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References and Notes

- (1) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, 347, 354.
- (2) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* 1990, 94, 8630.
- (3) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* 1990, 94, 8634.
- (4) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* 1991, 91, 1213.
- (5) The March 1992 issue of *Acc. Chem. Res.* (1992, 25, 97-175) is entirely dedicated to fullerene research and describes the chemistry and physics of these new carbon allotropes in 11 review articles written by various authors.
- (6) Diederich, F.; Whetten, R. L. In ref 5, pp 119-126.
- (7) Li, Q.; Wudl, F.; Thilgen, C.; Whetten, R. L.; Diederich, F. *J. Am. Chem. Soc.* 1992, 114, 3994.
- (8) Smalley, R. E. In ref 5, pp 98-105.

- (9) Peters, G.; Jansen, M. *Angew. Chem.* 1992, 104, 240; *Angew. Chem., Int. Ed. Engl.* 1992, 31, 223.
- (10) Howard, J. B.; McKinnon, J. T.; Makarovskiy, Y.; Lafleur, A. L.; Johnson, M. E. *Nature* 1991, 352, 139.
- (11) Maissel, L. I.; Glang, R., Eds. *Handbook of Thin Film Technology*; MacGraw-Hill: New York, 1970.
- (12) Bunshah, R. F., Ed. *Deposition Technologies for Films and Coatings*; Noyes Publications: Park Ridge, NJ, 1982.
- (13) Hayashi, C. *Phys. Today* 1987, 40, 44.
- (14) Suh, T. G.; Umarjee, D. M.; Prakash, S.; Doerr, H. J.; Deshpandey, C. V.; Bunshah, R. F. *Surf. Coatings Technol.* 1991, 49, 304-310.
- (15) (a) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* 1991, 113, 495. (b) Ross, M. M.; McElvany, S.; Goroff, N.; Rubin, Y.; Diederich, F., manuscript in preparation.
- (16) Yerezian, C.; Hansen, K.; Diederich, F.; Whetten, R. L. *Nature*, in press.
- (17) Olah, G. A., Ed. *Cage Hydrocarbons*; Wiley: New York, 1990.
- (18) For mass spectrometric detection of C_{60}^+ ions generated by kilo- and megaelectronvolt bombardment of polymers, see: (a) Feld, H.; Zurmühlen, R.; Leute, A.; Benninghoven, A. *J. Phys. Chem.* 1990, 94, 4595. (b) Brinkmalm, G.; Barofsky, D.; Demirev, P.; Fenyö, D.; Håkansson, P.; Johnson, R. E.; Reimann, C. T.; Sundqvist, B. U. R. *Chem. Phys. Lett.* 1992, 191, 345.

Endohedral Rare-Earth Fullerene Complexes

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The technique of carbon-arc evaporation has been successfully utilized to encapsulate a wide variety of rare-earth species in carbon cages. We have observed $M_m@C_n$ ($M = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, or Er$) species present in the toluene extracts of the carbon soot using laser desorption mass spectrometry. The presence of multiple-metal species appears to depend strongly on the metal-to-carbon atom ratio found in the starting rods, with the higher metal concentrations favoring multiple-metal incorporation. One often observed dimetallofullerene is $M_2@C_{80}$. Molecular orbital arguments are presented to support a possible icosahedral structure for C_{80} .

Introduction

The new family of hollow carbon cage molecules known as fullerenes has intrigued researchers since their discovery in 1985.¹ The insertion of atoms or ions inside the cages (endohedral incorporation) was first examined using laser vaporization techniques.²⁻⁵ Early photofragmentation studies provided strong evidence that the metals were inside the carbon cages.⁶ After a simple method for generating macroscopic quantities of fullerenes using a carbon evaporator was developed by Krätschmer, Huffman, et al. (K-H method),⁷ this technique was applied to the formation of endohedral metallofullerenes.⁸⁻¹³ These species appear to be soluble in common organic solvents including benzene, toluene, and carbon disulfide. Recent reports include the single-metal-containing fullerenes $La@C_{82}$,⁸ $Y@C_{82}$,⁹ $Sc@C_{82}$,¹² and $Fe@C_{60}$ ¹³ and the multiple-metal-containing fullerenes $La_2@C_{80}$,^{10,11} $Y_2@C_{82}$,^{5,9} and $Sc_3@C_{82}$.¹² EPR studies on $M@C_{82}$ species ($M = Sc, Y, or La$) demonstrate that the metals are in +3 oxidation states.^{9,12,15} Collision probes of $La_2@C_{80}$ and $Tb@C_{82}$ which yield no metal or fullerene fragments after impact with a silicon surface provide further evidence that the metals are strongly bound to the carbon cages.¹⁴

The fact that lanthanum can be successfully incorporated in fullerene cages suggests that other 4f block metals might be incorporated as well, owing to their similar electron configurations, oxidation states, ionic radii, and ionization potentials (see Table I). Here we report the successful encapsulation of cerium (Ce), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), and erbium (Er) in fullerene cages using carbon-arc evaporation techniques. Our studies indicate that if the metals or their ions formed from metal oxide evaporation are present in sufficient quantities during fullerene formation, some become trapped inside the carbon cages.

Higher concentrations of metal oxide lead to some multiple-metal encapsulation.

Experimental Methods

The gravity-driven resistive heating apparatus used has been described previously.¹⁰ In each case, metal oxides were mixed with graphite cement (HTGC-Dylon Industries) forming a thick paste which was pressed into 1.5 in. by 0.125 in. graphite rods (Poco Graphite Inc.) that had been hollowed out to 1.25 in. using a 0.056-in. drill bit. The metal oxide loadings were optimized to balance a high metal oxide content with a paste viscous enough to be pressed into the rods. The metal oxides and the metal-to-carbon atomic ratios for the rods were as follows: CeO_2 (99.9% Alpha), 1.0 Ce/100 C; Nd_2O_3 (99.9% Alpha) 1.1 Nd/100 C; Sm_2O_3 (Matheson Co.), 0.9 Sm/100 C; Eu_2O_3 (99.99% Alpha), 0.8 Eu/100 C; Gd_2O_3 (99.9% Atomergic), 1.0 Gd/100 C; Tb_4O_7 (99.9% Research Chemicals), 1.4 Tb/100 C; Dy_2O_3 (99.9% Atomergic), 1.5 Dy/100 C; Ho_2O_3 (99.9% Atomergic), 1.9 Ho/100 C; Er_2O_3 (96% Pechiney), 2.0 Er/100 C. All starting oxides were phase pure as indicated by powder X-ray diffraction. The metal oxide containing rods were cured at 200 °C for 1 day followed by heating at 900 °C under vacuum for at least 1 day. The soot produced by the resistive heating of these rods was refluxed in boiling toluene to extract fullerene and metallofullerene species. All samples were handled in air without special precaution. The toluene extracts were analyzed by a laser-desorption mass spectrometry (LDMS) procedure described previously.¹⁹ Radiation pulses (10^{-8} s) from an ArF laser operating at 193 nm (6.4 eV) were used to desorb the species from coated stainless steel rods and the positive ions formed were detected by a reflection mass spectrometer. Additionally for Eu, Gd, and Tb a Nd:YAG laser operating at 266 nm (4.7 eV) was used to obtain spectra.

TABLE I: Physical Properties of Selected Rare-Earth Metals

element	electronic config	oxid states ¹⁶	ionic radii ¹⁷ M ³⁺ (pm)	first ionization potential ¹⁸ (eV)	major isotopes ²⁰ (>5% nat abundances)
La	[Xe]5d6s ²	3	118.5	5.58	139: 99.9%
Ce	[Xe]4f ² 6s ²	3, 4	115	5.47	140: 88.5%, 142: 11.1%
Nd	[Xe]4f ⁴ 6s ²	3	112.3	5.49	142: 27.2%, 143: 12.2%
					144: 23.8%, 145: 8.3%
					146: 17.2%, 148: 5.7%
					150: 5.6%
Sm	[Xe]4f ⁶ 6s ²	3, 2	109.8	5.63	147: 15.0%, 148: 11.2%
					149: 13.8%, 150: 7.4%
					152: 26.7%, 154: 22.8%
Eu	[Xe]4f ⁷ 6s ²	3, 2	108.7	5.67	151: 47.8%, 153: 52.2%
Gd	[Xe]4f ⁷ 5d6s ²	3	107.8	6.14	155: 14.8%, 156: 20.5%
					157: 15.7%, 158: 24.8%
					160: 21.9%
Tb	[Xe]4f ⁹ 6s ²	3, 4	106.3	5.85	159: 100%
Dy	[Xe]4f ¹⁰ 6s ²	3	105.2	5.93	161: 18.9%, 162: 25.5%
					163: 24.9%, 164: 28.2%
Ho	[Xe]4f ¹¹ 6s ²	3	104.1	6.02	165: 100%
Er	[Xe]4f ¹² 6s ²	3	103	6.1	166: 33.6%, 167: 22.9%
					168: 26.8%, 170: 14.9%

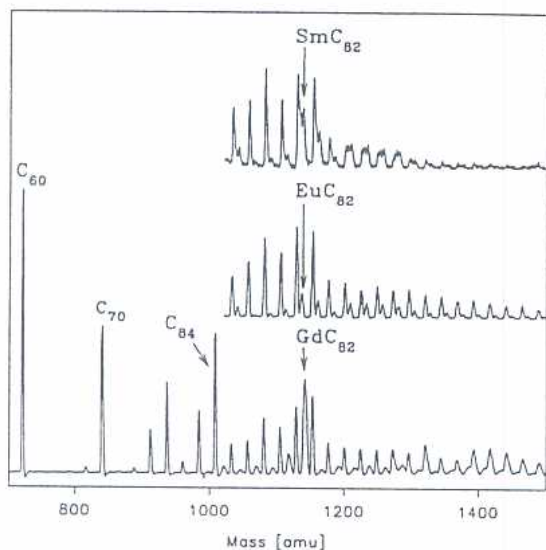


Figure 1. Positive-ion laser desorption mass spectra of toluene extracts obtained from soot produced by the arc-burning of carbon rods containing the rare-earth oxides Sm₂O₃ (top), Eu₂O₃ (middle), and Gd₂O₃ (bottom). All spectra have been optimized for 1100 amu.

A comparison of results from each laser showed the same relative intensities between observed species. The time-of-flight data was converted to a mass scale using a linear fit based on the positions of the prominent fullerene peaks.

Results and Analysis

The mass spectrometry results of the toluene extracts show many peaks corresponding to a wide variety of rare-earth metals associated with fullerene cages containing an even number of carbon atoms (Figures 1 and 2). These spectra are interleaved with the familiar pattern of the empty fullerenes C₆₀, C₇₀, C₇₆, C₇₈, C₈₄, etc.⁷ As seen in the figures, the mass spectrographic results can be divided into two categories consisting of single and multiple-metal-containing fullerenes. Figure 1 shows the LDMS positive ion results for fullerenes containing single Sm, Eu, or Gd metallofullerene species. A common feature of all three spectra is that M@C₈₂ is a prominent maximum in each case. As expected this peak shifts to higher masses on going from Sm to Eu to Gd, consistent with the increasing atomic masses of these metals. The metallofullerene peaks in Figure 1 (top) are broadened (up to 7 amu) due to the large distribution of seven major isotopes of Sm as given in Table I. The isotopic distribution is also responsible for the broadening of the Gd spectrum in Figure 1 (bottom).

Figure 2 shows the LDMS positive ion results for Ce, Tb, and Ho, all showing multiple-metal-containing fullerenes. Additionally, all three spectra have a prominent M@C₈₂ peak consistent with the Sm, Eu, and Gd fullerenes. Figure 2 (top) shows a strong

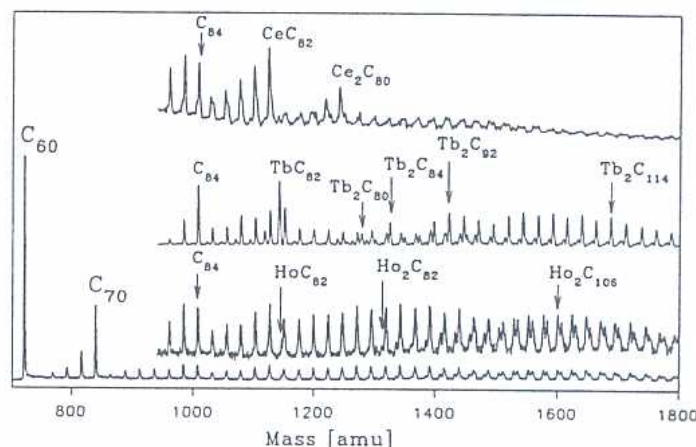


Figure 2. Positive-ion laser desorption mass spectra of toluene extracts obtained from soot produced by the arc-burning of carbon rods containing the rare-earth oxides CeO₂ (top), Tb₂O₃ (middle), and Ho₂O₃ (bottom). All spectra have been optimized for 1300 amu. The inset to the holmium fullerene spectrum starting at 940 amu has been enhanced by a factor of 5.

peak corresponding to Ce₂@C₈₀. Similar to earlier results on La₂@C₈₀,¹⁰ the M₂@C₈₀ species is the most intense peak of a series of even-numbered carbon cages containing two metals. The Tb_m@C_n spectrum in Figure 2 (middle) shows a relatively strong Tb₂@C₈₀ peak, but many stronger multiple metal peaks are also present. These include local maxima at Tb₂@C₈₄ and Tb₂@C₉₂. It is important to note that all major peaks from 1400 to 1800 amu correspond to Tb₂@C_n species. Figure 2 (bottom) shows the LDMS results for holmium. Here Ho@C₈₂ is present along with local maxima at Ho₂@C₈₄ and Ho₂@C₁₀₆. As before, all of the most intense peaks between 1530 and 1800 amu correspond to Ho₂@C_n.

The LDMS spectra of the neodymium and erbium samples were encouraging but hampered by the fact that the metal atomic weights are nearly identical to an even number of carbons (Nd = 144.2 g/mol ≈ 12 C and Er = 167.3 g/mol ≈ 14 C). In the case of neodymium there is a strong enhancement of the C₉₄ signal most likely due to a combination of C₉₄ (1128 amu) and Nd@C₈₂ (1128 amu). A similar occurrence is observed in the case of erbium with an enhanced C₉₆ peak (1152 amu) probably due to its overlap with Er@C₈₂ (1151 amu) and an enhanced C₁₁₀ (1320 amu) peak due to its combination with Er₂@C₈₂ (1319 amu). The dysprosium spectrum showed weak but characteristic peaks corresponding to Dy@C₈₂, Dy₂@C₈₀, and Dy₂@C₈₄.

Discussion and Conclusions

These results show that there is a division between the formation of soluble single-metal and multiple-metal fullerenes. As was

observed with the lanthanum system, the ratio of metal to carbon atoms in the starting rods can have a profound effect on whether multiple-metal fullerenes are observed. When the ratio is approximately 1 lanthanum/100 carbon atoms, only La@C_n species are observed.⁸ However, when the ratio is raised to nearly 2 La/100 carbon atoms, the $\text{La}_2\text{@C}_{80}$ signal appears in the mass spectrum.¹⁰ As can be seen by the loadings stated earlier, the smallest metal-to-carbon ratios result in only single metallofullerenes, while the more metal-rich starting rods lead to detectable amounts of dimetallofullerenes. For example, europium and samarium have metal-to-carbon atom ratios of 0.8:100 and 0.9:100, respectively, and show only single-metal fullerenes in the toluene extract. This is contrasted with terbium and holmium that have metal-to-carbon atom ratios of 1.4:100 and 1.9:100 and form an abundant variety of dimetallofullerenes (see Figure 2). This suggests that the concentration of atomic species in the vapor near the arc is important in determining which fullerene species coalesce and condense out.

There are obviously other factors that affect the formation of metallofullerenes because analysis of the toluene extracts of soot produced in analogous experiments with Al_2O_3 (2Al/100 C) and U_3O_8 (1.6 U/100 C) yielded only empty fullerenes. Recent studies have suggested a correlation between the ionization potential of the metal and its ability to form metallofullerenes.¹¹ There seems to be little correlation here between ionization potentials (IP) as given in Table I and the formation of single versus multiple-metal fullerenes, e.g., cerium (IP = 5.47 eV) with one of the smallest first ionization potentials of the rare earths and holmium (IP = 6.02 eV) with one of the largest both form dimetallofullerenes.

Although quantitative structural determination on any of the metallofullerenes awaits isolation and crystallization, it is worthwhile to speculate on structure based on available experimental and theoretical data. The stability of empty fullerenes has been related to the presence of a filled highest molecular orbital (HOMO) and a considerable gap between the lowest unoccupied molecular orbital (LUMO). This rational correctly predicts the stability of C_{60} , C_{70} , C_{76} , C_{78} , and C_{84} in agreement with what is observed experimentally.²¹ With the metallofullerenes, M_2C_{80} has shown up prominently in the lanthanum^{10,11} and cerium (Figure 2, top) systems and is significantly present in the terbium spectrum (Figure 2, middle). Hückel molecular orbital calculations predict seven isomers for C_{80} which obey the isolated-pentagon rule,^{22,23} a rule which reduces strain on the closed cage and has been followed by every fullerene structurally characterized to date. The two most symmetrical forms of C_{80} , I_h and D_{5h} , both have two electrons in a partially filled HOMO. The addition of six electrons (corresponding to two M^{3+} ions associated with the fullerene) results in HOMO-LUMO gaps of 0.98β and 0.70β respectively.^{23,24} These values compare favorably with C_{60} which has an energy gap of 0.76β ,²⁴ suggesting that $(\text{M}^{3+})_2\text{@C}_{80}^{6-}$ is a favorable formulation for this species. This is not unreasonable since both trivalent metal cations in fullerene cages^{9,12,15} as well as hexavalent C_{60} anions²⁵ are likely present in other systems. If one considers the size of a nearly spherical cage of C_{80} (i.e., I_h or D_{5h}) and assumes 1.45-Å C-C bond lengths, the cage is approximately 8 Å in diameter. This space can readily accommodate two or more rare-earth trivalent ions which have average diameters from 2.06 to 2.34 Å (see Table I). Another possibility which would reduce the charges on the lanthanides and the cage is metal-metal bonding.¹²

The arc-burning of rare-earth oxide filled graphite rods produces a wide variety of single- and multiple-metal fullerenes based on C_n cages which are not prevalent in pure fullerene mass spectra (i.e., C_{80} and C_{82}). This indicates that the encapsulated metals may help stabilize these cages through electron donation. The successful synthesis of fullerene cages encapsulating rare-earth metals offers the prospect that a host of new members of the fullerene family will be isolated. These compounds are important because they will enable new probes to be used, such as fluorescence spectroscopy to determine metal oxidation states (e.g.,

Eu^{2+} versus Eu^{3+}). Since EPR has shown La to be in a 3+ oxidation state, the isolation of $\text{M}^{3+}\text{@C}_{60}^{-3}$ species are of special interest because they should adopt a face-centered cubic (fcc) lattice in the solid like C_{60} , but have a half-filled HOMO. This would be the endohedral analogue of the potassium and rubidium compounds K_3C_{60} and Rb_3C_{60} , which are room-temperature conductors and low-temperature superconductors.^{26,27} One drawback with the alkali-fulleride superconductors is that they are very moisture sensitive. One expects these new endohedral rare-earth fullerenes to be more air stable because the metal ion is protected from hydrolysis by the closed carbon cage. The metallofullerenes investigated in this study appear stable for months. For example, a toluene extract of soot, from the arc burning of Sm_2O_3 and graphite, which was kept in a closed vial for 5 months yields a mass spectrum nearly identical to Figure 1 (top).

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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) 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.
- (3) Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. *J. Am. Chem. Soc.* 1986, 108, 2457.
- (4) Ross, M. M.; Callahan, J. H. *J. Phys. Chem.* 1991, 95, 5720.
- (5) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Haufler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* 1992, 190, 460.
- (6) Weiss, F. D.; Elkind, J. L.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *J. Am. Chem. Soc.* 1988, 110, 4464.
- (7) (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, 347, 354. (b) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* 1990, 94, 8630.
- (8) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* 1991, 95, 7564.
- (9) Metal-to-carbon ratios were estimated from data in the experimental section.
- (10) Shinohara, H.; Sato, H.; Saito, Y.; Ohkohchi, M.; Ando, Y. *J. Phys. Chem.* 1992, 96, 3571.
- (11) Alvarez, M. M.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Min, K. S.; Whetten, R. L. *J. Phys. Chem.* 1991, 95, 10561.
- (12) Ross, M. M.; Nelson, H. H.; Callahan, J. H.; McElvany, S. W. *J. Phys. Chem.*, submitted.
- (13) (a) Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato, T.; Saito, Y. *Nature* 1992, 357, 52. (b) Yannoni, C. S.; Hoinkis, M.; de Vries, M. S.; Bethune, D. S.; Salem, J. R.; Crowder, M. S.; Johnson, R. D. *Science* 1992, 256, 1191.
- (14) Pradeep, T.; Kulkarni, G. U.; Kannan, K. R.; Guru Row, T. N.; Rao, C. N. R. *J. Am. Chem. Soc.* 1992, 114, 2272.
- (15) Yeretzyan, C.; Hansen, K.; Alvarez, M. M.; Min, K. S.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Whetten, R. L. *Chem. Phys. Lett.*, in press.
- (16) Johnson, R. D.; de Vries, M. S.; Salem, J.; Bethune, D. S.; Yannoni, C. S. *Nature* 1992, 355, 239.
- (17) Emsley, J. *The Elements*, 1st ed.; Clarendon Press: Oxford, 1989.
- (18) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* 1970, B26, 1046. Reported radii are all six coordinate.
- (19) Martin, W. C.; Hagan, L.; Reader, J.; Sugar, J. *J. Phys. Chem. Ref. Data* 1974, 3, 771.
- (20) Beck, R. D.; St. John, P.; Alvarez, M. M.; Diederich, F.; Whetten, R. L. *J. Phys. Chem.* 1991, 95, 8402.
- (21) Isotopic Compositions of the Elements 1989. *Pure Appl. Chem.* 1991, 63, 991.
- (22) Fowler, P. W.; Manolopoulos, D. E. *Nature* 1992, 355, 428.
- (23) (a) Fowler, P. W.; Batten, R. C.; Manolopoulos, D. E. *J. Chem. Soc., Faraday Trans.* 1991, 87, 3103. (b) Manolopoulos, D. E.; Fowler, P. W. *Chem. Phys. Lett.* 1991, 187, 1.
- (24) Liu, X.; Schmaltz, T. G.; Klein, D., private communication.
- (25) Fowler, P. W. *Chem. Phys. Lett.* 1986, 131, 444.
- (26) Zou, O.; Fischer, J. E.; Coustel, N.; Kycia, S.; Zhu, Q.; McGhie, A. R.; Smith, A. B.; Cox, D. E. *Nature* 1991, 352, 701.
- (27) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* 1991, 350, 600.
- (28) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* 1991, 257, 1154.