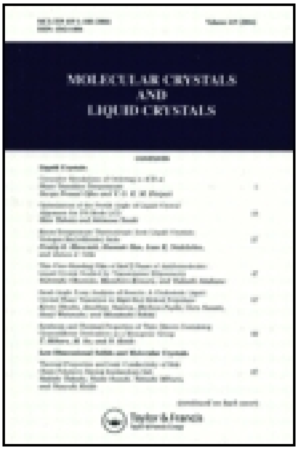

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theoretical Studies on Radical Spin Arrangements in the Cavity of Nanoporous Complexes

Takashi Kawakami [a] [b] , Satoshi Takamizawa [c] , Yasutaka Kitagawa [b] , Fumitake Matsuoka [b] , Tadashi Maruta [b] , Wasuke Mori [c] & Kizashi Yamaguchi [b]

[a] RIKEN, (The Institute of Physical and Chemical Research), Wako, Saitama, 351-0198, Japan

[b] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

[c] Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa, 259-1293, Japan

To cite this article: Takashi Kawakami, Satoshi Takamizawa, Yasutaka Kitagawa, Fumitake Matsuoka, Tadashi Maruta, Wasuke Mori & Kizashi Yamaguchi (2000): Theoretical Studies on Radical Spin Arrangements in the Cavity of Nanoporous Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 215-220

To link to this article: http://dx.doi.org/10.1080/10587250008023529

Mol. Cryst. and Liq. Cryst., 2000, Vol. 343, pp. 215-220
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Printed in Malaysia

Theoretical Studies on Radical Spin Arrangements in the Cavity of Nanoporous Complexes

TAKASH I KAWAKAMI[ab], SATOSH I TAKAMIZAWA[c],
YASUTAKA KITAGAWA[b], FUMITAKE MATSUOKA[b],
TADASHI MARUTA[b], WASUKE MORI[c] and KIZASHI YAMAGUCHI[b]

[a]*RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama, 351–0198, Japan,* [b]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560–0043, Japan and* [c]*Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259–1293, Japan*

Adsorption properties in nanoporous crystals, especially Zn(BDC) (BDC=1,4-benzenedicarboxylate) crystal, were studied theoretically. For sorbed molecules N_2 and CO_2 were employed and gas adsorption isotherms were obtained. In addition, O_2 as S=1 magnetic radical species was also treated in order to study the magnetic properties. Magnetic interaction between O_2 pairs exists and these cooperation might run in the nanoporous cavity. These results lead new approach to arrangement of organic spin radical sources and it is found that nanoporous organic-metal crystals are useful for controlling their position and orientation.

Keywords: adsorption; Monte Carlo simulation; molecular mechanics; *ab initio* MO calculation; magnetic interaction; effective exchange interaction

INTRODUCTION

Recently, dinuclear transition-metal dicarboxylates has been reported and it was found they adsorb a large amount of gases reversibly[1-5]. Recent progress in nanoporous study with metal-organic framework has started. These cavities are very useful for investigation of absorption phenomena, and both experimental and theoretical studies will make the nature clear. In another point of view, these nanoporous inorganic materials enable us to arrange molecules in suitable positions because of the rigid and stable cavities[6]. Thus, magnetic properties of oxygen which is physically adsorbed in Cu-trans-1,4-cyclohexanedicarboxylic acid (**1**) were studied by W. Mori and co-workers previously[1].

As the related materials, several crystals have been reported by many othe scientists[1-5]. O. M. Yaghi and co-workers reported several noteworthy materials[2,3]. One of them is $Zn_3(BDC)_3 \bullet 6CH_3OH$ (BDC=1,4-benzenedicarboxylate) (**2**) which have one dimensional cavities among the frameworks and we can obtain the detailed crystallographic structure data[3]. I. D. Williams and co-workers also reported $Cu_3(TMA)_2(H_2O)_3$ (TMA=benzene-1,3,5-tricarboxylate) crystal (**3**), where sphere holes exist and these size is about 9.5 or 13.3 Å across its diagonal[4]. These species are expected as novel materials beyond zeolite materials.

In addition to development of synthetic technique, theoretical calculation methods have also progressed and they enable us to evaluate amount of sorbed molecules with the Monte Carlo (MC) simulation method. On the other hand, the molecular mechanics (MM) method can give us information of orientation and direction of inside molecules. Furthermore, *ab initio* molecular orbital methods depend on quantum mechanics can evaluate magnetic interaction quantitatively.

CRYSTAL STRUCTURES

In this paper the crystal **2** was mainly treated as a stable metal-organic assembled species, since further crystal structural measurement for **1** had not been carried out[1,3]. This metal-organic assembled matter is consists

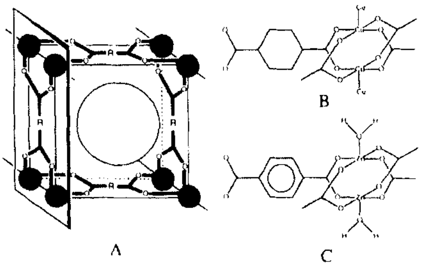

FIGURE 1 Nanoporous crystal structure(A) and its componet (B, C).

of dicarboxylate group and zinc metal atoms according to the X-ray measurement study. The common framework for both crystals is illustrated in Fig. 1A. In this figure the black balls indicate metal cations (Cu^{2+} for **1** and Zn^{2+} for **2**) which arrange in one line. The one dimensional nanoporous space of about 5 Å in diameter can be expected. In addition the component structural units in **1** and **2** are drawn in Figs. 1B and C, respectively. The differences between the both are only metal ion species and bridging hydrocarbon group (-R-).

The crystal **2** with inserted DMF molecules (DMF=N,N'-dimethylformamide) has unit cells classified by a space group of $P2_1/n$ and its cell parameters are a = 6.718(3) Å, b = 15.488(7) Å, c = 12.430(8) Å, and β = 102.83(4) °. The paper said that two water molecules which coordinated in axial positions of Zn were removed easily and Zn-O-Zn bonds might be establish. Though these inconsistency is inherent for this crystal, we employed the structure with water molecules for our following studies. Thus, coordinated water molecules were not removed, though all DMS guest molecules were taken away. For our theoretical adsorption simulation we had to build supercell as combination of two unit cells in a axis, since the disagree to cubic lead numerical errors.

SORPTION SIMULATION

A series of the MC simulation of single-gas adsorption was performed and we emploied Cerius^2 program packages for this purpose. In front of this simulation, force-field (FF) condition must be decided carefully. Suitable FF types on each atom in both framework and sorbed molecules were assigned manually. Through this simulation a general FF parameter set of "UNIVERSE_OFF 1.02" in Cerius^2 were introduced[7]. In regard to calculation of force and its division, the van der Waals (VDW) and Coulomb interactions were mainly taken into account but other effect was also considered. Here, the interaction radius of attract and/or repulsive effect was assumed to 20 Å, which was much longer than each cell constant.

The MC simulation is consistent of several process, that is, selection of a initial configuration, decision of moving molecules, trial to

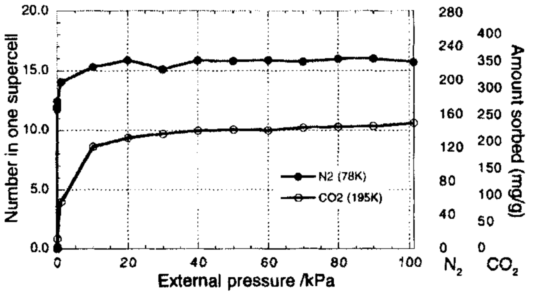

FIGURE 2 Amount of adsorbed N_2(a) and CO_2(b) adsorbed molecules.

add or remove molecules to the cavity. All of these procedure are handle using the normal Metropolis method with random number. In this study its sampling number was 6,000,000 and the first 1,000,000 cycles were discarded in order to improve the precision.

Pressure dependence of N_2 and CO_2 adsorption is shown in Fig. 2. In this figure, left scale indicates number of adsorption molecules in one supercell unit and right one indicates converted values to (mg weight sorbed) / [g of Zn(BDC)] in order to compare to experimental results in the paper[3]. The adsorption values increase and are saturated rapidly. The saturated values for N_2 and CO_2 reach about 16 molecules (=226 mg/g) and 10 molecules (222 mg/g), respectively. The tendency of the curvature is consistent to the experimental data, though these values are about 3 and 1.7 times as large as the experimental results, respectively. These inconsistency between calculated and experimental results may be derived from irregular stacking of unit cell and other effects.

ARRANGEMENTS OF O_2 MOLECULES AS S=1 RADICAL SPECIES

In addition to no magnetic species in the previous section, oxygen molecule was employed as radical species with S=1 spin par one molecule. The magnetic behavior of packed O_2 molecules was reported with their expectation of existence of Haldane gap[1].

First, we carried out similar calculations for O_2 molecule as sorbed species. Here, metal-organic framework **2** were employed because of lack of structural data for **1**. We assumed that there was no critical difference between two systems and same approximation was applied. Temperature dependence of O_2 adsorption calculated with the MC simulation is shown in Fig. 3, where right scale indicates converted values to (mol / 1 mol metal-ion) in order to compare to experimental results[1]. The adsorption decreases gradually below 200K and become to nearly zero above 250 K.

In order to understand these arrangement of adsorbed O_2 the mass density with MC adsorption simulation are depicted in Fig. 4A. The gray cloud is propagated in one dimensional waves. Control of O_2 arrangement is interesting in order to design magnetic interaction. The position and orientation in the cavity can be decided with the MM method as following to the MC calculations. One of these result is illustrated in Fig. 4B, though many styles of arrangement exist. Here, the intermolecular distance

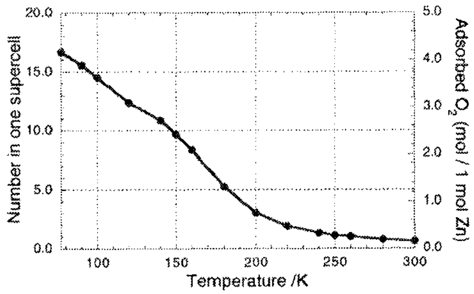

FIGURE 3 Temperature dependance of adsorbed O_2 molecules.

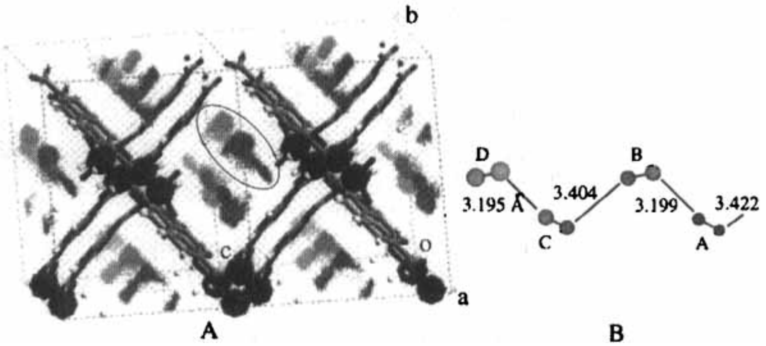

FIGURE 4 (A) Mass density of adsorbed O_2 molecules in two supercells. (B) One of the O_2 arrangement optimzed by MM method.

depends on framework structures. It is found that the alignment in this chain may compose one dimensional magnetic interactions. Thus, theoretical calculations with ab initio molecular orbital theory were carried out for O_2 pairs. The evaluate effective exchange integrals were antiferromagnetic (J_{ab}(UHF) = –0.030 cm^{-1}, J_{ab}(UB3LYP) = –1.158 cm^{-1} for Pair AB).

CONCLUDING REMARK

Theoretical adsorption calculation with the MC simulation for N_2 and CO_2 molecules were carried out for evaluating amount of adsorption molecules in nanoporous systems. The same tendency to experimental result is realized, though more molecules tend to enter into cavities. On the other hand, we investigated adsorption phenomenon of O_2 molecules into Zn framework but Cu. Magnetic interactions between O_2 pairs exist and these cooperation might run in nanoporous cavity. This study demonstrates the importance of nanoporous metal-organic frameworks for radical spin arrangement.

Acknowledgments

This work has been supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 10149105 "Metal-assembled Complexes") from Ministry of Education, Science, Sports and Culture, Japan. One of the present authors (T. K.) is supported by the Special Postdoctorial Researchers Program from RIKEN.

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