UNIVERSITAT DE BARCELONA
Química Inorgànica

Notícies Inorgàniques

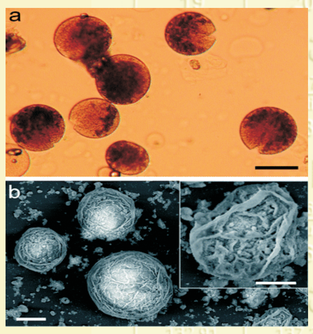
Any 10, Núm. 56, Setembre de 2011

http://www.ub.edu/inorgani/dqi.htm

Editors: Gabriel Aullón, Ramón Bosque i Joaquim Sales. Correspondència: noticies@qi.ub.es

La vida ve de la inorgànica?

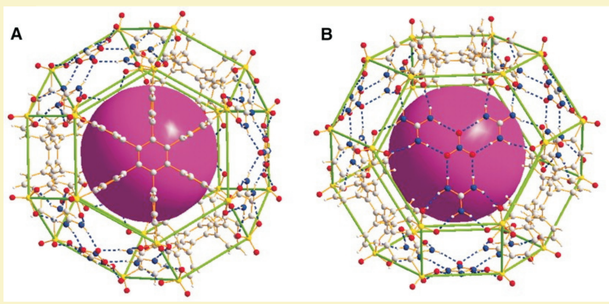
The basic components of cells can operate within the bounds of inorganic membranes made from nanoparticles . The authors (S. Mann et al. *Chem. Sci.*, **2011**, *2*, 1739) say such membranes provide an alternative model for explaining how the first cells evolved from simple, inorganic molecules. Chemists created silicon-based membranes with hydrophilic and hydrophobic properties akin to those of lipid bilayers in natural cells. Nanoparticles self-assembled in oil to form 'protocells', enclosing drops of water inside porous silicon shells. What was really interesting was that not only could they stabilise the droplets - which had been shown before - but that the nanoparticle-based shell could be considered as a primitive, semi-permeable inorganic membrane. To produce the desired water-loving/hating membrane, the researchers functionalised the surface of hydrophilic silica nanoparticles with silanol and dimethylsilane groups. Shaking the nanoparticles in oil and water made them pack together at the oil-water interface.The approach is simpler than chemical syntheses required to make artificial phospholipids, which are often used in artificial cell membranes. In a wider perspective, studies on bio-inorganic protocells could provide alternative models for evaluating potential prebiotic pathways prior to the emergence of lipid-based compartmentalization on the early Earth.



(a) Optical micrograph showing intact silica-stabilized microdroplets of the aqueous protein, ferritin, after shell reconstruction and transfer into water. The red-brown colouration of ferritin is associated specifically with the droplet interior, consistent with a sealed bio-inorganic compartment. Scale bar = 100 µm.
(b) SEM micrograph of silica-stabilized colloidosomes after shell reconstruction and transfer into water; scale bar = 100 µm. Inset, higher magnification image showing detail of partially collapsed inorganic membrane; scale bar = 50 µm

Casa a mida

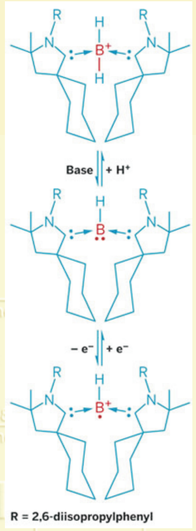
A new chemical cage is proving to be a more versatile trap for molecules, as well as a feat of molecular engineering. A team led Michael D. Ward (*Science*, **2011**, *333*, 436) created the novel structure out of 20 ions from three distinct molecules, all held together with 72 hydrogen bonds. Most molecular cages are built to house a specific guest molecule, but this new assembly is capable of capturing a variety of species, regardless of charge. The structure has the shape of a truncated octahedron and an interior space of 2,200 Å^3, and it can hold organic molecules, transition-metal complexes, and so-called ship-in-a-bottle nanoclusters that have not been observed outside the cage. It is hoped that the supramolecular assembly will find use as a structural support for building quantum dots, as a cage for confining components for molecular electronics and plasmonics, and as a molecular flask in which to carry out catalytic reactions. The assembly of the cage is constructed from two kinds of hexagonal molecular "tiles" with edges of roughly the same length and complementary hydrogen bonds. One tile is a tris(guanidinium)nitrate cluster with amino groups that hydrogen-bond to sulfonate moieties in the other type of tile, hexa(4-sulfonatophenyl)-benzene.



Two views of the truncated octahedron cage, delineated by green lines. Left structure shows the hexa(4-sulfonato-phenyl)benzene moiety as the central tile.
Right structure centers on the tris-(guanidinium)nitrate cluster. The purple sphere indicates the cage's interior space. S = yellow, N = blue, C = gray, O = red; hydrogen atoms omitted for clarity.

Transmutació àcid → base

Amines and boranes are the archetypical Lewis bases and acids, respectively. The former can readily undergo one-electron oxidation to give radical cations, whereas the latter are easily reduced to afford radical anions. The synthesis of a neutral tricoordinate boron derivative, which acts as a Lewis base and undergoes one-electron oxidation into the corresponding radical cation has been reported (G. Bertrand et al. *Science,* **2011**, *333*, 610). Unlike alchemists' fruitless efforts to turn base metals into gold, researchers have succeeded in transmuting conventional boron compounds, which are acidic, into stable borylene adducts, which are bases similar to amines. The adducts' basicity could lead to new catalysts. Borylenes, monovalent boron compounds with an electron lone pair and two vacant orbitals, have until now only been observed fleetingly, as transient intermediates. Stable species have been created by coordinating them with transition metals; but no stable, basic borylene adducts had been found. Now, the reaction of a carbene with a boron compound creates the first stable nonmetal borylene adduct, which is a base with a donatable electron lone pair.



A basic borylene adduct stabilized by two carbenes (center) forms a conjugate acid when protonated (top) or a radical cation when oxidized (bottom).

La Química reinterpreta l'economia

French researchers (Anne-Marie Desaulty et al. *Proc. Natl. Acad. Sci. USA*, **2011**, *108*, 9002) have used highly sensitive mass spectrometry to help solve a key question surrounding economic inflation in Europe during the 16th and 17th centuries. For decades historians have argued about why there was a gradual but inexorable increase in prices in Europe between around 1520 and 1650, known as the great Price Revolution. One influential school of thought postulates that the inflation was due to the Spanish economy being flooded with Mexican silver coins. But now, the high-precision isotope analysis of coins from Europe and the Americas from the relevant period and shown that there was no huge influx of Mexican silver into Spanish coinage at this time. The researchers profiled copper, lead and silver isotopes from coins from Europe and the Americas. The results showed that Mexican silver did not enter Spanish coinage from the 16th century to the beginning of the 17th century. On the other hand, Spanish coins struck under the reign of Philip V [1700-1746] have a purely Mexican signature. The findings suggest that inflation in Spain during the 16th and 17th centuries did not correlate with a massive influx of Mexican silver into Spanish currency, but that it took 80 years for Mexican silver to completely replace European silver in Spanish coinage. The results thus call into question the secular idea that the "prices revolution" is related to the massive arrival of American metals.

An eight reales silver cob struck in Potosi, Bolivia, under the reign of Philip II

Any Internacional de la Química 2011

• Coincidint amb la cloenda de l'Any Internacional de la Química, a finals del proper mes d'octubre s'instal·larà a la Biblioteca de Física i Química el mural «Homenatge als Elements» de l'artista visual Eugènia Balcells (Barcelona, 1943). L'obra és una versió particular de la Taula Periòdica constituïda pels espectres d'emissio del elements. Per tal d'afavorir la seva difusió se n'ha fet una versió en format pòster, que pot adquirir-se a la llibreria de la Facultat.

Avui recomanem

• La Mostra del Fons Històric que, per setè curs consecutiu, organitza la Biblioteca de Física i Química, enguany està dedicada a «L'utilltatge químic en llibres i catàlegs»

Breus

• Les determinacions més precises del moment dipolar elèctric fetes fins ara han demostrat que l'electró, contràriament a prediccions anteriors, continua sent esfèric. *Nature,* **2011**, *473*, 493.

• Ha estat detectat peròxid d'hidrogen a l'espai interstel·lar, fet que obliga a replantejar els models que expliquen la presència d'aigua i oxigen a l'espai. *Astron. Astrophys.*, **2011,** *531*, L 8.

L'element

Focs artificials verds de bari

L'element número 56, **bari**, fou preparat per Sir Humprey Davy el 1808, per electròlisi de l'òxid, BaO, fos. El 1774 Carl Scheele ja l'havia identificat encara que no fou capaç d'aïllar-lo. El nom prové del terme grec "barys" que vol dir pesant, atesa l'elevada densitat del seus compostos; la baritina, $BaSO_4$, que és el mineral més abundant, té una densitat de 4,5 g/cm^3. Com a element del grup dels alcalinoterris presenta una reactivitat elevada; l'abundància a la terra és moderada, 0,0425% l'escorça i 13 µg/L a l'aigua de mar, comparable a la del sofre.
Els compostos de bari no tenen gaires aplicacions, en part degut a la seva toxicitat. L'excepció n'és el $BaSO_4$ que s'empra com a contrast en les radiografies del sistema digestiu; la seva elevada insolubilitat anul·la el caràcter verinós. En menors quantitats el $Ba(NO_3)_2$, s'usa en els focs artificials per donar el color verd. Històricament s'emprava en la fabricació d'oxigen pur; es feia reaccionar l'òxid amb aire, a 500-600ºC, i el peròxid format, BaO_2, desprenia oxigen a 700ºC.