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Solvent-Soluble Coordination Polymer That Reconstructs Cyclic Frameworks That Trap a Kinetically Labile $[Cu(CO_3)_2]^{2-}$ Unit

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Supporting Information

ABSTRACT: A new 2D coordination polymer consisting of Cu^{II} ions, bis-imidazole-type ligands, and CO_3^{2-} was prepared. This compound converted to new pentanuclear complexes with cyclic frameworks, which trapped a kinetically labile $[Cu(CO_3)_2]^{2-}$ unit, by recrystallization from MeOH/Et_2O or EtOH/Et_2O.

Encapsulation of discrete molecules in the coordination cages is a unique method for the isolation of labile or unstable molecules that are difficult to isolate under ambient conditions.[1−4] As a typical example, Fujita and co-workers have successfully isolated cis forms of azobenzene and stilbene[1] and a mixed-valence dimer, $[(TTF)_2]^{+\cdot}$ (TTF = tetrathiafulvalene).[2] These guest molecules are difficult to isolate without deformation at ambient conditions. Raymond and co-workers have shown that the iminium ion, which is easily hydrolyzed by H_2O, can be isolated in aqueous media by encapsulation in coordination cages.[3]

Neutral multi-imidazole-type ligands[5] have been used for the construction of various molecular capsules.[6] We have focused on the self-assembled construction of coordination cages by Cu^{II} ions and 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bitb) ligands (Figure 1); this ligand forms an M_2L_4-type molecular capsule for ClO_4^- and BF_4^-, responding to the guest anions.[7] In continuing studies of the self-assembled system of Cu^{II} ions with bitb, we have synthesized a new coordination polymer constructed by Cu^{2+} ions, bitb, and CO_3^{2-} and have found that this coordination polymer reconstructs pentanuclear complexes, which have new cyclic frameworks including a kinetically labile $[Cu(CO_3)_2]^{2-}$ unit in the cage. This paper describes the syntheses and structures of a new Cu^{II}bitb coordination polymer, $\{[Cu(CO_3)(bitb)]\cdot 2H_2O\}_n$ (**1**), and the two reconstructed Cu^{II}bitb complexes $[Cu(CO_3)_2{\subset}Cu_4(\mu\text{-}OMe)_4(bitb)_4]CO_3\cdot 7.5MeOH\cdot 3H_2O$ (**2a**) and $[Cu(CO_3)_2{\subset}Cu_4(\mu\text{-}OEt)_4(bitb)_4]CO_3\cdot 3Et_2O\cdot 3EtOH$ (**2b**).

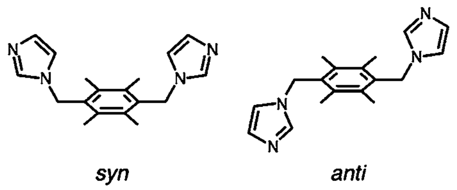

Figure 1. Syn and anti forms of bitb.

Complex **1** was obtained by the reaction of bitb with basic copper(II) carbonate, $CuCO_3\cdot Cu(OH)_2$. This complex was also obtained using copper(II) hydroxide, $Cu(OH)_2$, instead of basic copper(II) carbonate. The addition of an NH_3 aqueous solution of the copper salt to an EtOH solution of bitb produced a purple solid. Recrystallization of the crude product from MeOH/H_2O gave **1** as purple crystals, which were suitable for single-crystal X-ray analysis. The observed powder X-ray diffraction (PXRD) pattern of the crude product was consistent with the simulated PXRD pattern based on the solved structure (Figure S11 in the Supporting Information, SI), indicating that **1** is soluble in MeOH and can be recrystallized from MeOH/H_2O.

Structural characterization demonstrated that **1** has a network structure, as shown in Figure 2b. Each Cu^{II} center is based on a square-planar coordination geometry with two imidazole nitrogen atoms and two carbonate oxygen atoms (Figure 2a). The carbonate ion was disordered at the two positions by the imposed crystallographic C_2 axis, which runs through the Cu^{II} centers along the b axis. The Cu−O bonds [1.942(8) Å and 1.889(8) Å] are slightly shorter than the Cu−N bonds [2.007(6) Å] in the coordination environment.

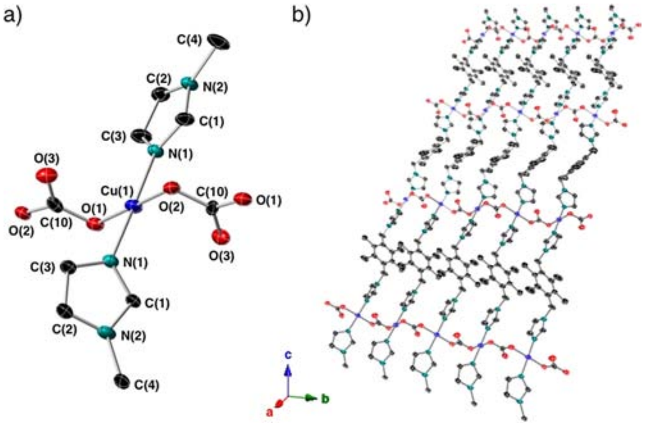

Figure 2. Coordination environment around the Cu^{II} center (a) and the 2D structure of **1** (b). Disorders of carbonate ions, solvent molecules, and hydrogen atoms are not shown for clarity.

Each Cu^{II} center is bridged by bitb to yield 1D chains along the $a-c$ vector. For the two different conformations, syn and anti, which the ligand can adopt because of the two methylene groups

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(Figure 1), the anti form is observed for bitb in the network framework of **1**. The carbonate ion bridges two Cu^{II} centers in the adjacent chains along the *b* axis, yielding a 2D structure with a grid motif.

During the single-crystal growth experiment for **1**, we found that diffusion of the MeOH solution of **1** into Et_2O affords a new pentanuclear complex, **2a**. When EtOH was used instead of MeOH, its ethoxy derivative, **2b**, was obtained. Their structures were clarified by single-crystal X-ray analysis studies.

Figure 3 shows the molecular structure of **2a**. The two imidazole nitrogen atoms and two MeO^- oxygen atoms bind to the Cu^{II} center at the cis positions. Two bitb with syn form connect two Cu^{II} centers, forming a $[Cu_2(bitb)_2]^{4+}$ unit. The four MeO^- groups connect the two $[Cu_2(bitb)_2]^{4+}$ units to form a cyclic framework $[Cu_4(\mu\text{-OMe})_4(bitb)_4]^{4+}$. A crystallographic inversion center exists in the center of the cyclic framework. The cyclic framework creates a cage with a size of approximately 11.0 × 5.0 × 4.0 Å^3.

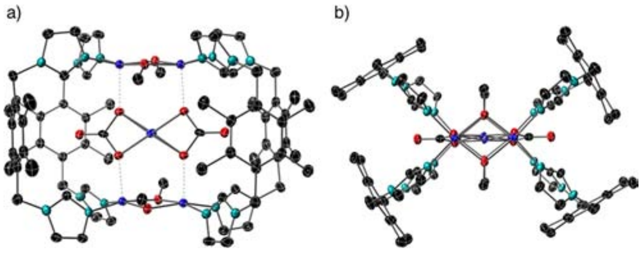

Figure 3. Side view (a) and top view (b) of the crystal structure of **2a**. Counteranions, solvent molecules, and hydrogen atoms are not shown for clarity. Color code: blue, copper; red, oxygen; cyan, nitrogen; black, carbon.

The cyclic framework traps a $[Cu(CO_3)_2]^{2-}$ unit in the cage by the four weak Cu–O interactions [2.311(4) and 2.256(4) Å] to the four carbonate oxygen atoms. A distorted square-pyramidal geometry around the Cu^{II} center in the cyclic framework is formed by association of the oxygen atom of the $[Cu(CO_3)_2]^{2-}$ unit at the apical site. The Cu–O bond distances for carbonate oxygen are longer than those of the other Cu–N (av. 1.977 Å) and Cu–O (av. 1.942 Å) bond distances because of the Jahn–Teller effect.

For the $[Cu(CO_3)_2]^{2-}$ unit in the cage, each CO_3^{2-} binds to the Cu^{II} center by four-membered chelation. The two C–O bond distances [1.333(7) and 1.322(5) Å] in the chelation ring are significantly longer than the other C–O bond distance [1.200(7) Å], showing localization of the two negative charges at the two coordinating oxygen atoms. This is in contrast to the case of the CO_3^{2-} ion, which has three similar C–O bond distances (Figure S7 in the SI) because of the delocalized negative charges, located outside the cyclic framework.

The structure of **2b** is shown in Figure S5 in the SI. Although the structural manner is the same as that of **2a**, the tilt of the $[Cu(CO_3)_2]^{2-}$ unit in the cage is significantly different. When the tilt angle is estimated from the plane–plane angle between the $[Cu(CO_3)_2]^{2-}$ unit and the Cu_4 plane that is defined by four Cu^{II} atoms in the cyclic framework, they are about 10° and 0° for **2a** and **2b**, respectively. This difference is connected with the longer Cu–Cu distance (6.711 Å) bridged by bitb in **2b** than in **2a** (6.666 Å).

Although the $[Cu(CO_3)_2(H_2O)_2]^{2-}$ species has been proposed as a plausible structure, which forms in an aqueous solution of Cu^{2+} ion and CO_3^{2-} at pH 8,[8] direct observation or isolation of the monomeric complex has not been established. Although $Rb_2[Cu(CO_3)_2]\cdot H_2O$ was structurally characterized by single-crystal X-ray analysis, this compound was shown to have a chain structure with carbonate bridges between the Cu^{II} centers.[9] To study the effect of the cyclic cages of **2a** and **2b** on the isolation of a $[Cu(CO_3)_2]^{2-}$ unit, we also attempted a crystal structure determination of another $Cu^{II}CO_3^{2-}$ complex, reported as $Na_2[Cu(CO_3)_2]\cdot 3H_2O$.[10] Although the preparation and cell parameters of this compound were mentioned, the crystal structure was not characterized.[8]

This complex crystallizes as $\{Na_2[Cu(CO_3)_2(H_2O)]\cdot 2H_2O\}_n$, which has a chain structure, as shown in Figure 4b. The Cu^{II} center is based on a distorted square pyramid with four carbonate oxygen atoms and a water molecule. For the two carbonate ions, one bridges two Cu^{II} ions to yield a chain structure. It is apparent that isolation of the monomeric $[Cu(CO_3)_2]^{2-}$ unit is difficult because of the infinite structure formation with $Cu^{II}-CO_3^{2-}-Cu^{II}$ bridges. This result means that the cyclic cages of $M_4L_4(\mu\text{-OR})_4$ just trap the kinetically labile $[Cu(CO_3)_2]^{2-}$ unit as a discrete anion.

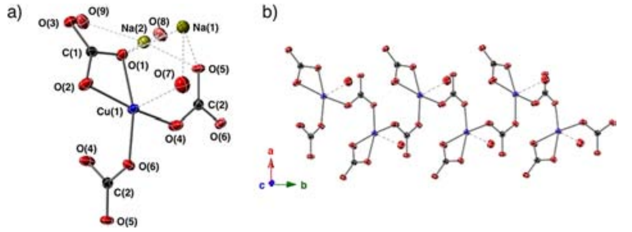

Figure 4. Coordination environment around the Cu^{II} center (a) and the chain structure (b) of $\{Na_2[Cu(CO_3)_2(H_2O)]\cdot 2H_2O\}_n$. Hydrogen atoms are not shown for clarity.

This Cu^{II}bitb-CO_3^{2-} system yielded different products, **1**, **2a**, and **2b**, depending on the solvent system used for recrystallization. To obtain insight into the effects of the recrystallization solvents, the structures present in the solutions were characterized.

The solid-state reflection spectra of **1**, **2a**, and **2b** show d–d bands at λ_{max} = 567, 631, and 639 nm, respectively (Figures S20–S22 in the SI). On the other hand, the solution spectra of these three complexes show similar d–d bands that depend on the solvents used for the measurements; they are at about 630 and 634 nm in MeOH and EtOH, respectively (Figures S24 and S25 in the SI).

Complex **2a** showed a similar spectrum pattern in its reflection spectrum in the solid state (λ_{max} = 631 nm) and absorption spectrum in MeOH (λ_{max} = 630 nm). The electrospray ionization time-of-flight (ESI-TOF) mass spectrometry (MS) spectrum of **2a** showed a parent ion peak at *m/z* 869.7 ascribed to $[Cu(CO_3)_2\subset Cu_4(\mu\text{-OMe})_4(bitb)_4]^{2+}$ (Figure S28 in the SI). These results indicate that the cyclic framework of **2a** is retained in MeOH.

Complex **1** showed different d–d absorptions in the solid state (λ_{max} = 567 nm) and solution state (λ_{max} = 630 and 634 nm in MeOH and EtOH, respectively). Their absorption patterns are rather similar to those of **2a** in MeOH and **2b** in EtOH. Interestingly, the ESI-TOF MS spectrum of **1** showed an intense peak at *m/z* 869.7 assigned to $[Cu(CO_3)_2\subset Cu_4(\mu\text{-OMe})_4(bitb)_4]^{2+}$ (Figure S26 in the SI). That is, **1** reconstructs the cyclic framework that traps a kinetically labile $[Cu(CO_3)_2]^{2-}$ unit in MeOH.

In the case of **2b**, although the reflection spectrum in the solid state ($\lambda_{max} = 639$ nm) and absorption spectrum in EtOH ($\lambda_{max} = 634$ nm) are similar, the ESI-TOF MS spectrum did not show a main peak for $[Cu(CO_3)_2 \subset Cu_4(\mu\text{-OEt})_4(bitb)_4]^{2+}$ but for $[Cu(CO_3)_2 \subset Cu_4(\mu\text{-OMe})_4(bitb)_4]^{2+}$ (m/z 869.7; Figure S30 in the SI) when MeOH was used as a mobile phase. Similarly, exchanges of MeO^- in the cyclic framework of **2a** with EtO^- were observed when EtOH was used as a mobile phase (Figure S34 in the SI). Apparently, EtO^- groups in **2b** were exchanged with MeO^-, which come from MeOH that was used as a mobile phase for the ESI-TOF MS spectrum measurement.

When the same amount of water was added to a MeOH solution of **1**, the intense peak at m/z 869.7 for the ESI-TOF MS spectrum was drastically decreased (Figures S26 and S27 in the SI). This result shows that the cyclic framework is decomposed by H_2O, and thus isolation of **1** by recrystallization from MeOH/H_2O is due to this process.

In summary, a new 2D coordination polymer, **1**, consisting of Cu^{II} ions, bitb, and CO_3^{2-} was prepared and structurally characterized. This coordination polymer was soluble in MeOH and EtOH. Diffusion of the MeOH or EtOH solution of **1** into Et_2O gave new pentanuclear complexes (**2a** and **2b**) with cyclic frameworks, which trapped a kinetically labile $[Cu(CO_3)_2]^{2-}$ unit. Systematic studies using ESI-TOF MS spectra indicate that **1** reconstructs the cyclic framework for **2a**, $[Cu(CO_3)_2 \subset Cu_4(\mu\text{-OMe})_4(bitb)_4]^{2+}$, in MeOH. Although this framework is decomposed by water, recrystallization from MeOH/H_2O yielded **1**, while recrystallization from MeOH/Et_2O afforded **2a**. The further construction of Cu-bitb self-assembled complexes is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, crystallographic data in CIF format, crystal structures, UV−vis and MS spectra, IR spectra, and PXRD patterns of the compounds. 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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