Title	Construction of Metallosupramolecular Frameworks Based on an Anionic Pentanuclear Complex with D-Penicillaminate
Author(s)	Surinwong, Sireenart
Citation	大阪大学, 2016, 博士論文
Version Type	VoR
URL	https://doi.org/10.18910/59531
rights	
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Form 3

Abstract of Thesis

Name	(Sireenart Surinwong)
Title	Construction of Metallosupramolecular Frameworks Based on an Anionic Pentanuclear Complex with D-Penicillaminate (D-ペニシラミンをもつアニオン性五核錯体をベースとする金属超分子フレームワークの構築)

Abstract of Thesis

Creation of metallosupramolecular frameworks has received continuous attention owing to their remarkable structures and properties. Attempts to construct metallosupramolecular frameworks possessing high stability and flexibility, in which merits from both coordination and hydrogen bonds are utilized, has been made in order to fulfil the requirement of further applications. For this purpose, the use of multinuclear complexes having multiple carboxylate groups as a molecular building block is one of the potential ways because multinuclear building units are able to provide not only expanded voids but also additional functions to the metallosupramolecular frameworks. Recently, an anionic rod-shaped $Co^{III}_{2}Au^{I}_{3}$ pentanuclear complex having six carboxylate arms, $(\Lambda)_2$-$[Co_2Au_3(\text{D-pen-}N,S)_6]^{3-}$ ($[1]^{3-}$; D-H_2pen = D-penicillamine), was prepared by Konno *et al.* This anionic pentanuclear complex was crystallized with Na^+ cations, constructing a metallosupramolecular framework with a well-fixed conformation with retention of the structure of the chiral pentanuclear building block. Thus, the $Co^{III}_{2}Au^{I}_{3}$ pentanuclear complex has a potential to construct a variety of metallosupramolecular frameworks.

In this thesis, the construction of diverse metallosupramolecular frameworks by employing an anionic $[1]^{3-}$ as a molecular building block in a combination with aqua metal cations, $[M(H_2O)_n]^{2+}$ ($M = Co^{2+}$, Ni^{2+}, Mn^{2+}, Zn^{2+}), was investigated. It has been expected that the formation of both coordination and hydrogen bonds is feasible. Diverse intermolecular interactions potentially create novel metallosupramolecular frameworks, which are restricted for general metallosupramolecular frameworks produced by using common ligands.

Firstly, a kinetic synthesis of metallosupramolecular frameworks involving $[1]^{3-}$ and $[Co(H_2O)_n]^{2+}$ was revealed. Impressively, a highly porous metallosupramolecular framework, $[Co(H_2O)_6]_3[Co_2Au_3(\text{D-pen-}N,S)_6]_2$ (**2a**), with a porosity of 80% was produced. In addition, **2a** was stepwise structural converted to thermodynamically more stable products with a denser framework, $[Co(H_2O)_6]_2[\{Co(H_2O)_4\}\{Co_2Au_3(\text{D-pen-}N,S)_6\}_2]$ (**2b**; porosity 60%) and $[\{Co(H_2O)_4\}_3\{Co_2Au_3(\text{D-pen-}N,S)_6\}_2]$ (**2c**; porosity 30%).

In order to study about the effects of different metal ions on the construction of metallosupramolecular frameworks, the use of other metals was investigated. The combination of $[1]^{3-}$ and $[Ni(H_2O)_n]^{2+}$ or $[Mn(H_2O)_n]^{2+}$ gave an isostructural pair of porous ionic crystals (**3a** and **4a**), followed by structural conversions. Owing to the nature of metal ions, the structural conversion phenomena occurred in the Mn^{II} complex were found to be different from those in the Co^{II} and Ni^{II} complexes, leading to different frameworks with different porosities, $[\{Ni(H_2O)_4\}_3\{Co_2Au_3(\text{D-pen-}N,S)_6\}_2]$ (**3b**; porosity 30%) and $[\{Mn(H_2O)_4\}\{Co_2Au_3(\text{D-Hpen-}N,S)(\text{D-pen-}N,S)_5\}]$ (**4b**; porosity 13%).

Furthermore, the effects of pH on the construction of metallosupramolecular frameworks were investigated by means of the reactions of $[1]^{3-}$ with $[Zn(H_2O)_n]^{2+}$ in sodium acetate buffer solutions. It was found that the production of two different frameworks, $[\{Zn(H_2O)_4\}\{Co_2Au_3(\text{D-Hpen-}N,S)(\text{D-pen-}N,S)_5\}]$ (**5a**) and $Na_9[\{Zn(OAc)_2\}\{Co_2Au_3(\text{D-pen-}N,S)_6\}_2][Co_2Au_3(\text{D-pen-}N,S)_6]$ (**5b**), with remarkably different porosities was successfully controlled only by a slight pH change.

Finally, this study demonstrated an expanded methodology for the construction of novel metallosupramolecular frameworks by using the rod-shaped heterometallic multinuclear complex that offers multiple carboxylate arms as a molecular building block, in combination with aqua metal cations. Thanks to the feasible utilization of both coordination and hydrogen bonds, a series of unique metallosupramolecular frameworks illustrating high flexibility and stability were created, in which the diversities from a dense framework to a highly porous framework are controlled by kinetics, metal-ion types, and solution pH.

様式 7

論文審査の結果の要旨及び担当者

氏　名　（　SURINWONG, SIREENART　）

論文審査担当者		（職）	氏　名
	主 査	教授	今野 巧
	副 査	教授	船橋 靖博
	副 査	教授	吉村 崇

論文審査の結果の要旨

本論文は、D-ペニシラミンをもつアニオン性硫黄架橋五核錯体とアクア金属イオンを組み合わせることにより、新規な金属超分子フレームワークを構築し、それらの構造を単結晶 X 線解析により決定するとともに、金属超分子フレームワーク特有の諸性質を明らかにしたものである。本研究により、アクアコバルト(III)イオンとの組み合わせにより、間隙率 80%の超分子フレームワークをもつイオン性結晶の合成に成功するとともに、この結晶が溶液中で間隙率 60%、さらには間隙率 30%のフレームワークをもつ結晶へと変換されることを見出している。また、形成される超分子フレームワークの安定性や構造が用いるアクア金属イオン種やわずかな pH 変化によって制御可能であることなど、構造制御に関する重要な知見を得るとともに、選択的な小分子吸着特性を見出している。これらの成果は、多核金属錯体をベーストする超分子フレームワークの合成化学および構造化学の今後の進展に対して、基礎的かつ重要な知見を与えるものである。よって、本論文は博士（理学）の学位論文として十分価値あるものと認める。