

# Noticies Inorganiques

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### Les proteïnes es pleguen al so del metall

The exquisite operation of many enzymes relies on slipping the correct metal ion into the protein's active site, yet the mechanism by which proteins choose one ion over another—say, copper over manganese—has long befuddled researchers. Now biochemists from Newcastle University, in England, led by Nigel Robinson, report that cells can ensure the enzyme picks the right metal ion by controlling which cellular compartment the protein folds in (*Nature* **2008**, *455*, 1138).

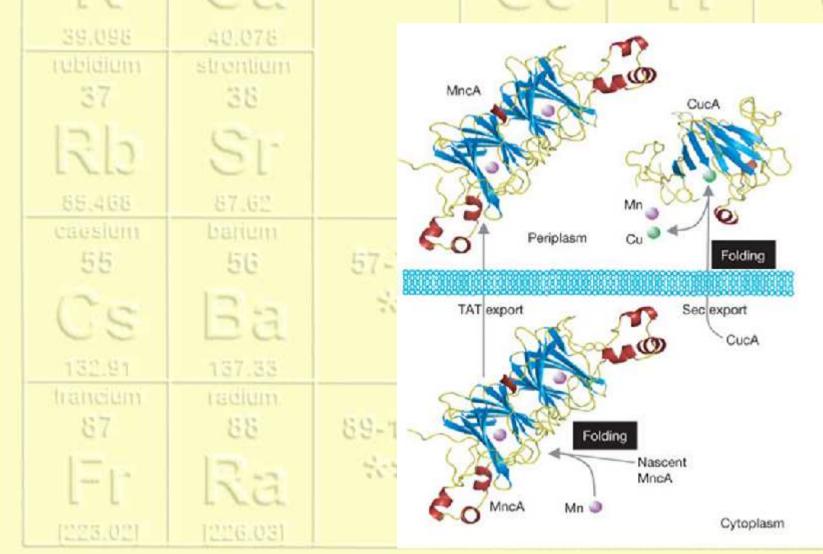
Recently, Robinson and his colleagues found in a cyanobacterium two proteins, CucA and MncA, that require copper and manganese, respectively, to be catalytically active. Strangely, both proteins used one glutamate and three histidine residues, in exactly the same orientation, to hold their catalytic metal ions in place.

It turns out that the cell places the correct metal in the protein by controlling where the nascent protein folds. Although both proteins are produced in the cytoplasm of the cell, only the manganese-containing protein is allowed to fold there. In the cytoplasm, the concentration of high-binding-affinity copper is negligible, allowing the manganese to slip into place. Meanwhile, the copper-containing protein is not allowed to fold in the cytoplasm, but is instead transported to an outer compartment in the bacterial cell called the periplasm, where there are higher concentrations of free copper that the protein can incorporate into its active site.

## Molibdè insaciable: MoZn<sub>12</sub>

Pushing the known boundaries of bonding in transition-metal compounds, a European research team has synthesized a highly coordinated complex containing a MoZn<sub>12</sub> core (*Angew. Chem. Int. Ed.* **2008**, *47*, 9150). The unusual [Mo{Zn<sub>12</sub>(CH<sub>3</sub>)<sub>9</sub>(Cp\*)<sub>3</sub>}] molecule, where Cp\* is the pentamethylcyclopentadienyl ligand, appears to have 12 metal-ligand bonds and provides a bridge between traditional transition-metal coordination compounds and main-group cluster compounds.

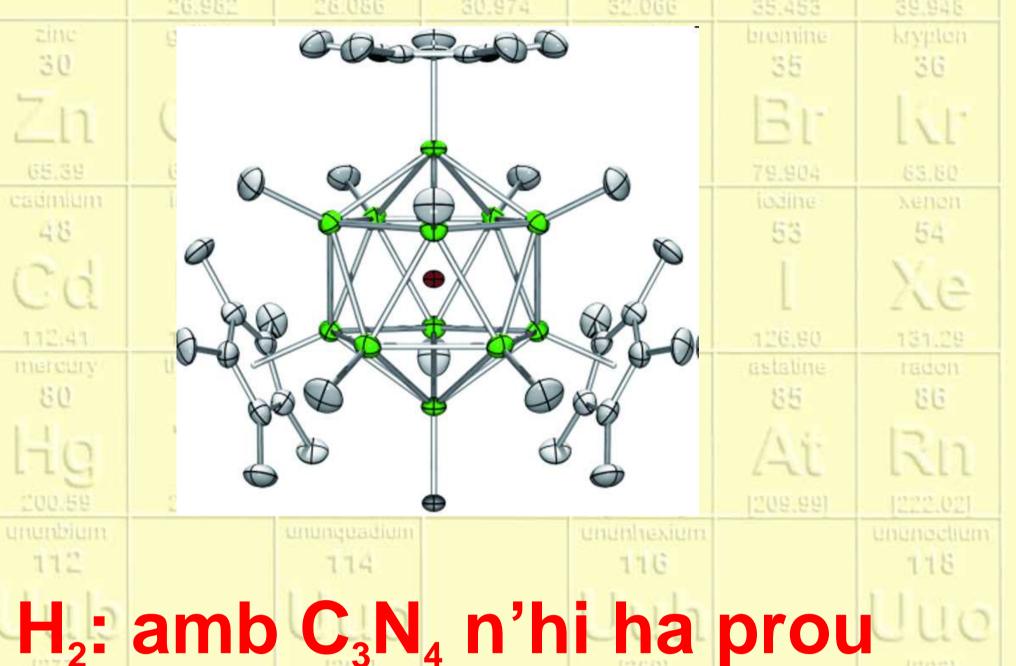
The complex obeys the 18-electron rule, a rule of thumb in transition-metal chemistry stating that complexes are most stable when 18 valence electrons are involved in the bonding. This rule typically limits the highest coordination number of ligands around a metal center to nine for standard two-electron bonds. But on the basis of spectroscopic, X-ray crystal structure, and computational studies, the researchers propose that molybdenum's six valence electrons together with six of the zinc valence electrons are engaged in six Zn–Mo–Zn "three-center, two-electron bonds," effectively forming 12 one-electron Mo–Zn bonds. The remaining six zinc valence electrons are delocalized over the zinc atoms surrounding molybdenum, forming weak Zn–Zn interactions.



# Un organometàl-lic de Ni(IV)

By reacting a nickel(0) complex with a strained cyclic alkene, a team of chemists has prepared the first reported all-alkyl nickel(IV) complex (*Angew. Chem. Int. Ed.* **2009**, *48*, 290). Earlier this year, Columbia University's Matthew Carnes and coworkers reported the synthesis of a unique dibenzocyclooctatetraene (DCOT) molecule that they are exploring as a monomer for ring-opening metathesis polymerization (*Angew. Chem. Int. Ed.* **2008**, *47*, 2982).

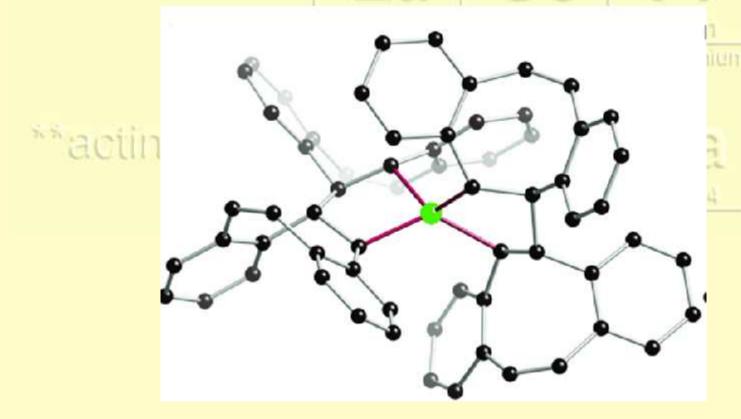
The central eight-membered tetraene ring has one trans double bond, which gives the molecule a spring-loaded helical twist. The researchers have now reacted DCOT with a nickel(0) complex under various conditions. One product is a chiral trimer in which three DCOT molecules surround a nickel atom. Under different conditions, the team ended up with the nickel(IV) tetraalkyl shown. It appears to form when the nickel atom in the trimer "slips" and forms a complex with four DCOT molecules, resulting in four Ni–C bonds. This unique chemistry is driven by DCOT working out the kink in its trans double bond.

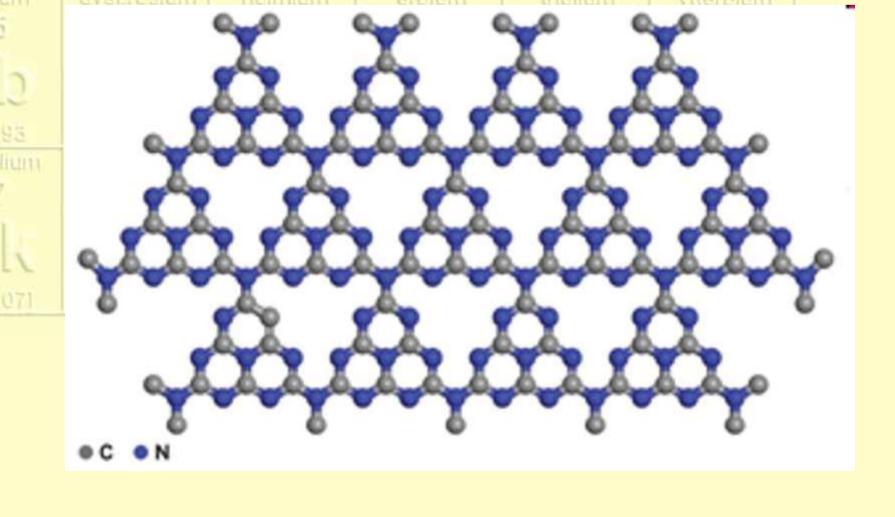


# Carbon nitride is an inexpensive, stable, and metal-free photocatalyst for producing hydrogen from water reports a group led by X. Wang of the International Joint

hydrogen from water, reports a group led by X. Wang of the International Joint Laboratory, a joint venture between the Max Planck Institute of Colloids & Interfaces, in Potsdam, Germany, and Fuzhou University, in China, and Kazunari Domen of the University of Tokyo (*Nat. Mater.* **2009**, *8*, 76).

Typical  $H_2$ -producing catalysts either require precious metals such as platinum or ruthenium or, in the case of synthetic polymer semiconductors, ultraviolet light. Wang, Domen, and colleagues found that "graphitic" carbon nitride —layers of  $C_3N_4$  sheets—can produce  $H_2$  in visible light without metal additives when triethanolamine is present as a sacrificial electron donor. Density functional computations indicate that the material likely oxidizes  $H_2O$  to  $O_2$  at the nitrogen atoms and reduces  $H_2$  to  $H_2$  at the carbon atoms. The unoptimized carbon nitride system produced up to  $4\mu$ mol of  $H_2$  per hour, roughly an order of magnitude less than photocatalysts that use precious metals.





### Breus

- Neix la revista Nature Chemistry: http://www.nature.com/naturechemistry
- La sisena companyia química mundial, Lyondell Chemical (EUA), ha fet fallida i ha arrossegat el Royal Bank of Scotland.
- Sembla ser que en les plantes tropicals l'activitat de la nitrogenasa ve controlada pel molibdè i no pel fosfat (A. R. Barron *et al.*, *Nature Geoscience* **2009**, *2*, 42)
- El H<sub>2</sub>S, conjuntament amb el NO, pot ser important en el control de la pressió sanguínia (R. Wang et al., *Science* **2008**, *322*, 587).

#### Avui recomanem

Fold it, un joc gratuït d'ordinador que permet contribuir a l'avançament de la ciència, concretament en el camp del plegament de les proteïnes.

http://fold.it

### L'element



L'element número 43, tecneci – l'existència del qual havia estat predita per Mendeléiev— fou preparat per C. Perrier i E. Segre a Itàlia, l'any 1937, en una mostra de molibdè que havia estat bombardejada amb nuclis de deuteri, a Berkeley. El nom prové del grec " que vol dir *artificial*, ja que fou el primer element sintètic. Al 1925, W. Noddack, O. Berg i I. Tacke, publicaren el descobriment de l'element 43, que anomenaren Masuri, basant-se en l'espectre d'emissió de raigs X de residus de la descomposició de minerals d'urani; aquests resultats no foren reconeguts en aquell moment, però revisions actuals d'aquelles mesures, han confirmat la proposta inicial.

El Tecneci, conjuntament amb el prometi, són els dos únics elements, abans de l'urani, que no es troben a la naturalesa; tots els seus isòtops són radioactius i les aplicacions estan relacionades amb la medicina nuclear.