

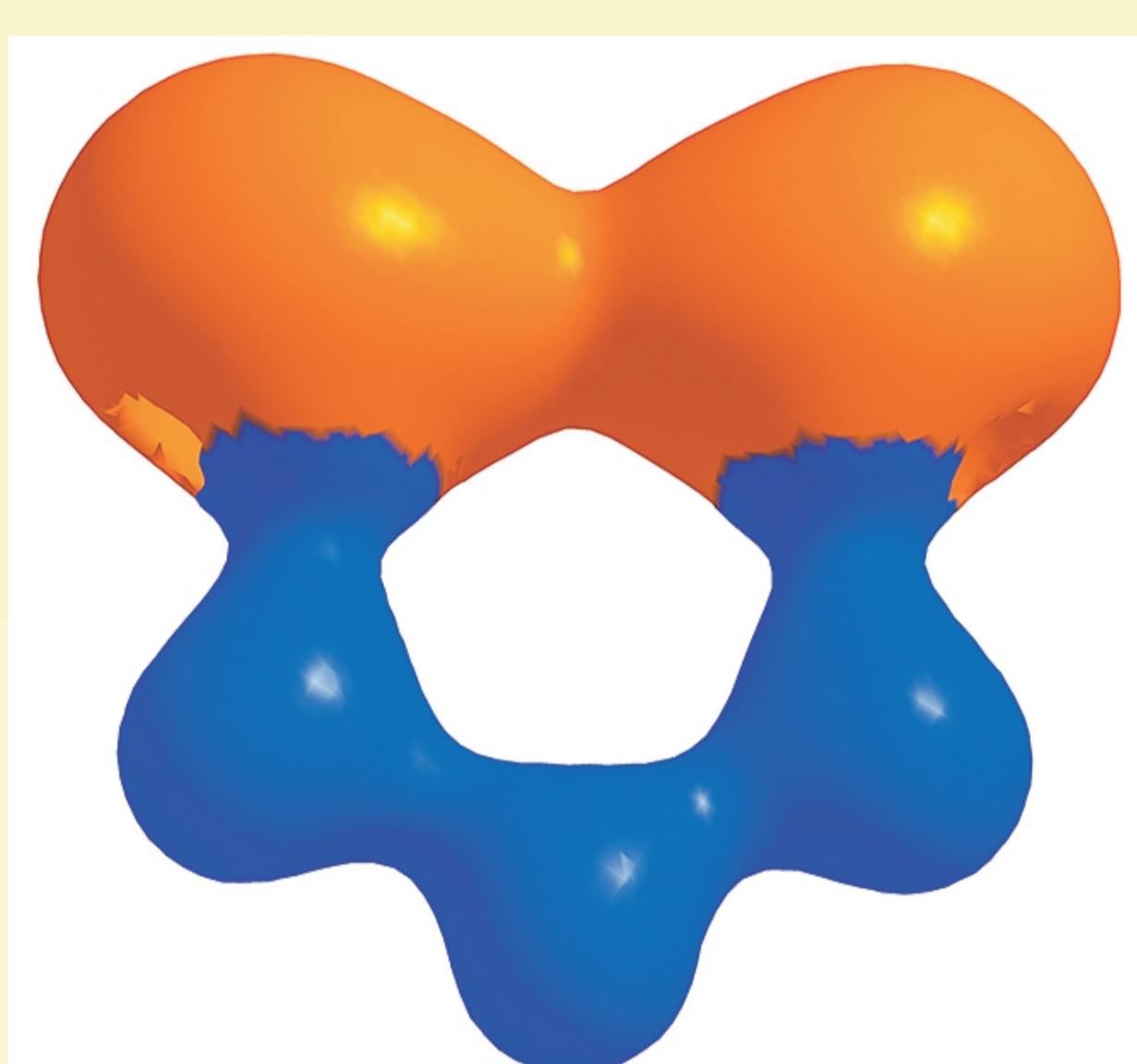
Notícies Inorgàiques

Any 14, Núm. 72, Setembre de 2015

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

Un Cp inorgànic

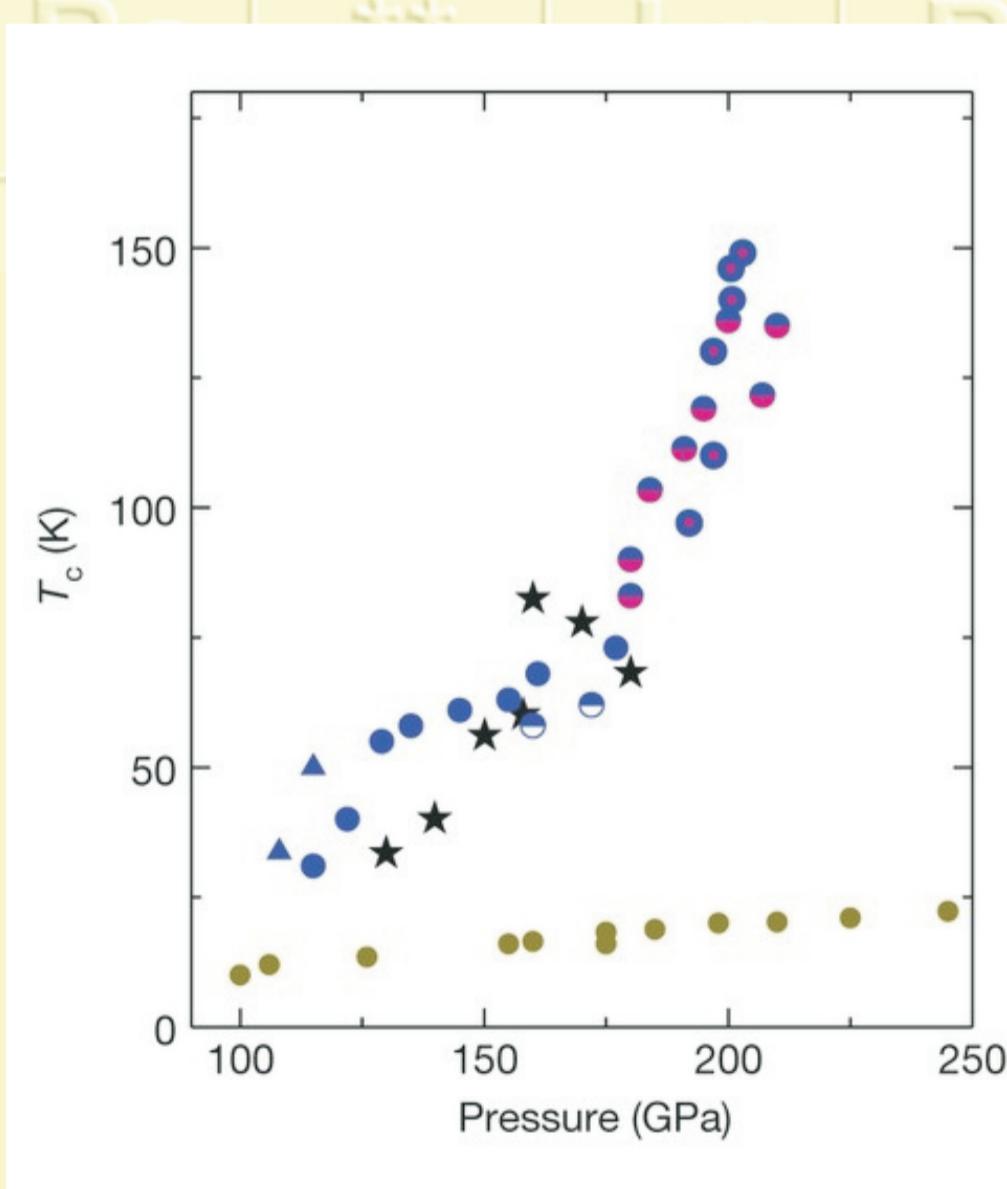
Chemists at MIT have created a stable aromatic anion composed solely of pnictogens—the elements that make up the periodic table column to the right of carbon (Ch. C. Cummins et al., *Science*, **2015**, 348, 1001; DOI:10.1126/science.aab0204). They made the inorganic aromatic ring, which has the formula $P_2N_3^-$, by transferring diphosphorus to the azide anion using a sodium cryptand cation. They crystallized a complex of the resulting salt and determined that the anion is planar and has an aromatic π -electron system, as indicated by electron structure calculations. Until now, the chemists note, to isolate compounds with multiple bonds between pairs of phosphorus atoms, chemists had to use bulky substituents to block the reactive π bond. But no such bulky groups were needed to isolate $P_2N_3^-$. Now, the stabilization is best construed as aromaticity, an effect traditionally reserved for the domain of organic chemistry.



This image shows the electron density of an all-pnictogen aromatic anion.
P = orange, N = blue.

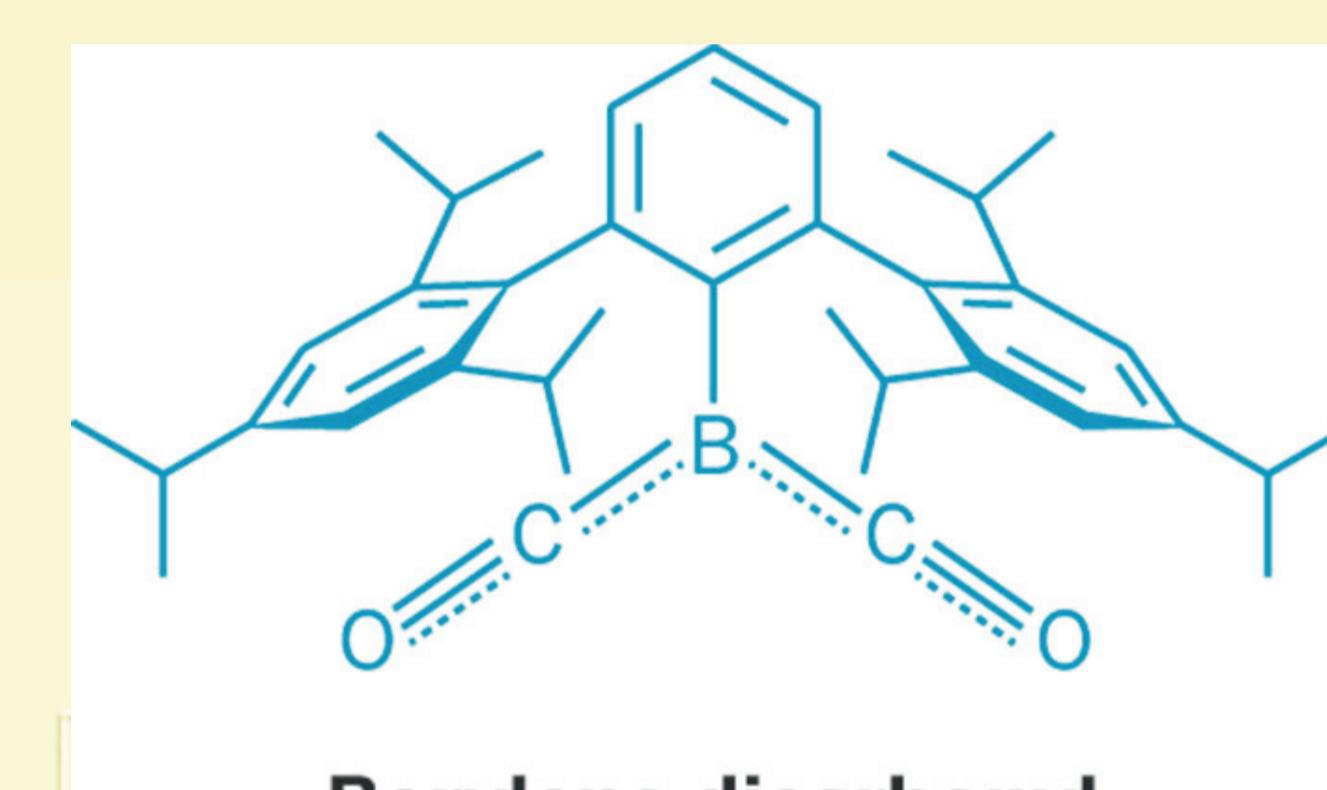
H₂S: nou record de superconductivitat

Squeezing hydrogen sulfide to extreme pressures results in a sulfur hydride phase that exhibits superconductivity at a record-setting 203 K (M.I. Eremets et al., *Nature*, **2015**, 525, 73; DOI: 10.1038/nature14964). Discovered just over a century ago, superconductors are a small group of materials that conduct electricity without losing energy in the form of heat. Such materials could be used to make energy-efficient electric motors and power distribution systems. Most superconductors, however, exhibit that property only when they are chilled below an impractically low critical transition temperature (T_c). The hydride's T_c is roughly 70 K warmer than that of the previous record holder, a copper oxide containing mercury, calcium, and barium. The analysis shows that as the researchers compressed H₂S to gigapascal pressures, the sulfide decomposed, yielding elemental sulfur and H₃S, the hydride responsible for the observed superconductivity. The finding confirms theoretical predictions that simple covalently bonded hydrogen-rich compounds can exhibit remarkably high T_c values and raises hopes for finding simple room-temperature superconductors.



Pressure dependence of T_c .

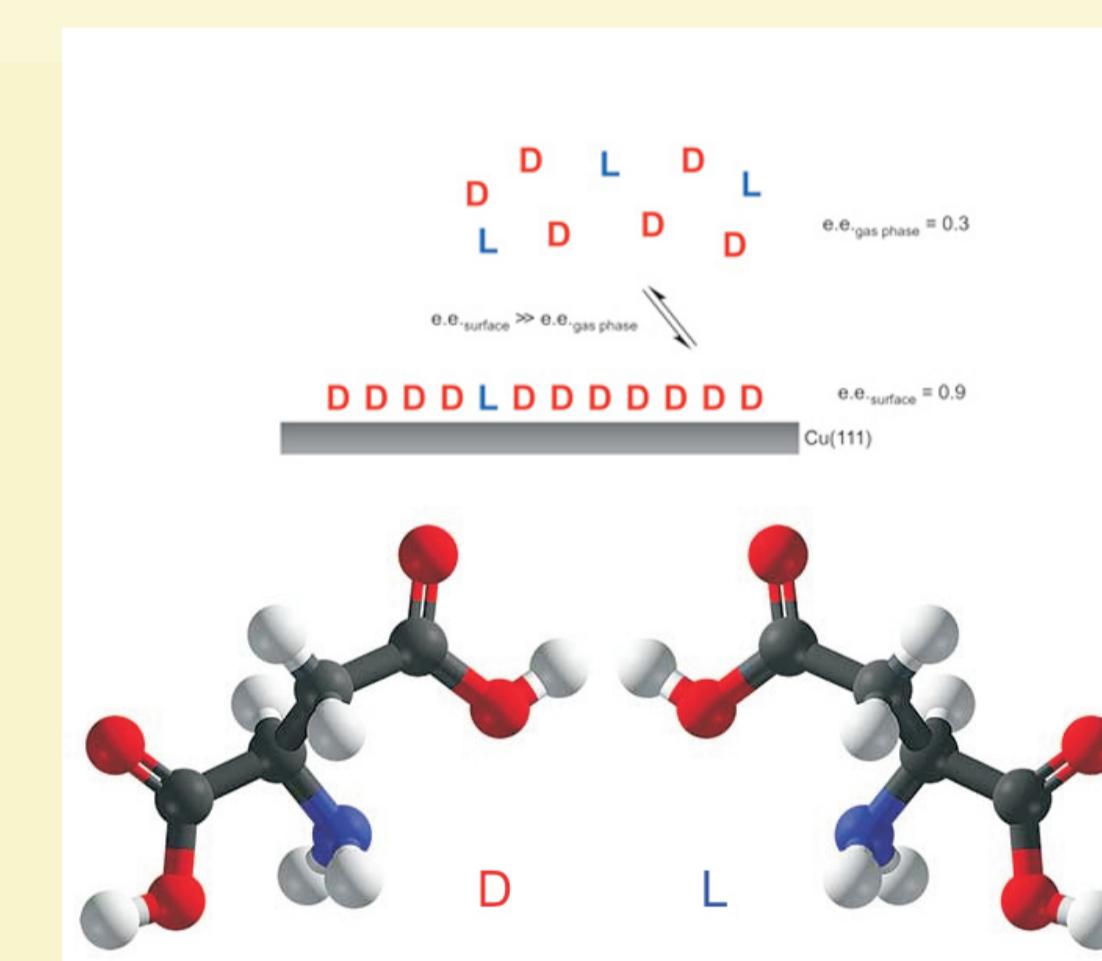
Chemists have built a new compound in which boron donates and accepts electron pairs when binding two carbon monoxide molecules, a peculiar situation that has the nonmetal main-group element acting like a transition metal (H. Braunschweig et al., *Nature* **2015**, 522, 327; DOI: 10.1038/nature14489). Until now, no elements outside of the transition metals have been observed to react directly with two or more CO molecules. Now, a team that figured out a way to make it happen. The researchers prepared a molybdenum pentacarbonyl complex bearing a borylene ligand, R₂Mo(CO)₅, where R is 2,6-di(2,4,6-trisopropylphenyl). After refluxing the complex in a CO-saturated benzene solution, they removed Mo(CO)₅ and isolated blue crystals of the borylene dicarbonyl compound, R₂(CO)₂. Boron has only three valence electrons and is known for the quirky ways it can form bonds. In borylenes, boron uses one electron to bond with the bulky substituent. The remaining two electrons form a lone pair in one orbital, and two orbitals remain vacant. Boron can therefore accept electrons from two CO molecules (σ bonding) as it contributes the lone pair to the CO molecules (π backbonding). This donor-acceptor behavior mimics that of transition-metal carbonyl complexes.



Borylene dicarbonyl

El coure metàl·lic augmenta la quiralitat

The curious observation that certain biochemical building blocks found in living organisms come almost exclusively in just one enantiomeric form—L for amino acids and D for sugars—has led scientists to propose mechanisms explaining its origins. Researchers have now added another piece to this homochirality-of-life puzzle. They determined that adsorption of gas-phase chiral molecules on an achiral surface can amplify the enantiomeric excess of the mixture (A.J. Gellman et al., *Nat. Chem.*, **2015**, 7, 520; DOI: 10.1038/nchem.2250). For years, scientists have studied the role that adsorption processes may play in enantioselectivity. But until now the focus has been on chiral surfaces, including naturally occurring chiral minerals such as quartz. Surprisingly, Yun and Gellman found that a chiral surface is not required for adsorption-based enantiomeric enrichment. The team exposed an achiral copper (111) surface to a ¹³C-labeled gas-phase mixture of D- and L-aspartic acid that was slightly enriched in the D isomer. On the basis of mass spectrometry analysis of adsorbed enantiomers and numerous control experiments, the team showed that adsorption on the achiral surface increased the D isomer's enantiomeric excess from roughly 30% to nearly 90%.



Breus

- Els «sleeping papers» - articles publicats fa moltes dècades que comencen a rebre moltes citacions - són cada cop més presents en la bibliografia química. A tall d'exemple, l'article de H. Freundlich «Models adsorption from solution/removal of metals drugs from drinking water», aparegut al *Z. Phys. Chem.* l'any 1909, ha rebut quasi 3000 cites des del 2002, l'any que va «despertar» (A. Flammini et al., *Proc. Natl. Acad. Sci. USA*, **2015**, 112, 7426; DOI: 10.1073/pnas.1424329112).
- S'ha fet un pas de gegant en el projecte de redefinir el kilo a partir de la constant de Planck, h, que està previst presentar l'any 2018. La nova aportació ha estat la determinació del nombre d'Avogadro amb una precisió de 1.8×10^{-8} (G. Mana et al., *J. Phys. Chem. Ref. Data*, 2015, 44, 031209; DOI: 10.1063/1.4921240).
- De les 50 empreses químiques més importants del món 19 són asiàtiques, 18 europees, 11 dels EUA, 1 del Brasil i 1 de Sud Àfrica. (*Chem. Eng. News*, **2015**, 93 (16), 14).

Avui recomanem

El llibre «*El tío tungsteno. Recuerdos de un químico precoz*» (Anagrama, Barcelona, 2003), unes memòries de la infantesa del neuròleg anglès, Oliver Sacks, traspassat el passat mes d'agost, que ha estat un dels grans divulgadors de la Taula Periòdica (*Not. Inorg.*, **2003**, 10).

L'element

L'element número 72, **hafni**, fou descobert l'any 1923, pels químics danesos Dirk Coster i Georg von Hevesy, en minerals de zirconi. El seu nom prové d'*Hafnia*, el terme llatí de Copenhaguen. La seva existència havia estat predicta per Mendeléiev l'any 1869, i conjuntament amb el reni – identificat el 1925 – són els dos últims elements no radioactius descoberts. La poca abundància – 3.3 ppm a l'escorça terrestre –, la dificultat de separar-lo del zirconi i les propietats molt semblants d'aquests dos elements, fan que no hi hagi gaires aplicacions específiques de l'hafni. Els usos més destacats són en la indústria nuclear, com a component de diversos aliatges que absorbeixen neutrons; s'ha emprat com a filament en làmpades d'incandescència. Es coneixen sis isotops de l'hafni natural, dels quals cinc són estables, i el ¹⁷⁴Hf és radioactiu amb una vida mitjana de 10^{15} anys que s'usa com a marcador geològic. No s'ha detectat la seva presència en el cos humà ni tampoc se li coneix cap activitat biològica.

