Flexible Hexagonal Tube Framework of a New Nickel Complex Assembled from Intermolecular Hydrogen Bonds

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A new nickel tubular framework compound, $[\mathrm{Ni(ima)_2(MeOH)_2}]\cdot 2\mathrm{MeOH}$ (where ima = 4-imidazoleacetato) has been synthesized, in which the nonmethanolated complex, $[\mathrm{Ni(ima)_2}]$, selectively reacts with methanol to reconstruct the initial porous framework, which can then incorporate other guest molecules.

The synthesis of coordination polymers with flexible channel frameworks has attracted intense attention in the development of new functional materials.[1–3] When isolated, coordination polymers have porous frameworks that generally include guest molecules in their channels. Although many porous coordination polymers do not retain their porous frameworks on removal of the guest molecules, they often reconstruct to form the initial porous framework by reinclusion of the guest molecule on contact.[3] A general schematic drawing showing this reconstruction process, known as Type I behavior, is shown in Figure 1. The initial porous framework usually does not have enough space for further addition of guest molecules, as the channels are already filled with guest molecules. Therefore, reconstruction of a porous framework that has enough channel spaces for other guest molecules is attractive from the viewpoint of a new flexible network system that exhibits a porous function when triggered by a chemical stimulus. However, such dynamic network systems, illustrated as Type II behavior in Figure 1, are still relatively unexplored.

Recently, we found that imidazole-carboxylate type chelates are useful for the synthesis of coordination frameworks connected by NH···O=C intermolecular hydrogen bonds.[4] During further synthetic studies of assembled metal complex systems incorporating imidazole-carboxylate sets, we have prepared $[\mathrm{Ni(ima)_2(MeOH)_2}]\cdot 2\mathrm{MeOH}$ (where ima = 4-imidazoleacetato) (**1**), and the dried, methanol-free amorphous compound $[\mathrm{Ni(ima)_2}]$ (**2**). Single crystal X-ray analysis shows that **1** has a porous structure constructed by hexagonal tubular frameworks that have enough space to incorporate guest molecules. We have found that **2** selectively reacts with methanol to reconstruct **1**, which then can adsorb other guest molecules in the hexagonal channels. This reconstruction system is of the Type II.

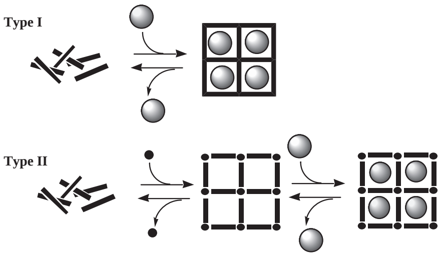

Figure 1. The two types of dynamic coordination networks. The stick assembly on the left-hand side shows the decomposed nonporous framework that is obtained by removal of guest molecules from the original porous framework (illustrated on the right-hand side). In Type I behavior, the original porous structures are reversibly recovered by reinclusion of the guest molecules, in which the guest molecules themselves occupy the channels. In Type II behavior, the reinclusion of the guest molecules reconstructs the initial porous structure that can include additional guest molecules.

Compound **1** was isolated as light-blue-colored columnar crystals by the diffusion of a methanol solution of the sodium salt of ima in an aqueous solution of a nickel perchlorate.[5] Figure 2 shows the assembled structure of **1**. This structure is isostructural to the Co analogue that was reported by Drozdzewski et al.[6] The nickel center exhibits octahedral coordination geometry surrounded by the two ima and two methanol ligands. These monomeric units are connected by two NH···O=C intermolecular hydrogen bonds (N–O = 2.758(3) Å) to yield a one-dimensional (1D) board framework along the *c* axis (Figure 2a). The nature of the intermolecular hydrogen bonds is similar to that of $[\mathrm{Cu(imc)_2}]$.[4] These 1D board frameworks are further connected by OH···O=C intermolecular hydrogen bonds formed between the coordinating methanol molecules and the O=C groups of the ima (O–O = 2.623(3) Å). As a result, a unique tube-assembled framework is created (Figure 2b). The size of the crevices

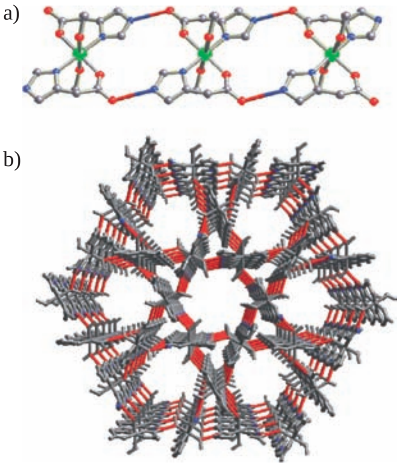

Figure 2. A view of the one-dimensional structure of **1** connected by NH···O=C intermolecular hydrogen bonds (a), and the tube-assembled structure assembled by OH···O=C intermolecular hydrogen bonds (b). The intermolecular hydrogen bonds are denoted by colored lines.

of the board framework, i.e., the 1D chain shown in Figure 2a, is less than 1 Å, indicating the creation of a sterically well-isolated tube framework. Each channel, whose effective size is about $6 \times 6\,\text{Å}^2$ based on the van der Waals radii, incorporates two guest methanol molecules per nickel ion. These methanol molecules, which are not located in the center of the channels but near the channel wall, form hydrogen bonds with the coordinating carboxylate oxygen atoms (O–O = 2.808(4) Å). As a result, **1** has enough space to incorporate further guest molecules in the channels. These tubular channels are connected to each other, as each board is shared between two hexagonal tube channels (Figure 2b). The resulting structure is composed of hexagonal and small trigonal columnar frameworks.

Thermogravimetric (TG) analysis shows that the included and coordinating methanol molecules are observed up until temperatures of 35 and 100 °C, respectively (see supporting information). We prepared the methanol-free dried compound $[\mathrm{Ni(ima)_2}]$ (**2**) by heating **1** at 130 °C under reduced pressure for 2 h. Compound **2** is an amorphous solid that exhibits no X-ray powder diffraction (XRPD) peaks. We studied the reconstruction properties of **2** to form **1** on contact with guest methanol molecules by monitoring the XRPD patterns, and observed that **1** is reconstructed on exposure of **2** to methanol vapor overnight. On the other hand, contact of **2** with water or other general organic solvents, such as ethanol, propanol, acetonitrile, or acetone, vapor does not yield **1** or any other crystalline solid. These experiments show that **2** selectively reacts with methanol to re-form **1**.

The selective reconstruction of the tubular assembled framework of **1** from the amorphous solid **2** in response to methanol exposure prompted us to study the adsorption properties against ethanol of **1** that was reconstructed by the addition of methanol to **2**. The preliminary results are shown in Figure 3, which shows plots of the relative volume of adsorbed ethanol and methanol molecules, which are normalized values against the equivalent and quarter equivalent of **2**, respectively.[7] The normalized volume of methanol adsorption reflects the rate of re-formed **1** in the reaction, and the volume of ethanol absorption reflects the molar rate of adsorbed ethanol to reconstructed **1**. Compound **2** and the equivalent volume of ethanol were immersed in *m*-xylene at 23 °C for 24 h. Even after a period of 24 h after mixing, no adsorption of ethanol was observed. After a period of 24 h, four equivalents of methanol to **2** were added to the reaction media. It was observed that the adsorption of methanol and ethanol began 1 h and 3 h, respectively, after the addition of methanol (see insert in Figure 3). The adsorption of methanol before the adsorption of ethanol could be due to an initial reaction of **2** with methanol, followed by an adsorption of ethanol in the reconstructed channels of **1**. This result demonstrates that **2** has a methanol-responsive porous function in connection with the reconstruction of the tubular framework assembly of **1**. After a period of 96 h from the addition of methanol, up to 40% of the methanol was absorbed, implying that 40% of **2** had transformed to **1** during this time. For the same period, 30% of the ethanol had been adsorbed, implying that **1** had adsorbed about 75% of the ethanol present. The slow reaction speed is most likely due to the difficulty of the methanol molecules gaining access to the center of the crystalline samples. Further studies on this functional system are currently in progress.

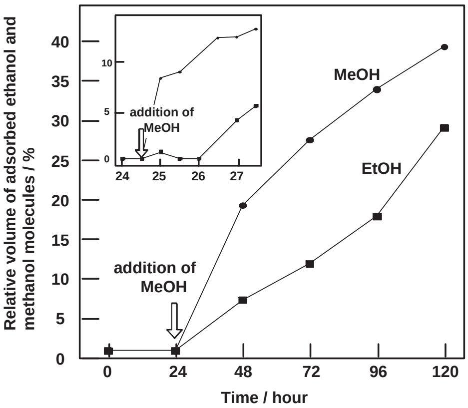

Figure 3. Plots of the relative volumes of methanol (circle) and ethanol (square) molecules normalized against equivalent and quarter equivalent of **2**.

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5 Crystal data: $M_r = 437.08$, trigonal, space group $R\bar{3}$ (No. 148), $a = b = 26.575(2)$, $c = 8.3321(8)$ Å, $V = 5096.1(6)\,\text{Å}^3$, $Z = 9$, $\mu(\text{Mo K}\alpha) = 0.898\,\text{mm}^{-1}$, $T = 293$ K, $R = 0.055$, w$R = 0.067$ for 2627 unique reflections ($R_{\text{int}} = 0.037$) with $I > 2\sigma(I)$ and 124 parameters. Highest electron density $0.54\,\text{e}\cdot\text{Å}^{-3}$. The data collection was performed on a Rigaku-CCD Mercury system. The structure was solved by direct methods using SIR-98. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms for the organic ligand were included but not refined. CCDC252033.

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7 Adsorption experiments. Compound **2** (16 mg, 0.05 mmol) was immersed in *m*-xylene (2.0 mL) containing the equivalent amount of ethanol (2.9 µL, 0.05 mmol). Four equivalents of methanol (8.0 µL, 0.20 mmol) were added to the solution after 24 h. The volume of adsorbed methanol and ethanol molecules was monitored using gas chromatography (GC). All the experiments were carried out at 23 °C.

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