electrical properties into the ligand and organize the compound on the surfaces for single-molecule or single-molecule layer study.

[1] G.L.J.A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493-494. [2] A.L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **1999**, *121*, 5302-5310. [3] M. Mannini, F. Pineider, Ph. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A.M. Talarico, M.-A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, *Nat. Mater.* **2009**, *8*, 194-197.

Keywords: magnetism, chirality, iron

MS66.P16

Crystal Structures and NLO properties of Quinoline Derivatives

Pedro S. Pereira Silva,[a] Hasnaa El Ouazzani,[b] Manuela Ramos Silva,[a] José António Paixão,[a] Bouchta Sahraoui,[b] *[a]CEMDRX, Physics Departament, University of Coimbra, Coimbra (Portugal). [b]Institut des Sciences et Technologies Moléculaires d'Angers, MOLTECH ANJOU, CNRS UMR 6200, Université d'Angers, Angers (France).* E-mail: psidonio@pollux.fis.uc.pt

The calculation of the nonlinear optical (NLO) properties of solids using structural data has been stimulated by the increasing importance of the communications industry and the parallel need for materials having suitable properties.

The following salts have been prepared by acid-base reactions and their structures have been determined by single-crystal X-ray diffraction: 6-methoxyquinolinium trifluoroacetate, 6-methoxyquinolinium hydrogensulphate trihydrate and 6-aminoquinolinium iodide monohydrate.

Using the methodology that we have developed recently [1], we calculated the nonlinear susceptibility tensor components for these non-centrosymmetric salts. The molecular hyperpolarizabilities were calculated using Time Dependent Density Functional Theory, Hartree-Fock and Semi-empirical methods.

The second and third order nonlinear optical properties of these salts will be presented.

The theoretical predictions will be compared with such experimental results.

[1] P.S. Pereira Silva, C. Cardoso, M.R. Silva, J.A. Paixão, A.M. Beja, M.H. Garcia, N. Lopes, *J. Phys. Chem A,* **2010**, *114*, 2607-617.

Keywords: nonlinear optical properties, structure-physical properties relationships, organic salts

MS66.P17

Distortion of the charged C_{60} fullerene cage in the ionic complexes

Salavat Khasanov,[a] Dmitri Konarev,[b] Alexey Kuzmin,[c] Sergey Simonov,[a] Leokadia Zorina,[a] *[a]Institute of Solid State Physics, Chernogolovka, Russia,[b]Institute of Problems of Chemical Physics, Chernogolovka, Russia, [c]Moscow State University, Moscow, (Russia).* E-mail: khasanov@issp.ac.ru

Ionic fullerene C_{60} complexes show a variety of promising physical properties such as metallic conductivity, superconductivity and ferromagnetism. Great interest is directed to the intrinsic structural and electronic properties of discrete fullerene C_{60}^{n-} anions. The Jahn-Teller theorem predicts a distortion of C_{60} from icosahedral symmetry when additional electrons are added to the degenerated t_{1u} LUMO orbital of C_{60}. The presence or absence of such distortion in the fullerene anions are of particular interest since the degeneracy strongly affects the electronic structure of fullerene and to a great extent defines such phenomena as superconductivity and ferromagnetism. Fullerene C_{60} is nearly a spherical molecule and fullerene anions are disordered in most ionic complexes and salts. Precise geometry of ordered fullerene anions was determined in a few compounds only [1-3]. The new complex {Co $(dppe)_2^+$}$\cdot(C_{60}^{\bullet-})\cdot(C_6H_4Cl_2)_2$ [4] gives another crystal structure with the ordered $C_{60}^{\bullet-}$ radical anions making it possible the $C_{60}^{\bullet-}$ distortion to be analyzed. An elongation of the fullerene cage by 0.025Å was found. Extended Hückel method calculations showed the 180 and 710 cm^{-1} splitting of the C_{60} degenerated LUMO levels. Additionally we present a comparative analysis of the C_{60} distortion parameters for the ordered structures known and compare the t_{1u} orbital splitting from extended Hückel method calculations and experimental data.

[1] W.C. Wan, X. Liu, G.M. Sweeney, W.E. Broderick, *J. Am. Chem. Soc.* **1995**, *117*, 9580. [2] B. Narimbetov, H. Kobayashi, M. Tokumoto, A. Omerzu, D. Mihailovic, *Chem. Commun.* **1999**, 1511. [3] P. Paul, Z. Xie, R. Bau, P.D. W.Boyd, C.A. Reed, *J. Am. Chem. Soc.*, **1994**, *116*, 4145. [4] D.V. Konarev, A.V. Kuzmin, S.V. Simonov, S.S. Khasanov, E.I. Yudanov, R.N. Lyubovskaya, *Dalton Trans.,* **2011**, *40*, 4453.

**Keywords: fullerene_structure, Jahn-Teller_distortion**

MS66.P18

Low dimensional Cu(II) complexes

Manuela Ramos Silva,[a] Consuelo Yuste-Vivas,[a] Ana Magalhães,[a] Laura C. J. Pereira,[b] Joana Coutinho,[b] José António Paixão,[a] *[a]CEMDRX, Physics Department, University of Coimbra, Coimbra, Portugal. [b]ITN, Sacavém, (Portugal).* E-mail: manuela@pollux.fis. uc.pt.

Molecular based magnets capitalize on the flexibility inherent in carbon chemistry. A rational choice of ligands can be made to control the dimensionality of the system in order to enhance quantum effects. Two new copper complexes were synthetized using the solvothermal technique and their structure determined using single crystal X-ray diffraction.

In compound 1, phenanthroline-isophtalic acid-Cu(II) compound, the metal ions are assembled in dimeric complexes. Each Cu(II) ion is in a distorted octahedral environment, surrounded by four nitrogen atoms from two phenanthroline molecules and by two oxygen atoms from an isophtalate ion. The isophtalate ion bridges two metal ions (see figure). The unit cell parameters are: a = 13.3116(4), b = 13.4168(4), c = 22.4838(6) Å, α = 83.800(2), β = 85.894(2), γ = 77.469(2)º, V = 3892.20(19) Å^3, space group P-1.
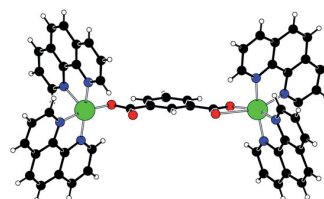
In compound 2, there is the formation of chains of phenanthroline-2,2'-iminobenzoic acid-Cu(II) units. The metal ion is in a distorted octahedral environment, four oxygen atoms from two 2,2'-iminobenzoate units and two nitrogen atoms from one phenantroline

molecule. Each 2,2'-iminobenzoate unit is linking two Cu(II) ions in a bis-bidentate mode, and the phenantroline unit is acting as a blocking ligand. The unit cell parameters are: a = 31.7600(5), b = 9.8517(2), c = 14.4899(3) Å, α = 90, β = 113.204(1), γ = 90º, V = 4167.00(14) Å^3, space group C 2/c.

The magnetic properties of both compounds, namely the magnetization in function of the applied magnetic field and the susceptibility in function of the temperature will be presented and discussed.

Keywords: coordination compound, molecular magnetism, Cu(II) chain

MS66.P19

Effect of low Sr-Ba on the transport and magnetic behaviour of $La_{0.67}Ca_{0.33}MnO_3$

M.Krishnaiah and B.Munirathinam *Department of Physics, Sri Venkateswara University, Tirupati, 517502 (India).* E-mail: profkrishnaiah.m@gmail.com.

The optimally doped composition (x=0.33) of the intermediate bandwidth manganite system $La_{1-x}Ca_xMnO_3$ has been studied extensively since the observation of large negative magneto resistance and strong ferromagnetism [Jin.S et al 1994]. In this compound, the double-exchange mechanism (DE) and electron-lattice coupling are believed to play major role in the occurrence of phenomena such as Ferromagnetism (FM), insulator-metal transition and colossal magneto resistance [Millis.A.J et al1995]. It is known that the substitution of cations of different size for A-site ions (La^{3+} and Ca^{2+}) affects the unit cell structure and the corresponding changes in the distortion or rotation of MnO_6 octahedrons give rise to wide variety of electronic properties [Hwang.H.Y et al 1995]. The conduction bandwidth of e_g electrons of Mn ions for instance is known to be strongly affected by the average size of A-site cations. By increasing the value of the latter by substitution method, both the conductivity and the paramagnetic to ferromagnetic transition temperature (T_C) may be increased. In this context the electronic transport and the magnetic susceptibility properties of optimally doped compounds $La_{0.67}Ca_{0.25}Sr_{0.04}Ba_{0.04}MnO_3$ (LCSBMO) and $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) synthesized under identical conditions are studied and compared. In the former composition, the average size of A-site ions has been increased lightly by simultaneous substitution of small percentage of large size ions such as Sr^{2+} and Ba^{2+} for Ca^{2+} ions. The focus of this work has been to study the effect of this low level substitution on the structural, microstructure, electronic transport and magnetic susceptibility properties of this widely studied LCMO. The electrical parameters which arise out of the fitting of standard models with resistivity data for T< T_{MI} and T > T_{MI} are compared and discussed in the above context apart from the paramagnetic to ferromagnetic transition temperatures (T_C)

Keywords: electronic transport, magnetic measurements, La0.67Ca0.33MnO3

MS66.P20

Classification of stacking interaction geometries of terpyridyl complexes

Jelena Andric,[a] Goran Janjić,[b] Agneš Kapor[c], Živadin D. Bugarčić,[d] and Snežana D. Zarić,[a] [a]*Department of Chemistry, University of Belgrade, Studentski trg 16, 11000, Belgrade, (Serbia).* [b]*IHTM, University of Belgrade, Njegoševa 12, 11000, Belgrade, (Serbia).* [c]*Department of Physics, Faculty of Sciences, University of Novi Sad, Trg D.Oradovića 4, 21000, Novi Sad, (Serbia).* [d]*Department of Chemistry, University of Kragujevac, Faculty of Science, R. Domanovića 12, P. O. Box 60, Kragujevac, 34000, (Serbia).* E-mail: jelenaandric.chem@gmail.com

Stacking interactions of terpyridyl square-planar complexes in crystal structures were studied analyzing data from the Cambridge Structural Database. In most of the crystal structures, two terpyridyl complexes were oriented "head-to-tail" or "head-to-head", with "head-to-tail orientation" being most prevalent. The number of structures with other orientations was very small. Based on the analysis of interacting geometries, we classified overlaps of terpyridyl complexes into six types. The types were defined by values of several geometrical parameters and all interactions of the same type had very similar overlap patterns. Stacking interactions of aromatic nitrogen-containing ligands were geometrically analyzed in crystal structures of metal complexes. The results show that nitrogen-containing aromatic rings usually form an offset (or parallel-displaced) stacking interactions.A terpiridine (2,2′;6′,2″-terpyridine) molecule coordinating to a metal ion forms a large planar system of five rings, three pyridine fragments and two chelate rings. This planar system has propensity to form stacking interactions. Stacking interactions between terpyridyl complexes were observed in crystal structures and in solution. Recent review papers present interesting properties of terpyridyl complexes from luminescence to biological activity. Propensity for stacking interactions is important for using these complexes in biochemistry, supramolecular and medicinal chemistry [1].

[1] G. Janjic, J. Andric, A. Kapor , Z.D. Bugarcic, S.D. Zaric, *CrystEngComm*, **2010**, *12*, 3773-377.

Keywords: stacking, CSD, terpyridine

MS66.P21

Structural Studies of N_4O_2 Iron(II) Spin Crossover Complexes

Mauricio Fuentealba, Andrés A. Goeta, Michael R. Probert, Alexander R. Whiting *Department of Chemistry. Durham University, Durham DH1 3LE, (United Kingdom).* E-mail: m.d.fuentealba@dur.ac.uk

Spin crossover (SCO) materials are molecular compounds switchable between a diamagnetic low-spin state (LS), which is stable at low temperatures and a paramagnetic high-spin state (HS), which is stable at higher temperatures. In general, the switching process in solid-state systems is controlled by cooperative intermolecular interactions. The correlation of structure with physical properties is crucial to the identification of these interactions and ultimately the understanding of the complex processes that control the SCO phenomenon.

We have carried out the syntheses and crystal structure analyses of iron(II) complexes with N_4O_2 coordination spheres using the tridentate Schiff base ligand, 4-hydroxy-N'-((pyridin-2-yl)-methylene)-benzohydrazide (**HL**) previously reported by Zhang *et al*. [1] In the mononuclear complex Fe**L**$_2$ the average bond lengths Fe-N and Fe-O are 0.25 and 0.14 Å shorter in the low-spin state compared with the high spin state. These variations allowed us to characterise the spin states of other N_4O_2 iron(II) complexes under different environmental conditions.

We have synthesised the mononuclear complexes Fe**L**$_2$ in methanol, ethanol, isopropanol and butanol to obtain different solvates. The crystals obtained from these reactions exhibit different spin states at room temperature indicating the importance of the crystal packing for the SCO phenomena. The figure shows the differences between (a) the structure of Fe**L**$_2$·EtOH (**LS**) and (b) Fe**L**$_2$· 2H$_2$O·iPrOH (**HS**). We have