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

Yoshiki Kubota,^{a,b} Akihiro Hori,^b Tatsuo C. Kobayashi,^c Ryotaro Matsuda,^d Kouichi Kindo,^e Kenichi Kato,^b Masaki Takata,^b Susumu Kitagawa,^{b,d,f} ^aDepartment of Physical Science, Osaka Prefecture University. ^bRIKEN/SPring-8 Center. ^cDepartment of Physics, Okayama University. ^dJapan Science and Technology Agency/ERATO. ^eUniversity of Tokyo. ^fiCeMS Kyoto University. (Japan). E-mail: kubotay@p.s.osakafu-u.ac.jp

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 physics 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.

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

Yan Zhang,^a Bin Zhang,^b Daoben Zhu,^b ^aInstitute of Condensed Matter and Material Physics, Department of Physics, Peking University, Beijing, 100871, (P R China). ^bOrganic Solid Laboratory, BNLMS, CMS & Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, (P R China). E-mail: zhang_yan@pku.edu.cn

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.

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

Naokazu Yoshikawa,^a Shinichi Yamabe,^b Nobuko Kanehisa,^c Tsuyoshi Inoue,^c ^aDepartment of Chemistry, Nara Women's Univ, ^bDepartment of Chemistry, Nara University of Education. ^cDepartment of Applied Chemistry, Graduate School of Engineering, Osaka University, (Japan). E-mail: naokazu@dream.com

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