UNIVERSITAT DE BARCELONA
Química Inorgànica

Notícies Inorgàniques

Any 16, Núm. 81, Novembre de 2017

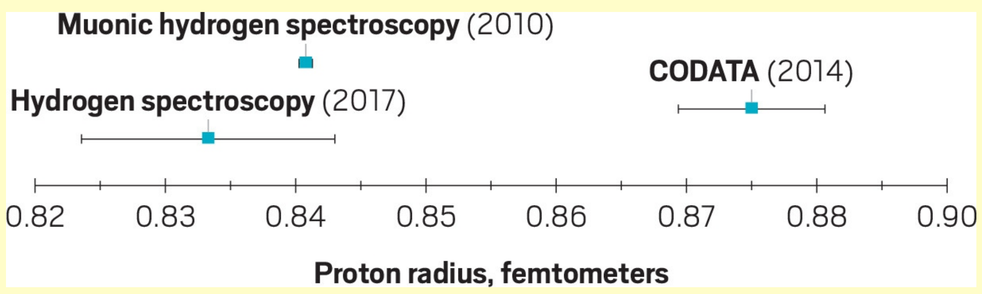
http://www.ub.edu/inorgani/dqi.htm

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

El protó més petit i més lleuger

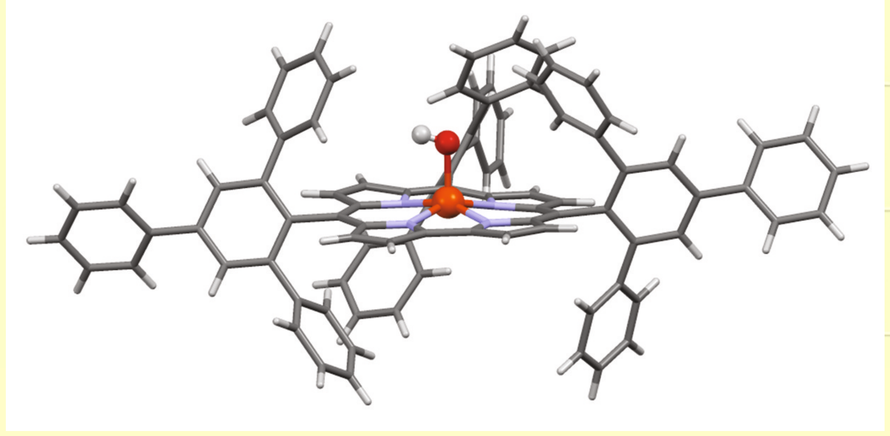
The radius of the proton has been puzzling scientists since 2010, when a study suggested that the proton's radius is significantly smaller than the consensus value, about 0.84 femtometers compared with 0.88 fm. New spectroscopic work measures the proton radius using hydrogen spectroscopy or electron scattering(A. Beyer et al., *Science* **2017**; DOI: 10.1126/science.aah6677) to yield a proton radius of 0.8335 fm.

On the other hand, the proton may be also significantly lighter than currently believed—1.007276466583 amu compared with 1.007276466879 amu— (S. Sturn et al., *Phys. Rev. Lett*. **2017;** DOI: 10.1103/PhysRevLett.119.033001). A lower proton mass could affect the values of physical constants such as the Rydberg constant, which represents the lowest-energy photon that can ionize a hydrogen atom from its ground state.



El citocrom P450, desempescat

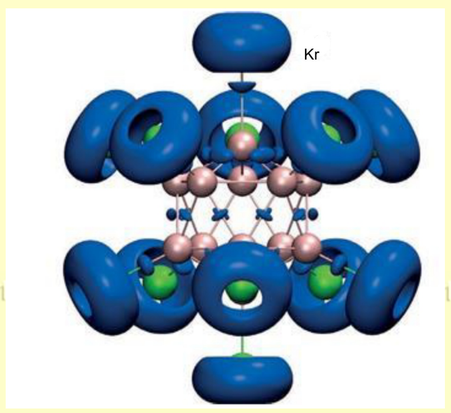
For more than 40 years, chemists and biologists have used the radical rebound mechanism to describe what happens when enzymes with transition metals, such as cytochrome P450, hydroxylate C–H bonds. Such enzymes first remove a hydrogen atom from a C–H bond using a high-valent metaloxo species. This produces a carbon radical and a metal-OH intermediate that then rebounds—the hydroxyl group moves onto the carbon radical and the metal is reduced by one electron. Although plenty of circumstantial evidence suggests this is what happens, observing the rebound step in this reaction has been impossible because it is fast compared with the hydrogen atom removal step. Now, a team has created the first model system in which the rebound reaction can be observed (D.P. Goldbrg, et. al., *J. Am. Chem. Soc*., **2017**; DOI: 10.1021/jacs.7b07979). The system features Fe–OH ensconced in a tris(triphenyl)phenyl corrole ligand, which stabilizes the high redox level of the Fe complex and has sufficient steric bulk to prevent dimerization—a problem that often plagues FeOH systems.



This model system makes it possible to observe the radical rebound reaction (C is gray, H is white, N is blue, O is red, Fe is orange)

Un anió electròfil!

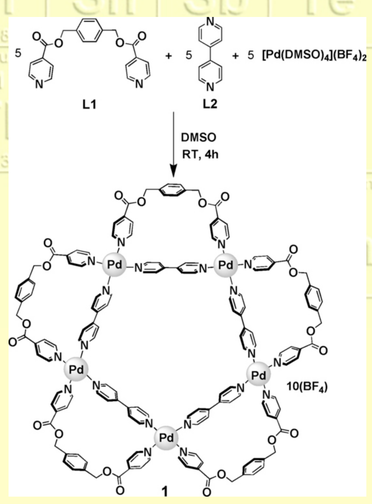
Although a superelectrophilic anion sounds like an oxymoron, a boron cluster that fits this description has been made. Usually, anions are described as nucleophilic: having a surplus of electrons and wanting to donate those to an electrophile, a chemical species short on electrons.A team (M Rhodenburg et al, *Angew. Chem., Int. Ed*., **2017**; DOI: 10.1002/anie.201702237) has now found a dodecaborate $[B_{12}Cl_{11}]^-$ that, despite being an anion, is electrophilic. It strongly binds the noble gases xenon and krypton – a property that chemists thought to be reserved for cationic compounds referred to as superelectrophiles. Having examined the $[B_{12}Cl_{11}]^-$ by mass spectrometry, infrared spectroscopy and through computational analysis, the scientists found that it binds well to nonpolar nucleophiles like nitrogen or noble gases, but not to polar nucleophiles such as water. The cluster reacts like a cationic, electrophilic boron atom inside a dianionic framework, leading the team to dub it a 'dipole-discriminating electrophilic anion'.



Visualisation of the orbital energies of $[B_{12}Cl_{11}]^-$ (chlorine – green; boron – pink) as it displays its surprising behaviour of binding to krypton, something that wouldn't be expected of an anion.

Ha nascut una estrella... molecular

One thing chemists have learned over the years is that geometry is innate in molecular structures. Besides regular polygons, unexpected shapes often emerge when researchers explore new combinations of metal and ligand components. In one of the latest examples, a team has built a "truncated molecular star," a pentagram-shaped palladium coordination complex (D. Kumar et al., *Chem.Eur. J*., **2017**; DOI: 10.1002/chem.201702264). The new molecular star is unique not just because of its pointless shape—a pentagon ringed by isosceles trapezoids—but also because it appears to be the first heteroleptic, nonchelating, multicompartment supramolecular coordination complex built with five palladium atoms. The researchers assembled the compound from a palladium(II) salt paired with equal amounts of 1,4-phenylenebis(methylene)diisonicotinate and 4,4′- bipyridine ligands in a one-pot reaction at room temperature.



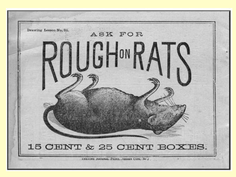
Breus

- Diverses editorials científiques, inclosa l'American Chemical Society, han presentat una demanda judicial contra *ResearchGate*, amb l'objectiu de limitar la difusió d'articles a les xarxes, sense respectar els drets d'autor. (*C&EN*, 9 d'octubre de 2017; p. 22)
- Una membrana constituïda per MOF ZIF-8, sotmesa a l'acció d'un camp elèctric, és capaç de separar propè de propà. (*Science* **2017**; DOI: 10.1126/science.aal2456)
- Dels 175 guardonats amb el Premi Nobel de Química, només quatre són dones: Marie Curie, Irène Joliot-Curie, Dorothy Crowfoot Hodgkin i Ada E. Yonath. En l'última reunió de l'ACS tingué lloc el col·loqui, "*Ladies in Waiting for Nobel Prizes: Overlooked Accomplishments of Women Chemists*", on es discutiren les aportacions de les dones que haurien merescut guanyar-lo. (*C&EN*, 11 de setembre de 2017; p. 22-24)

Avui recomanem

El video penjat a YouTube -*The 2017 Nobel Prize in Chemistry: Cryo-electron microscopy explained*- que explica la criomicroscopia electrònica. Aquesta tècnica permet la resolució estructural de biomolècules en solució, ha estat desenvolupada per Jacques Dubochet, Joachim Frank i Richard Henderson, fet pel qual han obtingut el Premi Nobel de Química d'enguany. (www.nobelprize.org/nobel_prizes/chemistry)

L'element



L'element número 81, **tal·li**, fou descobert per William Crookes l'any 1861, en fer anàlisis espectroscòpiques de residus de tel·luri, en una planta de fabricació d'àcid sulfúric. Paral·lelament el físic francès Claude-Auguste Lamy, aconseguí obtenir-ne un lingot, fet pel qual l'Acadèmia Francesa el reconegué com el descobridor del nou element. Crookes es queixà de manera furibunda i s'inicià una batussa dura i intensa, amb punts de xenofòbia inclosos. El nom prové del grec "θαλλός" (thallos) que vol dir branca verda, pel seu espectre d'emissió. No és un element rar, és 10 vegades més abundant que la plata, però es coneixen pocs minerals de tal·li –*crookesita* (Cu_7TlSe_4) i *lorandita* ($TlAsS_2$)– i es troba majoritàriament, en minerals de potassi i cesi. Aquest metall és molt tou i mal·leable i es pot tallar fins i tot amb un ganivet. Quan s'exposa a l'aire, primer té una lluïssor metàl·lica però ràpidament es torna d'un color gris blavós que recorda el plom. El tal·li i els seus compostos són molt tòxics i s'han de manipular amb molta cura, perquè el contacte amb la pell és molt perillós. Tradicionalment s'ha emprat com a raticida i insecticida. És un verí popular en la literatura de "lladres i serenos" en particular en l'obra d'Agatha Christie, i el seu ús en el vida real ha donat lloc a moltes llegendes urbanes.