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Synthesis and Crystal Structure of a One-dimensional Cu(II) Coordination Polymer Bridged by Inorganic $CH_3SO_3^-$ Anions Using Werner-type Cu(II) Complexes as Building Blocks

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The reaction of $[Cu(PF_6)_2(py)_4]$ (py: pyridine) with $[Cu(CH_3SO_3)_2(py)_4]$, both of which are Werner-type Cu(II) complexes, in a MeOH solution led to the formation of a one-dimensional framework composed of $[–\{Cu(1)_2(MeO)_2\}–Cu(2)–Cu(3)–Cu(3)–Cu(2)–]$ repeating units bridged by inorganic $CH_3SO_3^-$ anions.

Coordination polymers composed of 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 proper 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 anions with a strong Lewis basicity such as N_3^-, NCS^-, Cl^-, Br^-, I^-, and CN^- can also act as small bridging ligands for a wide variety of metal ions. On the other hand, it is not easy to purposely bridge metal ions by moderate or weak Lewis base inorganic anions such as PF_6^-, BF_4^-, $CF_3SO_3^-$, $CH_3SO_3^-$, and ClO_4^-. 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 moderate or weak Lewis base inorganic anions via electrostatic interactions. Indeed, many examples with a weak coordination of such inorganic anions have been reported in Cu(II) complexes.[2] Furthermore, bridging modes of such inorganic anions in Cu(II) coordination polymers have also been observed, although the numbers are not so large.[3]

In this manuscript, we report the synthesis and crystal structure of a one-dimensional Cu(II) coordination polymer, $\{[Cu_3(CH_3SO_3)_3(MeO)(py)_9]\cdot 2PF_6\cdot MeOH\}_n$ (**1**, py: pyridine), bridged by inorganic $CH_3SO_3^-$ anions. The bridged inorganic $CH_3SO_3^-$ anion structure in coordination polymers is very rare.[4] The choice of a Cu(II) ion as a metal source is a key point in achieving the formation of bridged $CH_3SO_3^-$ anions.

1 was synthesized as follows: Werner-type Cu(II) complexes of $[Cu(PF_6)_2(py)_4]$[5] (67 mg, 0.1 mmol) and $[Cu(CH_3SO_3)_2(py)_4]$[6] (57 mg, 0.1 mmol) were dissolved in MeOH (10 mL) and excess diethyl ether was added to the MeOH solution. Then, the MeOH/diethyl ether solution was allowed to stand in a refrigerator. After a few hours, blue prismatic crystals of **1** and needle crystals, which have not yet been characterized, were obtained.

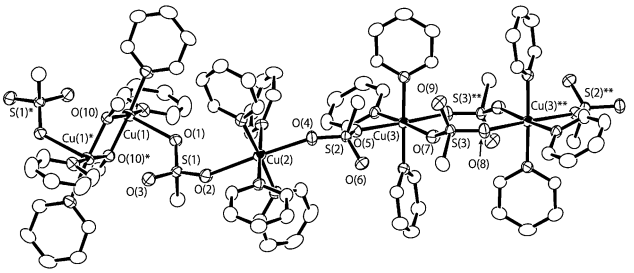

Figure 1. ORTEP drawing of the one-dimensional chain of **1** (50% probability; symmetry operations: $^*-x+1,\ -y+1,\ -z+1$, $^{**}-x,\ -y,\ -z$). The hydrogen atoms are omitted for clarity.

The crystal structure of **1** was determined by single-crystal X-ray diffraction analysis at 173 K.[7] Figure 1 shows the ORTEP view around the Cu(II) ions. In the crystal, there are three crystallographically independent Cu(II) ions bridged by inorganic $CH_3SO_3^-$ or organic MeO^- anions. Cu(1) has a square-pyramidal environment with two py molecules and two MeO^- anions in the equatorial plane and one $CH_3SO_3^-$ anion at an axial site. The Cu–O ($CH_3SO_3^-$) bond distance of 2.409(3) Å is considerably longer than the equatorial Cu–N (py) and Cu–O (MeO^-) distances (1.919(3)–2.011(3) Å), indicative of a Jahn–Teller effect. The remaining axial site is occupied by an oxygen atom of the $CH_3SO_3^-$ anion (Cu···O distance = 2.829(3) Å) bridging between Cu(1) and Cu(2). Two MeO^- anions bridge two Cu(1) ions to form the dinuclear core of $\{Cu_2(MeO)_2\}$, which has been seen in a large number of related Cu(II) complexes.[8] Cu(2) forms an elongated octahedral center with four py molecules in the basal plane and two $CH_3SO_3^-$ anions (Cu(2)–O(2) = 2.506(3) and Cu(2)–O(4) = 2.377(3) Å) at the axial sites. This coordination environment is similar to that of the starting material, $[Cu(CH_3SO_3)_2(py)_4]$. Cu(3) also has an elongated octahedral environment with three py molecules and one $CH_3SO_3^-$ anion (Cu(3)–O(7) = 2.000(3) Å) in the equatorial plane and two $CH_3SO_3^-$ anions (Cu(3)–O(5) = 2.451(3) and Cu(3)–O(8)** = 2.371(3) Å, symmetry operation: $^{**}-x,\ -y,\ -z$) at the axial sites. We found three crystallographically independent $CH_3SO_3^-$ anions. The first one bridges the Cu(1) and Cu(2) ions from the axial sites. The second one links the Cu(2) and Cu(3) ions from the axial sites. In contrast, the third one connects two Cu(3) ions from both axial and equatorial sites, as shown in Figure 1. As a result, the one-dimensional coordination framework composed of $[–\{Cu(1)_2(MeO)_2\}–Cu(2)–Cu(3)–Cu(3)–Cu(2)–]$ repeating units bridged by inorganic $CH_3SO_3^-$ anions is formed along the [111] direction. The MeOH molecules and PF_6^- anions are incorporated between the one-dimensional frameworks without significant intermolecular interactions.

The construction of **1** with the complicated one-dimensional framework cannot be interpreted as a simple junction of the two starting materials of $[Cu(PF_6)_2(py)_4]$ and $[Cu(CH_3SO_3)_2(py)_4]$. It is considered that some intermediate compounds are formed

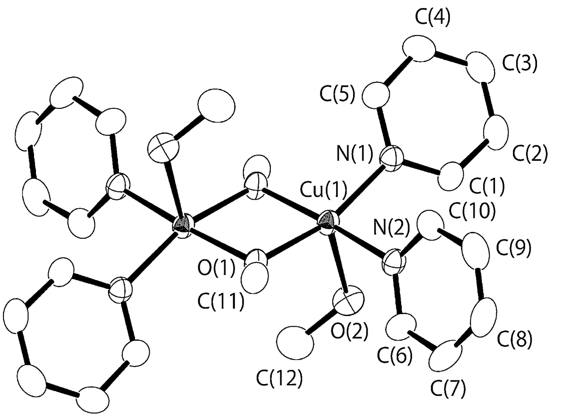

Figure 2. ORTEP drawing of the Cu_2 dimer of **2** (50% probability). The hydrogen atoms are omitted for clarity.

in a MeOH solution. One of the intermediate compounds, $\{[Cu_2(MeO)_2(py)_4(MeOH)_2]\cdot 2PF_6\}$ (**2**), was successfully isolated from a hot MeOH solution containing only $[Cu(PF_6)_2(py)_4]$.[9] In this reaction, two starting $[Cu(PF_6)_2(py)_4]$ units dimerize with the removal of weakly coordinated PF_6^- anions and some py ligands and with an attack by MeOH molecules and MeO^- anions. The dinuclear structure of **2** is shown in Figure 2.[10] Each Cu atom shows a square-pyramidal coordination, with the basal plane formed by two N atoms of py ($Cu–N = 2.000(2)$ and $2.005(3)$ Å) and two O atoms of MeO^- ($Cu–O = 1.931(2)$ and $1.935(2)$ Å) and one axial MeOH molecule ($Cu–O = 2.386(3)$ Å). The bond distances and angles within the basal plane are close to those in **1** and $[Cu_2(MeO)_2(ClO_4)_2(py)_4]$, which has a similar dinuclear structure except for the axial ligands.[8a,11] To compensate the charge balance, there are coordination-free PF_6^- anions in **2**.

Here, we discuss the formation mechanism of **2**. Because the Lewis basicity of PF_6^- anions is very weak, the Werner-type Cu(II) complex $[Cu(PF_6)_2(py)_4]$ is open to attack by other Lewis base molecules after the removal of PF_6^- anions.[2a,12] The coordinated py molecules also tend to be released from the Cu(II) center, which may be related to a deprotonation of MeOH molecules.[13] These two factors lead to a construction of **2** with bridged MeO^- anions from a MeOH solution containing $[Cu(PF_6)_2(py)_4]$. Hence, it seems that **2** derived from $[Cu(PF_6)_2(py)_4]$ is one of the intermediates in the formation of **1**. Other intermediates are now under investigation.

In conclusion, we succeeded in the synthesis and crystallographic characterization of the one-dimensional Cu(II) coordination polymer **1** with rare $CH_3SO_3^-$ bridges. The realization of such bridges is related to the use of a Cu(II) building block capable of capturing not-so-strong Lewis base anions at its axial sites. Further work is in progress to fabricate novel coordination polymers bridged by moderate or weak Lewis base inorganic anions that show unprecedented porous and magnetic properties.

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7 Crystallographic data of **1**. $C_{50}H_{61}Cu_3F_{12}N_9O_{11}P_2S_3$, $M_r = 1540.83$, triclinic, $P\bar{1}$ (#2), $a = 13.4391(5)$ Å, $b = 15.4390(5)$ Å, $c = 16.5396(5)$ Å, $\alpha = 84.3998(8)°$, $\beta = 68.9788(9)°$, $\gamma = 88.1873(9)°$, $V = 3188.04(17)$ Å^3, $T = 173$ K, $Z = 2$, $D_{calcd} = 1.605$ g cm^{-3}, $F_{000} = 1570.00$, $\lambda = 0.71075$ Å, $\mu(\text{Mo K}\alpha) = 12.371$ cm^{-1}, 34010 measured reflections, 14305 unique ($R_{int} = 0.0300$). $R_1 = 0.0448$ ($I > 2\sigma(I)$) and $wR_2 = 0.1472$ (all data) with GOF = 1.072. CCDC-875560. Selected bond distances and angles are listed in Table S1.[14]

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9 The details of the synthetic procedure are shown in Supporting Information.[14]

10 Crystallographic data of **2**. $C_{12}H_{18}CuF_6N_2O_2P$, $M_r = 430.80$, triclinic, $P\bar{1}$ (#2), $a = 8.8865(6)$ Å, $b = 9.4359(5)$ Å, $c = 10.9830(7)$ Å, $\alpha = 71.639(2)°$, $\beta = 83.363(2)°$, $\gamma = 75.622(2)°$, $V = 845.98(9)$ Å^3, $T = 173$ K, $Z = 2$, $D_{calcd} = 1.691$ g cm^{-3}, $F_{000} = 436.00$, $\lambda = 0.71075$ Å, $\mu(\text{Mo K}\alpha) = 14.545$ cm^{-1}, 8321 measured reflections, 3843 unique ($R_{int} = 0.0206$). $R_1 = 0.0421$ ($I > 2\sigma(I)$) and $wR_2 = 0.1236$ (all data) with GOF = 1.089. CCDC-875561. Selected bond distances and angles are listed in Table S2.[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.