FROM THE LITERATURE

by Fausto Calderazzo - Università di Pisa

◆ A review–article from the Università di Firenze [C. Andreini *et al.*, *Acc. Chem. Res.*, 2009, **42**, 1471] deals with metallo–proteoms, *i.e.* the metallo–proteins encoded by an organism. The use of bio–informatic methods for the study of these systems is reviewed with special consideration to zinc–containing proteomes. Applications to other transition metals (iron, copper, and molybdenum) were considered. ◆ *Highlights in Chemical Technology*, 2009, **6**, T95, deals with the problem of self–healing at a nanoscale level. Reference is consequently made to a recent review–article by V. Amendola and M. Meneghetti of the Università di Padova [*Nanoscale*, 2009, **1**, 74] reporting some self–healing systems found both in natural and artificial processes. Gold nanoparticles under laser irradiation represent an example of self–repairing system.

◆ The November 2009 issue of *Chem. Rev.*, volume **109**, is dedicated to *"Frontiers in Polymer Synthesis*", the contributions covering the pages from 4961 to 6540. The introduction by the Guest Editor Virgil Percec, University of Pennsylvania, contains the following statement: "*The goal of this thematic issue is to highlight with a group of 27 reviews the most recent advances in the development of new synthetic methods and strategies of polymer synthesis and discuss their use in the design of polymers with complex topology and architecture and the self–assembly of complex systems"*.

◆ Researchers from the Universities of Torino and Alessandria [F. Carniato *et al.*, *J. Organometal. Chem.*, 2009, **694**, 4241] have reported the reactions of $Co_2(CO)_8$ or $Co_2(CO)_6L$ (L=3–pentyn–1–ol, 1,4–butyn–diol, 2–methyl–3–butyn–2–ol) with 2(diphenylphosphino)ethyltriethoxysilane or tris(hydroxymethyl)phosphine for applications to sol–gel materials. One of the products reported in this paper, namely $Co_2(CO)_6[Ph_2PCH_2CH_2Si(OR)_3]_2$ was reacted with mesoporous silica SBA–15 and the resulting substance was characterized by several methods, including X–ray diffraction and scanning electron microscopy.

◆ The polyoxometalate complexes $Mn_{10}[Ru_4(H_2O)_4(\mu–OH)_2(\gamma–SiW_{10}O_{36})_2]$, M = Cs, Li, promote the oxidation of water, as for a contribution from the Università di Padova in collaboration with two research institutions in Tarragona [A. Sartorel *et al*, *J. Am. Chem. Soc.*, 2009, **131**, 16051]. High–valent intermediates are produced by cyclic voltammetry of the ruthenium–containing complexes. ◆ The Università di Torino and the University of Sydney [R.M. Yeates *et al.*, *Dalton Trans.*, **2009**, 8025] have jointly produced a paper concerning the vanadosilicate zeolite AM–6: several spectroscopic techniques have shown the substance to contain linear chains of alternating V=O and V–O bonds, with the unit–cell composition $(Na, K)VSi_5O_{13}•3\ H_2O$. The vanadium(IV) ions are ferromagnetically coupled, the susceptibility data being reproduced by a one–dimensional model with J=0.66 cm^{-1}.

◆ D.G. Nocera of MIT, Cambridge, Massachusetts, has written an Award Article [*Inorg. Chem.*, 2009, **48**, 10001] on the splitting of HY molecules (Y = halide, OH). Multielectron transfers, proton coupling, and activation of bonds in energy–poor substrates are the items discussed in this article. The profile of the Author contains the information that Professor Nocera is the Director of the ENI Solar Frontiers Center at MIT. ◆ Volume 38, year 2009 of *Chem. Soc. Rev.* is dedicated to Renewable Energy and contains an editorial by D.G. Nocera and D. Guldi and an article by J. Barber, Imperial College London, on natural and artificial photosynthetic energy, pp. 185–196. ◆ The group at the Università di Bologna headed by V. Balzani [P. Ceroni *et al.*, *Angew. Chem.*, 2009, **48**, 8516] has reported that the 2,2'–bipyridyl complex $[Ru(bpy)_3]^{2+}$ can undergo one–electron oxidation and redox processes, with possible applications for sensing and labelling. ◆ The Università di Messina and Centro Universitario per la Conversione dell'Energia Solare in the same town [G. La Ganga *et al.*, *Dalton Trans.*, **2009**, 9997] have reported the photoinduced oxidation of water to dioxygen by using a ruthenium dendrimer as the photosensitizer in a buffered aqueous solution containing nanoparticles of iridium–oxide as catalyst and $S_2O_8^{2-}$ as the sacrificial species.

◆ The collaboration of the Universities of Bologna and Urbino with IGS Innovations in New Jersey, with CIRSA in Ravenna and with Columbia University [A.J. Maliakal *et al.*, *Chem. Mater.*, 2009, **21**, 5519] has produced a paper reporting on the mechanism of O_2–enhanced photoconductivity in the condensed hydrocarbon rubrene: EPR data show the formation of both the hydrocarbon radical cation and O_2^+ during irradiation of the hydrocarbon in the presence of dioxygen.

◆ A contribution from the Università di Padova in collaboration with the Ruhr–Universität Bochum, and with the European Technologies Research Centre of Leicester reports the formation of thin films of lanthanide oxides by metal vapour deposition [A.P. Milanov *et al.*, *Chem. Mater.*, 2009, **21**, 5443]. As starting compounds for the deposition of Gd_2O_3 and Dy_2O_3 were chosen the corresponding isostructural derivatives of the two metals with the ligand *N,N'*–di–isopropyl–2–dimethylamido–guanidinato. The oxides were deposited in the presence of dioxygen in the range of temperature 300–700 °C.

◆ Two research institutions located in Bologna (Università and Istituto Nazionale di Scienza e Tecnologia dei Materiali) have published a paper [I. Conti *et al*, *J. Am. Chem. Soc.*, 2009, **131**, 16108] dealing with the pathway of adenine deactivation, as studied by CASPT/CASSCF calculations, in comparison with the available experimental data.

◆ The interest for sandwich metal complexes containing cyclic hydrocarbons is still quite high. S.K. Mohapatra *et al*. [*J. Am. Chem. Soc.*, 2009, **131**, 17014] report the selective lithiation of the titanium(0) derivative $Ti(\eta^7–C_7H_7)(\eta^5–C_5H_5)]$, as for a contribution from the Technische Universität Carolo–Wilhelmina in Braunschweig. ◆ In this connection, it is interesting to note that the isoelectronic sandwich cationic species containing two seven–membered rings of formula $[V(\eta^7–C_7H_7)(\eta^7–C_7H_8)]^+$, with vanadium in the formal zero oxidation state, was isolated as the hexacarbonylvanadate(–I) and converted to the tetraphenylborato derivative [F. Calderazzo *et al*., *Chim. Ind. (Milano)*, 1962, **44**, 1217]: the vanadium–containing cation was the primary product of the smooth reaction of $V(CO)_6$ with C_7H_8. ♦ INDO SCF MO calculations [D.W. Clack *et al*., *Theoret. Chim. Acta*, 1977, **46**, 313] have also appeared on the formally zerovalent metal complexes of formula $M(\eta^7–C_7H_7)(\eta^5–C_5H_5)$, M=Ti, V, Cr, and on the corresponding cationic species of chromium(I) and vanadium(I).

♦ Researchers of CNR in Bologna and of CNRS in Strasbourg [E. Treossi *et al*., *J. Am. Chem. Soc.*, 2009, **131**, 15576] have reported on the high–contrast visualization of graphite oxide on dye–sensitized glass, quartz or silicon.

♦ The complexes of copper(II) with the polypeptide $Ac–PEG_{11}–(PHGGGWGQ)_4–NH_2$ have been studied by spectroscopic (UV–VIS, EPR) and voltammetric methods [R.P. Bonomo *et al*., *Dalton Trans.*, **2009**, 2637]. Some square–pyramidal structures were detected, the coordination sites being occupied by imidazole peptidic nitrogen atoms and by carbonyl oxygen atoms, as for a contribution from the Università di Catania in collaboration with the Istituto di Biostrutture e Bioimmagini of the Consiglio Nazionale delle Ricerche (CNR), Section located in the same town. ♦ New DNA quadruplex groove binders have been reported [S. Cosconati *et al*., *J. Am. Chem. Soc.*, 2009, **131**, 16336], as for a contribution from the Università di Napoli, in collaboration with the Scripps Research Institute of La Jolla. Virtual screening (VS) calculations were successful in the identification of new chemotypes.

♦ The Università di Torino in collaboration with the Università di Firenze [G. Ambrosi *et al*., *Inorg. Chem.*, 2009, **48**, 10424] has reported on two amino–phenol macrocycles spaced by several linear tetra–amines. Trinuclear copper(II) complexes of the new ligands have been synthesized and characterized.

♦ A contribution from the Università di Firenze in collaboration with the Max–Planck–Institut für Biophysische Chemie, Göttingen, and with Bruker Biospin, Rheinstetten [M. Reese *et al*., *J. Am. Chem. Soc.*, 2009, **48**, 10424] has shown that Dynamic Nuclear Polarization (DNP) experiments in aqueous solution combined with high–resolution NMR detection are feasible in a DNP spectrometer. ♦ Time–resolved EPR measurements were carried out on Nafion, a polymer with a perfluorinated backbone and oligoether chains terminating with a SO_3H group. This is a contribution from the Università di Padova [F. Conti *et al.*, *Chem. Commun.*, **2009**, 7006]. Upon irradiation with UV light, Nafion can be excited to a singlet state S*, rapidly converting to a triplet T*, via inter–system crossing.

♦ The collaboration of three institutions located in Napoli with the Scuola Normale Superiore of Pisa has produced a paper [F. Santoro *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 15232] reporting on the decay of excited states in A–T DNA. The double–strand tetramer $(9–methyladenine)_2•(1–methylthymine)_2$ was examined in water as medium.

♦ The problem related to the black colour of melamine has been discussed in a contribution from the Università di Napoli [A. Pezzella *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 15270]. The species produced by oxidative polymerization of 5,6–dihydroxy–indole (DAI) were taken into consideration by using 5,6–dihydroxy–3–indolyl–1–thio–β–D–galactopyranoside as starting material. The resulting dark–brown polymer exhibited a band at 314 nm and a broad absorption in the VIS region. The conclusion was reached that a contribution to the black colour also derives from interchromophoric transitions depending on the oxidation and the degree of aggregation of the constituents.

♦ The ethylene complex of rhodium(I) of formula $Rh_2Cl_2(C_2H_4)_2(P^iPr_3)_2$ has been synthesized and characterized as a chloride–bridged dimer, according to a contribution from the Università di Bari in collaboration with the Universities of Torino and Parma and with the Hungarian Academy of Sciences, Budapest [A. Angelini *et al.*, *Dalton Trans.*, **2009**, 7924]. By reaction with H_2, the dimer gives $Rh_2Cl_2(H)_4(P^iPr_3)_2$, characterized by a high fluxionality both in solution and in the solid state. ♦ A contribution from several European institutions including the Università di Sassari and from the University of Kyoto [J. Nillson *et al.*, *Dalton Trans.*, **2009**, 7902] describes some oxo–vanadium(IV) derivatives derived from 2–{[bis(pyrid–2–yl)methylamine]}methylphenol, abbreviated as bp–OH, of formula $VO(bp–O)(HSO_4)$ and $VO(bp–OH)Cl_2•MeOH$. This study is justified by the established role of vanadium in sugar metabolism, with effects on patients affected by *diabetes mellitus*.

♦ The Università di Pisa in collaboration with the Università di Bologna [F. Marchetti *et al.*, *Dalton Trans.*, **2009**, 8096] has reported on the reactivity of the pentahalides of niobium and tantalum with 1,1–dialkoxyalkanes or 1,3–dioxolane. Several reaction pathways were observed depending on the nature of the metal and on the reaction conditions. The products of composition $[TaX_3(OMe)(\mu–OMe)]_2$, X=Cl, Br, and $[Me_2C=CHC(OMe)Me][NbCl_5OMe]$ were characterized by X–ray diffraction.

♦ The collaboration between the University of Athens with the ISOF–CNR Institution of Bologna has dealt with comparing the behaviour of the isoelectronic substances 8–oxo–7,8–dihydroxyguanidine and 8–aminoguanine in redox processes [P. Kaloudis *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 15895], namely one–electron oxidation and one–electron reduction.

Authors are cordially invited to submit recent or forthcoming accepted publications for consideration in this section of the journal by using the following e–mail address: facal@dcci.unipi.it Members of Società Chimica Italiana have access to the on–line edition of "La Chimica e l'Industria" at the following address: http://www.soc.chim.it/chimind/catalogo