



Title	Multinuclear Complexes Crystallized from a Mixture of Diphosphine Digold(I) Metalloligands with Cysteinate or Penicillamine
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Abstract of Thesis

	Name (Sasikarn Hanprasit)
Title	Multinuclear Complexes Crystallized from a Mixture of Diphosphine Digold(I) Metalloligands with Cysteinate or Penicillamate (システインあるいはペニシラミンをもつジフォスフィン金(I)二核錯体配位子の混合から結晶化する多核金属錯体)

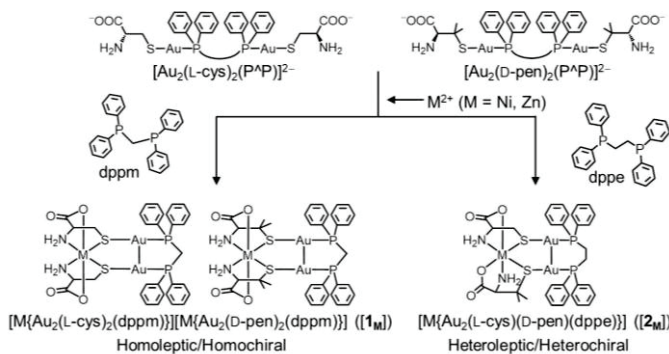
Abstract of Thesis

The self-assembly of metal ions and bridging ligands in solution has been one of the universal methods for creating metal complexes. However, the self-assembly of more than two kinds of components often results in the formation of two or more products. For example, when a mixture of two kinds of ligands (L_A and L_B) is reacted with a metal ion (M), a pair of coordination isomers, homoleptic complexes $[M(L_A)_2]$ and $[M(L_B)_2]$ and a heteroleptic complex $[M(L_A)(L_B)]$, are formed as the 1:2 complex. In some cases, the selective formation of one species from a mixture has been observed. Such a phenomenon is represented by the term ‘self-sorting’ and is classified into (i) homoleptic self-sorting and (ii) heteroleptic self-sorting, which show the selective formation of homoleptic and heteroleptic products, respectively. As a similar concept, chiral self-sorting phenomenon, showing the selective formation of homochiral (*e.g.*, $[M(R-L)_2]$ and $[M(S-L)_2]$) or heterochiral isomer (*e.g.*, $[M(R-L)(S-L)]$) from a pair of enantiomers of ligand (*e.g.*, $R-L$ and $S-L$), is also established and referred as the homochiral and heterochiral self-sorting, respectively. Usually, the self-sorting events are directed by ligand-ligand or ligand-metal repulsive or attractive interactions. Therefore, the preference of self-sorting is pre-determined by ligand structures. Thus, coordination systems that can switch the homoleptic *vs* heteroleptic and homochiral *vs* heterochiral isomers have rarely been reported. Recently, our laboratory has reported that a series of homoleptic digold(I) metalloligands with penicillamate (pen) and diphosphine ($P^{\wedge}P$), $[Au_2(pen)_2(P^{\wedge}P)]^{2-}$, can function as a metalloligand toward octahedral metal ions to form cyclic multinuclear complexes, such as $[M^{II}\{Au^I_2(D-pen)_2(dppm)\}]$ ($M = Ni, Zn$).

The studies presented in this thesis focused on the coordination behavior of a mixture of two or more kinds of digold(I) metalloligands $[Au_2(L)_2(P^{\wedge}P)]^{2-}$ ($L =$ cysteinate (cys), pen; $P^{\wedge}P =$ dppm, dppe) toward octahedral M^{2+} ions ($M = Ni, Zn$). Furthermore, the effects on the self-sorting behavior due to chemical modification and reaction condition were investigated.

Firstly, the coordination behavior of a mixture of two kinds of metalloligands, $[Au_2(L-cys)_2(P^{\wedge}P)]^{2-}$ and $[Au_2(D-pen)_2(P^{\wedge}P)]^{2-}$, toward M^{2+} ion ($M = Ni, Zn$) was investigated (Scheme 1). The homoleptic $Au^I_2M^{II}$ trinuclear complexes, $[M\{Au_2(L-cys)_2(dppm)\}][M\{Au_2(D-pen)_2(dppm)\}]$ (**[1M]**) were obtained for dppm system. On the other hand, the corresponding dppe system gave the heteroleptic $Au^I_2M^{II}$ trinuclear complex, $[M\{Au_2(L-cys)(D-pen)(dppe)\}]$ (**[2M]**). The molecular modeling study indicated that the matching of the directions of the P–Au bonds in the $[Au_2(P^{\wedge}P)]^{2+}$ unit and the lone pairs on the sulfur atoms of the $[M^{II}(L-cys \text{ or } D-pen)_2]^{2-}$ unit is a key factor for the coordination isomerism. Therefore, the ancillary $P^{\wedge}P$ ligand governs the coordination isomerism around the M^{II} center in **[1M]** and **[2M]**, leading to the selective homochiral and heterochiral self-sorting in this system.

In order to study the effect of solvent on the self-sorting, the coordination behavior of a mixture of four kinds of metalloligands, $[Au_2(D-cys)_2(P^{\wedge}P)]^{2-}$, $[Au_2(L-cys)_2(P^{\wedge}P)]^{2-}$, $[Au_2(D-pen)_2(P^{\wedge}P)]^{2-}$, and $[Au_2(L-pen)_2(P^{\wedge}P)]^{2-}$, toward M^{2+} ion ($M = Ni, Zn$) in various solvents (EtOH/H₂O, MeOH/H₂O, and MeOH) was examined (Scheme 2). In the dppm system, the reaction in EtOH/H₂O, which is a moderate polar solvent, formed the homochiral/heteroleptic

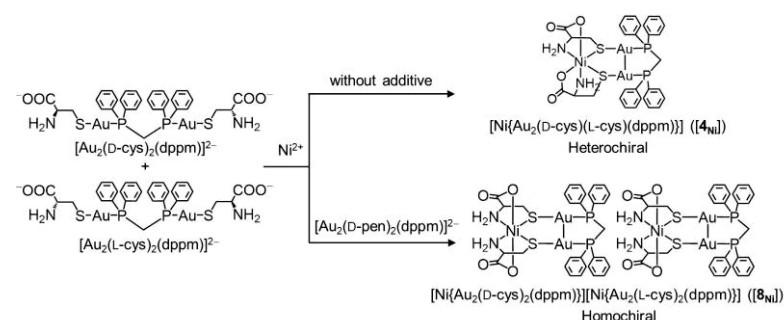


Scheme 1. Summary of the synthetic scheme for **[1M]** and **[2M]**.

$\text{Au}_2\text{M}^{\text{II}}$ trinuclear complexes, $[\text{M}\{\text{Au}_2(\text{D-cys})(\text{D-pen})(\text{dppm})\}][\text{M}\{\text{Au}_2(\text{L-cys})(\text{L-pen})(\text{dppm})\}]$ (**[3M]**). A similar reaction using MeOH and MeOH/H₂O, which is a less polar solvent and highly polar solvent, produced the heterochiral/homoleptic $\text{Au}_2\text{M}^{\text{II}}$ trinuclear complexes, $[\text{M}\{\text{Au}_2(\text{D-cys})(\text{L-cys})(\text{dppm})\}]$ (**[4M]**), and the homochiral/homoleptic $\text{Au}_2\text{M}^{\text{II}}$ trinuclear complexes, $[\text{M}\{\text{Au}_2(\text{D-pen})_2(\text{dppm})\}][\text{M}\{\text{Au}_2(\text{L-pen})_2(\text{dppm})\}]$ (**[5M]**), respectively. This trend is reasonable because the relatively polar *cys* complex may prefer to dissolve in the highest polar solvent. On the other hand, the *dppe* system showed the opposite trend; the heterochiral/homoleptic $\text{Au}_2\text{M}^{\text{II}}$ trinuclear complexes, $[\text{M}\{\text{Au}_2(\text{D-cys})(\text{L-cys})(\text{dppe})\}]$ (**[6M]**), were yielded in EtOH/H₂O that has the moderate polarity, whereas the homochiral/homoleptic $\text{Au}_4\text{M}^{\text{II}}_2$ hexanuclear complexes, $[\text{M}_2\{\text{Au}_2(\text{D-pen})_2(\text{dppe})\}_2][\text{M}_2\{\text{Au}_2(\text{L-pen})_2(\text{dppe})\}_2]$ (**[7M]**), were formed from less polar MeOH.

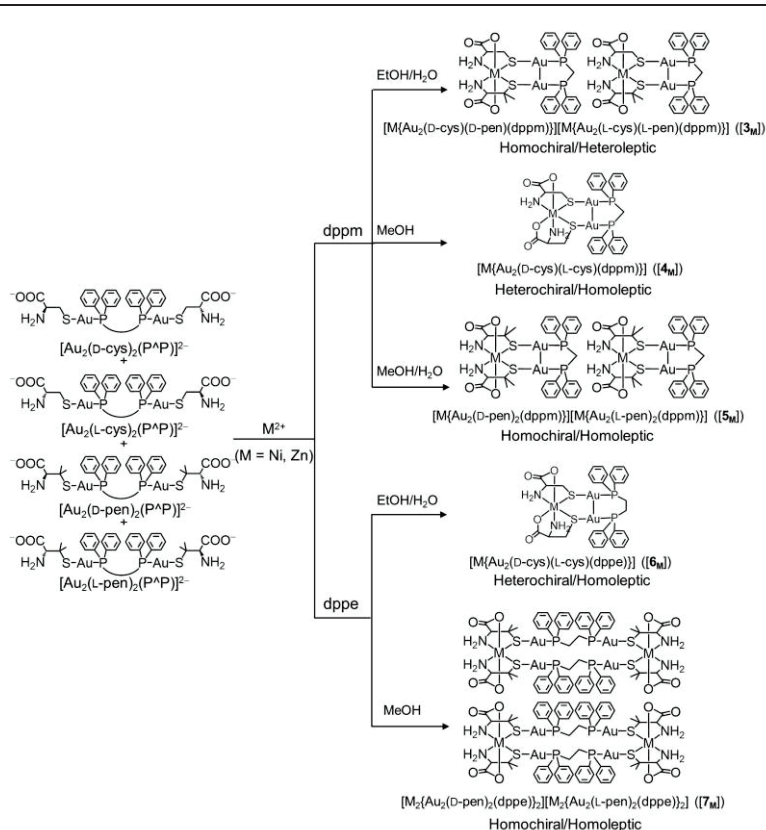
The preferable formation of hexanuclear complex in MeOH was explained by the non-polar D_2 symmetric structure of **[7M]**.

Furthermore, the coordination behavior of an enantiomeric mixture of the metalloligands, $[\text{Au}_2(\text{D-cys})_2(\text{P}^*\text{P})]^{2-}$ and $[\text{Au}_2(\text{L-cys})_2(\text{P}^*\text{P})]^{2-}$, toward Ni^{2+} ion was investigated. The reaction without the additive gave the heterochiral $\text{Au}_2\text{Ni}^{\text{II}}$ complexes, $[\text{Ni}\{\text{Au}_2(\text{D-cys})(\text{L-cys})(\text{P}^*\text{P})\}]$ ($\text{P}^*\text{P} = \text{dppm}$ (**[4Ni]**), dppe (**[6Ni]**)), indicating the heterochiral self-sorting phenomenon. Interestingly, the co-presence of $[\text{Au}_2(\text{D-pen})_2(\text{dppm})]^{2-}$ with the mixture of $[\text{Au}_2(\text{D-cys})_2(\text{dppm})]^{2-}$ and $[\text{Au}_2(\text{L-cys})_2(\text{dppm})]^{2-}$ gave the homochiral $\text{Au}_2\text{Ni}^{\text{II}}$ complex, $[\text{Ni}\{\text{Au}_2(\text{D-cys})_2(\text{dppm})\}][\text{Ni}\{\text{Au}_2(\text{L-cys})_2(\text{dppm})\}]$ (**[8Ni]**) (Scheme 3). Thus, the formation of **[8Ni]** is a kind of an



Scheme 3. Summary of the synthetic scheme for **[4Ni]** and **[8Ni]**.

Finally, this study demonstrated that the self-sorting behavior of multi-component metal complexes could be controlled by the subtle changes of ancillary ligands or reaction solvents. Indeed, eight of ten possible coordination isomers of the $[\text{M}\{\text{Au}_2(\text{L})_2(\text{P}^*\text{P})\}]$ -type complexes ($\text{L} = \text{D-cys}, \text{L-cys}, \text{D-pen}, \text{or L-pen}$) were successfully isolated in a controlled manner in the present study. Such a systematic preparation of coordination isomers of a multi-component coordination system has never been achieved so far. The chemical library obtained in this work should be a good platform for studying the relationship between the physical and chemical properties and the coordination isomerism in the future study.



Scheme 2. Summary of the synthetic scheme for **[3M]**, **[4M]**, **[5M]**, **[6M]** and **[7M]**.

additive-controlled crystallization. It is likely that the ratio of homochiral and heterochiral species in the reaction solution was changed by the additive, leading to the switching of the chiral self-sorting behavior. Such an additive-controlled formation was not observed in the *dppe* system, probably due to the high stability of the heterochiral structure.

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨		
本論文は、配位可能な部位を有する配位子として含硫アミノ酸（システインおよびペニシラミン）を、錯体配位子の機能を調節する連結配位子としてジホスフィンを導入した金(I)二核錯体配位子を合成し、含硫アミノ酸の異なる2種類の錯体配位子を混合させた場合に形成される $\text{Au}^{\text{I}}\text{Ni}^{\text{II}}$ および $\text{Au}^{\text{I}}\text{Zn}^{\text{II}}$ 多核金属錯体の構造と性質についてまとめたものである。L-システインをもつ錯体配位子とD-ペニシラミンをもつ錯体配位子を混合させた場合には、連結配位子の炭素鎖の違いにより、Homoleptic-Homochiral と Heteroleptic-Heterochiral の $\text{Au}_2\text{M}^{\text{II}}$ 三核錯体が選択的に結晶化し、一方、L-システインをもつ錯体配位子と D-システインをもつ錯体配位子を混合させた場合には、共存錯体配位子の有無により、Homochiral と Heterochiral の三核錯体が選択的に結晶化することを明らかにしている。また、DL-システインをもつ錯体配位子と DL-ペニシラミンをもつ錯体配位子の混合系においては、わずかに極性の異なる溶媒を用いることにより、可能な10種の錯体の中から、Homoleptic-Homochiral、Homoleptic-Heterochiral、および Homoleptic-Heterochiral の $\text{Au}_2\text{Ni}^{\text{II}}$ 三核錯体を選択的に得ることに成功している。これまで、このような多数の混合物から、Homoleptic と Homoleptic 錯体さらには Homochiral と Heterochiral 錯体の精密制御に成功した例はなく、外部因子による選択的多核錯体の結晶化を初めて実現した研究である。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。		