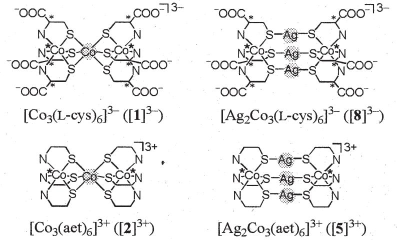
Title	Creation of Chiral Metalloaggregates Based on Multinuclear Complex Anions with L-Cysteinate
Author(s)	袁, 厚群
Citation	大阪大学, 2011, 博士論文
Version Type	
URL	https://hdl.handle.net/11094/58616
rights	
Note	著者からインターネット公開の許諾が得られていないため、論文の要旨のみを公開しています。全文のご利用をご希望の場合は、大阪大学の博士論文についてをご参照ください。

【41】

氏　　　　　名	袁（ユエン）　厚（ホウ）　群（チュイン）
博士の専攻分野の名称	博　士（理　学）
学 位 記 番 号	第　２４３３６　号
学位授与年月日	平成 23 年 3 月 25 日
学位授与の要件	学位規則第４条第１項該当 理学研究科化学専攻
学 位 論 文 名	Creation of Chiral Metalloaggregates Based on Multinuclear Complex Anions with L-Cysteinate （L-システィンをもつ多核金属錯体アニオンをベースとしたキラル分子集合体の創製）
論文審査委員	（主査） 教　授　今野　　巧 （副査） 教　授　石川　直人　　教　授　稲葉　　章

論文内容の要旨

Chiral metalloaggregates have been received considerable attention because of their significance in fundamental coordination stereochemistry and their potential and/or practical applications. However, the rational construction of chiral metalloaggregates with desired structures is still a great challenge. This study was focused on the aggregation of chiral multinuclear complex-anions with L-cysteinate (L-cys), which possess 6 free carboxylate groups, assisted by complex-cations or simple metal ions through non-covalent interactions, in order to achieve the rational construction of chiral metalloaggregates and to investigate the chiral effects of the complex-anions on the structures of the resulting chiral metalloaggregates. First, the diastereomers of the multinuclear complex-anions were treated with racemic complex-cations to investigate the chiral selectivity. Second, the diastereomers of the multinuclear complex-anions were treated with lanthanide ions to synthesize a series of chiral coordination polymers.



$[Co_3(L\text{-}cys)_6]^{3-}$ ($[\mathbf{1}]^{3-}$)　$[Ag_2Co_3(L\text{-}cys)_6]^{3-}$ ($[\mathbf{8}]^{3-}$)

$[Co_3(aet)_6]^{3+}$ ($[\mathbf{2}]^{3+}$)　$[Ag_2Co_3(aet)_6]^{3+}$ ($[\mathbf{5}]^{3+}$)

Scheme 1.

The $(\Lambda_{LLL})_2$ and $(\Delta_{LLL})_2$ isomers of the S-bridged trinuclear complex-anion, $[Co_3(L\text{-}cys)_6]^{3-}$ ($[\mathbf{1}]^{3-}$), having 6 free carboxylate groups and multiple chiral centers, were aggregated by using the $(\Delta)_2/(\Lambda)_2$ racemic trinuclear complex-cation, $[Co_3(aet)_6]^{3+}$ ($[\mathbf{2}]^{3+}$; aet = 2-aminoethanethiolate), which has an

S-bridged structure similar to that of [**1**]$^{3-}$. It was found that $(\Lambda_{\mathrm{LLL}})_2$-[**1**]$^{3-}$ exclusively selects the $(\Delta)_2$ isomer of [**2**]$^{3+}$ to form a heterochiral complex salt, $(\Delta)_2(\Lambda_{\mathrm{LLL}})_2$-$[\mathrm{Co_3(aet)_6}][\mathrm{Co_3(L\text{-}cys)_6}]$ (**3**). When $(\Delta_{\mathrm{LLL}})_2$-[**1**]$^{3-}$ was used, however, the complex salt, $[\mathrm{Co_3(aet)_6}][\mathrm{Co_3(L\text{-}cys)_6}]$ (**4**), was obtained only under a very concentrated condition, in which the $(\Lambda)_2$ isomer of [**2**]$^{3+}$ is preferentially selected. This difference in the chiral selectivity between the diastereomers of [**1**]$^{3-}$ is most likely due to the difference in the orientation of carboxylate groups between its $(\Lambda_{\mathrm{LLL}})_2$ and $(\Delta_{\mathrm{LLL}})_2$ isomers.

Then, the $(\Lambda_{\mathrm{LLL}})_2$ and $(\Delta_{\mathrm{LLL}})_2$ isomers of [**1**]$^{3-}$ were treated with the $(\Delta)_2/(\Lambda)_2$ racemic pentanuclear complex-cation, $[\mathrm{Ag_3Co_2(aet)_6}]^{3+}$ ([**5**]$^{3+}$), the structure of which is similar to that of [**2**]$^{3+}$, except the presence of an $\{\mathrm{Ag_3}\}^{3+}$ moiety between two terminal $[\mathrm{Co(aet)_3}]$ units in place of a $\mathrm{Co^{3+}}$ ion in [**2**]$^{3+}$. It was found that $(\Lambda_{\mathrm{LLL}})_2$-[**1**]$^{3-}$ exclusively selects the $(\Lambda)_2$ isomer of [**5**]$^{3+}$, which is in line with its enantioselectivity toward $(\Delta)_2$-[**2**]$^{3+}$. However, $(\Delta_{\mathrm{LLL}})_2$-[**1**]$^{3-}$ prefers the $(\Lambda)_2$ isomer of [**5**]$^{3+}$, as does $(\Lambda_{\mathrm{LLL}})_2$-[**1**]$^{3-}$, although its enantioselectivity is not excellent. Thus, both the $(\Delta_{\mathrm{LLL}})_2$ and $(\Lambda_{\mathrm{LLL}})_2$ isomers of [**1**]$^{3-}$ prefers the $(\Lambda)_2$ isomer of [**5**]$^{3+}$, indicating that the local chirality (L-cysteinate), rather than a helicoidal chirality about metal centers (Δ vs. Λ), predominates the chiral selectivity of [**1**]$^{3-}$ toward [**5**]$^{3+}$.

The chiral selectivity of the $(\Delta_{\mathrm{LLL}})_2$ isomer of a pentanuclear complex-anion, $[\mathrm{Ag_3Co_2(L\text{-}cys)_6}]^{3-}$ ([**8**]$^{3-}$) toward $(\Delta)_2/(\Lambda)_2$-[**2**]$^{3+}$ was also investigated. It was found that $(\Delta_{\mathrm{LLL}})_2$-[**8**]$^{3-}$ shows an excellent chiral selectivity toward the $(\Delta)_2$ isomer of [**2**]$^{3+}$, which is very different from the case for $(\Delta_{\mathrm{LLL}})_2$-[**1**]$^{3-}$. The introduction of an $\{\mathrm{Ag_3}\}^{3+}$ moiety in $(\Delta_{\mathrm{LLL}})_2$-[**8**]$^{3-}$, which causes additional intermolecular interactions and increases the distance between two terminal $[\mathrm{Co(L\text{-}cys)_3}]^{3-}$ units, is most likely responsible for this excellent enantioselectivity.

The aggregation of the $(\Lambda_{\mathrm{LLL}})_2$ and $(\Delta_{\mathrm{LLL}})_2$ isomers of [**1**]$^{3-}$ by lanthanide ions ($\mathrm{Ln^{3+}}$) was also investigated. It was shown that a series of heterometallic chiral metalloaggregates, $(\Lambda_{\mathrm{LLL}})_2$-Ln[**1**] and $(\Delta_{\mathrm{LLL}})_2$-Ln[**1**] composed of [**1**]$^{3-}$ and $\mathrm{Ln^{3+}}$ in a 1:1 ratio, were constructed, indicating that $(\Lambda_{\mathrm{LLL}})_2$- and $(\Delta_{\mathrm{LLL}})_2$-[**1**]$^{3-}$ can be used as an O-donating metalloligand. For the $(\Lambda_{\mathrm{LLL}})_2$ isomer of Ln[**1**], only a 3D structure, 2D and 3D structures, and only a 2D structure were formed for Ln = La and Ce, Ln = Pr and Nd, and Ln = Sm to Lu, respectively. On the other hand, for the $(\Delta_{\mathrm{LLL}})_2$ isomer of Ln[**1**], a 2D structure and a 3D structure were formed for bigger lanthanide ions (Ln = La to Tm) and smaller lanthanide ions (Ln = Yb and Lu), respectively. Thus, the dimensional structures of $(\Lambda_{\mathrm{LLL}})_2$-Ln[**1**] and $(\Delta_{\mathrm{LLL}})_2$-Ln[**1**] are highly dependent on the diastereoisomerism of [**1**]$^{3-}$, the difference of which causes the difference in the orientation of carboxylate groups, as well as on the ionic size of $\mathrm{Ln^{3+}}$.

In conclusion, the rational construction of chiral metalloaggregates by using chiral multinuclear complex-anions having several coordination and/or hydrogen-bonding sites was achieved in this study. It was found that the structures of chiral metalloaggregates are controlled by the diastereomerism of chiral multinuclear complex-anions, as well as the types of metal complexes or metal ions employed. In addition the chiral selectivity due to the chiral multinuclear complexes was found to be controlled by their diastereomerism because of the difference in the orientation of functional groups that interact with metal ions or complexes. Finally, it was shown that the presence of additional non-covalent interactions, besides hydrogen-bonding one, increases the efficiency of the chiral selectivity.

論文審査の結果の要旨

本論文は、L-システインを配位したアニオン性硫黄架橋多核錯体のカチオン性多核錯体やランタノイドイオンに対する反応性、ならびに形成される分子集合体の構造と諸性質についてまとめたものである。本研究により、この種のアニオン性多核錯体がカチオン性多核錯体に対して極めて優れたキラル認識能を有すること、そのキラル認識能が多核錯体のジアステレオ異性に大きく依存すること、さらには、多核錯体のジアステレオ異性やランタノイドのイオンサイズに基づいて分子集合体の次元構造が大きく変化することなど分子構造体の構築、ならびにそれらの構造と機能の制御に関する重要な知見が得られた。これらの成果は、錯体合成化学および錯体構造化学の今後の進展に対して基礎的かつ重要な知見を与えるものであり、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。