UNIVERSITAT DE BARCELONA B Química Inorgânica

Notícies Inorgàniques Any 6, Núm. 35, Setembre de 2007

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

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

Molècules: de la terra a l'infinit I - Hamburgueses terrenals

A team of researchers led by Takahiko Kojima at Osaka University, fused a molybdenumporphyrin complex and a tungsten polyoxometalate to form a compound they have named the porphyrin hamburger (*Chem. Commun.* **2007**, 3997).

Two saddle-shaped porphyrin complexes make up the burger buns, while a cluster of tungsten oxide anions surrounding a central silicon cation, known as a polyoxometalate, forms the meat sandwiched between them.

The structure combines two kinds of photoresponsive, redox-active molecules. This means the molecules can respond chemically to light and can participate in reduction-

Veïns ben avinguts

Zinc and gallium, chemically similar elements nestled next to each other in the periodic table, finally have been convinced to join together to form the first structurally characterized complexes containing a zinc-gallium bond (*Dalton Trans.* **2007**, 2997). Cameron Jones of Australia's Monash University and coworkers prepared several complexes by reacting a gallium heterocyclic precursor with zinc heterocyclic complexes.

The chemistry is part of a larger study by Jones and coworkers exploring the analogy between the cyclic gallium precursor and both N-heterocyclic carbene ligands and cyclic boron ligands, both of which are widely used to form transition-metal catalysts. In the past year, the gallium precursor has permitted the team to prepare a range of novel gallyl

oxidation processes. For example, polyoxometalates have been used in applications such as catalytic oxidation reactions and optoelectronics. The fusion of these two functional molecules will give rise to novel photofunctional materials for light energy conversion.

complexes, including compounds containing Ga-Sn, Ga-Cu, and Ga-Nd bonds. The researchers currently are studying the reactivity of the zinc gallyl complexes toward unsaturated organic molecules, such as alkynes, alkenes, and aldehydes.



Accumulation of extremely toxic methylmercury in the environment—particularly in fish—has triggered an effort by scientists to unravel the process by which a set of bacterial enzymes capture and then detoxify the compound. In a new development, Jonathan G. Melnick and Gerard Parkin of Columbia University report a synthetic mercury complex that provides insight into how one of these enzymes catalyzes cleavage of the Hg-C bond (*Science* **2007**, *317*, 225). The finding is expected to boost efforts to genetically modify plants to sequester HgCH₃⁺ for environmental cleanup.

In nature, microbes synthesize $HgCH_3^+$ from naturally occurring Hg^{2+} , as well as from mercury released in the emissions of coal-fired power plants. Organomercury compounds are toxic because the metal has a high affinity for sulfur, in particular the sulfur of thiol

(-SH) groups in cysteine units of proteins. Once the mercury binds, the normal function of

the proteins is disrupted. Bacteria resistant to $HgCH_3^+$ toxicity produce an enzyme named



From three simple ingredients has emerged a complex metal cage structure with arresting symmetries. Although its beauty stands out, the molecule also has shown some intriguing magnetic properties (Z. Zing *et al.*, *J. Am. Chem. Soc.* **2007**, *129*, 7016). In the synthesis, the researchers combined $La(NO_3)_3$, $Ni(NO_3)_2$, and iminodiacetic acid (IDA) in an aqueous solution, and subjected it to heating and slow cooling. Crystallographic analysis revealed a stunning architecture: a pair of nested, cagelike metal spheres bridged by IDA. The outer Ni(II) sphere's face of pentagons and triangles forms an icosidodecahedron (32 sides), while the inner La(III) sphere is a perfect dodecahedron (12 sides). Classified as a Kepler solid, or Keplerate, after the 16th-century astronomer who modeled the heavens with polyhedra, this metal cluster couldn't be more symmetric. Both sets of metal cages possess icosahedral symmetry, the highest possible symmetry for molecules.

In addition to the beauty of the chemical structure, this work presents some cool and potentially useful new chemistry. More specifically, when the researchers chilled the Keplerate to cryogenic temperatures (16 K), they observed ferromagnetic interactions between the outer cage's Ni(II) ions.

MerB, which has three cysteine residues in its active site that are known to be crucial for cleaving the Hg-C bond. But the exact way in which MerB coordinates to $HgCH_3^+$ and the intimate details of the reaction mechanism have been a mystery. Melnick and Parkin thus set out to decipher the mechanism of action of MerB. The researchers conclude that the ability of the mercury atom to coordinate to multiple

sulfur atoms sets up cleavage of the Hg-C bond. They envision that, for MerB, one cysteine is required to coordinate Hg CH_3^+ in a linear fashion, a second cysteine is required to activate the Hg-C bond, and a third cysteine is required to sever the bond.

III - Molècules còsmiques

Carbon-rich stars were previously considered the most likely source for the galaxy's complex chemical makeup, but Lucy M. Ziurys and colleagues at the University of Arizona have now observed that oxygen-rich stars may be just as chemically prolific. The researchers report seven unexpected compounds in the oxygen-rich shell of VY Canis Majoris, which brings the total known compounds present in the red supergiant to 17—more than the 10–12 compounds of other oxygen-rich stars and on par with the diversity of compounds in carbon-rich stars (*Nature* **2007**, *447*, 1094).

The researchers used microwave emission spectrometry to determine that the new compounds contain sulfur, phosphorus, silicon, or sodium and include the simple molecules HCN and NaCl.The detection of additional gas-phase molecules will help to draw a more complete picture of chemical synthesis in stars.



Breus

cohhe

29

63.546

28

46

120

26

44

76

93

95

Am

PU

96

Cim

98

97

Ek

1247.071 1247.071

45

• Amb motiu del centenari de la mort de D. I. Mendeléiev, la Biblioteca de Física i Química dedica enguany la tradicional exposició del seu fons històric a la Taula Periòdica.

• Ha estat publicada, a cura d'Elisabeth Bosch (UB) i Salvador Alegret (UAB), la versió catalana del *Llibre Taronja* de la IUPAC, "Compendi de Nomenclatura de Química Analítica. Regles definitives de 1997".

• El popular Chemical Abstracts fa cent anys (http://www.cas.org).

• S'ha demostrat que els dispersants utilitzats per netejar el petroli abocat al mar són més tòxics per als coralls que el propi petroli (*Environ. Sci. Technol.* **2007**, *41*,5571).

L'element número **35**, **brom**, va ser descobert l'any 1826 per Antoine J. Ballard a Montpeller (França). El seu nom prové del grec $\beta ? \mu$, que vol dir *pudor*.