

Gas-Occlusion Properties of a Novel Compound: Mononuclear Copper(II) Terephthalate-Pyridine

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Mononuclear copper(II) terephthalate-pyridine, which has a regular one-dimensional structure, occludes large amounts of gases. The maximum amount of N₂ gas that can be occluded by mononuclear copper(II) terephthalate-pyridine is 1.1 mole per mole of copper(II) salt, indicating the presence of a large number of micropores. A porous structure, which is formed by hydrogen bonding and self-assembly of the linear copper(II) terephthalate-pyridine, was determined by X-ray crystallography.

Previously, we reported that copper(II) dicarboxylates,¹ molybdenum(II) dicarboxylates,² and ruthenium(II,III) dicarboxylates^{3,4} reversibly occluded large amounts of gases such as N₂, Ar, O₂, CH₄, and Xe. The uniform linear micropores of these adsorbents were concluded as having been constructed by the stacking or bonding of two-dimensional lattices of dinuclear transition-metal dicarboxylates. Many excellent studies of adsorbent porous complexes have also been reported by Yaghi,⁵ Kitagawa,^{6,7} and Williams.⁸

Recently, it has been found that mononuclear copper(II) terephthalate-pyridine, which has a regular one-dimensional structure, also occludes large amounts of gases. In this paper, we report on the synthesis of a new copper(II) terephthalate-pyridine adsorbent and its magnetic and gas occlusion properties.

A form of copper(II) terephthalate-pyridine, capable of occluding gases, was synthesized as follows. An aqueous solution (200 cm³) of copper(II) formate (0.5 g) was added to a pyridine solution (200 cm³) of terephthalic acid (0.37 g). The mixture was then allowed to stand for several days at room temperature, after which deep blue, plate-like crystals precipitated out of the solution. [Cu(II)(μ-O₂CC₆H₄CO₂)(py)₂(H₂O)]·py·H₂O **1** Anal. Calcd for C₂₃H₂₃CuN₃O₆: C, 55.14; H, 4.63; N, 8.39%. Found: C, 55.17; H, 4.53; N, 8.09%. Complex **1** was dried under a vacuum at room temperature for 6 h, giving a pale blue powder capable of occluding gases. [Cu(II)(μ-O₂CC₆H₄CO₂)(py)₂(H₂O)] **2** Anal. Calcd for C₁₈H₁₆CuN₂O₅: C, 53.53; H, 3.99; N, 6.94%. Found: C, 53.32; H, 3.82; N, 6.54%.

Crystals suitable for a single-crystal X-ray structure determination were obtained from a dilute solution as being pyridine molecules in solvated form. The crystal structure was determined by X-ray diffraction using a Rigaku R-AXIS RAPID diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by the direct method and refined by full-matrix least-squares iterations. This complex crystallizes in the monoclinic space group *Cc* with *a* = 17.8636(9) Å, *b* = 5.9305(3) Å, *c* = 22.001(2) Å, β = 114.239(2)°, and *Z* = 4, *R*₁ = 0.055, *R*_w = 0.122. The distances of Cu–O₁H₂O, Cu–O₂, Cu–O₃, Cu–N₁, and Cu–N₂ are 2.272(5), 1.94(1), 1.91(1), 2.06(2), and 2.03(1) Å, respectively. The angles of O₁–Cu–O₂, O₁–Cu–O₃, O₁–Cu–N₁, O₁–Cu–N₂, O₂–Cu–N₁, O₂–Cu–N₂, O₃–Cu–N₁, and O₃–Cu–N₂ are 88.0(6), 90.2(6), 91.2(7), 96.0(7), 91.0(6), 88.0(5), 89.4(6), and 91.8(5)°, respec-

tively. The porous structure of complex **1** was examined on the basis of the crystal structure determined by X-ray diffraction (Figure 1a). The water hydrogen bonds (1.79 Å and 1.80 Å) between the H atoms (H1 and H2) of the coordinated water molecules of one linear chain and the O atoms (O4 and O5) of the carboxylate groups of the adjacent linear chain form a two-dimensional network (Figure 1b). In the process of crystallization, the micropores are occupied by the molecules of the solvent (pyridine). The pyridine molecules were removed from the micropores by treatment in vacuo (Figure 2).

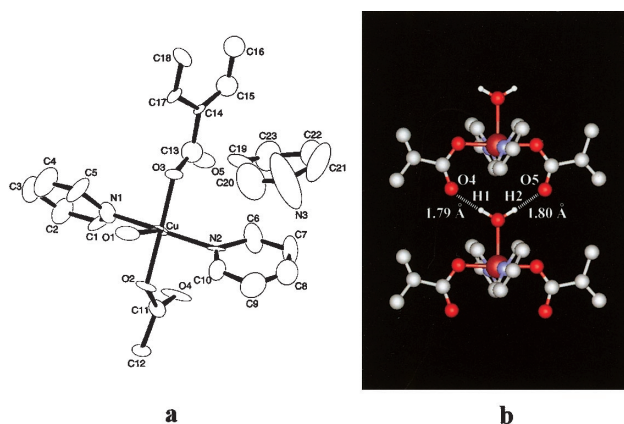


Figure 1. ORTEP view of the mononuclear unit of complex **1** showing the numbering scheme. For clarity, the hydrogen atoms have been omitted (a). Hydrogen bonding structure of complex **1** (b).

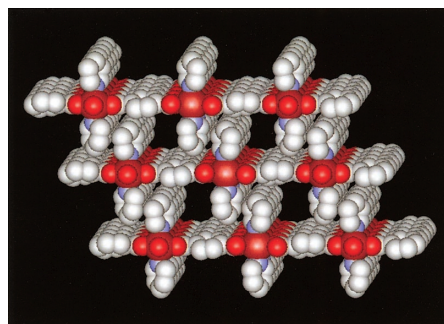


Figure 2. View of crystal structure of complex **1**. For clarity, the hydrogen atoms and the solvent molecules (pyridine) have been omitted.

The solid-state structure of complex **2** was determined by conventional X-ray powder diffraction data. The crystals are monoclinic, space group *Cc*, with *a* = 17.447(7), *b* = 5.887(5), *c* = 24.231(7) Å, β = 119.994(4)°, and *Z* = 4. The structure was refined by the Rietveld method using program packages, Cerius 2, down to *R*_p and *R*_{wp} values of 0.182 and 0.235, respectively, for

5500 data points measured at room temperature in the $5.01\text{--}60.0^\circ$ (2θ) range (Figure 3). The effective pore size deduced from the structure of complex **2** was $4.7\text{--}4.8\text{ \AA}$.

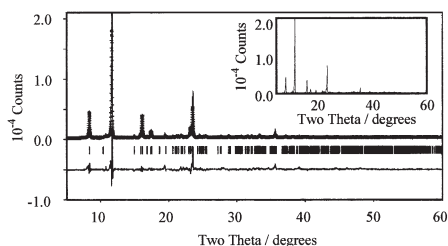


Figure 3. Observed (solid line) and calculated (dotted line) XRPD patterns for complex **2**. Reflection markers and a difference plot are at the bottom. Experimental data is shown in the insert.

The temperature dependence of the amount of occluded N_2 gas was determined by a Cahn 1000 electric balance at 20 Torr⁹ in the temperature range of $77\text{--}220\text{ K}$. The amount of occluded N_2 gas nearly reached saturation at 130 K (Figure 4). The maximum amount of occluded N_2 gas was 1.1 mole per mole of the copper(II) salt.

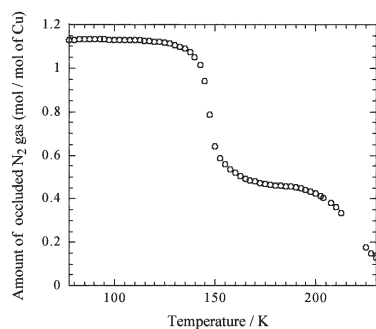


Figure 4. Temperature dependence of the amount of occluded N_2 gas of complex **2**.

Pore size distributions are shown in Figure 5. Pore size was calculated by the Horvath-Kawazoe equation¹⁰ from the absorption isotherm of complex **2** at the temperature of liquid argon. The resulting data indicated that the BET surface area and micropore volume were $110\text{ m}^2/\text{g}$ and $0.03713\text{ cm}^3/\text{g}$, respectively. A very narrow peak at ca. 4.8 \AA suggests regular and stable ultramicropores (Figure 2). A broad peak at ca. 10 \AA might indicate the existence of other micropores between the two-dimensional layers.

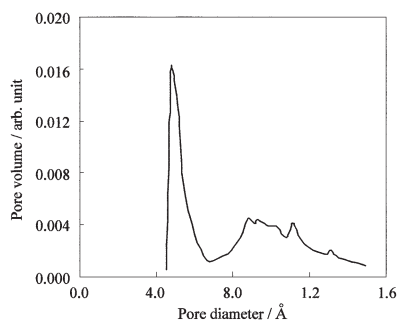


Figure 5. Micropore size distributions for complex **2**.

To investigate the structure in further detail, the temperature dependencies of the magnetic susceptibilities of complexes **1** and **2** were measured by a SQUID magnetometer (Quantum Design, MPMS-5S) in a temperature range of $2\text{--}300\text{ K}$. The effective magnetic moments (μ_{eff}) were calculated from the magnetic susceptibilities (Figure 6). The magnetic susceptibilities of complexes **1** and **2** obey the Curie-Weiss expression with $\theta = -1.4\text{ K}$ and $\theta = +9.4\text{ K}$, respectively (Figure 7). The θ value of complex **2** suggests a weak ferromagnetic coupling arising from hydrogen bonding.¹¹

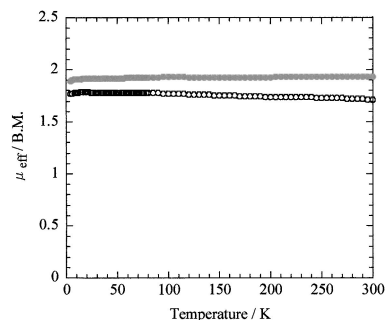


Figure 6. Temperature dependencies of the magnetic moments of complexes **1** (●) and **2** (○).

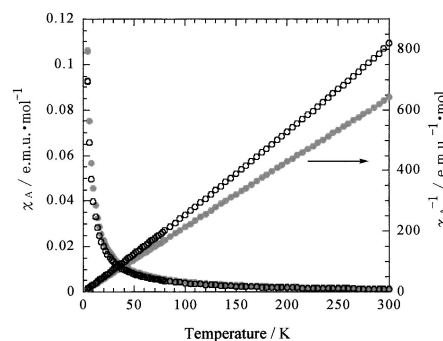


Figure 7. Temperature dependencies of the magnetic susceptibilities of complexes **1** (●) and **2** (○).

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References and Notes

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