



Title	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 Penicillamate and Bis(diphenylphosphino)ethane
Author(s)	Li, Chan; Lee, Raeun; Kuwamura, Naoto et al.
Citation	Inorganic Chemistry. 2015, 54(18), p. 8881–8883
Version Type	AM
URL	https://hdl.handle.net/11094/57158
rights	© 2015 American Chemical Society
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Chiral Scrambling and Independent Crystallization of D_4 , L_4 , and D_2L_2 Isomers of an $Au^I_4Co^{III}_2$ Hexanuclear Complex with Mixed Penicillamate and Bis(diphenylphosphino)ethane

Nobuto Yoshinari,[†] Chan Li,[†] Raeeun Lee,[†] Naoto Kuwamura,[†] Asako Igashira-Kamiyama,[†] Takumi Konno^{*,†,‡}

[†] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043 (Japan).

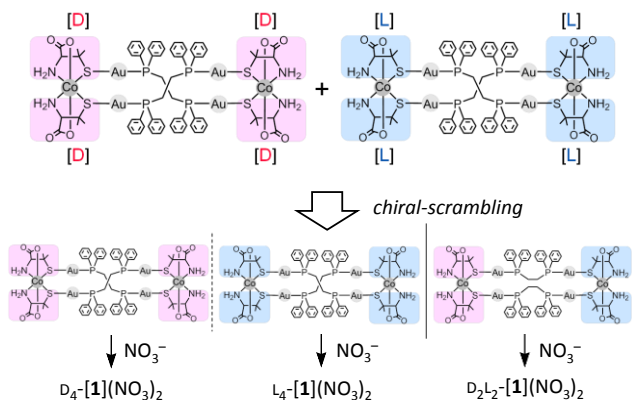
[‡] CREST, Japan Science and Technology Agency, Toyonaka, Osaka 560-0043 (Japan).

ABSTRACT: The 1:1 mixing of a pair of enantiomers of a cyclic $Au^I_4Co^{III}_2$ hexanuclear complex having penicillamate (pen) and 1,2-bis(diphenylphosphino)ethane (dppe), $[Au_4Co_2(dppe)_2(D-pen)_4]^{2+}$ ($D_4-[1]^{2+}$) and $[Au_4Co_2(dppe)_2(L-pen)_4]^{2+}$ ($L_4-[1]^{2+}$), in solution produced an additional stereoisomer, $[Au_4Co_2(dppe)_2(D-pen)_2(L-pen)_2]^{2+}$ ($D_2L_2-[1]^{2+}$), due to 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 $D_2L_2-[1](NO_3)_2$, showing a unique example of self-recognition and organization of three stereoisomers on crystallization.

Self-recognition and organization among enantiomers of chiral molecules is essential for the rational synthesis of chiral functional materials, such as chiral separators, asymmetric catalysts, and ferroelectric and non-linear 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 In a molecular level, the 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 the homochiral recognition in a crystalline level, which is referred to as 'spontaneous resolution' on crystallization.⁴ To date, a great number of reports on the homochiral assembly in either molecular or crystalline level has appeared in organic chemistry, coordination chemistry, 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 non-classical 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-penicillamate (D-pen) and a linking 1,2-bis(diphenylphosphino)ethane (dppe) ligands, $[Au_2(dppe)(D-pen)_2]^{2-}$, reacts with Co^{2+} under aerobic conditions to form a cyclic $Au^I_4Co^{III}_2$ hexanuclear complex, $[Au_4Co_2(dppe)_2(D-pen)_4]^{2+}$ ($D_4-[1]^{2+}$).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 metallo-supramolecular 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 ten X^- anions into an amazing adamantane-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, on crystallization with nitrate anions, three different kinds of crystals, $D_4-[1](NO_3)_2$, $L_4-[1](NO_3)_2$, and $D_2L_2-[1](NO_3)_2$, 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 the self-recognition and organization of the three stereoisomers on crystallization. To our knowledge, such a precise self-recognition of three stereoisomers into the 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 $D_2L_2-[1](NO_3)_2$, which provides us an insight into the importance of homochirality to the formation of the unique crystal structure found in D_4- or $L_4-[1](NO_3)_2$.



Scheme 1. Formation of D_4 , L_4 , and D_2L_2 isomers of $[1]^{2+}$ by mixing its D_4 and L_4 isomers and their independent crystallization with NO_3^- .

Crystals of the homochiral $Au^I_4Co^{III}_2$ 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 soluble in methanol or a mixture of water and ethanol. Therefore, solutions containing $D_4-[1]^{2+}$ or $L_4-[1]^{2+}$, which are *in situ* prepared from $[Au_2(dppe)(D-Hpen)_2]$ or $[Au_2(dppe)(L-Hpen)_2]$, cobalt(II) acetate, and PbO_2 in ethanol/water,^{12b} were used in this study.¹⁴ The quantitative formation of $D_4-[1]^{2+}$ or $L_4-[1]^{2+}$ in each solution was confirmed by the 1H NMR spectrum, which is essentially the same as that of the isolated crystals.¹⁵ To prepare a solution containing $D_4-[1]^{2+}$ and $L_4-[1]^{2+}$ exactly in a 1:1 ratio, the mixing of a solution of $D_4-[1]^{2+}$ and a solution of $L_4-[1]^{2+}$ was finely adjusted until the CD spectrum of the mixture solution became silent. To this solution containing $D_4-[1]^{2+}$ and $L_4-[1]^{2+}$ in a 1:1 ratio was added an excess amount of $NaNO_3$ as a source of counter anions. 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.¹⁶ 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 were in good agreement with a formula for the nitrate salt of $[1]^{2+}$.¹⁴ The IR spectra of A and B are 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 is assigned to the expected nitrate salt of $[1]^{2+}$.

Single-crystal X-ray analysis revealed that one of crystals A crystallizes in a chiral cubic space group of $F23$ and that its structure is identical with that of the previously reported homochiral $Au^I_4Co^{III}_2$ hexanuclear complex, $D_4-[1](NO_3)_2$ (Figure 1a). In this crystal, six $D_4-[1]^{2+}$ are self-assembled to form a cationic $\{D_4-[1]^{2+}\}_6$ supramolecular octahedron, accommodating a nitrate anion in its center (Figure 1b). Furthermore, the $\{D_4-[1]^{2+}\}_6$ octahedrons are closely packed in a face-centered cubic (fcc) structure to construct a homochiral crystal consisting only of $D_4-[1]^{2+}$ (Figure 1d). The anomalous aggregation of ten nitrate anions into an adamantane-like $\{NO_3^-\}_{10}$ structure was also observed (Figure 1c). On the other hand, another crystal A was found to contain $L_4-[1]^{2+}$, six of which are self-assembled to form the homochiral $\{L_4-[1]^{2+}\}_6$ supramolecular octahedron.¹⁴ Again, only the homochiral $\{L_4-[1]^{2+}\}_6$ octahedrons are closely packed in a homochiral fcc structure, with the concomitant aggregation of ten nitrate anions

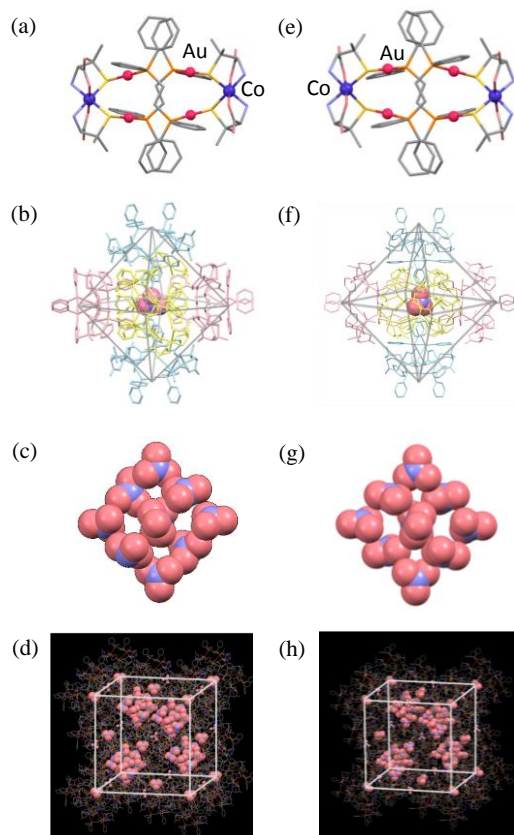


Figure 1. Perspective views of (a, e) complex cation, (b, f) supramolecular octahedron accommodating a NO_3^- ion, (c, g) $\{NO_3^-\}_{10}$ cluster, and (d, h) packing structure in $D_4-[1](NO_3)_2$ and $L_4-[1](NO_3)_2$, respectively. The crystal structure of $D_4-[1](NO_3)_2$ has been reported.¹²

into an adamantane-like arrangement (Figure 1e-h). These observations imply that A is the conglomerate consisting of homochiral crystals of $D_4-[1](NO_3)_2$ and homochiral crystals of $L_4-[1](NO_3)_2$. Note that only an enantiomeric pair ($\{D_4-[1]^{2+}\}_6$ and $\{L_4-[1]^{2+}\}_6$) was formed for the cationic supramolecular octahedrons from $D_4-[1]^{2+}$ and $L_4-[1]^{2+}$ and that $\{D_4-[1]^{2+}\}_6$ and $\{L_4-[1]^{2+}\}_6$ are independently aggregated with nitrate anions to create the homochiral crystals that exclusively contain the $\{D_4-[1]^{2+}\}_6$ or $\{L_4-[1]^{2+}\}_6$ octahedrons. Thus, this is a rare example of metallosupramolecular systems that show a high degree of self-recognition of chiral molecules on crystallization.⁶ The formation of multiple intermolecular $NH\cdots O$ hydrogen-bonding and $CH\cdots\pi$ interactions in the homochiral crystals¹² is most likely responsible for the self-recognition and organization of $D_4-[1]^{2+}$ and $L_4-[1]^{2+}$ on crystallization, constructing a homochiral fcc structure that accommodates ten 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 $P-1$ for this crystal.¹⁴ The asymmetric unit of crystal B contains two crystallographically independent, yet essentially the same complex cations ($D_2L_2-[1]^{2+}$), besides nitrate anions and water molecules. In $D_2L_2-[1]^{2+}$, each of two $[Au_2(dppe)(pen)_2]^{2-}$ 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 $[Co(pen)_2]^-$ octahedral units, like in $D_4-[1]^{2+}$ and $L_4-[1]^{2+}$ (Figure 2a). However, each $[Au_2(dppe)(pen)_2]^{2-}$ moiety consists of D-pen and

L-pen to give $[\text{Co}(\text{D-pen})_2]^-$ and $[\text{Co}(\text{L-pen})_2]^-$ units, constructing a heterochiral meso-type structure in $[\text{Au}_4\text{Co}_2(\text{dppe})_2(\text{D-pen})_2(\text{L-pen})_2]^{2+}$. It is interesting to note that the 18-membered metalloring in $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ is not twisted with the close Au...Au distances (av. 3.136 Å), indicative of the presence of an aurophilic interaction.¹⁷ This is distinct from the twisted metalloring structure in $\text{D}_4\text{-[1]}^{2+}$ or $\text{L}_4\text{-[1]}^{2+}$, which does not possess an aurophilic interaction. In packing structure, each $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ 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 $\text{CH}\cdots\pi$ interactions between methyl group of pen and phenyl group of dppe, constructing a grid-like 2D sheet structure. Each nitrate ion is accommodated in each void space surrounded by the $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ complex-cations (Figure 2b), illustrating an alternate arrangement of cations and anions. This arrangement, which is quite normal for crystal structures, is in sharp contrast to that in $\text{D}_4\text{-[1]}^{2+}$ or $\text{L}_4\text{-[1]}^{2+}$, implying that the molecular homochirality is an important factor for creating the unusual aggregation of the $\text{D}_4\text{-[1]}^{2+}$ or $\text{L}_4\text{-[1]}^{2+}$ cations and inorganic anions in crystal.

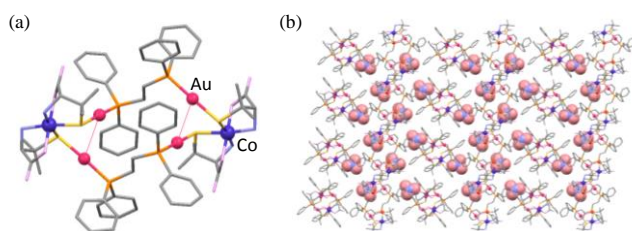


Figure 2. Perspective views of (a) complex cation and (b) packing structure in $\text{D}_2\text{L}_2\text{-[1]}(\text{NO}_3)_2$.

It should be noted that the heterochiral $\text{D}_2\text{L}_2\text{-[1]}(\text{NO}_3)_2$ was crystallized, together with the homochiral $\text{D}_4\text{-[1]}(\text{NO}_3)_2$ and $\text{L}_4\text{-[1]}(\text{NO}_3)_2$, from the 1:1 mixture solution of $\text{D}_4\text{-[1]}^{2+}$ and $\text{L}_4\text{-[1]}^{2+}$. This finding clearly indicates that a certain chiral-scrambling reaction occur in the course of the crystallization process. Since the heterochiral $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ is composed of $[\text{Co}(\text{D-pen})_2]^-$ and $[\text{Co}(\text{L-pen})_2]^-$ units, it is reasonable to assume that the chiral-scrambling is induced by the cleavage of Au^I-P and/or Au^I-S bonds in $\text{D}_4\text{-[1]}^{2+}$ and $\text{L}_4\text{-[1]}^{2+}$ in solution.^{18,19} In order to check the formation of $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ in solution, the ¹H NMR spectrum of a 1:1 mixture solution of $\text{D}_4\text{-[1]}^{2+}$ and $\text{L}_4\text{-[1]}^{2+}$ in CD_3OD was monitored at room temperature. As a result, no obvious spectral changes were observed even after 6 days.^{14,20} However, the ¹H NMR signals became broad as lowering the temperature below -60°C .¹⁴ This suggests that the chiral-scrambling between $\text{D}_4\text{-[1]}^{2+}$, $\text{L}_4\text{-[1]}^{2+}$, and $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ is fast on the ¹H NMR time scale.

In summary, we showed a unique, excellent example of self-recognition and organization of three stereoisomers (D_4 , L_4 , and D_2L_2) of the cyclic $\text{Au}^{\text{I}}_4\text{Co}^{\text{III}}_2$ hexanuclear complex, $[\text{Au}_4\text{Co}_2(\text{dppe})_2(\text{pen})_4]^{2+}$ ([1]^{2+}), on crystallization. We found that $\text{D}_2\text{L}_2\text{-[1]}^{2+}$ is generated through a quick chiral scrambling process on mixing a solution of $\text{D}_4\text{-[1]}^{2+}$ and a solution of $\text{L}_4\text{-[1]}^{2+}$, giving a solution containing all $\text{D}_4\text{-[1]}^{2+}$, $\text{L}_4\text{-[1]}^{2+}$, and $\text{D}_2\text{L}_2\text{-[1]}^{2+}$. Remarkably, the three stereoisomers co-existed in solution were independently crystallized into three different kinds of crystals, homochiral crystals of $\text{D}_4\text{-[1]}(\text{NO}_3)_2$, homochiral crystals of $\text{L}_4\text{-[1]}(\text{NO}_3)_2$, and heterochiral crystals of

$\text{D}_2\text{L}_2\text{-[1]}(\text{NO}_3)_2$, without producing any other crystals that are composed of all the three or two of the three stereoisomers. Since homochiral crystals of $\text{D}_4\text{-[1]}(\text{NO}_3)_2$ or $\text{L}_4\text{-[1]}(\text{NO}_3)_2$ can be regarded as arising from the homochiral aggregation of the $\{\text{D}_4\text{-[1]}^{2+}$ or $\text{L}_4\text{-[1]}^{2+}\}_6$ octahedrons, each of which is the homochiral aggregate of $\text{D}_4\text{-[1]}^{2+}$ or $\text{L}_4\text{-[1]}^{2+}$, 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 $\text{D}_4\text{-[1]}(\text{NO}_3)_2$ or $\text{L}_4\text{-[1]}(\text{NO}_3)_2$, the heterochiral crystal of $\text{D}_2\text{L}_2\text{-[1]}(\text{NO}_3)_2$ 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

X-ray crystallographic data in CIF format and crystallographic, experimental, and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: konno@chem.sci.osaka-u.ac.jp.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported in part by Grants-in-Aids for Science Research (No. 23350026) from the Ministry of Education, Culture Sports, Science and Technology of Japan. The synchrotron radiation experiments were performed at the BL19B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2014B1022).

REFERENCES

- (1) (a) Cronin, J.; Reisse, J. in *Lectures in Atrobiology*, (Ed. Gargaud, M.), Springer, Verlag Berlin Heidelberg, **2006**, Vol. I, p. 473. (b) Guisjarro, A.; Yus, M. *The Origin of Chirality in the Molecules of Life*, RSC Publishing, **2009**.
- (2) (a) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305-326. (b) Amabilino, D. B.; Veciana, J. *Top. Curr. Chem.* **2006**, *265*, 253-302. (c) Amabilino, D. B. *Chem. Soc. Rev.* **2009**, *38*, 669-670. (d) Liu, Y.; Xuan, W.; Cui, Y. *Adv. Mater.* **2010**, *22*, 4112-4135. (e) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 1051-1095.
- (3) (a) Perez-Garcia, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2007**, *36*, 941-967. (b) Safont-Sempere, M.; Fernández, G.; Würthner, F. *Chem. Rev.* **2011**, *111*, 5784-5814. (c) Duan, P.; Cao, H.; Zhang, L.; Liu, M. *Soft Matter*, **2014**, *10*, 5428-5448.
- (4) (a) Yacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, racemates and resolutions*, John Wiley & Sons, New York, **1981**. (b) Amouri, H.; Gruselle, M. *Chirality in Transition Metal Chemistry*, John Wiley & Sons, Chichester, **2008**. (c) Dupray, V. in *Recrystallization* (Ed. K. Sztwiertnia), InTech, **2012**, Chapt. 17.
- (5) (a) Katsuki, I.; Matsumoto, N.; Kojima, M. *Inorg. Chem.* **2000**, *39*, 3350-3354. (b) Katsuki, I.; Motoda, Y.; Sunatsuki, Y.; Matsumoto, N.; Nakashima, T.; Kojima, M. *J. Am. Chem. Soc.* **2002**, *124*, 629-640. (c) Ou, G.-C.; Jiang, L.; Feng, X.-L.; Lu, T.-B. *Inorg. Chem.* **2008**, *47*, 2710-2718. (d) Lee, H.; Noh, T. H.; Jung, O.-S. *Angew. Chem. Int. Ed.* **2013**, *52*, 11790-11795. (e) Yokoi, A.; Yoshinari, N.; Konno, T. *Chem. Lett.* **2013**, *42*, 885-887. (f) Brewer, G.; Alvarado, L. J.; Brewer, C. T.;

Butcher, R. J.; Cipressi, J.; Viragh, C.; Zavalij, P. Y. *Inorg. Chim. Acta* **2014**, *421*, 100-109.

(6) (a) Xie, Z.; Stepanenko, V.; Radacki, K.; Würthner, F. *Chem.-Eur. J.* **2012**, *18*, 7060-7070. (b) Lin, N.-T.; Jentzsch, A. V.; Guénée, L.; Neudörfl, J.-M.; Aziz, S.; Berkessel, A.; Orentas, E.; Sakai, N.; Matile, S. *Chem. Sci.* **2012**, *3*, 1121-1127. (c) Roche, C.; Sun, H.-J.; Prendergast, M. E.; Leowanawat, P.; Partridge, B. E.; Heiney, P. A.; Araoka, F.; Graf, R.; Spiess, H. W.; Zeng, X.; Ungar, G.; Percec, V. *J. Am. Chem. Soc.* **2014**, *136*, 7169-7185. (d) Dressel, C.; Reppe, T.; Prehm, M.; Brautzu, M.; Tschierske, C. *Nature Chem.* **2014**, *6*, 971-977.

(7) Gao, E.-Q.; Bai, S.-Q.; Wang, Z.-M.; Yan, C.-H. *J. Am. Chem. Soc.* **2003**, *125*, 4984-4985.

(8) (a) Kondepudi, D. K. *Science* **1990**, *250*, 975-976. (b) Soai, K.; Niwa, S.; Hori, H. *J. Chem. Soc. Chem. Commun.* **1990**, 982-983. (c) Kondepudi, D. K.; Asakura, K. *Acc. Chem. Res.* **2001**, *34*, 946-954. (d) Rybak, W. K.; Skarzynska, A.; Głowiak, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 1725-1727. (e) Hein, J. E.; Cao, B. H.; Viedma, C.; Kellogg, R. M.; Blackmond, D. G. *J. Am. Chem. Soc.* **2012**, *134*, 12629-12636.

(9) (a) Konno, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 627-649. (b) Igashira-Kamiyama, A.; Konno, T. *Dalton Trans.* **2011**, 40, 7249-7263.

(10) (a) Konno, T.; Yoshimura, T.; Aoki, K.; Okamoto, K.; Hirotsu, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1765-1768. (b) Aridomi, T.; Kawamoto, T.; Konno, T. *Inorg. Chem.* **2007**, *46*, 1343-1353. (c) Aridomi, T.; Takamura, K.; Igashira-Kamiyama, A.; Kawamoto, T.; Konno, T. *Chem.-Eur. J.* **2008**, *14*, 7752-7755. (d) Yoshinari, N.; Igashira-Kamiyama, A.; Konno, T. *Chem.-Eur. J.* **2010**, *16*, 14247-14251. (e) Yoshinari, N.; Konno, T. *Dalton Trans.* **2011**, 40, 12191-12200. (f) Yamashita, U.; Lee, P.; Kuwamura, N.; Yoshinari, N.; Konno, T. *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1450-1452.

(11) (a) Hashimoto, Y.; Yoshinari, N.; Naruse, D.; Nozaki, K.; Konno, T. *Inorg. Chem.* **2013**, *52*, 14368-14375. (b) Hashimoto, Y.; Yoshinari, N.; Matsushita, N.; Konno, T. *Eur. J. Inorg. Chem.* **2014**, 3474-3478. (c) Oji, K.; Igashira-Kamiyama, A.; Yoshinari, N.; Konno, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 1992-1996. (d) Yoshinari, N.; Kakuya, A.; Lee, R.; Konno, T. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 59-68. (e) Hashimoto, Y.; Yoshinari, N.; Kuwamura, N.; Konno, T. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1144-1146.

(12) (a) Lee, R.; Igashira-Kamiyama, A.; Motoyoshi, H.; Konno, T. *CrystEngComm* **2012**, *14*, 1936-1938. (b) Lee, R.; Igashira-Kamiyama, A.; Okumura, M.; Konno, T. *Bull. Chem. Soc. Jpn.* **2013**, *86*, 908-920.

(13) (a) Wheaton, C. A.; Puddephatt, R. J. *Angew. Chem. Int. Ed.* **2007**, *46*, 4461-4463. (b) Hao, H.-Q.; Liu, W.-T.; Tan, W.; Lin, Z.-J.; Tong, M.-L. *CrystEngComm* **2009**, *11*, 967-971.

(14) See the Supporting Information (SI).

(15) The L_4 isomer of the $Au_4Co^{III}_2$ hexanuclear complex (L_4 -[1](NO₃)₂) was prepared by using L-H₂pen, instead of D-H₂pen, according to the literature procedure for D₄-[1](NO₃)₂.^{1b} Its assignment was made by IR, absorption, circular dichroism (CD), and ¹H and ³¹P NMR spectroscopy, together with elemental and fluorescence X-ray analyses.¹⁴

(16) The 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 with those simulated from the crystal structure of D₂L₂-[1](NO₃)₂ most likely due to the efflorescence of crystals B.

(17) Pyykkö, P. *Chem. Soc. Rev.* **2008**, *37*, 1967-1997.

(18) 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.^{10a,10c}

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

(20) The ¹H and ³¹P NMR and absorption spectra of D₄- or L₄-[1]²⁺ were almost identical with those of D₂L₂-[1]²⁺.¹⁴

Mixing of a pair of enantiomers (D_4 , L_4) of the cyclic $Au^I_4Co^{III}_2$ hexanuclear complex resulted in a mixture of three stereoisomers (D_4 , L_4 , D_2L_2) through the chiral-scrambling process. The three stereoisomers were independently crystallized to give three kinds of crystals due to self-recognition and organization of complex-cations on crystallization.

