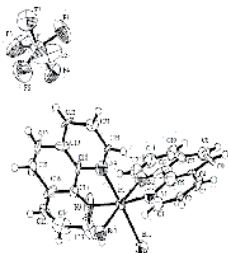


with a ligand replacement. For example, IrBr₃ (0.5 mmol) and phen (0.180 g, 1.0 mmol) were mixed in ethylene glycol (15 ml). The suspended mixture was refluxed for 15 min in a microwave oven. Next, the mixture was cooled to room temperature. A saturated aqueous solution of KPF₆ (20 ml) was added as a 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 Ir³⁺ centered polypyridine complexes were studied systematically. The computed geometry is in good agreement with the experimental one. Two geometric isomers of [IrX₂(bpy)₂]⁺ and [IrX₂(phen)₂]⁺ and the isomerization transition states were obtained with X = Cl⁻ Br⁻ and NO₃⁻ ligands. For X = 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

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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]

Fe^{III} spin-crossover complexes have been used as templating cations. By using different synthetic conditions the compounds [Fe(sal₂-trien)][MnCr(ox)₃·(CH₂Cl)₂] (**1**) and [Fe(sal₂-trien)][MnCr(ox)₃·0.75(CH₃OH)·0.5(CH₃CN)] (**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 [Fe(sal₂-trien)]⁺, which is complete in the case of **1**.[2] Furthermore, **1** shows an unexpected property for Fe^{III} such as the observation of LIEST effect.[3]

In an attempt to improve these results, this strategy has been extended to derivatives of [Fe^{III}(sal₂-trien)]⁺ with different substituents on the position 5 and 3 of the salicylaldimine ring. [Fe^{III}(5-NO₂sal₂-trien)]⁺ complex gives rise to a 2D network, whereas

[Fe^{III}(5-CH₃Osal₂-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 [Fe(sal₂-trien)]⁺ cation mentioned above. These results show that it is possible to tune the spin state of the inserted Fe^{III} compound depending on the electron-withdrawing or electron-donating character of the substituent of sal₂-trien. Compounds with Cl or Br in the 5th position of the salicylaldimine ring show a 3D chiral network. [5] Finally, other compounds with different structures have been obtained by using Fe^{II} and Mn^{III} complexes as templating cations.

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

MS66.P15

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An Enantiopure Fe^{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 Fe^{III}₄ cluster, they characterized the Single-Molecule Magnet (SMM) properties on the gold surface and confirmed that the molecule Fe^{III}₄ maintained the SMM behavior on the surface.^[2,3] Can these Fe^{III}₄ type SMMs be chiral and show optical activity simultaneously? In our laboratory, we have prepared a pair of novel chiral star shaped Fe^{III}₄ compounds, [Fe₄(L_R)₆]·5DMF·H₂O (**1R**) and [Fe₄(L_S)₆]·5DMF·H₂O (**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 χ'' can be fitted by the Arrhenius law giving τ₀ = 4.0 × 10⁻⁷ s and ΔE/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 Fe³⁺ 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 Fe^{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