## UNIVERSITAT DE BARCELONA B Química Inorgânica

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### Polioxometal-lats quirals i estables

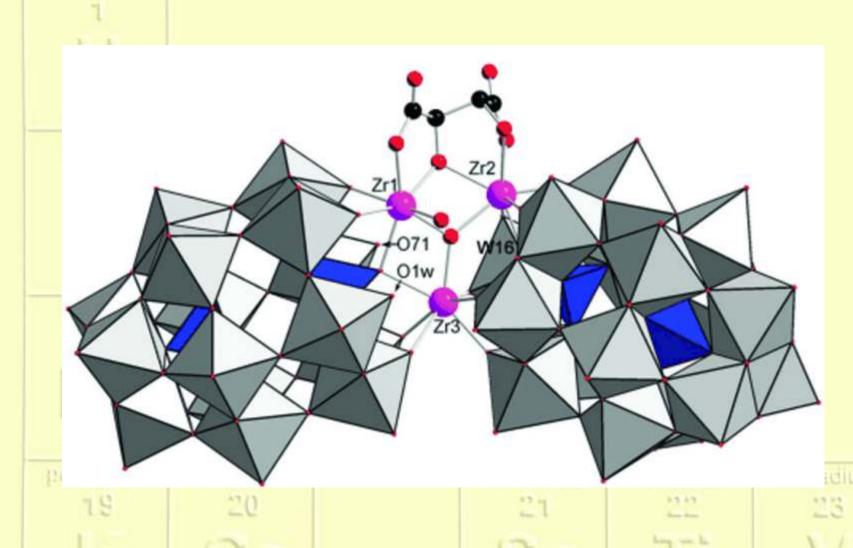
The first chiral, nanosized metal-oxide complexes that retain their enantiomeric purity under chemical and thermal conditions that normally cause racemization have been synthesized and characterized [C.L. Hill and coworkers, *Angew. Chem. Int. Ed.*, **2005**, *44*, 3540]. Enantiopure polyoxometalates (POMs) of this kind have long been sought for potential applications such as microporous solids, asymmetric catalysts, and inorganic pharmaceuticals (chiral cluster antiviral agents, for example).

Chiral POM complexes synthesized in earlier studies either have a chiral POM unit that is not enantiopure or have an achiral POM unit linked to a chiral organic ligand. In contrast, the new POM complexes are enantiopure, owe their chirality primarily to the POM unit (not to the organic ligand), and are stable in both solid-state and solution forms.

## Oxigen diamagnètic a pressió elevada

A solid-state transformation in oxygen that physicists had long thought might occur has finally been observed. Oxygen is a highly magnetic molecular solid at low temperatures, but physicists had for years speculated that its magnetism disappears at high pressures. Now Igor Goncharenko from the Laboratoire Léon Brillouin (LLB) in Saclay, near Paris, has found that oxygen becomes non-magnetic at about 80,000 times atmospheric pressure [*Phys. Rev. Lett.*, **2005**, *94*, 205701].

Solid oxygen is the only elementary molecular magnet known. At atmospheric pressure (about  $10^{-4}$  gigapascals) it is an anti-ferromagnetic insulator but becomes a superconductor and metal at about 96 gigapascals. Theory predicts that oxygen should lose its magnetic properties before it transforms into a superconductor, but this non-magnetic state has never been seen directly in an experiment before. Now Goncharenko has observed this magnetic "collapse" for the first time in experiments at the LLB.



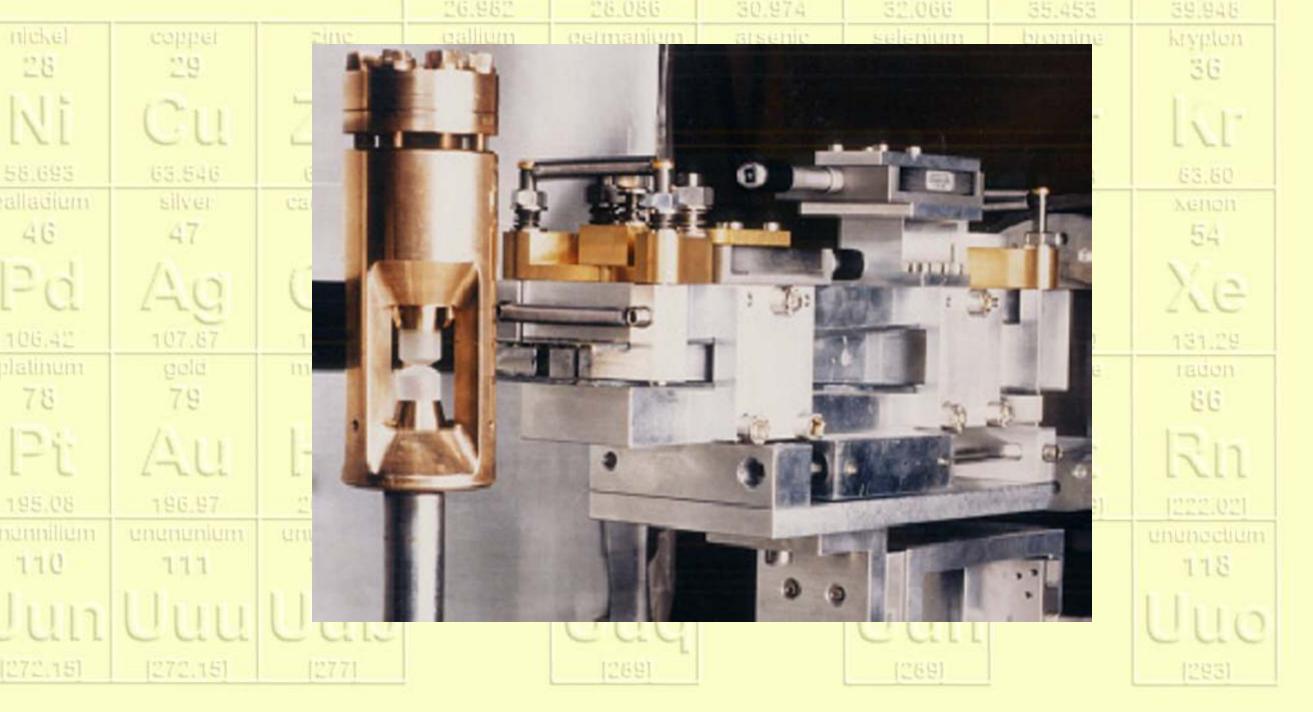
In complex synthesized by Hill and coworkers, two large polyoxotungstate units (in which blue = phosphate) are assembled around a hub of zirconium ions (purple) and tartrate (red = oxygen, black = carbon).

## Metal-lúrgia en solució

A solution-phase technique to make multimetallic nanocrystals of high structural complexity has been developed by assistant chemistry professor Raymond E. Schaak and his group at Texas A&M University. The approach allows materials to be prepared at relatively low temperatures in only a few minutes compared to traditional solid-state reactions involving high-temperature sintering or melting that can take days or weeks to carry out.

The technique is a modification of standard nanocrystal synthesis methods that the Texas A&M chemists call "metallurgy in a beaker." Schaak's group originally developed the process while working with gold and copper nanoparticles, which aggregate in solution to form nanocomposites that thermally transform at low temperatures into bimetallic nanocrystals. The composition of the compounds can be controlled by the ratio of reactants. The researchers have found the process to be general and have extended it to make trimetallic AuCuSn<sub>2</sub> and AuNiSn<sub>2</sub> nanocrystals that have new structures not observed in bulk systems [*J. Am. Chem. Soc.* **2005**, *127*, 7326].

The experiment involved scattering neutrons from a tiny polycrystalline sample of solid oxygen just 0.5 cubic millimetres in size. The sample could be compressed to high pressures using two tiny anvils. By monitoring how the neutrons scattered from the sample as the pressure increased, Goncharenko found that the long-range magnetic order completely disappears at about 8 gigapascals, which is far below the insulator-metal or superconductor transition.



#### Un clúster molt ric en hidrogen

A platinum-rhenium bimetallic cluster with an unusually high degree of electronic

unsaturation around the metal atoms has been discovered to add an equally unusual

amount of hydrogen, forming a hydride complex. The discovery could provide new

insight into hydrogenation catalysis and hydrogen storage applications, according to

Richard D. Adams and Burjor Captain of the University of South Carolina, Columbia,

who conducted the research [Angew. Chem. Int. Ed. 2005, 44, 2531].

They prepared AuCuSn<sub>2</sub> by heating a solution of HAuCl<sub>4</sub>,  $Cu(C_2H_3O_2)_2$ , SnCl<sub>2</sub>, and poly(vinylpyrrolidone) in tetraethylene glycol to 70 °C, then adding dilute NaBH<sub>4</sub> and heating to 120 to 200 °C for 10 minutes.

# Adams' group has been synthesizing platinum and palladium compounds containing the bulky tri-tert-butylphosphine ligand (L), including a trigonal bipyramid cluster, $Pt_3Re_2(CO)_6(L)_3$ , which is deficient by 10 electrons. It reacts at room temperature with $H_2$ (a good source of electrons) to form the hexahydride complex shown.

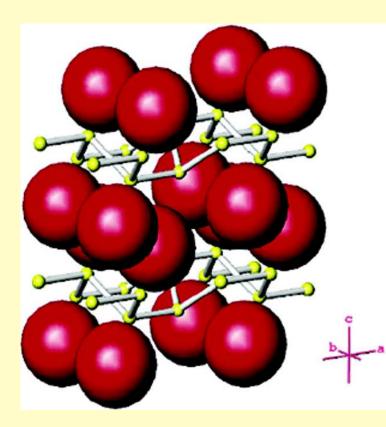
Nanocrystals of AuCuSn<sub>2</sub> (shown in micrograph) prepared by solution processing are made up of alternating layers of gold atoms (gray) and copper atoms (blue), with tin atoms (red) occupying interstitial holes.

## **El OsB**<sub>2</sub>, dissenyat per ser dur

Valence electron density and bond covalency can serve as design parameters for preparing novel incompressible materials, a new study shows [*J. Am. Chem. Soc.* **2005**, *127*, 7264]. Incompressible, hard materials are widely used to provide durable and wear-resistant coatings for drilling and cutting tools and in other applications.

Sarah H. Tolbert, Richard B. Kaner, and their coworkers at the University of California,

Los Angeles, note that incompressibility (or bulk modulus) and valence electron density are correlated in many materials. Likewise, bulk modulus and hardness are often correlated, as is the case for diamond, the hardest known substance. Osmium's valence electron density and bulk modulus are close to the values for diamond. Diamond is much harder than metallic osmium, the team explains, because of diamond's highly covalent and directional bonds. To introduce covalent bonding and thereby increase osmium's hardness, the team developed solid-state synthesis procedures for preparing  $OsB_2$  (shown, red = Os; yellow = B). Qualitative scratch tests indicate that  $OsB_2$  is indeed hard and that it has a bulk modulus between 365 and 395 GPa (diamond = 442 GPa).



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95

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Cin

• El procés de consulta gratuïta de les publicacions científiques (*open access*) guanya terrent dia a dia [*Chem. Eng. News*, 16 maig 2005, 40].

• Es compleixen 300 anys del descobriment del pigment blau de Prússia,  $Fe_4[Fe(CN)_6]_3[Chem. Eng. News, 2 maig 2005, 32].$ 

• S'ha aïllat un metal·loenzim que conté cadmi en un microorganisme marí [T. W. Lane *et al.*, *Nature*, **2005**, *435*, 42]

• Es proposa que en el rang de pH d'interès bioquímic i geoquímic (4.3 - 7.0) l'alumini forma l'espècie pentacoordinada  $[Al(H_2O)_4(OH)]^{2+}$  [T. W, Swaddle *et al*, *Science*, **2005**, *308*, 1450].

L'element número **22**, **titani**, va ser descobert el 1791 per William Gregor. El seu nom prové del mot *Tità*, que en la mitologia grega designava a cadascun dels fills mascles d'Urà i Gea..