

FROM THE LITERATURE by Fausto Calderazzo - Università di Pisa

An article has appeared about the structure adopted by proteins in solution (C. Leggio et al., Phys. Chem. Chem. Phys., 2008, 10, 6741). Through Small Angle X-ray Scattering (SAXS) measurements, it has been shown that defatted human serum albumin (HSA) in solution adopts a more open heart-shaped structure than in the crystal. Proteins in solution may be present in several conformations. On the other hand, SAXS measurements cover an average over several conformations, a property which makes this type of experiments useful for proteins in solution.

A family of polynuclear carboxylato-salicylaldiminato (sao) complexes of manganese(III) has been reported (L.F. Jones et al., Dalton Trans., 2008, 6205) as for a contribution from the School of Chemistry, Edinburgh, UK, and from the University of Patras, Greece. The new complexes of $3d^4$ electronic configuration, of general formula $Mn_6O_2(R-sao)_6X_2(Et-OH)_6]$, R being Et for X=Br, and Me for X=I, have been found to exhibit a single-molecule magnetic behaviour with spin Hamiltonian parameters S=12, g=1.98, and D=-0.36. This field of research about polynuclear aggregates of transition elements has been actively investigated by D. Gatteschi and his coworkers of the Università di Firenze: see, for example, D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press, Oxford, 2006. It is of some interest to compare these data with some earlier ones obtained through the reaction of Mn(C₅H₅)₂ with RNH₂/CO₂ (A. Belforte et al., J. Chem. Soc., Dalton Trans., 1988, 2921) on a series of N,N-dialkylcarbamato complexes of manganese(II). The X-ray diffraction data on the hexanuclear complex Mn₆(O₂CNEt)₁₂ thus obtained show the presence of four five-coordinated manganese atoms, while the remaining two central metal atoms are hexacoordinated. A further contribution reports the synthesis, X-ray structural investigation and magnetic properties of a tetranuclear diethanolaminato (DEA) nickel(II) derivative of formula Ni₄Cl₄(DEA)₄, as a contribution from several research institutions located in UK, France, and USA (A. Ferguson et al., Dalton Trans., 2008, 6409). The molecule, of S_4 symmetry, crystallizes in the 141/a tetragonal space group, each of the hexacoordinated nickel atoms being surrounded by the nitrogen atoms and by the oxygen donor atoms of the tridentate ligand. Magnetic exchange coupling was observed within the four nickel atoms. New wheel-shaped dodecanuclear manganese complexes of formula $Mn_{12}(adea)_8(CH_3COO)_{14} \cdot 7$ MeCN, $Mn_{12}(edea)_8(CH_3CH_2COO)_{14}$ and Mn₁₂(edea)₈(CH₃COO)₂(CH₃CH₂COO)₁₂, with adea=N-allyl-diethanolaminato and edea=N-ethyl-diethylaminato, have been reported as a contribution from the University of California at San Diego, the University of Central Florida and Florida State University (S.J. Shah et al., Inorg. Chem., 2008, 47, 9569). In these mixed-valent compounds, six manganese(II) and six manganese(III) centres are present, alternating in a wheel-shaped arrangement. Magnetic susceptibility data have been

obtained in the 1.8–300 K temperature range. As a further sign of the considerable interest in these polynuclear compounds, mention should be made of the mixed-valent compound of formula [Mn₂₅O₁₈(OH)₂ $(N_3)_{12}(pdm)_6(pdmH)_6|Cl_2$, pdm = pyridine-2,6-dimethanolato, containing six Mn(II), eighteen Mn(III), and one Mn(IV), characterized by a barrel-like cage structure. This product was reported by researchers operating at the University of Florida, and at the Institut Néel of the French CNRS (M. Murugesu et al., Inorg. Chem. 2008, 47, 9459). Variable-temperature direct current magnetic susceptibility data were presented, as obtained in the 1.8-300 K temperature range in a 0.1 T field.

A contribution from several international research institutions including the Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, and the Istituto Nazionale di Scienze e Tecnologia dei Materiali, Milano, has reported the synthesis of a new aluminium derivative containing 1,4-naphthalene-dicarboxylato (1,4-NDC) as ligand, of formula Al(OH)(1,4-NDC)·2 H₂O (A. Comotti et al., J. Am. Chem. Soc., 2008, 130, 13664). Selective uptake of xenon was observed for this product. A series of papers have appeared dealing with different aspects of metal oxides and their use in solid-state phenomena. A group of researchers of the Università di Padova, and of Istituto Nazionale di Scienza dei Materiali, Trieste, has investigated the perovskite-type oxide of formula $La_{0.6}Sr_{0.4}Co_{1-x}Fe_vO_{3-\delta}$, (y=0.2, 0.5, 0.8), as prepared by the citrate gel method, and the influence of the cobalt/iron molar ratio on the chemical and structural properties (M.M. Natile et al., Chem. Mater., 2008, 20, 2314). In addition, the catalytic properties towards alcohol steam reforming were studied. For the characterization, X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), thermal analysis, Kr physisorption surface area, scanning electron microscopy (SEM), and temperature-programmed reduction (TPR) were employed. Researchers of the Università di Pavia, in collaboration with the Institut Laue-Langevin of Grenoble (L. Malavasi et al., Chem. Mater., 2008, 20, 2343) have reported an extensive neutron diffraction study, carried out at high temperature, on the proton conducting substance of formula BaCe_{0.8}Y_{0.2}O_{2.9}. The monoclinic structure at room temperature is converted to the orthorhombic Imma space group at 500 °C, and to a rhombohedral structure in the range 600-700 °C; finally the solid converts to the more symmetric cubic structure at 800 °C.

A contribution from an INSTM unit located in Trieste, and from the Università di Trieste, in collaboration with a Pakistani Institute located in Islamabad (A. Hameed et al., J. Am. Chem. Soc., 2008, 130, 9658) has reported on the surface modifications induced by UV-Vis irradiation leading to nanocomposites of formula Bi₂O₃/Bi₂O_{4-x}. The photocatalytic performance of the nanocomposite was evaluated in comparison with that of the individual Bi₂O₃ and Bi₂O_{4-x} in the degradation of methylene blue, methyl orange and phenol. The conclusion of this study was that the ${\rm Bi_2O_3/Bi_2O_{4-x}}$ system is promising as a photocatalyst. A contribution from some Italian institutions (R. Scotti *et al.*, *Chem. Mater.*, 2008, **20**, 4051) has described the sol–gel synthesis of ${\rm TiO_2}$ from ${\rm TiCl_4}$ in the presence of the triblock co–polymer Pluronic P-123 (Basf code) as templating agent. Mesoporous and nanocrystalline ${\rm TiO_2}$ samples (anatase, rutile, and mixed phases), after calcination at 400 °C, were characterized by TEM, HRTEM, XRD, and surface area measurements. A paper contributed by two institutions of the Università di Perugia (L. Valentini *et al.*, *Chem. Mater.*, 2008, **20**, 32) has introduced a new diaryl–anthracene molecule containing hexyloxy groups in the aryl moieties, the flexible side chains leading to a higher solubility.

Two research institutions of the Università di Catania (G.M.L. Messina et al., Chem. Commun., 2008, 5031) have reported on the combination of plasma surface modified polymer thin films with colloidal nanosphere litography in order to produce two-dimensional nanopore arrays used as nanocontainers of proteins. Polyhydroxymethyl siloxane was the polymeric material used in this study. A contribution by the laboratories of the Centro Ricerche Fiat, Orbassano, Italy, in collaboration with a CNR institution located in Napoli, i.e. Istituto dei Materiali Compositi e Biomedici, and the Ludwig-Maximilian Universität in München has reported a simple method for producing highly luminescent gold-containing films by thermal decomposition of dodecylthiolatogold(I) (A.S. Susha et al., Chem. Mater., 2008, 20, 6169). The gold(I) complex was embedded in a polystyrene matrix, and the thermal treatment of the resulting composite was followed by UV-Vis spectroscopy: the spectra of the films undergo a change from that typical of the starting gold(I) complex to the broad plasmon peak of gold(0) at about 600 nm. The syntheses of new substituted thiols have been reported (G. Zotti et al., Chem. Mater., 2008, 20, 397) as a contribution from two CNR institutions located in Padova and Milano. The compounds form self-assembled monolayers on gold with high coverages in the range 2÷4x10⁻¹⁰ mol x cm⁻².

The preparation has been reported of novel bifunctional conjugates resulting from the linkage of inorganic nanoparticles (gold or an iron oxide) to organic oligothiophene fluorophores (OTF). The OTF/nanoparticles were characterized by gel electrophoresis, photoluminescence spectroscopy and dynamic light scattering, as for a contribution from research institutions of CNR and INFM located in Lecce and Bologna (A. Quarta et al., J. Am. Chem. Soc., 2008, 130, 10545). The iron oxide/OTF conjugates preserve the magnetic properties and the fluorescence, after uptaking by human tumour cells.

A contribution resulting from the collaboration within three research institutions located in London, Lausanne and Napoli (S.R. Martin *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 9963) has reported on the behaviour of proteins in the presence of low concentrations of three

alcohols, namely CF_3CH_2OH , or CH_3CH_2OH , or CH_3OH . This study suggests that at low concentration and at physiological pH, alcohols widen the temperature range of stability of Yfh1, the yeast ortholog of the human frataxin.

A contribution from two research institutions located in Bologna (Università and INSTM) has reported the structural parameters of some selected cobalt– and mixed cobalt/nickel hexacyanoferrates (M. Giorgetti et al., Inorg. Chem., 2008, 47, 6001). The CN bond length has been determined with a statistical error of a few thousandths of an angstrom.

The hexanuclear $\mathrm{Fe_6S_6}$ aggregate present in [FeFe] hydrogenase has been studied by a DFT approach, as for a contribution from the Università di Milano-Bicocca (M. Bruschi *et al.*, *Inorg. Chem.*, 2008, **47**, 6056). A satisfactory agreement with the experimental data was obtained in the case of the solvated complexes, consistent with a possible delocalization of the large negative charge of the aggregate.

Researchers operating in several Italian research institutions, including the Università di Roma "La Sapienza", have reported some new palladium(II) complexes derived from tetrakis[2,3–(5,6–di–2–pyridylpyrazino) porphyrazine], including their physico–chemical properties (M.P. Donzello *et al.*, *Inorg. Chem.*, 2008, **47**, 3903). Among the products isolated, this paper reports the properties of a pentanuclear species, where the central pyrazinoporphyrazine core is surrounded by four PdCl₂ units coordinated to the pyridine N atoms.

A new class of conducting discotic liquid crystals has been reported (M. Talarico *et al., Chem. Mater.*, 2008, **20**, 6589) as a contribution of the Università della Calabria, in collaboration with the Instituto de Ciencia de Materials de Madrid and the Universidad de Zaragoza. The compounds studied in this contribution are based on derivatives of an extended π -system with three carbazole units sharing an aromatic ring. The highest mobility was measured for the product with the lower degree of alkyl substitution within the carbazole unit.

A collaboration of three research institutions located in Firenze with the Dipartimento di Scienze Farmaceutiche, Università di Padova, has produced a contribution (C. Bazzicalupi *et al., Inorg. Chem.*, 2008, **47**, 5473) reporting a comparison of the hydrolytic properties on plasmid DNA by a mononuclear Zn(II) complex and a dinuclear one formed by two monocyclic N-containing ligands. The dinuclear complex was found to be considerably more active than the mononuclear one.

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