Microporous Structure of a Chain Compound of Copper(II) Benzoate Bridged by Pyrazine

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Reaction of copper(II) benzoate with pyrazine (pyz) gave a compound, $[Cu_2(bz)_4(pyz)]_n$ (**1**) which has a gas-occlusion property. The X-ray structure analysis of **1**·2nCH$_3$CN shows a microporous structure formed by chains where the carboxylate dimer units are linked by pyrazine molecules.

Recently, it has been found that some coordination polymers constructed by the metal complexes and bridging ligands have microporous strctures.[1-3] For instance, the polymeric compounds $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot xH_2O\}_n$ reveal adsorbing property for small molucules, CH_4, N_2, and O_2.[1] We and others have been engaged in chemistry of metal carboxylate dimers in order to produce new type of chain compounds and isolated several chain compounds of metal carboxylate.[3-8] Interestingly, some of them show gas-occlusion properties,[3] giving us a new aspect of chain compounds. Herein, we report preparation and X-ray crystal structure of a chain compound of copper(II) benzoate bridged by pyrazine, which is capable of adsorbing N_2 gas.

When copper(II) benzoate was treated with an equivalent amount of pyrazine in acetonitrile, chain compound of copper(II) carboxylate was isolated as in the case of copper(II) pivalate.[7] Microanalysis figures of C, H, and N agree with the formulation $[Cu_2(bz)_4(pyz)]_n$ (**1**). Crystals suitable for a single-crystal X-ray structure determination were obtained from a solution as those with solvated acetonitrile molecules, $[Cu_2(bz)_4(pyz)]_n\cdot 2n\mathrm{CH_3CN}$ (**1**·2nCH$_3$CN) by a slow diffusion technique.[9] A perspective view of **1**·2nCH$_3$CN is shown in Figure 1. The complex has the crystallographic inversion centers at the centers of the $Cu_2(bz)_4$ core and pyrazine molecule, respectively. The Cu-Cu' separation is 2.604(1) Å. The pyrazine molecules link the $Cu_2(bz)_4$ units with a Cu-N distance of 2.187(3) Å. The Cu'-Cu-N angle is 171.1(1)°. In spite of the chain structure, temperature dependence of the magnetic susceptibility per $[Cu_2(bz)_4(pyz)]$ unit (5–300 K) can be interpreted in terms of the Bleaney-Bowers equation [Figure 2, g = 2.09, $2J$ = -339 cm^{-1}, the mole fraction of paramagnetic impurity (assumed to mononuclear Cu(II) ions) 2.3 × 10^{-4}, and $N\alpha$ = 120 × 10^{-6} cgs emu].[10] This means that interdimer interaction through the pyrazine molecules is negligibly small in **1** as the case for chain compounds of copper(II) pivalate $[Cu_2(piv)_4L]_n$ (L = pyz, 4,4'-bpy, and dabco).[7]

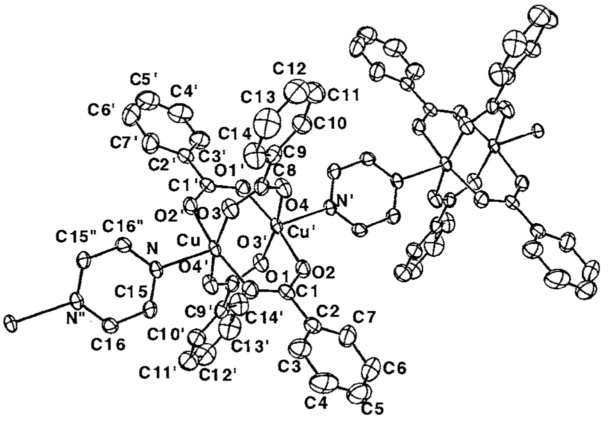

Figure 1. Perspective view of **1**·2nCH$_3$CN. Selected bond distances (l/Å) and angles (ϕ/°): Cu-Cu' 2.604(1), Cu-O1 1.954(3), Cu-O2' 1.970(3), Cu-O3 1.957(3), Cu-O4' 1.972(3), Cu-N 2.187(3); O1-Cu-O3 88.8(1), O1-Cu-O4' 88.4(1), O3-Cu-O2' 89.7(1), O2'-Cu-O4' 91.1(1), O1-Cu-N 99.1(1), O3-Cu-N 99.9(1), O2'-Cu-N 91.8(1), O4'-Cu-N 91.1(1). The acetonitrile molecules are omitted.

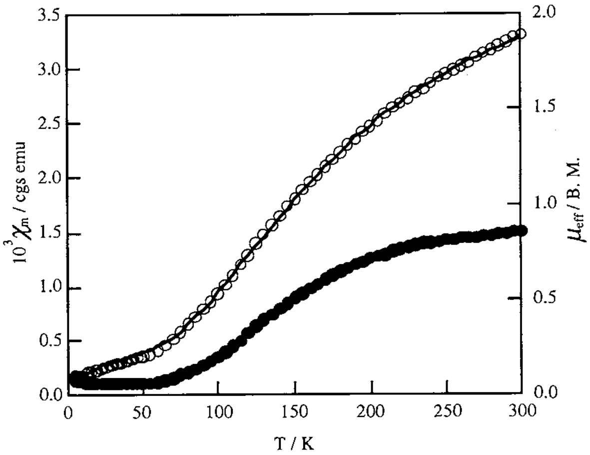

Figure 2. Temperature dependence of magnetic susceptibilities (filled circle) and magnetic moments (empty circle) of **1**. The solid lines shows the best fit curve of the Bleaney-Bowers equation with g = 2.09, $2J$ = -339 cm^{-1}, paramagnetic impurity 2.3 × 10^{-4}, and $N\alpha$ = 120 × 10^{-6} cgs emu.

The adsorption isotherms of nitrogen gas, water vapor, and carbon tetrachloride vapor were measured using the automatic volumetric adsorption apparatus described elsewhere.[11] Before the gas adsorption experiments, **1** was pretreated at 298 K *in vacuo* for 4 h. Figure 3 shows the adsorption-desorption isotherm of nitrogen gas at 77 K (curve A)[12] and the adsorption-desorption isotherm of water vapor at 283 K (curve B) for **1**. The adsorbed amounts of the adsorbates are expressed as the molar ratio (N_2 or water vapor / $[Cu_2(bz)_4(pyz)]$). The adsorption isotherm of curve A corresponds to Type I according to the isotherm classification,[13] showing that **1** is highly microporous. The low-pressure hysteresis in the adsorption-desorption branches indicates that the size of the micropores present in **1** is very close to the diameter of nitrogen molecule (d_{N_2} = 0.43 nm); the once adsorbed molecules are hardly removed from the micropores. The larger molecule, carbon

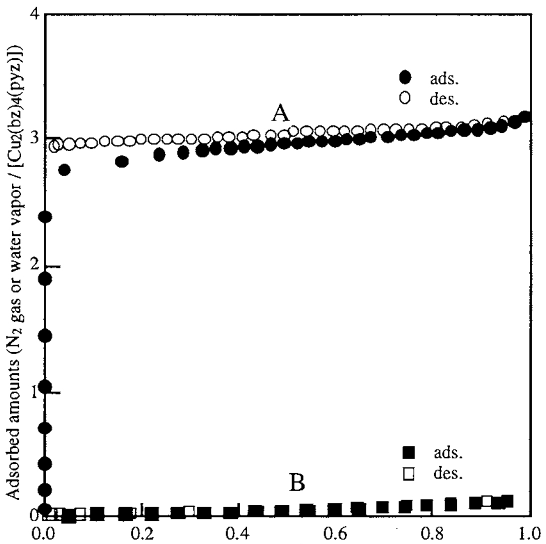

Figure 3. Adsorption isotherm of N_2 gas at 77 K (A) and adsorption isotherm of water vapor at 283 K (B) for **1**.

tetrachloride whose molecular diameter is 0.60 nm, cannot be adsorbed into the micropores.

The porous structure of **1** was examined on the basis of the crystal structure of **1**·2*n*CH_3CN determined by the X-ray diffraction method (Figure 4). The micropores are occupied by the solvent molecules (acetonitrile) in the process of crystallization. The acetonitrile molecules are easily removed from the micropores by treatment of **1**·2*n*CH_3CN *in vacuo* at 298 K. The size of the micropores estimated from the crystal structure of **1**·2*n*CH_3CN is 0.4 x 0.5 nm. As can be seen in Figure 3, the adsorbed amounts of **1** are three nitrogen molecules per [$Cu_2(bz)_4(pyz)$] unit. This is reasonable, because the distance of the linearly arranged three nitrogen molecules in micropores (*ca.* 1.2 nm) is approximately equal to the corresponding depth of the micropores in **1**·2*n*CH_3CN (1.1 nm). The crystal structure of **1**·2*n*CH_3CN reveals also that each micropore is surrounded by hydrocarbons of the benzoate groups and pyrazine molecules, giving hydrophobic nature of the micropores of **1**.[14] The hydrophobicity of **1** was examined by the adsorption experiment of water vapor. As seen in curve B of Figure 3, the adsorbed amounts of water molecules are very small compared with those of nitrogen (*cf.* curve A), which means that the micropores of **1** are extremely hydrophobic. The hydrophobicity of **1** is remarkably greater than that of the typical hydrophobic active carbons.[15]

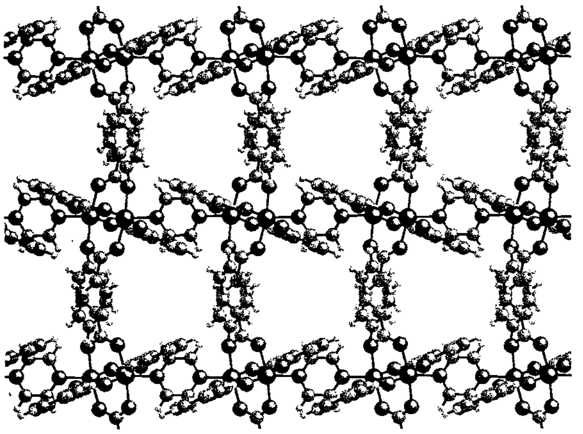

Figure 4. View of the crystal structure of **1**·2*n*CH_3CN. The acetonitrile molecules are omitted for clarity.

The present results show that chain compound **1** has a unique micropore structure which exclusively adsorbs nitrogen molecules because of the size and hydrophobic character of the micropores. This kind of chain compounds are promising to produce new type of microporous materials.

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9 Crystal data for **1**·2*n*CH_3CN: $C_{36}H_{30}Cu_2N_4O_8$, *F.W.* = 773.75, monoclinic, space group $P2_1/n$, $a = 10.585(3)$, $b = 19.270(2)$, $c = 9.692(2)$ Å, $\beta = 113.24(1)°$, $V = 1816.5(7)$ Å^3, $Z = 2$, $D_c = 1.42$ gcm^{-3}, $D_m = 1.42$ gcm^{-3}, μ(Mo-Kα) = 12.26 cm^{-1}, $F(000) = 792$, $T = 298$ K, crystal size 0.49 × 0.41 × 0.26 mm, 2953 reflections measured ($2\theta_{max} = 48°$), 1921 [$I \geq 3\sigma(I)$] used in the refinement, $R = 0.035$, $R_w = 0.042$. Intensity data ware collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.

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