

In the preceding report of this series mention was made of a paper contributed by the Università di Padova in collaboration with the Eindhoven University of Technology (S. Lovat *et al.*, *Inorg. Chem.*, 2009, **48**, 4724) reporting an oligomeric trisilanolato complex of vanadium(V) catalyzing the cumylhydroperoxide-promoted oxidation of sulfides to sulfoxides and of amines to the corresponding *N*-oxides. The addition of a Lewis base as a co-ligand affects reactivity, stability, and chemo- and stereoselectivity of the reaction. ♦A Perspective Article from a research group operating at the Università di Padova (G. Licini *et al.*, *Dalton Trans.*, 2009, 5265) describes some amine-triphenolato complexes of Main Group- and transition metals: the crystal structures of several complexes of this class have been described and, moreover, some of these complexes were used as catalysts in polymerization (Ti, Zr, Hf) and oxidation (Ti, V) reactions. Concerning the latter aspect, extensive work in the related area of oxidation processes has been carried in the Laboratories of Ente Nazionale Idrocarburi (ENI), and an account of this activity can be found in a 2006 review-article (M. G. Clerici *et al.*, *Enciclopedia degli Idrocarburi*, Istituto della Enciclopedia Italiana, Vol. 2, pp. 661-685) dealing with oxidation processes with hydrogen peroxide and hydroperoxides, catalyzed by titanium silicalite, a crystalline product resulting from the partial substitution of silicium by titanium in the corresponding oxide, as reported in the early Eighties of last century (M. Taramasso *et al.*, US Patent 4,410,501 to SnamProgetti). Intense activity in the field of polymerization of olefins is still present in the literature. ♦A research group operating at the NAIST Institute of Takayama, Japan, has reported some half-titanocene derivatives used in the catalytic polymerization of ethylene (I. Saeed *et al.*, *Inorg. Chem.*, 2009, **48**, 5011). The catalytic precursors contain  $\eta^2$ -pyrazolato ligands. ♦A paper resulting from the collaboration of researchers operating at the Università di Venezia and at the Università di Ferrara (M. Bortoluzzi *et al.*, *Organometallics*, 2009, **28**, 3247) has described some mixed-ligand organometallic complexes of palladium(II) containing both bis(pyrazol-1-yl)methane (BPM) and phosphites: the cationic acetyl palladium(II) complex containing both acetyl- and P(OEt)<sub>3</sub> as ligands catalyzes styrene polymerization and the CO/styrene co-polymerization. ♦Isotactic CO/*p*-styrene copolymerization has been reported by using aryl- $\alpha$ -diimine complexes of palladium(II) as catalytic precursors (C. Carfagna *et al.*, *Organometallics*, 2009, **28**, 3212), according to a contribution from the Università di Urbino, in collaboration with the Università di Firenze. As a function of the substituent on the aryl moiety, the resulting products range from atactic to stereoblock isotactic polymers.

A considerable number of papers have recently appeared discussing subjects related to biochemistry, in some cases including a discussion of the role of metals in these systems. ♦A communication result-

ing from the collaboration of the Università di Padova with the French Laboratoire d'Immunologie et Chimie Thérapeutique, Strasbourg (P. Geotti-Bianchini *et al.*, *Chem. Commun.*, 2009, 3178), has reported the three-dimensional structure of a thymine-based  $\alpha$ -nucleopeptide. ♦A NMR investigation has appeared concerning the interaction of zinc(II) with the single repeat region of the prion-related protein Pr-P-rel-2 from the zPrP63-70 fragment of zebrafish (F. Camponeschi *et al.*, *Dalton Trans.*, 2009, 4643), according to a contribution of the Università di Siena in collaboration with the University of Wrocław. This study was carried out by using NMR data and molecular dynamics calculations: no sulfur-metal interaction could be detected, the largest chemical shift variations being observed for the protons bonded to two nitrogen atoms of the interacting chain. ♦The International School for Advanced Studies (SISSA-ISAS) of Trieste has studied (F. Pietrucci *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 11811) the binding mechanism of a peptide substrate to the wild-type HIV-1 protease through molecular dynamics simulations in water. The calculated free energy of binding is -6 kcal x mol<sup>-1</sup> and the kinetic constants are 1.3x10<sup>6</sup> M<sup>-1</sup>s<sup>-1</sup> (association) and 57 s<sup>-1</sup> (dissociation). ♦A contribution from the Università di Parma in collaboration with research organisations in India, UK and France (S. Banerjee *et al.*, *Dalton Trans.*, 2009, 6849) has reported four new dinuclear hydrazone complexes of copper(II) performing a selective cell inhibitory effect towards leukemic and normal lymphocytes. All the complexes were studied by X-ray diffraction methods, and the degree and nature of the solid-state interactions were reported.

Nuclease enzymes hydrolyzing phosphodiester bonds in nucleic acids play an important role in genetic information. ♦A paper from the Università di Padova (R. Bonomi *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 11278) describes the mechanism of phosphate diesters cleavage by using two complexes of Zn(II) based on bis(2-amino-pyridyl-6-methyl)amine: one of the complexes carries an ammonium group, while the other is uncharged. The reactivity of charged and uncharged systems were compared. These results were preceded by a paper (R. Bonomi *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 15744) in which the hydrolysis of phosphate diester and DNA were carried out using a catalyst resulting from self-assembling multiple copies of thiolato ligand on the surface of monolayer-protected gold nanoparticles. ♦The Section of ETH Zürich located in Lugano (M. Bonomi *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 13938) has applied molecular dynamics simulations to the case of  $\beta$ -hairpin folding. ♦In a paper from the Università di Roma "La Sapienza" in collaboration with research institutions located in Spain and Portugal (M. Cano *et al.*, *Inorg. Chem.*, 2009, **48**, 6229) were studied the supramolecular interactions between Schiff-base complexes of zinc(II) and some biologically relevant

anions. The lifetimes of the photogenerated triplet state of the resulting compounds were measured by nanosecond laser flash photolysis. ♦A contribution from the Università di Napoli in collaboration with the University of Joannina, Greece, and the Medical Research Council in London (D. Sanfelice *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 11662) has reported on the domain of stability of the muscle protein I28, through NMR methods. The study was carried out both in aqueous solution and in a medium constituted by polyethyleneglycol and polyacrylamide. ♦Researchers of the Dipartimento di Scienze Ambientali in collaboration with the Dipartimento di Biotecnologie e Bioscienze, both of the Università di Milano-Bicocca (C. Greco *et al.*, *J. Organometal. Chem.*, 2009, **694**, 2846), have reported the effect of the electronic properties on a series of complexes of formula  $[\text{Fe}_2(\text{SCH}_2\text{XCH}_2\text{S})(\text{CN})_2(\text{CO})\text{L}]^n$ ,  $\text{L}=\text{CO}$ ,  $\text{Me}_2\text{S}^-$ ,  $\text{MeO}^-$ ,  $\text{F}^-$ , and  $\text{X}=\text{CH}_2$ ,  $\text{NH}$ ,  $\text{O}$ . Hard ligands favour isomers with two *trans* CO groups. ♦In a paper resulting from studies carried out at the Università di Sassari (D. Sanna *et al.*, *Inorg. Chem.*, 2009, **48**, 5747) the complexation was studied of the  $\text{VO}^{2+}$  cation in several systems modelling the transport of vanadium in blood serum. The study was carried out by measuring the EPR spectra of the vanadyl cation in three different media; the results are claimed to favour the understanding of the distribution of  $\text{VO}^{2+}$  within the components of blood serum. ♦The dinuclear copper enzyme tyrosinase catalyzes the hydroxylation of monophenols and the oxidation of *o*-diphenols to *o*-quinones. By using 3,5- $\text{C}_6\text{H}_3\text{F}_2(\text{OH})$ , a slow substrate, it has been shown that the ternary complex tyrosinase/ $\text{O}_2$ /phenol has the spectral features of a  $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxidodicopper(II)}$  species. This conclusion originates from a joint contribution of the Universities of Padova and Pavia (A. Spada *et al.*, *Dalton Trans.*, 2009, 6468). ♦A group of researchers operating in Sardinia (Università di Sassari and Centro Ricerche at Porto Conte, Alghero) has studied the interaction of nickel(II) ions with the C-terminal sequence of Cap43, a stress-responsive protein, believed to be involved in cancerous processes (M.A. Zoroddu *et al.*, *Dalton Trans.*, 2009, 5523). The discussion was based on a series of mono- and bidimensional NMR data. ♦The collaboration of the Università di Torino with the firm Sea Marconi Technologies located in Collegno, Torino, and with the Imperial College of London (G. Di Nardo *et al.*, *Dalton Trans.*, 2009, 6507) has produced a paper describing the catalytic properties of catechol-1,2-dioxygenase from *Acinetobacter radioresistens* S13 immobilized on nanosponges. A small-scale reactor was assembled and found to be able to convert catechol into *cis*, *cis*-muconic acid along a period of 70 d. ♦The complexes of copper(II) with the polypeptide  $\text{Ac-PEG}_{11}\text{-(PHGGGWGQ)}_4\text{-NH}_2$  have been studied by spectroscopic (UV-VIS, EPR) and voltammetric methods (R.P. Bonomo *et al.*, *Dalton Trans.*, 2009, 2637). Similar

square-pyramidal geometries were detected, the coordination sites being occupied by imidazole, peptidic nitrogen atoms and carbonyl oxygens. This is 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 Catania. ♦As a result of the collaboration of the Università di Roma with a CNR laboratory located in Roma (Y. Ivarsson *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 11727), the protein folding pathway has been investigated of an engineered circularly permuted postsynaptic family. An interpretation of the folding mechanism has been presented. ♦The Università di Pavia and the Université de Bourgogne (F. Denat *et al.*, *Dalton Trans.*, 2009, 6751) have produced a joint paper reporting the copper(II) complex of a new tetra-aza-macrocyclic ligand, bearing a  $-\text{CH}_2\text{NHR}$  side arm. This amino group does not coordinate apically around the metal centre even upon deprotonation.

Also in view of their potential use in cancer therapy, some papers have recently appeared on the synthesis and properties of ruthenium complexes. M. Vaccaro *et al.* (*Chem. Commun.*, 2009, 1404) describe a uridine derivative, further complexed to ruthenium by using  $[\text{H}(\text{DMSO})_2][\text{RuCl}_4(\text{DMSO})_2]$  as precursor. ♦The ruthenium(II) cation  $[\text{Ru}(\text{bpy})(\text{AP})]^{2+}$ , containing the 2,2'-bipyridine group, has been reported to undergo photodissociation of the AP (4-aminopyridine) ligands upon light excitation at 510 nm (L. Salassa *et al.*, *Inorg. Chem.*, 2009, **48**, 1469), as for a contribution from the Scuola Normale Superiore of Pisa, in collaboration with the Università di Torino and the University of Warwick, the products being *mer*- $[\text{Ru}(\text{bpy})(\text{AP})_3(\text{H}_2\text{O})]^{2+}$  and *trans*- $[\text{Ru}(\text{bpy})(\text{AP})_2(\text{H}_2\text{O})_2]^{2+}$ . Photodissociation occurs in two consecutive steps, the quantum yields being  $\varphi_1 = (6.1 \pm 1.0) \times 10^{-3}$  and  $\varphi_2 = (1.7 \pm 0.1) \times 10^{-4}$ . ♦A contribution from the Università di Firenze in collaboration with the Ecole Normale Supérieure de Montpellier, the Université de Guelma (Algeria) and the Université de Montpellier II (M. Stiti *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 16130) reports the preparation of gold nanoparticles coated with a carbonic anhydrase inhibitor, performing selective activity towards certain types of cancer. ♦A collaboration of the Institute ICCOM-CNR, Sesto Fiorentino, Firenze, with the EPFL-Lausanne and the Universität Wien (A.K. Renfrew *et al.*, *Organometallics*, 2009, **28**, 1165) resulted in the isolation of a series of ruthenium and osmium complexes of general formula  $[\text{M}(\eta^6\text{-arene})(\text{ptn})\text{Cl}]\text{X}$ ,  $\text{ptn}=3,7\text{-dimethyl-7-phospha-1,3,5-triazabicyclo}[3.3.1]\text{nonane}$ .

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