

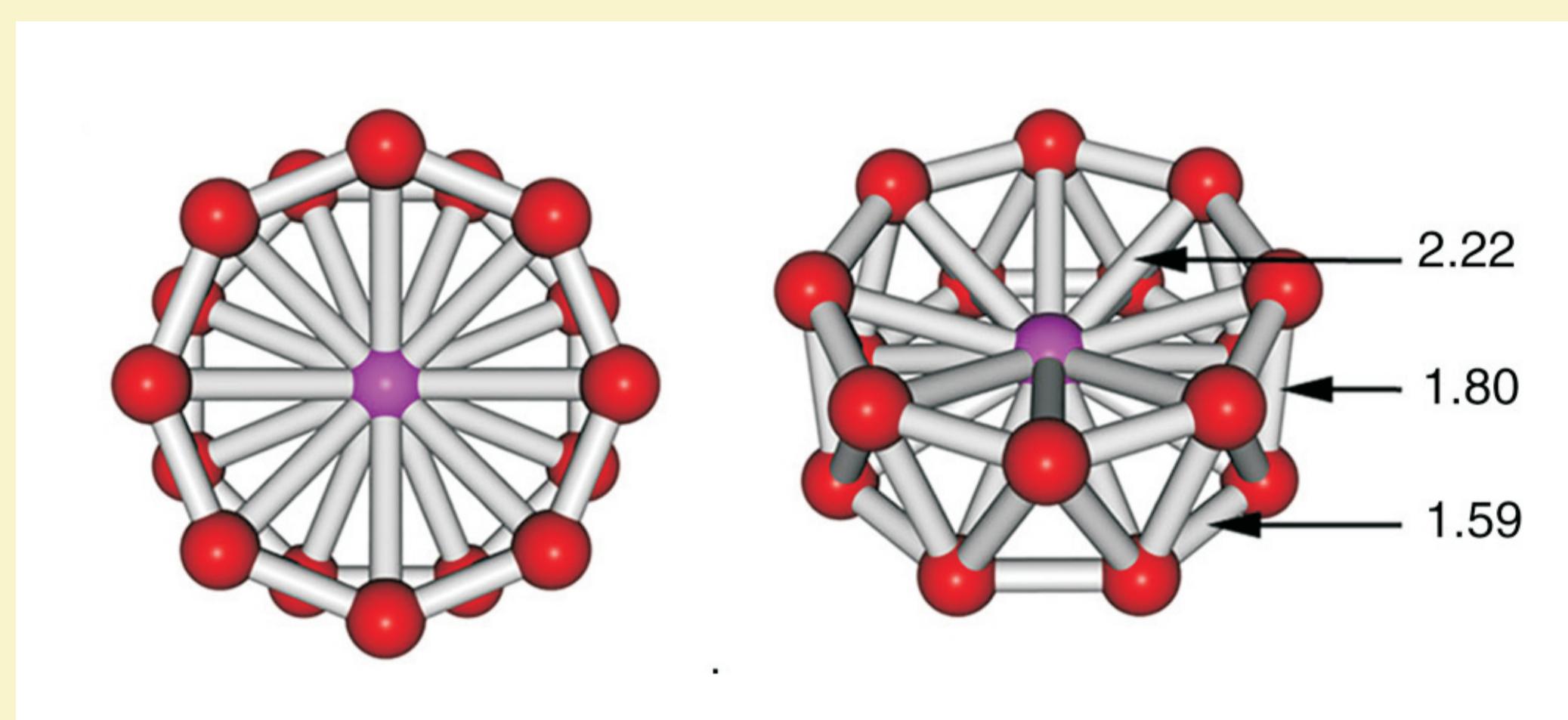
# Notícies Inorgàiques

Any 14, Núm. 73, Novembre de 2015

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

## Un nou rècord de coordinació: 16!

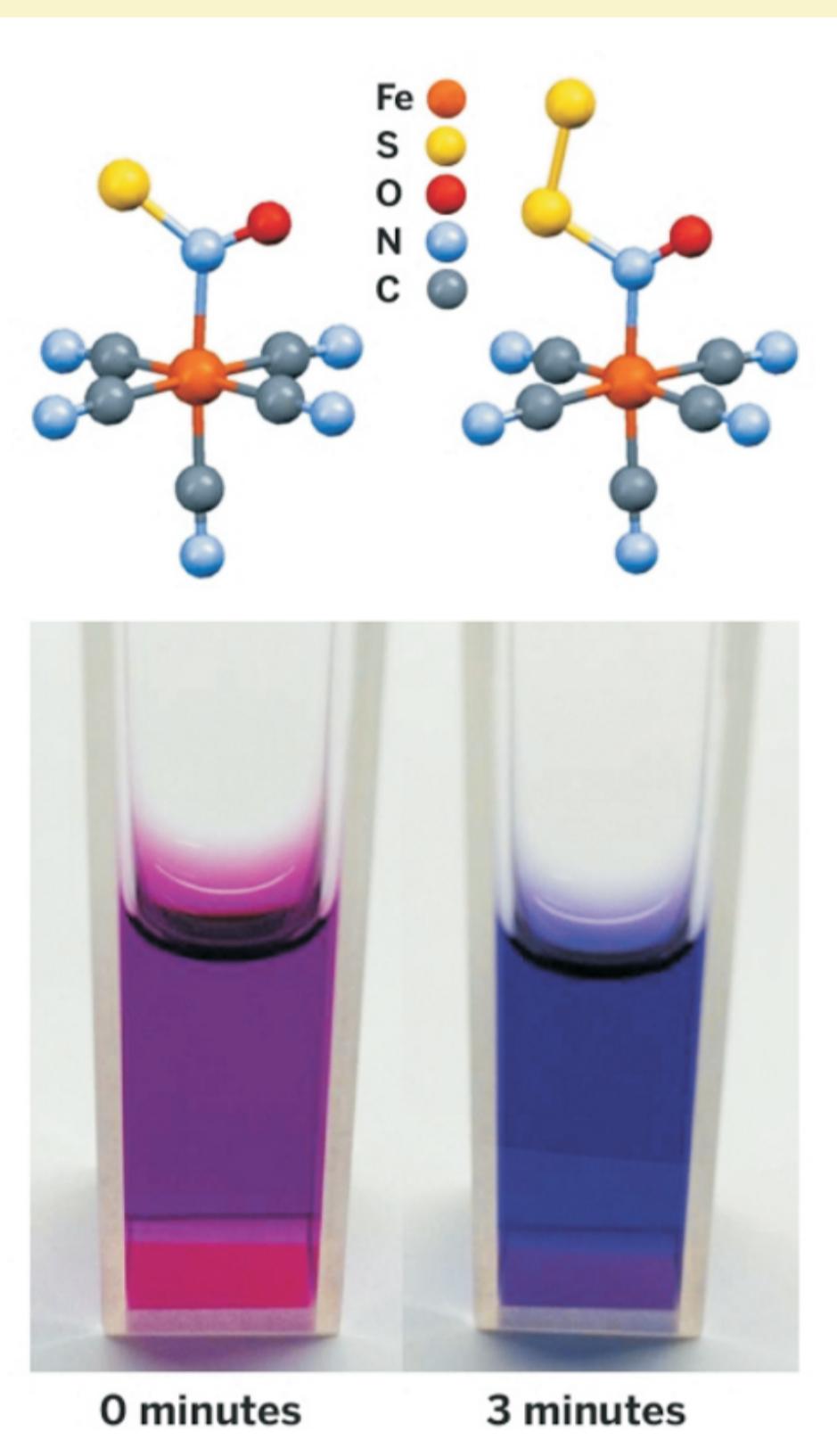
A multinational research team has created a drum-shaped cobalt-boron species in the gas phase,  $\text{CoB}_{16}^-$ , which sets a record for highest coordination number in a molecule. The sandwich complex created (A. Boldyrevet al., *Nat. Comm.*, **2015**, *6*:8654; DOI:10.1038/ncomms9654) consists of two  $\text{B}_8$  rings connected to the central cobalt atom via 16 bonds, the theoretical maximum based on the number of available atomic orbitals. Boron is particularly useful in such efforts because the electron-deficient element tends to share electron pairs with multiple other atoms to form strongly bonded network structures. The researchers made  $\text{CoB}_{16}^-$  by pressing cobalt and boron into a pellet and then vaporizing it with a laser beam. They used a mass spectrometer to select  $\text{CoB}_{16}^-$  clusters from the product mixture and analyzed them with photoelectron spectroscopy. The previous record stood with a 15-coordinate thorium complex,  $\text{Th}[(\text{H}_3\text{B})_2\text{N}(\text{CH}_3)_2]_4$ , which remains the most-coordinated molecule that has been isolated in a condensed state.



A top view (top) and side view (bottom) of the  $\text{CoB}_{16}^-$ . The connections between atoms help visualize the structure but do not necessarily indicate bonds.

## Un misteri de 170 anys resolt

A 170-year-old chemical color mystery has been solved with  $^{17}\text{O}$  NMR spectroscopy and other analytical techniques. The Gmelin reaction, first observed in the 1840s by German chemist Leopold Gmelin, is considered one of the most intense color-forming reactions. When nitroprusside ( $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ ) and sulfide combine they produce a brilliant red-violet intermediate that converts rapidly to a deep-blue intermediate. The red-violet intermediate has been proposed to be  $[\text{Fe}(\text{CN})_5(\text{HSNO})]^{3-}$  or  $[\text{Fe}(\text{CN})_5(\text{SNO})]^{4-}$ , but its structure was never confirmed. The identity of the blue intermediate has remained unknown, as has that of its decomposition products. Now, (Gang Wu et al., *Chem. Eur. J.* **2015**, DOI: 10.1002/chem.201503353), have now used  $^{17}\text{O}$ ,  $^{15}\text{N}$ , and  $^{13}\text{C}$  NMR along with UV-visible and infrared spectroscopy and quantum chemical computations to show that the red-violet intermediate is  $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{S}]^+$  and the blue molecule is  $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SS}]^+$ .



## Breus

- El Premi Nobel de Química d'enguany ha estat atorgat a Tomas Lindal (Francis Crick Institute, UK), Paul Modrich (Duke University, USA) i Aziz Sancar (University of North Carolina, USA), pels seus estudis sobre els mecanismes de reparació de l'ADN. S'ha de lamentar que, un any més, l'Acadèmia Sueca no hagi valorat descobriments ni aportacions més properes a la Química bàsica.
- L'iterbi és una mica més lleuger del que es creia. Una nova determinació del pes atòmic acceptada per la IUPAC, dóna el valor de 173.045, corregeix així l'anterior de 173.054.
- A l'última reunió de l'ACS, celebrada aquest estiu a Boston, s'ha analitzat en detall el paper que fa i, sobretot, pot fer la **Viquipèdia** en l'ensenyament de la Química a tots els nivells educatius, i fa una crida als professors a convertir-se en editors de l'enciclopèdia (*Chem. Eng. & News*, **93** (3), 14 de setembre de 2015).

## Avui recomanem

La web de l'Any de la llum declarat per l'ONU, **International Year of Light and Light-based Technologies (IYL 2015)** amb l'objectiu: «which will highlight to the citizens of the world the importance of light and optical technologies in their lives, for their futures, and for the development of society. It is a unique opportunity to inspire, educate, and connect on a global scale» (<http://www.light2015.org/Home.html>).

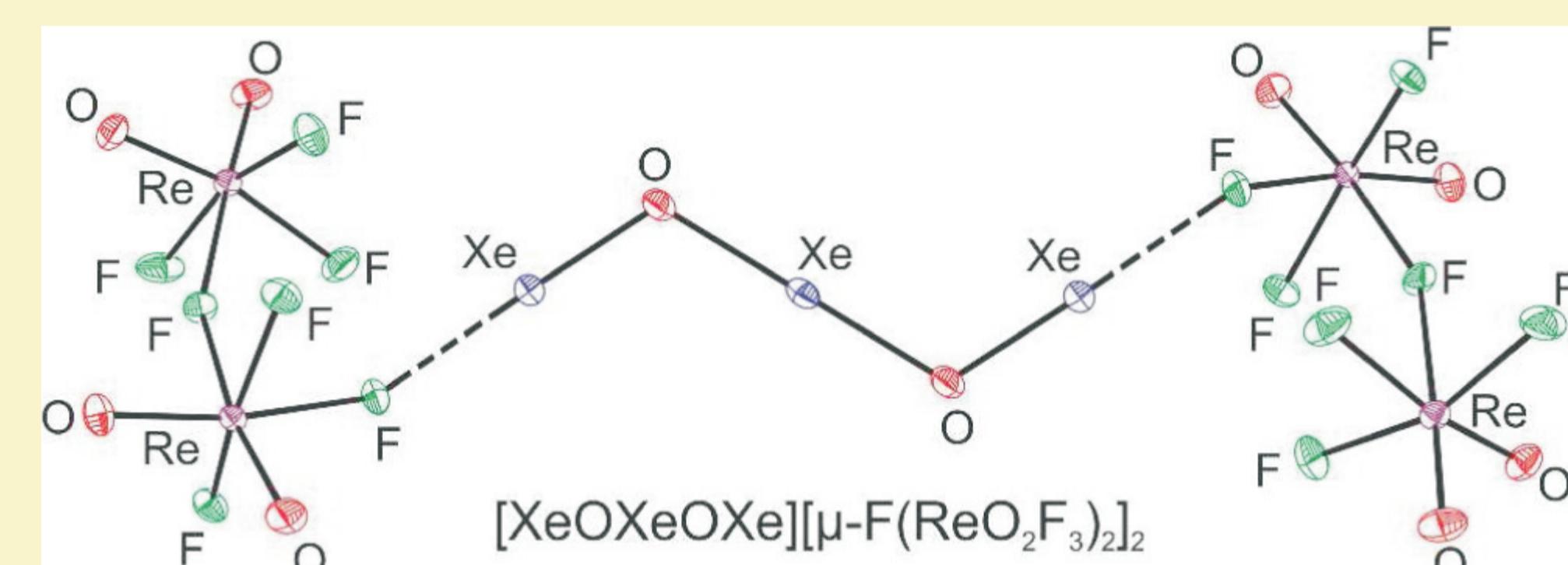
## L'element



L'element número 73, **tàntal**, fou descobert pel químic suec Anders Ekeberg l'any 1802, però la major part de químics pensaven que era el mateix element que el niobi. Després de moltes propostes i contrapropostes, la seva existència fou confirmada l'any 1866 per Jean Charles Galissard de Marignac. A l'estat pur no fou preparat fins el 1903, per Werner von Bolton. El seu nom prové de la mitologia grega "Tantalos", pare de "Niobe". És un element rar amb una abundància a l'escorça terrestre de  $1.5 \times 10^{-4}\%$ , unes quinze vegades menys que l'or. El principal mineral per a la seva extracció és el *coltan*, nom comercial que rep una mescla de columbita – principal font del niobi, que anteriorment s'anomenava columbi – i la tantalita. La principal aplicació és com a component de diversos aparells electrònics: telèfons mòbils, reproductors de DVD, GPS, videoconsoles, etc. El principals productors de *coltan* són Austràlia, amb el 10% de les reserves mundials, Brasil amb el 5%, Tailàndia amb un altre 5% i la regió dels Grans Llacs Africans (República Democràtica del Congo), aquesta última amb una estimació del 80% de les reserves mundials. L'explotació en aquesta zona fou una de les principals causes de la denominada «Segona guerra del Congo» o «Guerra del *coltan*», que entre 1998 i 2003 provocà la mort de més de 5 milions de persones. No s'ha detectat la seva presència en el cos humà ni tampoc se li coneix cap activitat biològica, fet que el fa apropiat en cirurgia com a material de diversos implants dentals i ossis. Com a curiositat, una forma del TaC és més dur que el diamant i té un p. f. de 3738 °C.

## Un compost amb tres xenons i més...

The noble gases, which occupy the last column of the periodic table, were once thought to be inert and not capable of forming molecules. It has now been more than 50 years since that thinking has been debunked, and in that time an array of noble-gas compounds have been reported. Even so, when new versions are announced they are still considered noteworthy. In the latest examples, (G. J. Schrobilgen, et al., *J. Am. Chem. Soc.*, **2015**, *137*, 13398; DOI: 10.1021/jacs.5b08765), have reported two new types of xenon molecules. In one case, the researchers ran a reaction of  $\text{XeF}_2$  with  $\text{ReO}_3\text{F}$  in anhydrous HF to prepare the bridging complex  $[\text{XeOXeOXe}][\mu\text{-F}(\text{ReO}_2\text{F}_3)_2]$ . The cation is an unprecedented example of a xenon(II) oxide and noble-gas oxocation, as well as a rare example of a noble-gas dication. In a second case, (G. J. Schrobilgen, et al., *Angew. Chem. Int. Ed.*, **2015**, *47*, 14169; DOI: 10.1002/anie.201507635) the researchers treated the potent oxidant  $\text{XeF}_6$  with acetonitrile in a chlorofluorocarbon solvent to make the shock-sensitive compounds  $\text{F}_6\text{XeNCCH}_3$  and  $\text{F}_6\text{Xe}(\text{NCCH}_3)_2\cdot\text{CH}_3\text{CN}$ . These are the first examples of molecules with  $\text{Xe(VI)}-\text{N}$  bonds; with X-ray crystal structures and computational analysis, the researchers provide additional insight into xenon's electronic structure and bonding abilities.



## Energia solar de ferro

Some materials scientists have been on a quest to build energy transformation and storage devices, such as solar cells, using Earth-abundant materials. Now, researchers in Sweden have designed an iron-based light-harvesting complex that collects solar energy and transmits it to semiconductor particles with exceptional efficiency (*Nat. Chem.*, **2015**, DOI: 10.1038/nchem.2365). Those processes are the first steps in producing electric power in the widely studied family of photovoltaic devices known as dye-sensitized solar cells (DSSCs). Shining sunlight on a DSSC excites electrons in a layer of light-absorbing molecules. These molecules, which are referred to as dyes or sensitizers, inject the excited electrons into semiconductor particles such as  $\text{TiO}_2$ , to which the molecules are anchored. From there, the electrons migrate to an electrode to produce electric current.

