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Acta Cryst. (2011) A67, C641**Molecular arrangement and magnetic properties of O₂ in the nanoporous materials**

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Molecular oxygen is an only element gas molecule which has magnetic moment with S=1. Intermolecular interaction between O₂ is due to not only electrostatic interaction but also magnetic interaction. The correlation between the molecular arrangement and magnetic properties of aligned O₂ has attracted the attention to physicists for a long time. It is suggested from the theoretical study that the magnetic properties of O₂ dimer is related not only to the intermolecular distance but also to the orientation of molecular axis. Therefore the precise structural information of O₂ including the molecular orientation is indispensable in the discussion of magnetic properties of O₂.

In 2002, we have succeeded in direct observation of array of O₂ adsorbed in the nanochannels of a porous coordination polymer (PCP) CPL-1 (Coordination polymer with pillared layer structure 1 : Cu-pyrazine-2,3-dicarboxylate). We determined molecular arrangement of O₂ in the nanochannels by an in-situ synchrotron powder diffraction of gas adsorption. O₂ molecules were found to be adsorbed forming dimer with H-geometry. From the magnetic susceptibility measurement, adsorbed O₂ was found to have antiferromagnetic ground state. But the meta-magnetic like behavior observed in the high-field magnetization process could not be explained by Heisenberg antiferromagnetic dimer model [1].

In the case of CuCHD (Cu-trans-1,4-cyclohexanedicarboxylic acid) [2] that have comparable size of nanochannels with CPL-1, O₂ molecules were also adsorbed forming dimer as same as CPL-1. The adsorbed O₂ dimer has H-geometry corresponding to the ground state with S=0 at 20 K and the geometry changed to S-type with increasing temperature. This shows that the thermally excited state of O₂ with S=2 was observed and the data of magnetic susceptibility and high-field magnetization process were well explained using spin-dependent intermolecular potential. These results suggest the magnetic field induced rearrangement of O₂ [3].

In comparing these two materials, CPL-1 shows the transformation of host framework in gas adsorption, which is one of the most characteristic features of PCPs. However the framework of CuCHD did not change so much. CPL-1 has larger host-guest interaction than CuCHD and larger magnetic field is needed in order to change molecular orientation in magnetization process. In addition, we have observed structural phase transition of O₂ adsorbed MFI zeolite at low temperature, which was not observed in N₂ adsorbed material. This implies that the phase transition was triggered by the intermolecular magnetic interaction between O₂ molecules. Our studies showed that the arrangement of adsorbed O₂ in nanopores is apparently related not only to the host-guest interaction but also to the intermolecular magnetic interaction.

[1] R. Kitaura, et al., *Science* **2002**, 298, 2358-2361. [2] W. Mori, et al. *Mol. Cryst. Liq. Cryst.* **1997**, 306, 1-7. [3] T. C. Kobayashi, et al. *Prog. Theor. Phys.* **2005**, 59, 271-279.

Keywords: metal-organic framework, synchrotron powder diffraction, gas adsorption

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Acta Cryst. (2011) A67, C641**Dynamic CuCl₂-(1,4-dioxane)-H₂O Crystal**

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In coordination compounds, the weak interaction of guest molecules, coordination geometry distortion, and coordination number change can effectively modulate the physical properties as magnetism, absorption, and chirality, so dynamic molecular crystals as crystal-to-crystal transformation involving changes on the dimensionality, color, and physical properties are very attractive for their potential applications in molecular devices as switches and sensors. The crystal-to-crystal transformation observed from red antiferromagnetic chain compound CoCl₂(1,4-dioxane)(H₂O)₂ to blue ferromagnetic diamond framework CoCl₂(1,4-dioxane)₂ was reported by us [1]. Recently, the work on dynamic crystal on CuCl₂-(1,4-dioxane)-H₂O showed the crystal composed of mononuclear compound CuCl₂(1,4-dioxane)₂(H₂O)₂ (**1**) in a hydrogen bond three-dimension framework can be transformed to crystal composed of layered coordination polymer (CuCl₂)₃(1,4-dioxane)₂ (**2**) by desolvation with changes on crystal composition, crystal color, crystal structure and magnetism as the antiferromagnetic interaction decreased with the Weiss constants changed from -66.7 K(**1**) to -3.2 K(**2**) and the temperature which a maximum observed on χ -vs-T plot decreased from 38 K to 7.8 K. [2] It proves the way to obtain crystal quantitatively by crystal-to-crystal transformation with drastic changes on molecular formula, crystal structure, crystal color and magnetism and provides crystalline materials to be used as sensor or switch in near future.

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[1] Z. M. Duan, Y. Zhang, B. Zhang, D. B. Zhu, *Journal of the American Chemical Society*, **2009**, 131, 6934-6935. [2] B. Zhang, D. B. Zhu, Y. Zhang, *Chemistry, A European Journal* **2010**, 16, 9994-9997.

Keywords: crystal-to-crystal transformation, hydrogen bond, magnetic properties

MS66.P13

Acta Cryst. (2011) A67, C641-C642**Electronic structures in the triplet states of polypyridine iridium(III) complexes**

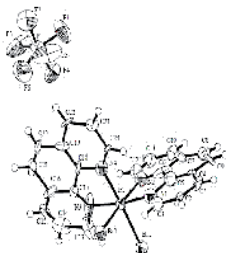
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Polypyridine complexes of d⁶ transition metals have been widely studied because of their useful spectroscopic and photophysical properties. Complexes of second-row and third-row transition metals with polypyridine ligands are particularly interesting, because they exhibit strong phosphorescence due to the mixing of singlet and triplet excited states via spin-orbit coupling. In this work, we prepared and performed DFT calculations of several Ir(III) complexes with bidentate ligands and X (halide ion) = Cl⁻, Br⁻ and NO₂⁻ ligands to seek the source of intense emission. Electronic structures of the triplet biradical complexes were carefully examined.

The desired complexes were prepared by a sequential procedure

with a ligand replacement. For example, 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 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 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 $\text{X} = \text{Cl}^-$, Br^- and 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

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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 $[\text{Fe}(\text{sal}_2\text{-trien})][\text{MnCr}(\text{ox})_3 \cdot (\text{CH}_2\text{Cl}_2)]$ (**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 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 $[\text{Fe}^{\text{III}}(\text{sal}_2\text{-trien})]^+$ 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 Fe^{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 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.

[1] M. Clemente-León, E. Coronado, C. Martí-Gastaldo, F.M. Romero, *Chem. Soc. Rev.* **2011**, 40, 473. [2] M. Clemente-León, E. Coronado, M. López-Jordà, G. Mínguez Espallargas, A. Soriano-Portillo, J. C. Waerenborgh, *Chem. Eur. J.* **2010**, 16, 2207. [3] M. Clemente-León, E. Coronado, M. López-Jordà, C. Desplanches, S. Asthana, H. Wang, J. F. Létard, *Chem. Sci.* **2011**, 2, 1121. [4] M. Clemente-León, E. Coronado, M. López-Jordà, *Dalton Trans.* **2010**, 39, 4903. [5] M. Clemente-León, E. Coronado, M. López-Jordà, J. C. Waerenborgh *Manuscript in preparation*.

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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, $[\text{Fe}_4(\text{L}_R)_6] \cdot 5\text{DMF} \cdot \text{H}_2\text{O}$ (**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 χ'' 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 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 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