

Two New Cu(II) Coordination Polymers with 2D and 1D Frameworks that Show Reversible Structural Transformations Depending on the Present Solvents

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Two New Cu(II) Coordination Polymers with 2D and 1D Frameworks that Show Reversible Structural Transformations Depending on the Present Solvents

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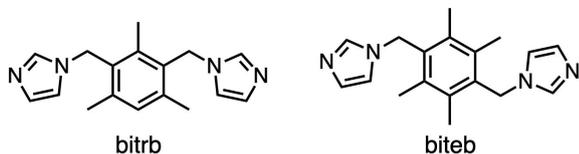
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Two new Cu^{II} coordination polymers with bis-imidazole ligand, bitrb, were synthesized and characterized. Reaction of CuSO₄·5H₂O with bitrb in a MeOH-H₂O mixed solution produced a 2D coordination polymer, while a similar reaction in a THF-MeOH mixed solution gave a 1D coordination polymer. The former compound converts to the latter in a THF-MeOH mixed solvent, while the reversed reaction proceeds in MeOH-H₂O media. Their crystal structures and the reversible transformations depending on the present solvents are described.

1 Keywords: bis-benzimidazole, Coordination polymer,
2 Reversible structural transformation.

1 For syntheses of multinuclear frameworks, flexible
2 bridging ligands can expand the obtainable structures
3 comparing to those constructed with rigid bridging ligands
4 such as 4,4'-bipyridine.^{1,2} 1,3-Bis-(imidazol-1-ylmethyl)-
5 2,4,6-trimethylbenzene (bitrb) and 1,4-bis-(imidazol-1-
6 ylmethyl)-2,3,5,6-tetramethylbenzene (biteb) have been
7 used for syntheses of many multinuclear Cu^{II} coordination
8 compounds that have M₂L₂,³⁻⁶ M₂L₄,^{3,4,7-9} and M₃L₃ cages^{10,11}
9 as well as network structures.^{3,11-13}

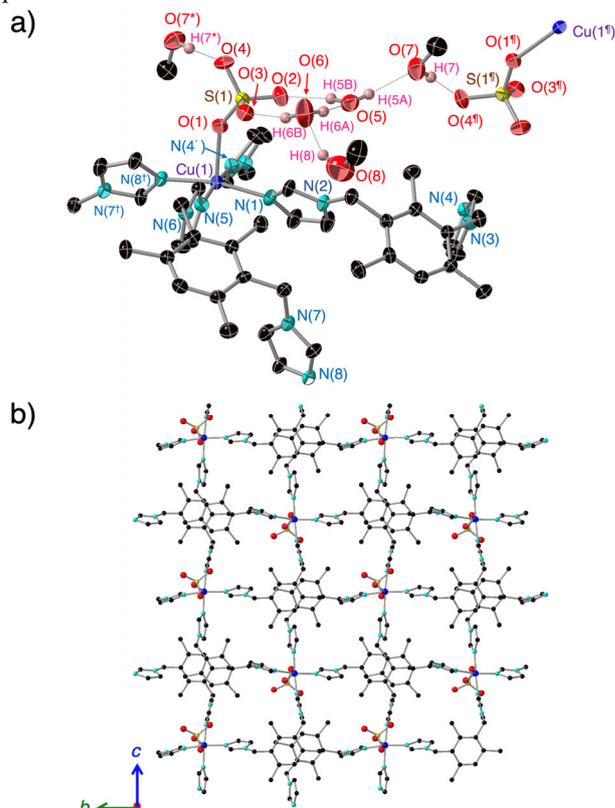
1 Reconstructions or structural transformations of
2 multinuclear coordination compounds caused by external
3 stimuli such as temperature variation and present solvents
4 are examples of the unique functions for the compounds.¹⁴⁻
5 ^{19, 20, 21-26} We have previously reported the irreversible
6 transformation of 1D coordination polymer with biteb,
7 [Cu(biteb)₂(NCS)](NCS)(MeOH)₂(H₂O), to the discrete
8 trinuclear coordination compound [Cu₃(biteb)₄(NCS)₆] by
9 contact with MeCN.



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1 On continuing work, we have synthesized and
2 characterized two new Cu^{II} coordination polymers with bitrb.
3 This paper reports the syntheses, crystal structures of the
4 new 2D and 1D Cu^{II} coordination polymers with bitrb, and

1 the reversible structural transformations depending on the
2 present solvents.



1
2 **Figure 1.** Thermal ellipsoids of the coordination
3 environment around the Cu^{II} center of **1** at 30% probabilities.
4 Color code: blue, copper; red, oxygen; yellow, sulfur; cyan,
5 nitrogen; black, carbon; pink, hydrogen. Symmetry
6 operation † $-X, 1/2+Y, 1-Z,$ ′ $-X, 1/2+Y, -Z,$ * $1-X, 1/2+Y, -$
7 $Z,$ † $1-X, -1/2+Y, -Z.$ Hydrogen atoms and methyl groups of
8 the ligand in (b) are omitted for clarity. Selected bond
9 distances are Cu(1)–N(1) = 1.995 (6); Cu(1)–N(5) = 1.984
10 (5); Cu(1)–N(4′) = 1.76 (5); Cu(1)–N(8†) = 1.992 (6);
11 Cu(1)–O(1) = 2.203 (5); O(2)⋯O(5) = 2.810(11);
12 O(3)⋯O(6) = 2.697(13); O(4)⋯O(7*) = 2.716(11);
O(5)⋯O(7) = 2.804(12); (6)⋯O(8) = 2.78(2) Å.

1 The ligand bitrb was prepared according to the
2 literature method.¹⁰ Reaction of CuSO₄·5H₂O with bitrb in a

1 MeOH-H₂O mixed media gave
 2 [Cu(bitrb)₂(SO₄)](MeOH)₂(H₂O)₂ (**1**) as deep blue powder.
 3 Crystal structure of **1** was determined by single crystal X-
 4 ray diffraction study.²⁷ The coordination environment and
 5 the 2D structure are shown in Figure 1. The Cu^{II} center is
 6 based on the distorted square pyramid surrounded by four
 7 imidazole nitrogen atoms in the basal plane and a sulfur
 8 oxygen atom at the apical site. The averaged Cu—N
 9 distance is 1.987 Å; each Cu—N distance is shown in
 10 caption of Figure 1. The Cu—O distance (2.203 (5) Å) is
 11 longer than those of Cu—N distances due to the Jahn-Teller
 12 distortion. The Cu^{II} atom is pulled about 0.167 (4) Å from
 13 the N₄ plane defined by the four coordinating nitrogen
 14 atoms toward the sulfate oxygen atom.

15 The Cu^{II} atoms are bridged by bitrb, yielding a 2D
 16 structure expanding in the *bc* plane as shown in Figure 1b.
 17 Because of the bent form of the bitrb, the 2D layer has about
 18 11.5 Å in thickness (Figure S1). The sulfate anions stick out
 19 from the layer to the upper and lower sides of the 2D layer.

20 As shown in Figure 1a, a MeOH molecule and two
 21 water molecules form hydrogen bonds with the sulfate
 22 oxygen atoms. The O···O distances are in the range from
 23 2.69 Å to 2.81 Å; each distance is shown in caption of
 24 Figure 1. The water molecule with O(5) forms the hydrogen
 25 bond with the MeOH molecule with O(7) that associates to
 26 the sulfate oxygen atom (O(4[#])) in its adjacent layer. This
 27 result means that the two sulfate anions in the adjacent
 28 layers create hydrophilic space between the sulfate ions, and
 29 trap two MeOH and two water molecules in it. Because their
 30 hydrophilic space are not connected but capped by the
 31 network frameworks, channel structures are not formed in **1**.
 32 (Figure S2)

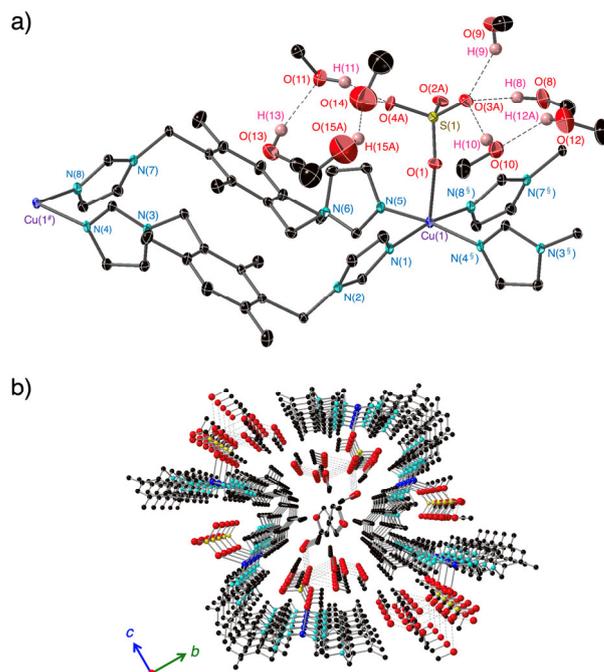
33 Diffusion of a THF solution of the ligand into a MeOH
 34 solution of CuSO₄·5H₂O gave
 35 [Cu(bitrb)₂(SO₄)](MeOH)₈(THF)_{0.5} (**2**) as deep blue powder.
 36 Figure 2 shows the crystal structure of **2**.²⁸ The Cu^{II} center is
 37 based on the distorted square pyramid formed by four
 38 imidazole nitrogen atoms in the basal plane and a sulfur
 39 oxygen atom at the apical site. The Cu^{II} atom is pulled about
 40 0.182 (2) Å from the N₄ plane defined by the coordinating
 41 nitrogen atoms toward the sulfate oxygen atom.

42 For **2**, the Cu—N distances around the Cu^{II} centers are
 43 almost the same (avg. 2.006 Å). The Cu(1)—O(1) distance
 44 (2.244 (4) Å) is significantly longer than these values
 45 because of the Jahn-Teller distortion. Each Cu^{II} center is
 46 connected by two bitrb, yielding 1D chain along the *a* axis.
 47 The sulfate anion was disordered at the two positions, and
 48 was solved with occupancies of 0.7 and 0.3. Figure 2a
 49 reveals a sulfate ion with occupancies of 0.7 for the two
 50 disordered sulfate ions. The anions stick out from the 1D
 51 chain to the same directions.

52 Compound **2** includes eight MeOH and 0.5 THF
 53 molecules per one Cu^{II} ion. Among them, five MeOH
 54 molecules bind to the sulfate ion by hydrogen bonds as
 55 shown in Figure 2a. The five MeOH molecules also form
 56 hydrogen bonds with the disordered sulfate ion. (Figure S3)
 57 The other three MeOH molecules are hydrogen bonded to
 58 the three MeOH molecules that connect to the sulfate ion
 59 directly. The hydrogen bonded O···O distances are in the

60 range from 2.54 to 2.89 Å; each distance is shown in caption
 61 of Figure 2 and Figure S3.

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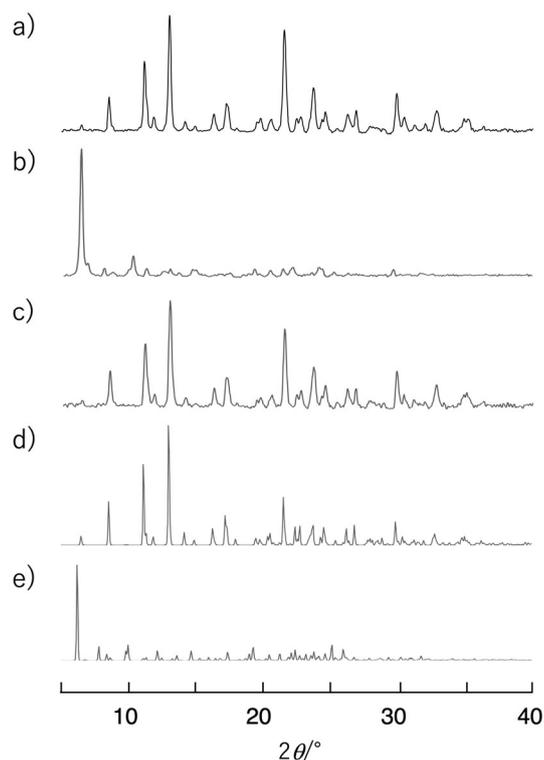
64 **Figure 2.** Thermal ellipsoids of the coordination
 65 environment around the Cu^{II} center of **2** at 30% probabilities
 66 (a) and the perspective view of **2** that shows the
 67 hydrophobic circumstance around the THF molecules (b).
 68 Color code: blue, copper; red, oxygen; yellow, sulfur; cyan,
 69 nitrogen; black, carbon; pink, hydrogen. Symmetry
 70 operation $\$ 1+X, Y, Z, \# X-1, Y, Z$. The disordered sulfate ion
 71 and THF molecules, and hydrogen atoms except for
 72 hydrogen atoms that bind to the O atoms are omitted for
 73 clarity. Selected bond distances are Cu(1)—N(1) = 2.001 (4),
 74 Cu(1)—N(2) = 2.002 (4); Cu(1)—N(5) = 2.006 (4[#]); Cu(1)—
 75 N(8[#]) = 2.013 (4); Cu(1)—O(1) = 2.244 (4); O(3A)···O(8) =
 76 2.858 (12); O(3A)···O(9) = 2.726 (12); O(3A)···O(10) =
 77 2.801 (14); O(4A)···O(11) = 2.785 (19); O(4A)···O(14) =
 78 2.73 (2); O(10)···O(12) = 2.785 (8); O(11)···O(13) = 2.889
 79 (7); O(14)···O(15A) = 2.61 (2) Å.

80

81 The THF molecule included is disordered at the two
 82 positions due to the crystallographic inversion center. They
 83 are trapped in the hydrophobic space created by the methyl
 84 groups of the MeOH molecules around the sulfate ion and
 85 bitrb as shown in Figure 2b. The size of channel-like space
 86 created among the [Cu(bitrb)₂(SO₄)] is only about 2.5 × 2.3
 87 Å². (Figure S4)

88 Compound **1** was obtained by the reaction of
 89 CuSO₄·5H₂O with bitrb in a MeOH-H₂O mixed solution,
 90 while **2** was formed in a THF-MeOH mixed solution. These
 91 results indicate that the presence of THF in the reaction
 92 solvent importantly affects the obtained structures and
 93 prompted us to study structural transformation from **1** to **2**
 94 by contact with a THF-MeOH mixed media.

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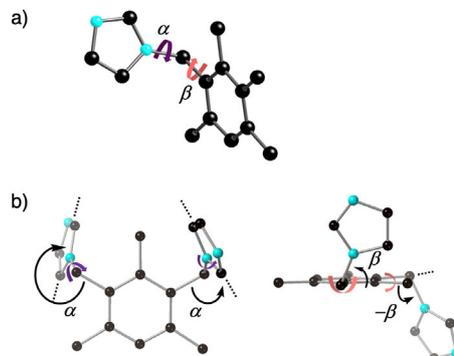


1
2 **Figure 3** PXRD (Cu K α) charts of a fresh sample of **1** (a),
3 the powder sample obtained by treatment of **1** with a THF-
4 MeOH (1:1 v/v) mixed solvent (b), the powder sample
5 obtained by the following treatment with a mixed MeOH-
6 H₂O (1:1 v/v) solvent (c), and simulated PXRD patterns of **1**
7 (d) and **2** (e).
8

9 The changes of the structures of the compounds were
10 monitored by measuring the powder X-ray diffraction
11 (PXRD) pattern. Figure 3a shows a fresh bulk sample of **1**.
12 The powder was stirred in a THF-MeOH (1:1 v/v) mixed
13 solvent overnight, and then collected by filtration. Figure 3b
14 shows the PXRD chart of the powder obtained from **1** by the
15 treatment. The pattern in Figure 3b is quite different from
16 that of Figure 3a, and well consistent with that of the
17 simulated PXRD pattern of **2** (Figure 3e). This result
18 demonstrates that **1** changes to **2** in a THF-MeOH mixed
19 solvent. Compound **1** didn't proceed **2** by a treatment in
20 THF (Fig. S5), indicating that both THF and MeOH are
21 necessary for the transformation.

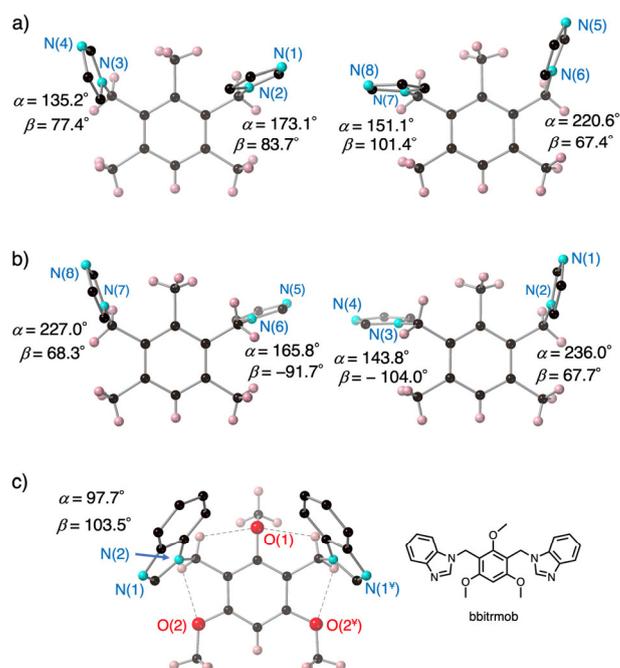
22 We further studied whether the reverse transformation
23 proceeds or not. The powder sample of **2** obtained from **1**
24 was dried under reduced pressure, and then stirred in a
25 MeOH-H₂O (1:1 v/v) solvent overnight. Figure 3c shows
26 the PXRD chart of the obtained powder, which is well
27 consistent with that of the simulated PXRD chart of **1**
28 (Figure 3d), exhibiting the re-formation of **1** by the
29 treatment. These results demonstrate that the structural
30 transformations are reversible. Although **1** and **2** show low
31 solubilities in MeOH and THF, the transformations would
32 proceed via recrystallization process.

33 The PXRD patterns of **1** and **2** were not changed
34 essentially after heating them at about 60°C in MeOH-H₂O
35 (1:1 v/v) and THF-MeOH (1:1 v/v) mixed media for an hour
36 (Figs. S6, S7), indicating that the transformations are not the
37 results of the reactions from the kinetic product to the
38 thermal one.^{29,30}
39



40

41 **Scheme 2.** Rotation of N-C and C-C bonds of the
42 methylimidazole groups (a) and definitions of the torsion
43 angles α and β (b).
44



45

46 **Figure 4.** Structures and the observed torsion angles, α and
47 β , for bitrb in **1** (a) and **2** (b) and bbitrmob in
48 [Cu₂(SO₄)₂(bbitrmob)₂](MeCN)(H₂O) (c). Hydrogen atoms
49 of the imidazole and benzimidazole rings are omitted for
50 clarity. Symmetry operation $\frac{1}{2}X, 1-Y, Z$.
51

52 Although bitrb has flexibilities due to the two C-N and
53 two C-C bonds (Scheme 2a), the rotations would be
54 restricted by the steric hindrance of two adjacent methyl
55 groups. We have recently synthesized a new Cu^{II}
56 coordination polymer [Cu₂(SO₄)₂(bbitrmob)₂](MeCN)(H₂O)

1 (bbitrmob = 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-
2 trimethoxybenzene (bbitrmob) (**3**), and proposed that the
3 replacements of the methyl groups with methoxy groups
4 relax the restrictions due to the attractive C-H...O
5 interactions. We have successfully characterized the crystal
6 structures of coordination polymers constructed by Cu^{II} ion,
7 sulfate ion, and bitrb in this work. To investigate the effects
8 of the methyl and methoxy groups on the structural
9 conformations of the bitrb and bbitrmob, we compared the
10 ligand structures in **1**, **2**, and **3**.

11 The conformations of bitrb and bbitrmob can be
12 estimated by rotation angles around the C-N and C-C bonds
13 as defined in Scheme 2b. Figure 4 exhibits structures of the
14 bitrb in **1** and **2**, and bbitrmob in **3**. The ligands in **1** and **3**
15 have so called the *syn* form, in which two imidazole rings
16 orient to the same directions from the trimethylphenyl plane,
17 while the ligand in **2** has the *anti* form. These results
18 demonstrate that bbitrmob shows the remarkably small α
19 (97.7°) and significantly large β (103.5°) angles.

20 In summary, we have prepared two new coordination
21 polymers with bitrb by the reactions of CuSO₄·5H₂O with
22 bitrb. The 2D and 1D coordination polymers are obtained
23 depending on the reaction solvents. That is, THF-MeOH
24 mixed solvent produced 2D coordination polymer **1**, while
25 MeOH-H₂O mixed solvent formed 1D coordination polymer
26 **2**. It was found that the two coordination polymers
27 reversibly convert the structures depending on the present
28 solvents. The ligand conformations affected by the steric
29 hindrances from the two adjacent methyl groups are
30 discussed.

31
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34 for support in obtaining the elemental analysis data.

35
36 Supporting Information is available on
37 <http://dx.doi.org/xx.xxxx>
38

39 References and Notes

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97 27 Data collection for **1** was carried out on a Rigaku CCD mercury
98 system fitted with a monochromated Mo-K α radiation (sealed X-
99 ray source). Crystallographic data for **1**: C₃₆H₅₂CuN₈O₈S (MW:
100 820.45), monoclinic, space group P2₁ (No. 4), $a = 8.975$ (8), $b =$
101 15.877 (13), $c = 13.603$ (11) Å, $\beta = 90.509$ (13) $^\circ$, $V = 1938$ (3) Å³,
102 $Z = 2$, $\rho(\text{caclcd}) = 1.406$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 0.678$ mm⁻¹, $T =$
103 293 K, $\lambda = 0.71073$ Å, ω scan, reflections collected/unique
104 reflections/ parameters refined: 14871/7402/503, $R_{\text{int}} = 0.0485$,
105 final $R1 = 0.0693$ ($I > 2\sigma(I)$), $wR2 = 0.0772$ (all data), GOF =
106 1.073. CCDC 2082655.
107 28 Data collection for **2** was carried out on a Rigaku VariMax Saturn
108 using multi-layer mirror monochromated Mo-K α radiation (1.2-
109 kW rotating anode). Crystallographic data for **2**:
110 C₄₄H₇₆CuN₈O_{12.5}S (MW: 1012.72), monoclinic, space group P2₁/n
111 (No. 14), $a = 12.4458$ (4), $b = 28.4042$ (7), $c = 15.6813$ (5) Å, $\beta =$
112 111.258 (4) $^\circ$, $V = 5166.3$ (3) Å³, $Z = 4$, $\rho(\text{caclcd}) = 1.302$ g cm⁻³,
113 $\mu(\text{Mo K}\alpha) = 0.529$ mm⁻¹, $T = 173$ K, $\lambda = 0.71075$ Å, ω scan,
114 reflections collected/unique reflections/ parameters refined:
115 110927/13554/687, $R_{\text{int}} = 0.0871$, final $R1 = 0.0997$ ($I > 2\sigma(I)$),
116 $wR2 = 0.1237$ (all data), GOF = 1.109. CCDC 2082656.
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