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Rational Synthesis of a Porous Copper(II) Coordination Polymer Bridged by Weak Lewis-Base Inorganic Monoanions Using an Anion-Mixing Method

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Supporting Information

ABSTRACT: The use of divalent Cu^{II} ions and an anion-mixing method led to the rational construction of a porous coordination polymer bridged by weak Lewis-base inorganic $CF_3SO_3^-$ monoanions.

Coordination polymers composed of transition-metal ions and bridging ligands have attracted much attention as functional materials because they show interesting porous, magnetic, conductive, optical, dielectric, and dynamic properties and combined properties that can be finely tuned by selecting and assembling appropriate building units.[1] Organic bridging ligands such as benzenedicarboxylate, 4,4′-bipyridine, and their derivatives have often been used to fabricate infinite coordination frameworks. Inorganic dianions such as AO_4^{2-} (A = S, Mo, and Cr) and XF_6^{2-} (X = Si and Ge) and inorganic monoanions with a stronger Lewis basicity, such as N_3^-, NCS^-, Cl^-, Br^-, I^-, and CN^-, can act as small bridging ligands for a wide variety of metal ions.[2,3] Weaker Lewis-base inorganic monoanions such as PF_6^-, BF_4^-, and $CF_3SO_3^-$ are also useful building blocks as hydrogen-bonding sites, flexibilizers, and interaction sites for guest molecules.[4] For example, a positively charged carbon atom of CO_2 gas interacts with the negatively charged fluorine atom of the PF_6^- anion in the two-dimensional porous coordination framework $[Cu(PF_6)_2(4,4'\text{-bipyridine})_2]_n$, which causes highly selective CO_2 adsorption.[4b] However, it is not easy to deliberately make them coordinate to metal ions. In particular, examples of air-stable coordination polymers with divalent transition-metal ions and coordinated weak Lewis-base monoanions are rare. This is because (1) the coordination of weak Lewis-base monoanions is prohibited by the preferential coordination of relatively stronger Lewis-base solvents coexisting during reactions and (2) coordinated weak Lewis-base monoanions are easily replaced by atmospheric H_2O molecules with relatively stronger Lewis basicity. The divalent copper ion, Cu^{II}, is an exceptional case: a Cu^{II} ion has weak coordination sites at the axial positions because of a Jahn−Teller effect, which enables the intentional coordination of such weak Lewis-base inorganic monoanions via electrostatic interactions. Charged monoanions prevent neutral H_2O molecules from interacting with Cu^{II} centers, and tolerance for atmospheric H_2O molecules is enhanced by the combination of monoanions and Cu^{II} ions. Indeed, we and other groups have reported many examples with a weak coordination of such inorganic monoanions in copper(II) complexes.[4−6] In contrast, the bridging modes of such inorganic monoanions in copper(II) coordination polymers have been limited, and the development of a useful strategy to fabricate such coordination polymers is a challenging problem.[2a,7]

In this manuscript, we report the rational synthesis of a two-dimensional porous copper(II) coordination polymer, $\{[Cu(CF_3SO_3)(bpp)_2]\cdot PF_6\cdot\text{acetone}\}_n$ [**1**⊃acetone; bpp = 1,3-bis(4-pyridyl)propane], with bridged inorganic $CF_3SO_3^-$ monoanions. The bridged inorganic $CF_3SO_3^-$ monoanion structure in coordination polymers is very rare.[7d−f] The choice of a Cu^{II} ion as a metal source and the coexistence of two types of inorganic monoanions with different Lewis basicities is a key point in achieving the rational formation of bridged $CF_3SO_3^-$ monoanions.

1⊃acetone was obtained under the condition of the coexistence of $CF_3SO_3^-$ and PF_6^- monoanions. The crystal structure of **1**⊃acetone was determined by single-crystal X-ray diffraction (XRD) analysis at 173 K. Figure 1a shows the unit cell of **1**⊃acetone viewed along the *a* axis, in which the two-dimensional $[Cu(CF_3SO_3)(bpp)_2]_n$ layers are stacked, incorporating PF_6^- anions and acetone guests. The structure around the Cu^{II} center is shown in Figure 1b, in which the Cu^{II} center has an octahedral environment exhibiting a Jahn−Teller axial elongation with four bpp nitrogen atoms in the basal plane [Cu−N distance = 2.033(2) Å] and two $CF_3SO_3^-$ oxygen atoms at the axial sites [Cu−O distance = 2.714(4) Å]. There is only one crystallographically independent bpp molecule with a *TT* conformation.[8] The bpp ligands bridge the Cu^{II} centers with a Cu···Cu distance of ca. 12.5 Å to form one-dimensional doubly linked chains along the *a* axis, as illustrated in Figure 1c. Each one-dimensional chain is further linked by inorganic $CF_3SO_3^-$ anions with a Cu···Cu distance of ca. 7.8 Å, thereby forming two-dimensional layers (Figure 1c). Uncoordinated PF_6^- anions are intercalated between the layers and interact with the bpp ligands

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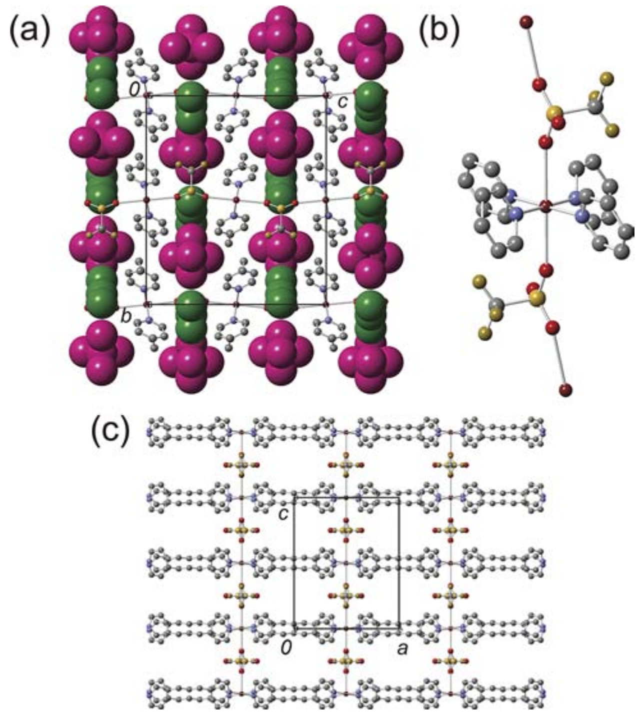

Figure 1. Crystal structure of **1**⊃acetone. (a) Unit cell viewed along the *a* axis (PF_6^- anions and acetone molecules are colored pink and green, respectively). (b) Coordination environment around the Cu^{II} center. (c) Two-dimensional layer structure projected along the *b* axis (PF_6^- anions and acetone molecules are omitted for clarity). In all figures, hydrogen atoms are omitted for clarity. Vermilion represents copper, blue for nitrogen, gray for carbon, red for oxygen, gold for fluorine, and orange for sulfur.

via weak hydrogen bonds (Figure S1 in the Supporting Information, SI). The guest acetone molecules are located inside two-dimensional layers and interact with coordinated $CF_3SO_3^-$ anions and uncoordinated PF_6^- anions via weak hydrogen bonds [C···O = 3.34(2) Å and C···F = 3.11 (2) Å; see Figure S2 in the SI].[9]

The use of a Cu^{II} building block and an anion-mixing method is essential to construct coordination polymers bridged by weak Lewis-base inorganic monoanions. As mentioned above, a Cu^{II} ion has the ability to capture weak Lewis-base anions at its axial sites via electrostatic interactions.[4−7] In the case of a single monoanion system, the Cu^{II} cation tends to form monodentate coordination of monoanions as a result of the charge balance and coordination number. If there exist two types of inorganic monoanions with different Lewis basicities (monoanions B_s and B_w with relatively strong and weak Lewis basicities, respectively), the monoanion B_w has difficulty participating in a competition for coordination to the Cu^{II} ion. Hence, the mixing of monoanions B_s and B_w with different Lewis basicities increases the probability of selective bidentate (bridged) coordination of relatively strong Lewis-base inorganic monoanions B_s. In this study, a PF_6^- anion was selected as a relatively weak Lewis base B_w. The Lewis basicity of this anion is very weak and comparable to that of a tetraphenylborate anion.[10] To confirm the universality of our synthetic strategy, we synthesized another copper(II) coordination polymer with bridged inorganic monoanions, $\{[Cu(CH_3SO_3)(pyridine)_4]\cdot PF_6\}_n$ (**2**), by mixing $CH_3SO_3^-$ and PF_6^- monoanions in a 1:1 ratio. Here, pyridine was selected as another type of organic ligand that coordinates to a metal center in a monodentate fashion. In **2**, the Cu^{II} center has an elongated octahedral environment with four pyridine nitrogen atoms in the basal plane [Cu−N distance = 2.027(4)−2.050(4) Å] and two $CH_3SO_3^-$ anions at the axial sites [Cu−O distance = 2.413(4) and 2.469(4) Å]. The $CH_3SO_3^-$ anions bridge the Cu^{II} centers to form a one-dimensional chain with a Cu···Cu distance of ca. 6.8 Å (Figure S3 in the SI). The weaker Lewis-base PF_6^- anions are not coordinated, as expected. The phase purity for **1**⊃acetone and **2** was confirmed by XRD patterns of microcrystalline samples (Figures S4 and S5 in the SI). Control experiments were also performed (see the SI), in which monoanion-bridged coordination polymers were not formed in the single monoanion system. Hence, we can conclude that this anion-mixing method is an efficient technique for constructing coordination polymers bridged by weak Lewis-base inorganic monoanions.

We succeeded in determining the crystal structure of a desolvated single crystal of **1** obtained by heating **1**⊃acetone at 413 K under vacuum. Desolvated **1** maintains its framework and single crystallinity after the removal of acetone molecules. As shown in Figure S6 in the SI, the one-dimensional channels are formed along the *c* axis. The channels have a unique form, comprising an alternating arrangement of two types of large (6.7 × 6.4 Å^2) and narrow (4.9 × 2.6 Å^2) tubes. The space with large apertures is adequate to accommodate an acetone molecule. The accessible void space calculated by the *PLATON* program is 20%.[11] The calculated specific pore volume is 0.14 $cm^3\cdot g^{-1}$. The thermal gravimetric (TG) curve of **1**⊃acetone (Figure S8 in the SI) shows that the acetone guest molecules are retained stably in the channels up to a temperature of 130 °C and then are completely ejected by 200 °C (obsd 7.4%; calcd 7.1%). Such a high retention temperature is due to an entrance-blocking effect at narrow pore apertures. The desolvated **1** again adsorbed guest acetone molecules with single crystallinity, which was confirmed by a single-crystal XRD analysis (Table S1 in the SI).

To evaluate the porous properties of **1**, we measured adsorption/desorption isotherms for several gases and vapors. **1** showed a rapid increase in the adsorbed amount of CO_2 gas (Lennard-Jones parameter = 2.98 Å)[12] at 195 K and low pressure (Figure 2), indicating a permanent porosity, which was also confirmed by reversible H_2 adsorption at 77 K (Figure S9 in the SI). The saturated adsorbed amount of CO_2 is 50 $cm^3(STP)\cdot g^{-1}$, which corresponds to roughly 1.7 CO_2 molecules per formula

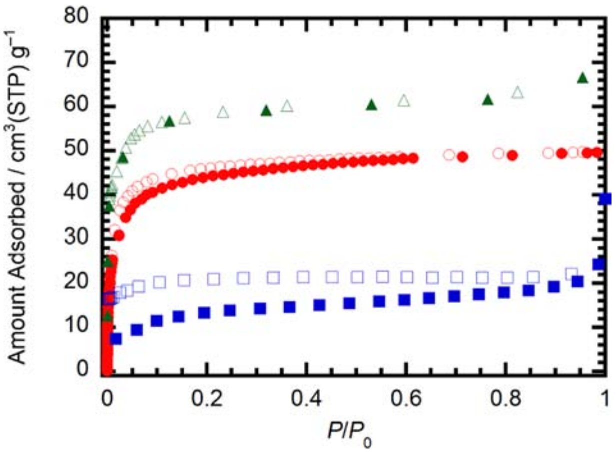

Figure 2. Adsorption (filled symbols) and desorption (open symbols) isotherms for CO_2 (red, 195 K), N_2 (blue, 77 K), and O_2 (green, 77 K) in **1**.

unit. The Brunauer−Emmett−Teller and Langmuir specific surface areas were found to be 226 and 283 $m^2 \cdot g^{-1}$, respectively. The micropore volume calculated from the CO_2 adsorption data (0.062 $cm^3 \cdot g^{-1}$) is considerably smaller than that calculated from the crystal structure of **1**. This may be because CO_2, with its large quadrupole moment and polarizability, interacts with small and permanent pores, preventing deep diffusion into the pores. The isosteric heat of CO_2 adsorption, Q_{st}, was calculated to be an average of 37 $kJ \cdot mol^{-1}$, which is caused by small pores and moderate acid−base interaction between CO_2 and inorganic anions. Although the N_2 and O_2 adsorption isotherms also showed type I curves (Figure 2), the specific micropore volumes calculated from their adsorption data are considerably different from each other (0.024 $cm^3 \cdot g^{-1}$ for N_2 and 0.072 $cm^3 \cdot g^{-1}$ for O_2). The larger N_2 molecules (Lennard-Jones parameters = 3.32 Å)[12] hardly diffuse through the permanent one-dimensional channels because of a blocking effect at narrow pore apertures. Despite O_2 having a larger size than CO_2 (Lennard-Jones parameter = 3.11 Å),[12] the micropore volume for O_2 is slightly higher than that for CO_2. The O_2 molecule has a smaller quadrupole moment and polarizability than CO_2, which causes relatively easy diffusion deep into the pores.

We investigated the effect of large and narrow pores from the adsorption and desorption isotherms for vapors (Figure S12 in the SI). For acetone, the isotherm showed a type I curve. The saturated adsorption amount is ca. 0.5 $mol \cdot mol^{-1}$, which is lower than the value of 1.0 $mol \cdot mol^{-1}$ calculated from the crystal structure of **1**⊃acetone. As is evident from the results of the crystal structure and the TG curve, acetone guests stably remain in one-dimensional channels because of the presence of narrow channel apertures. Therefore, acetone guests do not diffuse deeply into the one-dimensional channels. **1** also adsorbed MeCN and MeOH. Their saturated adsorbed amounts are different from each other. The MeCN molecule is in the shape of a rod; that is, it has a small minimum cross-sectional area compared with acetone. Thus, MeCN guests can diffuse deep into the one-dimensional channels. The MeOH molecule has a proton-donating OH group. Because this OH group interacts with inorganic anions via hydrogen bonds, the diffusion of MeOH into the one-dimensional channels is slow.

In conclusion, we succeeded in the rational synthesis of a two-dimensional copper(II) coordination polymer **1** with rare $CF_3SO_3^-$ bridges. The realization of such bridges is related to the use of a Cu^{II} building block capable of capturing weak Lewis-base anions at its axial sites and to the mixing of two types of inorganic monoanions with different Lewis basicities. Further work is in progress to fabricate novel coordination polymers bridged by weak Lewis-base inorganic monoanions that show interesting porous properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental details, crystal structures, XRD patterns, ATR-IR spectra, TG-DTA, and adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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