

FROM THE LITERATURE

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A review-article from the City University of New York and the Rockefeller University (C.M. Drain *et al.*, *Chem. Rev.*, 2009, **109**, 1630) deals with self-organized porphyrinic materials which may form macroscopic robust domains with a great potential in opto-electronics and presumably in the fabrication of photovoltaic devices.

The collaboration of the Universities of Messina and Ferrara with the Université de Montreal and the Université Pierre et Marie Curie has produced (M.-P. Santoni *et al.*, *Dalton Trans.*, **2009**, 3964) a report on the photoinduced energy transfer in rod-like dinuclear ruthenium(II) complexes containing 1,4-bis-2,2':6,2"-terpyridin-4'-y)benzene as bridging ligand and 2,4-bis(2-pyridyl)6-*p*-bromophenyl-1,3,5-triazine and/or (*p*-bromophenyl)-2,2':6',2"-terpyridine in the periphery. The new complexes were investigated for their steady-state absorption, redox behaviour and photophysical properties. Each subunit of the dyad maintains its properties, in agreement with the supramolecular character of the systems. In a somewhat related paper (T. Lazarides *et al.*, *Dalton Trans.*, **2009**, 3971) from the Istituto ISOF-CNR located in Bologna, in collaboration with the University of Sheffield and the University of Manchester, the $[M(\text{bipy})_3]^{2+}$ chromophore, M=Ru, Os, with a pendant aza-18-crown-6 macrocycle, was bonded to neodymium(III) or ytterbium(III): a Ru(II) \rightarrow Nd(III) energy transfer band was consequently observed with a rate constant of $6.8 \times 10^6 \text{ s}^{-1}$.

A contribution from the ISOF-CNR of Bologna in collaboration with Spanish and German Institutions (A.I. Oliva *et al.*, *Dalton Trans.*, **2009**, 4023) has reported the thermodynamics of the assembly process of a trinuclear zinc-porphyrin induced by coordination to a bipyridyl-functionalized perylene-bis-imide. The zinc-porphyrin units of the trimer behave independently.

The trimerization of ethylene has been reported (J. Zhang *et al.*, *Organometallics*, 2009, **28**, 2935) in a contribution from the National University of Singapore, in collaboration with the Chinese University of Xiamen. In this study, some intermetallic Cr-Al complexes have been isolated and structurally characterized. The complexes result from the interaction of AlMe_3 , or methylalumoxane (MAO), with the chromium(III) precursor containing a tridentate pyrazolyl ligand.

A contribution from the Università di Pisa, in collaboration with the Scuola Normale Superiore di Pisa and the Università di Torino (G. Uccello-Barretta *et al.*, *J. Organometal. Chem.*, 2009, **694**, 1813) describes the formation of mesitylene-solvated platinum particles. The growth process of the platinum particles can be retarded by addition of 1,3-divinyl-tetramethylsiloxane.

A contribution from the Istituto Italiano di Tecnologia located in Genova, in collaboration with the University of York and the Institute for Medical Research of Harrow, UK (A.J. Atkin *et al.*, *Dalton Trans.*, **2009**, 3653) has described some CO-releasing molecules, able to efficiently contrast some negative physiological phenomena such as homolytic diseases, growth retardation, homolytic anaemia, renal and vascular damages. The compounds taken into consideration in this study are the

well-established μ -alkyne-hexacarbonyl derivatives of cobalt(0), first reported several years ago by the US Bureau of Mines (H. Greenfield *et al.*, *J. Am. Chem. Soc.*, 1956, **78**, 120).

A collaboration of the Università di Padova with the University of Vermont (C. Musetti *et al.*, *Dalton Trans.*, **2009**, 3657) has resulted in the publication of a paper describing the assembly of small planar ligands to produce structures capable of recognizing G-quadruplex DNA arrangements. To this end, 9,10-phenanthroline derivatives containing alkyl chains functionalized with amino groups were prepared. These were further reacted with Ni^{2+} and Cu^{2+} ions and the resulting products were tested in the recognition process.

A contribution from the Università di Roma "La Sapienza" in collaboration with the Weizmann Institute of Science (M. Radoul *et al.*, *Inorg. Chem.*, 2009, **48**, 3913) has reported some spectroscopic data [W band (94.9 GHz), EPR, ENDOR, HYSCORE] aimed at characterizing the nitrosyl heme complex of nitrite reductase from *Pseudomonas aeruginosa*.

A contribution from the Università de L' Aquila (S. Della-Longa *et al.*, *Inorg. Chem.*, 2009, **48**, 3934) deals with the structure of tetramesitylporphirinatonickel(II), as studied in dilute toluene solution through Full-Multiple-Scattering (FMS), X-Ray Absorption Near-Edge Scattering (XANES), and X-Ray Absorption Spectroscopy (XAS). This study contributed to derive the structural parameters of short-lived photoexcited molecular transients.

A paper resulting from the contribution of the Università di Firenze with those of Padova, Camerino and Insubria (A. Bencini *et al.*, *Inorg. Chem.*, 2009, **48**, 4044) used Dispersion-Corrected Density Functional Theory (DFT-D) calculations, Electron Paramagnetic Resonance (EPR), and magnetic moment measurements at variable temperature to investigate the structure and the electronic/magnetic properties of bis(pyrazolato)copper(II) and its hydration product.

A contribution from the Università di Salerno (A. Poater *et al.*, *Inorg. Chem.*, 2009, **48**, 4062) reports a reaction pathway for the activation of di-oxygen by a tetra-azamacrocyclic complex of copper(I), thus concluding that a hydroperoxo complex of copper(II) is a fundamental intermediate in the C-H hydroxylation reaction. Complex formation between the human prion protein HuPrP(76-114) and copper(II) ions has been studied (G. Di Natale *et al.*, *Inorg. Chem.*, 2009, **48**, 4239) by potentiometric measurements, UV-VIS spectroscopy, circular dichroism (CD), Electron Paramagnetic Resonance (EPR) and Electrospray Ionization Mass-Spectrometry, as for a contribution of the Università di Catania in collaboration with the Università di Sassari, two CNR institutions located in Sassari and Catania and with the University of Debrecen. The HuPrP(76-114) protein binds four metal ions.

A contribution from four different research institutions located in France and in Italy (I. Ascone *et al.*, *Inorg. Chem.*, 2008, **47**, 8629) has described the reaction of bovine serum albumin (BSA) with the

ruthenium(III) complex [*trans*-RuCl₄(DMSO)(imidazole)]⁻, as its imidazolium derivative, a potential anticancer drug. The investigation, which was also carried out by X-ray absorption spectroscopy, confirms that the central metal atom maintains its +III oxidation state upon protein binding.

A study of the Università di Sassari (G. Micera *et al.*, *Dalton Trans.*, **2009**, 1914) has reported density functional (DFT) calculations of the ⁵¹V hyperfine coupling constants for several oxo-vanadium complexes with different donor sets, electric charges and geometries. An excellent agreement with the experimental results was obtained.

M. Delferro *et al.* (*Dalton Trans.*, **2009**, 544) of the Università di Parma have reported the reaction of the zwitterionic ligand EtNHC(S)Ph₂P=NPPH₂C(S)N₂Et with Ru₃(CO)₁₂ leading to different trinuclear products of carbonyl substitution. The X-ray diffraction data of three of the resulting products have been published.

A joint paper involving the Universidad Nacional de Rosario and the Università di Firenze (L.A. Abriata *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 1939) reports the binuclear copper site contained in *Thermus thermophilus* Cu_A in its oxidized form. The study was carried out by detecting the ¹H- and ¹³C NMR data from the cysteine and imidazole ligands. The presence of a hydrogen bond to a coordinated sulphur atom was detected.

Research groups operating at the Universities of Parma, Catania and Bologna (E. Biavardi *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 7447) have reported that a Si(100) surface features molecular recognition properties through covalent functionalization with a tetraphosphonato cavitand complexing a positively charged species.

Two papers contributed by the Università di Bologna report the synthesis of metal clusters containing carbonyl groups as ligands. In one of these papers, published in collaboration with the University of Liverpool, the Università di Siena and the Institute of Chemical and Engineering Sciences of Singapore (C. Femoni *et al.*, *Dalton Trans.*, **2009**, 2217) the electron-deficient heteronuclear icosahedral clusters [Rh₁₂Sn(CO)₂₆]⁴⁻ and [Rh₁₂Sn(CO)₂₅]⁴⁻ were reported as their tetra-alkyl ammonium derivatives. The second paper (C. Femoni *et al.*, *Inorg. Chem.*, 2009, **48**, 1599) reports the anion [Fe₄H(CO)₁₂]³⁻, as obtained by treating [Fe₄(CO)₁₃]²⁻ or [Fe₃H(CO)₁₁]⁻ with a 6 M solution of KOH/MeOH. The iron-carbonyl derivative [NEt₄]₃[Fe₄H(CO)₁₂] was reported, being characterized both spectroscopically and crystallographically. The protonation of [Fe₄H(CO)₁₂]³⁻ probably occurs at one of the carbonyl groups to primarily give the unstable [Fe₄H(CO)₁₁(COH)]²⁻.

Heteronuclear carbonyl clusters of rhenium have been reported in a contribution from the Università di Venezia in collaboration with the Universidade de Vigo (G. Albertin *et al.*, *Organometallics*, 2009, **28**, 1270). The new complexes, of formula Re₂{Sn₂(μ-S)(μ-SO₃)₂}(CO)₄L₂, L=PPh(OEt)₂, CN^tBu, were prepared by reacting the tri-hydrido stannyl precursor Re(SnH₃)(CO)₂L₂ with sulphur dioxide. The X-ray crystal

structures of both Re₂{Sn₂(μ-S)(μ-SO₃)₂}(CO)₄[PPh(OEt)₂]₆, and Re₂{Sn₂(μ-S)(μ-SO₃)₂}(CO)₄[PPh(OEt)₂]₄(CN^tBu)₂ were reported.

The reactions of the rhenium-carbonyl derivative Re₂(CO)₆(thf)₂, containing the labile tetrahydrofuran ligand, with several silsesquioxanes have been reported as for a contribution from the Università di Milano and the INSTM unit of Milano, in collaboration with the University of Bern (C. Dragonetti *et al.*, *Organometallics*, 2009, **28**, 2668). The crystal structures of two of the resulting silicon-containing dinuclear compounds have been solved, the rhenium-rhenium separation being 3.018(8) or 3.004(9) Å.

A paper contributed by the Università di Siena in collaboration with other institutions located in Germany, Russia and USA (W. Siebert *et al.*, *Organometallics*, 2009, **28**, 2707) has described the preparation of triple-decker complexes of ruthenium and cobalt containing a carbocyclic C₅ ligand bridged by a diborolyl ligand, of general formula Co(η⁵-C₅H₅)(μ-1,3-C₃B₂Me₃)M(ring), M(ring) = Ru(η⁵-C₅H₅), Ru(η⁵-C₅Me₅), or Co(C₄Me₄).

The reactions of substituted titanocene precursors with 4,4'-azobispyridine have been reported in a contribution from the Universität Oldenburg (O. Theilmann *et al.*, *Organometallics*, 2009, **28**, 2799). The reactions of the precursors to Ti(η⁵-C₅Me₅)₂ and Ti(η⁵-C₅H₄^tBu)₂ with *trans*-4,4'-azobispyridine led to new tetranuclear titanium organometallics in which the substituted bis-cyclopentadienyl titanium-containing fragments are joined by two aza-ligands. This paper is relevant to the problem of the stabilization of the bis(cyclopentadienyl)titanium(II) fragment. Some years ago (P. Biagini *et al.*, *Gazz. Chim. Ital.*, 1987, **117**, 27) the reduction of Ti(η⁵-C₅H₅)₂X₂, X = Cl, Br, I, with CoCp₂ was reported to be a function of both the nature of the halide and the solvent: in tetrahydrofuran (THF), the bromo- and the iodo-derivatives give Ti(η⁵-C₅H₅)₂X(THF). By reductive treatment under CO, Ti(η⁵-C₅H₅)₂X₂, X = Br, I, gave good yields of Ti(η⁵-C₅H₅)₂(CO)₂.

The carbonylation has been studied of a methyl derivative of platinum(II) containing a tridentate carbon- and nitrogen-based ("pincer") ligand (M.L. Scheuermann *et al.*, *Organometallics*, 2009, **28**, 1613) as for a paper from the Californian Colleges in collaboration with the University of California. The methyl → acetyl conversion was shown to occur by a methyl migration mechanism, upon cleavage of a Pt-N bond, followed by coordination of CO. A similar mechanism was first shown to operate in the case of the paradigmatic MnMe(CO)₅ → Mn(COMe)(CO)₅ transformation (K. Noack *et al.*, *J. Organometal. Chem.*, 1967, **10**, 101) by using ¹³C-labelled compounds under IR monitoring.

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