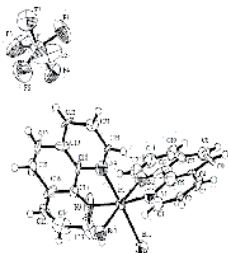


with a ligand replacement. For example,  $\text{IrBr}_3$  (0.5 mmol) and phen (0.180 g, 1.0 mmol) were mixed in ethylene glycol (15 ml). The suspended mixture was refluxed for 15 min in a microwave oven. Next, the mixture was cooled to room temperature. A saturated aqueous solution of  $\text{KPF}_6$  (20 ml) was added as a counter ion, and a yellow product began to precipitate. Yellow single crystals were obtained by recrystallization from acetonitrile and water.

In the adsorption and emission spectra, a contrast has been found. While the former ones are similar between dichloro- and dibromo- containing complexes, the latter ones are different. In order to investigate the source of the contrast, B3LYP calculations were carried out. Emission and electronic properties of eight  $\text{Ir}^{3+}$  centered polypyridine complexes were studied systematically. The computed geometry is in good agreement with the experimental one. Two geometric isomers of  $[\text{IrX}_2(\text{bpy})_2]^+$  and  $[\text{IrX}_2(\text{phen})_2]^+$  and the isomerization transition states were obtained with  $\text{X} = \text{Cl}^- \text{Br}^-$  and  $\text{NO}_3^-$  ligands. For  $\text{X} = \text{Cl}^-$  complexes, triplet-biradical isomers have nonequivalent bpy and phen ligands through the Jahn-Teller geometric distortion. Complexes with the asymmetric spin density distributions were found to correspond to strong emission spectra.



**Keywords:** triplet, DFT, iridium

## MS66.P14

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### Oxalate-based compounds with 2d and 3d structures showing coexistence of spin-crossover and ferromagnetism

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One of the most exciting developments in molecular magnetism is the preparation of multifunctional compounds that combine two (or more) physical properties of interest. This may lead to materials in which these properties coexist in an independent way, or interact synergistically leading to the emergence of new properties. These cooperative properties can be tuned by external stimuli such as light, pressure or temperature.

Spin crossover cations are particularly suitable to prepare switchable multifunctional magnetic materials since they represent one of the best examples of molecular bistability.

The first step to reach this goal is the insertion of these cations into magnetic extended networks. Oxalate-based networks have been used as they have reported many examples of multifunctional compounds. [1]

$\text{Fe}^{\text{III}}$  spin-crossover complexes have been used as templating cations. By using different synthetic conditions the compounds  $[\text{Fe}(\text{sal}_2\text{-trien})][\text{MnCr}(\text{ox})_3 \cdot (\text{CH}_2\text{Cl}_2)]$  (**1**) and  $[\text{Fe}(\text{sal}_2\text{-trien})][\text{MnCr}(\text{ox})_3 \cdot 0.75(\text{CH}_3\text{OH}) \cdot 0.5(\text{CH}_3\text{CN})]$  (**2**) have been prepared. [1] The structure of **1** presents a 2D honeycomb anionic layer while that of **2** presents an unusual 3D achiral network. [2] The magnetic properties indicate that these compounds undergo a long-range ferromagnetic ordering at ca. 5 K and a spin-crossover of the intercalated  $[\text{Fe}(\text{sal}_2\text{-trien})]^+$ , which is complete in the case of **1**. [2] Furthermore, **1** shows an unexpected property for  $\text{Fe}^{\text{III}}$  such as the observation of LIESST effect. [3]

In an attempt to improve these results, this strategy has been extended to derivatives of  $[\text{Fe}^{\text{III}}(\text{sal}_2\text{-trien})]^+$  with different substituents on the position 5 and 3 of the salicylaldimine ring.  $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{sal}_2\text{-trien})]^+$  complex gives rise to a 2D network, whereas

the  $[\text{Fe}^{\text{III}}(5\text{-CH}_3\text{Osal}_2\text{-trien})]^+$  complex, leads to the formation of an achiral 3D network. [4] In these two cases only one type of structure is obtained in contrast with the flexibility of  $[\text{Fe}(\text{sal}_2\text{-trien})]^+$  cation mentioned above. These results show that it is possible to tune the spin state of the inserted  $\text{Fe}^{\text{III}}$  compound depending on the electron-withdrawing or electron-donating character of the substituent of  $\text{sal}_2\text{-trien}$ . Compounds with Cl or Br in the 5<sup>th</sup> position of the salicylaldimine ring show a 3D chiral network. [5] Finally, other compounds with different structures have been obtained by using  $\text{Fe}^{\text{II}}$  and  $\text{Mn}^{\text{III}}$  complexes as templating cations.

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**Keywords:** spin-crossover, metal-complexes, molecular-magnetism

## MS66.P15

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### An Enantiopure $\text{Fe}^{\text{III}}_4$ Single Molecule Magnet

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Recently, the development of enantiopure chiral molecule-based magnets has been a topic of growing interest for synthetic chemists. Chiral Magnet has opened up a new field of research on molecular materials possessing both magnetic and optical properties. Such materials appear to be good candidates to present a cross effect between circular dichroism (CD) and magnetochiral dichroism (MChD). [1]

R. Sessoli et al reported a star shaped  $\text{Fe}^{\text{III}}_4$  cluster, they characterized the Single-Molecule Magnet (SMM) properties on the gold surface and confirmed that the molecule  $\text{Fe}^{\text{III}}_4$  maintained the SMM behavior on the surface. [2,3] Can these  $\text{Fe}^{\text{III}}_4$  type SMMs be chiral and show optical activity simultaneously? In our laboratory, we have prepared a pair of novel chiral star shaped  $\text{Fe}^{\text{III}}_4$  compounds,  $[\text{Fe}_4(\text{L}_R)_6] \cdot 5\text{DMF} \cdot \text{H}_2\text{O}$  (**1R**) and  $[\text{Fe}_4(\text{L}_S)_6] \cdot 5\text{DMF} \cdot \text{H}_2\text{O}$  (**1S**), which behaved as chiral SMMs.

Frequency dependence of AC susceptibility and hysteresis loop, the very important evidence for SMM, were observed for the title complex at low temperature. Below 1.5 K, the change of peak temperature with frequency for  $\chi''$  can be fitted by the Arrhenius law giving  $\tau_0 = 4.0 \times 10^{-7}$  s and  $\Delta E/k_B = 5.9$  K. At 0.5 K, a butterfly-shaped hysteresis loop emerges.

The optical activity and enantiomeric nature of compounds **1R** and **1S** were confirmed by circular dichroism (CD) spectra in both solution and solid state. The very well mirror symmetry spectra demonstrated the chirality has successfully transferred from ligand to the coordination environment of  $\text{Fe}^{3+}$  ion. Theoretical calculations were carried out to reveal the origin of CD signals from the fragment structures of the compounds.

This work is a successful example for preparing chiral SMMs from chiral ligands with designed absolute configuration, and the enantiopure  $\text{Fe}^{\text{III}}_4$  SMM may be a good candidate for studying the possible MChD behavior and enhanced MCD property. In next step we will try to tune the anisotropy barriers by introducing functional groups with different

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

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**Keywords:** magnetism, chirality, iron

## MS66.P16

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### Crystal Structures and NLO properties of Quinoline Derivatives

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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.

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

## MS66.P17

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### Distortion of the charged C<sub>60</sub> fullerene cage in the ionic complexes

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Ionic fullerene C<sub>60</sub> 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<sub>60</sub><sup>n-</sup> anions. The Jahn-Teller theorem predicts a distortion of C<sub>60</sub> from icosahedral symmetry when additional electrons are added to the degenerated t<sub>1u</sub> LUMO orbital of C<sub>60</sub>. 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<sub>60</sub> 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)<sub>2</sub><sup>+</sup>·(C<sub>60</sub><sup>•-</sup>)·(C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub>} [4] gives another crystal structure with the ordered C<sub>60</sub><sup>•-</sup> radical anions making it possible the C<sub>60</sub><sup>•-</sup> distortion to be analyzed. An elongation of the fullerene cage by 0.025 Å was found. Extended Hückel method calculations showed the 180 and 710 cm<sup>-1</sup> splitting of the C<sub>60</sub> degenerated LUMO levels. Additionally we present a comparative analysis of the C<sub>60</sub> distortion parameters for the ordered structures known and compare the t<sub>1u</sub> orbital splitting from extended Hückel method calculations and experimental data.

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**Keywords:** fullerene structure, Jahn-Teller distortion

## MS66.P18

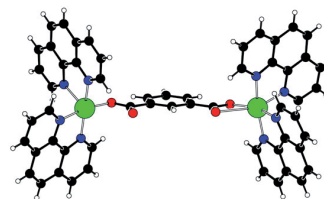
*Acta Cryst.* (2011) **A67**, C643-C644

### Low dimensional Cu(II) complexes

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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 synthesized using the solvothermal technique and their structure determined using single crystal X-ray diffraction.

In compound 1, phenanthroline-isophthalic 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 isophthalate ion. The isophthalate 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,  $\alpha = 83.800(2)$ ,  $\beta = 85.894(2)$ ,  $\gamma = 77.469(2)^\circ$ ,  $V = 3892.20(19)$  Å<sup>3</sup>, 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 phenanthroline