

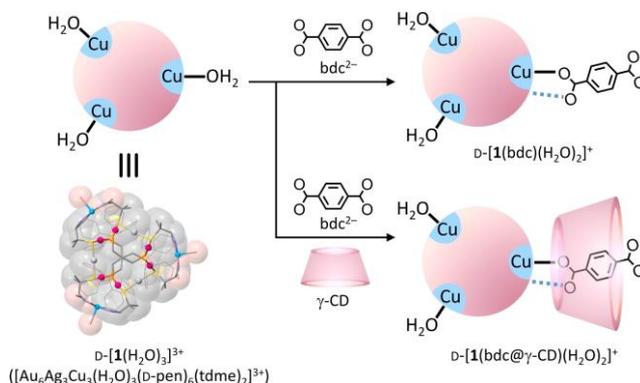
A Pseudorotaxane Structure with γ -Cyclodextrin Controlled by Chiral Recognition of an $\text{Au}^{\text{I}}_6\text{Ag}^{\text{I}}_3\text{Cu}^{\text{II}}_3$ Molecular Cap

(¹Graduate School of Science, Osaka University) ○Tatsuhiro Kojima,¹ Hiroto Takeda,¹ Naoto Kuwamura,¹ Takumi Konno¹

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Pseudorotaxane is a well-known supramolecule in which a macrocyclic molecular ring is threaded by a rod-shaped molecular axle, with its terminal position connected to a bulky molecular cap. The use of cyclodextrins (CDs) as molecular rings has been a target of intensive studies in recent decades because of their versatile molecular recognition abilities. Although the evaluation of intermolecular interactions between ring and axle molecules is essential to understand molecular recognition, most previous studies on pseudorotaxanes containing CDs as a molecular ring have been performed mainly via NMR spectroscopy in solution rather than X-ray crystallography in the solid state, and reports on the X-ray crystal structures of this class of supramolecules are scarce. In this presentation, we report a pseudorotaxane system with γ -CD controlled by chiral recognition of $[\text{Au}_6\text{Ag}_3\text{Cu}_3(\text{H}_2\text{O})_3(\text{D-pen})_6(\text{tdme})_2]^{3+}$ ($\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$; pen^{2-} = penicillamate, tdme = 1,1,1-tris(diphenylphosphinomethyl)ethane), the structure of which was established by single-crystal X-ray crystallography.¹

Soaking crystals of $\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$ in aqueous Na_2bdc (bdc^{2-} = 1,4-benzenedicarboxylate) yielded crystals containing $\text{D-}[\mathbf{1}(\text{bdc})(\text{H}_2\text{O})_2]^+$ due to the replacement of a terminal aqua ligand in $\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$ by a monodentate bdc^{2-} ligand. When γ -CD was added to aqueous Na_2bdc , $\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$ was transformed to $\text{D-}[\mathbf{1}(\text{bdc}@-\gamma\text{-CD})(\text{H}_2\text{O})_2]^+$, where a γ -CD ring was threaded by a bdc^{2-} molecule to construct a pseudorotaxane structure. While the use of dicarboxylates with an aliphatic carbon chain instead of bdc^{2-} afforded analogous pseudorotaxanes, such pseudorotaxane species were not formed when crystals of $[\text{Au}_6\text{Ag}_3\text{Cu}_3(\text{H}_2\text{O})_3(\text{L-pen})_6(\text{tdme})_2]^{3+}$ ($\text{L-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$) were soaked in aqueous Na_2bdc and γ -CD, affording only crystals containing $\text{L-}[\mathbf{1}(\text{bdc})(\text{H}_2\text{O})_2]^+$.



1) T. Kojima, H. Takeda, N. Kuwamura, T. Konno, *Chem. Eur. J.* **2021**, *27*, 15981.