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A Pseudorotaxane System Containing γ-Cyclodextrin Formed via Chiral Recognition with an $Au^{I}_{6}Ag^{I}_{3}Cu^{II}_{3}$ Molecular Cap

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Dedication ((optional))

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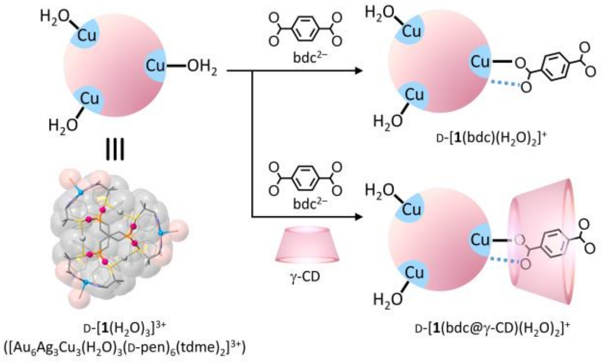
Abstract: Solvent-mediated crystal-to-crystal transformations of $[Au_6Ag_3Cu_3(H_2O)_3(\text{D-pen})_6(tdme)_2]^{3+}$ (D-$[\mathbf{1}(H_2O)_3]^{3+}$; pen^{2-} = penicillaminate, tdme = 1,1,1-tris(diphenylphosphinomethyl)ethane) to form unique supramolecular species are reported. Soaking crystals of D-$[\mathbf{1}(H_2O)_3]^{3+}$ in aqueous Na_2bdc (bdc^{2-} = 1,4-benzenedicarboxylate) yielded crystals containing D-$[\mathbf{1}(bdc)(H_2O)_2]^{+}$ due to the replacement of a terminal aqua ligand in D-$[\mathbf{1}(H_2O)_3]^{3+}$ by a monodentate bdc^{2-} ligand. When γ-cyclodextrin (γ-CD) was added to aqueous Na_2bdc, D-$[\mathbf{1}(H_2O)_3]^{3+}$ was transformed to D-$[\mathbf{1}(bdc@\gamma\text{-CD})(H_2O)_2]^{+}$, 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 $[Au_6Ag_3Cu_3(H_2O)_3(\text{L-pen})_6(tdme)_2]^{3+}$ (L-$[\mathbf{1}(H_2O)_3]^{3+}$) enantiomeric to D-$[\mathbf{1}(H_2O)_3]^{3+}$ were soaked in aqueous Na_2bdc and γ-CD, affording only crystals containing L-$[\mathbf{1}(bdc)(H_2O)_2]^{+}$.



Scheme 1. Synthetic routes of D-$[\mathbf{1}(bdc)(H_2O)_2]^{+}$ and D-$[\mathbf{1}(bdc@\gamma\text{-CD})(H_2O)_2]^{+}$ from D-$[\mathbf{1}(H_2O)_3]^{3+}$ via solvent-mediated structural transformations. Colors: red, Au; blue, Cu; gray, Ag; pink ring, γ-CD.

Introduction

Rotaxanes and pseudorotaxanes are well-known supramolecules in which a macrocyclic molecular ring is threaded by a rod-shaped molecular axle, with its terminal position(s) connected to bulky molecular cap(s).[1] While a variety of macrocyclic molecules have been employed as molecular rings for the creation of rotaxane and pseudorotaxane architectures,[2] the use of cyclodextrins (CDs) as molecular rings has been a target of intensive studies in recent decades[3] because of their versatile molecular recognition abilities[4] that lead to a wide range of applications, such as molecular motors,[5] drug delivery,[6] and hydrogel systems.[7] Although the evaluation of intermolecular interactions between ring and axle molecules is essential to understand molecular recognition, most previous studies on rotaxanes and 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,[8] and reports on the X-ray crystal structures of this class of supramolecules are scarce.[9] In particular, only one crystal structure containing γ-CD as a molecular ring has been reported[10] because of the large cavity size of γ-CD, which hinders the formation of effective intermolecular interactions with the axle molecule.

Here, we report a pseudorotaxane system containing γ-CD as a molecular ring, the structure of which was established by single-crystal X-ray crystallography. This system was prepared from a chiral $Au^{I}_{6}Ag^{I}_{3}Cu^{II}_{3}$ complex with D-penicillaminate, D-$[\mathbf{1}(H_2O)_3]^{3+}$ = $[Au_6Ag_3Cu_3(H_2O)_3(\text{D-pen})_6(tdme)_2]^{3+}$ (tdme = 1,1,1-tris(diphenylphosphinomethyl)ethane, D-pen = D-penicillaminate),[11] in combination with dicarboxylate and γ-CD via solvent-mediated crystal-to-crystal transformations (Scheme 1). We found that the γ-CD ring was threaded by a molecular axle of dicarboxylate attached to a molecular cap of an $Au^{I}_{6}Ag^{I}_{3}Cu^{II}_{3}$ complex in a largely distorted manner such that the smaller opening, rather than the larger opening, unusually interacts with the $Au^{I}_{6}Ag^{I}_{3}Cu^{II}_{3}$ molecular cap. Notably, the use of the corresponding $Au^{I}_{6}Ag^{I}_{3}Cu^{II}_{3}$ complex with L-penicillaminate (L-$[\mathbf{1}(H_2O)_3]^{3+}$) did not afford an analogous pseudorotaxane species without including γ-CD in the structure. This is the first example of a structurally characterized pseudorotaxane system prepared via chiral recognition between a γ-CD ring and a chiral molecular cap.

Results and Discussion

Transformation of D-[**1**$(H_2O)_3]^{3+}$ in aqueous bdc^{2-}

Blue crystals of D-[**1**$(H_2O)_3](tfa)_3$ (tfa = trifluoroacetate), in which D-[**1**$(H_2O)_3]^{3+}$ cations are surrounded by tfa^- anions in a 2D layer structure (Figure S1), were prepared according to the procedure described in our recent publication.[11,12] When blue crystals of D-[**1**$(H_2O)_3](tfa)_3$ with a hexagonal block shape were soaked in an aqueous solution containing Na_2bdc (bdc^{2-} = 1,4-benzenedicarboxylate) at room temperature, the original crystals immediately lost its transparency and disappeared with the concomitant formation of a blue-white suspension in a few days, from which blue crystals of D-**2** with a thin hexagonal plate shape gradually appeared over two weeks. Completion of the crystal transformation was confirmed by the powder X-ray diffraction of the product, which exhibited a single set of diffractions that are distinct from those of D-[**1**$(H_2O)_3](tfa)_3$ (Figure S2).[12] The diffuse reflection and circular dichroism spectra of D-**2** in the solid state are essentially the same as those of D-[**1**$(H_2O)_3](tfa)_3$ (Figure S3),[12] indicating the retention of the $Au^I_6Ag^I_3Cu^{II}_3$ dodecanuclear structure during the crystal transformation. However, the IR spectrum indicated that the tfa^- anions in D-[**1**$(H_2O)_3](tfa)_3$ are replaced by bdc^{2-} in D-**2** (Figure S4).[12] On the basis of these results, together with the X-ray fluorescence and elemental analyses, D-**2** was determined to have a chemical formula of [**1**]$(bdc)_{1.5}\cdot nH_2O$.

The structure of D-**2** was determined by single-crystal X-ray diffraction analysis, which revealed the presence of complex cations and bdc^{2-} counteranions in a 1:1 ratio. The complex cation in D-**2** contains two trigold(I) metalloligands $[Au_3(tdme)(D\text{-}pen)_3]^{3-}$ [13] spanned by three linear Ag^I and three square-planar Cu^{II} centers to form a spherical $Au^I_6Ag^I_3Cu^{II}_3$ dodecanuclear structure, with its apical positions covered by tdme phenyl groups and its equatorial positions surrounded by three square planar Cu^{II} centers (Figures 1a and 1b). This structural feature is the same as that of the $Au^I_6Ag^I_3Cu^{II}_3$ complex cation in D-[**1**$(H_2O)_3](tfa)_3$.[11] However, one of the three water molecules coordinated to the three different Cu^{II} centers in D-[**1**$(H_2O)_3]^{3+}$ is replaced by a monodentate bdc^{2-} ligand with an occupancy of 0.5 in D-**2**. This implies that D-**2** has a 1:1 mixture of D-[**1**$(bdc)(H_2O)_2]^+$ and D-[**1**$(H_2O)_3]^{3+}$ as complex cations, corresponding to the chemical formula [**1**$(bdc)_{0.5}(H_2O)_{2.5}$](bdc). In the D-[**1**$(bdc)(H_2O)_2]^+$ cation, a carboxyl group in bdc^{2-} forms an intramolecular $NH_2\cdots OOC$ ($N\cdots O$ = 2.64 Å) hydrogen bond with an adjacent amine group in D-pen (Figures 1a and 1b), which appears to sustain the axle structure of bdc^{2-} perpendicular to the square planar Cu^{II}. In the crystal packing structure of D-**2**, D-[**1**$(bdc)(H_2O)_2]^+$ and D-[**1**$(H_2O)_3]^{3+}$ cations form a dimeric assembly through an intermolecular $OH_2\cdots OOC$ ($O\cdots O$ = 2.83 Å) hydrogen bond (Figure 1c). The dimers are further linked in a 1D chain structure through intermolecular $NH_2\cdots OH_2$ ($N\cdots O$ = 2.90 Å) hydrogen bonds (Figure 1d).[12]

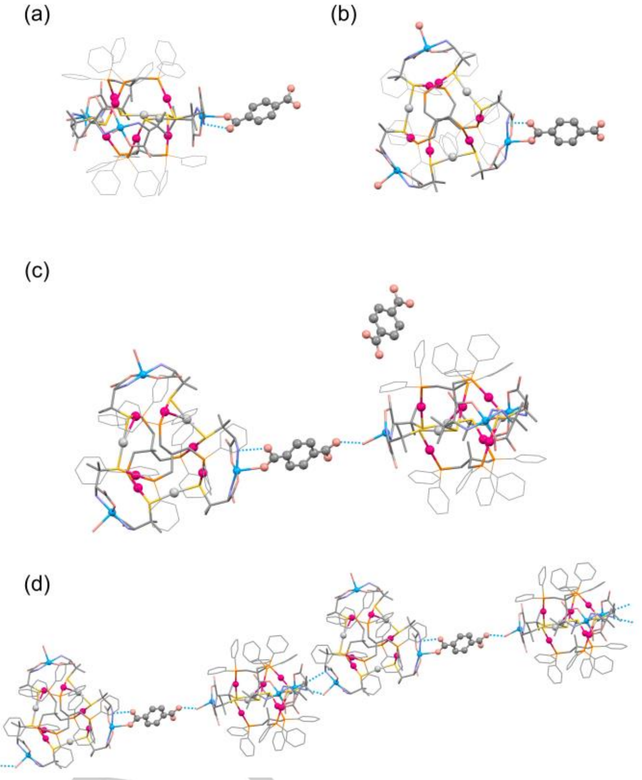


Figure 1. Crystal structure of D-**2**. Side (a) and top (b) views of the $Au^I_3Ag^I_3Cu^{II}_3$ complex cation of D-[**1**$(bdc)(H_2O)_2]^+$. (c) Dimeric structure composed of D-[**1**$(H_2O)_3]^{3+}$ and D-[**1**$(bdc)(H_2O)_2]^+$. (d) 1D chain formed via intermolecular $NH_2\cdots OH_2$ hydrogen bonds. Colors: red, Au; silver, Ag; blue, Cu; orange, P; yellow, S; pink, O; pale blue, N; gray, C. H atoms are omitted for clarity.

Transformation of D-[**1**$(H_2O)_3]^{3+}$ in aqueous bdc^{2-} and γ-CD

Following the formation of [**1**$(bdc)(H_2O)_2]^+$ with a pendent bdc^{2-} axle molecule, crystals of D-[**1**$(H_2O)_3](tfa)_3$ were soaked in aqueous Na_2bdc containing excess γ-CD to insert the axle molecule of bdc^{2-} into the γ-CD ring. This procedure yielded blue crystals of D-**3** via solvent-mediated crystal-to-crystal transformation.[14] Again, completion of the crystal transformation from D-[**1**$(H_2O)_3](tfa)_3$ to D-**3** was proven by the powder X-ray diffraction (Figure S2),[12] and the retention of the $Au^I_6Ag^I_3Cu^{II}_3$ dodecanuclear structure in the course of the transformation was confirmed by the solid-state diffuse reflection and circular dichroism spectroscopy (Figure S3),[12] together with the X-ray fluorescence analysis. The presence of both bdc^{2-} and γ-CD in D-**3** was shown by the IR spectroscopy (Figure S4).[12]

Single-crystal X-ray analysis revealed that D-**3** contains complex cations and tfa^- anions in a 1:1 ratio. The complex cation has an $Au^I_6Ag^I_3Cu^{II}_3$ dodecanuclear structure in D-[**1**$(bdc)(H_2O)_2]^+$ with a pendent bdc^{2-} ligand (Figures 2a and 2b), which is essentially the same as that of the D-[**1**$(bdc)(H_2O)_2]^+$ cation found in D-**2**. In D-**3**, however, the pendent bdc^{2-} is enclosed by a γ-CD ring to form a pseudorotaxane structure in D-[**1**(bdc@γ-CD)$(H_2O)_2]^+$, with the smaller opening of the γ-CD ring facing the $Au^I_6Ag^I_3Cu^{II}_3$ molecular cap. In pseudorotaxane structures reported to date, a molecular cap is commonly located on the larger opening of the CD ring with secondary hydroxyl groups rather than the smaller opening with primary hydroxyl groups,[15] which is a result of the ease of inserting a molecular axle into the larger opening of a CD ring. This is also the case for a pseudorotaxane structure containing γ-CD and fullerene as a molecular ring and a molecular cap, respectively, which is the only pseudorotaxane containing γ-CD that has been structurally characterized to date.[10] Thus, D-[**1**(bdc@γ-CD)$(H_2O)_2]^+$ is the first example of a structurally characterized pseudorotaxane in which the smaller opening of the CD ring faces a molecular cap. Inspection of the crystal structure of D-**3** revealed that two *trans* carboxyl groups in the $[Cu(D\text{-}pen)_2]^{2-}$ moiety in the $Au^I_6Ag^I_3Cu^{II}_3$ molecular cap form O-H$\cdots$O ($O\cdots O$ = 2.74 Å, 2.84 Å) hydrogen

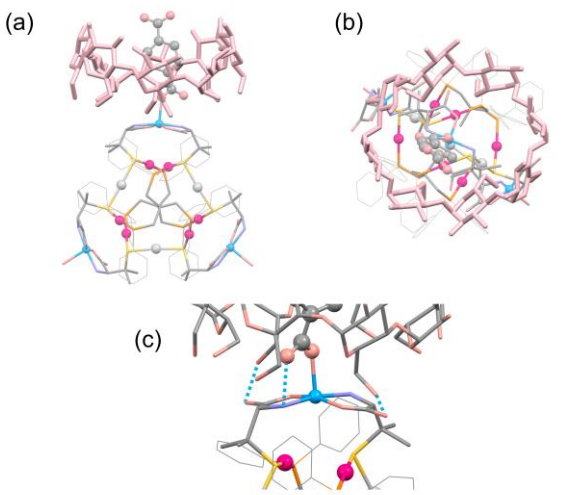


Figure 2. Crystal structure of D-**3**. Side (a) and top (b) views of the pseudorotaxane structure in D-[**1**(bdc@γ-CD)(H$_2$O)$_2$]$^+$. (c) Hydrogen bonding interaction between the square planar [Cu(D-pen)$_2$]$^{2-}$and the smaller opening of γ-CD. Colors: same as in Figure 1. H atoms are omitted for clarity.

bonds with two primary hydroxyl groups of the γ-CD ring located diagonally with an O⋯O separation of 10.22 Å (Figure 2c). Such a hydrogen-bonding motif is not possible for the larger opening of γ-CD with secondary hydroxyl groups because of the large separation between the diagonal hydroxyl groups. The hydrogen-bonding interaction between the [Cu(D-pen)$_2$]$^{2-}$ moiety and the γ-CD ring induces not only opposite host-guest interactions but also the ring shape of γ-CD in D-**3;** the γ-CD ring threaded by the bdc^{2-} molecular axle is largely distorted such that its diagonal positions are pulled by the hydrogen-bonding interaction (Figure 3). To our knowledge, such a large distortion of γ-CD has never been observed in crystal structures. In D-**3**, the pseudorotaxane molecules of [**1**(bdc@γ-CD)(H$_2$O)$_2$]$^+$ are closely packed in a zigzag fashion, without forming intermolecular hydrogen bonds via noncoordinating carboxylate groups of bdc^{2-} (Figure S5).[12] Here, it should be noted that soaking crystals of D-[**1**(H$_2$O)$_3$](tfa)$_3$ in aqueous γ-CD in the absence of bdc^{2-} did not accommodate γ-CD in the crystal but resulted in partial decomposition of D-[**1**(H$_2$O)$_3$]$^{3+}$ to form a neutral Au$^I_6$Cu$^{II}_3$ complex [Au$_6$Cu$_3$(H$_2$O)$_3$(D-pen)$_6$(tdme)$_2$] that cocrystalizes with D-[**1**(H$_2$O)$_3$](tfa)$_3$ (Figure S6).[12] Thus, the presence of an axle molecule is essential for the inclusion of γ-CD, fixing a γ-CD molecule near the Au$^I_6$Ag$^I_3$Cu$^{II}_3$ molecular cap.

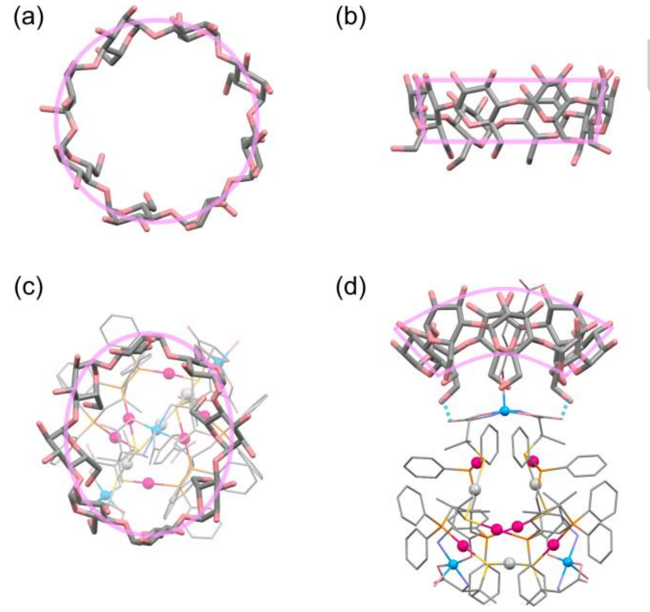


Figure 3. Comparison of the ring structures of γ-CD. Top (a) and side (b) views of free γ-CD.[16] Top (c) and side (d) views of γ-CD in D-**3.** Transparent orange lines represent molecular outlines. The radius of the free γ-CD ring (r) is 13.7 Å. The radii of the γ-CD ellipses in D-**3** (r_a and r_b, $r_a < r_b$) are 11.4 Å and 13.0 Å, respectively.

Transformation of D-[1(H$_2$O)$_3$]$^{3+}$ in aqueous adp^{2-}/sbr^{2-}/sbc^{2-} and γ-CD

To investigate whether a similar pseudorotaxane structure with a distorted γ-CD ring is formed when dicarboxylate anions with an aliphatic carbon chain are used instead of bdc^{2-} with an aromatic benzene ring, crystals of D-[**1**(H$_2$O)$_3$](tfa)$_3$ were soaked in an aqueous solution containing adipate (adp^{2-}; $C_4H_8(COO^-)_2$), suberate (sbr^{2-}; $C_6H_{12}(COO^-)_2$), and sebacate (sbc^{2-}; $C_8H_{16}(COO^-)_2$) in the presence of excess γ-CD, which led to the production of crystals D-**4**, D-**5**, and D-**6**, respectively, via solvent-mediated crystal-to-crystal transformation.[14] The presence of D-[**1**]$^{3+}$, dicarboxylate, and γ-CD in D-**4**, D-**5**, and D-**6** was confirmed by the solid-state reflection, circular dichroism, and IR spectroscopy (Figures S7 and S8),[12] together with the X-ray fluorescence and elemental analyses. Single-crystal X-ray analysis established that D-**4**, D-**5**, and D-**6** have pseudorotaxane structures very similar to that of D-**3**, except for the presence of an axle molecule with an aliphatic carbon chain in place of bdc^{2-} in D-**3** (Figure 4). Similar to that in D-**3**, the γ-CD rings in D-**4**, D-**5**, and D-**6** are largely distorted, forming O-H⋯O hydrogen bonds with the Au$^I_6$Ag$^I_3$Cu$^{II}_3$ molecular cap of D-[**1**(H$_2$O)$_2$]$^{3+}$ via primary hydroxyl groups of its smaller opening. This indicates that the hydrogen-bonding interaction between the molecular of the pseudorotaxane structure in this system. Contrary to that in D-**3**,

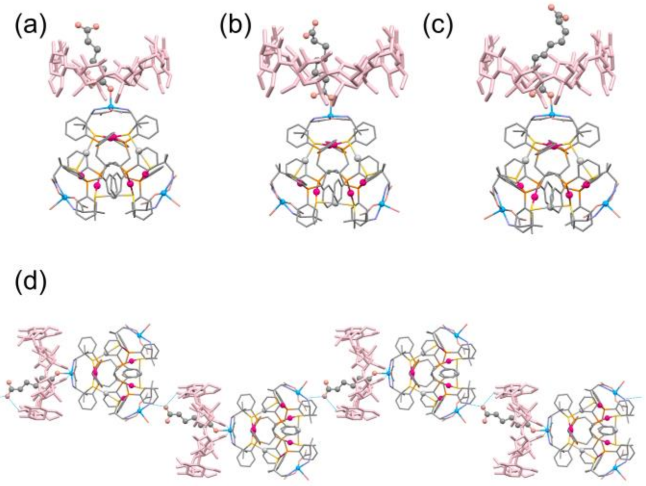


Figure 4. Side views of the pseudorotaxane structures in D-**4** (a), D-**5** (b), and D-**6** (c). Polyrotaxane-like chain structure in D-**4** (d). Colors: same as in Figure 1. H atoms are omitted for clarity.

the noncoordinating carboxyl group of each axle molecule (adp^{2-}, sbr^{2-}, sbc^{2-}) in the crystals of D-**4**, D-**5**, and D-**6** is hydrogen-bonded with an adjacent pseudorotaxane molecule to form a polyrotaxane-like chain structure (Figure 4d and S9).[12]

Transformation of L-$[\mathbf{1}(H_2O)_3]^{3+}$ in aqueous bdc^{2-} and γ-CD

Since the molecular cap of D-$[\mathbf{1}(H_2O)_2]^{3+}$ is chiral due to the presence of asymmetric D-pen ligands, we next used L-$[\mathbf{1}(H_2O)_3](tfa)_3$ with L-pen instead of D-$[\mathbf{1}(H_2O)_3](tfa)_3$ with D-pen in the reaction to evaluate the importance of chirality in the formation of the pseudorotaxane structure. Soaking crystals of L-$[\mathbf{1}(H_2O)_3](tfa)_3$ in aqueous Na_2bdc in the presence of γ-CD under the same conditions yielded crystals of L-**2**. The diffuse reflection, circular dichroism, and IR spectra in the solid state (Figures S10 and S11),[12] together with the X-ray fluorescence and elemental analyses, indicated that L-**2** has a chemical formula of $[\mathbf{1}(bdc)_{0.5}(H_2O)_{2.5}](bdc)$, corresponding to that of D-**2** rather than that of D-**3**, which lacks γ-CD. The crystal structure of L-**2** is entirely enantiomeric to that of D-**2**, as confirmed by single-crystal X-ray analysis (Figure S12).[12] Thus, L-$[\mathbf{1}(bdc)(H_2O)_2]^+$ bearing a molecular cap of L-$[\mathbf{1}(H_2O)_2]^{3+}$ does not accept a γ-CD ring in the structure. Molecular modeling suggested that steric repulsion, rather than hydrogen-bonding interaction, exists between the primary hydroxyl groups of γ-CD and carboxyl groups of pen ligands when D-pen ligands in D-$[\mathbf{1}(bdc)(H_2O)_2]^+$ are replaced by L-pen (Figure S13).[12] While a number of reports on chiral recognition due to CD have appeared to date,[8c,17] such a structurally established supramolecular system with CD, which shows the formation of a rotaxane/pseudorotaxane structure controlled by the chirality of a molecular cap rather than a molecular axle, is unprecedented.

Conclusion

In this study, we showed the solvent-mediated crystal-to-crystal transformation of D-$[\mathbf{1}(H_2O)_3](tfa)_3$ to D-$[\mathbf{1}(bdc@\gamma\text{-}CD)(H_2O)_2](bdc)$ (D-**3**) in an aqueous solution containing bdc^{2-} and γ-CD. Single-crystal X-ray crystallography revealed that in D-**3,** bdc^{2-} is bound perpendicular to the $[Cu(D\text{-}pen)_2]^{2-}$ plane of D-$[\mathbf{1}(H_2O)_2]^{3+}$ through coordination and hydrogen bonds, and a γ-CD ring is inserted to generate a pseudorotaxane structure. Remarkably, the γ-CD ring is largely distorted, with its smaller ring side facing the $[Cu(D\text{-}pen)_2]^{2-}$ plane to form intermolecular hydrogen bonds. While an analogous pseudorotaxane structure was also generated by using adp^{2-}, sbr^{2-}, and sbc^{2-} instead of bdc^{2-}, the employment of L-$[\mathbf{1}(H_2O)_3](tfa)_3$ for the reaction did not accommodate γ-CD in the structure because of the chirality mismatch between the molecular cap of L-$[\mathbf{1}(H_2O)_2]^{3+}$ and the γ-CD ring. Thus, we established a novel class of pseudorotaxane systems, in which the unusual inclusion mode and large distortion of γ-CD are induced by an intermolecular interaction with a chiral molecular cap via chiral recognition.

Crystal Structures

Deposition Number(s) <url href="https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.20210XXX"> 2096869 (for D-**2**), 2096870 (for D-**3**), 2096871 (for D-**4**), 2096872 (for D-**5**), 2096873 (for D-**6**), 2096874 (for L-**2**), 2096875 (for D-$[\mathbf{1}(H_2O)_3](tfa)_3\cdot[Au_6Cu_3(D\text{-}pen)_6(tdme)_2]$)</url> contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <url href=" http://www.ccdc.cam.ac.uk/structures ">Access Structures service</url>.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Pseudorotaxane • γ-CD • Multinuclear complex • Chiral recognition • X-ray crystallography

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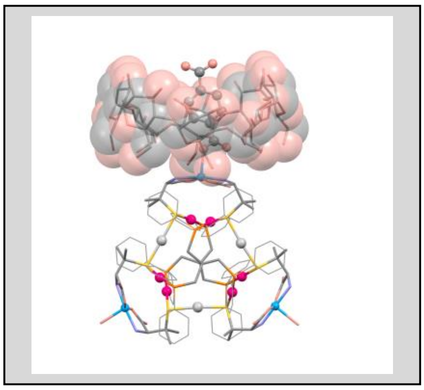

Pseudorotaxanes are created from an $Au^I_6Ag^I_3Cu^{II}_3$ complex with D-penicillamine combined with dicarboxylate and γ-CD via a solvent-mediated crystal-to-crystal transformation. In the structure, a γ-CD ring is threaded by a dicarboxylate axle such that the smaller opening of γ-CD faces an $Au^I_6Ag^I_3Cu^{II}_3$ complex cap in a largely distorted manner. The corresponding complex with L-penicillamine does not accept a γ-CD ring in the structure.

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