FROM THE LITERATURE by Fausto Calderazzo - Università di Pisa

◆ Giacomo Chiari, of the Getty Conservation Institute in Los Angeles has utilized a XRD/XRF approach to analyse the outdoor sculptures and manuscripts of the Getty Museum; this method is expected to be soon utilized in the study of the ruins of Hercoleaneum [*Chemistry World*, March 2010, p. 50-53].

◆ Natural and artificial photosynthetic energy conversion has been discussed in a review article by J. Barber of Imperial College London [*Chem. Soc. Rev.*, 2009, **38**, 185]. Particular attention has been paid to Photosystem II, the water splitting enzyme providing the appropriate reducing equivalents to convert carbon dioxide into organic molecules.

 Ferrocenyl-based bimetallic indenyl complexes were reported by researchers of the Università di Padova, in collaboration with the CNR Istituto di Chimica Inorganica e delle Superfici located in the same town [S. Santi et al., Organometallics, 2009, 28, 3319]. The complexes have the general composition $[\eta^5-(2-\text{ferrocenyl})]$ indenyl]ML_n, and the compound with $ML_n = Cr(CO)_3$ was studied by X-ray crystallography. Electrochemical oxidation of the compounds allowed the authors to evaluate the metal-metal electronic coupling between the ferrocenyl-containing moiety and several metallic fragments, namely {Ru(η^5 -C₅Me₅)}, {(Fe η^5 -C₅H₅)}, {Ir(COD)}, {Mn-(CO)₃}, and {Cr(CO)₂NO}. ♦ A contribution from the Università di Torino [J.G. Vitillo et al., Inorg. Chem., 2009, 48, 5439] deals with grafting the Cr(CO)₃ moiety on doubly p-substituted six-membered rings. The effect of the electronic properties of the substituents on the carbonyl stretching vibrations has been reported. • Some earlier papers report the thermal synthesis of $Cr(\eta^6-arene)(CO)_3$ from the hexacarbonyl and the aromatic compound [E.O. Fischer et al., Chem. Ber., 1957, 90, 2543; G. Natta et al., Gazz. Chim. Ital., 1958, 40, 2875; B. Nicholls et al., Proc. Chem. Soc., 1958, 152]. ♦ As a contribution from the University of Georgia, a paper has appeared [A.M. Ricks et al., J. Am. Chem. Soc., 2009, 131, 9176] dealing with the problem of seven-coordinate metallic derivatives containing carbonyl groups. Mass-spectrometry of the positively charged metal carbonyl derivatives were obtained by laser vaporization in a supersonic expansion of carbon monoxide. The most abundant carbonyls for vanadium and tantalum are the hexacarbonyl and the heptacarbonyl, respectively.

◆ Research activity carried out at the Politecnico di Milano and at the Università di Parma [M. Galletta *et al.*, *Dalton Trans.*, 2010, **39**, 2546] dealt with the extraction of radioactive materials (actinide/lanthanide separation). Calix[6]arene–based picolinamide derivatives were used as coordinating agents.

◆ A sol-gel route to prepare carbon/TiO₂ composite structures was developed at the General Motors Research and Development Center in USA [S. Donthu *et al.*, *Chem. Comm.*, **2009**, 4203]. The resulting

substrates were doped by using [PtCl_e]²⁻ as the platinum source and ethylene glycol as the reducing agent.

The structural control of mesoporous platinum deposition process [Y. Kuroda et al., Chem. Commun., 2010, 46, 1827] has been carried through the use of both a silica nanoparticle assembly and Pluronic 123. • A contribution from Cornell University [M.C. Orilall et al., J. Am. Chem. Soc., 2009, 131, 9389] reports the incorporation of platinum nanoparticles in a composite constituted by niobium oxide and carbon. Loading of Carbon Vulcan with several metals including platinum has been reported. • As mentioned in a preceding report of this series, work carried out at the Università di Pisa in collaboration with Alta SpA. Pisa [L. Romeo et al., 43rd Joint Propulsion Conference, July 2007, Cincinnati; 5th Int. Spacecraft Propulsion Conference, May 5-8 2008, Heraclion, Crete, Greece; 44th Joint Propulsion Conference and Exhibit, Hartford, Conn., USA, July 2008] has shown the possibility of preparing catalytic beds based on transition metals, including platinum, by using silica or γ -Al₂O₃ as the support. \blacklozenge A mesoporous organosilica, functionalized with carboxylic groups, has been prepared [S. Fiorilli et al., Chem. Commun., 2009, 4402], as a contribution from the Università di Torino. Silver nanoclusters have been deposited on Engelhard titanosilicalite ETS-10, according to researchers of the Università di Torino, in collaboration with other Institutions located in France [G. Agostini et al., Chem. Mater., 2009, 21, 1343]: by thermal- and chemical treatments, and through irradiation with UV light, the isolated silver ions aggregate into nanoclusters of increasing nuclearity. • A silica-zirconia matrix has been treated with some N.N-dialkylcarbamato derivatives of copper(II), as a contribution from the Universities of Stuttgart, Giessen and Wien, in collaboration with the Universities of Pisa, Milano-Bicocca and Padova [D. Belli Dell'Amico et al., Chem. Eur. J., 2009, 15, 4931]. The grafting of the copper(II) precursor was monitored by FTIR, XPS, EPR, XAS, XRD, TEM, and dinitrogen absorption.

◆ A contribution from the Università di Perugia in collaboration with the Université de Montpellier [G. Ciancaleoni *et al.*, *Organometallics*, 2009, **28**, 960] has reported on the self–aggregation of ruthenium(II) complexes of general formula RuX(*N*,*N*)(*p*–cymene), *N*,*N* referring to the ligated atoms of an aminoamidato ligand and X=Cl, or H. The dimerization process occurs through the NH/SO₂ interaction of the two partners.

• A μ_4 -oxo-centered structure of zinc carrying 1,4-benzenedicarboxylato functions further connected to tricarbonylchromium(0) functionalities has been reported [S.S. Kaye *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 806], as a contribution from the University of California. The resulting products are expected to perform gas absorption properties. • μ_4 -Oxo-centered structures for carboxylato derivatives of zinc(II) are well-established in the literature and *N*,*N*-dialkyl-

carbamato complexes of this element have been studied at the Università di Pisa. For example, the diethylcarbamato derivative $Zn_4(\mu_4-O)(O_2CNEt_2)_6$ was prepared [A. Belforte et al., Inorg. Chem., 1991, **30**, 3778] by reacting finely divided zinc with NHEt₂ and carbon dioxide under pressure at 150 °C: the resulting product was crystallographically established to have the μ_4 -oxo-centered structure, the oxo group being suggested to originate from deoxygenation of carbon dioxide. • Simplified synthetic procedures were further discovered and it was found that ZnSO₄ was converted to the carbamato derivative [D. Belli Dell'Amico et al., Chem. Rev., 2003, 103, 3857], whose molecular structure was established by X-ray diffractometry. The synthesis was more simply carried out by solvent extraction from an aqueous solution of a soluble zinc salt in the presence of the amine under carbon dioxide. Furthermore, ZnO was reported [D. Belli Dell'Amico et al., Inorg. Chim. Acta., 2003, 350, 661] to react with [NH2Me2][O2CNMe2] in MeCN leading to the crystallographically established μ_4 -oxo derivative of formula $Zn_4(\mu_4-O)(O_2CNMe_2)_6$.

◆ A contribution from the Université de Lausanne has appeared [A. Casini *et al.*, *Dalton Trans.*, 2010, **39**, 2239] dealing with the characterisation and biological properties of gold(III) compounds containing substituted bipyridine– and bipyridylamine–based ligands, see also: A. Casini *et al.*, *J. Inorg. Biochem.*, 2008, **102**, 995.

♦ The collaboration of the Università di Cagliari with the SuperSTEM Daresbury Laboratory [D. Carta *et al.*, *Chem. Mater.*, 2009, **21**, 945] produced a paper dealing with the characterization of CoFe₂O₄/SiO₂ and NiFe₂O₄/SiO₂ aerogels. These nanocomposites consist of two separate phases containing ferrihydrate and the hydroxo-silicate of cobalt or nickel. ♦ The collaboration of the Università di Trieste with some Institutions located in France and USA resulted in the publication of a paper reporting the electric behaviour of mixed oxides containing lanthanum, nickel and iron, upon doping with Sr²⁺ [T. Montini *et al.*, *Chem. Mater.*, 2009, **21**, 1768]. These systems, of formula La_{1-x}Sr_xNi_{0.6}Fe_{0.4}O₃, were prepared by co-precipitation and further calcined at 1000 °C.

• Methanolysis of VCl₄ yielded the chloro-methoxide derivative, which can be further hydrolyzed [M. Epifani *et al.*, *Chem. Mater.*, 2009, **21**, 1618]. Thin films and microcrystalline aggregates of V_2O_5 were prepared and treated at 500 °C. The resulting product was used to detect ammonia and ethanol over a broad range of concentrations. This is a contribution from several Institutions located in Spain and in Italy.

• The search for antitumor inorganic systems is still a hot subject. A review–article [K.S. Lovejoy, S.J. Lippard, *Dalton Trans.*, **2009**, 10651] from M.I.T., Cambridge, USA, describes non–traditional platinum compounds for tumor targeting. Mention is made of the compound of formula PtCl(CH₃COO)(NH₃)(C₆H₁₁NH₂), the first oral drug

with an antitumor activity. • A publication of the Università di Roma in collaboration with the University of California [F. Ricci et al., Chem. Comm., 2010, 46, 1742] deals with the detection of anti-DNA antibodies providing insight into the progression of some autoimmune diseases: the use is presented of an electrochemical DNA sensor operating at nanomolar concentrations. • A paper resulting from the collaboration of the Università di Firenze with the Ecole Polytechnique Fédérale de Lausanne [C.G. Hartinger et al., J. Inorg. Biochem, 2008, 102, 2136] reports the interaction of $Ru(\eta^{6}-p-cymene)(1,3,5-triaza-7-phospha-adamantane)$ with the tripeptide glutathione GSH (g-L-Glu-L-Cys-Gly) and with ubiguitine as a model protein: the corresponding adducts were studied by Fourier transform ion cyclotrone resonance mass spectrometry (FT-ICR MS). • An article resulting from the collaboration of the Università di Trieste with the SISSA Institution of the same town and with the CNRS Institut de Biologie Moléculaire et Cellulaire of Strasbourg [C. Samorì Chem. Comm., 2010, 46, 1494] reports that the conjugation of multi-walled carbon nanotubes (MWCNT) with the anticancer drug methotrexate (MTX) using some appropriate cleavable linkers performs some citotoxic activity for breast cancer cells.

♦ A colorimetric test for oxidized carbon nanotubes has been reported in a contribution from several Italian institutions including the Università di Torino [S. Visentin et al., Chem. Comm., 2010, 46, 1443]. For this purpose, thionin acetate was contacted with the carbon nanotube as such or oxidized, carboxylic groups resulting in the latter case. Both Raman spectroscopic- and thermogravimetirc analyses were used to monitor this type of interaction. • Single-wall carbon nanotubes deposited on stainless-steel as new electrodes for solar cells based on the synthetic dye [Ru(2,2'-dipyridyl-4,4'-dicarboxylic acid)₂(NCS)₂] have been published as a contribution from the Università di Messina in collaboration with Cambridge University [G. Calogero et al., Dalton Trans., 2010, 39, 2903]: for this purpose, commercially available carbon nanotubes were used. • Platinum dispersed on carbon nanotubes is also the subject of a contribution from the New Jersey Institute of Technology [Y. Chen et al., Chem. Commun., 2010, 46, 1652], the uniform distribution of the metal particles being established by SEM and TEM measurements.

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