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Chiral Scrambling and Independent Crystallization of D$_4$, L$_4$, and D$_2$L$_2$ Isomers of an Au$^{I}_4$Co$^{III}_2$ Hexanuclear Complex with Mixed Penicillaminate and Bis(diphenylphosphino)ethane

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Supporting Information

ABSTRACT: The 1:1 mixing of a pair of enantiomers of a cyclic Au$^{I}_4$Co$^{III}_2$ hexanuclear complex having penicillaminate (pen) and 1,2-bis(diphenylphosphino)ethane (dppe), [Au$_4$Co$_2$(dppe)$_2$(D-pen)$_4$]$^{2+}$ (D$_4$-[**1**]$^{2+}$) and [Au$_4$Co$_2$(dppe)$_2$(L-pen)$_4$]$^{2+}$ (L$_4$-[**1**]$^{2+}$), in solution produced an additional stereoisomer, [Au$_4$Co$_2$(dppe)$_2$(D-pen)$_2$(L-pen)$_2$]$^{2+}$ (D$_2$L$_2$-[**1**]$^{2+}$), because of the scrambling of [Co(D-pen)$_2$]$^-$ and [Co(L-pen)$_2$]$^-$ units between D$_4$-[**1**]$^{2+}$ and L$_4$-[**1**]$^{2+}$. Upon crystallization with NO$_3^-$, the three stereoisomers were independently crystallized to form three different kinds of crystals, homochiral crystals of D$_4$-[**1**](NO$_3$)$_2$, homochiral crystals of L$_4$-[**1**](NO$_3$)$_2$, and heterochiral crystals of D$_2$L$_2$-[**1**](NO$_3$)$_2$, showing a unique example of the self-recognition and organization of three stereoisomers upon crystallization.

Self-recognition and organization among enantiomers of chiral molecules are essential for the rational synthesis of chiral functional materials, such as chiral separators, asymmetric catalysts, and ferroelectric and nonlinear optical materials, as well as for the understanding of homochirality in nature.[1,2] In this context, the control of self-recognition/organization upon chiral molecular assembling and crystallization processes has attracted much attention in synthetic chemistry for many years.[3−5] At a molecular level, chiral recognition leads to the selective formation of a pair of enantiomers (racemic isomer).[3] On the other hand, a racemic mixture of enantiopure crystals (conglomerate crystals) is produced by homochiral recognition in a crystalline level, which is referred to as "spontaneous resolution" upon crystallization.[4] To date, a great number of reports on the homochiral assembly at either the molecular or crystalline level have appeared in organic, coordination, and supramolecular chemistry.[5] In recent years, interests of researchers in this research field have shifted to explore more complicated recognition systems that are closer to living systems, such as a high degree of chiral recognition that involves a hierarchical chiral-sorting process,[6] partial spontaneous resolution that generates both conglomerate and racemic crystals in a crystallization process,[7] and chiral autocatalysis that leads to a single enantiopure product through a spontaneous symmetry-breaking process.[8] Examples of such nonclassical phenomena are still limited in number, and the finding of a novel system that shows unique recognition/sorting behavior of chiral molecules is of great demand in this research field.

In the course of our continuing studies on the rational creation of chiral metallosupramolecular architectures by using multifunctional metalloligands with thiol-containing amino acids,[9−11] we recently reported that a digold(I) metalloligand with two terminal D-penicillaminate (D-pen) ligands and a linking 1,2-bis(diphenylphosphino)ethane (dppe) ligand, [Au$_2$(dppe)(D-pen)$_2$]$^{2-}$, reacts with Co^{2+} under aerobic conditions to form a cyclic Au$^{I}_4$Co$^{III}_2$ hexanuclear complex, [Au$_4$Co$_2$(dppe)$_2$(D-pen)$_4$]$^{2+}$ (D$_4$-[**1**]$^{2+}$).[12] Interestingly, D$_4$-[**1**]$^{2+}$ was found to crystallize with several monovalent inorganic anions (X = Cl$^-$, NO$_3^-$, ClO$_4^-$, BF$_4^-$, N$_3^-$) to produce metallosupramolecular ionic crystals, in which six D$_4$-[**1**]$^{2+}$ cations are self-assembled to form a big cationic {D$_4$-[**1**]$^{2+}$}$_6$ supramolecular octahedron, with the concomitant aggregation of 10 X$^-$ anions into an amazing adamantine-like anionic {X$^-$}$_{10}$ cluster. To investigate the importance of homochirality to the formation of such an anomalous crystal structure, which shows a separate aggregation of cationic and anionic species, we carried out the 1:1 mixing of the homochiral D$_4$-[**1**]$^{2+}$ and its enantiomer of L$_4$-[**1**]$^{2+}$ in solution, expecting the formation of racemic crystals that are composed of D$_4$-[**1**]$^{2+}$ and L$_4$-[**1**]$^{2+}$ in a 1:1 ratio. We found that, upon crystallization with nitrate anions, three different kinds of crystals, D$_4$-[**1**](NO$_3$)$_2$, L$_4$-[**1**](NO$_3$)$_2$, and D$_2$L$_2$-[**1**](NO$_3$)$_2$, are produced by this treatment, without forming any crystals that contain both D$_4$-[**1**]$^{2+}$ and L$_4$-[**1**]$^{2+}$ (Scheme 1). This is indicative of the scrambling of [Co(D-pen)$_2$]$^-$ and [Co(L-pen)$_2$]$^-$ units in solution, followed by self-recognition and organization of the three stereoisomers upon crystallization. To our knowledge, such a precise self-recognition of three stereoisomers into three different kinds of crystals is unprecedented, although chiral-scrambling phenomena through ligand-exchange reactions have been reported.[13] In addition, the normal alternate arrangement of cations and anions was observed in the crystal structure of D$_2$L$_2$-[**1**](NO$_3$)$_2$, which provides us insight into the importance of homochirality to the formation of the unique crystal structure found in D$_4$- or L$_4$-[**1**](NO$_3$)$_2$.

Crystals of the homochiral Au$^{I}_4$Co$^{III}_2$ hexanuclear complexes, D$_4$-[**1**]X$_2$ and L$_4$-[**1**]X$_2$ (X = Cl$^-$, NO$_3^-$, ClO$_4^-$, BF$_4^-$, N$_3^-$), are insoluble in any common solvents, although they are only slightly

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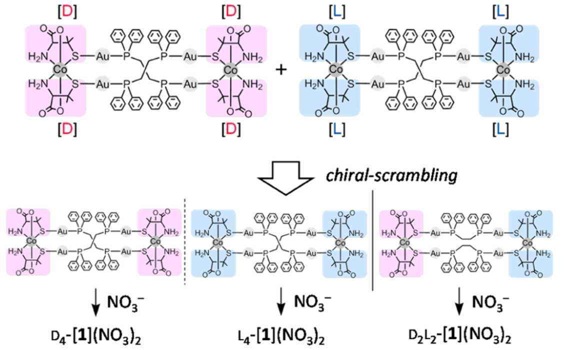
Scheme 1. Formation of D_4, L_4, and D_2L_2 Isomers of $[\mathbf{1}]^{2+}$ by Mixing Its D_4 and L_4 Isomers and Their Independent Crystallization with NO_3^-



soluble in methanol or a mixture of water and ethanol. Therefore, solutions containing D_4-$[\mathbf{1}]^{2+}$ or L_4-$[\mathbf{1}]^{2+}$, which are in situ prepared from $[Au_2(\text{dppe})(\text{D-Hpen})_2]$ or $[Au_2(\text{dppe})(\text{L-Hpen})_2]$, cobalt(II) acetate, and PbO_2 in ethanol/water,[12b] were used in this study.[14] The quantitative formation of D_4-$[\mathbf{1}]^{2+}$ or L_4-$[\mathbf{1}]^{2+}$ in each solution was confirmed by the ^1H NMR spectrum, which is essentially the same as that of the isolated crystals.[14] To prepare a solution containing D_4-$[\mathbf{1}]^{2+}$ and L_4-$[\mathbf{1}]^{2+}$ exactly in a 1:1 ratio, the mixing of a solution of D_4-$[\mathbf{1}]^{2+}$ and a solution of L_4-$[\mathbf{1}]^{2+}$ was finely adjusted until the circular dichroism (CD) spectrum of the mixture solution became silent. To this solution containing D_4-$[\mathbf{1}]^{2+}$ and L_4-$[\mathbf{1}]^{2+}$ in a 1:1 ratio was added an excess amount of $NaNO_3$ as a source of counteranions. When the mixture was allowed to stand at room temperature for several days, two kinds of purple crystals with different shapes, triangular pyramid (**A**) and square plate (**B**), appeared and were separated manually for characterization.[15] X-ray fluorescence analysis indicated that both **A** and **B** contain Co and Au atoms in a 1:2 ratio, and each of their elemental analysis data was in good agreement with a formula for the nitrate salt of $[\mathbf{1}]^{2+}$.[14] The IR spectra of **A** and **B** were quite similar to each other, showing several strong bands due to pen, dppe, and NO_3^-.[14] From these results, each of **A** and **B** was assigned to the expected nitrate salt of $[\mathbf{1}]^{2+}$.

Single-crystal X-ray analysis revealed that one of crystals **A** crystallized in a chiral cubic space group of *F*23 and that its structure was identical with that of the previously reported homochiral $Au^I_4Co^{III}_2$ hexanuclear complex, D_4-$[\mathbf{1}](NO_3)_2$.[14] In this crystal, six D_4-$[\mathbf{1}]^{2+}$ were self-assembled to form a cationic $\{\text{D}_4\text{-}[\mathbf{1}]^{2+}\}_6$ supramolecular octahedron, accommodating a nitrate anion in its center. Furthermore, the $\{\text{D}_4\text{-}[\mathbf{1}]^{2+}\}_6$ octahedra were closely packed in a face-centered-cubic (fcc) structure to construct a homochiral crystal consisting only of D_4-$[\mathbf{1}]^{2+}$. The anomalous aggregation of 10 nitrate anions into an adamantane-like $\{NO_3^-\}_{10}$ structure was also observed. On the other hand, another crystal **A** was found to contain L_4-$[\mathbf{1}]^{2+}$, six of which were self-assembled to form the homochiral $\{\text{L}_4\text{-}[\mathbf{1}]^{2+}\}_6$ supramolecular octahedron.[14] Again, only the homochiral $\{\text{L}_4\text{-}[\mathbf{1}]^{2+}\}_6$ octahedra were closely packed in a homochiral fcc structure, with the concomitant aggregation of 10 nitrate anions into an adamantane-like arrangement. These observations imply that **A** is the conglomerate consisting of homochiral crystals of D_4-$[\mathbf{1}](NO_3)_2$ and homochiral crystals of L_4-$[\mathbf{1}](NO_3)_2$. Note that only an enantiomeric pair ($\{\text{D}_4\text{-}[\mathbf{1}]^{2+}\}_6$ and $\{\text{L}_4\text{-}[\mathbf{1}]^{2+}\}_6$) was formed for the cationic supramolecular octahedra from D_4-$[\mathbf{1}]^{2+}$ and L_4-$[\mathbf{1}]^{2+}$ and that $\{\text{D}_4\text{-}[\mathbf{1}]^{2+}\}_6$ and $\{\text{L}_4\text{-}[\mathbf{1}]^{2+}\}_6$ were independently aggregated with nitrate anions to create the homochiral crystals that exclusively contained the $\{\text{D}_4\text{-}[\mathbf{1}]^{2+}\}_6$ or $\{\text{L}_4\text{-}[\mathbf{1}]^{2+}\}_6$ octahedra. Thus, this is a rare example of metallosupramolecular systems that show a high degree of self-recognition of chiral molecules upon crystallization.[6] The formation of multiple intermolecular NH···O hydrogen-bonding and CH···π interactions in the homochiral crystals[12] is most likely responsible for the self-recognition and organization of D_4-$[\mathbf{1}]^{2+}$ and L_4-$[\mathbf{1}]^{2+}$ upon crystallization, constructing a homochiral fcc structure that accommodates 10 nitrate anions in each tetrahedral interstice.

Single-crystal X-ray analysis was also performed for the other purple crystal **B**, which revealed a centrosymmetric space group of $P\bar{1}$ for this crystal.[14] The asymmetric unit of crystal **B** contains two crystallographically independent, yet essentially the same, complex cations $\{[Au_4Co_2(\text{dppe})_2(\text{D-pen})_2(\text{L-pen})_2]^{2+}$ (D_2L_2-$[\mathbf{1}]^{2+}$), besides nitrate anions and water molecules. In D_2L_2-$[\mathbf{1}]^{2+}$, each of two $[Au_2(\text{dppe})\ (\text{pen})_2]^{2-}$ moieties binds to two octahedral Co^{III} centers in a bis(tridentate-N,O,S) mode, form a cyclic $Au^I_4Co^{III}_2$ hexanuclear structure composed of two $[Co(\text{pen})_2]^-$ octahedral units, like in D_4-$[\mathbf{1}]^{2+}$ and L_4-$[\mathbf{1}]^{2+}$ (Figure 1a). However, each $[Au_2(\text{dppe})\ (\text{pen})_2]^{2-}$ moiety consisted of D-pen and L-pen to give $[Co(\text{D-pen})_2]^-$ and $[Co(\text{L-pen})_2]^-$ units, constructing a heterochiral meso-type structure inD_2L_2-$[\mathbf{1}]^{2+}$. It is interesting to note that the 18-membered metalloring in D_2L_2-$[\mathbf{1}]^{2+}$ was not twisted with the close Au···Au distances (ave. 3.136 Å), indicative of the presence of an aurophilic interaction.[16] This is distinct from the twisted metalloring structure in D_4-$[\mathbf{1}]^{2+}$ or L_4-$[\mathbf{1}]^{2+}$, which does not possess an aurophilic interaction. In the packing structure, each D_2L_2-$[\mathbf{1}]^{2+}$ complex cation is connected to two adjacent complex cations through intermolecular hydrogen bonds between carboxylate and amine groups of pen to form a 1D chain. The 1D chains are further connected to each other through intermolecular CH···π interactions between the methyl group of pen and the phenyl group of dppe, constructing a gridlike 2D sheet structure. Each nitrate ion is accommodated in each void space surrounded by the D_2L_2-$[\mathbf{1}]^{2+}$ complex cations (Figure 1b), illustrating an alternate arrangement of cations and anions. This arrangement, which is quite normal for crystal structures, is in sharp contrast to that in D_4-$[\mathbf{1}]^{2+}$ or L_4-$[\mathbf{1}]^{2+}$, implying that the molecular homochirality is an important factor for creating the unusual aggregation of the D_4-$[\mathbf{1}]^{2+}$ or L_4-$[\mathbf{1}]^{2+}$ cations and inorganic anions in the crystal.

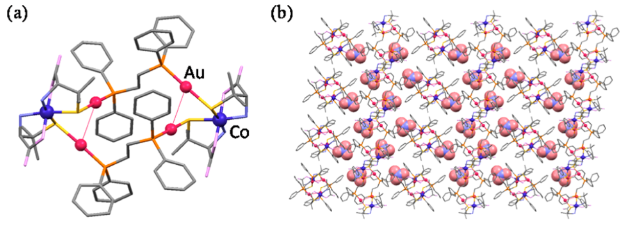


Figure 1. Perspective views of the (a) complex cation and (b) packing structure in D_2L_2-$[\mathbf{1}](NO_3)_2$.

It should be noted that the heterochiral D_2L_2-$[\mathbf{1}](NO_3)_2$ was crystallized, together with the homochiral D_4-$[\mathbf{1}](NO_3)_2$ and L_4-$[\mathbf{1}](NO_3)_2$, from a 1:1 mixture solution of D_4-$[\mathbf{1}]^{2+}$ and L_4-$[\mathbf{1}]^{2+}$. This finding clearly indicates that a certain chiral-scrambling reaction occurs in the course of the crystallization process. Because the heterochiral D_2L_2-$[\mathbf{1}]^{2+}$ is composed of $[Co(\text{D-pen})_2]^-$ and $[Co(\text{L-pen})_2]^-$ units, it is reasonable to assumed that the chiral scrambling is induced by the cleavage of Au^{I}−P and/or Au^{I}−S bonds in D_4-[**1**]$^{2+}$ and L_4-[**1**]$^{2+}$ in solution.[17,18] In order to check the formation of $\mathrm{D}_2\mathrm{L}_2$-[**1**]$^{2+}$ in solution, the ^{1}H NMR spectrum of a 1:1 mixture solution of D_4-[**1**]$^{2+}$ and L_4-[**1**]$^{2+}$ in CD_3OD was monitored at room temperature. As a result, no obvious spectral changes were observed even after 6 days.[14,19] However, the ^{1}H NMR signals became broad as the temperature was lowered below −60 °C.[14] This suggests that the chiral scrambling between D_4-[**1**]$^{2+}$, L_4-[**1**]$^{2+}$, and $\mathrm{D}_2\mathrm{L}_2$-[**1**]$^{2+}$ is fast on the ^{1}H NMR time scale.

In summary, we showed a unique, excellent example of self-recognition and organization of three stereoisomers (D_4, L_4, and $\mathrm{D}_2\mathrm{L}_2$) of the cyclic $\mathrm{Au}^{I}_4\mathrm{Co}^{III}_2$ hexanuclear complex $[\mathrm{Au}_4\mathrm{Co}_2(\mathrm{dppe})_2(\mathrm{pen})_4]^{2+}$ ([**1**]$^{2+}$) upon crystallization. We found that $\mathrm{D}_2\mathrm{L}_2$-[**1**]$^{2+}$ is generated through a quick chiral-scrambling process upon mixing of a solution of D_4-[**1**]$^{2+}$ and a solution of L_4-[**1**]$^{2+}$, giving a solution containing all D_4-[**1**]$^{2+}$, L_4-[**1**]$^{2+}$, and $\mathrm{D}_2\mathrm{L}_2$-[**1**]$^{2+}$. Remarkably, the three stereoisomers that coexisted in solution were independently crystallized into three different kinds of crystals, homochiral crystals of D_4-[**1**]$(NO_3)_2$, homochiral crystals of L_4-[**1**]$(NO_3)_2$, and heterochiral crystals of $\mathrm{D}_2\mathrm{L}_2$-[**1**]$(NO_3)_2$, without producing any other crystals that are composed of all three or two of the three stereoisomers. Because homochiral crystals of D_4- or L_4-[**1**]$(NO_3)_2$ can be regarded as arising from the homochiral aggregation of $\{\mathrm{D}_4$- or L_4-[**1**]$^{2+}\}_6$ octahedra, each of which is the homochiral aggregate of D_4- or L_4-[**1**]$^{2+}$, the production of the homochiral crystals is a result of a high degree of self-recognition and organization of the homochiral species. Unlike the homochiral crystal of D_4- or L_4-[**1**]$(NO_3)_2$, the heterochiral crystal of $\mathrm{D}_2\mathrm{L}_2$-[**1**]$(NO_3)_2$ possesses a normal alternate arrangement of complex cations and nitrate anions. This is indicative of the importance of homochirality to the future design and creation of unique supramolecular architectures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01549.

Crystallographic, experimental, and spectroscopic data (PDF)

X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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(14) See the Supporting Information.

(15) Powder X-ray diffraction showed two kinds of signals, sharp and broad ones (see Figure S7),[14] which supports the formation of two kinds of crystals (**A** and **B**), although the broad signals do not match those simulated from the crystal structure of $\mathrm{D}_2\mathrm{L}_2$-[**1**]$(NO_3)_2$, most likely because of the efflorescence of crystals **B**.

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(17) The cleavage of Au−S/P bonds in solution has been recognized in the related gold(I) coordination systems with mixed phosphine and thiolate ligands.[11a,c]

(18) It is assumed that the scrambling of D-pen and L-pen, which results in the formation of the $[\mathrm{Co}(\mathrm{D}\text{-pen})(\mathrm{L}\text{-pen})]^-$ unit, does not occur because of the inert character of Co^{III} centers.

(19) The ^{1}H and ^{31}P NMR and absorption spectra of D_4- or L_4-[**1**]$^{2+}$ were almost identical with those of $\mathrm{D}_2\mathrm{L}_2$-[**1**]$^{2+}$.[14]