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E-MRS Spring Meeting 2003
June 10 - 13, 2003

SYMPOSIUM K

Design, characterisation and modelling of
molecule-based magnetic materials

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E-MRS 2003 SPRING MEETING

SYMPOSIUM K

Tuesday, June 10, 2003
Mardi 10 juin 2003

Morning
Matin

08:45

OPENING

Session I

K-I.1 9:00 -Invited-

OXYGEN BRIDGED POLYMETAL AGGREGATES AS BUILDING BLOCKS FOR EXTENDED MOLECULE-BASED MAGNETIC STRUCTURES

Annie K Powell, Muralee Murugesu, Christopher E Anson, University of Karlsruhe, Institute for Inorganic Chemistry, Engesserstrasse 15, 76128 Karlsruhe, Germany

Hydrolysis reactions are a feature of the chemistry of many metal ions and usually lead to the formation of oxo- and hydroxo-bridged aggregates and then hydroxide, hydroxyoxide or oxide minerals. This chemistry can be controlled by supplying templating ligands which direct the size and shape of the intermediate aggregated species in a manner similar to that employed in Nature in biomineralisation processes. This makes it possible to favour the formation of molecular polymetal-oxo clusters which can have different magnetic properties from the related extended mineral phases as a result of the strong boundary effects which operate in such systems. Furthermore, it is possible to functionalise the encapsulating ligands or supply linking synthons in order to enhance different types of supramolecular interactions amongst the molecules. In this way it is possible to create arrays of linked magnetic particles which can be arranged in 1-D chains, 2-D sheets or 3-D arrays. Structure determination using single crystal X-ray diffraction has been used in conjunction with a variety of magnetic property studies in order to characterise these systems.

K-I.2 9:30

SYNTHESES AND CRYSTAL STRUCTURES OF A SERIES OF MULTIVALENT HIGH-NUCLEARITY PLATINUM CARBONYL CLUSTERS DISPLAYING AN ELECTRON SPONGE BEHAVIOUR

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It has been suggested that large homoleptic carbonyl metal clusters (LHCMC) are assimilable to molecular nanosized capacitors in that the metal core, shielded by carbonyl ligands, is a quantum dot in which the cluster valence electrons are confined. They could represent valid building blocks for assembling devices for data storage in microelectronics. Moreover, there is a widespread belief that LHCMC containing interstitial metal atoms could behave as electron sponges, exhibiting multivalence or at least reversible redox properties. This contribution is to show that large homoleptic carbonyl Pt clusters (LHCpC) fulfilling the above structural requirements are excellent tools for supporting such expectations. Indeed LHCpC such as [Pt₁₉(CO)₂₂]⁴⁻ and [Pt₂₄(CO)₃₀]²⁻ display several redox steps with electrochemical reversibility and, in the latter compound, a multivalence behaviour with at least three stable oxidation states, including either close- and open-shell electronic configurations. Here we report the syntheses and the single-crystal structural characterizations of [Pt₂₄(CO)₃₀]ⁿ⁻ (n=0,1,2) belonging to a multivalent supercubane ccp Pt₂₄ core. The related LHCpC anions, viz. [Pt₂₆(CO)₃₂]²⁻ and [Pt₃₈(CO)₄₄]²⁻, which also contain interstitial Pt atoms, display as well a multivalence behaviour which will be discussed in some detail.

K-I.3 9:50

MAGNETO-STRUCTURAL CORRELATIONS IN DOUBLE CARBOXYLATO-OXYGEN BRIDGED GADOLINIUM(III) COMPLEXES

Catalina Ruiz-Pérez(a), María Hernández-Molina(a), M. Milagros Laz(b), Trinidad López(c), Francesc Lloret(d) and Miguel Julve(d), (a)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Física Fundamental II, Universidad de La Laguna, Tenerife, Spain, (b)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Edafología y Geología, Universidad de La Laguna, Tenerife, Spain, (c)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Física Básica, Universidad de La Laguna, Tenerife, Spain, (d)Instituto de Ciencia Molecular/Dpto de Química Inorgánica, Universitat de València, Burjassot, Valencia, Spain

Coordination compounds with lanthanide cations have attracted the interest of researchers in materials science because of their luminescence and/or magnetic properties. The rather large magnetic moment of most of the lanthanide(III) cations (Ln(III)) together with their anisotropy make them very appealing in the preparation of magnetic materials. A great number of 4f-3d or 4f-organic radical systems have been described. However, except for the isotropic Gd(III), which has an 8S_{7/2} single-ion ground state, very little is known concerning neither the nature and magnitude of the coupling in such compounds nor the evolution of the magnetic properties along the lanthanide series. One of the reasons for this situation is the orbital contribution occurring for most of the Ln(III) ions, i.e., the ligand field effects on the magnetic properties of the ions displaying spin-orbit coupling.

In the present work we present our first magneto-structural results on polynuclear gadolinium(III) complexes where two single carboxylato-oxygen atoms act as bridges. At the stage we are, it seems clear that the value of the angle at the bridging carboxylato-oxygen atom plays a key role on the nature and magnitude of the magnetic coupling observed. This situation remains that of the di-μ-hydroxodicopper(II) family where the intradimer magnetic coupling is ferro- or antiferromagnetic depending mainly on the value of the angle at the hydroxo bridge. Work is in progress (magneto-structural studies coupled with DFT type calculations) in order to design new examples of ferromagnetically coupled oxo-bridged Gd(III) compounds and to understand the exchange mechanism involved.

10:10

BREAK

Session II

K-II.1 10:30

TOWARD THE DESIGN OF MOLECULAR MAGNETIC MATERIALS THROUGH WEAK INTERACTIONS

J. Pasán(a), J. Sanchiz(b), C. Ruiz-Pérez(a), F. Lloret(c) and M. Julve(c), (a)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Física Fundamental II, Universidad de La Laguna, Tenerife, Spain, (b)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Química Inorgánica, Universidad de La Laguna, Tenerife, Spain, (c)Instituto de Ciencia Molecular/Dpto de Química Inorgánica, Universitat de València, Burjassot, Valencia, Spain

Malonate-bridged copper(II) complexes (malonate = dianion of 1,3-propanedioic acid) appear as very interesting compounds from structural and magnetic points of view. We have found that the flexibility and versatility of the malonate dianion results in the ferromagnetic interaction always dominant in our malonate-bridged copper(II) compounds. This fact led us to consider the use as a ligand of substituted malonate derivatives aiming at increasing the dimensionality and keeping the ferromagnetic interaction.

In our synthetic work, we planned to use intermolecular forces (π-π-stacking benzene herringbone interactions, hydrogen bonding) to control the relative arrangement of the molecules in the crystal. While the control of crystal packing is still a challenge, the use of relatively strong interactions such as π-π ones allows to get reasonable predictions of short-range intermolecular interactions. Having in mind that the phenylmalonate anion (the phenyl ring being attached to the central carbon atom of the malonate) has the ability to establish π-π interactions and to create a hydrophobic layer of phenyls groups, we focus here on its use as a ligand toward copper(II) ions. We present here our most recent results of a family of phenylmalonate-bridged copper(II) complexes with pyridine-like ligands built up by the same structural motif: [Cu(phmal)(L)] (H₂phmal = phenylmalonic acid; L = pyrimidine, pyrazine, 4-cyanopyridine, 3-cyanopyridine)

- K-II.2** 10:50 NOVEL THREE-DIMENSIONAL 3d-4f-3d TRIMETALLIC MOLECULAR MAGNETS
M. Ohba, T. Shiga, H. Okawa, Kyushu Univ., JST PRESTO, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan
 We are systematically studying the structure, magnetic and magneto-optical properties of cyanide-bridged bimetallic assemblies. One of our recent targets is a trimetallic system having a 4f ion with a hope to modulate magnetic and magneto-optical properties. Here we report novel three-dimensional trimetallic assemblies, $[\text{Co}_2\text{Ln}(\text{L})_2][\text{Cr}(\text{CN})_6]_n\text{H}_2\text{O}$ ($\text{Ln}^{3+} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$; $\text{L}^2 = 2,6\text{-bis}(\text{acetoacetyl})\text{pyridine}$).
 The trimetallic assemblies were obtained in a crystalline form by 1 : 1 reaction of trinuclear complex, $[\text{Co}_2\text{Ln}(\text{L})_2(\text{NO}_3)_3]$, and $\text{K}_3[\text{Cr}(\text{CN})_6]$ in water. X-ray crystallography has revealed that these assemblies are isomorphous. $[\text{Cr}(\text{CN})_6]^{3-}$ coordinates to Co^{2+} centers to form 2-D grid on the ab plane. Ln^{3+} centers combine the grids along the c axis and to form a 3-D network. The $\text{Co}_2\text{La-Cr}$ compound shows a metamagnetic behavior below 7.4 K. On the other hand, the other compounds show a ferrimagnetic ordering with $T_c = 9 - 11$ K. In each case a ferromagnetic interaction operates between Cr^{3+} and Co^{2+} through cyanide-bridge and spins align in parallel on the grid-layer. In the case of $\text{Ln} = \text{La}$, the magnetic interaction between Co^{2+} centers through diamagnetic La^{3+} is weakly antiferromagnetic. In the others, the magnetic interaction between Co^{2+} and Ln^{3+} ions through enolate-bridge is antiferromagnetic. Thus, the bulk magnetic property of $[\text{Co}_2\text{Ln}(\text{L})_2][\text{Cr}(\text{CN})_6]_n\text{H}_2\text{O}$ can be modulated by the change in the metal-combination of the Co_2Ln trinuclear component.
- K-II.3** 11:10 NANOPATTERNING OF MOLECULAR MAGNETS BY STAMP-ASSISTED SELF ORGANISATION AND MICROTRANSFER MOLDING
M. Cavallini(a), M. Massi(a), F. Biscarini(a), D. Ruiz-Molina(b), J. Gomez(b), C. Rovira(b), J. Veciana(b), (a)CNR-ISMN, Via P. Gobetti 101, 40129 Bologna, Italy, (b)Institut de Ciencia de Materials de Barcelona (C.S.I.C.), Campus Universitari de Bellaterra, 08193 Cerdanyola, Spain
 We present two methods based on unconventional parallel nanolithography for patterning molecular magnets on a large area and with nanometer resolution. The former termed lithographically controlled wetting (LCW) uses a solution of molecular magnets, viz. Mn_{12} clusters, and is based on the wetting (or de-wetting) of the surface controlled by the capillary forces which are established between the surface and the stamp protrusions. By governing concentration of the solution, distance and pressure of the stamp, and interactions between the clusters and the surface, we can orderly pattern arrays of monolayer stripes or droplets made of molecular magnets.
 In the second application we show the fabrication at submicron resolution of an ordered pattern of molecular magnets dispersed in a polycarbonate matrix by modified micro-transfer molding and subsequent solvent exposure.
- K-II.4** 11:30 -Invited- MOLECULAR MAGNETS BASED ON $\text{Mn}^{2+}/[\text{Mo}(\text{CN})_7]^{4-}$ SYSTEM : TEMPLATING ROLE OF COUNTER CATIONS
 Stephanie Willemin(a), Xavier Le Goff(b), **Joulia Larionova**(a), Rodolphe Clérac(b), Bruno Donnadieu(c), Christian Guérin(a), Claude Coulon(b), (a)UMR 5637, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier, France, (b)CRPP, UPR CNRS 8641, av. Dr. A. Schweitzer, 33600 Pessac, France, (c)LCC, UPR CNRS 8241, 31077 Toulouse, France
 Molecular based magnets, molybdenum, magnetic materials
 In the past ten years, numerous bimetallic cyano-bridged molecular based networks have been synthesized and have aroused a great deal of interest for their possible applications in molecular electronics, in electron-transfer process, and as molecular magnets. The $\text{Mn}^{2+}/[\text{Mo}(\text{CN})_7]^{4-}$ system highlights perfectly the structural versatility and the magnetic property richness of materials containing heptacyanomolybdenum (III) as a building block. In this system, nature and coordination sphere of metal ions are not the only parameters to design new cyano-bridged architectures. Introduction of cations can affect the topology and the dimensionality of the network and therefore strongly influenced the magnetic properties. A family of compounds $[\text{Cat}]_2\text{Mn}_3(\text{H}_2\text{O})_n[\text{Mo}(\text{CN})_7]_2\text{-mH}_2\text{O}$ with different counter ions (K^+ , NH_4^+ , $\text{N}(\text{CH}_3)_4^+$) have been synthesized and crystallized. All compounds crystallize in the monoclinic system, and the lattice symmetries are relatively low. The organization, the dimensionality of the structures and thus the magnetic properties depend of the size and the nature of counter cations.

12:00

LUNCH

Tuesday, June 10, 2003
Mardi 10 juin 2003

Afternoon
Après-midi

Session III

K-III.1 14:00 -Invited-

AN UNUSUAL MAGNETIC STATE OF LITHIUM-DOPED MoS₂ NANOTUBES

D. Mihailovic, D. Arcon, A. Mrzel, A. Zorko, M. Remskar and V.V. Kabanov, Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, Z. Jaglicic, Institute of Mathematics, Physics and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia, R. Dominko, National Chemistry Institute, Hajdrihova 19, 1000 Ljubljana, Slovenia, C.J. Gómez-García, J.M. Martínez-Agudo, E. Coronado Instituto de Ciencia Molecular. Dpto. Quémica Inorgánica. Univ. de Valencia, 46100 Burjassot, Spain

We report on the very peculiar magnetic properties of an ensemble of very weakly coupled lithium-doped MoS₂ nanotubes. The temperature-independent magnetic susceptibility χ of the system is nearly three orders of magnitude greater than in typical Pauli metals, yet there is no evidence for any instability which would alleviate this highly frustrated state. Instead, the material exhibits peculiar paramagnetic stability down to very low temperatures, with no evidence of a quantum critical point (QCP) as $T \rightarrow 0$ in spite of clear evidence for strongly correlated electron behaviour. The exceptionally weak inter-tube interactions appear to lead to a realization of a near-ideal 1-dimensional state in which fluctuations prevent the system from re-ordering magnetically, or structurally.

K-III.2 14:30

SURPRISING ELECTRONIC-MAGNETIC PROPERTIES OF CLOSED PACKED ORGANIZED ORGANIC LAYERS

I. Carmeli(a), G. Leitus(b), S. Reich(b), Z. Vager(c), **R. Naaman**(a), (a)Department of Chemical Physics, (b)Department of Material and Interfaces, (c)Department of Particle Physics Weizmann Institute, Rehovot 76100, Israel

We investigated spin polarized electron transmission (SPET) through organized monolayers of a helices of polypeptides adsorbed on gold substrate. It is shown that the spin dependent transmission of polarized electrons through these layers depends both on the chirality of the molecules and on the direction of the dipole moment of the adsorbed molecules. In addition, grazing angle magnetic field dependent FTIR spectroscopy indicate that the polypeptide film posses permanent magnetic properties at room temperature. Temperature dependent SPET combined with contact potential difference (CPD) and two photon photoelectron spectroscopy reveal that the electronic properties and the magnetic behavior of the films vary with temperature. The temperature dependence is associated with a coherent coupling between the hydrogen bonds at low temperatures. A model is proposed that rationalizes all the observations.

K-III.3 14:50

SYNTHESIS, STRUCTURAL AND MAGNETIC CHARACTERIZATION OF ANISOTROPIC CYANIDE-BRIDGED Fe(III)Mn(II) BIMETALLIC COMPLEX

Rodrigue Lescouëzec(a), Francesc Lloret(a), Miguel Julve(a), Jacqueline Vaissermann(b) and Michel Verdaguer(b), (a)Dept. de Química Inorgànica/Instituto de Ciencia Molecular, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot (València), Spain, (b)Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Unité CNRS 7071, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

The control of the topology and dimension of polynuclear magnetic compounds is of considerable importance because of their influence on the magnetic properties. A well known approach to build magnetic compounds of desired architecture is the so-called self-assembly process. It consists of using a stable compound (Lewis base) as a ligand towards another entity (Lewis acid). The synthesis of *n*-dimensional (*n* = 0-3) compounds (such as high spin molecules [1] and photomagnetic polymers [2]) from hexacyanometallate precursors and aquocomplexes (or partially blocked complexes) illustrates the efficiency of this route.

In the context of the increasing interest for low-dimensional magnetic compounds in the cyanide-containing complexes, [3] we developed a new approach based on the use of the modified cyano-building block of general formula : $[M(L)(CN)_x]^{(x+1-m)-}$ (L = blocking ligand). Besides the tendency of these complexes to form low dimensional compounds (because of the reduced number of cyanide groups), the introduction of an adequate blocking ligand allows a better control of the properties of the precursor (coordinating ability and solubility,...) and consequently, those of the final product. Recently, we report the synthesis and magneto-structural characterization of the new mononuclear precursor *fac*-[Fe^{III}{HB(pz)₃}(CN)₃]⁻ [HB(pz)₃] = hydrotrispyrazolylborate] and that of the high spin molecule it undergoes by reacting with the hexoaquairon(III) cation [4]. Along these lines, we prepared the related monoanionic *mer*-derivative of formula *mer*-[Fe^{III}(bpca)(CN)₃]⁻ [bpca = bis(2-pyridylcarbonyl)amidate anion] and we use it as a ligand towards first row transition metal ions. We present here the first magneto-structural results concerning the precursor PPh₄[Fe(bpca)(CN)₃]·H₂O and the ladder-like chain compound obtained from it: [Mn(H₂O)₆{Fe(bpca)(CN)₃}]_n[Fe(bpca)(CN)₃]_n·3H₂O.

[1] T. Mallah, C. Auberger, M. Verdaguer, P. Veillet, *Chem. Commun.*, 1995, 61 ; A. Sculler, T. Mallah, A. Nivorozhkin, M. Verdaguer, P. Veillet, *New J. Chem.*, 1996, 1.

[2] V. Escax, A. Bleuzen, C. Cartier dit Moulin, F. Villain, A. Goujon, F. Varret, M. Verdaguer, *J. Am. Chem. Soc.*, 2001, 123, 12536; G. Champion, V. Escax, A. Bleuzen, F. Villain, F. Baudelet, E. Dartyge, M. Verdaguer, *J. Am. Chem. Soc.*, 2001, 123, 12544 and references herein.

[3] R. Lescouëzec, J. Vaissermann, F. Lloret, C. Ruiz Pérez, M. Julve, Y. Dromzé, M. Verdaguer, W. Wernsdorfer, D. Gatteschi, *Angew. Chem.*, march 2003, to be published ; J.J. Sokol, A.G. Hee, J.R. Long, *J. Am. Chem. Soc.*, 2002, 124, 7656

[4] R. Lescouëzec, F. Lloret, M. Julve, J. Vaissermann, M. Verdaguer, *Inorg. Chem.* 2002, 41, 5943.

K-III.4 15:10

SYNTHESIS AND CHARACTERIZATION OF TRANSPARENT SUPERPARAMAGNETIC $K_xCo(II)_y[Fe(III)(CN)_6]_z$ -SILICA NANOCOMPOSITES WITH TUNABLE PHOTOMAGNETISM

A.E. Stiegman(a), Joshua G. Moore(a), Eric J. Lochner(b), Chris Ramsey(a), Naresh S. Dalal(a), (a)Department of Chemistry, Florida State University, Tallahassee, Florida, USA, (b)Materials Research and Technology Center (MARTECH), Florida State University, Tallahassee, Florida, USA
We report the preparation of homogeneous, optically transparent, moldable silica xerogel nanocomposites containing this compound ferromagnetic Prussian-blue analog $K_xCo(II)_y[Fe(III)(CN)_6]_z$. Relative to the bulk, this new material exhibits a blue shift in the intervalence band of $\sim 2900\text{ cm}^{-1}$, superparamagnetic behavior below the blocking temperature ($T_b \sim 10\text{ K}$) and a tunable photomagnetic effect, which is facilitated by an in-situ ligand-substitution process. These properties are attributable to the arrested precipitation and sequestering of $\sim 8\text{-}10\text{ nm}$ nanoparticles of $Co(II)_3[Fe(III)(CN)_6]_2$ during the sol-gel process. This new approach to magnetic nanocomposites may have applications in advanced magnetooptics and photomagnetic information storage

15:30

BREAK

Session IV

K-IV.1 16:00 -Invited-

SYNTHESIS AND CHARACTERIZATION OF MAGHEMITE NANOPARTICLES ENTRAPPED IN PSEUDO SINGLE CRYSTALS OF CYCLODEXTRIN

D. Bonacchi(a), **A. Caneschi**(a), D. Gatteschi(a), C. Sangregorio(a), R. Sessoli(a), A. Falqui(b), (a)Department of Chemistry, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (Fi), Italy, (b)Department of Chemistry, University of Cagliari, SP Monserrato Sestu Km 0.700, 09042 Monserrato (Cagliari) Italy

During the attempt to synthesize polynuclear magnetic metal ion compounds using the family of cyclodextrin ligands with structures similar to those reported with lead and other non-magnetic ions,[1] we have found a new method to produce magnetic nanoparticles. Nanoparticles in general are produced with many different techniques, widely differing in the background principles used to limit their size and dispersion, but the present one appears to be quite original. Nanoparticles of iron, nickel or cobalt oxides can be entrapped in tiny single crystals of the organic host. Evidences of nanosize particles embedded in the organic crystals were obtained by HR-TEM which showed the occurrence of uniformly dispersed particles with average diameter of 18 \AA . The resulting crystals give diffraction patterns with crystallographic parameters very close to those of cyclodextrin crystals without metal-oxide nanoparticles. Up to now all the attempts to refine the structure were unsuccessful. The magnetic properties are those expected for an assembly of randomly oriented nanoparticles: irreversibility between the ZFC and FC magnetization appears below ca. 10 K while at lower temperature non zero coercivities are observed in hysteresis loops. Spin-glass like behaviour has been observed in AC susceptibility experiments where frequency dependent maxima are observed. We have also observed an anomalous dependence of the temperature of the maximum in the susceptibility, T_{max} , with the applied field. This behaviour has been attributed to the complex magnetic properties of the surface that shows the limits of classical models. We wish to discuss the general relevance and the possibilities of applications stemming from this novel finding.

K-IV.2 16:30

STRUCTURAL AND MAGNETIC INVESTIGATIONS ABOVE AND BELOW THE CRITICAL TEMPERATURE OF A MIXED-VALENCE IRON (II,III) 2D LAYER COMPOUND

Eva Rentschler, Jacob Overgaard, Grigore A. Timco, Finn K. Larsen Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, 45470 Mülheim, Germany, Department of Chemistry, University of Aarhus, Langelandsgade 140, 8000 Aarhus C, Denmark, Institute of Chemistry, Academy of Sciences of the Republic of Moldova, 2028 Chisinau, Moldova

Molecular species containing more than one metal ion offer the possibility of co-operative behavior between the metal ions, which may lead to new properties and reactivity. Nature utilizes such co-operative properties in enzymes that catalyze several different processes. In addition, magneto-structural correlations in oligonuclear metal complexes are of fundamental interest in the field of molecular based magnets. Oxo- and hydroxo-bridged polymetallic systems are the most thoroughly investigated examples of single molecule magnets. In order to investigate co-operative effects in transition metal complexes we used the trinuclear complex $[Fe_3O(O_2CBut)_6(H_2O)_3] \cdot O_2CBut$, a very versatile starting material, for the preparation of a variety of oligonuclear iron complexes. We have been successful in isolating several different oxo-, hydroxo-, and peroxy-bridged iron(III) compounds, as well as heterometallic complexes from this approach. Our present studies are motivated by our interest in investigating electron transfer processes in mixed-valence iron carboxylates. One example of such an iron(II)/(III) compound is the 2D-network $\{[Fe_2(O_2CH)_5(4\text{-pic})_3]_2\}_n$, in which the pivalato bridges have been replaced by formate ligands. This new polynuclear complex exhibits an overall antiferromagnetic ordering around 20 K , confirming extended spin-spin interactions. The present paper describes the crystal structure above and below the critical temperature. The magnetic properties and mössbauer spectra of this compound are discussed in detail.

K-IV.3 16:50

SELF ASSEMBLY OF SINGLE MOLECULE MAGNETS ON THE Au (111) SURFACE

D. Bonacchi (a), A. Caneschi (a), D. Gatteschi (a), A. Cornia (b), A.C. Fabretti (b), M. Pacchioni (b), L. Zobbi (b), R. Biagi (c), U. Del Pennino (c), H.S.J. Van der Zant (d), L. Gurevich (d), (a) Dipartimento di Chimica, INSTM and Università degli Studi di Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy, (b) Dipartimento di Chimica, INSTM and Università degli Studi di Modena e Reggio Emilia, Via G. Campi 183, 41100 Modena, Italy, (c) Dipartimento di Fisica, INFN and Università degli Studi di Modena e Reggio Emilia, via G. Campi 213/A, 41100 Modena, Italy, (d) Department of Applied Sciences and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

In the last decade, it was discovered that in principle single molecules can be used to store magnetic information. The research in this field started from the observation that a dodecamanganese(III,IV) cluster, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}\cdot 2\text{AcOH}$ (Mn₁₂-acetate), exhibits a hysteresis cycle under cryogenic conditions. This compound is considered the prototype of a class of materials referred to as Single-Molecule Magnets (SMMs), as their magnetic behavior is strongly reminiscent of bulk magnets. Practical applications of SMMs as molecular-scale units for information storage or qubits for quantum computation require the addressing of individual molecules, i.e. imaging, probing and eventually manipulating individual molecules. This goal can be most simply reached by depositing target molecules on a suitable substrate at monolayer or submonolayer coverage and by addressing them individually using scanning probe microscopies, like Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and Magnetic Force Microscopy (MFM). We have now been able to achieve the deposition of suitably derivatized Mn₁₂-type clusters on a Au(111) surface and wish to report their direct observation at the single-molecule level by STM. This is the first time that this goal is achieved and opens exciting perspectives for magnetic information storage in an individual cluster.

K-IV.4 17:10

CHIRAL MOLECULAR MAGNETS

David B. Amabilino(a), Christian Sporer(a), Maria Minguet(a), Daniel Ruiz-Molina(a), Jordi Gómez(a), Elsa Lhotel(b), Vincent Villar(b), Carley Paulsen(b), Vladimir Laukhin(a,c), Josep Fontcuberta(a), Benjamín Martínez(a), Klaus Wurst(d), Peter Jaitner(d), Dominique Luneau(e), Jaime Veciana(a), (a)Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193 Bellaterra, Spain, (b)CNRS UPR5001, 38054 Grenoble, France, (c)ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain, (d)Institut für Allgemeine Anorganische und Theoretische Chemie, Universität Innsbruck, 6020 Innsbruck, Austria, (e)CEA-Grenoble, 38054 Grenoble, France

Synergism between magnetism and chirality – and all of the optical properties that it implies – is of utmost interest for contemporary materials science. Our present research aims to probe these synergies in molecular materials.

The nitronyl nitroxides are interesting compounds for the preparation of chiral magnetic materials, since their stereochemistry can be dictated in a precise way during synthesis. We have prepared a manganese(II)bis(hexa-fluoroacetylacetonate) complex of an intrinsically chiral nitronyl nitroxide which shows intriguing magnetic behaviour. The complex is comprised of a chiral polymeric chain of alternating radical and manganese(II) ions which packs to give parallel ferrimagnetic chains, which order ferromagnetically at 3 K with observation of hysteresis loops at lower temperatures, in addition to a magnetic avalanche effect. The consequence of pressure on magnetic ordering will be presented. The circular dichroism spectrum of the complex shows significant Cotton effects arising from the radical component. In addition, crystallisation of a ferrocene bis(nitronyl nitroxide) with the same metal complex afforded a coordination polymer which shows spontaneous resolution of the enantiomers, as witnessed in the Circular Dichroism spectrum of one of the enantiomorphs. Chiral single molecule magnets of the dodecamanganese family will also be presented. They exhibit the typical magnetic behaviour of these compounds as well as pronounced optical activity.

K-IV.5 17:30

CHIRAL FERROMAGNETS BASED ON CYANIDE-BRIDGED BIMETALLIC COMPLEXES

Eugenio Coronado, Carlos Giménez-Saiz, Alicia Nuez, Francisco Romero, Universitat de Valencia, Química Inorgánica, Dr. Moliner 50, 46100 Burjassot, Spain

The combination of hexacyanometalates with different diamine metal(II) complexes results in the formation of extended bimetallic assemblies with a rich variety of structures and magnetic properties. Most of these compounds are two-dimensional and show ferromagnetic interactions within the layers as well as long-range magnetic ordering over the lattice. The bulk magnetic properties shift from ferromagnetism to metamagnetism depending on the interlayer magnetic interaction. Since one of the factors influencing the interlayer distance is the diamine ligand, bulky cyclohexane-1,2-diamine has been used in order to obtain compounds with long-range ferromagnetic ordering.

In fact, cyclohexane-1,2-diamine (chxn) is a mixture of the trans-racemic and the cis- meso form. Starting from enantiomerically pure trans-(1R,2R)-chxn and trans-(1S,2S)-chxn, chiral compounds $[\text{Ni}(\text{trans}-(1\text{R},2\text{R})\text{-chxn})_2]_3[\text{Fe}(\text{CN})_6]_2\cdot 2\text{H}_2\text{O}$ (1), $[\text{Ni}(\text{trans}-(1\text{S},2\text{S})\text{-chxn})_2]_3[\text{Fe}(\text{CN})_6]_2\cdot 2\text{H}_2\text{O}$ (2), $[\text{Cu}(\text{trans}-(1\text{R},2\text{R})\text{-chxn})_2]_3[\text{Fe}(\text{CN})_6]_2\cdot 4\text{H}_2\text{O}$ (3) and $[\text{Cu}(\text{trans}-(1\text{S},2\text{S})\text{-chxn})_2]_3[\text{Fe}(\text{CN})_6]_2\cdot 4\text{H}_2\text{O}$ (4) have been obtained. Whereas layered compounds 1 and 2 behave as ferromagnets, 3 and 4 consist of zig-zag chains and show no magnetic ordering. The chiral nature of the two enantiomeric pairs has been confirmed by circular dichroism (CD) measurements. Also compounds $[\text{Cu}(\text{trans}-(1\text{S},2\text{S})\text{-chxn})]_3[\text{Fe}(\text{CN})_6]_2\cdot x\text{H}_2\text{O}$ and $[\text{Cu}(\text{trans}-(1\text{R},2\text{R})\text{-chxn})]_3[\text{Fe}(\text{CN})_6]_2\cdot x\text{H}_2\text{O}$ have been obtained which show magnetic ordering. Work with cis-(1R,2S)-chxn, on the other hand, has led to the obtention of $[\text{Cu}(\text{cis}-(1\text{R},2\text{S})\text{-chxn})]_3[\text{Fe}(\text{CN})_6]_2\cdot 6\text{H}_2\text{O}$ (5) which presents a layered structure as well as ferromagnetic ordering.

1 E. Coronado, C. J. Gómez-García, A. Nuez, F. M. Romero, E. Rusanov, H. Stoeckli-Evans, Inorg. Chem. 2002, 41, 4615.

CYANIDE-BASED NANOPARTICLES: ANOTHER APPROACH TO SUPERPARAMAGNETIC AND PHOTOMAGNETIC NANOSYSTEMS

Laure Catala, Eric Rivière, Talal Mallah, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, 91405 Orsay, France, Thierry Gacoin, Jean-Pierre Boilot, Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, CNRS UMR 7643, Ecole Polytechnique, 91128 Palaiseau, France, Carley Paulsen, Elsa Lhotel, Centre de Recherche sur les Très Basses Températures (CRTBT), 38054 Grenoble, France

During the last decade, huge efforts have been directed to the elaboration of nanoscopic objects with functional properties, with the idea that brand new science as well as technological applications can emerge.

In this communication, nanoparticles made of various cyanide-based coordination polymers are presented. Microemulsion was used to control the size and distribution of the particles. These two criteria could be influenced by various parameters, namely the water/surfactant ratio, the concentration and the nature of the coordinating species. Magnetic studies are presented for all these new systems.

Wednesday, June 11, 2003
Mercredi 11 juin 2003

Afternoon
Après-midi

Session V

- K-V.1** 14:00 -Invited- RECENT EPR INVESTIGATIONS OF PHASE TRANSITIONS IN THIAZYL RADICALS
J.M. Rawson, C.M. Pask and A. Alberola-Catalan, University of Cambridge, E.J.L. McInnes, University of Manchester, G. Smith, University of St Andrews, U.K.
We have recently observed bistability near room temperature in a number of thiazyl radicals. The bistability arises through either solid-solid or solid-liquid phase transitions, with the high temperature solid or liquid phase exhibiting a metastable state. In all cases the low temperature phase is diamagnetic because of spin-paired dimerisation, whereas the high temperature phase is paramagnetic. The phase transition is accompanied by a large increase in paramagnetism which can be readily monitored by EPR spectroscopy.
Ferromagnetic resonance (FMR) and antiferromagnetic resonance (AFMR) studies on extended systems are well documented, but few studies of the EPR behaviour of molecule-based materials have been reported. Single crystal AFMR studies of the magnetic phase transition of the canted antiferromagnet, p-NCC6F4CNSSN at 36K are reported.
- K-V.2** 14:30 SINGLE-MOLECULE MAGNETS: SYNTHESIS OF NEW CATIONIC Mn12 DERIVATIVES
Eugenio Coronado, Alicia Forment-Aliaga, Francisco M. Romero, Carlos Giménez-Saiz, Instituto de Ciencia Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain
The synthesis of the first SMM, Mn12O12(O2CCH3)16(H2O)4*2CH3COOH*4H2O Mn12Ac, was reported by Lis in 1980.1 Later, Mn12Ac was found to be a useful starting material for the synthesis of different Mn12 complexes. In order to obtain the ultimate high-density memory device or a building block for quantum computing based on single molecule magnets, we need to be able to functionalize and organise these molecules. Our aim is to synthesise new Mn12 derivatives which are easier to organise in different ways: on gold surfaces, as Langmuir-Blodgett films, or into mesoporous silica.
One approach to obtain molecules easier to organise is to synthesise high charge Mn12 derivatives which are able to have electrostatic interactions with a surface. We have synthesised two new cationic Mn1216+ using carboxylate bridging ligands that introduces a positive charge with a tetraalkylammonium group, [Mn12O12(O2CPhCH2N(Bun)3)16(H2O)4][PF6]16 (1), and [Mn12O12(O2CCH2N(CH3)3)16(CH3CH2OH)4][PF6]16 (2). Complex 1 has been characterised by Electrospray Ionisation Mass Spectrometry.2 Complex 2 represents the first cationic Mn12 derivative for which the crystal structure has been determined. Here we present the structure, electrospray mass spectra and magnetic properties of this novel derivative. It crystallises in a tetragonal system in the I4- space group. Interestingly all the clusters in the crystal have the same orientation and they are extremely well isolated thanks to the PF6- anions around the Mn12 clusters. Now we are trying to organise these cations on anion-coated gold surfaces and in LB films.
- K-V.3** 14:50 " NEW MOLECULAR CONDUCTORS BASED ON [Mo3S7]CLUSTER UNIT
Rosa Llusar(a), Santiago Uriel(b), Cristian Vicent(a), Eugenio Coronado(c), Carlos, J. Gomez-García(c), (a)Departament de Ciències Experimentals, Campus de Riu Sec, Box 224, 12071 Castellón, Spain, (b)Departamento de Química Orgánica- Química Física. Centro Politécnico Superior, María de Luna 3, 50015 Zaragoza. (c)Instituto de Ciencia Molecular. Universidad de Valencia. Dr. Moliner 50, 46100 Bujassot (Valencia), Spain
Transition metal complexes with 1,2-dithiolenes such as C3S52- (dmit2-) have been intensively studied as materials with nonlinear optical and electrical properties.1,2 The coordination of dithiolene ligand to transition metal clusters will combine the redox activity of both moieties by allowing the electronic delocalization between the terminal ligand and the metal core. Clusters with a Mo3Q7 (Q = S, Se) core and an ideal symmetry C3v, are readily accessible by ligand exchange reactions of [Mo3S7Br6]2- with non-reducing reagents. In this work, we present the synthesis of 1,2-dithiolene (dmit2-, mnt2-, dsit2-) complexes derived from the [Mo3Q7] core and their crystal structures and electrochemical properties.3,4
Electrochemical or chemical oxidation of [Mo3S7(dmit)3]2- gives the neutral complex [Mo3S7(dmit)3] which crystallize forming a 3D structure through extensive cluster to ligand interactions. This compound exhibits a semiconductor behavior with a room temperature conductivity of 2 S cm-1 in pressed pellet. Cluster [Mo3S7Br6]2- has been used for the preparation of (BEDT-TTF)3[Mo3S7Br6]2 and (BEDT-TTF)2[Mo3S7Br6] cation-radical salts by electrocrystallization. The crystal structure of former salt shows the presence of a [BEDT-TTF]2- anion, which has been obtained in mild conditions. X-ray structures, transport and magnetic properties will be presented.
1 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, Coord. Chem. Rev., 1991, 110, 115-160
2 Jie Dai et. al, J. Am. Chem. Soc. 2000, 112, 11007-11008
3 R. Llusar, S. Uriel, C. Vicent, M. G. Humphrey, N. T. Lucas, (to be published)

- K-V.4** 15:10 SINGLE CHAIN MAGNET BEHAVIOR" IN A HETEROMETALLIC Mn(III)-Ni(II) CHAIN
Rodolphe Clérac(a), Hitoshi Miyasaka(b), Claude Coulon(a), Masahiro Yamashita(b), (a)Centre de Recherche Paul Pascal, CNRS UPR 8641, avenue du Dr. A. Schweitzer, 33600 Pessac, France, (b)Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan
 The new heterometallic chain of MnIII and NiII ions, [Mn(saltmen)]₂[Ni(pao)₂(py)₂](ClO₄)₂ (1) (saltmen: N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneimine)); pao: pyridine-2-aldoximate) is the second example of "Single Chain Magnet" behavior[1] predicted in 1963 by Glauber for Ising 1-D systems.[2] In the structure, chains are well separated which ensures their magnetic isolation. At high temperature, the magnetic susceptibility of (1) is well described in a mean field approximation as an assembly of trimers (Mn-Ni-Mn) with Ni-Mn antiferromagnetic interactions ($J = -21$ K) connected though ferromagnetic Mn-Mn interaction ($J' = +0.7$ K). Below 60 K, the susceptibility is strongly anisotropic and can be fitted in the chain direction to a 1-D Ising model leading to same J' . Below 3.5 K, hysteresis loops are observed and combined ac/dc measurements show slow relaxation of the magnetization. These results indicate the presence of a metastable magnet state without magnetic long-range order. This material is the first experimental design of a heterometallic chain with $S = 3$ magnetic units showing a "Single Chain Magnet" behavior. This work opens new perspectives for 1-D systems to obtain high temperature metastable magnets by combining high spin magnetic units, strong inter-unit interactions and uni-axial anisotropy.[3]
 [1] A. Caneschi et al, Angew. Chem. Int. Ed. 2001, 40, 1760.
 [2] R. J. Glauber, J. Math. Physics 1963, 4, 294.
 [3] R. Clérac et al, J. Am. Chem. Soc. 2002, 124, 12837.
- K-V.5** 15:30 EFFECTS OF INTER-CLUSTER COUPLING IN HIGH SPIN MOLECULAR MAGNETS
M. Affronte(a), R. Sessoli(b), D. Gatteschi(b), W. Wernsdorfer(c), J.C. Lasjaunias(d), S.L. Heath(e), A. Fort(f), A. Rettori(f), (a)I.N.F.M.-S3 National Research Centre and Università di Modena, v. G. Campi 213A, 41100 Modena, Italy, (b)I.N.S.T.M. and Dipartimento di Chimica, Università di Firenze, 50019 Sesto Fiorentino, Italy, (c)Laboratoire L. Néel, C.N.R.S., BP166, 24 Av. des Martyrs, 38042 Grenoble, France, (d)C.R.T.B.T. C.N.R.S., BP166, 24 Av. des Martyrs, 38042 Grenoble, France, (e)Department of Chemistry, University of York, Heslington, York YO105DD, U.K., (f)I.N.F.M. and Dipartimento di Fisica, Università di Firenze, 50019 Sesto Fiorentino, Italy
 Inter-cluster interactions are in general weak in molecular nanomagnets, yet at low temperatures they play a role in the dynamic of the magnetization and they may be strong enough to lead high spin systems to cooperative phenomena. Here we report evidences for transition to antiferromagnetic (AF) state in Fe₁₉ and in (enH₂)₂Fe₆ molecular clusters. Fe₁₉metheidi is a new molecular nanomagnet with a total spin $S = 33/2$ while (enH₂)₂Fe₆ has a $S = 5$ ground state. Low temperature susceptibility shows a very weak antiferromagnetic coupling (Weiss temperature $= -1.7$ K) among Fe₁₉ clusters and anomalies are clearly observed at 1.19 K in the heat capacity and in the low-field magnetization of Fe₁₉metheidi. When metheidi is replaced by etheidi the anomaly in the heat capacity is shifted to 1.07 K, while for (enH₂)₂Fe₆ a broad peak is found at 0.99 K. Since in Fe₁₉metheidi the dipolar interaction between clusters is estimated to be ~ 190 mK, the origin of the AF transition is probably due to super-exchange in this case. The analysis of specific heat at very low temperature reveals a $C \sim T^3$ decrease for (enH₂)₂Fe₆ as expected for an antiferromagnet while an exponential T-scaling of C is observed for Fe₁₉. The latter can be ascribed to the presence of an energy gap in the spin wave spectra. The relaxation of the magnetization of Fe₁₉metheidi can not be fitted by a simple law but using a single scaling function $f(t/\tau(T))$, we found that τ is of the order of days and tends to saturate below 100 mK.
- 15:50 **BREAK**
- 16:30-18:00 **POSTER SESSION I**
- K/PI.01** DIVALENT TRANSITION METAL IONS AND PYRIMIDINOLS: SIMPLE PLAYERS FOR A RICH STRUCTURAL MAGNETO-CHEMISTRY
 Jorge A.R. Navarro(a), Juan M. Salas(a), Elisa Barea(a), Norberto Masciocchi(b), Simona Galli(b), and Angelo Sironi(b), (a)Departamento de Química Inorgánica, Universidad de Granada, 18071 Granad, Spain, (b)Dipartimento di Scienze Chimiche Fisiche e Matematiche, Università dell'Insubria, 22100 Como, Italy, (c)Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, 20133 Milano, Italy
 The combination of first-row divalent transition metal ions with 2-pyrimidinol or 4-pyrimidinol is used as a very simple strategy for constructing extended 1-D, 2-D and 3-D frameworks. The resulting assemblies are principally directed by metal and pyrimidine geometrical requirements. Thus, we have found that combination of metals with blocked bonding positions with 120° bonding angles provided by pyrimidines lead to 1-D polymers. When "naked" metal ions are employed instead, higher dimensionalities are obtained. The magnetic properties of these materials are dominated by antiferromagnetic coupling transmitted through the pyrimidinolate bridges leading to Heisenberg antiferromagnets. It is noteworthy, however, the spin-canted behaviour of [Co(2-pymo)₂]_n 3-D framework.
 We are thankful to The Spanish Ministry of Science and Technology (BQU2001-2955-CO2-01). EB thanks The Spanish Ministry of Education, Culture and Sport for a FPU grant.

K/P-I.02 A NOVEL ASYMMETRIC END-ON DOUBLE AZIDO BRIDGED COPPER(II) COMPLEX WITH UNPRECEDENTED LOW Cu-N(AZIDE)-Cu ANGLES

Subratanath Koner, Sandip Saha, Tallal Mallah and Ken-ichi Okamoto, Department of Chemistry, Jadavpur University, Jadavpur, Calcutta 700 032, India Université Paris-Sud, Bat. 420, Laboratoire de Chimie Inorganique UMR CNRS 8613, 91405 Orsay, France, Department of Chemistry, Tsukuba University, Tsukuba, Ibaraki 305-8566, Japan

Investigation into the structural and magnetic properties of the polynuclear transition metal complexes has become a fascinating subject in the field of coordination chemistry, materials chemistry and condensed matter physics. The azide ion is found to be one of the most efficient ligand as regards the super-exchange pathways between paramagnetic centers. The versatility and efficiency of azido ligand lies on its functionality as a bridging bi, tri, tetradentate ligand. But the simplest complex among them is the azido-bridged copper(II) dimer. It is well established that the nature of magnetic interaction depends on mode of coordination of copper(II) ions and bridging azido groups. For an end-on azido bridged copper(II) complex the interaction is ferromagnetic if the Cu-N(azide)-Cu angles of the complex is close to 90 degrees. This interaction also depends on another minor structural factor viz. the Cu-N-Cu distance. The cut-off Cu-N distance for a ferromagnetic interaction is found to be 2.05 Å. It is noteworthy that all the end-on azido bridged copper(II) complexes reported so far have shown ferromagnetic coupling only. Here we wish to disclose the synthesis, structural and magnetic study of a rare asymmetric end-on double-bridged copper(II) azido complex. In this complex the Cu-N(azide)-Cu = 89.1 degrees but the magnetic coupling between two copper ions is found to be antiferro-magnetic in nature, instead.

K/P-I.03 PROTONATED MALONATE: THE INFLUENCE OF THE HYDROGEN BONDS ON THE MAGNETIC BEHAVIOUR

Fernando S. Delgado (a), Yolanda Rodríguez-Martín(a), Joaquín Sanchiz(b), Catalina Ruiz-Pérez(a), Francesc Lloret(c) and Miguel Julve(c), (a)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Física Fundamental II, Universidad de La Laguna, Tenerife, Spain, (b)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Química Inorgánica, Universidad de La Laguna, Tenerife, Spain, (c)Instituto de Ciencia Molecular/Dpto de Química Inorgánica, Universitat de València, Burjassot, Valencia, Spain

In previous studies we have shown how the versatility of malonate ligand (dianion of 1,3-propanedioic acid, H₂mal) can lead to a great diversity of structural motifs (mononuclear species, one-, two, and three-dimensional compounds) and very different and interesting magnetic interactions between the metal ions that it bridges. Malonate-bridged complexes have provided examples of extensive hydrogen bonding interactions, spin-canting, etc....

New perspectives are opened when malonate ligand is partially protonated. A family of new compounds containing monoprotonated malonate was prepared by us and their crystal structure and magnetic properties were investigated. These compounds are interesting because they allow us to illustrate the influence of the hydrogen bonding interactions on the magnetic properties (even in mononuclear complexes). Two different monomeric compounds Cu[Hmal]₂ and Co[Hmal]₂ are presented where the magnetic behaviour is controlled by the hydrogen bonds. Remarkably, in spite of being isostructural species, they exhibit very different magnetic properties, the hydrogen bonding interactions accounting for this difference. Finally, we also show how the dimensionality can be increased by the introduction of a protonated ligand. In our current research work, we have obtained several structural motifs with copper(II) and malonate ions, but the highest dimensionality obtained was only one. We were able to prepare a new two-dimensional copper(II)-malonate compound with monoprotonated malonate. In this way, we increased the dimensionality without adding a new ligand. The magnetic properties of this compound are investigated and analyzed.

K/P-I.04 SELF-ASSEMBLY OF NEW ARCHITECTURES COMBINING MALONATE AND 2,2'-BIPYRIDINE AS BUILDING BLOCKS

M. Milagros Laz (a), Yolanda Rodríguez-Martín(b), Catalina Ruiz-Pérez(b), Joaquín Sanchiz(c), Francesc Lloret(d) and Miguel Julve(d), (a)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Edafología y Geología, Universidad de La Laguna, Tenerife, Spain, (b)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Física Fundamental II, Universidad de La Laguna, Tenerife, Spain, (c)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Química Inorgánica, Universidad de La Laguna, Tenerife, Spain, (d)Instituto de Ciencia Molecular/Dpto de Química Inorgánica, Universitat de València, Burjassot, Valencia, Spain

A great interest has been devoted to the development of rational synthetic routes to novel polynuclear compounds of tunable dimensionality which may have applications as molecular-based magnetic materials. Focusing on the approach of having transition metals as spin carriers, the declared target consists of optimizing the number of chemical links between the magnetic centers in order to get a greater contribution from intramolecular interactions and the same time, to decrease the influence of the weaker intermolecular contacts.

In our research, the use of malonate as a bridging ligand in transition metal complexes has shown the versatility of this dicarboxylate type ligand. The variety of coordination modes of the malonate ligand accounts for the structural complexity of its metal complexes. The ability of the carboxylate group to mediate significant ferro- or antiferromagnetic interactions between the paramagnetic centres that it bridges enhances the interest in the malonate ligand, aiming at designing extended magnetic systems. The use of the potentially bis-chelating 2,2'-bipyridine (bpym) molecule as coligand in the malonate-bridged complexes increases the structural diversity and provides an additional exchange pathway in the resulting mixed-ligand species. In the present communication, we present the first magneto-structural results that we obtained concerning the use of malonate and bpym as ligands towards some first-row transition metal ions. The structures and magnetic properties of the heteroleptic species [Cu(bpym)(mal)(H₂O)]·6H₂O (1) (mononuclear), [Cu₂(bpym)(mal)₂(H₂O)₂]·4H₂O (2) (dinuclear) and [M₂(H₂O)₂(bpym)(mal)₂]·3/2EtOH [M = Zn (3), Co (4)] (honeycomb layered material) illustrate well the possibilities of our strategy.

- K/P-I.05** HYDROGEN- AND COORDINATION-BONDED METAL COMPLEX ASSEMBLIES OF PYROMELLITATE
María Hernández-Molina(a)*, M. Milagros Laz(b), Catalina Ruiz-Pérez(a), Francesc Lloret(c) and Miguel Julve(c), (a)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Física Fundamental II, Universidad de La Laguna, Tenerife, Spain, (b)Laboratorio de Rayos X y Materiales Moleculares, Dpto de Edafología y Geología, Universidad de La Laguna, Tenerife, Spain, (c)Instituto de Ciencia Molecular/Dpto de Química Inorgánica, Universitat de València, Burjassot, Valencia, Spain, *Present adress: Laboratoire de Chimie Inorganique et Matériaux Moleculaires, Unite Associee au C.N.R.S. 7071, Case 42, Batiment F74, Universite Pierre et Marie Curie, Paris, France
 Synthesis of metal-organic hybrid materials using the concept of supramolecular engineering is one of the most active research areas in material science. The most useful strategy by which to construct such extended systems is to employ appropriate bridging ligands capable of binding metal centers through direct bond formation, promoting magnetic interactions. Di- and polycarboxylates are good candidates as bridging ligands for the construction of such extended systems. In line with our studies of long-range magnetic order in low-dimensional metal complexes, we have been trying to develop metal di-carboxylate hybrid materials (metal-malonate complexes). Tri- and tetra-carboxylate as multi-connecting ligands are also good candidates for the synthesis of hybrid materials.
 To extend the possibilities, our investigations have focused on the use of pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid or H₄pm) as structural building block for the synthesis of new metal-organic hybrid materials. We will report the synthesis, single crystal structures and magnetic properties of three Metal(II)-pyromellitate compounds (M = Cu(II), Co(II) and Ni(II))
- K/P-I.06** FROM MONOMERIC TO POLYMERIC COPPER(II)-2-PHENYLMALONATE COMPLEXES BEARING BIPYRIDINE, BIPYRIDINE AND RELATED LIGANDS. SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES
 J. Pasan(a) and C. Ruiz-Pérez(a), J. Sanchez(b), F. Lloret(c) and M. Julve(c), (a) Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental II, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38206 La Laguna (Tenerife), Spain, (b) Laboratorio de Rayos X y Materiales Moleculares, Departamento de Química Inorgánica, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38204 La Laguna (Tenerife), Spain, (c) Departament de Química Inorgánica/Instituto de Ciencia Molecular, Facultat de Química, Universitat de València, 46100 Burjassot (València), Spain
 Previous studies have shown the structural versatility of the malonate ligand (the dianion of the 1,3-propanedioic acid). Combined with other ligands and metallic ions this ligand is able to generate mono-, di-, tri-, tetra-nuclear molecules, infinite chains, 2D and 3D networks. Additionally the malonate ligand is able to mediate significant magnetic coupling among the paramagnetic centres and adopts coordination geometries and bridging modes that make the metallic ions to become ferromagnetically coupled in a very high frequency, much higher than that exhibited by other carboxylate bridged complexes. One of the reasons of its versatility seems to be the flexibility provided by the -CH₂- group that bridges the two carboxylate groups. The -CH₂- group can move above or below the equatorial plane of the complexes adopting the most stable conformation. We are now intensively exploring the effect in the structures and in the magnetic properties of the introduction of a rigid phenyl group as a substituent. In particular we present herein the structure and the magnetic properties of the complexes of formula [Cu(phenmal)(2,2'-bipy)(H₂O)] 2H₂O, [Cu(phenmal)(2,2'-bipym)], [Cu(phenmal)(2,4'-bipy)(H₂O)], and [Cu(phenmal)(4,4'-bipy)] H₂O. (H₂phenmal = 2-phenyl-1,3-propanedioic acid, bipy = bipyridine, bipym = bipyrimidine).
- K/P-I.07** SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF MANGANESE(II) COMPLEXES WITH 2,2'-BIPYRIDINE (BPYM) AND 2,3-BIS(2-PYRIDYL)PYRAZINE (DPP) LIGANDS
 Donatella Armentano(a), Giovanni De Munno(a), Francesca Guerra(a), Miguel Julve(b) and Francesc Lloret(b), (a)Dipartimento di Chimica, Università della Calabria, Arcavacata di Rende (CS), Italy, (b)Departament de Química Inorgánica/Instituto de Ciencia Molecular, Universitat de Valencia, Valencia, Spain
 Crystal engineering techniques have received a remarkable support since the introduction of the concept of building block. In particular, small organic ligands can be used to organize metal ions into expected networks through the so-called building block strategy. Our attention is focused on systems formed by 3d metal ions and potentially bridging organic ligands which can mediate magnetic interactions between the metal centres that they link. In this communication, we compare the reactivity of Mn(II) ion towards two poly-pyridyl ligands in order to check their ability to propagate magnetic interactions. Three new complexes of Mn(II) with 2,2'-bipyrimidine (bpym) and 2,3-bis(2-pyridyl)pyrazine (dpp) have been synthesized and characterized structurally and magnetically. Bpym can act either as a chelating or as a bis-chelating ligand, affording mono-, dinuclear and higher nuclearity compounds. We here report a chain compound of formula [Mn₂(bpym)Cl₂(H₂O)₂]_n, where bpym mediates a relatively strong antiferromagnetic interaction. Dpp, on the other side, is a very versatile ligand acting also as a terminal or bridging ligand. It can also mediate antiferromagnetic interactions, but they weaker respect to that mediated across bpym. We have observed the bis-chelating coordination mode of dpp in the chain compound [[Mn(dpp)(H₂O)₂](ClO₄)₂·1.5H₂O]_n whereas the bidentate coordination mode occurs in the dinuclear complex [Mn₂(m-Cl)₂(dpp)₂(H₂O)₂Cl₂]·2H₂O. These compounds exhibit weak antiferro- and ferromagnetic interactions, respectively.
- K/P-I.08** DESIGN OF NEW IRON(III) MOLECULE-BASED MAGNETS CONTAINING OXALATO AND OXO AS BRIDGES
 Donatella Armentano(a), Giovanni De Munno(a), Teresa Mastropietro(a), Miguel Julve(b) and Francesc Lloret(b), (a)Dipartimento di Chimica, Università della Calabria, Arcavacata di Rende (CS), Italy, (b)Departament de Química Inorgánica/Instituto de Ciencia Molecular, Universitat de Valencia, Valencia, Spain
 During the past decade, the oxalate ion (ox) has appeared as a very appealing bridging ligand in the design of molecule-based magnets. Recently, the oxalate ion has allowed the construction of two- and three- dimensional metal networks, which are polyfunctional materials. In a recent work, we have shown how the use of an oxo bridge together with the oxalate ligand afforded the unprecedented three-dimensional oxalato- and oxo-bridged iron(III) complex of formula {(NH₄)₂[Fe₂(ox)₂Cl₂(m-O)]·2H₂O}_n (1) exhibiting a spin canted structure at low temperatures (T_c = 40 K). As an extension of this research work concerning the synthesis of new molecule-based magnets we have investigated the possibilities offered by this iron(III) system by varying the nature and size of the counterion. Our preliminary results show that MeNH₃⁺ and Me₂NH₂⁺ cations (Me = methyl group), allow the formation of three-dimensional compounds of formula {X₂[Fe₂(ox)₂Cl₂(m-O)]·2H₂O}_n where X = MeNH₃⁺ (2) and Me₂NH₂⁺ (3). The anionic network in 2 and 3 constitute, basically, a three-dimensional pattern analogous to the previous compound 1. Also these compounds exhibit a ferromagnetic phase transition at low temperatures due to a weak spin canting, behaving as ferrimagnets. Bulkier cations such as the trimethyl- or tetramethyl-ammonium afford only one-dimensional oxalato-bridged compounds of formula {X₂[Fe₂(ox)₂Cl₄·H₂O]_n with X = Me₃NH⁺ (4) and Me₄N⁺(5). Antiferromagnetic coupling between the iron(III) centers through oxalato-bridges occurs in 4 and 5. The two types of compounds (three- and one-dimensional) were obtained in the case of the dimethylammonium cation. In this communication we present the crystal structure determination and magnetic characterization of this family of Fe(III) complexes.

K/P-I.09 [M(CTH)]₂: A VERSATILE BUILDING BLOCK FOR THE DESIGN OF NOVEL CYANO-BRIDGED BIMETALLIC MAGNETIC ASSEMBLIES

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Coordinating unsaturated ML_x complexes with two available coordination positions have been infrequently used together with cyanometallates as building blocks in the design of cyanide-bridged bimetallic assemblies, despite the fact that new and interesting architectures can be obtained. In view of this, we have envisaged the use of hexacyanomethylate to connect high thermodynamically stable [M'L]₂⁺ units (L=tetraazamacrocyclic), which can adopt both the planar and folded configurations leading to trans and cis dispositions of the two available positions on M', respectively. We have used the [M'(rac-CTH)]₂⁺ (rac-CTH=rac-5,7,7,12, 14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) building block for the synthesis of new cyanobridged bimetallic assemblies.

We are thankful to The Spanish Ministry of Science and Technology for economical support (BQU2001-3221) and a FPI grant.

K/P-I.10 NULL INTERMOLECULAR MAGNETIC EXCHANGES IN THE NEW DINUCLEAR [Cu₂(bptd)Cl₄(H₂O)] AND [Ni₂(bptd)2Cl₄(H₂O)₄]Cl₄·(H₂O)₃

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A number of dinuclear transition metal compounds showing interactions via diazine bridges have been prepared and characterized in the last 10 years. They systematically show antiferromagnetic couplings through M-N-N-M superexchanges (J values depending on the M nature, the ligand, and the molecular geometry). In any cases, it involves the magnetically active MO's to lie in the aromatic plane. Using the 2,5-bis(2-pyridyl)-1,3,4-thiadiazole (bptd), we recently prepared the new [Cu₂(bptd)Cl₄(H₂O)] and [Ni₂(bptd)2Cl₄(H₂O)₄]Cl₄·(H₂O)₃ in which magnetic centres are connected through one diazine + one chloro and two diazine ligands bridges, respectively. These two compounds are the first examples that show no-intramolecular magnetic interactions despite M-M distances close to 3.7 Å within perfectly plane edifices :

- Down to T_t = 125 K, [Cu₂(bptd)Cl₄(H₂O)] is paramagnetic while, below T_t, half of the Cu₂⁺ interact, leading to residual paramagnetism of one Cu₂⁺/f.u. Magnetic measurements, EPR and pulsed EPR study indicate the original intermolecular nature of AF exchanges. - [Ni₂(bptd)2Cl₄(H₂O)₄]Cl₄·(H₂O)₃ susceptibility obeys a Curie-law involving pure paramagnetism. Moreover, its EPR spectrum can be interpreted on the basis of virtual S=1 monomers. Below 70 K, Zero Field Splitting (D~300 Gauss) due to dipolar interactions without magnetic exchanges could be responsible for the LT spectra splitting. Considering the previous works on related compounds, only the sulphur of the thiadiazole groups could be responsible for the original behaviours and for the probable tilting of the magnetically active MO's towards apical orientations.

K/P-I.11 2D METAL ORGANIC HEISENBERG ANTIFERRO-MAGNET WITH COPPER(II) IONS COUPLED THROUGH FOUR DIFFERENT BRIDGES

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One-pot reaction of Cu(NO₃)₂, 2-Hydroxypyrimidine (2-Hpymo) and 4,4'-bypirimidine (4,4'-bpy) in aqueous ammonia solution results in an extended two dimensional network with formula [Cu₃(m-OH)₂(m-Cl)₂(m-2-pymo)(m-4,4'-bpy)1.5](NO₃)₂·nH₂O. This framework is built up of cationic layers containing threenuclear Cu₃(m-OH)₂(m-Cl)₂ cores bridged by 2-pymo and 4,4'-bpy ligands acting in the N,N' exo-bidentate bridging mode (Figure 1). The magnetic behavior is dominated by strong antiferromagnetic coupling through the m-OH and m-2-pymo bridges.

We are thankful to the Spanish Ministry of Science and Technology for economical support (BQU2001-2955-CO2-01). EB thanks the Spanish Ministry of Education, Culture and Sport for a FPU grant.

K/P-I.12 STRUCTURAL AND MAGNETIC PROPERTIES OF M(II)-HYDROXY-TEREPHTHALATE (M= Cu AND Co)

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In the aim to elaborate new multifunctional materials, associating in their structure a mineral component responsible, for example, of the magnetic properties and an organic component bringing optical properties (chromophore molecules), standard compounds were elaborated. They are Copper(II) and cobalt(II) hydroxy-terephthalate(tp) with lamellar structures and the have structural formula (Cu, Co)₂(OH)₂(C₈H₄O₄). They consist of layers metal(3d) hydroxydes bridged by the anions bidentates tp. Accurate crystallographic data of these well structured materials make it possible to establish the link between magnetic properties and crystallographic structures.

K/P-I.13 ORGANIC HIGH-SPIN SYSTEMS; SYNTHESIS, ELECTROCHEMICAL AND ETSF STUDIES OF A SERIES OF TETRAARYL m-PHENYLENEDIAMINES

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Organic molecules with plural redox active sites are the focus of contemporary issues in the field of chemistry and molecular spin science. Recently, pi-conjugated oligoarylamines have attracted much attention as precursors for genuinely organic high-spin systems. Previously, we reported that oligotriarylamines with two or three meta-connected diarylamino groups exhibit triplet or quartet ground state upon multi-electron oxidation, respectively. A relationship between the structures of oligoarylamines and the stabilities of their corresponding oligocations is an important subject to establish a molecular design rule for extended oligoarylamines based high-spin systems. Although p-substituted triarylamines are widely known to give very stable monocation radicals, few studies were reported for stabilities of oligoarylamines based open shell systems.

In this study, we have systematically designed and synthesized a series of tetraaryl m-phenylenediamines with various substituents on central and/or peripheral aromatic rings. In order to elucidate the stabilities of corresponding mono/dicationic species, cyclic voltammetry (CV) and electron transfer stopped flow (ETSF) technique were applied. The lifetime of oxidized state strongly depends on the positions and electronic nature of substituents.

K/P-I.14 CHARACTERIZATION OF STRUCTURE AND MAGNETIC PROPERTIES OF THE COMPLEX OF IRON WITH 2-HYDROXY-1-NITROZONAPHTHALENE

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In the present report the structure, temperature dependence of EPR spectrum and magnetic behavior of metal-organic magnet - the complex of iron with 2-hydroxy-1-nitrozonaphthalene $\text{Na}[\text{Fe}(\text{C}_{10}\text{H}_6\text{ONO})_3]$ has been investigated over the temperature range of 4,2-300 K. Anionic complex in the form of sodium salt was characterized by IR, UV-spectroscopy, thermogravimetry and elemental analysis. In this compound the ferrous ion surrounded by three nitrozonaphthole ligands and connected with nitrogen and oxygen atoms of each ligand to formation the pentagonal helat cycle. According to X-ray powder diffraction [1] this complex salt has a low symmetry, it's structure is monoclinic with lattice parameters: $a=1,116$ nm; $b = 0,876$ nm; $c = 0,620$ nm; $\beta = 92,40$. Similar to hybrid materials on the base of conjugated polyarenes doped by $\text{K}_3\text{Fe}(\text{CN})_6$ and FeCl_3 [2,3] the unusual temperature dependence in the EPR spectrum has been manifested. The EPR spectrum is a superposition of two lines which behavior under temperature change is a contrast. A change in temperature leads to a redistribution of the absorption intensities between the LT and HT spectra. This behavior is evidence of unusual dynamics of the molecules surrounding the Fe^{3+} ion, which has a significant influence on the various properties of the substance. Preliminary results on investigations of the dc magnetization and ac susceptibility show that this compound exhibits a features which are characteristic of spin-glass system.

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K/P-I.15 THIN FILMS OF MOLECULE-BASED MAGNETS

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Molecule-based magnets represent a highly interesting alternative to conventional systems in future generation of devices. For such applications, processing these low weight materials, derived from organometallic species, as thin films is essential. We report here on the use of chemical vapor deposition to grow thin films of $\text{M}(\text{TCNE})_x$ ($\text{M} = \text{V}, \text{Cr}, \text{Nb}, \text{Mo}$; TCNE = tetracyanoethylene). The deposition was studied on oxide-free micro-porous $\text{Si}(001)$.

Chemical vapor deposition was carried out in a conventional hot-wall apparatus using $\text{M}(\text{C}_6\text{H}_6)_2$ ($\text{M} = \text{V}$ or Cr), $\text{Nb}(\text{iPr}_2\text{-dad})_3$ ($\text{iPr}_2\text{-dad} = 1,4\text{-diisopropyl-1,4-diazabuta-1,3-diene}$), $\text{Mo}(\text{C}_6\text{H}_5\text{CH}_3)_2$, and TCNE as starting compounds. $\text{M}(\text{TCNE})_x$ deposits were made of small micro-grains paving the substrate surface. The infrared spectra showed two broad CN bands at ~ 2200 and ~ 2105 cm^{-1} , indicating the formation of the TCNE radical anion. According to XPS measurements, the V 2p, Cr 2p, Nb 3d and Mo 3d lines showed binding energies typical for low-oxidation state organometallic compounds. Magnetization curves vs applied magnetic field for both $\text{V}(\text{TCNE})_x$ and $\text{Cr}(\text{TCNE})_x$ evidenced hysteresis loops at 300 K, demonstrating long-range magnetic ordering at this temperature. Magnetization measurements also revealed that $\text{Nb}(\text{TCNE})_x$ and $\text{Mo}(\text{TCNE})_x$ as thin films are magnetically ordered at 2 K. The chromium K-edge spectrum (XANES) of $\text{Cr}(\text{TCNE})_x$ revealed an irregular octahedral environment. At the chromium K-edge, the Fourier transform of the EXAFS signal gave the following data : 6 nitrogen neighbors around chromium, a mean Cr-N distance of 2.03  , a N-C distance of 1.30   and a 160° Cr-N-C angle.

K/P-I.16 TRIMETALLIC MOLECULAR MAGNETS COMPRISED OF 3d/4f MIXED-METAL COMPLEX AND HEXACYANO-METALLATE

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Trinuclear 3d-4f mixed-metal complexes, $[\text{M}_2\text{Ln}(\text{L})_2(\text{NO}_3)_3]$ ($\text{M} = \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}$; Ln = lanthanide; L = 2,6-di(acetoacetyl)pyridine) have been prepared in our laboratory. We report here an extension of the trinuclear complexes to trimetallic assemblies $[\text{M}_2\text{Ln}(\text{L})_2][\text{M}'(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Cu}, \text{Ni}$; $\text{M}' = \text{Co}, \text{Fe}, \text{Cr}$) which are derived by the reaction of $[\text{M}_2\text{Ln}(\text{L})_2(\text{NO}_3)_3]$ with $\text{K}_3[\text{M}'(\text{CN})_6]$ in water. $[\text{Cu}_2\text{Ln}(\text{L})_2][\text{M}'(\text{CN})_6]$ forms a 1-D zigzag chain structure and shows no long range magnetic ordering, whereas $[\text{Ni}_2\text{Ln}(\text{L})_2][\text{M}'(\text{CN})_6]$ forms a 1-D double chain or 2-D sheet structure and shows a tendency of magnetic ordering in the bulk. The magnetic properties of the latter class are studied in view of Ln ions.

K/P-I.17 GROWTH OF CRYSTALS OF MOLECULAR MAGNETS AT THE AIR-WATER INTERFACE

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Prussian Blue Analogues (PBA) are of interest because of their potential as molecular magnets. Tc values above room temperature have been reported for these hexacyanometallates. Structural information on PBAs is indispensable for understanding their magnetic behaviour, but their high FCC symmetry is often accompanied by inherent disorder among different cationic sites, making it difficult to grow single crystals. We report the results of our efforts to grow thin crystalline films of PBAs at the air-water interface, under the Langmuir monolayer of the surfactant octadecylamine (ODA), which was used as a template to promote the crystallization.

We shall report on the growth of crystalline films of Ni(II)-hexacyanoferrate(III) under the ODA monolayer and their characterization using several techniques like XRD, electron diffraction, TEM, XPS, FTIR spectroscopy, UV-visible spectroscopy and cyclic voltammetry. Similarly, we shall describe the growth of highly oriented cubic crystals of Co(II)-hexacyanoferrate(III) at the air-water interface under the ODA monolayer. XRD and electron diffraction studies on them indicate that the crystals are oriented with their {100} plane parallel to the monolayer. TEM and AFM investigations reveal that cubic crystals with sides of 50-300 nm get initially formed, which grow further with time to coalesce into a thin film. Cyclic voltammetry of these films transferred onto gold-coated glass indicate the presence of the couple corresponding to the Fe(III)/Fe(IV)-hexacyanate system.

- K/P-I.18** ISOLATED SINGLE-MOLECULE MAGNETS ON A POLYMERIC THIN FILM
Jordi Gómez-Segura(a), Daniel Ruiz-Molina(a), Marta Mas(a), Neus Domingo(b), Javier Tejada(b), Concepció Rovira(a), Jaume Veciana(a), (a)Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, (b)Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
 Single-molecule magnets (SMM) have a large-spin ground state with appreciable magnetic anisotropy, resulting in a barrier for the spin reversal. As a consequence, interesting magnetic properties such as out-of-phase ac magnetic susceptibility signals and stepwise magnetization hysteresis loops are observed. In addition to resonant magnetization tunnelling, during the last few years several other interesting phenomena have also been reported. The origin of the slow magnetization relaxation rates as well as of other phenomena are due to individual molecules rather than to long-range ordering; as confirmed by magnetization relaxation and heat capacity studies. Therefore, SMM represent nanoscale magnetic particles of a sharply defined size that offer the potential access to the ultimate high-density information storage devices as well as for quantum computing applications. However, if a truly molecular computational device based on SMM is to be achieved, new systematic studies that allow us to find a proper way to address properly oriented individual molecules or molecular aggregates onto the surface of a thin film, where each molecule or molecular aggregate can be used as a bit of information, are highly required. Here we report a new soft, reliable and simple methodology to address individual Mn12 molecules onto a film surface, as revealed by Atomic Force Microscopy (AFM) and Magnetic Force Microscopy (MFM) images. Moreover, the advantageous properties of polymeric matrices, such as flexibility, transparency and low density, make this type of materials very interesting for potential applications.
- K/P-I.19** Mn12 SINGLE-MOLECULE MAGNETS INCORPORATED INTO MESOPOROUS MCM-41 SILICA
 Eugenio Coronado, Miguel Clemente-León, Alicia Forment-Aliaga, J.M. Martínez-Agugo, Instituto de Ciencia Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain, Pedro Amorós, Instituto de Ciencia de Materiales, Universitat de València, 46071 Valencia, Spain
 Single-molecule magnets are one of the topics of major interest in molecular magnetism. A current challenge is to organize them in 1, 2 or 3 dimensions. Here, we present the incorporation of four Mn12 derivatives, namely [Mn12O12(O2CR)16(H2O)4] (R = CH3 (1), CH3CH2 (2), C6H5 (3), C6F5 (4)), into the hexagonal channels of the MCM-41 mesoporous silica. Only the smallest clusters 1 and 2 that are those with compatible size with the pores of MCM-41 could be incorporated into the mesoporous silica. Powder X-ray diffraction analysis and N2 adsorption-desorption isotherm experiments show that the well-ordered hexagonal structure of MCM-41 is preserved and that the Mn12 clusters are inside the pores. The magnetic properties of the MCM-41/1 and MCM-41/2 nanocomposite materials indicate that the structure of the cluster is maintained after incorporation into the MCM-41 walls, but some differences appear between 1 and 2 that may be related to the solvent used in the synthesis. Calcination of the nanocomposite samples gives rise to a material with magnetic properties different to those of Mn3O4 that it is the compound obtained after calcination of pristine Mn12. We can conclude that the organization of the clusters within the channels of the mesoporous silica changes the thermal decomposition of the clusters.
- K/P-I.20** A LOW SYMMETRY PLANAR OCTANUCLEAR COMPOUND AS INTERMEDIATE IN THE FORMATION OF A HIGHLY SYMMETRICAL 2-D NET
Milagros Tomás, Inmaculada Escorihuela and Larry R. Falvello, University of Zaragoza - C.S.I.C., Department of Inorganic Chemistry, Plaza San Francisco s/n, 50009 Zaragoza, Spain
 The knowledge of processes by which building blocks form larger aggregates is fundamental in designing and constructing supramolecular compounds and 1-D, 2-D or 3-D polymers. To date few examples are available of the isolation and characterization of the intermediate compounds and aggregates involved in the formation of complex supramolecular structures. We present the structure of a heterometallic octanuclear compound which is an intermediate in the formation of a 2-D supramolecular net. The structure of the Pt4Cu4 compound [(NH3)4Cu(μ-CN)Pt(CN)2(μ-CN)]2{[Pt(CN)2(μ-CN)2Cu(NH3)2]2} shows that the isolated building blocks do not necessarily possess the same symmetry that they do when assembled into the more complex structure, and that an intermediate compound can have the same connectivity but a different shape from that which it possesses in the final supramolecular aggregate. The chemical issues involved in substituting Pt by magnetically active 4d and 5d transition metals will be discussed.
- K/P-I.21** FERRIMAGNETIC CHAIN COMPOUNDS [CuL]ReCl6 × H2O and [CuL]ReBr6 (WHERE L = 6,13-BIS(DODECYLAMINOMETHYLIDENE)-1,4,8,11-TETRAZACYCLOTETRADECA-4,7,11,14-TETRAENE)
 Jerzy Mrozinski, Alina Tomkiewicz, Bohdan Korybut-Daszkiewicz, University of Wrocław, Faculty of Chemistry, F. Joliot-Curie 14, 50-383 Wrocław, Poland
 Recently, we synthesized a new type of highly unsaturated bismacrocylic face-to-face transition metal complexes interacting with a guest molecule via strong p-p interactions. Comparison of electrochemical behavior of bismacrocylics and their corresponding catenanes in the solution reveals the 'mediator' role of the electron-rich component. As a result one observes an increased communication between the metal centers reflected in the values of the conproportionation constants higher than in the parent bismacrocylic complexes [1]. On the other hand, synthesis of heteropolymetallic systems with extended structures consists frequently, in self-assembly processes, an anionic building blocks, which contain a paramagnetic ion, and assembling complexed cations able to interact with them [2].
 We present the magnetic properties for the system build of highly unsaturated cyclidene copper(II) complex cation [CuL]2+ (L = 6,13-Bis(dodecylaminomethylidene)-1,4,8,11-tetrazacyclocotetradeca-4,7,11,14-tetraene) and anionic building blocks, hexachlororhenate(IV) or hexabromorhenate(IV). Their magnetic behavior is typical for a ferrimagnetic Cu(II)Re(IV) bimetallic chain. The intrachain interaction parameter has been found as JReCu = -3.03 cm-1 for [CuL]ReCl6 × H2O and JReCu = -4.08 cm-1 for [CuL]ReBr6 exhibits weak antiferromagnetic interactions between ReIV and CuII unit. The temperature dependence of the magnetization for both complexes has revealed a crossover from one-dimensional ferrimagnetic system to 3D magnetic ordering. References: [1] B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domaga^a and K. Woźniak, J. Am. Chem. Soc., 2001. [2] S. Tanase, M. Andruh, A. Müller, M. Schmidtman, C. Mathoniere and G. Rombaut, Chem. Commun., 2001, 1084-1085.

K/P-I.22 DENDRITIC POLYCHLOROTRIPHENYLMETHYL POLYRADICALS WITH NANOSCOPIC DIMENSIONS. APPROACHING THE "LIMIT GENERATION"

Nora Ventosa, Daniel Ruiz-Molina, José Vidal-Gancedo, Concepció Rovira, Jaume Veciana, Institut de Ciència de Materials de Barcelona, (ICMAB-CSIC), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

The development of magnetic materials with nanoscopic size is an area of increasing interest due to its potential applications in high density storage devices. Among the different approaches followed so far, the obtaining of high-spin purely organic macromolecules with nanoscopic dimensions is a current topic of great interest, since properties are expected to be rationally designed by a systematic modification of organic molecular structures. This motivation was further fueled by increased synthetic capabilities especially for obtaining large molecules with nanoscopic dimensions. One of the general approaches towards ferro- or superparamagnetism in purely organic macromolecules is based on large p-conjugated polyradicals with topologically polarized spins. There are two prerequisites to realize this objective. First, stable open-shell building blocks are required, and second, ferromagnetic couplings between the spins of these blocks are necessary.

Our choice was the use of polychlorinated triphenylmethyl radicals, which show high thermal and chemical stabilities due to the presence of bulky chlorine atoms around the radicals centers. Furthermore, the topology of the covalent connections permits to expect the presence of ferromagnetic couplings between the radical units. Following this approach, different nanoscopic dendritic molecules have been obtained, although the presence of large steric congestions turned out to extremely influence not only their synthesis but also their properties.

K/P-I.23 INCOMPLETE SPIN CROSSOVER IN A TETRANUCLEAR {CR(III)-FE(III)₃} CYANO-BRIDGED COMPLEX

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A novel heteronuclear complex $[\text{Cr}^{\text{III}}\{\text{CN}\}\text{Fe}^{\text{III}}(\text{5L})\}_3\text{CN}\}_3$ was synthesized by combination of mononuclear Fe(III) precursor - $[\text{Fe}^{\text{III}}(\text{5L})\text{Cl}]$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$ in the ratio 6:1 in methanol. A pentadentate ligand 5LH₂ = saldptn where prepared by the Schiff condensation of the 1,7-diamino-4-azaheptane with the salicylaldehyde.

Different techniques have been applied to characterize the compound. From the Mössbauer spectroscopy it follows up that two types of iron (III) are present in the sample. Temperature dependence of the Mössbauer spectra reveals that ratio of these two kinds of iron (III) centers is changing. It results in spin transition from low spin to high spin state. A trinuclear spin crossover model of the Ising-type was proposed first but the mole fraction of the high-spin molecules becomes too high and no good fit was obtained. Moreover, the X-ray structure determination shows that the surroundings of iron centers are different. Thus, a binuclear spin cross-over Ising-like model was applied to fit the experimental data, and one center was fixed to high spin state at all temperatures. Fitting procedure was done using an error functional comprises data from magnetic susceptibility measurement, magnetization and Mössbauer spectroscopy all at once. The corresponding spin Hamiltonian matrices for the $\{1/2, 1/2, 5/2, 3/2\}$, $\{1/2, 5/2, 5/2, 3/2\}$ and $\{5/2, 5/2, 5/2, 3/2\}$ spins have been diagonalized and the energy levels used for evaluating the magnetization and susceptibility through the partition function.

Thursday, June 12, 2003
Jeudi 12 juin 2003

Morning
Matin

Session VI

- K-VI.1** 9:00 -Invited- ELECTRON TRANSFER AND PHOTOMAGNETISM IN THE Cu²⁺ / [MoIV(CN)₈]⁴⁻
Corine Mathonière(a), Isabelle Bord(a), Guillaume Rombaut(a), Juan-Manuel Herrero(b), Valérie Marvaud(b), (a)Groupe des Sciences Moléculaires, Institut de Chimie de la Matière Condensée, UPR CNRS N°9048, 33608 Pessac cedex, France, (b)Laboratoire de Chimie Inorganique et Matériaux Moléculaires, URA CNRS N°7071-Université de Paris VI, 75252 Paris cedex 05, France
The first results published in 1996 by Hashimoto's group about photo-induced magnetic ordering in the compounds belonging to the family of prussian blue systems opens a new active field in molecular magnetism [1]. Recently, we initiated in our group a project consisting of the synthesis and characterization of new potential photomagnetic molecular materials.
In this presentation, we will focus on the bimetallic compounds formed with the [MoIVCN₈]⁴⁻ precursor and Cu²⁺, ranging from finite molecules to 3D networks. These compounds present in their optical spectra InterValence Charge Transfer bands corresponding to the electron delocalisation between Mo and Cu centers. The photomagnetic studies revealed reversible photoinduced electron transfer leading to magnetic ordering or exchange-coupled systems [2,3]. These results will be discussed by focusing on relations between structures and properties. In particular, we will try to identify the key factors for the observation of photo-induced magnetic effect in our compounds.
[1] O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 272 (1996) 704.
[2] G. Rombaut, M. Verelst, S. Golhen, L. Ouahab, C. Mathonière, O. Kühn, *Inorg.Chem.*, 41 (2001) 1151.
[3] G. Rombaut, C. Mathonière, P. Guionneau, S. Golhen, L. Ouahab, M. Verelst and P. Lecante, *Inorg. Chim. Acta* 2001 326 27-36.
- K-VI.2** 9:30 ANISOTROPIC GIANT NEGATIVE MAGNETORESISTANCE ORIGINATING FROM THE d-p INTERACTION IN A MOLECULE
H. Tajima, N. Hanasaki, M. Matsuda, Institute for Solid State Physics, The University of Tokyo, 277-8581 Kashiwa, Japan and T. Naito, T. Inabe, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
We have studied TPP[FeIII(Pc)(CN)₂]₂, PTMA_x[FeIII(Pc)(CN)₂]_y(MeCN) and PXX [FeIII(Pc)(CN)₂], a new series of charge-transfer salts containing the axial-substituted phthalocyanine (Pc), [FeIII(Pc)(CN)₂]⁻. These three salts exhibit anisotropic Curie-Weiss behavior, and spontaneous magnetization at low temperatures. The resistivity of TPP[FeIII(Pc)(CN)₂]₂ at 25 K decreases down to less than 1% of the zero field value for the magnetic field of 38 T applied perpendicular to the crystallographic c-axis. Similar behavior was observed in other two salts. We show that the orbital angular moment still remains in the [FeIII(Pc)(CN)₂]⁻ molecular unit, and explain various magnetic phenomena based on molecular regime.
1) H. Tajima, N. Hanasaki., M. Matsuda, F. Sakai, T. Naito, T. Inabe, *J. Solid State Chemistry*, in press.
2) N. Hanasaki, H. Tajima, M. Matsuda, T. Naito, T. Inabe, *Phys. Rev. B*, 62, 5839-5842(2000).
- K-VI.3** 9:50 NEW MOLECULAR SWITCHES BASED ON THE REDOX BEHAVIOR OF FERROCENE-SUBSTITUTED POLYCHLOROTRIPHENYLMETHYL RADICALS
Christian Sporer(a), Imma Ratera(a), Daniel Ruiz-Molina(a), Klaus Wurst(b), Concepció Rovira(a), Jaume Veciana(a), (a)Institut de Ciència de Materials de Barcelona, (ICMAB-CSIC), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, (b)Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck, Innrain 52a, 6020 Innsbruck, Austria
The development of molecular systems whose physical properties (electric, magnetic or optical properties) may be controlled and reversibly switched at will by means of different external stimuli, such as optical stimulation or an electric field, has attracted considerable interest in the last few years. Such systems are considered excellent candidates to be used as building blocks for the development of switching devices at the molecular level.
Here we present a new multiarray, based on the interesting redox behavior of a ferrocenyl based polychlorotriphenylmethyl radical, of four electronic states with different non-linear optical properties, magnetic ground states and electronic properties that can interconvert reversibly between them by means of an electrochemical stimuli. This work was supported by the Programa Nacional de Materiales de la Dirección General de Investigación (Spain), under project MAGMOL, and by the Fond zur Foerderung Wissenschaftlicher Forschung (FWF) Austria (J2103) .
- 10:10 **BREAK**

Session VII

K-VII.1 10:30

THE EXPLORATION OF MAGNETIC PHOTOEXCITED STATES USING ORGANOMETALLIC COUPLERS BASED ON THE SILOLE PATTERN

Nans Roques, Philippe Gerbier, Christian Guérin, Université Montpellier 2, UMR 5637, cc007, Place E. Bataillon, 34095 Montpellier Cedex 5, France, Satoru Nakajima, Yoshio Teki, Departement of Material Science, Graduate University, 3-3-138 Sugimoto Sumiyoshi-ku, Osaka 558-8585, Japan, School of Science, Osaka City, Jean-Pascal Sutter, Laboratoire des Sciences Moléculaires, ICMCB-CNRS, 87, Ave Dr. Schweitzer, 33608 Pessac, France, Vladimira Videva, Philippe Turek, Université Louis Pasteur, Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France

Intramolecular spin alignment and exchange interactions in purely organic spin systems are essential topics in the field of molecule-based magnetism. Since most studies are limited to the ground state, synthetic efforts are actually devoted to design high-spin compounds that are based on conjugated polyradicals with topologically polarized Pi-spins able to give rise to ferromagnetic interactions between the spin carriers. Therefore, topologies that are expected to give rise to antiferromagnetic interactions, yielding a singlet or low spin ground state, have been generally discredited.

Recently, the observation of high spin excited states in purely organic π -conjugated spin systems with a singlet ground state has opened a new strategy for photoinduced/photoswitching magnetic spin systems, and has relaunched an interest in systems with a "wrong" topology. One of the major requirement for the organic coupler in such a strategy is that it has to possess an accessible photoexcited triplet state. In this context, 2,5-disubstituted silacyclopentadienes or siloles are promising candidates. Compared to conventional π -systems, the siloles take advantage of the σ^* - π^* conjugation between the π^* orbital of the silicon moiety and the π^* orbital of the butadiene fragment, leading to an unusually low-lying LUMO leading to a photoexcited triplet state shown theoretically and experimentally.

We report therein the synthesis, characterization and magnetic studies of a series of biradicals connected through the silole ring. The ability of the silole pattern to magnetically couple the radicals in the ground state and its efficiency to achieve a photoinduced spin alignment upon irradiation will be discussed in details.

K-VII.2 10:50

MAGNETO-OPTICAL (MO) EFFECT AND MAGNETIZATION-INDUCED SECOND HARMONIC GENERATION (MSHG) OF CYANO-BRIDGED METAL ASSEMBLY

Shin-ichi Ohkoshi, Kazuhito Hashimoto, Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

The phenomenon caused by the interaction between magnetism and light is one of the most attractive topics in the field of magnetic materials, e.g., photo-magnetism, magneto-optical (MO) effect, and magnetization-induced second harmonic generation (MSHG). In this work, we have studied the MO effect and MSHG of molecule-based magnets. Electrochemically synthesized hexacyanochromate-based magnetic thin films showed Faraday effects in the visible region below their curie temperatures [1]. In addition, the optical control and humidity control of Faraday effects were achieved in these films. In the electrochemically synthesized iron(II)-chromium(II) hexacyanochromate(III) magnetic films, we have observed the SHG signal. The SH intensity changed with depending on magnetization values and the plane of SH polarized light was rotated by the external magnetic field, suggesting that the MSHG from the bulk appeared in this system.

[1] S. Ohkoshi, M. Mizuno, G. J. Hung, and K. Hashimoto, J. Phys. Chem. B, 104, 9365-9367 (2000).
[2] K. Ikeda, S. Ohkoshi, K. Hashimoto, Chem. Phys. Lett., 349, 371 (2001).

K-VII.3 11:10

MULTIFUNCTIONAL MOLECULAR MAGNETS: DESIGN OF FERROMAGNETIC CONDUCTORS

Antonio Alberola, Eugenio Coronado, José R. Galán-Mascarós, Carlos Giménez-Saiz, Carlos J. Gómez-García, Eugenia Martínez-Ferrero, Ana M. Murcia-Martínez, Instituto de Ciencia Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain

An attractive approach to the field of molecular dual-action materials, those combining two cooperative properties, is to build two-network solids from the appropriate building blocks able to bring to the material the desired properties. Following this strategy, a few years ago we reported the first molecular material combining metal-like conductivity and bulk ferromagnetism.1

After this discovery, we have prepared a whole family of (ferro)magnetic conductors of general formula $(\text{TTFs})_x[\text{MM}'(\text{ox})_3](\text{CH}_2\text{Cl}_2)$ [TTFs = BEDT-TTF, BEDS-TTF, BEDT-TSF, BEDO-TTF; M= Mn(II), Co(II); M' = Cr(III), Rh(III); $2.5 < x < 3$]. All these compounds present the same structural features: alternating layers of conducting stacks of the organic p-electron donors with magnetic layers of a bimetallic oxalato complex. Here we report on the correlations between structure and physical properties found in these series. We will show how changes in the organic donor have resulted in the formation of different stack motifs, the so-called a and b phases. We will also focus on the tuning of the magnetic properties when different metal cations are present in the bimetallic lattice. And finally we will also show how the interplay between ferromagnetism and metallic conductivity in these molecular materials gives unusual phenomena, as negative magneto-resistance below the critical temperature of magnetic ordering. In this regard, the synthesis of the Rh(III) derivatives is key to understand these features, since it allowed to obtain paramagnetic analogues, with absence of magnetic ordering, while maintaining the overall solid state structure. [1] E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, V. Laukhin, Nature, 2000, 408, 447-449.

K-VII.4 11:30 -Invited-

QUANTUM PHENOMENA IN MOLECULAR NANO-CLUSTERS

F. Luis(a), F. Mettes(b), M. Evangelisti(b), A. Morello(b) and L.J. de Jongh(b), (a)Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain, (b)Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

Molecular crystals are ideal to investigate quantum phenomena at the mesoscopic level. The spin of magnetic clusters, such as Mn₁₂, Fe₈, and Mn₄, can flip by quantum tunneling (QT) across the energy barrier associated with the magnetic anisotropy. At sufficiently high temperatures and for zero magnetic field, QT takes place via thermally populated magnetic states. By applying a field perpendicular to the anisotropy axis, QT via lower lying states, down to the ground state doublet, is promoted at any temperature [1]. Specific heat experiments show that QT enables the electronic spins to reach thermal equilibrium with the lattice. For still higher fields, the tunnel splitting of the magnetic ground state can be made large compared to perturbations such as hyperfine and dipolar interactions. The equilibrium specific heat measured at the lowest temperature gives then evidence for the presence of this splitting, thus showing that coherent QT can occur in these systems [1]. At zero field, QT is induced by off-diagonal terms of the crystal field Hamiltonian. The magnitude of these can be increased by changing the shell of ligand molecules around the magnetic core, as we have done for a series of Mn₄ compounds [2]. If the spin-lattice relaxation rate remains sufficiently fast down to temperatures of order 0.1 K, dipole-dipole interactions between the electronic spins can induce a transition to a ordered magnetic phase [2,3].

[1] F. Luis et al., Phys. Rev. Lett. 85, 4377 (2000); F. Luis, F. L. Mettes, and L. J. de Jongh in Magnetism: Molecules to Materials, edited by J. S. Miller and M. Drillon (Wiley-Vch, Weinheim 2002), vol. III, p. 169. [2] M. Evangelisti, et al., Polyhedron (2003), in press. [3] A. Morello, et al., Phys. Rev. Lett. 90, 017206 (2003).

12:00

LUNCH

Thursday, June 12, 2003
Jeudi 12 juin 2003

Afternoon
Après-midi

Session VIII

K-VIII.1 14:00 -Invited-

MAGNETIC AND OPTICAL PROPERTIES OF NITROXIDES RADICALS AND THEIR LANTHANIDES COMPLEXES

D. Luneau, Laboratoire des Multimatériaux et Interfaces (UMR 5615), Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France and C. Reber, Université de Montréal, Montréal QC H3C 3J7, Canada

Nitroxides are stable free organic radicals that are extensively used in the field of molecular based magnetic materials. In contrast, the optical spectroscopy of these systems have received little attention until recently.

We present the absorption, luminescence and Raman spectroscopy of some of these radicals and their lanthanides complexes. A distinguishing property of these compounds is that both radical and metal center may exhibit unprecedented red to near-IR luminescence effect. The spectroscopic information provide insight in the understanding of magnetic properties of nitroxide-lanthanide complexes. Moreover, the result is important in the frame of multifunctional materials coupling magnetism with optical properties.

1) C. Hirel, D.Luneau, J. Pécaut, L. Öhrström, G. Bussièrè, C. Reber Chem. Eur J 2002, 8, 3157-3161

2) C. Lescop, D. Luneau, P. Rey, G. Bussièrè, C. Reber Inorg. Chem. 2002, 41, 5566-5574

K-VIII.2 14:30

1D TRIAZOLE-BASED IRON(II) SPIN-CROSSOVER POLYMERIC MATERIALS : MEASURE OF COOPERATIVITY AND DESIGN OF NEW POTENTIALITIES

Olivier Roubeau, Ramón Burriel, Jaap G. Haasnoot, J. Reedijk, Centre de Recherche Paul Pascal (CNRS), 115 avenue du Dr. Schweitzer, 33600 Pessace, France, Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300RA, Leiden, The Netherlands, Instituto de Ciencia de Materiales de Aragon, CSIC-Universidad de Zaragoza, Plaza San Francisco, 54005 Zaragoza, Spain

Several series of 1D polymeric materials possessing spin-crossover properties have been synthesised with the ligands 4-R-1,2,4-triazole (R being an alkyl, methoxyalkyl or formylamino substituent) and various counteranions. The influence of the different synthetic parameters on the final bulk properties, i.e. transition temperature, abruptness of the spin crossover, presence of hysteresis etc. was studied. In particular, the latter two parameters, often discussed in terms of cooperativity, were systematically evaluated by calorimetric measurements.

Some of these materials present potentiality as temperature threshold sensors (white in the High-Spin $S = 2$ state and purple in the Low-Spin $S = 0$ state), either thanks to their intrinsic crossover properties, or because of the synergy between loss of solvent molecules and change of spin. Eventually, these materials also allowed to observe for the first time in spin-crossover Fe(II) compounds the coexistence of liquid crystals behaviour and spin conversion.

K-VIII.3 14:50

PHOTOINDUCED MAGNETIC STATE OF $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ STUDIED BY POLARISED NEUTRON DIFFRACTION

A. Goujon, B. Gillon, A. Gukasov, Laboratoire Léon Brillouin (LLB), CEA-CNRS, CEN Saclay, 91191 Gif-sur-Yvette Cedex, France, J. Jelic, Ecole Nationale de Chimie de Rennes (ENSCR), UMR CNRS 6052, Av. du Général Leclerc, Campus de Beaulieu, 35700 Rennes, France, E. Codjovi, F. Varret, Laboratoire d'Optique et de Magnétisme de Versailles (LMOV), CNRS-Université de Versailles, 45 Avenue des États Unis, 78035 Versailles Cedex, France

The photo-induced magnetisation density of the photo-switchable $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ spin crossover compound is reported. The photo-switching process is observed by using a new experimental setup allowing both light illumination and polarised neutron diffraction measurements (PND). We studied the photo-excitation kinetics and the photo-induced magnetic properties of the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ compound. A complete photo-process has been evidenced. The photo-induced magnetisation density and Fe^{2+} magnetic form factor have been obtained. Thermal relaxation towards the stable electronic state was observed in the 55-60K temperature interval. Hence, we suggest that the large possibilities of PND in providing information on the magnetic coupling scheme, the magnetisation density distribution and spin delocalisation effects could be useful for other photo-magnetic crystals.

- K-VIII.4** 15:10 **LINESHAPE OF MAGNETODIPOLE TRANSITIONS AND MAGNETIZATION RELAXATION IN MN12AC STUDIED BY FREQUENCY-DOMAIN MAGNETIC SPECTROSCOPY**
 S. Vongtragool(a), B. Gorshunov(a), J. van Slageren(a), M. Dressel(a), A. Mukhin(a,b), (a)1.Physikalisches Institut, Universität Stuttgart, Germany, (b)General Physics Institute, Russian Academy of Sciences, Moscow, Russia
 Frequency-domain magnetic spectra (50-1000 GHz) recorded on Mn12ac (S = 10 ground state) single crystals yielded information on its zero field splitting parameters, the cluster environment and internal fields. The lineshape of the magnetodipole transitions is found to depend on the history of the magnetic state. In the nonmagnetized (zero field cooled) state, the absorption line has a symmetric, Gaussian shape whereas in a magnetized (field cooled) state, the line is asymmetric even in the absence of an external magnetic field. These asymmetric lineshapes are quantitatively explained by inhomogeneous broadening of the crystal field states (D strain) in the crystal. ($\Delta D = 0.01 D$). We also present detailed studies of quantum tunneling of the magnetisation and relaxation phenomena which are directly observed by our technique, which can probe local populations of separate crystal field levels. The spin relaxation of Mn12ac is studied by magnetizing the sample and subsequently reversing the external magnetic field. Below T~2 K resonant quantum tunneling is directly observed as a 'tunnel dip' in the absorption spectra of polycrystalline samples.
- K-VIII.5** 15:30 **DI(PHENYLETHENYL)-PYRIDINE, TERPYRIDINE AND DIPYRAZOLYL-PYRIDINE BASED NITRONYL-NITROXIDE RADICALS FOR ORGANIC MAGNETS**
M. Baumgarten, C. Rajadurai, G. Zoppellaro, A. Geies, V. Enkelmann, A. Ivanova, Max Planck Institute for Polymer Research, PO 3148, 55021 Mainz, Germany
 Recently we have synthesised novel high spin molecules based on nitronyl-nitroxides and imino-nitroxide radicals attached to phenylacetylenes, 2,6- and 3,5-di(phenylethynyl) pyridine, terpyridine and dipyrazolyl- pyridine as building blocks for organic magnets. Detailed EPR, UV-Vis and X-ray characterizations were performed for the mono-, bi-, and triradicals, demonstrating that even the extinction of optical spectroscopy can be used to count the spin units. EPR liquid solution spectra show that all the biradicals are strongly exchange coupled with $J/AN \gg 1$, even through large distances (~ 2.4 nm). For identification of the ground spin states and zero field splittings also cryogenic EPR measurements were performed down to 4 K. The synthetic efforts were supported by parallel semi-empirical (with large CI) and DFT calculations showing the triplet-ground state for meta-pyridine bridged biradicals. While further work on metal complexations for the pyridine containing moieties is ongoing, 1-D polymeric chains from monoradicals through H-bonding and by Cu(hfac)₂ and Mn(hfac)₂ ligation were obtained.
- 15:50 **BREAK**
- 16:30-18:00 **POSTER SESSION II**
- K/P-II.01** **INTERPLAY OF ANTIFERROMAGNETIC COUPLING AND SPIN CROSSOVER IN DINUCLEAR IRON(II) COMPLEXES**
Ana B. Gaspar(a), Vadim Ksenofontov(a), Hartmut Spiering(a), Sergey Reiman(a), M. Carmen Muñoz(c), José A. Real(b), Philipp Gülich(a), (a)Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität, Staudinger Weg 9, 55099 Mainz, Germany, (b)Departament de Química Inorgànica/Institut de Ciència Molecular, Universitat de València, Doctor Moliner 50, 46100 Burjassot, València, Spain, (c)Departament de Física Aplicada, Universitat Politècnica de València, Camí de Vera s/n, 46071 València, Spain
 The development of molecular switching units capable of storing and transferring information is currently one of the most attractive research areas in molecular science. Six coordinate iron(II) spin crossover compounds represent a class of switchable molecular systems. They change reversibly from a low-spin(LS) diamagnetic state to a high-spin(HS) paramagnetic state by the action of temperature, pressure or light irradiation.
 In this way, the family of dinuclear compounds of the common formula $\{[Fe(L)(NCX)_2]_2bpy\}$ (X: S and Se; L = bpy (2,2'-bipyrimidine) and bt (2,2'-bithiazoline) represents one of the most unique systems in SC field because they are the simplest examples of polynuclear SC complexes exhibiting a rich variety of magnetic behaviour: magnetic coupling and / or spin transition depending on the nature of external ligand and the counterion. So far there has been no direct method to determine directly the spin state of molecules in dinuclear iron(II) compounds. The molecular fractions of high spin (HS) and low spin (LS) species have been deduced mainly from magnetic susceptibility and zero field Mössbauer spectroscopy data irrespective to whether they belong to LS-LS, HS-LS and HS-HS pairs. However, this distinction becomes possible if Mössbauer measurements are carried out in an external magnetic field. The proposed method enables to explore the microscopic features of spin crossover and the photoinduced conversion of pairs.

- K/P-II.02** AB-INITIO X-RAY POWDER DIFFRACTION CHARACTERISATION OF MOLECULE-BASED MAGNETIC MATERIALS
S. Galli, N. Masciocchi, DSCFM, University of Insubria, via Valleggio 11, 22100 Como, Italy and A. Sironi, DCSSI, University of Milano, via Venezian 21, 20133 Milano, Italy
 During the past decade, the oxalate ion (ox) has appeared as a very appealing bridging ligand in the design of molecule-based magnets. Recently, the oxalate ion has allowed the construction of two- and three- dimensional metal networks, which are polyfunctional materials. In a recent work, we have shown how the use of an oxo bridge together with the oxalate ligand afforded the unprecedented three-dimensional oxalato- and oxo-bridged iron(III) complex of formula $\{(NH_4)_2[Fe_2(ox)_2Cl_2(m-O)] \cdot 2H_2O\}_n$ (1) exhibiting a spin canted structure at low temperatures ($T_c = 40$ K). As an extension of this research work concerning the synthesis of new molecule-based magnets we have investigated the possibilities offered by this iron(III) system by varying the nature and size of the counterion. Our preliminary results show that $MeNH_3^+$ and $Me_2NH_2^+$ cations (Me = methyl group), allow the formation of three-dimensional compounds of formula $\{X_2[Fe_2(ox)_2Cl_2(m-O)] \cdot 2H_2O\}_n$ where X = $MeNH_3^+$ (2) and $Me_2NH_2^+$ (3). The anionic network in 2 and 3 constitute, basically, a three-dimensional pattern analogous to the previous compound 1. Also these compounds exhibit a ferromagnetic phase transition at low temperatures due to a weak spin canting, behaving as ferrimagnets. Bulkier cations such as the trimethyl- or tetramethyl-ammonium afford only one-dimensional oxalato-bridged compounds of formula $\{X_2[Fe_2(ox)_2Cl_4] \cdot H_2O\}_n$ with X = Me_3NH^+ (4) and Me_4N^+ (5). Antiferromagnetic coupling between the iron(III) centers through oxalato-bridges occurs in 4 and 5. The two types of compounds (three- and one-dimensional) were obtained in the case of the dimethylammonium cation. In this communication we present the crystal structure determination and magnetic characterization of this family of Fe(III) complexes.
- K/P-II.03** FREQUENCY SWEPT EPR SPECTROSCOPY OF MOLECULAR MAGNETS
J. van Slageren(a), S. Vongtragool(1), B. Gorshunov(a,b), and M. Dressel(a), (a)1. Physikalisches Institut, Universität Stuttgart, Germany, (b)General Physics Institute, Russian Academy of Sciences, Moscow, Russia
 Field swept high frequency EPR has been widely applied to study zero field splitting in molecular magnetic materials. This technique keeps the irradiation frequency fixed while sweeping the magnetic field until the resonance condition is achieved. From the observed resonance fields, the zero field parameters are obtained to second and often up to fourth order. In contrast, we apply a technique which is based on sweeping the frequency, rather than the field, which is kept fixed at some finite or zero value. The radiation source in our setup is a backward-wave oscillator (BWO) which produces coherent, monochromatic, frequency-tunable radiation in the millimeter-submillimeter spectral range. The frequency can be continuously scanned in the range 40 - 1300 GHz and the magnetic field can be applied up to 8 Tesla. By using a Mach-Zehnder interferometer, the change of the phase of the radiation passed through the sample is measured, in addition to the power-transmission coefficient. Using these two measured quantities, the real and the imaginary parts of the magnetic and dielectric permeabilities can be easily calculated. With this technique traditionally "EPR silent" ions such as NiII, as well as exchange coupled systems, can be studied directly, without application of an external magnetic field. In this way true zero-field splitting parameters can be measured directly. Furthermore, it is shown that this technique allows the observation of magnetisation relaxation in single molecule magnets, and that quantum tunneling of the magnetisation can be observed. In this case, the advantage is that the populations of the spin sublevels can be directly probed in contrast to bulk methods such as magnetisation measurements.
- K/P-II.04** SPIN DENSITIES AND NMR SPECTROSCOPY. SPIN TRANSFER ACROSS METALLOCENE LINKERS
 H. Heise, F.H. Köhler, Anorganisch-chemisches Institut, Technische Universität München, 85747 Garching, Germany, P. Jaitner, C. Sporer, K. Wurst, Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, 6020 Innsbruck, Austria, J.J. Novoa, Department de Química Física, Universitat de Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain, D. Ruiz-Molina, J. Veciana, Institut de Ciència de Materials de Barcelona, Campus Universitari de Bellaterra, 08193 Cerdanyola, Spain
 Magnetic exchange interaction, which is expected upon coupling of building blocks having unpaired electrons, can be studied in much detail by looking at the spin distribution within the compound. This is particularly true for the coupling unit. Its nature and the building block's relative position at the coupling unit determine, whether the interaction is ferromagnetic or antiferromagnetic and whether it is weak or strong.
 Ferrocene and ruthenocene have been used as new types of coupling units between two nitronyl nitroxide radicals. In order to analyze the spin distribution, these compounds have been subjected to solid-state 1H and ^{13}C NMR spectroscopy. This contribution presents magic angle spinning NMR spectra with shift ranges up to about 40 ppm and 2000 ppm, respectively. The signal shifts are converted to spin densities, which are compared with data
- K/P-II.05** SYNTHESIS, MAGNETIC PROPERTIES AND THEORETICAL CALCULATIONS ON TERPYRIDINE AND DIPYRAZOLYL-PYRIDINE BASED BIRADICALS
G. Zoppellaro, A. Geies, C. Rajadurai, A. Ivanova, V. Enkelmann, M. Baumgarten, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
 We have synthesized novel stable nitronyl-nitroxides (NIT) and imino-nitroxide (IN) radicals attached to 2:2',6':2''-terpyridine, dipyrazolylpyridine and pyrazolylbipyridine rings as high spin building blocks for organic magnets. The optical spectra of the biradicals show characteristic absorptions around 600 nm (NIT) and around 460 nm (IN). The EPR solution spectra exert well resolved 9 and 13 lines-pattern for the NIT and IN biradicals, respectively, indicating strong exchange coupling ($J/AN \gg 1$). The low temperature EPR studies down to 4 K performed on the biradicals showed Curie-like behaviour. The triplet ground states have been also supported by semiempirical calculations. Since all the ligands share similar tridentate nitrogen-binding motifs, their metal chelation appears very promising to be further pursued.
- K/P-II.06** CHARGE AND SPIN DENSITY DISTRIBUTION IN Y(III) AND Gd(III)-SEMIQUINONE COMPLEXES
M. Souhassou(a), B. Gillon(b), N. Claiser(a), C. Lecomte(a), Y. Pontillon(c), A. Caneschi(d), C. Carbonera(d), F. Bencini(d), D. Gatteschi(d), (a)Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, Univ. H. Poincaré Nancy 1, Faculté des Sciences, BP 239, Vandoeuvre-les-Nancy Cedex, France, (b)Laboratoire Léon Brillouin (CEA-CNRS), CE Saclay, 91191 Gif/Yvette Cedex, France, (c)Centre d'Etudes Nucléaires de Grenoble, 17 Rue des Martyrs, 38054 Grenoble Cedex 9, France, (d)Department of Chemistry, University of Florence, Via Maragliano 77, 50144 Firenze, Italy
 Most of the Gd complexes with Nitronyl Nitroxide radicals present a ferromagnetic intramolecular interaction. At the opposite, the Gd complex with a semiquinone radical $Gd(Hbpz)_2(DTBSQ)$ presents an antiferromagnetic interaction. We have undertaken theoretical calculations, and experimental spin and charge density studies in order to precise the interaction mechanism on the Gd complex and the isomorphous Y complex (with a non magnetic ion Y^{3+}). The results of theoretical/experimental studies will be discussed.

K/P-II.07 SINGLE-ION VS MOLECULAR ANISOTROPIES OF AN Fe(III)-OXO DIMER STUDIED BY SINGLE-CRYSTAL W-BAND ELECTRON PARAMAGNETIC RESONANCE

Etienne Goovaerts, Mariana Stefan, Peter ter Heerdt, Department of physics, Univ. of Antwerp, Belgium, Andrea Cornia, Department of Chemistry, Univ. of Modena and Emilia Region, Italy, Andrea Caneschi, Department of Chemistry, Univ. of Florence, Italy

Typical single molecule magnet behaviour is observed in a series of FeIII-oxo complexes. Two dimers of this family are studied by single-crystal W-band EPR.

The first complex is a GaIII dimer doped with a small amount of FeIII-ions. The second complex is an isomorphous FeIII dimer. The first compound is used to derive the single-ion zero field splitting tensor of the FeIII-ion. This FeGa dimer can be thought of as an FeIII monomer in which the basic single-ion properties can be studied. The next step is to use the single-ion properties of the FeIII center and separate them from other major interactions, like dipolar contributions. The principal values of the FeIII ZFS tensor and the orientation of the principal directions relative to the crystalline axes are determined. The resulting ZFS parameters are consistent with the parameters derived from high-frequency powder EPR measurements at 525 GHz. The principal axes are pointing in arbitrary directions with respect to the directions of the different bonds. From the FeIII spectra the principal values and axes of the complete anisotropic spin-spin interaction are determined. The principal values and directions demonstrate that the dipolar interaction is not the dominant contribution to the spin-spin interactions. The anisotropic exchange interaction therefore has a significant contribution to the overall magnetic anisotropy of molecular magnets of the FeIII-oxo family.

K/P-II.08 RAMAN SCATTERING STUDY OF HIGH-PRESSURE PHASE TRANSITION IN TCNE

R. Rao, T. Sakuntala, R. Mukhopadhyay, S.K. Deb, Bhabha Atomic Research Center, Mumbai 400085, India

Tetracyanoethylene (TCNE) is a planar molecule and a strong electron acceptor due to the presence of the cyano (C N) group. Thus it forms many charge transfer complex compounds exhibiting interesting magnetic and other properties. Recently, an interesting photo-induced magnetic compound Mn(TCNE)_xy(CH₂Cl₂) has been synthesized where the magnetization states can be switched using visible light. TCNE in solid form exists in cubic and monoclinic phases and these phases show a series of interesting pressure-induced phase transitions; Study of phase transitions in TCNE is of considerable interest because, the phase changes will lead to corresponding changes in the properties of various charge transfer complex compounds and it is necessary to understand the structure and dynamics of the transition. Although many techniques have been used to study these transitions, vibrational spectroscopy is of special importance, because many of the interesting electronic properties may be mediated through electron-phonon interaction. We report a Raman scattering study of high-pressure phase transition in cubic and monoclinic forms of TCNE. Our results indicate that the cubic phase is stable upto 7-8 GPa beyond which it transforms to a lower symmetry phase as revealed by splitting of several modes. The monoclinic phase shows a reversible transition beyond 3Gpa with considerable hysteresis. Both phases turn opaque at high pressure (12 GPa for cubic and 4.5 GPa for monoclinic) – a possible polymerized phase. However, we do not observe any clear Raman signature for polymerization.

K/P-II.09 ELECTRON SPECTROSCOPY AND DENSITY-FUNCTIONAL STUDY OF "FERRIC WHEEL" MOLECULES

A.V. Postnikov, S.G. Chiuzaian and M. Neumann, University of Osnabrueck, Department of Physics, 49069 Osnabrueck, Germany

The Li-centered "ferric wheel" molecules with six oxo-bridged iron atoms [1] form molecular crystals. We probed their electronic structure by X-ray photoemission and soft X-ray emission spectroscopy, the former revealing the total density of states (DOS) in the valence band while the latter - the local 3d-DOS on Fe sites, due to the resonant excitation of iron 2p states (L-emission line). In parallel, we calculated electronic structure of a single "ferric wheel" molecule from first principles by applying the SIESTA method [2] which incorporates local density (LDA) and generalized gradient (GGA) approximations of the density functional theory, using norm-conserving pseudopotentials and numerical basis orbitals. The Fe local moments correspond to S=2 in ferromagnetic (FM), different antiferromagnetic (AFM) and ferrimagnetic trial configurations. GGA favours somewhat higher localization of magnetic moments on the Fe sites, as compared to LDA. The ground-state is AFM; energy differences with inverted-spin states allow to estimate interatomic exchange parameters, which are then compared with neutron-scattering data [3].

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K/P-II.10 THE ORIGIN OF STRONG TEMPERATURE INDEPENDENT PARAMAGNETISM OF TRIGONAL LOW-SPIN RE(II) COMPLEXES

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A model is developed to explain the unusual magnetic behavior of two low-spin Re(II) compounds [Re(triphos)(CH₃CN)₃][BF₄]₂ and [Et₄N][Re(triphos)(CN)₃]. The model involves eight lowest cubic crystal field terms split and mixed by strong trigonal crystal field and spin-orbit coupling. The combined effect of the last two interactions is the stabilization of two close in energy Kramers doublets originating mainly from the 2T₂ term. The efficient mixing of these Kramers doublets with those arising from the 6A₁ and 4T₁ terms is shown to result in the small low-temperature effective magnetic moments and the anomalously strong temperature independent paramagnetism in accordance with the observed magnetic behavior. The obtained best-fit parameters reproduce well the magnetic susceptibility curves being at the same time in a qualitative agreement with the observed light absorption spectra.

Financial support of MRDA/CRDF (Award MP2-3022) and SCSTD of Moldova (grant 111) is highly appreciated.

- K/P-II.11** PSEUDO-JAHN-TELLER ORIGIN OF THE METASTABLE STATES IN SODIUM NITROPRUSSIDE
 E. Coronado(a), S. Klokishner(b), O. Reu(b), B. Tsukerblat(c), (a)Instituto de Ciencia Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain, (b) State University of Moldova, Mateevich str.60, Kishinev 2009, Moldova, (c) Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
 A new model for the photochromic effect in sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ based on the concept of the pseudo-Jahn-Teller effect is proposed. The model takes into account the electron transfer from the Fe^{2+} ion to the orbitals of the NO-ligand as well as the vibronic mixing of three low-lying electronic states of the Fe-NO fragment through the non-symmetric and full symmetric modes. The problem is solved within the adiabatic approximation. Under certain conditions the lower sheet of the adiabatic potential is shown to possess three minima with the increasing energies that correspond to the N-bound, sideways bound and O-bound NO group. The barriers between the minima are estimated and the excited minima are attributed to the MS2 and MS1 metastable states observed experimentally.
 Financial support of INTAS (Project 2000-0651) and Supreme Council on Science and Technological Development of Moldova (grant 111) is highly appreciated.
- K/P-II.12** MAGNETIC PROPERTIES OF LANGMUIR FILMS OF POLYMETHINE RADICALS - A THEORETICAL STUDY
A. Ivanova(a), N. Tyutyulkov(a,b), F. Dietz(b), (a)University of Sofia, Faculty of Chemistry, Chair of Physical and Theoretical Chemistry, Bulgaria, (2)University of Leipzig, Faculty of Chemistry and Mineralogy, "Wilhelm Ostwald" Institute for Physical and Theoretical Chemistry, Germany
 One of the approaches towards the assessment of purely organic ferromagnetic materials is the organization of organic radicals (or ion-radicals) in 2-D lattices at a gas/liquid interface, such as insoluble surfactant monolayers. The theoretical study of various systems is a powerful tool in the design of ferromagnetically coupled molecular aggregates. Earlier studies on low-dimensional high-spin systems [1,2] and on electric properties of insoluble monolayers [3] prompted the computational strategy of this investigation.
 Magnetic properties of model 2-D Langmuir films of stacked cation-radicals were addressed, considering quasi-1-D stacks with lateral interaction in the second dimension. Different alignments of the radicals within the stack were calculated by means of a combined procedure including Monte Carlo/MM simulation followed by semi-empirical structure optimization in order to find the minimum energy stack arrangement at the gas/water interface. Further application of the band theory of open-shell pi-electron systems allowed estimation of the effective exchange interaction and design of assemblies with ferromagnetic ordering.
 [1] A. Ivanova, M. Baumgarten, S. Karabunarliev, N. Tyutyulkov, Phys. Chem. Chem. Phys., 2002, 4, 4795
 [2] F. Dietz, N. Tyutyulkov, M. Staneva, M. Baumgarten and K. Müllen, J. Phys. Chem. B, 2001, 105, 7972
 [3] A. Ivanova, A. Tadjer, B. Radoev, Int. J. Quant. Chem., 2002, 89, 397
- K/P-II.13** A MODEL HAMILTONIAN CALCULATED BY AB INITIO METHODS FOR MIXED VALENCE MOLECULES
Hélène Bolvin, Université Louis Pasteur, Strasbourg, France
 The so-called Creutz Taube molecule, $[(\text{NH}_3)_5\text{Ru} \text{ pz Ru} (\text{NH}_3)_5]^{5+}$, which is a mixed valence molecule has been the purpose of many experiments and theories. We propose new insight on this molecule. First, the whole spectrum is analyzed with ab initio methods. Secondly, model parameters are calculated to modelize the superexchange phenomenon. The proposed method permits to evaluate the metal ligand transfer integral and for longer bridges, the ligand-ligand transfer integral. In this presentation, we shall show that a two-parameter model is suitable to reproduce the excited states of the Creutz Taube molecule. The transferability of the parameters is analyzed for molecules with longer bridge. This work validates the models usually proposed to modelize electron transfer through bridges.
- K/P-II.14** DFT MODELING OF LIGAND FIELDS AND EXCHANGE COUPLING IN TRANSITION METAL-RARE EARTH DIMER HALOGENIDE COMPLEXES
M. Atanasov(a), C. Daul(b), H.U. Guedel(c), (a)Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, (b)Département de Chimie, Université de Fribourg, Switzerland, (c)Institut fuer Chemie und Biochemie, Universität Bern, Bern, Switzerland
 A newly developed DFT based ligand field theory has been used to study theoretically the ligand field and magnetic exchange coupling in dimers of Mn(II) and Yb(III) hexa-coordinate halogenide complexes with corner-, edge- and face- sharing bridging geometries. The results have been utilized to shed some light into the intimate mechanism of light up-conversion which has been recently discovered in these systems.
- K/P-II.15** Shifted to K-VI.3
- K/P-II.16** PRESSURE-INDUCED ELECTRON TRANSFER IN FERRIMAGNETIC PRUSSIAN BLUE ANALOGUES
Vadim Ksenofontov(a), Georgiy Levchenko(a), Sergey Reiman(a), Philipp Gütllich(a), Anne Bleuzen(b), Virginie Escax(b), Michel Verdaguer(b), (a) Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Staudinger Weg 9, 55099 Mainz, Germany, (b) Laboratoire de Chimie Inorganique et Matériaux moléculaires, Unité CNRS 7071, Université Pierre et Marie Curie, Bât F 74, 4 place Jussieu, 75252 Paris Cedex 05, France
 Mössbauer and magnetic susceptibility measurements were performed under pressure in three Prussian blue analogues, $\text{K}_0.1\text{Co}_4[\text{Fe}(\text{CN})_6]_2.7 \times 18\text{H}_2\text{O}$, $\text{K}_0.28\text{Co}_4[\text{Fe}(\text{CN})_6]_2.76 \times 18\text{H}_2\text{O}$ and $\text{Cs}_0.7\text{Co}_4[\text{Fe}(\text{CN})_6]_2.9 \times 16\text{H}_2\text{O}$. They found a pressure-induced electron transfer $\text{Co}^{2+}(\text{S}=3/2)\text{-Fe}^{3+}(\text{S}=1/2) \rightarrow \text{Co}^{3+}(\text{S}=0)\text{-Fe}^{2+}(\text{S}=0)$. The "scanning" of the ligand field strength by applying an external hydrostatic pressure allows to explore the distribution of CoNnO_{6-n} ($0 \leq n \leq 6$) configurations. It reveals a narrow distribution of configurations centered around the most probable CoN_4O_2 configuration in $\text{K}_0.1\text{Co}_4[\text{Fe}(\text{CN})_6]_2.7 \times 18\text{H}_2\text{O}$ and a broad CoNnO_{6-n} distribution in $\text{K}_0.28\text{Co}_4[\text{Fe}(\text{CN})_6]_2.76 \times 18\text{H}_2\text{O}$ and $\text{Cs}_0.7\text{Co}_4[\text{Fe}(\text{CN})_6]_2.9 \times 16\text{H}_2\text{O}$. This evolution of site distribution caused by alkali doping, explored here for the first time, is shown to play an important role in the photoinduced magnetization process.

K/P-II.17 SPIN, ELECTRON AND MAGNETIC PROPERTIES OF THE 4f-5d ELECTRONIC CONFIGURATION OF TRIVALENT RARE EARTH IONS

A.C. Cefalas(a), E. Sarantopoulou(a), S. Kobe(b), (a) National Hellenic Research Foundation, TPCI, 48 Vas. Constantinou Av., Athens 11635, Greece, (b) Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

The interest of investigating the spin, electronic and magnetic properties of the 4f-15d electronic configuration of the trivalent rare earth (RE) ions in wide band gap dielectric hosts is based on current and future optical and magnetic applications [1].

Regarding their optical properties, the strong radiative interconfigurational 4f-15d \rightarrow 4f transitions of the RE ions, in wide band gap dielectric crystals, suggest that these materials can be used for generating coherent VUV or UV light [1]. In addition the investigation of their magnetic properties could trigger a new variety of applications on magnetic semiconductors, as coherent spin & transport properties could be realized rather in paramagnetic semiconductors than ferromagnetic ones. In this communication we investigate the spin, electronic and magnetic properties of 4f-15d electronic configuration of the trivalent rare earth (RE) ions in wide band gap dielectric hosts by exciting crystal samples with laser light at 157nm in the presence of magnetic field of 1 Tesla. With this experimental configuration direct observation of the transient magnetic moment of the 4f-15d electronic configuration with ~ 20nsec lifetime was made possible for the first time.

[1] & VUV Laser Spectroscopy of Trivalent Rare Earth Ions in Wide Band-Gap Fluoride Crystals”, E. Sarantopoulou and A. C. Cefalas. In“Ultraviolet spectroscopy and UV lasers” edited by Marcel and Dekker, New York 2002.

K/P-II.18 CRYSTALLOGRAPHIC, ELECTRONIC AND MAGNETIC STRUCTURES OF GAM (M = CR, MN OR FE) ALLOYS

Olivier Gourdon and Gordon J. Miller, Department of Chemistry and Ames Laboratory, US Department of Energy, Iowa State University, Ames Iowa 50011-3111, USA

The crystallographic structure of the binaries compounds GaM (M=Cr, Mn or Fe) has been reinvestigated using X-ray and neutron diffraction. The structure is quite different from that proposed previously. Although GaM (M=Cr, Mn or Fe) is reported crystallize with the Al8Cr5 structure type, space group R3m, we found that the centrosymmetric space group R-3m is more accurate. Moreover, the atomic positions and the atomic displacements parameters, which are missing in the previous study are now refined. Band structure calculations using self-consistent spin-polarized TB-LMTO-ASA method were carried out to understand the electronic structure and the magnetic properties of these compounds. Analyses from the band structure, the density of states and the magnetic moments obtained show the stability of two different magnetic models relative to the nonmagnetic one for GaMn since only one is found for GaFe and GaCr. Moreover, calculations show that from Cr to Fe a change of the magnetic interactions from an antiferromagnetic coupling to a ferromagnetic coupling is observed. Finally, magnetic susceptibility measurements have been performed on GaFe and GaCr to support these theoretical studies.

K/P-II.19 NONCOLLINEAR MAGNETISM FOR VARIOUS CR SURFACES

N.S. Yartseva(a), C. Demangeat(b), V.M. Uzdin(c), S.V. Yartsev(a), J.C. Parlebas(b), (a)Institute of Metal Physics, UAS, Ekaterinburg, 620219 Russia, (b)IPCMS, CNRS, UMR 7504, BP 43, 67034 Strasbourg cedex 02, France, (c)St. Petersburg State University, ICAPE, St. Petersburg 199178, Russia

Chromium is a very intriguing transition metal, especially as far as the magnetism of its surface is concerned. More than two decades ago Allan [1] described the Cr surface as a layered antiferromagnetic structure with a surface magnetic moment 4 times higher than in the bulk. Quite recently there has been some additional evidence of a spin polarized Cr(001) surface with Auger Electron Spectroscopy [2]. These works motivated us to theoretical study of the Cr surface in the aspect of noncollinear magnetism on the atomic scale.

In the most theoretical models the perfectly flat surface have been assumed. In practice, the terraces can happen and result in zero magnetic moment at the Cr(001) surface. A breakdown of spatial homogeneity and magnetic frustrations can cause the noncollinearity in the magnetic structure. Here we present the results of self-consistent calculations of stepped and rough Cr(001) surfaces by using a real space recursion method for the Vector Periodic Anderson Model [3]. Comparison is also made with a stepped and rough Cr(110) surfaces and various iron surfaces. This work was partially supported by INTAS-01-0386, and bilateral exchange program CNRS-RAS. [1] G. Allan Surf. Sci. 74 (1978) 79 [2] L. Niebergall, Dr. rer. nat. Dissertation (2000) Math. Nat. Tech. Dept., Martin-Luther Univ. of Halle-Wittenberg (Germany) [3] V.M. Uzdin, N.S. Yartseva Comp. Mat. Sci. 10 (1998) 211

K/P-II.20 SYNTHESIS, STRUCTURAL AND MAGNETIC CHARACTERIZATION OF ANISOTROPIC CYANIDE-BRIDGED MIIIMnIII (M = Cr, Fe) HETERODINUCLEAR COMPLEXES

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The discovery in 1993 of the superparamagnetic like behavior exhibited by the so-called Mn₁₂ polynuclear complex represents a breakthrough in the development of molecular magnetism [1]. Nowadays, many research groups are involved in this field but most of the systems investigated deal with oxo-bridged species. Only very recently, such a behaviour has been observed in a cyanide-bridged polynuclear compound abbreviated as [MnIIIMoIII₆(CN)₁₈] [2] showing that this phenomenon is not constrained to a limited family of complexes. These systems have in common the occurrence of a strong anisotropy which is one of the requirements to observe superparamagnetism.

Having this in mind, we allow to react [MIIILCN_x]- (L = blocking ligand) mononuclear precursors (that we have designed and which are specially adapted for the synthesis of low dimensional compounds) [3] with anisotropic MnIII-Schiff base preformed complexes. Although the use of pentadentate Schiff base blocking ligands appears as the best choice for the synthesis of discrete polynuclear systems, our results with tetradentate Schiff base ligands show that lower denticity blocking ligands around Mn(III) also work. We present here the first magneto-structural results that we obtained using [MIII(bpy)(CN)₄]- [(M = Cr, Fe) and (bpy = 2,2'-bipyridine)] and [FeIII(bpca)(CN)₃]- [bpca = bis(2-pyridylcarbonyl)amidate anion] as ligands toward the [MnIII(MeOsalen)]ClO₄ complex.

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Friday, June 13, 2003
Vendredi 13 juin 2003

Morning
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Session IX

- K-IX.1** 8:30 -Invited- METAL-RADICAL SPIN COUPLING IN MODEL SYSTEMS AS STUDIED BY FIRST PRINCIPLES MOLECULAR ORBITAL THEORY AND MAGNETIC SPECTROSCOPY
Frank Neese, Max Planck Institut für Strahlenchemie, Stiftstr. 34+36, 45481 Mülheim an der Ruhr, Germany
This contribution will describe recent efforts to combine theory and experiment in the study of magnetic interactions in metal-radical model systems. A number of recent theoretical developments will be discussed that allow the calculation of the complete EPR and Mössbauer spectra based on density functional theory. In addition recent methodological developments in the correlated ab initio treatment of large transition metal complexes will be discussed and applications to systems studied experimentally will be described.
- K-IX.2** 9:00 PRESSURE TUNING OF THE MOLECULAR SHAPE OF THE TWO-DIMENSIONAL ANTIFERROMAGNET trans-[Ni(cyan)2(NH3)4] AT TWO TEMPERATURES
Larry R. Falvello(a), Robert W. Henning(b), Fernando Palacio(c), Arthur J. Schultz(b), Milagros Tomás(a) and Xiaoping Wang(b), (a)University of Zaragoza-C.S.I.C., Department of Inorganic Chemistry, Plaza San Francisco s/n, 50009 Zaragoza, Spain, (b)Intense Pulsed Neutron Source, Building 360, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439-4814, USA, (c)Instituto de Ciencia de Materiales de Aragon, C.S.I.C.-Universidad de Zaragoza, Plaza San Francisco s/n, 50009 Zaragoza, Spain
Single crystals of the compound trans-[Ni(cyan)2(NH3)4] [cyan = cyanurate, C3H2N3O3(-)] display a second-order phase transition which operates up to about 310 K, giving rise to the unprecedented phenomenon of reversible, non-destructive molecular shape tuning in the crystalline state.(1) The compound displays Curie-Weiss behavior through the temperature range of the most pronounced shape changes, but antiferromagnetic interactions become significant below 50 K; antiferromagnetic ordering takes place at 2.61 K. The temperature-dependent capacity for molecular shape tuning in the solid has been further characterized as a function of pressure. The crystal structure, which is dominated by an unbounded, hydrogen-bonded supramolecular aggregate formed by self-recognition of the cyanurate ligands, has been further characterized by single crystal time-of-flight neutron diffraction at 20 K and 223 K with the sample subjected to a pressure of 2000 bar. At T = 223 K the effects of this pressure are equivalent to a temperature drop of approximately 70 K, while at T = 20 K the pressure exerts an influence equivalent to an effective temperature drop of about 25 K.
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- K-IX.3** 9:20 MECHANISM OF THE MAGNETIC INTERACTION IN POLYMERIC-C60
Jordi Ribas and Juan J. Novoa, Dept. Química Física and CER Química Teórica, Fac. Química, Univ. Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain
Polymeric-C60 is the solid resulting when pressing and heating pristine C60. At certain values of pressure and temperature the resulting solid presents magnetic properties which are taken by some as indication of ferromagnetism up to values above room temperature. However, despite the potential impact that this material can have in the field of magnetism, little is understood about the basic characteristics of its magnetic interaction. Among other important unknown properties, a key one is determine where are the magnetic moments.
In this work we present the results of ab initio theoretical studies on dimers and other aggregates of C60 balls, which shed light on to the mechanism of the magnetic interaction in polymeric-C60. Our results allow to identify where are the magnetic moments, the process of their creation and how they interact within the solid, thus allowing an indepth understanding of the magnetism in this solids.
- K-IX.4** 9:40 ELECTRONIC STRUCTURE CALCULATIONS FOR SPIN-CROSSOVER MATERIALS
H. Paulsen and A.X. Trautwein, Institut für Physik, Universität zu Lübeck, Ratzeburger Allee 160, 23538 Lübeck, Germany
Spin-crossover (SCO) complexes exhibit a transition from a low-spin (LS) to a high-spin (HS) state that can be reversibly induced by changing temperature or pressure or by irradiation with light. With respect to electronic-structure calculations, SCO complexes are intricate objects since the total electronic energy difference between HS and LS states, which is in the order of some 10 kJ/mol, results from a delicate balance of various factors.
The total electronic energy difference has been calculated for a large set of monomeric, dimeric, and trimeric SCO complexes containing various transition metal centers (Cr, Mn, Fe, Co, Ni). The calculations have been performed for free molecules using several different density functional methods. For selected complexes the effect of solvents has been studied using self-consistent reaction field models. Calculations with periodic boundary conditions have been performed to investigate the influence of intermolecular interactions on the energy difference. The accuracy of the current calculations is not sufficient to predict the equilibrium temperature for the HS and LS state. However, for a series of complexes with ligand substitutions the calculations can be used to predict the shift of equilibrium temperature.

10:00

BREAK

Session X

- K-X.1** 10:30 **MODELLING OF ANTIFERROMAGNETIC EXCHANGE INTERACTIONS USING META-GGA**
Ilaria Ciofini and Carlo Adamo, Laboratoire d'Electrochimie, ENSCP, Paris, France, Francesc Illas, Departament de Química Física, Universitat Barcelona, Spain
The antiferromagnetic exchange interaction in magnetic materials such as La₂CuO₄, KNiF₃ and K₂NiF₄ has been studied using an embedded cluster approach and Density Functional Theory. In particular, the effect, on the computed singlet-triplet energy gap, of the inclusion of semi-local (the kinetic energy density, t) or non-local (the exact, Hartree Fock exchange) exchange terms has been investigated. The results obtained with local (LDA) gradient corrected (GGA), semi-local (meta-GGA) and hybrid exchange functionals have been compared. Although meta-GGA functionals do not include exact Hartree Fock exchange, they are able to significantly improve the results obtained with standard GGA towards those of hybrid approaches. These results are encouraging since meta GGA are computationally less demanding than hybrid functionals and easier to implement in solid states codes.
- K-X.2** 10:50 **A DFT BASED LIGAND FIELD MODEL FOR MAGNETIC EXCHANGE COUPLING IN TRANSITION METAL DIMER COMPLEXES**
M. Atanasov(b) and C.A. Dau(a), (a)Departement de Chimie, Université de Fribourg, Perolles, 1700 Fribourg, Switzerland, (b)Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad.G.Bontchev Str. Bl.11, 1113 Sofia, Bulgaria
A DFT based ligand field model for magnetic exchange coupling in homonuclear transition metal dimer complexes will be presented. It is based on a model of localized d-electrons and on a procedure allowing to express the model parameters in terms of exchange and Coulomb integrals from DFT calculations of a homonuclear dimer complex. We describe a recipe to relate the latter integrals with the manifold of all Slater determinants of the active space originating from the magnetic electrons of the dimer. The method is applied to d⁹ and d¹ model clusters involving Cu(II) and Ti₂Cl₉(³⁻). In this work we present in addition an extension of this model to magnetic ions with more than one magnetic electrons per site. As a first application the exchange constant of the (NH₃)Cr(III)(OH)3Cr(III)(NH₃)₃³⁺ model cluster has been calculated in nice agreement with experiment. The new approach helps analyse the exchange integral in terms of antiferromagnetic and ferromagnetic contributions to show that the usual neglect of the latter in theoretical studies is not justified. Using all these results the performance of the up-to-date functionals for magnetic exchange is discussed.
- K-X.3** 11:10 **PROTONIC MODULATION OF MOLECULAR MAGNETISM: COMPLETE SPIN CROSSOVER OF A SELF-ASSEMBLED [2X2] IRON GRID COMPLEX THROUGH DEPROTONATION**
Jonathan Nitschke and Jean-Marie Lehn, ISIS, Université Louis Pasteur, Strasbourg, France
The phenomenon of spin crossover provides means for gaining control over the magnetism of a molecular material through external stimuli. Iron(II), the transition metal ion for which spin-crossover properties have been most fruitfully studied, can be reversibly switched from a high-spin quintet state to a diamagnetic singlet state in certain ligand environments through changes in temperature, pressure and light, as demonstrated for a tetra-iron(II) [2x2] grid complex.[1] We have recently succeeded in controlling the spin crossover of such a species by means of protonation/deprotonation equilibria. Each complex contains four ligands which each bear two acidic protons. Progressive removal of these protons renders the ligands anionic, which increases the ligand field and triggers spin crossover, as monitored by NMR and UV-Vis spectroscopy. The magnetism of the grid complex may thus be reversibly extinguished through sequential addition of base and acid. Such protonic modulation of the spin properties of a molecular entity is of special interest in the context of the emerging field of "spintronics."
[1] E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Guetlich, E. Wegelius, K. Rissanen. *Angew. Chem. Int. Ed.* 2000, 39, 2504.
- K-X.4** 11:30 -Invited- **MAGNETIC MATERIALS WITH TRANSITION METALS: ANALYSIS AND DESIGN USING THEORETICAL TOOLS**
Eliseo Ruiz, Antonio Rodríguez-Forteza, Miquel Llunell, Santiago Alvarez, Departament de Química Inorgànica, *Departament de Química Física and Centre de Recerca en Química Teòrica (CERQT), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
Theoretical methods based on density functional theory have been employed successfully to study the magnetic properties of binuclear transition metal complexes.[1-3] This approach has been useful for the understanding of the magnetic properties with more intuitive models as well as an excellent tool to probe magnetic properties for new compounds that have not yet synthesized. However, as much in the field of the molecular magnetism as for the applied use of magnetic compounds, the materials are polynuclear complexes containing several paramagnetic centers or extended structures.
In this communication, we want to present an extension of the methodology employed for binuclear complexes to large polynuclear complexes and extended structures. The first part will be devoted to show that the magnetic properties for this kind of complex materials can be reproduced with the similar accuracy that for binuclear complexes using the same methodology. In the second part we will analyze with more detail the magnetic properties as some polynuclear and extended compounds, such as the Fe₈ complex, layered Cu(II) compounds and transition metal dicianamides. 1) E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* 1997, 119, 1297. 2) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* 1998, 120, 11122. 3) Desplanches, C., E. Ruiz, A. Rodríguez-Forteza, S. Alvarez, *J. Am. Chem. Soc.* 2002, 124, 5197.

12:00

LUNCH

Friday, June 13, 2003
Vendredi 13 juin 2003

Afternoon
Après-midi

Session XI

K-XI.1 14:00 -Invited-

DFT-BASED SIMULATION OF MOLECULAR MAGNETS

Mark Pederson(a), Noam Bernstein(a), Jens Kortus(b), Tunna Baruah(c), Kyungwha Park(d), Stephen Hellberg(a), (a)Naval Research Laboratory, Washington DC., USA, (b)Max-Planck-Institute, Stuttgart, Germany, (c)Georgetown University, Washington DC., USA, (d)Howard University, Washington DC., USA

We describe density-functional-based electronic structure calculations on molecular magnets which we have performed to address several characteristics of these systems. The calculations are performed using the massively parallel NRLMOL code. The geometrical degrees of freedom are optimized by using standard derivative-based procedures. The optimal spin orientation is determined by starting off the calculation with various spin instabilities and allowing the SCF procedure to either accept or reject the input instability. Once the lowest geometrical and spin configuration is determined the anisotropy Hamiltonian and exchange parameters are then calculated. Results on the Mn12-Acetate molecule, the Mn4-dimer, and Co4 monomer will be highlighted but results from several other molecular magnets will be included for comparison between experiment and theory. Particular emphasis will be on the calculation of the spin-vibron interaction from density-functional theory. We show that the spin-vibron interaction contributes to the tunnel splittings in several ways. We compare our original calculations of the spin-vibron interaction, which lead to Stephenson coefficients that were smaller than the experimentally deduced values, to more recent frozen phonon calculations. Recent work aimed at determining anisotropic exchange hamiltonians will also be discussed with applications to the Mn4 dimer.

K-XI.2 14:30

A MAGNETIC NANOPOROUS SPONGE

Daniel MasPOCH(a), Daniel Ruiz-Molina(a), Klaus Wurst(b), Neus Domingo(c), Massimiliano Cavallini(d), Fabio Biscarini(d), Javier Tejada(c), Concepció Rovira(a) and Jaume Veciana(a), (a)Institut de Ciència de Materials de Barcelona, (ICMAB-CISC), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, (b)Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, 6020, Innsbruck, Austria, (c)Facultad de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, (d)CNR-Istituto per lo Studio dei Materiali Nanostrutturati (CNR), Via P. Gobetti 101, 40129 Bologna, Italy

The exceptional characteristics of nanoporous materials have prompted their technological applications in different fields such as molecular sieves, sensors, ion-exchangers and catalysis. In this context, the interest for metal-organic open-framework structures has increased enormously in the past few years because of the potential benefits of using crystal engineering techniques to yield nanoporous materials with predictable structures. Furthermore, the construction of open-frameworks from transition metal ions opens the possibility to design functional nanoporous materials with additional physical properties. Among them, the search for magnetic open-framework structures is a major challenge. Here we present a new efficient methodology for the preparation of metal-organic open-framework magnetic structures based on the use of a persistent organic free radical (PTMTC) properly functionalised with three carboxylic groups. Following such approach, the open framework structure [Cu₃(PTMTC)₂(py)₆(EtOH)₂(H₂O)] (MOROF-1), combining very large pores (2.8-3.1 nm) with a bulk magnetic ordering, is presented. Interestingly, such a structure shows a highly selective solvent-induced "shrinking-breathing" process involving large volume changes (25-35%) that influence severely the magnetic properties of the material.

K-XI.3 14:50

SYNTHESIS AND MAGNETIC PROPERTIES OF GOLD-COATED PERMALLOY (Fe_{0.2}Ni_{0.8}) NANOPARTICLES

Brian L. Cushing and Charles J. O'Connor, Advanced Materials Research Institute, University of New Orleans, New Orleans LA 70148, USA

Permalloy, due to its high magnetic permeability and low hysteresis loss, is used extensively in logic devices, thin-film recording heads and magnetic shielding. We have developed a synthetic route for 5 - 30 nm diameter permalloy particles by reduction of aqueous cations in reverse micelles. Additionally, a method for coating the particles with a thin layer of gold, forming a core-shell structure, has been developed to reduce the particles' susceptibility to oxidation. Preliminary experiments by Energy Dispersive X-ray (EDX) and Transmission Electron Microscopy (TEM) indicate that the ~10 nm particles contain Fe, Ni and Au in an approximate 1:4:5 atomic ratio, in good agreement with the expected result, and Powder X-ray Diffraction (XRD) results are consistent with the formation of Au-coated permalloy. Magnetic susceptibility measurements on a SQUID magnetometer indicate that the particles are superparamagnetic at room temperature with a blocking temperature, T_B, of 12 K. Details of the synthetic procedure and the magnetic properties of the products will be presented, with emphasis on the variation of physical properties with particle size. The effects of low- to intermediate-temperature annealing will also be discussed.

- K-XI.4** 15:10 REDOX-TUNABLE VALENCE TAUTOMERIC COMPLEXES AS MULTIFUNCTIONAL MOLECULAR SWITCHING ARRAYS
Daniel Ruiz-Molina, Klaus Wurst, Jaume Veciana, Institut of Materials Science of Barcelona, LMO, Campus UAB, 08193 Cerdanyola, Spain
There is currently active interest in the development of molecular electronic devices that can be used as optical and/or magnetic data storage media. Compounds of specific interest are bistable molecular materials having two nearly degenerated states with different optical and/or magnetic properties. These complexes have an appreciable sensitivity to the environment so an external perturbation, like photons or temperature, may lead to an interconversion between the two degenerated electronic states. Examples of electronic labile complexes are valence tautomeric complexes. Valence tautomerism has been observed to occur for a series of transition metal complexes such as Mn or Co with ligands derived from substituted o-benzoquinones. Most of these complexes exhibit localized electronic structures with well-defined charges for the metal and the ligands where the charge distribution is dictated by the nature of the conterligand and the metal center. Here we present the redox-tunable valence tautomerism of the aforementioned systems, which allowed us to establish a multistate array of several states exhibiting different optical and magnetic properties that can interconvert reversibly either thermally or by a reversible oxidation process.
- K-XI.5** 15:30 -Invited- DIRECTED ASSEMBLY OF HIGH-SPIN METAL-CYANIDE CLUSTERS
Jennifer J. Sokol, Matthew P. Shores, Miriam V. Bennett and **Jeffrey R. Long**, Department of Chemistry, University of California, Berkeley CA, USA
The remarkable observation of magnetic bistability in certain high-spin metal-oxo clusters has permitted elucidation of new physical phenomena and suggests possible applications in computing. In an effort to produce further examples of molecules exhibiting this behavior, we are exploring directed assembly routes to high-nuclearity metal-cyanide clusters. The use of multidentate capping ligands has led to the synthesis of a range of cluster geometries featuring as many as 27 metal centers. Substitution of selected transition metal ions into these structures is shown to permit adjustment of the ground state spin and magnetic anisotropy associated with the molecules. The behavior of single-molecule transistors incorporating certain of these clusters will also be described briefly.
- 16:00 CLOSING