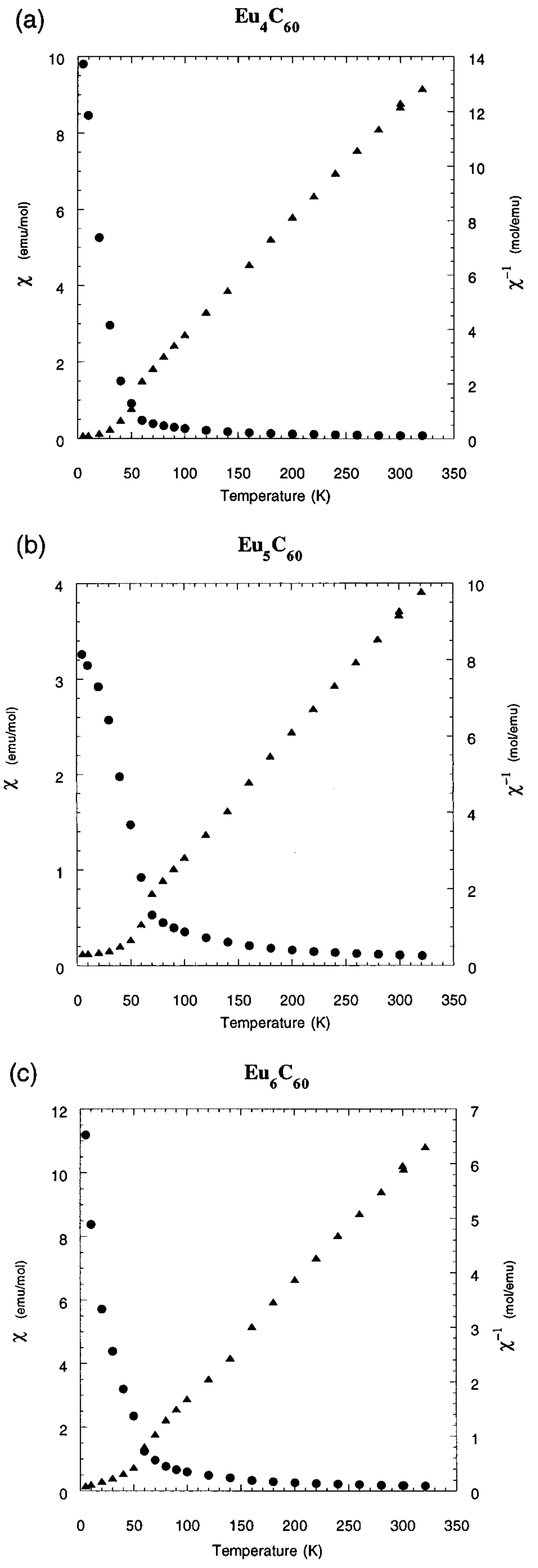

Figure 5. Plots of magnetic susceptibility (●) and inverse magnetic susceptibility (▲) versus temperature for (a, top) Eu_4C_{60}, (b, middle) Eu_5C_{60}, and (c, bottom) Eu_6C_{60}.

Table 1. Curie−Weiss Parameters and Effective Magnetic Moments for Eu_xC_{60} (x = 4−6)[a]

compound	χ_0 (emu/mol)	θ (K)	C (emu K/mol)	$\mu_{eff}\,\mu_B$/Eu
Eu_4C_{60}	5 (2) × 10^{-3}	14 (2)	22.0 (6)	6.6 (1)
Eu_5C_{60}	5 (2) × 10^{-3}	14 (2)	29.7 (8)	6.9 (1)
Eu_6C_{60}	5 (3) × 10^{-3}	24 (3)	25.9 (9)	5.9 (1)

[a] Data were fit for T = 70−300 K, H = 1000 G.

those bands observed for Eu_1C_{60} and Eu_2C_{60}. The band at 1352 cm^{-1} is indicative of transfer of charge from the Eu to the C_{60}. This strong mode is also seen in Rb_xC_{60} and K_xC_{60} which has been studied by IR and Raman spectroscopy.[31] The 1428 and 1399 cm^{-1} bands decrease in intensity. The energy of the 1352 cm^{-1} band is consistent with C_{60}^{6-} and suggests that Eu is present in the +2 oxidation state. In addition, the 577 cm^{-1} band in Eu_xC_{60} increases in intensity as x increases and the 527 cm^{-1} band decreases. This is similar to what is observed in A_xC_{60} samples.[31] Figure 4 shows the FTIR spectra of C_{60} and Eu_xC_{60}, x = 4−6. In the spectra for Eu_xC_{60}, x = 4−6, the 1428 and the 527 cm^{-1} bands are significantly diminished in intensity compared with C_{60}. The 577 cm^{-1} band increases in intensity with increasing x from Eu_4C_{60} to Eu_6C_{60} and shifts slightly to 571 cm^{-1}. The band at 1352 cm^{-1} does not shift upon further doping but becomes significantly broader, and the shoulder at 1311 cm^{-1} also increases in intensity. Additional features are observed in Eu_4C_{60} at 1263 and 1231 (very weak) cm^{-1}. Eu_5C_{60} shows the weak 1263 and 1231 cm^{-1} bands and a new broad band at 801 cm^{-1}. The band at 1263 cm^{-1} in Eu_6C_{60} is obscured and the 1231 cm^{-1} is enhanced. In addition, in Eu_6C_{60} there is a very weak new band at 762 cm^{-1}. These additional features do not coincide with Raman active modes and cannot be attributed to the formation of a C_{60} polymer.[16]

Magnetic Susceptibility. Figure 5 shows the magnetic susceptibility and the inverse magnetic susceptibility versus temperature for Eu_xC_{60}, x = 4−6. All samples showed a very small ferromagnetic impurity with T_C near 65 K. This is consistent with the presence of EuO which has a reported T_C of 70 K.[33,34] The data in the range 70−300 K were fit to the Curie−Weiss law: $\chi_m = C/(T - \theta) + \chi_0$. Table 1 provides the effective magnetic moments and the Curie constant, C, Weiss constant, θ, and χ_0. The Weiss constants, θ, are small and positive indicating near-neighbor ferromagnetic interactions of the Eu ions. The calculated moment for Eu^{2+} is 7.94 μ_B and Eu^{3+} is 0 μ_B.[35] Typically the experimentally determined magnetic moments for Eu^{3+} compounds are in the 3.4−3.6 μ_B range.[35] The experimental moment of approximately 7 μ_B for Eu_4C_{60} and Eu_5C_{60} is most consistent with the europium being present as Eu^{2+}, although some of the europium may be present as Eu^{3+}. The experimental moment of 5.9 μ_B for Eu_6C_{60} is more reduced and may indicate a larger amount of Eu^{3+} present in the sample.

Summary. Powder X-ray diffraction shows that these europium fullerides are amorphous. This is somewhat surprising since Eu^{2+} is approximately the same size as Sr^{2+}, which forms a crystalline phase, Sr_6C_{60}.[3] Further investigation of these materials with Mo Kα or synchrotron radiation may provide more information concerning structure. The fact that the product of the reaction of Eu in liquid ammonia is

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amorphous and insoluble in common organic solvents is reminiscent of the reaction of Eu with cyclopentadiene.[36] Eu and Yb complexes have been prepared by dissolving the metal in liquid ammonia and adding C_5H_6 or C_8H_8. The Eu complexes were found to be amorphous and insoluble in all solvents. Crystal structures of related divalent Yb complexes show oligomerization in the solid state via bridging cyclopentadienyl rings.[37] In the ytterbium fulleride, $Yb_{2.75}C_{60}$, whose structure has been reported, there is evidence for short-range, covalent interactions.[8] This suggests that europium does not react with the fullerenes according to a simple intercalation reaction, but reacts to form covalently bound europium fullerides where the Eu^{2+} ion interacts strongly with the fullerene. More recently, this type of behavior has been suggested for Sm_xC_{60}.[38,39] To obtain materials with better defined structures, it would be worthwhile to explore the reaction of fullerenes with lanthanides in solvents other than ammonia. Mössbauer and EPR measurements would provide additional insight as to the state of Eu in these phases. Perhaps derivatized fullerenes will allow for facile crystallization of new rare-earth fullerides. There is much more fullerene chemistry to be explored, and the investigation of rare-earth fullerides may open up a new field of organolanthanide chemistry.

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