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Synthesis, Crystal Structure, and Adsorption Properties of Werner-type Cu(II) Complex [Cu(CF_3SO_3)$_2$(4-methylpyridine)$_4$]

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A Werner-type Cu(II) complex, α-[Cu(CF_3SO_3)$_2$(4-mepy)$_4$] (α-**PAC-1-CF_3SO_3**, PAC: porous assembly of coordination complex and 4-mepy: 4-methylpyridine), was synthesized, crystallographically characterized, and its adsorption properties were compared with those of the derivative α-[Cu(PF_6)$_2$(4-mepy)$_4$] (α-**PAC-1-PF_6**).

Porous assemblies of coordination complexes (PACs), which are formed by the assembly of discrete coordination complexes without internal spaces via intermolecular interactions (van der Waals, electrostatic, and hydrogen-bonding interactions) that are weaker than coordination bonds,[1–3] have the potential to provide the following unique host–guest features: (i) diversity in assembled structures with guest molecules, resulting from weak and flexible intermolecular interactions;[1h,1i] (ii) formation of host frameworks consisting of two or more different discrete coordination complexes;[1j] (iii) facile fabrication of films because of high solubility;[1k,1l] and (iv) polymorphism without guest molecules, which is controlled by a kind of preadsorbed guests.[1c,1i] These characteristics of PACs could supply not only fundamental information about their pores but also unprecedented, useful porous functions.

The Werner-type complex [Ni(NCS)$_2$(4-mepy)$_4$] (4-mepy: 4-methylpyridine) and its derivatives are well known as examples of PACs; their preparation and guest-inclusion abilities were first reported in 1957.[1a] Among them, [Ni(NCS)$_2$(4-mepy)$_4$] has been thoroughly studied because of its interesting guest-inclusion properties derived from pseudopolymorphism, such as a dense α-form, and guest-including β- and γ-forms. The α-form has no space for including guest molecules because of its dense packing structure, whereas the β- and γ-forms are channel-type and layer-type clathrates, respectively.[1i] In particular, this complex easily affords an empty β-form that adsorbs several gases with type I isotherms.

We have recently found that a Cu(II)-based PAC, [Cu(PF_6)$_2$(4-mepy)$_4$] (**PAC-1-PF_6**), which is a quasi-Werner-type metal complex, has interesting guest-recognition abilities.[4] The dense α-form, α-**PAC-1-PF_6**, has inorganic PF_6^- anions covered with only fluorine atoms in the framework, and it adsorbs CO_2 gas with structural transformations; this is the first example of gas-adsorption properties in the dense α-form. On the other hand, when α-**PAC-1-PF_6** is recrystallized from acetone/*n*-hexane and 2-butanone/*n*-hexane, some of the weakly coordinated PF_6^- anions are easily released from the axial sites and Lewis-base guests (acetone and 2-butanone) attach to these sites instead, forming the guest-including γ-form, γ-{[Cu(PF_6)$_2$(4-mepy)$_4$][Cu(PF_6)(4-mepy)$_4$(acetone)]·PF_6·4acetone} (γ-**PAC-1-PF_6**$\supset$2.5acetone), γ-{[Cu(PF_6)$_2$(4-mepy)$_4$][Cu(PF_6)(4-mepy)$_4$(2-butanone)]·PF_6·3.5(2-butanone)} (γ-**PAC-1-PF_6**$\supset$2.25(2-butanone)). The prefix "quasi-" derives from such labile axial bonds. These unprecedented phenomena have never been observed in any other Werner-type metal complexes. These results clearly indicate that Cu(II)-based PACs are useful for the construction of porous materials with multiguest-recognition properties.

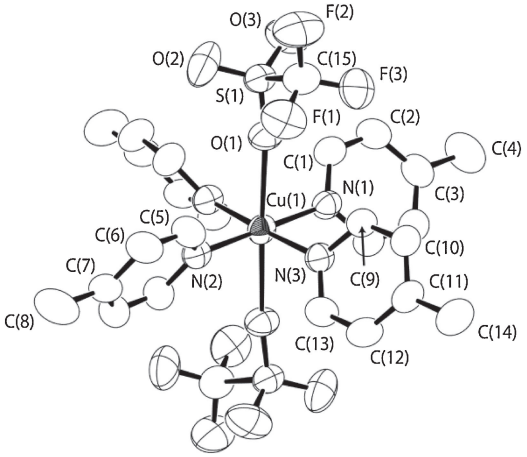

Figure 1. ORTEP drawing around the Cu(II) center in α-**PAC-1-CF_3SO_3**. The hydrogen atoms are omitted for clarity.

In this letter, we report the synthesis, crystal structure, and adsorption properties of a derivative of α-**PAC-1-PF_6**, α-[Cu(CF_3SO_3)$_2$(4-mepy)$_4$] (α-**PAC-1-CF_3SO_3**), to investigate the effect of inorganic anions on the adsorption properties. The introduction of $CF_3SO_3^-$ anions enhanced the intermolecular interactions through the oxygen atoms of the anions and inhibited gas adsorption with structural changes.

α-**PAC-1-CF_3SO_3** was synthesized as follows: Cu(CF_3SO_3)$_2$ (362 mg, 1.0 mmol) and 4-mepy (466 mg, 5.0 mmol) were dissolved in acetone (20 mL) and excess *n*-hexane was added to the acetone solution, forming blue microcrystals of α-**PAC-1-CF_3SO_3**. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from $CHCl_3$/*n*-hexane.

The crystal structure of α-**PAC-1-CF_3SO_3** was determined by single-crystal X-ray diffraction analysis at 173 K.[5] Figure 1 shows the ORTEP view around the Cu(II) ion. The Cu(II) ion has an elongated octahedral environment with four 4-mepy molecules in the equatorial plane and two $CF_3SO_3^-$ anions at the axial sites. The Cu–O bond distance of 2.468(2) Å is considerably longer than the equatorial Cu–N values (2.014(4)–2.025(3) Å), indicating that the Jahn–Teller axis is formed along the O–Cu–O direction. The axial bonds in α-**PAC-1-CF_3SO_3** are shorter than those in α-**PAC-1-PF_6** (Cu–F bond dis-

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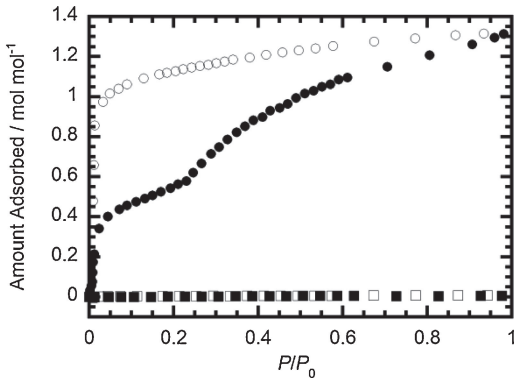

Figure 2. Adsorption (filled symbols) and desorption (open symbols) isotherms for CO_2 at 195 K on **α-PAC-1-CF_3SO_3** (squares) and **α-PAC-1-PF_6** (circles).

tances = 2.478(2), 2.528(2), 2.586(2), and 2.629(2) Å),[6] which is a reasonable result because $CF_3SO_3^-$ anions have stronger Lewis basicity than PF_6^- anions.[7] Each mononuclear Cu(II) complex is densely packed, resulting in the assembled structure having no pores (accessible void space calculated using the PLATON program is 0%).[8]

The adsorption and desorption isotherms for CO_2 at 195 K on **α-PAC-1-PF_6** and **α-PAC-1-CF_3SO_3** were measured to compare the effects of inorganic anions. As shown in Figure 2, **α-PAC-1-PF_6** shows CO_2 adsorption. Because **α-PAC-1-PF_6** possesses no vacant space, the observed adsorption behavior with large hysteresis should be associated with gate-opening processes, in which adsorption occurs with structural transformations.[4] On the other hand, **α-PAC-1-CF_3SO_3** scarcely adsorbs CO_2 gas over the entire pressure range. In general, the gate-opening pressure depends on the strength of host–host and/or host–guest interactions. Weak host–host and strong host–guest interactions decrease the gate-opening pressure. First, host–host interactions were checked from the viewpoint of (1) the type of intermolecular interactions, and (2) their distances and angles. In **α-PAC-1-CF_3SO_3**, there are weak intermolecular hydrogen bonds between noncoordinated oxygen atoms of $CF_3SO_3^-$ anions and hydrogen atoms of 4-mepy ligands (O···C = 3.33, 3.40, and 3.42 Å, Figure 3). **α-PAC-1-PF_6** bears slightly shorter intermolecular contacts between noncoordinated fluorine atoms of PF_6^- anions and hydrogen atoms of 4-mepy ligands (F···C = 3.19–3.32 Å, see Supporting Information).[14] However, considering the van der Waals radii of oxygen and fluorine atoms (1.52 and 1.47 Å, respectively) and the C–H(pyridyl)···O(F) angles (see Table S2),[9,14] the slight difference observed in the intermolecular distances may not reflect a difference in the strength of the intermolecular interactions. On the other hand, as confirmed by DFT calculations for α-$[Cu(A)_2(py)_4]$ (**α-PAC-2-A**, A = PF_6 and CF_3SO_3, py: pyridine), **α-PAC-2-PF_6** bears an almost uniform negative potential over all the surface fluorine atoms of PF_6^-. In contrast, the $CF_3SO_3^-$ anions in **α-PAC-2-CF_3SO_3** have negative potentials on their oxygen atoms; their magnitude is higher than that on the fluorine atoms in **α-PAC-2-PF_6**.[10] Moreover, a fluorine atom, with a small polarizability, weakens intermolecular interactions. These results imply that host–host interactions (including acid–base and van der Waals interactions) in **α-PAC-1-PF_6** are weaker than those in **α-PAC-1-CF_3SO_3**. Next, host–guest interactions were compared. It is known that a CO_2 molecule interacts with these fluorinated anions via weak acid–base interactions in ionic liquids.[11] As mentioned above, the Lewis basicity of $CF_3SO_3^-$ anions is stronger than that of PF_6^- ones. Furthermore, the results of DFT and MP2 calculations show that the binding energy in the $CF_3SO_3^-$–CO_2 complex is slightly higher than that in PF_6^-–CO_2.[12] Hence, the host–guest interaction between the $[Cu(PF_6)_2(4\text{-mepy})_4]$ unit and CO_2 is probably weaker than that between the $[Cu(CF_3SO_3)_2(4\text{-mepy})_4]$ unit and CO_2. This comparison of host–host and host–guest interactions indicates that host–host interactions predominantly influence gate-opening adsorptions in these PACs.

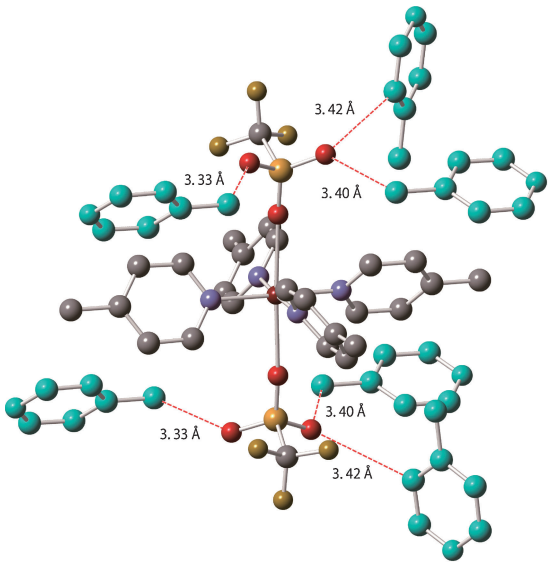

Figure 3. View of the intermolecular interactions in **α-PAC-1-CF_3SO_3**, in which the red dashed lines indicate hydrogen bonds. The 4-mepy molecules of other mononuclear complexes are represented in sky blue. The hydrogen atoms are omitted for clarity.

A similar tendency has been observed in the two-dimensional Cu(II) porous coordination polymers (PCPs) $[Cu(A)_2(4,4'\text{-bpy})_2]_n$ (A = PF_6 and CF_3SO_3, 4,4′-bpy: 4,4′-bipyridine).[10,13] Both PCPs have similar two-dimensional frameworks with weakly coordinated inorganic anions, PF_6^- and $CF_3SO_3^-$, at the axial sites and show two kinds of adsorption events: micropore filling in open voids and gate-opening adsorption with expansion of the layers. The gate-opening pressures for $[Cu(PF_6)_2(4,4'\text{-bpy})_2]_n$ are considerably lower than those for $[Cu(CF_3SO_3)_2(4,4'\text{-bpy})_2]_n$. These results can also be explained by the difference in the strengths of host–host interactions.

In conclusion, we achieved the synthesis and crystallographic characterization of the Werner-type Cu(II)-based PAC α-$[Cu(CF_3SO_3)_2(4\text{-mepy})_4]$ (**α-PAC-1-CF_3SO_3**). The weak hydrogen-bonding interactions between the oxygen atoms of the $CF_3SO_3^-$ anions and the hydrogen atoms of the 4-mepy ligands make the assembled structure rigid, resulting in the suppression of CO_2 adsorption with structural transformations. This finding could help in designing flexible PCPs that show gate-opening adsorption. In addition, although **α-PAC-1-CF_3SO_3** did not

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show porosity for CO_2 gas, other organic vapors, such as alcohols, ketones, and benzene, may adsorb on **α-PAC-1-CF_3SO_3** with structural transformations.[4] Further work is therefore in progress to isolate the guest-including **β-** and **γ-PAC-1-CF_3SO_3** and check the vapor-adsorption properties of **α-PAC-1-CF_3SO_3**.

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5 Crystallographic data of **α-PAC-1-CF_3SO_3**. $C_{26}H_{28}CuF_6N_4O_6S_2$, $M_r = 734.19$, Orthorhombic, *Pbcn* (#60), $a = 10.9762(5)$ Å, $b = 17.8294(10)$ Å, $c = 16.5322(8)$ Å, $V = 3235.4(3)$ Å^3, $T = 173$ K, $Z = 4$, $D_{calcd} = 1.507$ g cm^{-3}, $F_{000} = 1500.00$, $\lambda = 0.71075$ Å, μ(Mo Kα) = 8.830 cm^{-1}, 29498 measured reflections, 3687 unique ($R_{int} = 0.0312$). $R_1 = 0.0440$ ($I > 2\sigma(I)$) and $wR_2 = 0.1597$ (all data) with GOF = 1.078. CCDC-877849. Selected bond distances and angles are listed in Table S1.[14]

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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