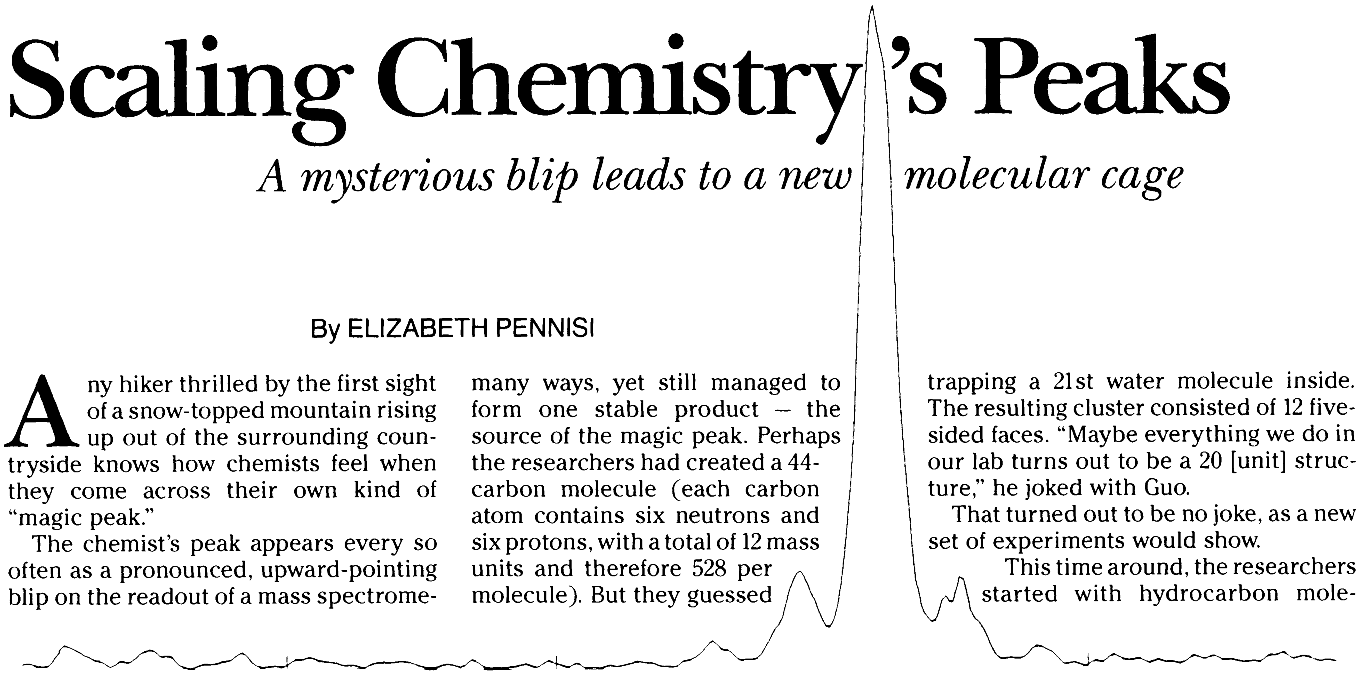
Scaling Chemistry's Peaks

A mysterious blip leads to a new molecular cage

By ELIZABETH PENNISI



Any hiker thrilled by the first sight of a snow-topped mountain rising up out of the surrounding countryside knows how chemists feel when they come across their own kind of "magic peak."

The chemist's peak appears every so often as a pronounced, upward-pointing blip on the readout of a mass spectrometer, an instrument that sorts and registers molecules by their masses. Researchers find such a peak magical — and baffling — because its height suggests that an experiment has yielded a large number of molecules of one particular size, rather than the typical mess of a few of many kinds of molecules, which creates a landscape of undistinguished hills on the mass spectrum.

Just that kind of peak led to the discovery of the buckyball, one of a class of cage-like carbon molecules called fullerenes that has riveted the chemistry, physics and materials science communities for almost two years (SN: 8/24/91, p.120).

Another such peak, recently observed at Pennsylvania State University in University Park, has pointed researchers to yet another class of cage-like molecules with as much, if not more, potential for practical application as the fullerenes.

Chemist A. Welford Castleman Jr. first saw this anomaly last December, when he, Penn State colleague Baochuan C. Guo and graduate student Kevin P. Kerns were studying the behavior of clusters, groups of atoms or molecules that bunch to form a "supermolecule."

In this particular series of experiments, they were studying the interaction between organic molecules and titanium. The researchers used a technique called laser vaporization to create and then manipulate clusters in a plasma reactor. They then analyzed the results with a mass spectrometer.

"We suddenly noticed this rather striking, prominent peak," recalls Castleman. The peak indicated that the chemists had made a new molecule with 528 atomic mass units — the total number of protons and neutrons. Somehow, they thought, inside the plasma reactor these organic molecules had collided, fallen apart and regrouped, perhaps many times and in many ways, yet still managed to form one stable product — the source of the magic peak. Perhaps the researchers had created a 44-carbon molecule (each carbon atom contains six neutrons and six protons, with a total of 12 mass units and therefore 528 per molecule). But they guessed they had made a hydrocarbon with a metal atom or two attached.

However, there was something very strange about this product. "All kinds of different [compounds] gave us this one peak," Castleman told SCIENCE NEWS. The researchers tried methane (CH_4), then ethylene (C_2H_4), then acetylene (C_2H_2) and finally two other hydrocarbon compounds, propylene (C_3H_6) and benzene (C_6H_6). Each time, they got the same results. But when they reacted the hydrocarbons with metal atoms other than titanium, they found that each metal led to a new peak at a slightly different location than the original one.

To pin down what atoms were in this putative hydrocarbon, they repeated the experiments, this time using organic compounds made with deuterium, a heavy isotope of hydrogen. If the new compound contained hydrogen, then the peak should shift by one mass unit for each hydrogen atom incorporated into the molecule.

Still the magic peak appeared right at 528. "That told us we were getting rid of all the hydrogens," says Castleman, who admits being a little discouraged at that point. "We were on the wrong track."

Weeks later, while preparing a talk, Guo made transparencies of the various peaks. As he and Castleman were trying to make sense of them, they happened to stack a few transparencies on top of each other. Suddenly they realized that the different locations of these peaks could be accounted for if the mystery molecule contained several metal atoms, not just one or two.

Then something about the peaks reminded Castleman of work his lab group had done last year showing that water tended to form clusters of 20 molecules, trapping a 21st water molecule inside. The resulting cluster consisted of 12 five-sided faces. "Maybe everything we do in our lab turns out to be a 20 [unit] structure," he joked with Guo.

That turned out to be no joke, as a new set of experiments would show.

This time around, the researchers started with hydrocarbon molecules that contained a heavier isotope of carbon. The magic peak shifted: The amount of the increase in mass meant that this new compound contained 12 carbon atoms.

"We didn't expect more than one or two metal atoms at most [in the molecule]," says Castleman. "Yet everything shifted as if it had eight metal atoms. Then we got really excited. This is quite a different cage-like structure."

The most famous cage-like structures are the all-carbon molecules called fullerenes. During the past year, several researchers have worked hard to modify these round, hollow molecules, sometimes by replacing a few carbon atoms with other atoms. To date, they have succeeded only in getting up to six atoms to stand in for as many carbon atoms.

Theorists have shown that the buckyball could handle many more. But too many replacements in smaller fullerenes might cause these hollow molecules to form links across their core as well as around their perimeter, says Daniel A. Jelski, a theoretical chemist at the State University of New York, Fredonia. His calculations indicate, for example, that with more than a dozen or so boron, nitrogen or silicon substitute atoms, the 44-carbon fullerene would begin to collapse. Thus, it seems unlikely that a stable, round molecule with just 12 carbon atoms and almost as many metal atoms could exist.

Yet the new ball-like molecule they discovered has eight titanium atoms, the Penn State group reports in the March 13 SCIENCE. The researchers cite as evidence an experiment in which they first used mass spectrometry to separate out their new molecule and then added ammonia ions to the reaction chamber. These ions pair only with titanium, not carbon. With a second mass spectrometer, the scientists determined that eight ammonia ions latched on to the new molecule, indicating that eight titanium atoms occupied equivalent places on the outside of the molecule.

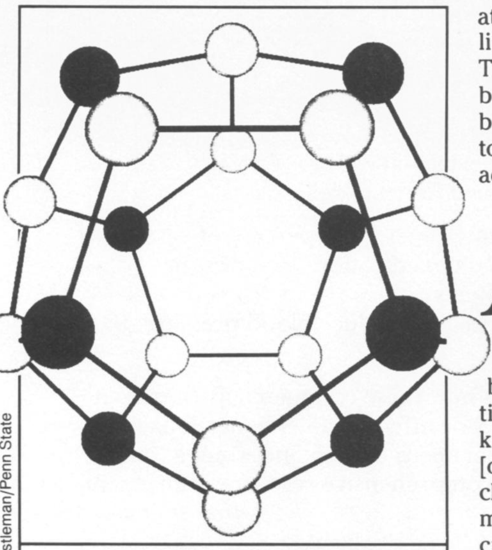
They concluded that their new molecule's eight titanium and 12 carbon atoms arrange in pentagons and link to form a symmetrical 12-sided ball that could be round or puckered. Two titanium and three carbon atoms make up each pentagon, and each titanium connects to three carbon atoms. The Penn State group calls this type of molecule a metallo-carbohedrene, "met-car" for short.

Electrons from transition metals such as titanium distribute themselves in the met-car such that the structure is less strained than when 20 carbon atoms come together this way. The Penn State group suspects that in each pentagon, some of the titanium's electrons may rove about freely. These "delocalized" electrons could impart very interesting electronic and magnetic properties and they hint that the new molecules could prove useful in information storage, pollution control and the development of new catalysts.

"It's very elegant work," says Jelski. "I found the evidence very convincing. And the fact that they've gotten a [closed] structure this small is an achievement in itself."

However, with just enough carbon atoms to make up two flat benzene rings, this molecule will surely raise some eyebrows. The smallest fullerenes that hang together long enough to show up in mass spectra contain at least 30 carbon atoms. Anything with fewer tends to fall apart because of the strain in the sharply bent carbon connections. Investigations of fullerene structures — which have carbons arranged in 12 pentagons and a varying number of hexagonal rings — indicate that the molecule is most stable when the pentagons are farthest apart, Jelski says.

This new molecule shoves three pentagons together, and while having them meet at a titanium atom may make the connections more feasible, "you still have very high strain between the pentagons," notes Jelski. "So I don't think it will be the perfect dodecahedron that they have drawn," he adds.



Guo, Kerns, Castleman/Penn State

This hollow molecule's eight titanium (black) and 12 carbon (white) atoms arrange in 12 five-sided faces.

Also, even though carbon and titanium usually share, give or gain four electrons in linking up with other atoms, they are by no means twin atoms. These elements differ enough in size — titanium is almost four times as big as carbon — that Jelski expects some of the met-car's bonds to be longer than others. Thus, this cage may lack the incredible symmetry of the buckyball. Finally, the molecule may be small enough that some bonds extend across the center of the cage, making it less hollow.

"It is really a different thing than a fullerene," says Richard E. Smalley, whose group at Rice University in Houston was the first to see the buckyball's magic peak in 1985. Rice chemists have since been the first to put atoms inside the fullerene or in place of the cage's carbon atoms. "The titanium atoms are not bonded in such a way that they are completely surrounded by carbon [atoms]," Smalley notes. He thinks that because of how each titanium in met-car attaches to three carbon atoms, the metal atoms may be eager to link with something else. Thus, pure Ti_8C_{12} may be difficult to isolate and may be unstable outside these reaction chambers. "On the other hand, it may work out to be a very happy molecule," Smalley adds.

A happy molecule would make chemists happy, too. Already the Penn State chemists have made met-car molecules with metals other than titanium, opening up the possibility of tailoring the molecule's properties to a particular need. "One can get all kinds of different chemical reaction sites [on the molecule]," Jelski says. Adding a chemical side group or atom to met-car might allow chemists to disrupt the molecule's symmetry and perhaps "get a whole bunch of unique properties," he adds. "It becomes very complex but also very powerful. You'll be able to make a large number of richer materials."

The high proportion of metal in these molecules makes them particularly appealing as potential catalysts, adds Donald M. Cox, a physicist at the Exxon Research and Engineering Co.'s Corporate Research Laboratory in Annandale, N.J.

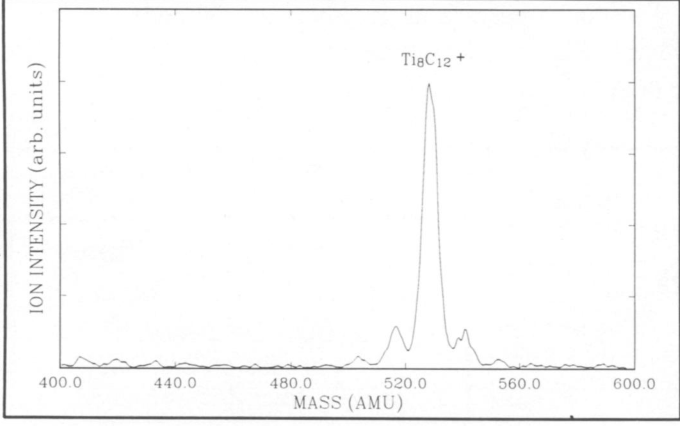
Like others, however, Cox awaits the next steps, which in the case of fullerenes took more than five years: Scientists must collect and purify enough of the new molecule to study its properties and confirm its structure.

"I would say there is some 'magic' in the magic [peak] that the authors discuss but would emphasize that now we need to make tens of milligrams to take a closer look at the structure," says Rodney Ruoff of SRI International in Menlo Park, Calif. "The absolute skeptic will wish that enough of these molecules are obtained in a vial, and a crystal grown, and the molecular structure obtained from X-ray diffraction."

Castleman's mass spectrometer could not register anything larger than 1,200 atomic mass units, but he and others hope they will one day discover that met-cars come in a variety of sizes, just as fullerenes do. Also, they hope to come up with a way to produce larger quantities of the material.

As other laboratories gear up to make their own met-cars, the Penn State group tries to keep one step ahead in scaling this new peak in chemistry. "We've got some stuff in the bottle; whether it's [met-car] or not is yet to be seen," says Castleman.

Meanwhile, his colleagues cite this new cage molecule as evidence of a vast range of chemical clusters waiting to be discovered. "It's an interesting tidbit that suggests the possibilities of other materials," says Cox. "It shows that there are other things that we should be looking for in the three-dimensional world." ☐



Guo, Kerns, Castleman/Penn State

A readout from a mass spectrometer shows that a reaction between titanium and methane has produced a relatively large number of molecules — all with a mass of 528 atomic mass units.