



Title	Chiral Behavior of S-Bridged M ₃ M' ₂ (M = AuI, AgI; M' = CoIII, RhIII) Pentanuclear Complexes with L-Cysteinate
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論文内容の要旨

氏名 (LEE, PEI-SHAN)	
論文題名	Chiral Behavior of S-Bridged $M_3M'_2$ ($M = Au^I, Ag^I; M' = Co^{III}, Rh^{III}$) Pentanuclear Complexes with L-Cysteinate (L-システインをもつ硫黄架橋 $M_3M'_2$ ($M = Au^I, Ag^I; M' = Co^{III}, Rh^{III}$) 五核錯体のキラル挙動)
論文内容の要旨	

Chiral coordination compounds have received immense attention because of their fundamental importance in modern stereochemistry and potential applications. The preparation of optically active chiral compounds is mainly achieved by two ways; one is the asymmetric synthesis and the other is the optical resolution of a racemic compound into its enantiomers. The formation of a diastereomeric ion-pair is a powerful way for the optical resolution. For this purpose, optically pure organic compounds such as tartaric acid and alkaloids have widely been used as resolving reagents for cationic and anionic coordination compounds, respectively. Recently, Konno and co-workers reported that the $(\Delta_{LLL})_2$ isomer of $[Co_3(L-cys-N,S)_6]^{3-}$ ($L-cys = L$ -cysteinate), in which two octahedral $\Delta_{LLL-fac}-[Co(L-cys-N,S)_6]^{3-}$ units are linked by a Co^{III} atom through sulfur atoms, acts as an efficient anionic resolving reagent toward the racemic (Δ_2/Λ_2) polynuclear complexes, $[Co_3(aet)_6]^{3+}$ and $[Ag_3Co_2(aet)_6]^{3+}$ ($aet = 2$ -aminoethanethiolate), forming the complex-salts that contains only the $(\Delta)_2$ isomer of $[Co_3(aet)_6]^{3+}$ and the $(\Lambda)_2$ isomer of $[Ag_3Co_2(aet)_6]^{3+}$, respectively. This result implies that optically active polynuclear complex-anions can be used as an appropriate resolving reagent toward racemic polynuclear complex-cations.

To extend this chemistry, in this study, the chiral behavior of S-bridged $M_3M'_2$ pentanuclear complex-anions, $(\Delta_{LLL})_2-[M_3M'_2(L-cys-N,S)_6]^{3-}$ ($M = Au^I, Ag^I; M' = Co^{III}, Rh^{III}$), in which two terminal $\Delta_{LLL-fac}-[M'(L-cys-N,S)_3]^{3-}$ units are linked by three linear M atoms was investigated. It is expect that the introduction of $\{Au^I_3\}^{3+}$ or $\{Ag^I_3\}^{3+}$ moieties, in place of the central Co^{III} atom in $[Co_3(L-cys-N,S)_6]^{3-}$, leads to the formation of additional intermolecular interactions to show different chiral behavior. In this thesis, the resolving ability of these optically active multinuclear complex-anions and their Rh^{III} analogues toward the racemic $[Co_3(aet)_6]^{3+}$, together with the unique chiral and structural conversions of $(\Delta_{LLL})_2-[Co_3Au_2(L-cys-N,S)_6]^{3-} ([1]^{3-})$ in the course of the crystallization with $[Co_3(aet)_6]^{3+}$, is presented.

At first, the S-bridged $Au^I_3Co^{III}_2$ pentanuclear complex-anion, $(\Delta_{LLL})_2-[Au_3Co_2(L-cys-N,S)_6]^{3-} ([1]^{3-})$, was newly prepared, and its crystallizing behavior with the racemic $[Co_3(aet)_6]^{3+}$ was investigated. When $K_3[1]$ was treated with the racemic $[Co_3(aet)_6](NO_3)_3$ in a neutral aqueous solution, a 1:1 complex-salt of $[Co_3(aet)_6][1]$ was formed, retaining the pentanuclear structure with the $(\Delta_{LLL})_2$ configuration of $[1]^{3-}$. On the other hand, a similar reaction in a basic solution resulted in the chiral and structural conversions from $[1]^{3-}$ to $(\Delta_{LLL})_2-[Au_6Co_4(L-cys-N,S)_{12}]^{6-} ([2]^{6-})$, affording a 2:1 complex-salt of $[Co_3(aet)_6]_2[2]$. Such a coordination system that shows a multiple chiral inversion and a structural conversion in the course of the formation of a complex-salt is unprecedented.

Next, the chiral selectivity of $[1]^{3-}$, $[2]^{6-}$, $(\Delta_{LLL})_2-[Ag_3Co_2(L-cys-N,S)_6]^{3-} ([3]^{3-})$, $(\Delta_{LLL})_2-[Au_3Rh_2(L-cys-N,S)_6]^{3-} ([4]^{3-})$, and $(\Delta_{LLL})_2-[Ag_3Rh_2(L-cys-N,S)_6]^{3-} ([5]^{3-})$ toward the racemic $[Co_3(aet)_6]^{3+}$ was investigated. The optical purity of $[Co_3(aet)_6]^{3+}$ incorporated with these complex anions in each complex-salt was checked by column chromatography and the subsequent absorption and CD spectral measurements, along with X-ray crystallography. It was found that the presence of Ag^I in the anionic pentanuclear structure, which forms intermolecular $Ag-OOC$ coordination bonds, is key to the appearance of an excellent chiral selectivity toward the racemic $[Co_3(aet)_6]^{3+}$.

In conclusion, this study provides not only the fundamental understanding for the chiral behavior in coordination chemistry, but also the further development of chiral switching systems in material science. From the chiral recognition behavior of the multinuclear complex-anions toward the racemic $[Co_3(aet)_6]^{3+}$ found in this study, it is evident that the increase in the intermolecular-interaction sites between complex-anions and complex-cations improves chiral selectivity. Thus, to achieve an excellent chiral selectivity, the introduction of several non-covalent bonding sites into optically active metal complexes that act as a resolving reagent should be required.

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		
<p>本論文は、L-システインを配位したキラルなアニオン性硫黄架橋五核錯体の合成と構造決定、それらのキラルなカチオン性三核錯体に対する反応性、ならびに形成されるイオン結晶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のキラル認識能が五核錯体を構成する連結金属イオン (Ag^+ vs. Au^+) に大きく依存すること、その要因が分子間相互作用にあることなどキラル構造制御に関する重要な知見を得ている。また、Au^+連結五核錯体においては、わずかなpHの調整による前例のない多重キラル反転、それに伴う分子カップリング反応がイオン結晶生成過程において生じる事を発見している。これらの成果は、光学活性な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。</p>		