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## COMMUNICATION

## Two New Coordination Polymers, a Trinuclear Metal Complex and Their Interconversion depending on Solvent

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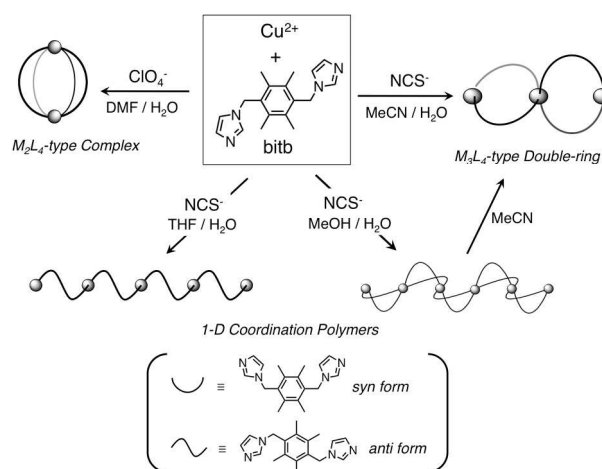
Two new 1-D coordination polymers and a discrete trinuclear complex with a double-ring framework were synthesized and structurally characterized. The unique irreversible conversion from the trinuclear complex to one of the 1-D coordination polymers by contact with MeCN is described.

Selective constructions of multinuclear metal complexes by self-assembly processes are fundamental subjects in supramolecular chemistry.<sup>1</sup> Bis-imidazole- and bis-benzimidazole-type ligands with two methylene groups<sup>2</sup> have produced coordination polymers<sup>3</sup> as well as discrete molecules<sup>4,5,6</sup> that have M<sub>2</sub>L<sub>4</sub>, M<sub>2</sub>L<sub>2</sub>, and M<sub>3</sub>L<sub>4</sub>-type cage structures. The metal ions, anions, and solvents used in the syntheses are important factors in the obtained structures. In many cases, the anion is included in the cage of the obtained compounds, because they act as a template guest to create the cage frameworks. Among the discrete metal complexes, M<sub>3</sub>L<sub>4</sub>-type complexes are still rare.<sup>5</sup> This is because it is quite difficult to terminate the multinucleation at the trinuclear structure when the formation of polynuclear structures could be obtainable.

We have focused on the self-assembled system constructed from 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bitb) and Cu<sup>2+</sup> ions.<sup>6,7</sup> When ClO<sub>4</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup> ions are present, the combination of Cu<sup>2+</sup> and bitb yields an M<sub>2</sub>L<sub>4</sub>-type molecular capsule, which includes the anion in the cage. When CO<sub>3</sub><sup>2-</sup> is used as the anion of the system, a 2-D coordination polymer is obtained.<sup>7</sup> Interestingly, this coordination polymer converts to the pentanuclear Cu(II) complex including the [Cu(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> anion by treatment with MeOH or EtOH. This conversion from the 2-D coordination polymer to the pentanuclear metal complexes would be induced by the template anion [Cu(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup>.

Structural changes in response to the solvents present have often been observed in some coordination polymers.<sup>8,9</sup> As a typical example, [Zn<sub>2</sub>(oba)<sub>2</sub>(dmf)<sub>2</sub>]<sub>n</sub> (oba = 1,4-bisoxo-benzoate) with a porous framework reversibly converts to [Zn(oba)(H<sub>2</sub>O)]<sub>n</sub> without a porous framework, depending on the solvents present, H<sub>2</sub>O or DMF.<sup>9</sup> However, structural changes from coordination polymers to discrete molecules are still limited.<sup>7</sup> To explore this conversion reaction, we have continued our synthetic studies of the Cu<sup>II</sup>-bitb system and have succeeded in isolating two new Cu<sup>II</sup>-bitb coordination polymers and a new M<sub>3</sub>L<sub>4</sub>-type trinuclear complex. Their formations are largely dependent on the solvents used in the reactions. This communication reports the syntheses, structures, and a new structural conversion from coordination

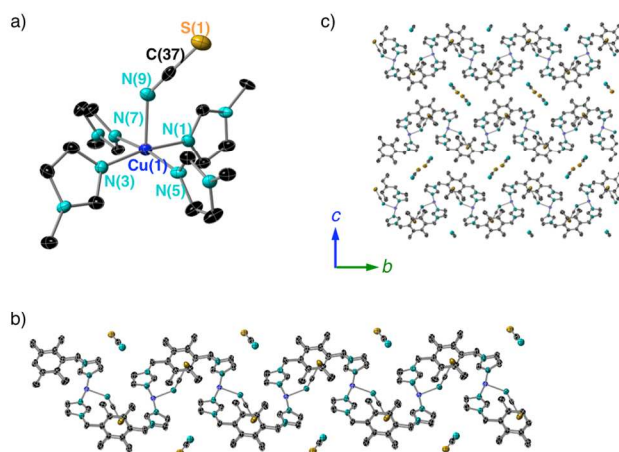
polymer to trinuclear M<sub>3</sub>L<sub>4</sub>-type complex responding to the solvent.



Scheme 1. Schematic images of structural motifs of Cu<sup>II</sup>-bitb complexes and the irreversible conversion from the coordination polymer to the discrete trinuclear complex observed in this work.

The Cu<sup>II</sup>-bitb self-assembled system in this work is schematically summarized in Scheme 1. A methanol solution (30 ml) of bitb (0.141 g, 0.48 mmol), a MeOH:H<sub>2</sub>O (1:1 v/v) mixed solution (30 ml) of NaSCN (0.039 g, 0.48 mmol), and an aqueous solution (30 ml) of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.060 g, 0.24 mmol) were mixed. The reaction solution was stirred for a few days to yield {[Cu(bitb)<sub>2</sub>(NCS)]NCS·2MeOH·H<sub>2</sub>O}<sub>n</sub> (**1**) as a blue powder, which was collected by filtration (0.097 g, 0.11 mmol, 47.5%). Calcd for C<sub>40</sub>H<sub>54</sub>CuN<sub>10</sub>O<sub>3</sub>S<sub>2</sub> (850.60): C, 56.48; H, 6.40; N, 16.47. Found: C, 56.55; H, 6.22; N, 16.51. When THF was used instead of MeOH, {[Cu(bitb)(NCS)<sub>2</sub>(H<sub>2</sub>O)]THF}<sub>n</sub> (**2**) was obtained as a deep green powder in 64.3% yield. Calcd for C<sub>24</sub>H<sub>32</sub>CuN<sub>6</sub>O<sub>2</sub>S<sub>2</sub> (564.22): C, 51.09; H, 5.72; N, 14.89. Found: C, 51.30; H, 5.74; N, 14.41. On the other hand, similar treatment of CuCl<sub>2</sub>·2H<sub>2</sub>O with bitb and NaSCN in MeCN/H<sub>2</sub>O media produced [Cu<sub>3</sub>(bitb)<sub>4</sub>(NCS)<sub>6</sub>] (**3**) as a green powder in 61.4% yield. Calcd for C<sub>78</sub>H<sub>88</sub>Cu<sub>3</sub>N<sub>22</sub>S<sub>6</sub> (1716.70): C, 54.57; H, 5.17; N, 17.95. Found: C, 54.58; H, 5.18; N, 18.01. The single crystals of each compound for X-ray diffraction studies were obtained by the diffusion method at about 33%, 41%, and 50% yield respectively.

The structures of **1**, **2**, and **3** were clarified by single-crystal X-ray diffraction studies. Figure 1 shows the coordination environment of the Cu<sup>II</sup> center and the infinite network structures of **1**. The Cu<sup>II</sup> center is based on a square pyramid with four imidazole nitrogen atoms of bitb, and an NCS<sup>-</sup> nitrogen atom at the apical site (Figure 1a). The Cu–N bond distance (2.182(6) Å) formed between the Cu<sup>II</sup> center and the NCS<sup>-</sup> nitrogen is slightly longer than those of the other Cu–N bonds (avg. 2.009 Å) formed between the Cu<sup>II</sup> center and the imidazole nitrogen atoms. As shown in Figure 1b, each Cu<sup>II</sup> center is connected by two bitb in the syn form to yield a 1-D structure along the *b*-axis. The imidazole nitrogen atoms of the two bitb ligands that bridge the pair of Cu<sup>II</sup> ions occupy the *cis*-positions at the Cu<sup>II</sup> center. As a result, a unique zigzag chain motif is constructed.



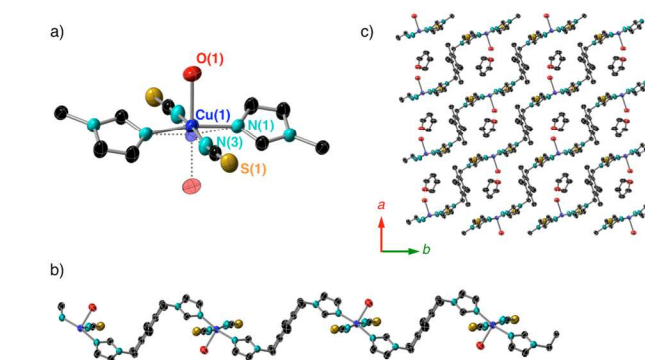
**Figure 1.** Thermal ellipsoids of the coordination environment around the Cu<sup>II</sup> center of **1** (a). The 1-D structure along the *b*-axis (b) and the overall structure (c) of **1**. Hydrogen atoms, and water and MeOH molecules included in the channels are omitted for clarity.

The NCS<sup>-</sup> binds to the Cu<sup>II</sup> center with remarkably bent Cu–N–C bond angles (139.7(6)<sup>o</sup>). Although the sulfur atom of the NCS<sup>-</sup> orients to the vacant site of the Cu<sup>II</sup> ion in the same chain, the longer Cu–S distance (*ca.* 3.9 Å) indicates that there is no significant interactions between the Cu<sup>II</sup> center and the sulfur atom. As shown in Figure 1c, the 1-D chains assemble to create 1-D channels along the *a*-axis with a size of about 1.5 × 1.5 Å<sup>2</sup>. While **1** involves two NCS<sup>-</sup> ions per Cu<sup>II</sup> ion, one does not bind to the Cu<sup>II</sup> center. The channels are occupied with the metal-free NCS<sup>-</sup> ions, water and methanol molecules.

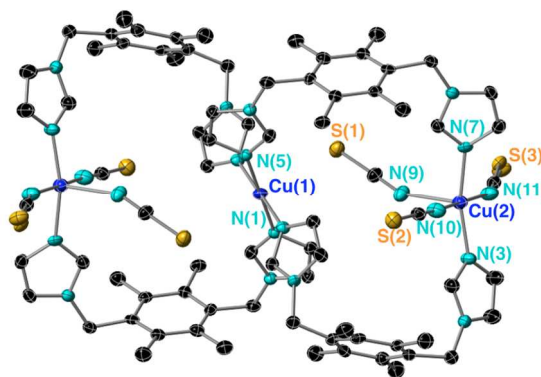
Figure 2 shows the coordination environment and network structure of **2**. The Cu<sup>II</sup> center is based on a square pyramid with two imidazole nitrogen atoms of bitb, two NCS<sup>-</sup> nitrogen atoms, and a water oxygen atom at the apical position. The Cu–O bond distance (2.687(14) Å) is significantly longer than the Cu–N bond distances (1.92 ~ 2.03 Å) because of the Jahn–Teller effect. As shown in this figure, the Cu–O unit is disordered at the two positions by the crystallographic inversion center located between the two Cu<sup>II</sup> centers. The Cu atom is pulled about 0.2 Å from the plane defined by the four coordinating nitrogen atoms

toward the water oxygen atom. The Cu–N bond distances between the Cu<sup>II</sup> ion and the imidazole nitrogen atoms (avg. 2.012 Å) are slightly longer than those between the Cu<sup>II</sup> and NCS<sup>-</sup> ions (avg. 1.952 Å). Two NCS<sup>-</sup> ions bind to the Cu<sup>II</sup> center with nearly linear Cu–N–C bond angles (avg. 172.8<sup>o</sup>).

Each Cu<sup>II</sup> center is connected by bitb in the anti form to yield zigzag 1-D chains along the (*a* + *b*) vector (Figure 2b). Compound **2** contains a THF molecule per Cu<sup>II</sup> atom. The THF molecule, which is disordered at the two positions, forms a hydrogen bond with the coordinating water molecule (O···O = avg. 2.988 Å).



**Figure 2.** Thermal ellipsoids of coordination environment around the Cu<sup>II</sup> center of **2** (a). The disordered Cu(1) and O(1) atoms are shown by the transparent ellipsoids. The 1-D structure along the (*a* + *b*) vector (b). Hydrogen atoms are omitted for clarity. Disorders are also omitted in (b) and (c) for clarity.

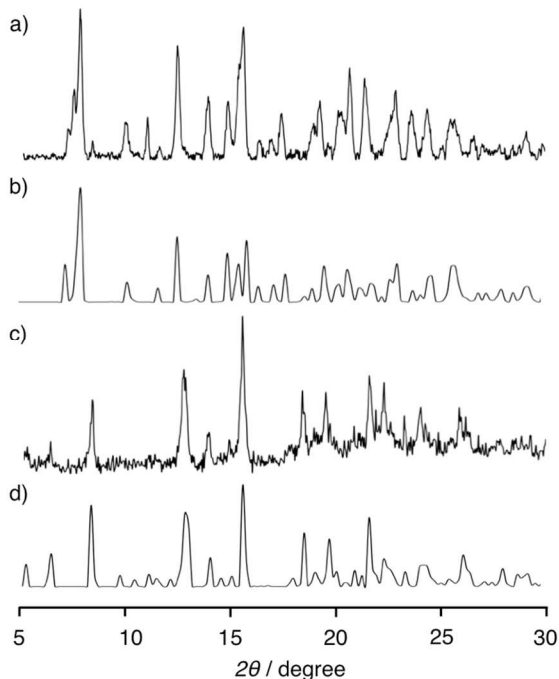


**Figure 3.** Thermal ellipsoids of molecular structure of **3**. Hydrogen atoms are omitted for clarity.

In contrast to **1** and **2**, **3** has a discrete trinuclear structure with double-ring framework, which is also called a twin-cage framework. As shown in Figure 3, this framework is constructed by connections of three Cu<sup>II</sup> ions by four bitb ligands to give double rings connected at the Cu(1) atom. The crystallographic inversion center is located at the Cu(1) atom. For the three Cu<sup>II</sup> centers, Cu(2) atoms located in both edges of the double-ring framework are based on the square pyramidal coordination environment with two imidazole nitrogen atoms and three NCS<sup>-</sup> nitrogen atoms. For the three crystallographically independent NCS<sup>-</sup> ligands in **3**, N(10)–C(38)–S(2)<sup>-</sup> binds with the Cu<sup>II</sup> ion with a nearly linear Cu–N–C bond angle (171.0(5)<sup>o</sup>), while the other two

NCS<sup>-</sup> ligands show remarkably bent Cu–N–C bond angles (149.9(5)° and 154.7(5)°). Of the five Cu–N bonds, the Cu(1)–N(9) bond (2.275(6) Å) is longer than the others (avg. 1.991 Å) because of the Jahn–Teller effect. The sulfur atom of one of the NCS<sup>-</sup> ligands orients to the axial site of the Cu(1) atom. The Cu(1)–S(1) distance (*ca.* 3.1 Å) is shorter than the sum of the van der Waals radii of copper (1.4 Å) and sulfur (1.85 Å) atoms, indicating an association of the S(1) atom to the Cu(1) atom. As a result, the Cu(1) atom is based on the elongated octahedral geometry with four imidazole nitrogen atoms and the sulfur atoms.

Compounds **1**, **2**, and **3** were obtained depending on the organic solvents included in the reaction solutions when they were prepared. We studied whether or not these three organic solvents induce structural conversions among **1**, **2**, and **3**. Because these three compounds were only sparsely soluble in their solvents, MeOH, THF, and MeCN, the structural changes were monitored by measurements of X-ray powder diffraction (XRPD) patterns of each bulk sample before and after stirring in the solvents for a week. We found that **1** is converted to **3** irreversibly in this condition. Figure 4 shows the XRPD charts of a fresh sample of **1**, the powder sample obtained after stirring of **1** in MeCN for a week, and simulated XRPD patterns of **1** and **3**, which were obtained based on their crystal structures.



**Figure 4.** XRPD (Cu K $\alpha$ ) pattern of a fresh sample of **1** (a) and the powder sample obtained after stirring **1** in MeCN for a week (c) with the simulated XRPD pattern for **1** (b) and **3** (d).

The XRPD peaks characteristic for **1** disappeared on treatment with MeCN, and the XRPD peaks of a pattern similar to the simulated pattern of **3** appeared. This result indicates that **1** converts to **3** by treatment with MeCN. We also studied whether or not the reverse conversion, *i.e.*, from **3** to **1**, was induced by contact with MeOH. The XRPD pattern of the bulk sample of **3**

was not changed essentially after stirring the bulk sample in MeOH for 2 weeks (Figure S12 in Supplementary Information), indicating that conversion from **3** to **1** did not occur on treatment with MeOH in this condition. This result reveals that **1** converts to **3** irreversibly.

The conversion from **1** to **3** was also confirmed by measurement of reflectance spectra. Compounds **1** and **3** show d-d absorption at  $\lambda_{\text{max}} = 673$  and 696 nm in the reflectance spectra (Figure S18 and S20). The spectrum of the powder sample obtained by contact of **1** with MeCN for a week was quite similar to that of **3** (Figure S21), although the change of the color was not clear in visible. For the conversion reaction, the XRPD peaks of **1** disappeared within 4 days because of the formation of amorphous state, and then new peaks ascribed to **3** appeared within additional three days (Figure S11). For construction of the double-ring framework of **3** from **1**, cleavages of Cu–N (imidazole) bonds and formations of new Cu–N (imidazole) and Cu–N (NCS<sup>-</sup> anions) bonds are involved. The dynamic rearrangements which yield double-ring frameworks selectively would be difficult in the solid state. Despite **1** is sparsely soluble in MeCN (one piece of crystal is not soluble in 100 mL of MeCN) and other general organic solvents, the conversion from **1** to **3** could proceed by recrystallization process.

Although we also studied structural conversions between **1** and **2** by contact with THF and MeOH, and between **2** and **3** by contact with MeCN and THF, these combinations did not induce structural changes under the above conditions. Their XRPD charts are shown in the Supplementary Information (Figure S9, S10, S13, S14).

In conclusion, treatments of CuSO<sub>4</sub>·5H<sub>2</sub>O or CuCl<sub>2</sub>·2H<sub>2</sub>O, bitb, and NaSCN yielded two new coordination polymers and a new discrete trinuclear complex with an M<sub>3</sub>L<sub>4</sub>-type double-ring structure. Their formations are dependent on the kinds of organic solvents included in the reaction solvents. To clarify the effects of the organic solvents on the obtained structures, we studied the structural changes among the three compounds by contact with the organic solvents, MeOH, THF, and MeCN. This study showed that **1** converts to **3** irreversibly by contact with MeCN, while no other conversions were observed after treatment of the bulk samples in the solvents.

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## Notes and references

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† Electronic supplementary information (ESI) available: Materials and methods, crystallographic data, XRD charts, UV-vis. reflectance spectra, IR spectra. CCDC 990125 (1), 990127 (2), 990126 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C5DT00000A

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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## Graphical Abstract

Irreversible conversion of 1-D coordination polymer to a discrete trinuclear complex by contact with MeCN is described.

