

FROM THE LITERATURE

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A review-article by the Departamento de Química Inorgánica, Universidad de Sevilla (E. Carmona, A. Galindo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6526) has reviewed the recent findings on $\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2$ and related organometallics of Group 12, as summarized recently in an earlier report of this series.

An article by M. Jacoby appeared in the August 18th issue of the year 2008, p. 38, of *Chem. Eng. News*, entitled *Recognizing a pioneer*, is dedicated to Eligio Perucca, born in Potenza in 1890, with a degree in Physics from the Università di Pisa in 1910, before becoming Professor of Experimental Physics at the Politecnico di Torino. Some of the scientific acquisitions by Perucca deal with a new type of electrometer, and with studies on the photoelectronic and thermoionic effects, and on crystal dyeing.

The construction of assemblies containing transition- or Main Group elements, connected intermolecularly through electrostatic interactions, or through hydrogen bonds, or more tightly by bridging ligands, is a subject of considerable current interest. These systems are expected to perform important properties in relation to gas storage, electronic conduction, catalytic activity or magnetic cooperativity. A microporous coordination polymer of formula $[\text{Cu}(5\text{-fluoropyrimidin-2-olato})_2(\text{H}_2\text{O})_{1.25}]_n$ has been prepared and structurally characterized (J.A.R. Navarro *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 3978), as reported in a paper contributed by the Università di Milano, the Universidad de Granada, the Instituto Nacional del Carbon de Oviedo, and by the Università dell'Insubria. The solid selectively absorbs H_2 , or N_2 , or CO_2 , and, at 77 K, selective absorption of H_2 from a H_2/N_2 mixture was demonstrated. Single-crystal X-ray diffraction of the copper-containing precursor is reported showing slightly distorted square-planar copper(II) centres, while thermodiffraction experiments on polycrystalline samples have been conducted in the range of temperature 303–473 K. Some so-called supramolecular memory systems (SuMeS) have been reported (A. Mammana *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 8062), as for a contribution from two institutions based in Catania (Università and Istituto CNR).

An article (D. Belli Dell'Amico *et al.*, *Inorg. Chim. Acta*, 2008, **361**, 2997) has reviewed the scientific acquisitions obtained at the Università di Pisa on the synthesis of heavier halides of transition metals by halide exchange using the easily accessible chlorides in the presence of hydrogen halides HX or alkyl halides RX (X = Br, I) in a dry organic solvent.

A tetranuclear μ_4 -oxo derivative of formula $\text{Zn}_4(\mu_4\text{-O})(1,3,5\text{-benzenetribenzoato})$ was found to convert to a second modification upon a short exposure to moisture (S.S. Kaye *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 14176), as for a communication from the University of California at Berkeley, the General Motors Corporation, the Purdue University. The absorption of H_2 by this material was found to be as high as 7%

by weight at 77 K. It is interesting to note that μ_4 -oxo derivatives of zinc have been prepared by treating ZnO with a secondary amine and CO_2 , of formula $\text{Zn}_4(\mu_4\text{-O})(\text{cbm})_6$, cbm being a dialkyl-carbamato ligand (M. Casarin *et al.*, *J. Chem. Soc. Faraday Trans.*, 1993, **89**, 4363). In a somewhat related subject, a joint paper by Chiba University, Nippon Steel Corporation, and the Università di Milano (A. Kondo *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 12362) has reported N_2 absorption by a so-called metal-organic framework formed through solvent removal from $\text{Cu}(\text{OTf})_2(\text{bpy})_2 \cdot (\text{H}_2\text{O}) \cdot 2\text{EtOH}$, a bis-derivative of copper(II), with 4,4'-bipyridine as additional ligand. A paper contributed by some Italian, French and Swiss research institutions (K. Bernot *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 1619) has reported the reaction of meso-tetraphenylporphyrin(acetato)manganese(III) with phenylphosphinic acid leading to the one-dimensional product of minimal formula $\text{Mn}(\text{TPP})(\text{OPPh}(\text{OH})) \cdot \text{H}_2\text{O}$, which behaves as a single-chain magnet, according to measurements carried with a magnetometer operating in the range of temperature 1.8–300 K.

The adsorption of self-assembled monolayers of long-chain alkane-thiols on gold(111) has been reported in a collaborative study by some Italian and US institutions (A. Cossaro *et al.*, *Science*, 2008, **321**, 943). A kinetic study of the reaction of alkyl- and arylpalladium complexes containing pyridyl-thioethers or quinoline-phosphines with some isocyanides has appeared (L. Canovese *et al.*, *Organometallics*, 2007, **26**, 5590), as a contribution from the Universities of Venezia and Padova. Squaraines are the condensation products of electron-rich molecules with squaric acid, the squarate dianion $\text{C}_4\text{O}_4^{2-}$ being the product of the electrochemical reduction of CO (G. Silvestri, *et al.*, *Gazz. Chim. Ital.*, 1972, **102**, 818; G. Silvestri, *et al.*, *Electrochim. Acta*, 1978, **23**, 413; R. Ercoli, *et al.*, *Gazz. Chim. Ital.*, 1973, **55**, 156), according to studies carried out at the Università di Palermo. Three classes of singlet oxygen sensitizers belonging to the family of symmetric squaraines have now been reported (L. Beverina *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 1894) in a joint paper from the Universities of Padova and Milano and from the Consiglio Nazionale delle Ricerche, CNR, Istituto di Scienza e Tecnologia dei Materiali, Milano. Further details about these systems can be found in a subsequent paper by the same group of authors (L. Beverina *et al.*, *Chem. Mater.*, 2008, **20**, 3242).

A paper has appeared describing the manganese-catalyzed *cis*-hydroxylation of alkenes with H_2O_2 (J.W. de Boer *et al.*, *Chem. Commun.*, 2008, 3747). For example, 2,2'-dimethylchromene is *cis*-hydroxylated in a full-conversion reaction leading to the hydroxylated product with a 54% enantiomeric excess. In a somewhat related area, the iron-catalyzed oxidation of aromatic hydrocarbons to phenols has been studied in the Research Laboratories of Eni at Novara (D. Bianchi *et al.*, *Angew. Chem., Int. Ed.*, 2000, **39**, 4321; idem, *J. Mol. Catal. A: Chemical*, 2003, **204-205**, 419).

The electrocatalytic generation of dihydrogen mediated by Fe–hydrogenase has been studied using the sulfur-bridged *dinuclear* Fe(II)/Fe(II) system of formula $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_6$ as model: according to a theoretical study by researchers of the Università di Milano-Bicocca (C. Greco *et al.*, *Inorg. Chem.*, 2007, **46**, 108), a dinuclear species containing terminal hydrido ligands is the more likely candidate to be a precursor to dihydrogen formation. Strictly related to this study is the recent paper contributed by some German institutions describing the crystal structure, at 1.75 Å resolution, of the *mononuclear* iron–hydrogenase from *Methanocaldococcus jannaschii* (S. Shima *et al.*, *Science*, 2008, **321**, 572).

A contribution from four different institutions (Università di Firenze, European Molecular Biology Laboratory in Hamburg, and the Institute of Crystallography of the Russian Academy of Sciences in Moscow) has reported the structural data of a matrix metalloproteinase (MMP) in solution (NMR and SAXS) and in the solid state (I. Bertini *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 7011).

Carbon nanotubes (CNT) have been studied: [(a) D. Paolucci *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 7393 – a contribution from the Universities of Trieste and Bologna and from the Laboratory of the French CNRS at the Université Bordeaux-I; (b) D. Gozzi *et al.*, *Chem. Mater.*, 2008, **20**, 4126 – a contribution from the Università di Roma and the Laboratorio IMEM–CNR of Parma; D. Gozzi *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 10269]. Fullerene derivatives [(c) A. Mateo-Alonso *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 1534 – a contribution from the Università di Trieste and the University of Patras] keep a relevant position in the chemical literature. In (a), voltammetric and VIS–NIR data on solutions of the material are presented; (b) reports the use of CNT in the Boudouard reaction ($\text{C} + \text{CO}_2 \rightarrow 2 \text{CO}$); (c) describes two different conformations of the product exhibiting a substantial difference in their third-order non-linear optical (NLO) response.

Single-walled carbon nanohorns (SWNH), *i. e.* tubes of $\varnothing = 2\text{--}5 \text{ nm}$ and $l = 30\text{--}50 \text{ nm}$, have been functionalized with ethylene glycol chains and porphyrins, as for a paper in collaboration from the Universities of Trieste, Bologna, Padova and Erlangen–Nürnberg (C. Cioffi *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 3938): the products were analyzed by electrochemistry, photoelectrochemistry and a series of steady-state and time-resolved spectroscopies.

A joint paper from the Universities of Milano and Torino (G. Pacchioni *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 8690) reports experimental evidence and DFT calculations concerning the stabilization and chemical activation of gold nanoclusters on MgO.

The interaction of native calf-thymus DNA with a copper(II) complex in liquid crystals of tetraethyleneglycol monododecyl ether (C_{12}E_4) has been studied by UV spectrophotometry, circular dichroism, and small-angle X-ray scattering, as reported in a paper from the

Università di Palermo (G. Barone *et al.*, *J. Chem. Soc., Dalton Trans.*, 2008, 4172): dramatic changes were noted on going from aqueous solution to the liquid-crystalline system.

The group of G. Longoni at the Università di Bologna has reported (C. Femoni *et al.*, *Angew. Chem., Int. Ed.*, 2008, **47**, 6666) the results obtained by studying the oxidation of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ with $[\text{AuCl}]_4^-$ in acetone under an inert atmosphere. The crystallographically established products thus obtained are the anions $[\text{Au}_{22}[\text{Fe}(\text{CO})_4]_{12}]^{6-}$, $[\text{Au}_{21}[\text{Fe}(\text{CO})_4]_{10}]^{5-}$, $[\text{Au}_{28}\{[\text{Fe}(\text{CO})_3]_4[\text{Fe}(\text{CO})_4]_{10}\}]^{8-}$, and $[\text{Au}_{34}[\text{Fe}(\text{CO})_3]_6[\text{Fe}(\text{CO})_4]_8]^{8-}$, as their tetraethylammonium derivatives. A group operating at the Università di Padova (S. Antonello *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 9836) has reported the electrochemical electron-transfer processes on the thiolato complexes of gold of formula $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$, with a core diameter of $\sim 11 \text{ Å}$, a monolayer-protected cluster (MPC). The cyclic voltammetric experiments show that the periphery of the cluster can undergo ligand-exchange processes.

A contribution from the Universities of Trieste and Urbino (J. Durand *et al.*, *J. Chem. Soc., Dalton Trans.*, 2008, 2171) has described a number of new atropisomeric bidentate bipyridine-based ligands (N–N), which were used to prepare the corresponding palladium(II) complexes of formula $[\text{Pd}(\text{N–N})_2][\text{PF}_6]_2$. These and other similar complexes were used in the CO/4-methylstyrene copolymerization in 2,2,2-trifluoroethanol at $p_{\text{CO}} = 40 \text{ atm}$, leading to perfectly alternating polyketones.

A paper in collaboration within four institutions (Università di Teramo, Istituto CNR di Metodologie Chimiche and Università di Roma, ICCOM–CNR Firenze) describes the use of the phosphorous derivative PCp_2Ph for assembling heteropolymetal complexes (A. Ricci *et al.*, *Organometallics*, 2008, **27**, 1617).

The interaction between solid hemin and a poly(amidoamine)dendrimer has been studied at the Universities of Messina and Siena (M.A. Castriciano, *Chem. Comm.*, 2008, 688), an enhanced catalytic activity being observed after spontaneous self-assembling on a solid surface. Trialkylstannyl complexes of manganese and rhenium have been reported resulting from a collaboration between the Università di Venezia and the Universidade de Vigo (G. Albertin *et al.*, *Organometallics*, 2008, **27**, 2789).

A contribution from the Università di Bari (F. Babudri *et al.*, *J. Organometal. Chem.*, 2008, **27**, 2789) reports the preparation of a poly(*p*-phenylenevinylene, PPV), through a Suzuki–Miyama polymerization of (*E*)-4,4'-dibromostilbene and 2,5-dioctyloxy-1,4-benzenediboronic acid, in the presence of a Pd-based catalyst.

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