

Departament de Química Inorgànica

Editors: M. Gómez i J. Sales. Disseny: R. Bosque. Correspondència: noticies@qi.ub.es

Noticies Inorganiques

Any 2, Núm. 11, Setembre de 2003

Ful-lerens sense carboni

Buckminsterfullerene (C_{60}) possesses the highest possible of all symmetries: icosahedral. But there are other icosahedral molecules out there, and two striking examples that have fullerene-like structures but aren't based on carbon were unveiled recently in *Science* [300, 778 and 781 (2003)].

One example, reported by Bryan W. Eichhorn's group at the University of Maryland, is the $[As@Ni_{12}@As_{20}]^{3-}$ ion. This cluster consists of an As_{20} pentagonal dodecahedron that encapsulates a Ni_{12} icosahedron, which contains an arsenic atom at its center. The As_{20} cage is related to the smallest fullerene, C_{20} .

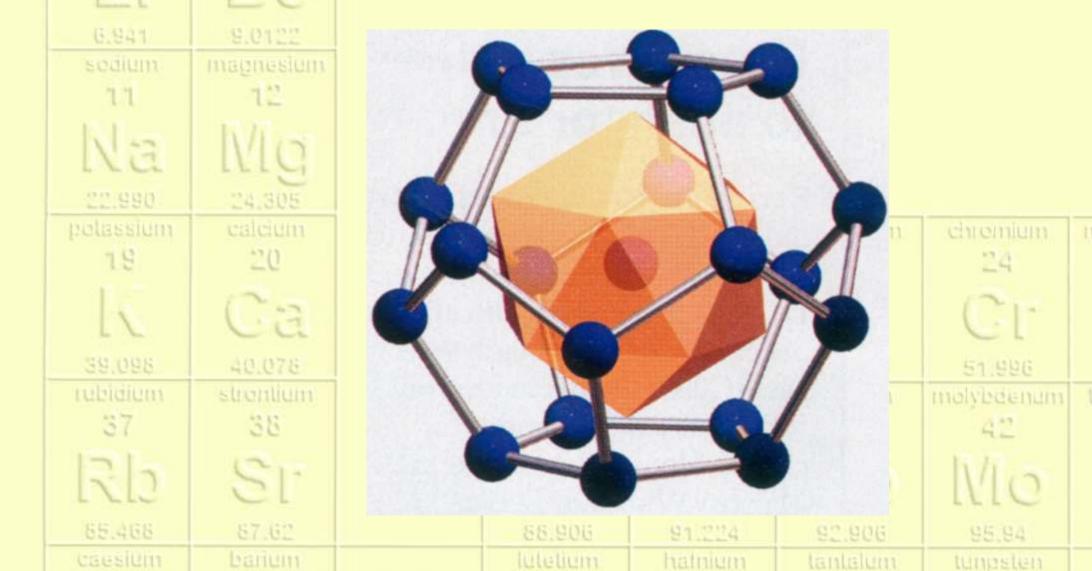
The other example of an inorganic fullerene-like molecule was reported by Manfred Scheer of the University of Karlsruhe and his colleagues. They reacted copper(I) chloride with a ferrocene-like complex consisting of an iron atom sandwiched between two ligands, one of them being cyclo- P_5 . In the spherical cluster that results, the P_5 rings have been stitched together by CuCl moieties to form a P_{60} Cu₂₅Cl₅ cage.

Clústers metàl·lics antiaromàtics

Aromatic compounds--stabilized by 4n + 2 electrons--were once thought to be purely the domain of organic chemistry. But in the past few years, chemists have discovered several aromatic all-metal cluster systems. Now, the concept of antiaromaticity--destabilization observed in cyclic systems with 4n electrons--is following suit.

Alexander I. Boldyrev of Utah State University and coworkers have made Li₃Al₄⁻ in which the Al₄⁴⁻ anion has four electrons [*Science*, **300**, 622 (2003)].

 Li_3Al_4^- was prepared by laser vaporization of a LiAl alloy and separated from other Li_xAl_y^- species using time-of-flight mass spectrometry. It was characterized by photoelectron spectroscopy and *ab initio* calculations to determine the optimized structure and molecular orbital pictures, verifying the presence of the four electrons. The bonding patterns and the rectangular shape of the Al_4^+ unit are analogous to cyclobutadiene, which is the quintessential antiaromatic organic compound.



Nous materials per transportar hidrogen

There is no convenient way for the public to store and transport large quantities of hydrogen safely. However, some advances in storage materials have been reported.

Omar M. Yaghi and their coworkers at Michigan, Los Alamos National Laboratory, and Arizona State University have developed new materials [*Noticies Inorganiques*, any 1, núm 3, maig de 2002], composed of metal-organic frameworks with a cubic three-dimensional extended porous structure, which can adsorb up to 2% by weight of hydrogen (orange spheres in the figure) at room temperature and about 10 atm of pressure [*Science*, **300**, 1127 (2003)]. At lower temperatures, hydrogen uptake as high as 4.5% has been achieved.

The materials, which remain stable even after solvent molecules are removed, are made up of cubes in which each corner is occupied by an $OZn_4(CO_2)_6$ cluster that is bridged by six carboxylates of an organic linker. The group prepared crystals using various linkers

2.58 A C1 A1 35.453 39.948 bromine krypton 35 36 B1 L1 78.904 83.80 iodine xenon 53 54 L1 114.82 118.71 121.76 127.60 126.90 131.29 y thallium lead bismuth polonium astatine radon

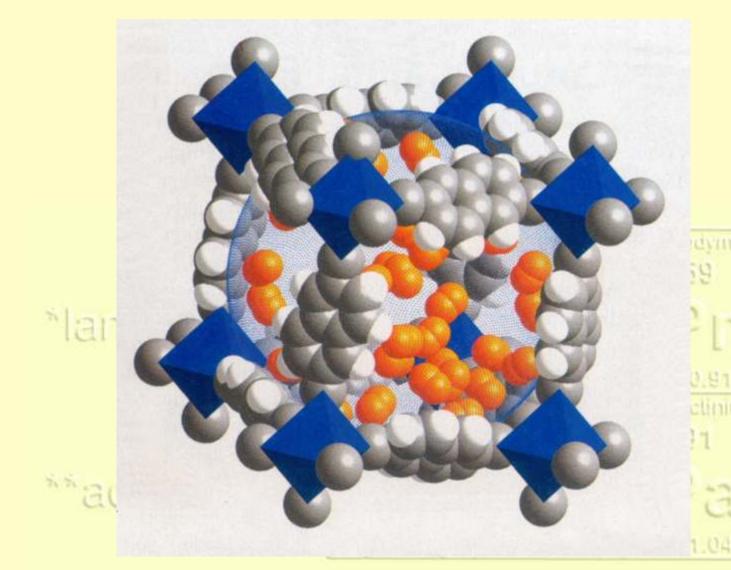
El polimorfisme permet nanocristalls ramificats

A few years ago, A. Paul Alivisatos and his coworkers at the University of California, Berkeley, and Lawrence Berkeley National Laboratory noticed that some nanocrystals would unexpectedly form branched structures. Now, the researchers can make those branched structures controllably and reproducibly [*Nat. Mat.*, **2**, 382 (2003)].

The branching happens because CdTe has two different stable crystal structures that are close--but not too close--in energy and that have atomically identical facets. Branches form by switching between conditions that favor one structure over the other. Alivisatos and coworkers manipulate the conditions so that the cubic structure is preferred during the nucleation phase and the hexagonal structure is preferred during the growth phase.

The length and width of the tetrapod arms are controlled by changing the ratios of cadmium to tellurium and to the surfactant. As the Cd/Te ratio increases, the arms get longer. As the Cd/surfactant ratio increases, the arms get fatter. Additionally, within a few percent, the four arms of the tetrapods are of equal length.

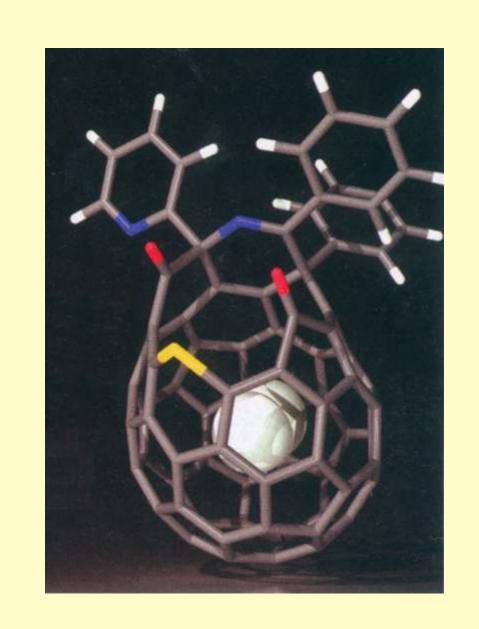
Such controllable syntheses could be especially useful for solar cells, where the diameter of the arms dictates the wavelength and the length determines the amount of energy absorbed. In contrast to nanorods, the tetrapods spontaneously orient themselves correctly.



On the other hand, Japanese chemists for the first time have prepared an open-cage fullerene derivative with an orifice large enough to allow a hydrogen molecule to be inserted into the cage in 100% yield [K. Komatsu et al, *J. Am. Chem. Soc.*, **125**, 7152 (2003)].

The new molecule was prepared from C_{60} in three steps in 40% overall yield. When the researchers expose the compound to hydrogen gas at 800 atm and 200 °C in an autoclave, 100% encapsulation is achieved within eight hours.

None of the encapsulated hydrogen escaped when a solution of the endohedral complex was monitored for more than three months at room temperature. However, hydrogen was released slowly when the solution was heated above 160 °C.



ZB(111) ZB(111) ZB(111) ZB(111)

Breus

- La Real Sociedad Española de Química compleix cent anys.
- Recentment s'ha demostrat que el ²⁰⁹Bi és radiactiu, amb una vida mitjana de 1,9·10¹⁹ anys. En conseqüència, l'element estable més pesant és el plom.
- El vidre dopat amb LaB₆ deixa passar la llum, però no la calor [S. Schelm and G.B. Smith; *Appl. Phys. Lett.*, **82**, 4346 (2003)].
- Una pàgina web amb 8400 setis d'Internet relacionats amb la Química: http://www.liv.ac.uk/Chemistry/Links/links.html.

L'element número **11**, **sodi**, va ser preparat l'any 1807 per Humpry Davy. El seu nom prové de la paraula anglesa *soda*, mentre que el símbol prové del llatí *natrium*.