A Polymer Complex $[Cu(O_2CC_6F_5)_2(pyz)]_n$ Formed from Copper(II) Pentafluorobenzoate and Pyrazine

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The reaction of copper(II) pentafluorobenzoate ($[Cu_2(O_2CC_6F_5)_4]$) with pyrazine (pyz) in methanol gave a polymer complex $[Cu(O_2CC_6F_5)_2(pyz)]_n$. The pyz-bridged structure of $Cu(O_2CC_6F_5)_2$ was characterized by X-ray crystal structure analysis. Temperature-dependent magnetic susceptibility showed the existence of an antiferromagnetic interaction ($J = -3.0\,cm^{-1}$) within the polymer.

Copper(II) carboxylates ($[Cu_2(O_2CR)_4]$) have a lantern-like dimer structure without a direct metal–metal bond and strong antiferromagnetic interaction operates through the carboxylato ions between copper(II) ions within the dimer, which has been explained by a super-exchange mechanism.[1] The dinuclear complexes have been lately used as building blocks in combination with bridging ligands such as pyrazine (pyz).[2–4] We have reported that a polymer complex of copper(II) benzoate bridged by pyrazine $[Cu_2(O_2CC_6H_5)_4(pyz)]_n$ (**1**) has interesting nitrogen-adsorbing properties due to its porous structure, three nitrogen molecules per copper(II) dimer unit being adsorbed.[3] Similar polymeric compounds using lantern-like dinuclear complexes with other metal ions and bridging ligands have been reported for their gas-storing properties.[4] In this study, we used copper(II) pentafluorobenzoate ($[Cu_2(O_2CC_6F_5)_4]$) for combination with pyz because we expected the formation of polymer complexes with an alternating arrangement of the copper(II) dimer and pyz, possibly showing a new gas occlusion property based on the introduction of electron-withdrawing fluorine groups onto the phenyl ring. Despite this expectation, the complex obtained from the reaction of $[Cu_2(O_2CC_6F_5)_4]$ with pyz in methanol was found to be the polymer chain complex $[Cu(O_2CC_6F_5)_2(pyz)]_n$ (**2**), of which chain structure is built up by the alternating arrangement of $Cu(O_2CC_6F_5)_2$ units and the pyz bridging ligands. The crystal structure and magnetic properties of **2** will be presented in this report.

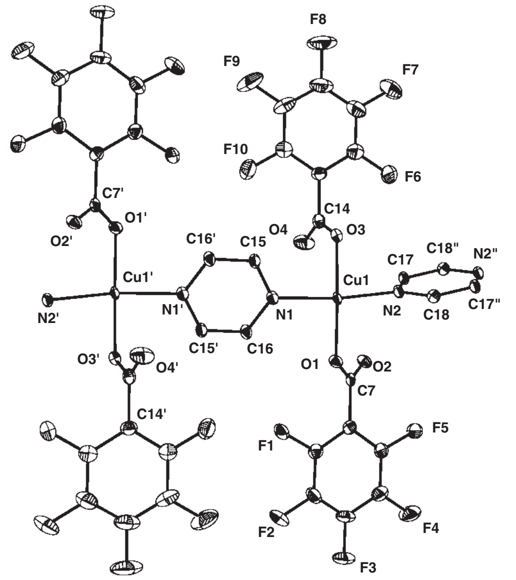

Figure 1. Crystal structure of **2**. Primes and double primes refer to the equivalent positions $(1 - x, -y, 1 - z)$ and $(-x, 1 - y, 1 - z)$, respectively.

The elemental-analytical result for the obtained complex from the reaction solution of $[Cu_2(O_2CC_6F_5)_4]$ and pyz in methanol revealed that it had a structure with $Cu(O_2CC_6F_5)_2$: pyz = 1:1, which corresponds to that of **2**. The crystal structure of **2** is shown in Figure 1, where it is clearly shown that the lantern-like dinuclear framework is broken to form a mononuclear $Cu(O_2CC_6F_5)_2$ unit linked by the bidentate bridging ligand pyz. We have confirmed that the polymer structure is built up in the repeated X-ray determining work for the crystal obtained by the reaction of $[Cu_2(O_2CC_6F_5)_4]$ and pyz in methanol.[5] In Figure 2, the crystal packing features of the polymer chains with alternating arrangement of the $Cu(O_2CC_6F_5)_2$ unit and pyz is displayed. The copper(II) ion is coordinated by carboxylate oxygens with Cu–O distances of 1.939(3) (for Cu1–O1) and 1.934(3) Å (for Cu1–O3), respectively, as well as two pyrazine nitrogens with Cu–N distances of 2.035(4) (for Cu1–N1) and 2.005(4) Å (for Cu1–N2), respectively. The oxygen atoms designated with O2 and O4 do not participate in the coordination to the copper(II) ion within the chain, although the carboxylate oxygen (O2) axially coordinates to the copper(II) ion of the neighboring chain with a distance of 2.199(3) Å. The coordination environment around the copper(II) ion is an axially elongated square-pyramid with the axial coordination, which is depicted with a green line in Figure 2. To our knowledge, there have been only two X-ray crystallographic reports for the present type of ligand-bridged copper(II) polymer complexes with unsymmetrically coordinating carboxylate ions, on which substituent groups (3-thiophenemethyl[6] and methyl[7]) are rather electron-donating; the polymer complexes were prepared from the copper(II) carboxylate dimers and bridging ligands with nitrogen donors (1,3-bis(4-pyridyl)propane[6] or 4,4′-dithiodipyridine[7]). It should be noted that they both have flexible bridging ligands compared

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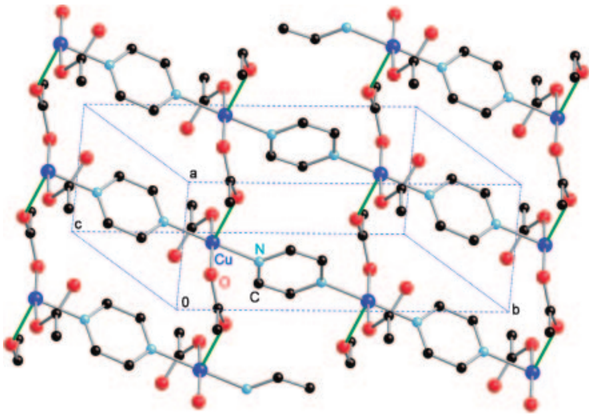

Figure 2. Crystal packing of **2**. C_6F_5 moieties are omitted for clarity.

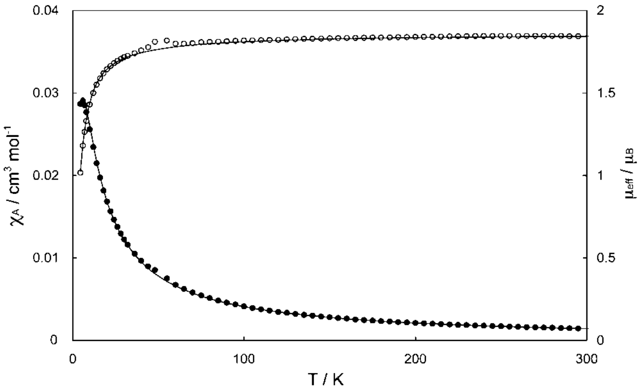

Figure 3. Temperature dependences of magnetic susceptibility (●) and effective moment (○) of **2**.

with pyz in **2**. In the case of the 1,3-bis(4-pyridyl)propane-bridged polymer, the copper(II) ion has a square-pyramidal geometry with an apical carboxylato oxygen ($Cu–O_{ax} = 2.695(3)$ Å), which equatorially coordinates to the copper(II) ion in the neighboring polymer chain. This leads to a ferromagnetic coupling between copper(II) ions through the oxygen atom, resulting in the triplet ground state,[6] which is in contrast to the case of **2** (see later).

Since pyz was considered to be the bridging ligand preferable for mediating the magnetic interaction between the copper(II) ions, magnetic measurement was performed for **2**. The temperature dependences of magnetic susceptibility and moment are displayed in Figure 3. The magnetic moment is 1.84 μ_B at room temperature, which correspond to $S = 1/2$ spin of the copper(II) ion, although the moment decreases gradually with lowering the temperature till ca. 30 K and then falls steeply down to 1.0 μ_B at 4.5 K, which is indicative of the existence of antiferromagnetic interaction between copper(II) ions. The temperature-dependent profile was simulated using the equation introduced by Bonner and Fisher for the chain of $S = 1/2$.[8] The parameters obtained by the simulation are $J = -3.0\,\text{cm}^{-1}$ and $g = 2.15$, where J is the spin-coupling constant for the interaction between copper(II) ions through pyz and g is the g factor for the copper(II) ion. The J value is similar to those for the pyz-bridged polymeric complexes consisting of copper(II) monomeric units.[9]

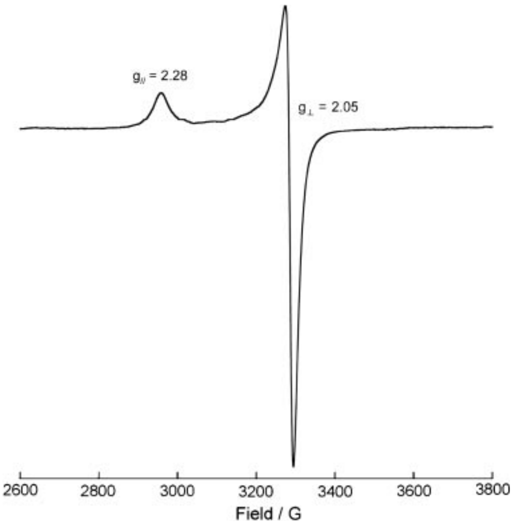

Figure 4. EPR spectrum of **2** at room temperature in the solid.

The EPR spectrum (Figure 4) of **2** at room temperature in the solid state exhibits signals at $g_\perp = 2.05$ and $g_{//} = 2.28$, which corresponds to the essentially isolated $S = 1/2$ magnetic centers. The mean value defined by $(2g_\perp + g_{//})/3$ is 2.13, which is close to the g value (2.15) obtained from magnetic susceptibility data. The anisotropic spectral feature is basically the same even if the temperature is cooled down to 4 K. This implies that uncoupled spins still exist at 4 K, being consistent with the fact that the susceptibility does not die away at 0 K as has been described by the Bonnor and Fisher's equation for the equally spaced copper(II) ($S = 1/2$) chain system.[8]

The complex **2** does not show the N_2-adsorbing properties in contrary to the case of the polymer complex of copper(II) benzoate dinuclear units bridged by pyrazine $[Cu_2(O_2CC_6H_5)_4(pyz)]_n$ (**1**). In the crystal of **2**, the distances between the carbon atoms belonging to the different neighboring polymer chains are smaller than 4.725(1) Å, which indicates that it has only small open spaces less than ca. 1.3 Å, when taking the van der Waals radii (1.7 Å) for the C–H bond into the consideration. This may be the reason that **2** does not adsorb N_2 gas; **1** crystallized as the one with the reaction solvent molecules (**1**$\cdot 2n CH_3CN$) and adsorbs three N_2 molecules per $[Cu_2(O_2CC_6H_5)_4(pyz)]$ unit, corresponding to the space ($4 \times 5 \times 11$ Å^3) occupied by the solvent molecules in the crystal of **1**$\cdot 2n CH_3CN$.[3]

Experimental

Copper(II) pentafluorobenzoate ($[Cu_2(O_2CC_6F_5)_4]$) was prepared by stirring the solution of copper(II) acetate monohydrate (0.50 g, 1.3 mmol) and pentafluorobenzoic acid (2.4 g, 11 mmol) in ethyl acetate (100 mL) at room temperature, the resultant precipitate being filtered, washed with small amount of ethyl acetate, and dried by heating under vaccum.[10] Pyrazine (pyz) was obtained from Wako Chem. Co.

Synthesis of Complex 2. To a methanolic solution (15 mL) of copper(II) pentafluorobenzoate (0.15 g, 0.15 mmol) was added a methanolic solution (15 mL) of pyz (30 mg, 0.38 mmol). The resultant solution was stirred overnight to give a precipitation,

Table 1. Crystal Data and Data Collection Details of **2**

Formula	$C_{18}H_4CuF_{10}N_2O_4$
Formula weight	565.77
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	4.7247(13)
b/Å	12.876(4)
c/Å	15.031(4)
α/°	89.488(5)
β/°	88.841(6)
γ/°	87.335(5)
V/Å^3	913.2(4)
Z	2
D_{calcd}/g cm^{-3}	2.058
μ(Mo Kα)/mm^{-1}	1.330
Crystal size/mm^3	0.22 × 0.10 × 0.06
2θ range/°	2.72–57.00
Total No. of reflections measured	5635
No. of unique reflections with $I \geq 2\sigma(I)$	4050
$R1$, $wR2$ $[I > 2\sigma(I)]$[a]	0.0706, 0.1744
Goodness-of-fit on F^2	1.122

a) $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

which was dissolved by adding methanol. Blue single-crystals were formed in the solution after leaving it for several days at room temperature. The crystals were collected by suction and washed with methanol. The yield was 22.6% based on $[Cu_2(O_2CC_6F_5)_4]$. Anal. Found: C, 38.09; H, 1.42; N, 4.98%. Calcd for $C_{18}H_4CuF_{10}N_2O_4$: C, 38.21; H, 0.71; N, 4.95%.

Measurements. Elemental analysis for carbon, hydrogen, and nitrogen was carried out using a Yanaco CHN CORDER MT-5. The temperature dependence of the magnetic susceptibility was measured with a Quantum Design MPMS-5S SQUID susceptometer operating magnetic field of 0.5 T over a temperature range of 4.5–300 K. The susceptibility was corrected for the diamagnetism of the constituent atoms using Pascal's constants.[11] The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per copper atom. EPR spectrum was recorded on a Bruker E500 spectrometer. N_2-Adsorption isotherms were measured by a Quantachrome Autosorb 1-C at the boiling temperature of liquid nitrogen. Prior to the adsorption, the samples were outgassed at 298 K for 2 h.

X-ray Crystal Structure Analysis. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation at 123 K. Crystal data and selected bond distances and angles are given in Tables 1 and 2, respectively.

The structure was solved by direct methods using SHELXS-97[12] and refined by full-matrix least-squares on F^2 using SHELXL-97.[13] The hydrogen atoms were inserted at their calculated positions and fixed there. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-725516. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Selected Bond Distances/Å and Angles/° for **2** with Their Estimated Standard Deviations in Parentheses[a)]

Cu1–O1	1.939(3)	O1–C7	1.268(6)
Cu1–O3	1.934(3)	O2–C7	1.217(6)
Cu1–N1	2.035(4)	O3–C14	1.272(6)
Cu1–N2	2.005(4)	O4–C14	1.211(6)
Cu1–O2‴	2.199(3)		
O1–Cu1–O3	173.9(1)	N2–Cu1–N1	172.6(2)
O1–Cu1–N2	96.2(2)	O1–Cu1–O2‴	93.8(1)
O3–Cu1–N2	83.6(2)	O3–Cu1–O2‴	92.3(1)
O1–Cu1–N1	90.2(2)	N1–Cu1–O2‴	88.3(1)
O3–Cu1–N1	89.6(2)	N2–Cu1–O2‴	94.9(2)

a) Triple primes refer to the equivalent position ($x + 1$, y, z).

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