Form 3

Abstract of Thesis

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Title	Characteristics of Porous Crystalline Frameworks Composed of Nonanuclear $Au^{I}_{6}Cd^{II}_{3}$ Complex Molecules ($Au^{I}_{6}Cd^{II}_{3}$九核錯分子からなる多孔質結晶性フレームワークの特性)

Abstract of Thesis

Nowadays, the creation of porous materials is one of the trending topics in scientific fields, especially in material science and chemistry. Generally, the attractiveness of porous materials is caused by their characters, such as permeability for inducing guest molecules, high energy absorption, and large specific surface area. Since the first porous crystalline material that originated from the discovery of synthetic zeolites, hybrid materials composed of organic linkers and metal ions were developed to produce extended frameworks such as metal-organic framework (MOF). Recently, single-crystal X-ray diffraction (SCXRD) technique has been used not only for the structural determination but also for the investigation of a new insight in specific chemical reactions such as post synthetic modification (PSM), single-crystal-to-single-crystal (SCSC) transformation, and crystalline sponge. In some cases, porous crystalline frameworks can not maintain the crystallinity after being exposed to an external stimulus, which makes it impossible to use SCXRD.

In this doctoral thesis, the characteristics of the porous crystalline framework of $[\{Au^{I}_{6}Cd^{II}_{3}(tdme)_{2}(D\text{-}pen)_{6}\}_{12}Cd_{4}Na_{4}](NO_{3})_{12}$ (**1_{CdNa}**) composed of the nonanuclear $Au^{I}_{6}Cd^{II}_{3}$ complex cations was investigated. The investigation scope is not finite to determine the crystal structure. Some specific phenomena for the crystalline porous material in the course of chemical reactions (*e.g.*, metal exchange) under the control of temperature were also investigated in detail based on X-ray crystallographic evidences, together with related characterizations. The topics of this doctoral thesis are divided into three main chapters.

In Chapter II, the SCSC transmetallation reaction of **1_{CdNa}** was investigated. By soaking single crystals of **1_{CdNa}** in an aqueous $Cu(NO_{3})_{2}$, the isostructural cage-of-cage of $[\{Au^{I}_{6}Cu^{II}_{3}(tdme)_{2}(D\text{-}pen)_{6}\}_{12}Cu_{8}](NO_{3})_{16}$ (**1_{Cu}**) was produced within 30 minutes as a kinetic product. Single crystal X-ray structure analysis of **1_{Cu}** revealed that Cd^{II}-to-Cu^{II} metal replacement proceeded not only in the Na^{I}/Cd^{II} linker sites but also in the three Cd metal centers in the nonanuclear $Au^{I}_{6}Cd^{II}_{3}$ complex cations. The metal substitution of Cd^{II} centers by Cu^{II} centers afforded the coordination geometry transformation from $N_{2}O_{2}S_{2}$ octahedral to $N_{2}S_{2}$ square planar or $N_{2}OS_{2}$ square pyramidal geometries. Further soaking crystals for 3 days generated the more stable crystals of $[\{Au^{I}_{6}Cu^{II}_{3}(tdme)_{2}(D\text{-}pen)_{6}\}_{12}Cu_{8}]_{0.5}[\{Au^{I}_{6}Cu^{II}_{6}(tdme)_{2}(D\text{-}pen)_{6}(H_{2}O)_{6}\}_{12}Cu_{8}]_{0.5}(NO_{3})_{52}$ (**$1'_{Cu}$**). Compound **$1'_{Cu}$** contained two kinds of cage-of-cages, **A** and **B**. Type **A** has the same cage-of-cage structure as **1_{Cu}** with chemical formula of $[Au^{I}_{6}Cu^{II}_{3}(tdme)_{2}(D\text{-}pen)_{6}]$. Type **B** has a structure slightly different from type **A**; three additional Cu^{II} exist on the outer position and each binds to a flipping D-pen ligand and two water molecules to give the chemical formula of $[Au^{I}_{6}Cu^{II}_{6}(tdme)_{2}(D\text{-}pen)_{6}(H_{2}O)_{6}]^{6+}$. Hydrogen-bonding interactions between cage-of-cage **A** and **B** are formed and provides a more robust framework, which is suitable for using it as a crystalline flask. It was found that **$1'_{Cu}$** underwent an anion exchange reaction of NO_{3}^{-} with MoO_{4}^{2-} to generate compound **2**. In addition, a condensation of oxomolybdate species in **2** was induced by adjusting the pH to around 7 and 1 to form polyoxomolybdates, $Mo_{7}O_{24}^{6-}$ (**3**) and β-type $Mo_{8}O_{26}^{4-}$ (**4**), respectively, demonstrating an availability of **$1'_{Cu}$** as a crystalline flask.

In Chapter III, the SCSC transmetallation reaction of **1_{CdNa}** with aqueous $Co(NO_{3})_{2}$, which proceeds in a moderate speed, was investigated by SCXRD snapshot technique. By soaking single crystals of **1_{CdNa}** in an aqueous $Co(NO_{3})_{2}$, the isostructural cage-of-cage of $[\{Au^{I}_{6}Co^{II}_{3}(tdme)_{2}(D\text{-}pen)_{6}\}_{12}Co_{8}](NO_{3})_{16}$ (**1_{Co}**) was obtained after 6 days with

retaining the single crystallinity. The crystal structure of $\mathbf{1}_{Co}$ showed the metal replacement of Cd^{II} by Co^{II} proceeded at all Na^{I}/Cd^{II} linkers and Cd^{II} metal centers in nonanuclear $Au^{I}_{6}Cd^{II}_{3}$ complexes. In contrast to Cd^{II}-to-Cu^{II} metal replacement, the coordination geometry remained unchanged after the transmetallation, adopting an $N_2O_2S_2$-octahedral geometry. The moderate rate of the SCSC transmetallation reaction enabled to observe the intermediate state by SCXRD snapshot technique. Based on the site occupancies on the M1-M5 sites of the intermediate states, two intermediate states, $[\{Au^{I}_{6}Cd^{II}_{3}(tdme)_2(D\text{-}pen)_6\}_{12}Cd_4Co_4](NO_3)_{16}$ ($\mathbf{1}_{CdCo}^{1h}$) and $[\{Au^{I}_{6}Cd^{II}Co^{II}_{2}(tdme)2(D\text{-}pen)_6\}_{12}Cd_4Co_4](NO_3)_{16}$($\mathbf{1}_{CdCo}^{1d}$), were found during the SCSC transmetallation reaction of $\mathbf{1}_{CdNa}$, the crystals of which were soaked in a $Co(NO_3)_2$ aqueous solution. Porous cavities in $\mathbf{1}_{CdNa}$ allows a smooth diffusion of Co species to induce the homogeneous Cd^{II}-to-Co^{II} transmetallation event. This is the first example of the observation of intermediate states in the SCSC transmetallation reaction by X-ray crystallography evidence.

In Chapter IV, the formation of water cluster inside $\mathbf{1}_{CdNa}$ and its phase transition were deeply studied. In $\mathbf{1}_{CdNa}$, there exist four kinds of cavity spaces that are occupied by solvated water molecules owing to the pseudo-primitive cubic packing of cage-of-cage complex cations. It was found that, by cooling a single crystal of $\mathbf{1}_{CdNa}$ rapidly, solvated water molecules in the cavity A were arranged in a specific pattern corresponding to that of ice I_c, which is difficult to be formed generally. In the cavity A, a total of 143 water molecules were found, which form a water cluster with an ice I_c arrangement. Although a large number of studies on the formation of ice I_c in porous materials was reported, this is the first successful finding and direct evidence of the formation of an ice I_c arrangement of water cluster by SCXRD technique. Here, three important structural factors are proposed, i) spherical shape, ii) large enough space, iii) symmetry of the cavity. Especially, the molecular arrangement in 432 crystallographic point group is essential for the formation of ice I_c arrangement in 23 crystallographic point group. In addition, from the screening of the temperature control, it was proposed that the cooling rate is crucial for the formation of an ice I_c arrangement of water cluster. While rapid cooling afforded well-ordered ice I_c arrangement, slow cooling gave less-ordered arrangement presumably owing to the difference between homogeneous and heterogeneous thermal conductions. By elevating the temperature, a phase transition was observed at 200 K from a drastic volume reduction. At the same time, SCXRD observed directly the disappearance of the water cluster with an ice I_c arrangement. The appearance of an endothermic peak in the DSC profile supported that the phase transition is a pseudo-melting from ice I_c to disordered water molecules. This is also the first observation of the phase transition from ice I_c to another phase of water cluster not via ice I_h. After the observation of the pseudo-melting, it was demonstrated that the arrangement of water molecules can be reverted back to ice I_c by cooling.

In conclusion, the structural changes in the porous single crystals of $\mathbf{1}_{CdNa}$ cage-of-cage complex, i) the transmetallation (Cd^{II}-to-Cu^{II} and Cd^{II}-to-Co^{II}) ii) the condensation of oxomolybdates to form polyoxometalates, iii) the formation of ice I_c water cluster and its pseudo-melting were observed in this study. These phenomena found in this study are all distinct from those in non-porous materials because of the usage of porous spaces in the crystalline materials. This study demonstrated the importance of the design of highly symmetrical porous spaces that are large enough, providing a significant direction to develop porous materials for the study of chemical reactions and unique phenomena in the solid state.

様式 7

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

細孔物質は、ゲスト分子の取り込みや解離があり、その界面の反応が興味深く、反応の表面積も大きい等の特性を有するため、それらを利用した高機能性材料を開発する材料化学の分野で有望視されている。多孔性材料として先行するゼオライトに続いて、金属原子と架橋有機分子から成る金属−有機構造体（MOF: Metal-Organic Frameworks）が開発され、近年においてはその細孔の分子構造の解明のみならず、外部刺激による細孔物質全体の構造変化や細孔内のゲスト分子の反応挙動が単結晶 X 線構造解析により検討されている。すなわち、結晶性の固体状態における①はじめの結晶相とは異なる結晶相への変化や、②細孔内の分子変換と修飾、および③ゲスト分子の構造解析を行う結晶スポンジ法などである。本論文では新規の結晶性 MOF として、D-penicillamine (D-H_2pen)と 1,1,1-tris(diphenylphosphinomethyl)ethane を用いた九核 Au_6Cd_3 錯体を開発し、その多孔質結晶性フレームワークについて化学的特性の精密な評価を行い、以下の Chapter II, III, IV にその詳細が述べられている。

Chapter II では、九核 Au_6Cd_3 錯体を有する多孔質結晶性フレームワークに対して、外部刺激として銅(II)イオン（Cu^{2+}）の添加を行い、①はじめの結晶相とは異なる結晶相への変化を、単結晶 X 線構造解析をはじめとする各種の手法により追跡した。同様に外部刺激としてモリブデン酸イオン（MoO_4^{2-}）の添加を行い、さらに反応条件を整えると細孔内部でポリオキソメタレートである $Mo_7O_{24}^{6-}$や $Mo_8O_{26}^{4-}$が生成することを示した。以上の成果により、分子性固体の細孔物質におけるカチオンやアニオンの交換による①結晶相の変化だけでなく、それを利用して②細孔内の分子変換と修飾の現象を明確に見出した。

Chapter III では、九核 Au_6Cd_3 錯体を有する多孔質結晶性フレームワークに対して、外部刺激としてコバルト(II)イオン（Co^{2+}）の添加を行い、①はじめの結晶相とは異なる結晶相への変化を各種の手法により追跡した。このカチオン交換反応が二価金属イオンに特有の配位子交換反応の速度に依存することを利用している。このCo^{2+}添加の系においては、結晶相の変化が段階的な中間体種を経由して進むことを、単結晶 X 線構造解析により分子構造のレベルで明確にした。これは MOF において初めての例である。

Chapter IV では、九核 Au_6Cd_3 錯体を有する多孔質結晶性フレームワークに対して、外部刺激として温度変化を行い、①はじめの結晶相とは異なる結晶相への変化を、単結晶 X 線構造解析や熱化学的測定をはじめとする各種の手法により検討した。それにより、急速冷却した場合に細孔内に取り込まれた多数の水分子が”Cubic packing”と呼ばれる水の結晶相としては特異な水分子クラスターを形成することが分かった。これは多孔質結晶性フレームワークの持つ細孔を利用して、③ゲスト分子の構造解析を行う結晶スポンジ法であり、その成果は狭小空間で形成した水クラスターの構造に関する重要な知見である。

以上、本研究では、九核 Au_6Cd_3 錯体を有する多孔質結晶性フレームワークを用いて、各種の外部刺激に対する応答を系統的に検討し、この結晶性 MOF の外部応答の過程と特性に関して多くの知見を得ている。これらの成果は、多孔性材料の分野の基礎研究として新規かつ重要な成果であると評価できる。したがって、本論文は博士（理学）の学位論文として十分な内容を有すると認める。