Creation of Discrete Silver(I) Coordination Compounds with Nonbridging Chlorides by the Use of Mono(D-penicillaminato)cobalt(III) Metalloligand

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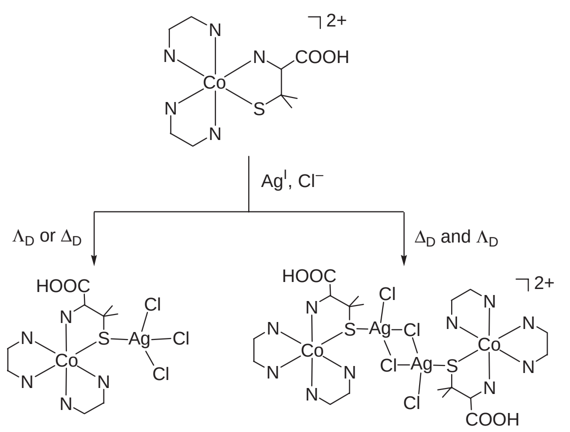
The reactions of the Λ_D or Δ_D isomer of [Co(D-Hpen-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (**1**; D-H$_2$pen = D-penicillamine) with AgNO$_3$ in water, followed by the addition of NaCl and HCl, led to the formation of discrete Co^{III}Ag^{I} dinuclear complexes, Λ_D- or Δ_D-[AgCl$_3${Co(D-Hpen-*N*,*S*)(en)$_2$}]. A similar reaction using a 1:1 mixture of the Λ_D and Δ_D isomers of **1**, followed by the addition of NaCl, afforded a Co$^{III}_2$Ag$^{I}_2$ tetranuclear complex, $\Lambda_D\Delta_D$-[Ag$_2$Cl$_4${Co(D-Hpen-*N*,*S*)(en)$_2$}$_2$]$^{2+}$.

Silver chloride has attracted much attention for many years because of its peculiar properties such as light sensitivity, ionic conductivity, and catalytic activity.[1] In addition, the poor solubility of silver chloride in any common solvents has been applied to extract Ag$^+$ or Cl$^-$ ions from solutions by the addition of chloride or silver(I) salts.[2] Despite the poor solubility of silver chloride, a number of silver(I) coordination compounds with chloride ligands have been prepared by mixing with an appropriate organic or inorganic ligand.[3,4] In many cases, chloride ligands tend to bridge silver(I) centers, and thus the isolation of silver(I) compounds with more than two nonbridging chloride ligands is very rare.[3f] During the course of studying the binding ability of thiolato-type metalloligands toward a silver(I) center,[5] we noticed that an aqueous suspension containing [Co(D-Hpen-*N*,*S*)(en)$_2$]$^{2+}$ and AgCl turns to a clear solution by the addition of excess Cl$^-$, suggesting the formation of some discrete Co^{III}Ag^{I} species with nonbridging chloride ligands. In this paper, we report that the Co^{III}Ag^{I} species isolated from the reaction using the Λ_D or Δ_D isomer of [Co(D-Hpen-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (**1**) has a S-bridged Co^{III}Ag^{I} dinuclear structure bearing three nonbridging chloride ligands (Scheme 1). As far as we know, these are the first examples of discrete silver(I) coordination compounds with more than three nonbridging chloride ligands, except [AgCl$_3$]$^{2-}$ and [AgCl$_4$]$^{3-}$.[4] Remarkably, the use of a 1:1 mixture of the Λ_D and Δ_D isomers of **1** was found to produce a Co$^{III}_2$Ag$^{I}_2$ tetranuclear structure with two bridging and two nonbridging chloride ligands, the result of which is also reported here.



Scheme 1. Synthetic routes of **2** or **3** (left) and **4** (right) from **1**.

Treatment of a dark-brown aqueous solution of Λ_D-[Co(D-Hpen-*N*,*S*)(en)$_2$](ClO$_4$)$_2$[6] (Λ_D-**1**) with AgNO$_3$ in a 1:1 ratio gave a dark-red solution. When a saturated aqueous NaCl solution was added to this solution, a precipitate of AgCl appeared to afford a dark-brown suspension, which turned to a clear red-brown solution by the addition of 1 M aqueous HCl. From this reaction solution, red-brown crystals **2** were isolated by allowing it to stand at room temperature.[7] Compound **2** was also obtained by the direct reaction of Λ_D-**1** with AgCl in water, followed by the addition of 1 M aqueous HCl. X-ray fluorescence spectrometry implied that **2** contains Co and Ag atoms in a 1:1 ratio, and its elemental analytical data were in good agreement with the formula for a 1:1 adduct of [Co(D-Hpen-*N*,*S*)(en)$_2$]$^{2+}$ and [AgCl$_3$]$^{2-}$. The presence of a protonated COOH group in **2** was confirmed by the IR spectrum that gives a ν(C=O) band at 1702 cm^{-1}.[8] The structure of **2** was determined by single-crystal X-ray analysis.[9] As shown in Figure 1a, **2** is a neutral complex molecule consisting of a Λ_D-[Co(D-Hpen-*N*,*S*)(en)$_2$]$^{2+}$ unit and a [AgCl$_3$]$^{2-}$ moiety. The thiolato S atom of the [Co(D-Hpen-*N*,*S*)(en)$_2$]$^{2+}$ unit binds to a Ag^{I} atom of the [AgCl$_3$]$^{2-}$ moiety to form a S-bridged Co^{III}Ag^{I} dinuclear structure in Λ_D-[AgCl$_3${Co(D-Hpen-*N*,*S*)(en)$_2$}]. The Ag^{I} atom is situated in a tetrahedral geometry, coordinated by three nonbridging Cl atoms (av Ag–Cl = 2.622(1) Å), besides a S atom from the [Co(D-Hpen-*N*,*S*)(en)$_2$]$^{2+}$ unit (Ag–S = 2.513(1) Å). In **2**, there exists a weak intramolecular hydrogen bond between chloro and en amine groups (Cl···N = 3.369(4) Å).[10]

A similar reaction using the Δ_D isomer of **1**, instead of its Λ_D isomer, also produced red-brown crystals **3**.[11] Compound **3** was assigned to have a Co^{III}Ag^{I} dinuclear structure, analogous to that of **2**, by X-ray fluorescence spectrometry and elemental analysis, together with IR spectrum (ν(C=O) = 1738 cm^{-1}).[12] The structure of **3** was also determined by X-ray analysis.[13] As shown in Figure 1b, **3** contains a Δ_D-[Co(D-Hpen-*N*,*S*)(en)$_2$]$^{2+}$

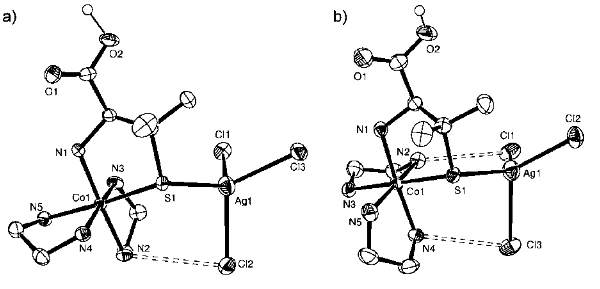


Figure 1. ORTEP views of **2** (a) and **3** (b) with the atomic labeling scheme.

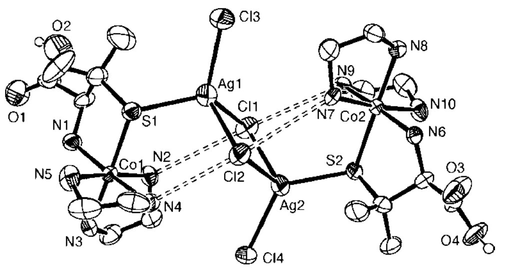


Figure 2. ORTEP view of **4** with the atomic labeling scheme.

unit that is connected by a $[AgCl_3]^{2-}$ moiety through a Ag–S bond to form a S-bridged $Co^{III}Ag^{I}$ dinuclear structure in Δ_D-$[AgCl_3\{Co(\text{D-Hpen-}N,S)(en)_2\}]$. Like in **2**, the Ag^{I} atom in **3** has a tetrahedral geometry, coordinated by three nonbridging Cl atoms and a S atom. However, the Ag–S (2.489(1) Å) and Ag–Cl (av 2.600(1) Å) distances in **3** are slightly shorter than the corresponding distances in **2**. In **3**, the dinuclear structure is supported by two weak intramolecular $Cl\cdots H–N_{en}$ hydrogen bonds (av 3.419(5) Å).

To investigate whether **2** or **3** is preferentially isolated from a reaction solution, a 1:1 mixture of the Λ_D and Δ_D isomers of **1** was treated with $AgNO_3$, followed by the addition of a saturated aqueous NaCl solution. Interestingly, a precipitate of AgCl, which initially appeared, was dissolved on stirring the reaction mixture at room temperature without the addition of HCl, and brown crystals **4** were isolated from the reaction solution.[14] While X-ray fluorescence and elemental analytical results of **4** were consistent with the expected formula for $[Co(\text{D-Hpen-}N,S)(en)_2][AgCl_3]$, single-crystal X-ray analysis revealed that **4** is a complex salt consisting of a divalent complex cation and two chloride counter anions.[15] As shown in Figure 2, the complex cation of **4** contains Λ_D- and Δ_D-$[Co(\text{D-Hpen-}N,S)(en)_2]^{2+}$ units that are linked by a $[Ag_2Cl_4]^{2-}$ moiety through Ag–S bonds to construct a $Co^{III}{}_2Ag^{I}{}_2$ tetranuclear structure in $\Lambda_D\Delta_D$-$[Ag_2Cl_4\{Co(\text{D-Hpen-}N,S)(en)_2\}_2]^{2+}$. While each Ag^{I} atom in **4** is situated in a tetrahedral geometry with a Cl_3S donor set, like in **2** and **3**, two of four Cl atoms bridge two Ag^{I} centers. In **4**, each bridging Cl atom is weakly hydrogen-bonded with two en amine groups from the Λ_D- and Δ_D-$[Co(\text{D-Hpen-}N,S)(en)_2]^{2+}$ units (av $Cl\cdots N = 3.495(10)$ Å), which appears to stabilize the $Co^{III}{}_2Ag^{I}{}_2$ tetranuclear structure in **4**.[16] The Ag–S bond distances (av 2.489(3) Å) in **4** are very similar to the Ag–S distance in **2** having two intramolecular $Cl\cdots H–N_{en}$ hydrogen bonds. As expected, the $Ag–Cl_{bridging}$ bonds (av 2.683(4) Å) are elongated compared to the $Ag–Cl_{terminal}$ bonds (av 2.546(4) Å).

In summary, we showed that discrete silver(I) coordination compounds containing nonbridging chloride ligands are isolated by the use of $[Co(\text{D-Hpen-}N,S)(en)_2]^{2+}$ as a bulky S-donating metalloligand in combination with AgCl.[17] While the use of Λ_D- or Δ_D-$[Co(\text{D-Hpen-}N,S)(en)_2]^{2+}$ gave a $Co^{III}Ag^{I}$ dinuclear structure with three nonbridging chloride ligands (**2** or **3**), a $Co^{III}{}_2Ag^{I}{}_2$ tetranuclear structure was constructed from a 1:1 mixture of Λ_D- and Δ_D-$[Co(\text{D-Hpen-}N,S)(en)_2]^{2+}$. Thus, the bridging vs. nonbridging binding mode of chloride toward silver(I) centers could be controlled by the combination of the chiralities (Λ and Δ) of cobalt(III) metalloligands, leading to the creation of silver(I) coordination compounds with different nuclearities.

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References and Notes

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7 Calcd for $\mathbf{2}\cdot H_2O = [AgCl_3\{Co(\text{D-Hpen})(en)_2\}]\cdot H_2O$: C, 19.32; H, 5.04; N, 12.52%. Found: C, 19.29; H, 4.86; N, 12.48%. Yield: 48%.

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9 Crystal data for $\mathbf{2}\cdot H_2O$: Λ_D-$[AgCl_3\{Co(\text{D-Hpen})(en)_2\}]\cdot H_2O$, fw 559.57, Orthorhombic, $P2_12_12_1$, $a = 12.808(2)$, $b = 18.097(2)$, $c = 8.395(2)$ Å, $V = 1945.9(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.910$ g/cm^3, 2536 reflections measured, 2536 independent. $R_1 = 0.0262$ ($I > 2\sigma(I)$), $wR_2 = 0.0684$ (all data). CCDC: 641467.

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11 Calcd for $\mathbf{3}\cdot H_2O\cdot 0.25NaCl = [AgCl_3\{Co(\text{D-Hpen})(en)_2\}]\cdot H_2O\cdot 0.25NaCl$: C, 18.83; H, 4.92; N, 12.20%. Found: C, 18.87; H, 4.84; N, 12.33%. Yield: 36%.

12 In **2**, the COOH group forms intermolecular hydrogen bonds with an en amine group and a water molecule ($O\cdots N = 2.914(5)$ Å and $O\cdots O = 2.570(5)$ Å), whereas the COOH group in **3** is weakly hydrogen-bonded with a Cl atom ($O\cdots Cl = 3.001(5)$ Å), which is responsible for the higher-energy shift of the $\nu(C{=}O)$ band for **3** compared with that for **2**.

13 Crystal data for **3**: Δ_D-$[AgCl_3\{Co(\text{D-Hpen})(en)_2\}]$, fw 541.56, Orthorhombic, $P2_12_12_1$, $a = 10.441(2)$, $b = 19.626(2)$, $c = 9.143(2)$ Å, $V = 1873.4(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.920$ g/cm^3, 3091 reflections measured, 3091 independent. $R_1 = 0.0345$ ($I > 2\sigma(I)$), $wR_2 = 0.0946$ (all data). CCDC: 641468.

14 Calcd for $\mathbf{4}\cdot 3H_2O\cdot 0.5NaCl = [Ag_2Cl_4\{Co(\text{D-Hpen})(en)_2\}_2]Cl_2\cdot 3H_2O\cdot 0.5NaCl$: C, 18.54; H, 5.01; N, 12.01%. Found: C, 18.61; H, 4.98; N, 12.08%. Yield: 34%.

15 Crystal data for $\mathbf{4}\cdot 4H_2O$: $\Lambda_D\Delta_D$-$[Ag_2Cl_4\{Co(\text{D-Hpen})(en)_2\}_2]Cl_2\cdot 4H_2O$, fw 1155.18, Monoclinic, $P2_1$, $a = 12.807(3)$, $b = 18.715(5)$, $c = 8.749(2)$ Å, $\beta = 96.19(2)°$, $V = 2084.7(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.840$ g/cm^3, 5150 reflections measured, 4941 independent ($R_{int} = 0.0765$). $R_1 = 0.0397$ ($I > 2\sigma(I)$), $wR_2 = 0.1287$ (all data). CCDC: 641469.

16 Molecular model examinations suggested that similar intramolecular $Cl\cdots H–N_{en}$ hydrogen bonds are not formed when two Λ_D- or Δ_D-$[Co(\text{D-Hpen-}N,S)(en)_2]^{2+}$ units are linked by a $[Ag_2Cl_4]^{2-}$ moiety because of the steric demand. This seems to be related to the formation of the dinuclear structure in **2** or **3**.

17 Compounds **2**, **3**, and **4** are immediately decomposed in water to give a AgCl precipitation.