buried in the native state of myoglobins and do not react with hydrogen ions.[4] The effective pK's of the remaining histidines and those of the glutamic and aspartic acid side chains are lowered considerably, compared to their intrinsic pK values, because of the electrostatic interactions in the native conformation.[14,16] As a result, the net positive charge on the native protein is lower than would be expected from the intrinsic pK values of the side chains. At lower pH values, the unfolding of the protein results in complete protonation of the buried histidines, disruption of the heme-globin interaction, and changes in the effective pK values of the side chains toward the intrinsic pK's.[11,15] Thus, the denatured state may be characterized by the absence of heme and a relatively higher positive charge on the globin. Conversely, the native state of myoglobin may be characterized by the presence of heme in the hydrophobic pocket and by a lower net positive charge on the protein molecule. In the present communication, we use these criteria to differentiate between the electrospray-produced ions of equine myoglobin in a native conformation and those produced from the denatured protein.

Figure 1A shows the spectrum obtained from an aqueous equine myoglobin solution[17] at pH = 3.35 (no salts or buffers added), a pH where the protein is known to be completely denatured.[15] The spectrum shows a single distribution of peaks, with protonation states ranging from 20+ to 10+, with 15+ the most intense. The average molecular mass measured from these peaks is 16 951 ± 1 u and corresponds to the calculated mass of apomyoglobin (16 951.5 u; without heme). These spectral characteristics are similar to those previously reported for the electrospray ionization of myoglobin.[20-23] If we assume that certain solution characteristics of the protein, such as the degree of protonation and the extent of heme-globin complexation, are preserved into the gas phase, then our mass spectrometric results confirm that the protein is in a denatured form in this solution (as evidenced by the high degree of protonation and the total absence of ions corresponding to the heme-globin complex).

Figure 1B shows an electrospray mass spectrum obtained from an equine myoglobin solution at pH 3.9 (no salts or buffers added). This pH is in a range of values where both native and denatured forms of myoglobin can coexist in solution.[14,15] The spectrum is different from that shown in Figure 1A because it exhibits two distinct distributions of charge states. The first ranges from 19+ to 9+, with 15+ the most intense. The average molecular mass calculated from this distribution is 16 949 ± 2 u and corresponds to that of apomyoglobin. The second distribution, in the higher m/z range, shows three peaks with protonation states 11+ to 9+ (shown circled in Figure 1B). The low charge state components (lower than 9+) of this distribution could not be observed because their m/z values lie beyond the range of our instrument (m/z < 2000).[19] Two important features make this distribution distinct from the first one and also from the distribution shown in Figure 1A. The charge states are comparatively lower, and the measured molecular mass is significantly higher (17 564 ± 2 u). This measured mass corresponds to that of the intact heme-globin complex (calculated molecular mass = 17 568.0 u). The correlation between the measured mass and the low charge states of this distribution suggests that these ions arise from the native protein in solution.[24] At a higher pH value (pH = 4.4), where the protein is predicted to be in a wholly native state,[14,15] the first distribution centered around 15+ disappeared completely while the 9+ charge state of the second distribution continued to be observed (data not shown).[26] Similar results were also obtained for dog myoglobin.

Our findings demonstrate that electrospray-ionization mass spectrometry can provide information on the conformation of myoglobin under different solution conditions and that the noncovalently bound heme-globin complex found in the native state can be measured mass spectrometrically. Although the data do not imply that the solution conformation is preserved into the gas phase, the results suggest that native, noncovalent associations of proteins and cofactors in solution can be preserved into the gas phase and observed by mass spectrometry.

Acknowledgment. This work was supported in part by Grants RR00862 and RR07065, Division of Research Resources, NIH, and GM38274, National Institute of General Medical Sciences, NIH.

(16) Matthew, J. B.; Gurd, F. R. N. *Methods Enzymol.* **1986**, *130*, 413-35.

(17) Aqueous solutions (acidified with acetic acid, no salts or buffers added) of equine skeletal muscle myoglobin (Sigma Chemical Company, St. Louis, MO) were electrosprayed through a 150 μm i.d. stainless steel syringe needle, whose tip was etched to a conical shape.[5,18] The electrospray mass spectrometer used in the present investigations has been described earlier.[19] The protein concentrations were in the range 20-40 μM, and the flow rates were 0.4-0.8 μL/min.

(18) Chowdhury, S. K.; Chait, B. T. *Anal. Chem.* **1991**, *63*, 1660-1664.

(19) Chowdhury, S. K.; Katta, V.; Chait, B. T. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 81-7.

(20) Mann, M.; Meng, C. K.; Fenn, J. B. *Anal. Chem.* **1989**, *61*, 1702-8.

(21) Berkel, G. J. V.; Glish, G. L.; McLuckey, S. A. *Anal. Chem.* **1990**, *62*, 1284-95.

(22) Henry, K. D.; Williams, E. R.; Wang, B. H.; McLafferty, F. W.; Shabanowitz, J. F.; Hunt, D. F. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 9075-8.

(23) Chowdhury, S. K.; Katta V.; Chait, B. T. In *Methods and Mechanisms for Producing Ions from Large Molecules*; Standing, K. G., Ens, W., Eds.; NATO ASI Series; Plenum Press: New York, 1990 (in press).

(24) Peaks corresponding to a complex of heme with apomyoglobin have been observed earlier.[9,25] However, these earlier studies were carried out under solution conditions that favored denaturation, and the charge distribution of the complex was similar to the distribution of apomyoglobin, which centered around 17+ to 19+. The nature and origin of the association complex in the earlier studies are thus uncertain.

(25) Edmonds, C. G.; Loo, J. A.; Barinaga, C. J.; Udseth, H. R.; Smith, R. D. *J. Chromatogr.* **1989**, *474*, 21-34.

(26) The spectra obtained from myoglobin solutions maintained at respectively pH = 3.35, pH = 3.9, and pH = 4.4 were all taken under identical mass spectrometric conditions.

A Synthetic *p*-Nitrophenyl Esterase with Remarkable Substrate Selectivity

Wilmer K. Fife,* Slawomir Rubinsztajn, and Martel Zeldin

Department of Chemistry
Indiana University-Purdue University at Indianapolis
1125 East 38th Street, Indianapolis, Indiana 46205

Received May 28, 1991

A new linear oligomer, **4** ($n \sim 10$), recently prepared and characterized in our laboratory,[1] has been evaluated as a catalyst for hydrolysis of *p*-nitrophenyl esters of alkanoic acids, **1**. This synthetic material not only exhibits high levels of catalytic efficiency and conforms to the Michaelis-Menten model but also demonstrates enzyme-like specificity for esters derived from acids of moderate chain length ($C_{12} \rightarrow C_{16}$) with **1** ($n = 14$) the optimum substrate ($V_{max} = 7.5 \times 10^{-7}$ M s^{-1}, $K_M = 2.9 \times 10^{-5}$ M, $k_{cal}/K_m = 1.1 \times 10^4$ M^{-1} s^{-1} at 30 °C in 1:1 MeOH-aqueous buffer (pH 8.0) with [cat.] = 2. 5 × 10^{-6} M). Significantly, catalysis is accompanied by rapid release of product from the catalytic site, a 4-(dialkylamino)pyridine.

Duplication of enzymic efficiency and selectivity with synthetic materials has been the goal of much research.[2-15] Studies directed

(1) Rubinsztajn, S.; Zeldin, M.; Fife, W. K. *Macromolecules* **1990**, *23*, 4026. (b) Rubinsztajn, S.; Zeldin, M.; Fife, W. K. *Macromolecules* **1991**, *24*, 2682.

(2) D'Souza, V. T.; Bender, M. L. *Acc. Chem. Res.* **1987**, *20*, 146.

(3) Lehn, J.-M. *Science* **1985**, *227*, 849.

(4) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.

(5) Breslow, R.; Trainor, G.; Veno, A. *J. Am. Chem. Soc.* **1983**, *105*, 2739.

(6) Cram, D. J.; Lam, P. Y.; Ho, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 839.

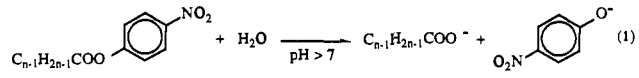
(7) Rebek, J.; Askew, B.; Killoran, M.; Demeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426.

(8) Ford, W. T., Ed. *Polymeric Reagents and Catalysts*; ACS Symposium Series 308; American Chemical Society: Washington, DC, 1986.

(9) (a) Kunitaki, T.; Okahata, Y.; Ando, R. *Macromolecules* **1974**, *7*, 140. (b) Kunitaki, T.; Shinkai, S. *Adv. Phys. Org. Chem.* **1980**, *17*, 435.

0002-7863/91/1513-8535$02.50/0

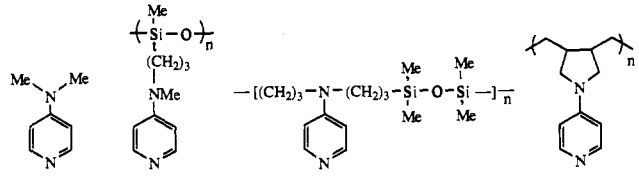
toward understanding enhancement of amide and ester hydrolysis frequently utilize **1** as a substrate to gain mechanistic insight (eq 1). Most studies have focused on increasing catalyst efficiency



1
(n = 2, 6, 8, 10, 12, 14, 16, 18)

to bring activity of synthetic catalysts to levels afforded by relevant enzymes. Our goal has been to examine structure/activity relationships in linear, water-soluble, polymeric catalysts that exhibit high levels of substrate selectivity and notable rate acceleration in hydrolysis of **1**. True enzyme-like behavior requires that "active sites" discriminate among structurally different *p*-nitrophenyl esters and effect hydrolysis at different reaction velocities with turnover.[16] Since variants of **1** differ by number of carbons in the alkanoate chain, binding between catalyst and substrate is controlled by hydrophobic–lipophilic interactions.[17-21]

The 4-(dialkylamino)pyridines (DAAP), of which 4-(dimethylamino)pyridine (**2**) is best known, are highly reactive "supernucleophilic" catalysts for transacylation reactions in aprotic solvents.[1,14,15,22-24] Simple monomeric DAAPs are known to be



2 **3** **4** **5**

relatively ineffective nucleophilic catalysts for transacylation reactions in aqueous media. Klotz et al. discovered that poly(ethylenimine) derivatives functionalized with DAAPs exhibit significant catalytic activity in the hydrolysis of **1** (n = 6).[14] Mathias and Vaidya described poly(4-diallylamino)pyridine (**5**), which exhibited increasing activity toward variants of **1** with increasing alkanoate chain length (C_2–C_{12}).[15] Recently we reported the synthesis and characterization of **3** and **4**, which differ significantly from one another and from the Klotz and Mathias catalysts. The solubility properties of **3** and **4** in water and their catalytic efficiency toward acylation of sterically hindered alcohols in aprotic solvent encouraged investigation of them as catalysts for reactions of electrophilic lipophiles in aqueous media.

Hydrolysis of **1** (n = 2–18, 30 °C, 1:1 (v/v) MeOH–aqueous buffer, pH 8.0) catalyzed by **2–5** was investigated by methods widely used for evaluation of enzymic catalysis.[25,26] The results

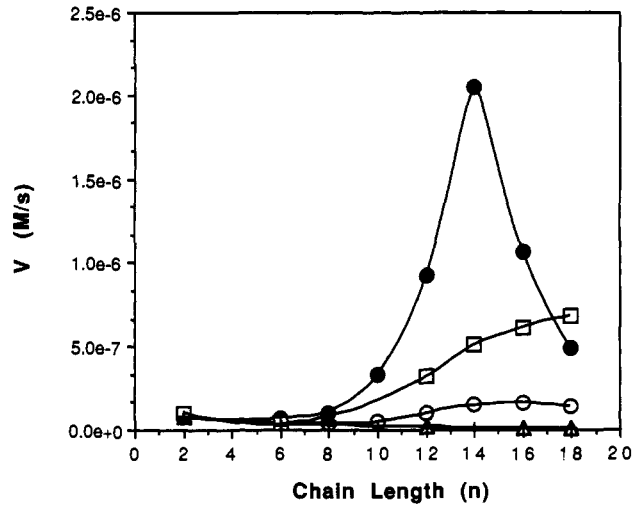


Figure 1. Dependence of reaction velocity (V) for hydrolysis of **1** on alkanoate chain length (n) at 30 °C in 1:1 (v/v) MeOH–aqueous buffer (0.05 M $H_2PO_4^-/HPO_4^{2-}$, pH 8.0): [**1**] = 5 × 10^{-5} M; [cat.] = 1.0 × 10^{-5} M. Catalyst: none, +; **2**, △; **3**, ○; **4** ●; **5**, □.

are illustrated in Figure 1. Macromolecule **4**, in contrast to **2**, **3**, and **5**, exhibits clear preference for **1** (n = 14); therefore, *this synthetic, linear oligomer exhibits enzyme-like subtrate selectivity.* Polymer **5**, however, shows a steady increase in reaction velocity with increasing alkanoate chain length. The dependence of reaction velocity on substrate concentration for C_6, C_{12}, C_{14}, and C_{16} esters was examined in the presence of **4**. *The three longer chain esters exhibited saturation kinetics over the concentration range studied, while the C_6 ester did not.* The pH dependence of reaction velocities for hydrolysis of **1** (n = 12) in 1:1 (v/v) methanol–aqueous buffer was measured in the presence of **2–4** at 30 °C. The reaction velocity increases linearly with pH from pH 7.0–9.0 for all three catalysts[27] and continues to increase at higher pH due to uncatalyzed reaction with OH^-. Kinetic studies used 10-fold excess substrate over catalyst concentrations, and reactions were followed for 4–5 half-lives. Velocity values are directly proportional to catalyst concentration over the range 8.0 × 10^{-7} M to 1.0 × 10^{-5} M. Thus, **3** and **4**, like DMAP, function as true catalysts.

As a further test of the ability of **4** to function as an enzyme mimic, the data from hydrolyses of **1** (n = 12, 14, 16) were subjected to Michaelis–Menten analysis.[16] Lineweaver–Burk plots ($1/V$ vs $1/[S]$) are linear, as predicted by the Michaelis–Menten equation ($(1/V = K_M/V_{max}[S] + 1/V_{max}$) where V_{max} is the maximum reaction velocity, K_M is the Michaelis constant, and [S] is the substrate concentration). The Michaelis–Menten parameters, where k_{cat}/K_M ($k_{cat} = V_{max}/[cat.]_{total}$) indicates specificity of an enzyme for competing substrates, are as follows: (n, V_{max}, k_{cat}, K_M, k_{cal}/K_M) 12, 6.1 × 10^{-7} M s^{-1}, 0.27 s^{-1}, 5.9 × 10^{-5} M, 4600 M^{-1} s^{-1}; 14, 7.5 × 10^{-7} M s^{-1}, 0.33 s^{-1}, 2.9 × 10^{-5} M, 11.400 M^{-1} s^{-1}; 16, 4.5 × 10^{-7} M s^{-1}, 0.20 s^{-1}, 2.4 × 10^{-5} M, 8300 M^{-1} s^{-1}. Substrate optimization at n = 14 is due to enhanced velocity of hydrolysis as given by k_{cal}. Values of K_M show a steady

(10) Letsinger, R. L.; Savereide, T. J. *J. Am. Chem. Soc.* **1962**, *84*, 3122.
(11) Overberger, C. G.; Salamone, G. C. *Acc. Chem. Res.* **1969**, *2*, 217.
(12) Kimura, Y.; Tanaka, A.; Nanga, M.; Kuroki, N. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 407.
(13) Tomko, R.; Overberger, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 279.
(14) (a) Hirl, M. A.; Gamson, E. P.; Klotz, I. M. *J. Am. Chem. Soc.* **1979**, *101*, 6020. (b) Delaney, E. J.; Wood, L. E.; Klotz, I. M. *J. Am. Chem. Soc.* **1982**, *104*, 799.
(15) Vaidya, R. A.; Mathias, L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5514.
(16) Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman: New York, 1985.
(17) (a) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698. (b) Menger, F. M.; Ladika, M. *J. Am. Chem. Soc.* **1987**, *109*, 3145.
(18) Guthrie, J. P. *Can. J. Chem.* **1973**, *51*, 3494.
(19) Jiang, X.-K. *Acc. Chem. Res.* **1988**, *21*, 362.
(20) Blyth, C. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3021.
(21) Murakami, Y.; Sunamoto, J.; Okamoto, H.; Kawanami, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1537.
(22) Hofle, G.; Steglich, W.; Vorbrungen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.
(23) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129.
(24) Katritzkey, A. R.; Duell, B. L.; Knier, B. L.; Durst, H. D. *Langmuir* **1988**, *4*, 192.

(25) Kinetic measurements: Reaction mixtures were made up in a 1.00-cm quartz cuvette. The cuvette was filled with 2.97 mL of a 1:1 mixture of methanol and aqueous buffer (0.05 M $H_2PO_4^-/HPO_4^{2-}$, pH 8.0). A stock solution of catalyst in methanol (usually 5 μL) was added by microsyringe, and the solution was equilibrated for 10 min in the thermostated cell compartment (30 ± 1 °C) of a Hewlett-Packard Model 8450 spectrophotometer. An appropriate aliquot (0.03 mL) of a stock solution of *p*-nitrophenyl alkanoate in dioxane was added by microsyringe. The reaction mixture was quickly mixed by shaking, and the absorbance at 400 nm was recorded as a function of time. The pseudo apparent first-order rate constants were obtained as slopes of plots of ln $[A_\infty/(A_\infty - A_t)]$ vs time, where A_∞ and A_t are the absorbances at infinite time and time t, respectively. Duplicate runs generally showed a measurement error of less than 5%.

(26) Catalytic activity is taken as equivalent to the reaction velocity, V, i.e., the initial velocity of product formation.

(27) The pH dependence of degree of protonation of **4** is complex and is the focus of current investigation.

decrease with increasing alkanoate chain length; however, k_{cat}/K_M maximizes at $n = 14$. These parameters are consistent with effective binding of substrate to catalyst and efficient catalysis of hydrolysis ($t_{1/2}$ for **1** ($n = 14$) is 15 s at [cat.] = 1.0×10^{-5} M). The factors that control substrate selectivity in **4** are believed to be those responsible for enzyme specificity.[16]

The performance of **4** as a *p*-nitrophenyl esterase was compared with those of cholesterol esterase ($k_{cat}/K_M = 125 \times 10^4$ M^{-1} s^{-1})[28] and chymotrypsin ($k_{cat}/K_M = 7.6 \times 10^4$ M^{-1} s^{-1}).[29] The enzymic reactions are only moderately faster and show optimum activity with substrates of shorter chain length (**1**, $n = 6$, for cholesterol esterase and **1**, $n = 7$, for chymotrypsin). An important distinction between **4** and the enzymes is that the latter utilize bifunctional catalysis with histidine imidazole and serine hydroxyl as key participants.[16,28]

Acknowledgment. We thank the Office of Naval Research for financial support of this work and L. J. Mathias for the sample of poly(DAAP) used in this study.

Supplementary Material Available: Plot of $1/V$ vs $1/[S]$ for **1** ($n = 14$) in the presence of **4** and tables that list Michaelis-Menten parameters for hydrolysis of **1** ($n = 12, 14, 16$) in the presence of **4** and compare **4** with cholesterol esterase, chymotrypsin, and active synthetic catalysts as a *p*-nitrophenyl esterase (4 pages). Ordering information is given on any current masthead page.

(28) Sutton, L. D.; Stout, J. S.; Quinn, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 8398.
(29) Marshall, T. H.; Akgün, A. *J. Biol. Chem.* **1971**, *246*, 6019.
(30) Sutton, L. D.; Quinn, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 8404.

Synthesis, Structure, and Superconducting Properties of Single-Phase Rb_3C_{60}. A New, Convenient Method for the Preparation of M_3C_{60} Superconductors

John P. McCauley, Jr.,[†] Qing Zhu,[†] Nicole Coustel,[†] Otto Zhou,[†] Gavin Vaughan,[†] Stefan H. J. Idziak,[†] John E. Fischer,*[,†] S. W. Tozer,[‡] David M. Groski,[‡] Nicholas Bykovetz,[†,§] C. L. Lin,[∥] Andrew R. McGhie,[†] Brent H. Allen,[†] William J. Romanow,[†] Arnold M. Denenstein,[†] and Amos B. Smith, III*[,†]

Departments of Chemistry, Physics, and Materials Science Laboratory for Research on the Structure of Matter University of Pennsylvania Philadelphia, Pennsylvania 19104
Central Research and Development Department E. I. du Pont de Nemours & Co., Inc. Experimental Station, Wilmington, Delaware 19880
Department of Physics, Temple University Philadelphia, Pennsylvania 19122

Received August 2, 1991
Revised Manuscript Received September 4, 1991

Several synthetic procedures have been developed to produce alkali metal intercalated fullerite superconductors (M_xC_{60}, $x = 3$). The UCLA version[1] of the original AT&T method[2] (vapor-phase reaction of stoichiometric amounts of M = K or Rb and C_{60}) is thus far the only protocol demonstrated to yield phase-pure material (i.e., K_3C_{60}).[3] A significant drawback of this method is the limited accuracy of stoichiometric control when only modest quantities of C_{60} are used (e.g., 3 mg of K + 20 mg of C_{60}). Moreover, we have been unable to completely reproduce the UCLA results using our C_{60} powder (ca. 1500 Å crystallite size, which according to the described doping model[1] may be an important processing variable). Solution techniques[4] promise greater versatility but also present problems of stoichiometric control. The difficulty of accurately weighing small amounts of reactive metals was reportedly overcome by treating C_{60} with alkali/heavy metal amalgams. Exploiting this approach, Kelty et al.[5] claim that the heavy metal acts merely as a spectator. However, Kraus et al.[6] find from weight uptake measurement that the heavy metal Tl is co-intercalated from the KTl (1.5) amalgam; the latter depresses the T_c value to 17.6 K from 19.3 K for the K_3C_{60} binary compound.[3] In all of these methods, the final product of desired stoichiometry (x) may be thermodynamically or kinetically limited by miscibility gaps in the binary phase diagram.

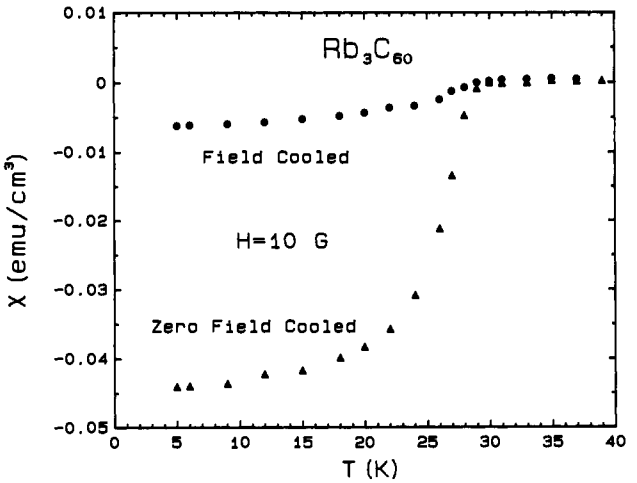


Figure 1. Diamagnetic susceptibility of Rb_3C_{60} (uncompacted powder, 3.5 mg). Circles: field cooled. Triangles: zero field cooled.

We describe here a new vapor-transport technique for producing M_xC_{60}. Stoichiometric control of small batches is markedly improved by reacting pristine C_{60} with the saturation-doped product,[7] which simply requires weighing two aliquots of C_{60}[8] outside the drybox. A weighed amount of C_{60} is treated with a large excess of alkali metal at 225 °C under vacuum. A small temperature gradient during cooldown prevents condensation of excess metal onto the powdered product. The crystallographic composition is M_6C_{60}, whereas repeated weight uptake measurements (K, Rb, or Cs) give x in the range 6.4–6.7.[7,9] This air-sensitive material is then diluted with C_{60} in the drybox to give a desired x. The two powders are ground together, sealed under vacuum, heated for 24 h at 250 °C, and then further annealed for 24 h at 350 °C, followed in some cases by 1 h at 400 °C or longer periods at 350 °C. Annealing is crucial to the process since the initial treatment usually yields a multiphase mixture. Extended annealing

[†] Departments of Chemistry, Physics, and Materials Science, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104.
[‡] Central Research and Development Department, E. I. du Pont de Nemours & Co., Inc., Experimental Station, Wilmington, DE 19880.
[§] On leave from Spring Garden College, Philadelphia, PA.
[∥] Department of Physics, Temple University, Philadelphia, PA 19122.

(1) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K. J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154.
(2) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600.
(3) Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-M.; Kaner, R. B.; Diederich, F.; Holczer, K. *Nature* **1991**, *351*, 632.
(4) Wang, H. H.; Kini, A. M.; Savali, B. M.; Carlson, K. D.; Williams, J. M.; Lykke, K. R.; Wurtz, P.; Parker, D. H.; Pellin, M. J.; Gruen, D. M.; Welp, U.; Kwok, W. K.; Fleshler, S.; Crabtree, G. W. *Inorg. Chem.* **1991**, *30*, 2838.
(5) Kelty, S. P.; Chen, C.-C.; Lieber, C. M. *Nature* **1991**, *352*, 223.
(6) Kraus, M.; Freytag, J.; Gärtner, S.; Vieth, H. M.; Krätschmer, W.; Lüders, K. *Z. Phys. B*, submitted.
(7) Zhou, O.; Fischer, J. E.; Coustel, N.; Kycia, S.; Zhu, Q.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III; Cox, D. E. *Nature* **1991**, *351*, 462.
(8) Prepared as described in the following: Fischer, J. E.; Heiney, P. A.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. R.; McCauley, J. P., Jr.; Smith, A. B., III. *Science* **1991**, *252*, 1288.
(9) Further analysis of the X-ray data is underway to determine if this "excess" metal exists in defect sites in the bcc structure.

0002-7863/91/1513-8537$02.50/0