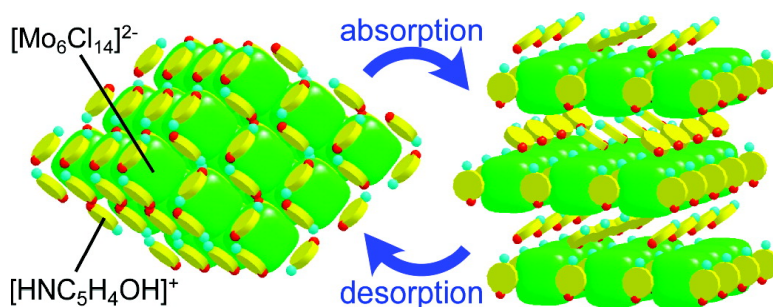Communication

Reversible Emergence of a Self-Assembled Layered Structure From Three-Dimensional Isotropic Ionic Crystal of a Cluster Compound (4-HNCHOH)MoCl Driven By Absorption of Water and Alcohols

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Reversible Emergence of a Self-Assembled Layered Structure From Three-Dimensional Isotropic Ionic Crystal of a Cluster Compound (4-HNC5H4OH)2Mo6Cl14 Driven By Absorption of Water and Alcohols

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Design of three-dimensional architectures at the nanometer scale is one of the current topics in materials chemistry. Porous coordination polymers or metal organic frameworks (MOF) provide three-dimensional structures constructed from a variety of molecular building blocks.[1–7] Ionic crystalline compounds can also form nanometer scale 3D architectures when they are composed of molecules with sizes of nanometer scale.[8–13] Ionic crystals comprising anionic and cationic hexanuclear clusters,[10] organic salts of hexanuclear compounds,[11] and salts of polyoxometalates with organometallic cations[12,13] were studied. Since Coulomb interaction is isotropic, the structures of these compounds are usually isotropic. Exceptions are found when the constituent molecules have anisotropic shapes and/or anisotropic interactions such as coordination and hydrogen bonds other than Coulomb interaction.[13]

Here we report a structural transformation where a "layered" structure emerges reversibly from an isotropic ionic crystal. Hydroxypyridinium salt of hexamolybdenumchloride cluster (4-HNC5H4OH)2Mo6Cl14 changes to a layered structure of which the interlayer spaces are filled with the absorbed molecules. This transformation is unusual and interesting because the salts comprised symmetric $[Mo_6Cl_{14}]^{2-}$ cluster anions. The "layers" are formed through Coulomb interactions. The structure changed reversibly between the layered and isotropic ones by absorption and removal of the guest molecules. These results highlight a novel chemistry of nanometer scale architectures of ionic crystals.

Figure 1a is a schematic illustration of the structural transformation. The salt with no absorbed molecules forms a monoclinic structure in which all hydroxypyridinium cationic molecules occupy structurally equivalent sites. Hydroxypyridinium cations are closely surrounded by cluster anions. When the crystal absorbs guest molecules to form the layered structure, the hydroxypyridinium cations are divided into two kinds of sites and play different roles in the structure: One is located in the interlayer spaces. The hydroxypyridinium cation at the other type of site attracts four cluster anions around it through Coulomb interactions to form two-dimensional arrays of the cluster anions (Figure 1a, right).

Figure 1b shows the crystal structure of the water-absorbed layered phase (4-HNC5H4OH)2Mo6Cl14·6 H2O determined by single-crystal X-ray structural analysis. The hydroxyl (OH) and NH groups of hydroxypyridinium cations in the [4-HNC5H4OH·Mo6Cl14]⁻ layers are directed toward the interlayer spaces. Hydroxypyridinium cations in the interlayer spaces bridge the two [4-HNC5H4OH·Mo6Cl14]⁻ layers. The NH group of hydroxypyridinium in the interlayer spaces is in contact with the terminal Cl atom (Cl−N distance = 0.323 nm), where the Cl has a large negative charge in the cluster anion. The N−O distances of the two different hydroxypyridinium are 0.353 and 0.335 nm, which are slightly longer than the sum of their van der Waals radii (0.307 nm) and are much longer than a typical hydrogen bond length
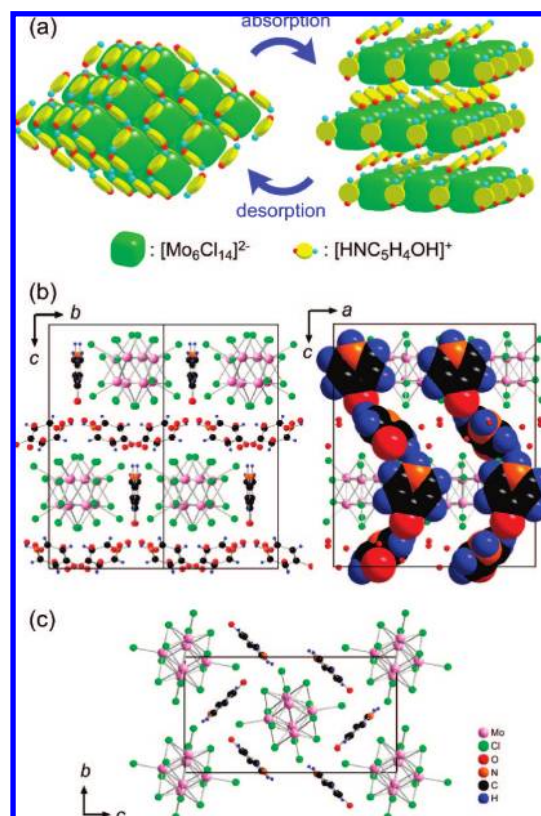

Figure 1. (a) Schematic illustration of the reversible structural change between layered structure and three-dimensional structure of the crystal. Absorbed molecules are omitted for clarity. In the three-dimensional structure, hydroxypyridinium cation has only one equivalent site. (b) Crystal structure of (HNC5H4OH)2Mo6Cl14·6 H2O. (c) Crystal structure of (HNC5H4OH)2Mo6Cl14 dehydrated phase. Hydrogen atoms of water and hydroxyl groups are omitted.

(0.28−0.29 nm), indicating they are interacting through Coulomb forces between the positively charged hydroxypyridinium group and the negatively charged hydroxyl oxygen, rather than direct hydrogen bonding. Figure 1c shows the structure of the dehydrated phase, which adopts monoclinic densely packed structure.

The reversible structural transformation was confirmed by in situ powder X-ray diffraction (Supporting Information Figure S1). The hydrated phase gave a powder pattern coinciding with the simulation using the result of single-crystal structural analysis. When the sample was evacuated at room temperature, the powder diffraction pattern changed in 30 min to that of the monoclinic dehydrated phase (Figure 1c). The powder pattern coincided with the simulated pattern from single-crystal structural data of the dehydrated phase. By contacting with water vapor (2.4 kPa), the powder diffraction
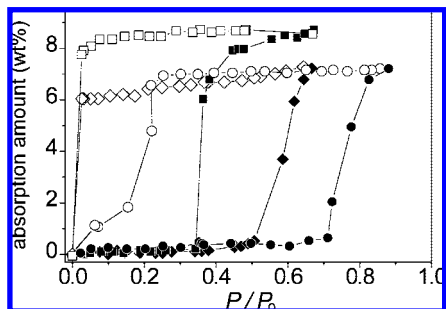
Figure 2. Absorption and desorption of water and some alcohol vapor on $(HNC_5H_4OH)_2Mo_6Cl_{14}$ at 288 K. Circles, water; squares, methanol; diamonds, ethanol. Solid and open symbols represent absorption and desorption data, respectively.

pattern was restored to that of the initial hydrated phase. Further repetition of evacuation and introduction of water vapor brought about the same structural transformation.

Water absorption behaviors of this crystal were also investigated by weight change measurements. At first, evacuation of the hydrated crystal brought about a weight decrease of 7.1%, which corresponds to 5.4 water molecules per 1 cluster anion. This means that most of the water molecules are removed from the hydrated phase by evacuation at 288 K. As shown in Figure 2 (open and solid circles), contact of the dehydrated crystal with water vapor (relative pressure $P/P_0 \sim 0.75$) brought about the reversible absorption of water. With decreasing water vapor pressure, the absorbed water was removed reversibly.

This crystal showed similar behavior upon methanol absorption–desorption cycles. The structural transformation between the layered structure and the three-dimensional salts was confirmed to be reversible by in situ powder X-ray diffraction and weight measurements. As shown in Figure 2 (solid and open squares), the crystal after evacuation at room temperature absorbs methanol vapor when it was contacted with methanol vapor of $P/P_0 > 0.4$. The absorption amount saturated at 8.7 wt %. It was confirmed that evacuation of the methanol-absorbed phase at room temperature resumed the crystal weight reversibly to the value before the absorption. As shown in the Supporting Information (Figure S1d), in situ powder X-ray diffraction demonstrated that methanol absorption at $P/P_0 \sim 0.5$ also transformed the crystal structure to a layered one, with an interlayer distance slightly wider than the hydrated structure. The crystal absorbed ethanol, as well. The transformation of the layered structure (Figure S1e) and the reversibility of the structure were confirmed also for ethanol by the in situ powder X-ray diffraction and weight measurement.

As for the reason for the anisotropic expansion of the ionic crystal driven by the molecular absorption, one should note the following points. Upon water absorption, the volume of the crystal increased by up to 15.5%. This brings about an increase in the Coulomb energy (i.e., Madelung potential) of the host crystal. The energy increase upon the expansion of the crystal is reduced by adopting

the configuration of the hydroxypyridinium molecule, where the positively and negatively charged parts were located closely to each other in the structure. The energy increase can be compensated for by the absorption energy of the guest molecules to stabilize the layered structure. The quantitative calculation on this point would be an interesting subject for future study.

In conclusion, we found anisotropic structural expansion of an ionic molecular crystal $(4\text{-}HNC_5H_4OH)_2Mo_6Cl_{14}$ driven by absorption of water and alcohols, which is unusual for isotropic three-dimensional molecular ionic crystals. The drastic changes between the layered and three-dimensional structures were reversible. This study highlights a novel chemistry of nanometer scale anisotropic architecture of ionic crystal composed of nanosized inorganic molecules.

Supporting Information Available: In situ powder X-ray diffraction patterns upon molecular absorption and desorption, experimental methods, and CIF files of single-crystal X-ray structural investigations of $(HNC_5H_4OH)_2Mo_6Cl_{14}\cdot6\ H_2O$ and $(HNC_5H_4OH)_2Mo_6Cl_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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