tion spectrum), yet it dominates the excited-state properties. It has a broad emission band without any detectable vibronic structure even at 6 K. All of these properties are characteristic of a charge-transfer state. Questions about the nature of this excited state and how it evolves with increasing cluster size remain to be addressed.

Finally, the solubility of this new crystalline cluster may be used in the production of polymer films, such as polyvinylcarbazole, doped with the CdS cluster simply by spin-coating from a pyridine solution. Such films have been found to exhibit good photoconductive properties (*10*), which points to a real utility for such soluble semiconductor clusters in the preparation of materials that go into electronic devices made for this and other thin-film applications.

REFERENCES AND NOTES

1. S. Datta, J. K. Furdyna, R. L. Gunshor, *Superlattices Microstruct.* **1**, 317 (1985); L. E. Brus, *J. Chem. Phys.* **80**, 4403 (1984).
2. C. N. Rao and J. Gopalakrishnan, *New Directions in Solid State Chemistry* (Cambridge Univ. Press, Cambridge, 1986), chap. 3; L. Spanhel and M. Anderson, *J. Am. Chem. Soc.* **113**, 2826 (1990).
3. C. R. Berry, *Phys. Rev.* **161**, 848 (1967); M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.* **23**, 183 (1990); A. Henglein, *Top. Curr. Chem.* **143**, 113 (1988); Y. Wang, N. Herron, W. Mahler, A. Suna, *J. Opt. Soc. Am. B.* **6**, 808 (1989).
4. Y. Wang and N. Herron, *J. Phys. Chem.* **95**, 525 (1991).
5. I. G. Dance, A. Choy, M. L. Scudder, *J. Am. Chem. Soc.* **106**, 6285 (1984); I. G. Dance, *Aust. J. Chem.* **38**, 1745 (1985).
6. G. S. H. Lee, D. C. Craig, I. Ma, M. L. Scudder, T. D. Bailey, I. G. Dance *J. Am. Chem. Soc.* 110, 4863 (1988).
7. W. E. Farneth, N. Herron, Y. Wang, *Chem. Mater.* **4**, 916 (1992).
8. A light-yellow, clear cubic block, 0.39 mm on a side, was mounted on an Enraf-Nonius (Delft, Holland) CAD4 diffractometer (graphite monochromatized Mo$K\alpha$ radiation, wavelength of 0.71069 Å) and cooled to −70°C. The cubic unit cell parameter was determined from the Bragg angles of 25 computer-centered reflections as $a = 21.856(2)$ Å. The space group was assigned as $P23$ (No. 195), and the structure later confirmed this assignment. We collected 12,924 data points, of which 1,672 were unique with $I \geq 3.0\sigma(I)$, where I is intensity. The structure was solved by direct methods and was refined by full-matrix least-squares techniques with scattering factors from *International Tables for X-ray Crystallography* (Mathematical Tables Series, Kluwer Academic, Norwell, MA, 1974), vol. IV, including the anomalous terms for Cd and S. The final refinement of 239 parameters (data to parameter ratio = 6.91), in which Cd, S, N, and C were anisotropic and H was fixed, converged at $R = 0.042$ and $R_w = 0.039$. The single molecule for each unit cell resides on a site of T symmetry.
9. N. Herron, Y. Wang, H. Eckert, *J. Am. Chem. Soc.* 112, 1322 (1990).
10. Y. Wang and N. Herron, *Chem. Phys. Lett.*, in press.
11. DuPont Contribution 6304. Supplementary data (atomic coordinates, bond lengths, and angles) are available on request. Atomic coordinates will also be deposited with the Cambridge crystallographic data files. We thank J. B. Jensen and S. J. Harvey for technical assistance and W. J. Marshall for x-ray manipulations.

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Stable Compounds of Helium and Neon: He@C$_{60}$ and Ne@C$_{60}$

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It is demonstrated that fullerenes, prepared via the standard method (an arc between graphite electrodes in a partial pressure of helium), on heating to high temperatures release ^{4}He and ^{3}He. The amount corresponds to one ^{4}He for every 880,000 fullerene molecules. The ^{3}He/^{4}He isotopic ratio is that of tank helium rather than that of atmospheric helium. These results convincingly show that the helium is inside and that there is no exchange with the atmosphere. The amount found corresponds with a prediction from a simple model based on the expected volume of the cavity. In addition, the temperature dependence for the release of helium implies a barrier about 80 kilocalories per mole. This is much lower than the barrier expected from theory for helium passing through one of the rings in the intact structure. A mechanism involving reversibly breaking one or more bonds to temporarily open a "window" in the cage is proposed. A predicted consequence of this mechanism is the incorporation of other gases while the "window" is open. This was demonstrated through the incorporation of ^{3}He and neon by heating fullerene in their presence.

An intriging feature of buckminsterfullerene is the hollow interior, which is large enough to enclose atoms. In contrast with other molecules that bind ligands through noncovalent forces, buckminsterfullerene and its higher homologs are like closed bottles. Atoms or small molecules can be contained and held without need for binding interactions. Smalley *et al.* have reported the preparation of metallofullerenes (*1*). Although there was early discussion about whether the metals might be covalently attached to the outside (*2*), the present evidence indicates that there are metal atoms inside the carbon cages (*3–6*). Cram *et al.* (*7*) have suggested the name carcerands for closed-surface compounds that trap atoms and molecules inside. Schwarz *et al.* have reported that collisions of C$_{60}$ cations with ^{4}He and ^{3}He in a mass spectrometer produce ions which have the additional mass of helium (*8, 9*). In order to provide evidence that the helium is inside, the ions were neutralized and then reionized with a four-sector tandem mass spectrometer. Helium retention was interpreted as indicating that the helium was inside (*10*). It would be extremely difficult to recover macroscopic quantities of fullerenes containing helium or other rare gas atoms after formation of such ions in a mass spectrometer.

How then could one prepare quantities of buckminsterfullerene containing helium? We considered the possibility that this had already been done. The common method of preparing bulk quantities of the fullerenes involves operating an arc between graphite electrodes in helium at about 150 torr. As each molecule closes, there is a chance that a helium atom will end up inside. How could one detect this helium? If enough were present, one might see it directly in the mass spectrum of buckminsterfullerene. However, the ion with four ^{13}C atoms (and no helium) will generally be present. This ion has a mass so similar to the ion with no ^{13}C but with ^{4}He that only extremely high resolution would resolve them. If only a small quantity were present, it would not be seen.

Helium itself can be detected with extremely high sensitivity in a mass spectrometer. One of us (R.J.P.) has been using an instrument designed to measure helium content in geological samples (*11*). A sample, after evacuation is heated to high temperature in an all-metal furnace and the released gases are analyzed. Helium and neon were measured with a VG 5400 noble gas mass spectrometer fitted with a Johnston electron multiplier with pulse-counting electronics on the axial collector [see (*11*) for details]. A resolution of 550 ($\Delta m/m$) achieved complete baseline separation of ^{3}He$^+$ from HD$^+$. A "high side" Faraday cup with a resolution of 200 was used for the ^{4}He measurement. Absolute abundances of ^{3}He, ^{4}He, and ^{22}Ne were calculated by peak height comparison to an air standard of known size (0.101 cm^3 standard temperature and pressure) and are accurate to ±3%. A split of the gas was also measured for ^{40}Ar abundance on a Dycor quadrupole mass spectrometer by peak height comparison with the air standard. The small amount of ^{22}Ne in all tempera-

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Table 1. Mass spectrometric analysis of fullerenes.

Heating time (min)	Temperature (°C)	^{4}He ($\times 10^{-9}$ cm^3)	^{22}Ne ($\times 10^{-9}$ cm^3)	^{40}Ar ($\times 10^{-6}$ cm^3)	^{3}He ($\times 10^{-12}$ cm^3)
Commercial sample (40 mg)					
55	110	0.2	<0.02	6	—
55	230	1	<0.03	19	—
55	350	4.7	0.04	12	—
115	510	9.6	0.03	<0.2	—
50	650	26	0.03	<0.2	0.009
50	780	310	<0.02	<0.1	0.078
90	850	950	<0.02	<0.1	0.24
60	940	90	<0.02	<0.1	0.025
Heated with ^{3}He at 600°C for 1 hour (14 μg)					
220	210	<0.1	<0.01	0.006	0.15
45	410	0.2	<0.01	0.006	13.4
45	610	2.0	0.04	0.012	339
50	780	2.2	0.59	0.041	277
90	900	0.5	0.23	0.062	42
Heated with neon at 600°C for 1 hour (22 mg)					
90	200	0.4	<0.02	0.01	
100	410	1.2	0.45	0.02	
45	600	8	0.87	0.02	
90	790	113	4.04	0.02	
150	900	72	1.65	0.02	
150	900	39	0.35	0.02	
150	900	3.9	0.08	0.02	

ture steps (3×10^{-11} cm^3) is equivalent to the average extraction blank. This provides a limit on possible contamination by air. Average blank levels are 1×10^{-10} cm^3 for ^{4}He and 2×10^{-16} cm^3 for ^{3}He.

When 40 mg of a commercial sample (*12*) of C_{60} (containing about 10% C_{70}) was heated in steps, 1.4×10^{-6} cm^3 of helium was measured, most of it appearing from 780° to 850°C (Table 1). This is equivalent to one molecule of He@C_{60} for every 880,000 molecules of fullerene. Helium-3 could also be measured (3.5×10^{-13} cm^3) in the same experiment. The ^{3}He/^{4}He isotopic ratio corresponds to tank helium (2.1×10^{-7}) rather than to atmospheric helium (1.4×10^{-6}). The helium must therefore have been introduced when the fullerene was made and cannot have exchanged with helium from the atmosphere. A small amount of ^{40}Ar (3.7×10^{-5} cm^3) was released at low temperature (200° to 350°C). The high temperature steps (>500°C) had Ar at blank levels (1×10^{-8} cm^3). We conclude that the argon is adsorbed in the solid, outside of the fullerene molecules, while the helium is inside them. Argon comprises 0.9% of the atmosphere in contrast to helium (5.2 ppm) and is a much stickier atom.

One might assume that the average concentration of helium inside the cavity when the last bond closes to create a fullerene is about the same as that in the gas outside (1.2×10^{18} atoms cm^{-3} corresponding to 150 torr at around 1000°C). The average number of helium atoms per fullerene should therefore be the volume of the cavity times the concentration of helium in the gas. Using this idea and the measured abundance of helium inside, one obtains a free volume equal to that of a sphere of diameter 1.2 Å. Although the diameter of buckminsterfullerene is 7 Å, one must subtract the size of the carbons to get the size of the hole. With a van der Waals radius of 1.7 Å for carbon one calculates a 3.6 Å cavity. Because the helium also must be considered to have effective size, the free volume (locations possible for the helium nucleus) will be reduced by the volume of the helium atom. The agreement of the amount of helium found with that expected from this crude, hard-sphere model is good, perhaps fortuitously so.

The release of helium from fullerene is strongly dependent on temperature (Table 1). The data for release of ^{4}He yield an Arrhenius activation energy of approximately 80 kcal mol^{-1}. Theoretical barriers for helium to penetrate the benzene rings of a fullerene are around 200 kcal mol^{-1} (*13*, *14*). The thermal release cannot occur via the ring penetration route. Any process that opens the fullerene cage would permit the helium to escape. There are two categories of mechanism that can be considered. Opening could be followed by subsequent (perhaps intermolecular) steps irreversibly leading to some form of degraded fullerene. However, if the initial opening occurs by breaking one (or perhaps two) bonds, the fullerene might well reform by closing the opened bond after the helium gets out. Such bond-opened species have 9- or 10-membered rings (12-, 13-, or 14-membered rings if two bonds break). We expect these rings to be large enough for atoms to pass in or out. One might call this possibility a "window" mechanism. (The window opens and then recloses.) An important consequence of a window mechanism is the possibility of an atom coming in as well as going out when the window is open.

If one bond breaks, a singlet diradical should be formed. The rate of its reclosure could compete with the rate for atoms to either leave or enter. However, intersystem crossing to a triplet might provide a species with a long enough lifetime so that atoms can go in and out, achieving equilibrium before an ultimate return to closed fullerene. If the latter mechanism is followed, the rate of atom escape should be equal to the rate of going to this triplet. The rate for atoms to enter, in any event, must be slower by a factor equal to the fraction of molecules occupied at the ambient pressure and temperature at equilibrium.

To test this window possibility, we sealed fullerene in a fused silica tube with one atmosphere of pure ^{3}He and heated it at 600°C for 1 hour which increased the pressure to three atmospheres. The product was dissolved in toluene, filtered, and evaporated to dryness. A small amount of it (10 to 20%) did not dissolve. Remaining solvent was removed in a vacuum line. A small sample was made by dissolving a weighed amount in toluene and using a small portion of this solution so that only 14 μg of the original material was introduced into the instrument. The quantity of ^{3}He released from it was 6.7×10^{-10} cm^3. However, the amounts of ^{4}He, ^{20}Ne, ^{22}Ne, and ^{40}Ar were so low, relative to the blanks (owing to slight leaks or gases emitted from the oven and sample container), that obtaining accurate values was not possible. The amount of ^{3}He released per milligram was 5,400,000 times greater than that of the original material. This corresponds to one atom for every 650,000 buckyballs. The temperature profile for the ^{3}He release was similar to that found for the original fullerene, providing strong evidence that the ^{3}He was inside rather than somehow bound to the exterior.

In a similar manner, fullerene was heated with three atmospheres of neon at 600°C for an hour. Heating 22 mg of the recovered fullerene yielded 7.4×10^{-9} cm^3 of ^{22}Ne. (^{20}Ne measurements are affected by interference by the doubly charged cation of ^{40}Ar.) With the normal isotopic ratio, this would be 8×10^{-8} cm^3 of total neon. This corresponds to one neon atom for every 8,500,000 buckyballs. Most of the neon came out in the same 700° to 900° range required to release helium, so it must have been inside the cavity.

The results presented here constitute

compelling evidence that helium is trapped within the cavity of fullerenes during normal preparation. The amount released on heating in a mass spectrometer is in accord with the idea that the probability of trapping is the product of the size of the cavity times the density of helium in the gas at the time the last hole closes. The release of helium occurs at temperatures far lower than those expected for a process where helium goes through a ring of the intact fullerene structure. Strong evidence for a mechanism where one or more bonds reversibly break to open a "window" allowing atoms to pass in or out is provided by demonstrating that ^{3}He and neon can be incorporated into fullerene by heating in their presence. To the best of our knowledge, no other stable compounds of helium or neon have previously been reported.

REFERENCES AND NOTES

1. J. R. Heath *et al.*, *J. Am. Chem. Soc.* **107**, 7779 (1985).
2. D. M. Cox, O. J. Trevor, K. C. Reichmann, A. Kaldor, *J. Chem. Phys.* **88**, 1588 (1988).
3. F. D. Weiss, J. L. Elkind, S. C. O'Brien, R. F. Curl, R. E. Smalley, *J. Am. Chem. Soc.* **110**, 4464 (1988).
4. Y. Chai *et al.*, *J. Phys. Chem.* **95**, 7564 (1991).
5. R. D. Johnson, M. S. deVries, J. Salem, D. S. Bethune, C. S. Yannoni, *Nature* **355**, 239 (1992).
6. C. S. Yannoni *et al.*, *Science* **256**, 1191 (1992).
7. D. J. Cram *et al.*, *J. Am. Chem. Soc.* **110**, 2554 (1988).
8. T. Weiske, D. K. Böhme, J. Hrušák, W. Krätchmer, H. Schwarz, *Angew. Chem. Int. Ed.* **30**, 884 (1991).
9. K. A. Caldwell, D. E. Giblin, C. S. Hsu, D. Cox, M. L. Gross, *J. Am. Chem. Soc.* **113**, 8519 (1991).
10. T. Weiske, T. Wong, W. Krätchmer, J. K. Terlouw, H. Schwarz, *Angew. Chem. Int. Ed.* **31**, 183 (1992).
11. R. J. Poreda and K. A. Farley, *Earth Planet. Sci. Lett.* **113**, 129 (1992).
12. Texas Fullerenes, Houston, TX.
13. J. Hrušák, D. K. Bohme, T. Weiske, H. Schwarz, *Chem. Phys. Lett.* **193**, 97 (1992).
14. T. Weiske, J. Hrušák, D. K. Böhme, H. Schwarz, *Helv. Chem. Acta* **75**, 79 (1992).
15. This work was supported by grants from the National Science Foundation. We acknowledge helpful discussions with K. Turekian of the Yale Geology Department which led to this collaboration and with F. A. L. Anet. We thank J. A. Berson and M. Cordes for the use of a furnace and for help in its operation.

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On the Application of the Minimal Principle to Solve Unknown Structures

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The Shake-and-Bake method of structure determination is a new direct methods phasing algorithm based on a minimum-variance, phase invariant residual, which is referred to as the minimal principle. Previously, the algorithm had been applied only to known structures. This algorithm has now been applied to two previously unknown structures that contain 105 and 110 non-hydrogen atoms, respectively. This report focuses on (i) algorithmic and parametric optimizations of Shake-and-Bake and (ii) the determination of two previously unknown structures. Traditional tangent formula phasing techniques were unable to unravel these two new structures.

The Shake-and-Bake procedure (*1*, *2*) has been designed and implemented on a variety of computing platforms for the purpose of determining crystal structures by means of minimizing a recently proposed minimal function (*2*–*5*). The focus of this report is on: (i) algorithmic and parametric optimizations we have made to the basic algorithm (*1*), based on successful applications of Shake-and-Bake to 14 known structures over six space groups, ranging from 25 to 127 non-hydrogen atoms in the asymmetric unit cell, and (ii) the application of this modified algorithm to solve two previously unknown structures. In particular, the algorithmic and parametric optimizations we present were guided predominantly by the experimentation on three known structures, namely, the 28 non-hydrogen atom 9α-methoxycortisol (*6*), the 84 non-hydrogen atom isoleucinomycin (*7*), and the 127 non-hydrogen atom isoleucinomycin analog (*8*).

The two previously unknown structures solved by our algorithm are two polymorphic forms of a cycloheptapeptide, ternatin(I), a 110 non-hydrogen atom structure (*9*), and ternatin(II), a 105 non-hydrogen atom structure (*10*).

The minimal function has not been applied previously to an unknown complex structure. A considerable effort to solve the ternatin(I) structure by traditional tangent formula methods proved unsuccessful. Approaches taken included the testing of $\sim$50,000 randomly generated phase sets (*11*) as well as an additional 500,000 permuted phase sets. Molecular replacement (*12*) was also invoked, but the models considered were constructed with seven L-amino acids, and as it turns out, the structure was later found to contain three L- and four D-configuration amino acids. [Details of the two new structures are given in (*13*).] It remains to be demonstrated whether these two structures could have been as easily determined by several other new promising techniques that are currently being developed, including the Sayre equation tangent formula (*14*), phase annealing (*15*), and low-density elimination (*16*). In any event, the Shake-and-Bake algorithm was able to determine each structure in $\sim$70 min of CPU time on a Connection Machine CM-5.

A general introduction to the crystallographic phase problem is given in Box 1. We have recently proposed that a particularly simple function of the phases takes on its constrained minimal value for the correct set of phases. A brief review of the minimal principle is given in Box 2. The minimal principle states that $R(P) < R(S)$ for N atom structures $S \neq P$ (the given structure). In other words, among all phases ϕ that satisfy the necessary identities, those corresponding to the true structure P, minimize $R(\phi)$. Inspection of the minimal function R shows it to be a weighted sum of squares of residuals, that is, the differences between cosines and their expected values, the ratios of the Bessel functions I_1/I_0. The known conditional probability distributions of the triple $T_{\mathbf{HK}}$, given the three magnitudes $|E|$ of Eq. 4, and the known conditional distributions of the quartet $Q_{\mathbf{LMN}}$ of Eq. 5, lead directly to the expected values of the corresponding cosines, $I_1(A_{\mathbf{HK}})/I_0(A_{\mathbf{HK}})$ and $I_1(B_{\mathbf{LMN}})/I_0(B_{\mathbf{LMN}})$, respectively. In addition, these same distributions show that the reciprocals of their variances are strongly correlated with $A_{\mathbf{HK}}$ and $|B_{\mathbf{LMN}}|$, respectively. Thus, in analogy with the principle of least squares, the minimal principle, which attempts to minimize the weighted sum of squares of residuals, Eq. 1, becomes plausible. Furthermore, it can be shown rigorously that the values of $R(\phi)$, when the phases are set equal to their true values for any choice of origin and enantiomorph, are indeed smaller than the values of $R(\phi)$ when the phases ϕ are chosen "at random."

Although a number of standard minimization techniques exist, including simulated annealing (*17*) and genetic algorithms (*18*), such techniques are targeted at minimization with respect to the range of a

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