A Remarkable $\mathrm{Co^{III}Mn^{II}Ag^{I}}$ Heterometallic Aggregate with L-Cysteinate That Accommodates Chiral Cobalt(III) Octahedra in a 1D Channel

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Treatment of an aqueous solution of Δ_{L}-[Co(L-Hcys-*N*,*S*)-(en)$_2$](ClO$_4$)$_2$ (L-cys = L-cysteinate) with AgNO$_3$ under a neutral condition, followed by the addition of excess Mn(NO$_3$)$_2$, led to the formation of a $\mathrm{Co^{III}Mn^{II}Ag^{I}}$ coordination polymer, $\{(\Delta_{\mathrm{L}})_5$-[Ag$_2Mn_3$(NO$_3$)$_2$(H$_2$O)$_{10}$\{Co(L-cys-*N*,*S*)(en)$_2$\}$_5$](NO$_3$)$_{6.5}$-(ClO$_4$)$_{4.5}\}_n$ (**1**). The crystal structure of **1**, which accommodates Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ molecules in a 1D channel, was determined by X-ray crystallography.

During the last decade, design and creation of metallosupramolecular species have attracted considerable interest because of their intriguing structural diversities and potential applications in functional materials.[1] While the majority of chemists constructed supramolecular structures from organic ligands and metal cations through spontaneous self-assembly, our synthetic strategy is the use of transition metal complexes as a metalloligand, which possess functional groups available for coordination to metal centers.[2] In particular, our recent research has been devoted to the construction of chiral heterometallic dimensional structures, utilizing mono(thiolato)-type cobalt(III) complexes with 2-aminoethanethiolate (aet) or L-cysteinate (L-cys) as a S-donating chiral metalloligand.[3,4] Recently, we have found that the reaction of Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with AgNO$_3$, followed by the addition of NaNO$_3$, produces a 2D honeycomb structure, in which a thiolato S and a carboxylate O atoms in each [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit coordinates to Ag$^{\mathrm{I}}$ and Na$^{\mathrm{I}}$ atoms, respectively.[4b] This result suggested that [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ acts as a bifunctional metalloligand having a *soft* thiolato S and a *hard* carboxylate O donor sites, which may selectively bind with *soft* and *hard* transition metal centers, respectively. Thus, we started to investigate the reactions of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with a *soft* Ag$^{\mathrm{I}}$ ion in the presence of a *hard* transition metal ion, in order to establish the utility of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ as a bifunctional metalloligand and to rationally construct quite rare examples of chiral dimensional systems consisting of three kinds of transition metal centers. In this paper, we report that a novel chiral coordination polymer consisting of Co$^{\mathrm{III}}$, Mn$^{\mathrm{II}}$, and Ag$^{\mathrm{I}}$ ions, which exhibits a fascinating metallosupramolecular stereochemistry, is created from Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ in combination with Ag$^{\mathrm{I}}$ and Mn$^{\mathrm{II}}$ under appropriate conditions.

A dark-brown aqueous solution of Δ_{L}-[Co(L-Hcys-*N*,*S*)-(en)$_2$](ClO$_4$)$_2$·H$_2$O[5] (0.40 mmol) neutralized by aqueous NH$_3$ was treated with AgNO$_3$ (0.14 mmol) in a 3:1 ratio, which gave a dark-red solution. When an equimolar of Mn(NO$_3$)$_2$·6H$_2$O (0.40 mmol) was added to the dark-red reaction solution, followed by allowing to stand at room temperature, only a S-bridged $\mathrm{Co^{III}Ag^{I}Co^{III}}$ trinuclear complex, $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag\{Co(L-Hcys-*N*,*S*)(en)$_2$\}\{Co(L-cys-*N*,*S*)(en)$_2$\}](NO$_3$)$_3$(ClO$_4$), was obtained.[4b,6] On the other hand, the addition of excess Mn(NO$_3$)$_2$·6H$_2$O (3.2 mmol) to the reaction solution led to the isolation of dark-red crystals (**1**), which were found to contain Co, Ag, and Mn atoms in a 5:2:3 ratio based on the plasma emission spectral analysis. The elemental analytical result of **1** was in agreement with the formula for a 5:2:3 adduct of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$, Ag$^+$, and Mn^{2+},[7] and its crystal structure was established by X-ray analysis.[8]

As shown in Figure 1, the asymmetric unit of **1** contains a $\mathrm{Co^{III}{}_2Mn^{II}Ag^{I}}$ part (Part A) and a $\mathrm{Co^{III}{}_3Mn^{II}{}_2Ag^{I}}$ part (Part B). In the extended structure of Part A, two Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are linked by a digonal Ag$^{\mathrm{I}}$ atom through S atoms to form a S-bridged $\mathrm{Co^{III}Ag^{I}Co^{III}}$ trinuclear moiety, $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag\{Co(L-cys-*N*,*S*)(en)$_2$\}$_2$]$^{3+}$ (av Ag–S = 2.444(6) Å). The $\mathrm{Co^{III}Ag^{I}Co^{III}}$ trinuclear moieties are connected by Mn$^{\mathrm{II}}$ atoms (Mn1) through *axial* carboxylate O atoms (av Mn–O = 2.22(1) Å) to afford a 1D zigzag $(\mathrm{Co^{III}{}_2Mn^{II}Ag^{I}})_n$ chain (Chain A; Figure 2a). Each Mn$^{\mathrm{II}}$ atom is situated in an octahedral environment, coordinated by two *trans* carboxylate groups, besides three H$_2$O molecules and a NO$_3{}^-$ ion. It should be noted that the NO$_3{}^-$ ion bound to a Mn$^{\mathrm{II}}$ center interacts with an adjacent Ag$^{\mathrm{I}}$ atom (Ag1···O12 = 2.90(2) Å), which seems to sustain the $(\mathrm{Co^{III}{}_2Mn^{II}Ag^{I}})_n$ chain structure.[9] The extended structure of Part B also forms a 1D zigzag $(\mathrm{Co^{III}{}_2Mn^{II}Ag^{I}})_n$ chain (Chain B; av Ag–S = 2.448(6) Å, Mn–O = 2.21(1) Å), which appears to be virtually the same as Chain A. However, in Chain B one of two carboxylate groups bound to the Mn2 atom further coordinates to another Mn$^{\mathrm{II}}$ atom (Mn3) (Mn3–O8 = 2.19(1) Å). In

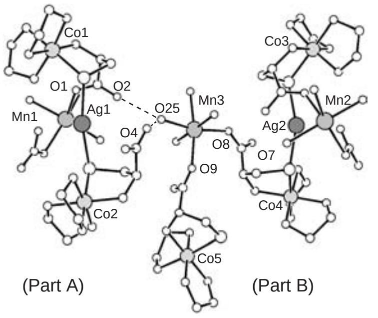

Figure 1. The asymmetric unit of the complex cation of **1**. The selected bond distances (Å) and angles (°): Co1–S1 = 2.276(6), Co2–S2 = 2.268(6), Co3–S3 = 2.287(6), Co4–S4 = 2.272(6), Co5–S5 = 2.255(6), Ag1–S1 = 2.451(6), Ag1–S2 = 2.436(6), Ag2–S3 = 2.464(5), Ag2–S4 = 2.431(6), Mn1–O1 = 2.20(2), Mn1–O3′ = 2.23(1), Mn2–O5 = 2.22(1), Mn2–O7′ = 2.20(1), Mn3–O8 = 2.19(1), Mn3–O9 = 2.14(2), S1–Ag1–S2 = 168.2(2), S3–Ag2–S4 = 161.4(2).

addition, one of the four water molecules (O25) bound to the Mn3 atom is hydrogen bonded with two carboxylato groups in Chain A (O2···O25 = 2.75(2) Å, O4···O25 = 2.79(2) Å), which constructs a unique $(\mathrm{Co^{III}}_4\mathrm{Mn^{II}}_3\mathrm{Ag^{I}}_2)_n$ ladder-like structure (Figure 2b). In the crystal of **1**, the $(\mathrm{Co^{III}}_4\mathrm{Mn^{II}}_3\mathrm{Ag^{I}}_2)_n$ ladders, which run parallel to the *c* axis, are connected with $\mathrm{NO_3}^-$ counter-anions through N–H···O hydrogen bonds (N···O = 2.83–3.25 Å) so as to form 1D channels. Of note is the accommodation of Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ molecules (Co5) in the channel (Figure 2c), each of which is attached to the linking Mn3 atom through an *axial* carboxylate O atom (Mn3–O9 = 2.14(2) Å) to complete a *cis*-Mn(carboxylato)$_2$(H$_2$O)$_4$ octahedron (Figure 1).

Attempts to synthesize a $(\mathrm{Co^{III}}_4\mathrm{Mn^{II}}_3\mathrm{Ag^{I}}_2)_n$ ladder-like complex were unsuccessful by treatment of the trinuclear $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ complex with excess Mn(NO$_3$)$_2$ in water. However, the addition of Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ to this reaction mixture led to the formation of **1**. On the other hand, the addition of Λ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$, instead of Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$, did not afford any desired products containing Co$^{\mathrm{III}}$, Mn$^{\mathrm{II}}$, and Ag$^{\mathrm{I}}$ atoms. Thus, it is considered that the $(\mathrm{Co^{III}}_4\mathrm{Mn^{II}}_3\mathrm{Ag^{I}}_2)_n$ ladder-like structure selectively incorporates the Δ_{L} isomer of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ in the 1D channel, which in turn stabilizes its extended structure.

The EPR spectrum of a solid sample of **1** at room temperature displays a broad isotropic signal with $g = 1.95$, consistent with the presence of Mn$^{\mathrm{II}}$ atoms in **1**. Furthermore, its magnetic moment (10.05 BM) is comparable with the spin-only value (10.25 BM) expected for **1**, which contains three Mn$^{\mathrm{II}}$ atoms with a high-spin d^5 configuration in the asymmetric unit. The electronic absorption and CD spectra of **1** in the solid state (nujol mull) resemble those of $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]-(ClO$_4$)$_3$, showing a broad d-d absorption band at *ca.* 500 nm and a negative (521 nm) and a positive (433 nm) CD bands in this region. However, it is noticed that these CD bands are significantly blue shifted relative to those for $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3$ (545 nm, 466 nm). In water, **1** exhibits absorption and CD spectra very similar to those of $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3$,[4b,7] suggestive of the dissociation into the Co$^{\mathrm{III}}$Ag$^{\mathrm{I}}$Co$^{\mathrm{III}}$ units because of the cleavage of COO–Mn bonds.

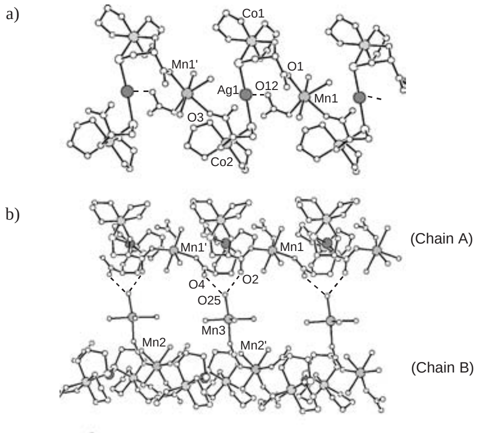

Figure 2. a) The chain structure (Chain A), b) the ladder-like structure, and c) the packing structure in **1**.

In summary, it was shown that Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ can bind with *hard* Mn$^{\mathrm{II}}$ and *soft* Ag$^{\mathrm{I}}$ ions through *hard* carboxylate O and *soft* thiolato S atoms, respectively, to produce a chiral coordination polymer consisting of three different transition metal ions (Co$^{\mathrm{III}}$, Mn$^{\mathrm{II}}$, Ag$^{\mathrm{I}}$) (**1**). Compound **1** was found to exhibit several unique, unprecedented features that would provide valuable insight into the development of chiral heterometallic aggregates: (a) the 1D zigzag $(\mathrm{Co^{III}}_2\mathrm{Mn^{II}}\mathrm{Ag^{I}})_n$ chain composed of the trinuclear [Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ units, which first indicates that [Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ could act as a "multinuclear metalloligand" using two carboxylate groups, (b) the ladder-like structure consisting of two $(\mathrm{Co^{III}}_2\mathrm{Mn^{II}}\mathrm{Ag^{I}})_n$ chains, which are bridged by transition metal ions (M = Mn$^{\mathrm{II}}$) through two different bonding interactions (COO–M coordination bond and COO···H$_2$O–M hydrogen bond), (c) the co-existence of three different binding modes of Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$[10] and two different geometries (*cis* and *trans*) of M(carboxylato)$_2$ fragments, which combine to generate a highly organized chiral molecular architecture, and finally (d) the chiral selective accommodation of Δ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ molecules in the 1D chiral channel made up of the parallel ladders. Work is in progress to incorporate different chiral complex molecules in the channel and to construct other heterometallic aggregates, not only based on the mononuclear [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ but also on the trinuclear [M{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ (M = Ag$^{\mathrm{I}}$, Au$^{\mathrm{I}}$).

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References and Notes

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6 Anal. Calcd for [Ag{Co(L-Hcys)(en)$_2$}{Co(L-cys)(en)$_2$}](NO$_3$)$_3$(ClO$_4$)$\cdot$0.5H$_2$O: C, 16.82; H, 4.44; N, 18.21%. Found: C, 16.68; H, 4.35; N, 18.38%.

7 Yield 56%. Anal. Calcd for **1**$\cdot$11H$_2$O = [Ag$_2$Mn$_3$(NO$_3$)$_2$(H$_2$O)$_{10}${Co(L-cys)(en)$_2$}$_5$](NO$_3$)$_{6.5}$(ClO$_4$)$_{4.5}\cdot$11H$_2$O: C, 13.04; H, 4.59; N, 14.55%. Found: C, 12.95; H, 4.55; N, 14.81%. UV–visible spectrum in H$_2$O [$\sigma_{\max}$, $10^3\,\mathrm{cm^{-1}}$ (log ε, $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$)]: 19.9 (2.84), 26.7 (3.18 sh), 35.0 (4.75). CD spectrum in H$_2$O [$\sigma_{\max}$, $10^3\,\mathrm{cm^{-1}}$ ($\Delta\varepsilon$, $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$)]: 19.3 (−14.28), 24.6 (+12.67), 35.0 (−15.18).

8 Crystal data for **1**$\cdot$6H$_2$O: FW = 3134.7, monoclinic, $P2_1$, $a = 15.272(3)$ Å, $b = 41.540(9)$ Å, $c = 9.102(1)$ Å, $\beta = 103.23(2)^\circ$, $V = 5621(1)$ Å^3, $Z = 2$, $D_c = 1.852\,\mathrm{g\,cm^{-3}}$, $R = 0.067$ for 8022 reflections with $I > 2.0\sigma(I)$.

9 Compatible with this, a similar reaction using excess Mn(ClO$_4$)$_2$, instead of Mn(NO$_3$)$_2$, produced only $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3$, indicating that nitrate anions are essential for the construction of the Co$^{\mathrm{III}}$Mn$^{\mathrm{II}}$Ag$^{\mathrm{I}}$ structure in **1**.

10 These are a bidentate-*O*,*S* mode (Co1, Co2, and Co3), a tridentate-*O*,*O*′,*S* mode (Co4), and a monodentate-*O* mode (Co5); the latter two modes are unprecedented.[4]