Title: Synthesis and Crystal Structure of a One-dimensional Cu(II) Coordination Polymer Bridged by Inorganic CH₃SO₃⁻ Anions Using Werner-type Cu(II) Complexes as Building Blocks

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Synthesis and Crystal Structure of a
One-dimensional Cu(II) Coordination Polymer Bridged by Inorganic CH$_3$SO$_3^-$ Anions Using
Werner-type Cu(II) Complexes as Building Blocks

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The reaction of [Cu(PF$_6$)$_2$(py)$_2$] (py = pyridine) with [Cu(CH$_3$SO$_3$)$_2$(MeO)$_2$], 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(II)(MeO)$_2$]–Cu(2)–Cu(3)–Cu(3)–Cu(2)–] repeating units bridged by inorganic CH$_3$SO$_3^-$ 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. Organic bridging ligands such as benzenedicarboxylate, 4,4'-bipyridine, and their derivatives have been often used to fabricate infinite coordination frameworks. Inorganic anions with a strong Lewis basicity such as N$_3^-$, NCS$^-$, CT$^-$, 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$_3$SO$_3^-$, CH$_3$SO$_3^-$, 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. Furthermore, bridging modes of such inorganic anions in Cu(II) coordination polymers have also been observed, although the numbers are not so large.

In this manuscript, we report the synthesis and crystal structure of a one-dimensional Cu(II) coordination polymer, [(Cu(CH$_3$SO$_3$)$_2$(MeO)(py)$_3$]$_2$PF$_6$·MeOH]$_n$ (1, py = pyridine), bridged by inorganic CH$_3$SO$_3^-$ anions. The bridged inorganic CH$_3$SO$_3^-$ anion structure in coordination polymers is very rare. The choice of a Cu(II) ion as a metal source is a key point in achieving the formation of bridged CH$_3$SO$_3^-$ anions.

1 was synthesized as follows: Werner-type Cu(II) complexes of [Cu(PF$_6$)$_2$(py)$_2$] (67 mg, 0.1 mmol) and [Cu(CH$_3$SO$_3$)$_2$(py)$_2$] (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, y + 1, z + 1. **x, y, z). The hydrogen atoms are omitted for clarity.

The crystal structure of 1 was determined by a single-crystal X-ray diffraction analysis at 173 K. 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$_3$SO$_3^-$ 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$_3$SO$_3^-$ anion at an axial site. The Cu–O (CH$_3$SO$_3^-$) 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$_3$SO$_3^-$ 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. Cu(2) forms an elongated octahedral center with four py molecules in the basal plane and two CH$_3$SO$_3^-$ 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$_3$SO$_3$)$_2$(py)$_3$]. Cu(3) also has an elongated octahedral environment with three py molecules and one CH$_3$SO$_3^-$ anion (Cu(3)–O(7) = 2.000(3) Å) in the equatorial plane and two CH$_3$SO$_3^-$ anions (Cu(3)–O(5) = 2.451(3) and Cu(3)–O(8) = 2.371(3) Å), symmetry operation: *x, y, z). We found three crystallographically independent CH$_3$SO$_3^-$ 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)Cu(2)Cu(3)] repeating units bridged by inorganic CH$_3$SO$_3^-$ 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)$_2$] and
[Cu(CH$_2$SO$_3$)$_2$(py)$_2$]. It is considered that some intermediate compounds are formed in a MeOH solution.
One of the intermediate compounds, [{Cu$_2$(MeO)$_2$(py)$_2$(MeOH)$_2$}PF$_6$] (2), was successfully isolated from a hot MeOH solution
containing only [Cu(PF$_6$)$_2$(py)$_2$]. In this reaction, two starting
[Cu(PF$_6$)$_2$(py)$_2$] 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. 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)$_2$], which has a similar
dinuclear structure except for the axial ligands. To
compensate the charge balance, there are coordination-free PF$_6^-$ anions in 2.

![Figure 2. ORTEP drawing of the Cu$_2$ dimer of 2 (50% probability). The hydrogen atoms are omitted for clarity.](image)

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)$_2$] is open to attack by other
Lewis-base molecules after the removal of PF$_6^-$ anions. The coordinated py molecules also tend to be released from
the Cu(II) center, which may be related to a deprotonation of
MeOH molecules. These two factors lead to a construction of 2 with bridged MeO$^-$ anions from a MeOH solution
containing [Cu(PF$_6$)$_2$(py)$_2$]. Hence, it seems that 2 derived from
[Cu(PF$_6$)$_2$(py)$_2$] 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$_2$SO$_3^-$ bridges.
The realization of such bridges is related to the use of a Cu(II)
bonding 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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Culture, Sports, Science, and Technology, Japan.

References and Notes

6 Crystallographic data of I. Cu$_2$H$_2$Cu$_2$F$_4$N$_2$O$_3$P$_2$S$_2$. M$_1$ = 1540.83, Triclinic, P$\overline{1}$ (–2), a = 13.4391(5) Å, b = 15.4390(5) Å, c = 16.5396(5) Å, α = 84.3998(8)º, β = 68.9788(9)º, γ = 88.1873º, V = 3188.04(17) Å$^3$, T = 173 K, Z = 2, D$_{calcd}$ = 1.605 g cm$^{-3}$, F$_{000}$ = 15700.00, λ = 0.1705 Å, μ(Mo Kα) = 12.371 cm$^{-1}$, 34010 measured reflections, 14305 unique (R$_{int}$ = 0.0300), R$_{1}$ = 0.0448 (I $> 2σ(I))$ and wR$_2 = 0.1472$ (all data) with CCDC 875560. Selected bond distances and angles are listed in Table S1.
8 The details of the synthetic procedure are shown in Supporting Information.
9 Crystallographic data of 2. C$_2$H$_2$Cu$_2$F$_4$N$_2$O$_3$.M$_2$. M$_1$ = 430.80, Triclinic, P$\overline{1}$ (–2), a = 8.8865(6) Å, b = 9.4359(5) Å, c = 10.9830(7) Å, α = 71.639(2)º, β = 83.363(2)º, γ = 75.622(2)º, V = 845.98(9) Å$^3$, T = 173 K, Z = 2, D$_{calcd}$ = 1.691 g cm$^{-3}$, F$_{000}$ = 436.00, λ = 0.71075 Å, μ(Mo Kα) = 14.545 cm$^{-1}$, 8321 measured reflections, 3843 unique (R$_{int}$ = 0.0206), R$_1$ = 0.0421 ($>$ 2σ(I)) and
$wR_2 = 0.1236$ (all data) with GOF = 1.089. CCDC-875561.

Selected bond distances and angles are listed in Table S2.\textsuperscript{14}


NOTE The diagram is acceptable in a colored form. Publication of the colored figures are free of charge.

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## Textual Information

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Synthesis and Crystal Structure of a One-dimensional Cu(II) Coordination Polymer Bridged by Inorganic CH$_3$SO$_3$⁻ Anions Using Werner-type Cu(II) Complexes as Building Blocks

**Authors’ Names**

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## Graphical Information

[Image of a diagram showing a one-dimensional Cu(II) coordination polymer bridged by inorganic CH$_3$SO$_3$⁻ anions using Werner-type Cu(II) complexes as building blocks]

\[
\text{[}\text{CH}_3\text{SO}_3\text{⁻[Cu(1)\text{MeO}_3]⁻CH}_3\text{SO}_3\text{⁻Cu(2)⁻CH}_3\text{SO}_3\text{⁻Cu(3)⁻(CH}_3\text{SO}_3\text{)}_2\text{⁻Cu(3)⁻CH}_3\text{SO}_3\text{⁻Cu(2)⁻]}\text{]}
\]