FROM THE LITERATURE by Fausto Calderazzo - Università di Pisa

♦ A contribution from the Università di Genova [M. Panizza et al., Chem. Rev., 2009, 109, 65411 discusses the anodic oxidation of organic pollutants. As a matter of fact, pollutants can undergo direct electrolysis at the anode surface, or else they can be oxidized by an electrogenerated active species.

♦ A recent edition of Highlights Chem. Sci. [2009, 6, C91] reports the results obtained by a group of researchers of the Università di Pisa [C. Chiappe et al., Green Chem., 2010, 12, 77]. A phenomenon known as the common-ion effect has been utilized to produce highly concentrated ionic liquid solutions. As a matter of fact, bis(triflylimide) or nitrato metal derivatives can be dissolved in ionic liquids containing the same anion. Thus, for example, a 1.1 M solution of copper(II) triflate can be obtained in 1-butyl-3-methylimidazolium triflate.

◆ The themed issue of Dalton Trans. dedicated to Metal Anticancer Compounds contains an introduction by P.J. Sadler of the University of Warwick and three contributions from research institutions operating in Italy, as specified hereinafter. • L. Ronconi and D. Fregona of the Università di Padova [Dalton Trans., 2009, 10670] are the Authors of a Perspective Article concerning the use of dithiocarbamato derivatives of gold(III) in cancer chemotherapy.
Moreover, a contribution from the Università di Trieste [T. Gianferrara et al., Dalton Trans., 2009, 10742] describes the combination of the porphyrin chromophore with ruthenium in order to obtain an antitumor effect. As a matter of fact, ruthenium derivatives have exhibited interesting antitumor activities: phototoxicity and tumor-localization properties of the porphyrin system are successfully combined with the cytotoxicity of the metal.
 Also, dinuclear bis-phosphonato derivatives of platinum(II) can be used in the treatment of brain tumors, as for a contribution from research institutions located in Bari and Padova [N. Margiotta et al., Dalton Trans., 2009, 10904]: the new complexes were evaluated for their activity in vitro.

♦ A paper resulting from the collaboration of the Università di Roma "Tor Vergata" with the Università di Bologna, Louisiana State University and the University of Houston [F. Mandoj et al., Inorg. Chem., 2009, 48, 10346] describes a novel porphyrin analogue, i.e. 6-azahemiporphycene and its methyl-containing derivatives.

♦ Among the "most-accessed articles" listed in one of the ACS publications, two papers have been cited, both printed in the J. Medicinal Chem. One of them, from the Università di Bologna [A. Cavalli et al., J. Medicinal Chem., 2008, 51, 347], is a Perspective Article dealing with multi-target-directed ligands of interest in the treatment of neurodegenerative diseases. • The other contribution is also a Perspective Article from several European institutions including the Università di Parma, the Università di Modena e Reggio Emilia, the Università del Piemonte Orientale and the Supercomputing Centre (CINECA) located in Casalecchio di Reno, Bologna [P. Cozzini et al., J. Medicinal Chem., 2008, 51, 6237]. The Authors have pointed out the importance of molecular flexibility in the design and discovery of new drugs, taking into

consideration the structures and conformations of hemoglobin.

♦ A contribution from three research institutions, namely Universitat de Barcelona, Cornell University and ICCOM-CNR in Sesto Fiorentino, Firenze [S. Alvarez, R. Hoffmann and C. Mealli, Chem. Eur. J., 2009, 15, 8358] concerns a debate about the presence or absence of a sulfur-sulfur bond in a trinuclear cationic cluster of formula $[Cu_3L_3(\mu_3-S)_2]^{3+}$, L = Me₂NCH₂CH₂NMe₂. The debate is still open, the first of the three authors believing that the cation does not contain an S-S bond, while Hoffmann and Mealli favour the existence of a true bond in between the two sulfur atoms.

• The problem of bonding in polynuclear metal carbonyls has been discussed in a contribution from the Università di Milano and from the Institute of Chemical Process Fundamentals of Prague [R. Ponec et al., Inorg. Chem., 2009, 48, 11024]. The systems containing bridging ligands exhibit the features typical of delocalized 3c-2e bonds. The alternative proposition is the presence of a direct metal-metal bond.

The methyl groups of tetramethylurea were found to be activated in the presence of cis-PtL₂(NO₃)₂, L=a tertiary phosphine, according to a contribution from the Università di Milano in collaboration with research institutions in Spain and UK [S. Fantasia et al., Dalton Trans., 2009, 8107]. Tri-coordinated species of platinum(II) were proposed to be involved in the process.

♦ A paper resulting from the collaboration of the Università di Bologna with the University of Groningen [T. Kudernac et al., J. Am. Chem. Soc., 2009, 131, 15655] discusses the formation of crystalline polymorphs of Schiff bases, with special attention to their photochromic and thermochromic properties. Polymorphism of 4-(dodecyloxy)-N-(4-dodecylphenyl)-2-hydroxybenzaldimine occurs in two--dimensional crystals absorbed on, for example, highly oriented pyrolytic graphite.

The mechanism of the insulin-degrading enzymes is operated by a zinc-containing protease found in bacteria, fungi, plants and animals. A theoretical study was carried out at the Università della Calabria [O. Amata et al., J. Am. Chem. Soc., 2009, 131, 14804]. Proteolysis was reported to be an exothermic process.

• The isomerization of the organic ligand in the cyclopentadienyl derivative of ruthenium(II) [Ru(Cp)(HCC₂CH)(PMe₃)₂]+ converting to the butatrienylidene derivative has been studied by density functional calculations [F. Creati et al., Organometallics, 2009, 28, 6603], according to a contribution from the Università di Chieti. The transformation was evaluated to proceed through an activation free energy of 19.6 kcalxmol⁻¹.

• Two Institutions located in Milano (Politecnico and Università) in collaboration with Solvay Solexis, Bollate, Milano, have reported [M. Sansotera et al., Chem. Mater., 2009, 21, 4498] on highly hydrophobic carbon black obtained by covalent bonding of perfluorocarbon chains to Cabot Vulcan XC 72R.

The Università di Padova in collaboration with the Università di Udine

and the CNR Istituto di Chimica Inorganica e delle Superfici, Padova, has produced a paper [P. Di Bernardo *et al.*, *Dalton Trans.*, **2009**, 4236] reporting the complexation equilibria of La(III), Gd(III) and Yb(III) with a new sulfonated tripodal polyaza–polycatechol–amine ligand.

◆ Researchers of the Università di Messina [A. Giannetto *et al.*, *Inorg. Chem.*, 2009, **48**, 10397] have published equilibrium studies concerning the interaction with pyridine of a series of 29 ion-pairs containing platinum(II), 19 of them being reported for the first time.

◆ The collaboration of the Università di Firenze with the Università di Urbino [G. Ambrosi *et al., Chem. Commun.,* **2009**, 7039] has produced a paper describing the interaction between a cyclam-based ligand, an amino-macrocycle, and Cu(II) or Zn(II) ions. The polyaza-macrocyclic ligand, upon coordination to the metal, produces fluorescence with different emission wavelengths, as measured in MeCN solution. ◆ Two research institutions located in Catania (Università and CNR Institute of Biostructures and Bioimaging), in collaboration with the University of Debrecen, have reported on the binding capacity of zinc(II) to a new polyethyleneglycol-conjugated peptide fragment [C.A. Damante *et al., Inorg. Chem.*, 2009, **48**, 10405]. The binding of Zn(II) was studied by several methods. The aminoacid region 1–16 is able to coordinate up to three Cu²⁺, the histidyl residues acting independently.

◆ The Università di Firenze in collaboration with with the University of Manchester and the Universität Bielefield [I.S. Tidmarsh *et al.*, *Dalton Trans.*, **2009**, 9402] has reported on the formation of polynuclear vanadium(III) complexes, studied magnetochemically and crystallographically: very weak antiferromagnetic exchange was found in these 3d³ systems. ◆ Complex formation of vanadium(V) with 2–hydrox-ypyridine–N–oxide or 2–mercaptopyridine–N–oxide has been reported in a contribution from the Università di Padova in collaboration with two Hungarian Universities (Szeged and Debrecen), *i.e.* T. Jakusch *et al.*, *Dalton Trans.*, 2010, **39**, 212.

♦ Non–alternating copolymerization of CO and C_2H_4 has been reported in a contribution from Pennsylvania State University [R. Luo *et al.*, *Organometallics*, 2009, **28**, 6994]. The process is catalyzed by a system consisting of palladium bonded to a phosphinesulfonato ligand. Copolymers with CO incorporation in the 1÷50 mol% range were obtained. The CO/olefin copolymerization was the subject of a review–article by C. Bianchini and A. Meli [*Coord. Chem. Rev.*, 2002, **225**, 35].

◆ A contribution from the Università di Torino in collaboration with the University of California and the Lawrence Berkeley Natl. Laboratory [E.L. Que *et al., Dalton Trans.,* 2010, **39**, 469] describes a method aimed at improving the performance of a magnetic resonance imaging contrast agent containing both gadolinium and copper, the cation being coordinated to a thioether receptor.

• The allyl dimers of palladium(II) $Pd_2(\mu-CI)_2(\eta^3-C_3H_5)_2$ and $Pd_2(\mu--$

Cl)₂(η^3 –C₃H₃Me₂)₂ undergo insertion of 2,6–Me₂C₆H₃–NC or ^tBuNC in between the Pd–C bond, according to a contribution from the Università Ca' Foscari of Venezia [L. Canovese *et al.*, *Organometallics*, 2009, **28**, 6762]. Experimental evidence favours the presence of η^1 –allyl intermediates. • A contribution from the Università di Milano in collaboration with the ETHZ–Zürich, the Universidad de Vallalolid and the Instituto Superior Tecnico of Lisbon [A. Moreno *et al.*, *Organometallics*, 2009, **28**, 6489] reports two substituted palladium–allyl derivatives of general formula [Pd(η^3 –allyl)(N,N–chelate)]BPh₄. Solution Overhauser studies and X–ray diffraction data show that the phenyl groups of the BPh₄⁻ anion have a close approach to the *N*,*N* –chelating ligand.

• The reaction of $Fe_3(CO)_{12}$ with 1,8-bis(diphenylphosphino)naphthalene (dppn) gives the tetranuclear "butterfly" cluster of formula $Fe_4(CO)_{10}(\mu_4-O)(dppn)$ [S. Ghosh *et al.*, *Organometallics*, 2009, **28**, 7047], as for a contribution from the Università di Torino in collaboration with the Universities of Jahangirnagar (Bangladesh) and Warwick and with the University College London.

◆ The ISM-CNR Institution located in Monterotondo Stazione, Roma, in collaboration with the Università di Roma "La Sapienza", the Democritos National Simulation Center of Trieste and with the Università di Udine, has published a theoretical investigation on systems obtained by combining some phthalocyanines with inorganic semiconductors [G. Mattioli *et al.*, *Chem. Mater.*, 2009, **21**, 4555].

♦ The Università di Sassari and the Università di Milano [M.A. Cinellu et al., Organometallics, 2009, **28**, 7015] have described adducts of gold(III) with chiral pyridinyl–oxazolines (pyox). The complexes have the formula [Au(pyox)Cl₂]+X⁻, X⁻ = PF₆⁻, AuCl₄⁻, and some of them were structurally characterized.

• A tetra-phosphonato cavitand was found to host a group of four water molecules, as for a contribution from the Università di Parma [C. Massera *et al.*, *Chem. Commun.*, 2010, **46**, 88]. The resulting system has C_4 symmetry.

◆ The collaboration of a CNR Institution located in Bologna with three groups of the French CNRS has produced a paper [S. Diring *et al., J. Am. Chem. Soc.*, 2009, **131**, 18177] dealing with two functional ethynyl–pyrene liquid crystals and gels for optoelectronics. The products were characterized by SEM and laser scanning confocal microscopy.

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