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# Magnetic properties of nitric oxide adsorbed within channel crystals

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**Abstract**

The crystalline one-dimensional compounds, $[M_2(bza)_4(pyz)]_n$ (bza = benzoate; pyz = pyrazine; M = $Cu^{II}$ (**1**)) and $[M_2(bza)_4(2\text{-mpyz})]_n$ (2-mpyz = 2-methylpyrazine; M = $Rh^{II}$ (**2**), $Cu^{II}$ (**3**)), demonstrate gas absorbency of NO. The amounts of adsorbed NO gas are 0.61 for **1**, 0.30 for **2**, and 0.23 for **3** per $M_2$ unit at 195 K (800 Torr). The crystals of **1** adsorbed more NO molecules than did those of **2** and **3**. The magnetic susceptibilities of the NO-inclusion crystals indicate that included NO molecules interact antiferromagnetically with neighboring guests without dimerization to $N_2O_2$. Magnetic behaviors indicated NO aggregation in the narrow 1D channels of **1**–**3** under unsaturated adsorption conditions.


*Keywords:* Adsorption; Host–guest systems; NO-inclusion compounds; Magnetic properties; Antiferromagnetic interaction

## 1. Introduction

Gas clathrate compounds have been attracting a large amount of attention for not only a wide range of possible applications such as gas purification, storage, and catalysts, but also for the physicochemical properties of specific aggregate structures with low dimensionality, particularly in oxygen molecules. Observations characterized using the single-crystalline state [1–3], but not the powdered state [4–6], would provide an exact aggregate structure for included guests that closely relate to their properties because single-crystal hosts can regulate the guest array with high integrity.

Recently, we have synthesized a series of single-crystal adsorbents, $[M_2(bza)_4(pyz)]_n$ (bza = benzoate; pyz = pyrazine; M = $Rh^{II}$ [7], $Cu^{II}$ (**1**) [8]) and $[M_2(bza)_4(2\text{-mpyz})]_n$ (2-mpyz = 2-methylpyrazine; M = $Rh^{II}$ (**2**) [9]) (Scheme 1), and have reported their gas adsorption properties and determination of their aggregation structure [7–19]. These crystals have 1D narrow channels, which can form 1D molecular chain systems of various adsorbed guests. In a previous study, we have reported the possibility of a change of intermolecular configuration between included $O_2$ molecules in the channel of **2** induced by an external magnetic field [9]. This report indicated that the high flexibility framework might provide prospects for the sensitive response of guest arrangements in various external fields, such as a magnetic field and an electric field in the use of paramagnetic or dipolar molecules [20].

Here, we focused on nitric oxide (NO) as the paramagnetic and dipolar guest molecule. NO is a high reactivity gas and of interest from the standpoint of magnetism and biology. NO molecules exhibit a diamagnetic nature in their solid phase at low temperatures due to dimerization [21–23]. Even at room temperature, diamagnetic dimers $(NO)_2$ are known to be formed and stabilized in the micropores of activated carbon fibers [24]. Further, elucidation of the details of NO arrangements in nanospace is an important factor in understanding characteristic physical properties, such as roles in the biological functions of biomolecular organisms. Herein, we report on the gas adsorption properties and the magnetic behavior of gas aggregates in the narrow spaces of **1**, **2**, and $[Cu_2(bza)_4(2\text{-mpyz})]_n$ (**3**) using different metals and substituents on the host lattice.

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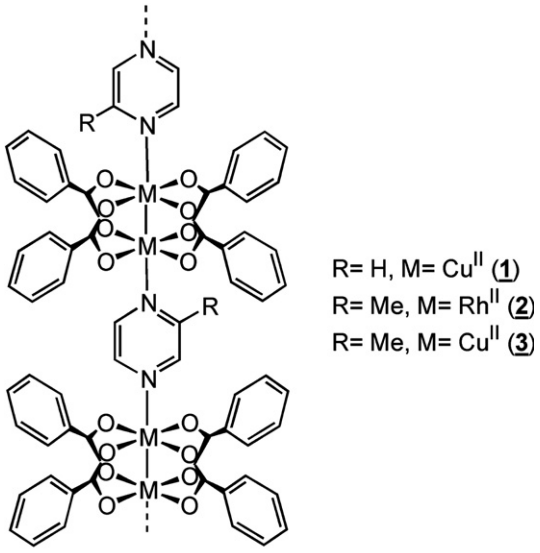


Scheme 1.

## 2. Experimental

Single-crystal hosts **1** and **2** were synthesized as described elsewhere [8,9]. Using the same synthetic procedure performed in **1** and **2**, blue plate crystals of $[Cu_2(bza)_4(2\text{-mpyz})]_n$ (**3**) were obtained by the careful vapor diffusion of 2-methylpyrazine into the methanol solution of copper(II) benzoate in 60% yield. Experimental procedures were performed under strict exclusion of oxygen and water vapor. Careful treatment, especially for NO gas, was taken because of its high degree of reactivity with oxygen.

### 2.1. Physical measurements

The NO gas used during the physical measurements had a purity of >99.9%. The NO adsorption isotherms for all adsorbents were measured by a volumetric method at 195 K on a Quantachrome Autosorb-1MP instrument (the pressure for the data collections ranged from 0.3 to 800 Torr for all adsorbents). Magnetic susceptibilities of the included NO molecules were measured on a Quantum Design SQUID magnetometer MPMS-XL with an applied magnetic field of 1 T. The crystals were sealed in glass tubes with pressurized NO gas (2.0 MPa for **1**, 2.6 MPa for **2**, and 2.5 MPa for **3**) at 195 K, which can separate from the condensed excess NO at low temperatures. Measurement of the pure NO was performed by using a sample tube containing solid NO, which corresponds to an inner pressure of 7.5 MPa at 298 K. Susceptibility was corrected by the trace background values of the cell and each empty crystal. Calculation of the molar magnetization and susceptibility of the included NO was based on a mass of 1.83 for **1**, 1.00 for **2**, and 1.14 for **3** per $M_2$ unit, which were estimated by theoretical Bohr magneton numbers applied for the observed maximum values at around 200 K.

## 3. Results and discussion

### 3.1. Gas adsorption properties

The NO adsorption isotherm curves of **1**, **2**, and **3** at 195 K are shown in Fig. 1. The sorption curves show a slight curve in **1** and a linear increase to 800 Torr in **2** and **3**; all curves smoothly return reversibly to the starting point without hysteresis. The isotherm curves reach 0.61 for **1**, 0.30 for **2**, and 0.23 for **3** per $M_2$ unit at 800 Torr. **1** adsorbed more NO molecules than did **2** and **3**. We have reported that, under a saturated inclusion state, the host possesses a one-dimensional channel even if the channel surface is modified by the substituents on the pyrazine linker, such as methyl and ethyl groups, and strong contacts are found between the guests and the substituents on the channel surface [9,25]. Therefore, the observed difference in the NO adsorption property is probably influenced by

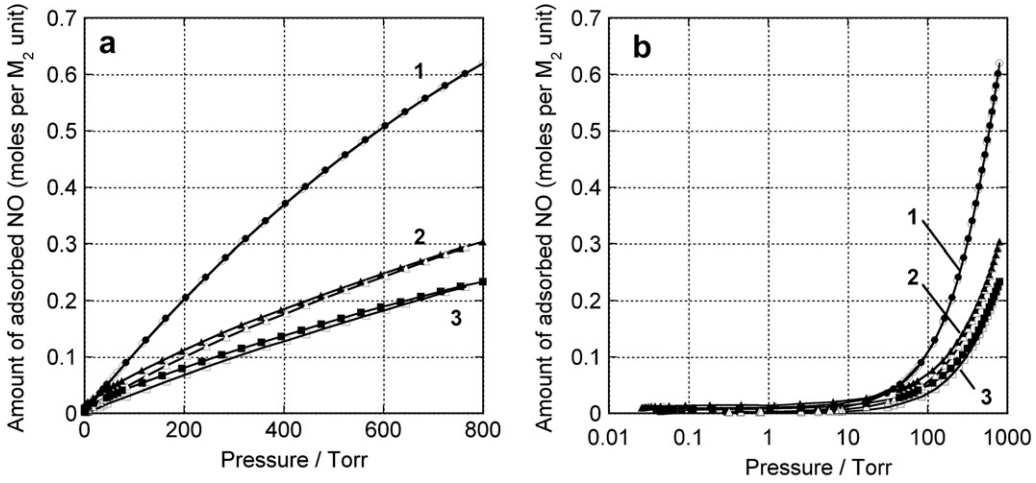


Fig. 1. NO sorption isotherm curves for **1**, **2**, and **3** at 195 K: adsorption process (open point), desorption process (solid point). (a) Linear plot, (b) log plot.