MATERIAL WITNESS

CAGED WATER

When fullerene chemistry took off in the 1990s, one enticing use of the carbon-cage molecules was as a protective wrapping for trapped molecules, isolating them from their environment. This, it was suggested, might offer a kind of matrix-isolation technique for studying sensitive chemical species under ambient conditions — a notion explored previously using other cage complexes[1]. Trapped metal atoms — the first class of endohedral fullerene compounds reported — might be used as contrast agents for magnetic resonance imaging, or perhaps even as qubits for quantum computing[2,3]. If encapsulation could be made reversible, maybe fullerenes could be used to chaperone drug molecules to their target cells.

Some of these possibilities continue to show promise; no doubt others will turn out to have been over-optimistic. The enterprise of trapping molecules to study in isolation has now been furthered significantly by Kurotobi and Murata, who have used inventive chemistry to open up a hole in C_{60}, insert a single water molecule, and then seal up the cage again[4]. They report a crystal structure of $H_2O@C_{60}$ (the @ sign denoting encapsulation) complexed to a nickel porphyrin, with the lone H_2O localized in the cage centre.

Kurotobi and Murata suggest that $H_2O@C_{60}$ might offer a rare opportunity to study the water molecule in a situation where it is not coordinated to other species via either hydrogen bonds or lone-pair dative bonding. Well, perhaps. The nominally hydrophobic interior of the fullerene cage might certainly lead one to imagine that the water molecule behaves almost as if *in vacuo*. And the ultraviolet-visible spectrum of the complex is almost identical to that of empty C_{60}, suggesting almost no interaction between the H_2O and the carbon cage, while the ^{13}C NMR spectrum shows all the carbons to be identical, indicating that the water molecule rotates rapidly on the NMR timescale. Yet it would be surprising if indeed there was no interaction between the hydrogen atoms and the aromatic rings of the cage, as hydrogen bonding to the π electrons of benzene rings has been reported for other encapsulated water molecules, both in synthetic supramolecular complexes[5] and in a hydrophobic protein cavity[6].

It's in the latter regard that $H_2O@C_{60}$ might prove to be a useful model compound. Several proteins have hydrophobic interior spaces in which a few water molecules might lodge. In the cytokine interleukin-1β, for example, such a cavity hosts between one and four water molecules on average[6]. There is predominantly a water dimer in the cavity itself, but it is not totally isolated: lone water molecules in two channels opening onto the cavity sometimes connect the dimer to the exterior[7].

Such trapped water molecules seem to have significantly slowed dynamics relative to the bulk[8], although it's not clear whether this depends on there being several water molecules present so that the dynamics become cooperative. If that's so, the trapped water might be expected to have a different dielectric constant from the bulk, altering its solvent properties[9]. If the same chemistry will work for larger fullerenes, Kurotobi and Murata might have devised a valuable method for exploring the characteristics of such small, hydrophobically encapsulated water clusters. ❐

PHILIP BALL

References

1. Cram, D. J., Tanner, M. E. & Thomas, R. *Angew. Chem. Int. Ed.* **30,** 1024–1027 (1991).
2. Harneit, W. *Phys. Rev. A* **65,** 032322 (2002).
3. Ju, C., Suter, D. & Du, J. *Phys. Rev. A* **75,** 012318 (2007).
4. Kurotobi, K. & Murata, Y. *Science* **333,** 613–616 (2011).
5. Atwood, J. L., Hamada, F., Robinson, K. D., Orr, G. W. & Vincent, R. L. *Nature* **349,** 683–684 (1991).
6. Somani, S., Chng, C. P. & Verma, C. S. *Proteins* **67,** 868–885 (2007).
7. Yu, B., Blaber, M., Gronenborn, A. M., Clore, G. M. & Caspar, D. L. D. *Proc. Natl Acad. Sci. USA* **96,** 103–108 (1999).
8. Modig, K., Rademacher, M., Lücke, C. & Halle, B. *J. Mol. Biol.* **332,** 965–977 (2003).
9. Despa, F., Fernández, A. & Berry, R. S. *Phys. Rev. Lett.* **93,** 228104 (2004).

SOLID ELECTROLYTES

Lithium ions on the fast track

The solvent-based electrolytes used at present in lithium-ion batteries can be unsafe for large-scale applications. A crystalline electrolyte with high ionic conductivity could soon enable all-solid energy storage systems.

Christian Masquelier

Electrochemical energy storage systems, which can deliver electricity on demand, lie at the heart of today's mobile electronic devices and electrically powered vehicles. On a larger scale, such systems can secure the supply of renewable energy through the buffering of intermittent resources such as wind and the Sun. The growing need for energy storage systems has prompted intense academic research activities and huge industrial investments in the field of rechargeable batteries[1,2]. The lithium-ion battery, which was introduced by Sony Corporation in 1991, now plays a major role in consumers'