First Aggregation of L-Cysteinato Cobalt(III) Octahedrons Assisted by Trigonal-Planar Silver(I) and Trigonal-Prismatic Sodium(I) Ions

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The reaction of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ with NaOH and AgClO$_4$ in a 2 : 2 : 1 ratio in water gave a 2 : 1 (Co:Ag) adduct, (Δ_L)$_2$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ ((Δ_L)$_2$-[**1**]$^{3+}$), while the corresponding reaction with AgNO$_3$ led to the isolation of a 3 : 1 adduct, (Δ_L)$_3$-[AgNa{Co(L-cys-*N*,*S*)(en)$_2$}$_3$]$^{5+}$ ((Δ_L)$_3$-[**2**]$^{5+}$). The discrete trinuclear structure in (Δ_L)$_2$-[**1**]$^{3+}$ and the 2D polymeric structure in (Δ_L)$_3$-[**2**]$^{5+}$ were determined by X-ray crystallography.

While it has been recognized that a single thiolato group in some mono(thiolato)-type cobalt(III) complex tends to bind with soft metal ions such as Ag$^\mathrm{I}$, Cu$^\mathrm{I}$, Pt$^\mathrm{II}$, and Hg$^\mathrm{II}$ to form S-bridged structures,[1] only a few polynuclear complexes composed of [Co(aet)(en)$_2$]$^{2+}$ (aet = 2-aminoethanethiolate) or [Co(SCH$_2$-COO)(en)$_2$]$^+$ units have been isolated and characterized for over 20 years.[2] Recently, we have found that the reaction of [Co(aet)(en)$_2$]$^{2+}$ with AgNO$_3$ in a 1 : 1 ratio gave a 1D zigzag chain complex-polymer, [Ag{Co(aet)(en)$_2$}](NO$_3$)$_3$, in which the same configurational (Δ or Λ) [Co(aet)(en)$_2$]$^{2+}$ units are linked by Ag$^\mathrm{I}$ ions through μ_3-thiolato S atoms.[3] A similar Co$^\mathrm{III}$Ag$^\mathrm{I}$ chain complex-polymer was expected to be formed by using Λ_L- or Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ (L-cys = L-cysteinate) instead of [Co(aet)(en)$_2$]$^{2+}$. However, the corresponding 1 : 1 reactions were found to produce a 2D sheetlike structure in Λ_L-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}](NO$_3$)$_2$ and a 1D left-handed helical structure in Δ_L-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}](NO$_3$)$_2$, owing to the bonding interaction of the COO$^-$ group in each Λ_L- or Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit with Ag$^\mathrm{I}$ ion.[4] This result suggested that the introduction of the simple L-cys ligand having a free COO$^-$ group, in place of the aet ligand, results in highly organized chiral molecular architectures. We therefore decided to investigate the reactions of Λ_L- or Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with Ag$^+$ by changing the reaction stoichiometry and counter anions, in order to find the key factors to control supramolecular structures based on metal octahedrons. Here we report that the 2 : 2 : 1 reaction of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ with NaOH and AgNO$_3$ produces a novel 2D aggregate containing Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units and Ag$^\mathrm{I}$ ions in a 3 : 1 ratio, (Δ_L)$_3$-[AgNa{Co(L-cys-*N*,*S*)(en)$_2$}$_3$]$^{5+}$ ((Δ_L)$_3$-[**2**]$^{5+}$), while the corresponding reaction with AgClO$_4$ gives an expected 2 : 1 adduct, (Δ_L)$_2$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ ((Δ_L)$_2$-[**1**]$^{3+}$), the structure of which corresponds well with that of the known S-bridged trinuclear complex, [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$.

Treatment of a dark-brown aqueous solution of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$·H$_2$O[5] with 1 molar equiv of NaOH and 0.5 molar equiv of AgClO$_4$ at room temperature gave a dark-red solution, from which dark-red crystals ((Δ_L)$_2$-[**1**](ClO$_4$)$_3$·4H$_2$O) were obtained by adding an aqueous solution of NaClO$_4$ (59% yield). The elemental and plasma emission analyses of this red product are in good agreement with the formula for the 2 : 1 adduct of Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ and Ag$^\mathrm{I}$.[6] Single-crystal X-ray analysis demonstrated that (Δ_L)$_2$-[**1**]$^{3+}$ is an expected S-bridged Co$^\mathrm{III}$Ag$^\mathrm{I}$Co$^\mathrm{III}$ trinuclear complex, (Δ_L)$_2$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$, in which the central Ag$^\mathrm{I}$ atom is coordinated by two thiolato S atoms from two octahedral Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units (average Co–S = 2.257(5) Å, Ag–S = 2.383(5) Å, S–Ag–S = 165.4(2)°).[7] The overall structure in (Δ_L)$_2$-[**1**]$^{3+}$ is very similar to that found in [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$ (Co–S = 2.259(2) Å, Ag–S = 2.400(1) Å, S–Ag–S = 164.50(8)°),[2b,3] except the presence of free COO$^-$ groups.

A similar 2 : 2 : 1 reaction of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$·H$_2$O with NaOH and AgNO$_3$ also gave a dark-red solution, and its absorption spectrum was the same as the reaction solution with AgClO$_4$. However, the addition of an aqueous solution of NaNO$_3$ to this reaction solution led to the isolation of dark-red crystals ((Δ_L)$_3$-[**2**](NO$_3$)$_4$(ClO$_4$)·3H$_2$O; 40% yield), analyzing as the 3 : 1 adduct {[Co(L-cys-N,S)(en)$_2$](NO$_3$)}$_3$·AgNO$_3$·NaClO$_4$·3H$_2$O.[8] Consistent with this, (Δ_L)$_3$-[**2**](NO$_3$)$_4$(ClO$_4$)·3H$_2$O was also obtained by treating an aqueous solution of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$·H$_2$O with NaOH and AgNO$_3$ in a 3 : 3 : 1 ratio (71% yield). The solid-state absorption spectrum (nujol paste) of this product shows a broad d-d absorption band at higher energy (20.70 × 10^3 cm^{-1}) than the d-d band for (Δ_L)$_2$-[**1**](ClO$_4$)$_3$·4H$_2$O (20.08 × 10^3 cm^{-1}), while their absorption and CD spectra in water are essentially identical.[6,8]

The crystal structure of (Δ_L)$_3$-[**2**](NO$_3$)$_4$(ClO$_4$)·3H$_2$O was established by X-ray analysis, which revealed the presence of an asymmetric unit consisting of one third of (Δ_L)$_3$-[AgNa{Co(L-cys-*N*,*S*)(en)$_2$}$_3$]$^{5+}$, four thirds of NO$_3$$^-$, one third of ClO$_4$$^-$, and a water molecule.[9] As shown in Figure 1, the octahedral Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit (Co–S = 2.255(2) Å) is bound to a Na$^\mathrm{I}$ ion through carboxylate O atom (Na–O = 2.376(6) Å), besides to a Ag$^\mathrm{I}$ ion through thiolato S atom (Ag–S = 2.519(2) Å); Ag$^\mathrm{I}$ and Na$^\mathrm{I}$ ions lie on the three-fold rotation axis. In the extended structure, each Ag$^\mathrm{I}$ ion is coordinated by three S atoms from three Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units in a trigonal-planar geometry (Ag–S–Ag = 113.22(4)°), while each Na$^\mathrm{I}$ ion is coordinated by six O atoms from three Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units and three water molecules in a trigonal-prismatic environment (O–Na–O = 75.2(2)°, 79.5(3)°, 95.9(2)°, 118.8(2)°, 144.6(2)°). As a result, in (Δ_L)$_3$-[**2**]$^{5+}$, the Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are linked alternatively by Ag$^\mathrm{I}$ and Na$^\mathrm{I}$ ions to construct a 2D honey-comb layer structure, in which three Ag$^\mathrm{I}$ and three Na$^\mathrm{I}$ ions form a hexagon (Figure 2). To the best of our knowledge, this is the first chiral extended structure consisting of three kinds of metal ions,[10] and furthermore, the

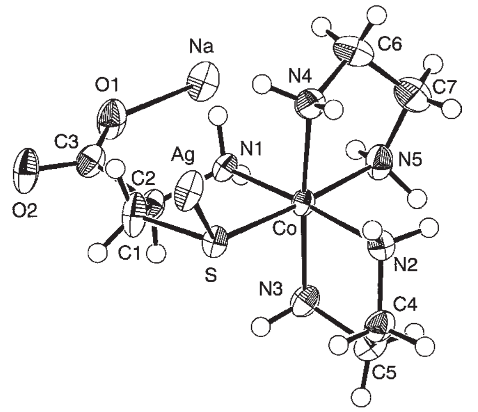

Figure 1. An ORTEP plot of the asymmetric unit for the complex cation $(\Delta_L)_3$-$[\mathbf{2}]^{5+}$.

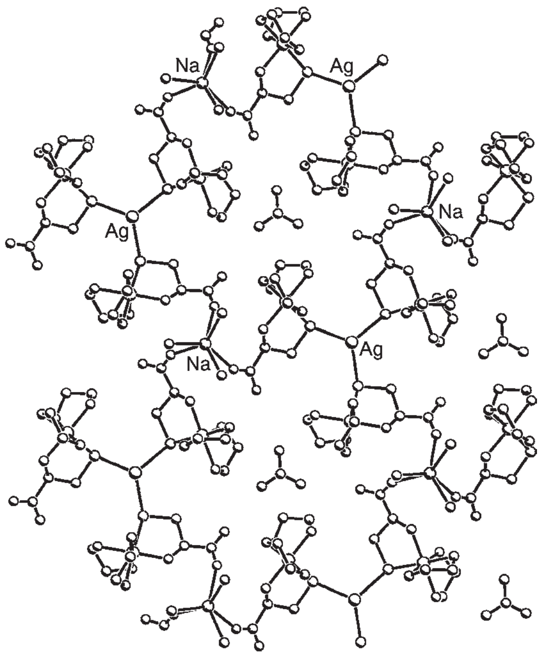

Figure 2. A perspective view for $(\Delta_L)_3$-$[\mathbf{2}](NO_3)_4(ClO_4)$ along the *c* direction. Only the nitrate anion located at the center of each hexagon is presented for clarity.

trigonal-planar geometry of Ag^I ion that bridges three hetero metal centers through thiolato S atoms is quite rare.[11] Here, it should be noted that one NO_3^- ion is situated at the center of each hexagon. Since the formation of $(\Delta_L)_3$-$[\mathbf{2}]^{5+}$ was not recognized for the reaction of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$(ClO_4)_2 \cdot H_2O$ with NaOH and $AgClO_4$, the presence of NO_3^- ion, the size of which is best fitted for the cavity of the hexagon, would stabilize the honey-comb structure of $[\mathbf{2}]^{5+}$ in crystal.

In summary, treatment of Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with $AgNO_3$ in the presence of Na^+ was found to give the unique $Co^{III}_3Ag^INa^I$ coordination polymer $(\Delta_L)_3$-$[\mathbf{2}]^{5+}$, besides the discrete $Co^{III}Ag^ICo^{III}$ trinuclear complex $(\Delta_L)_2$-$[\mathbf{1}]^{3+}$. This result demonstrates that Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ functions not only as a simple monodentate-*S* complex-ligand, but also as a bridging bidentate-*O*,*S* complex-ligand with use of both the coordinated thiolato S and the free carboxylate O atoms. Thus, a variety of chiral supramolecular architectures consisting of 'soft' and 'hard' metal ions could be systematically created from simple (L-cysteinato)cobalt(III) complexes by the control of the reaction stoichiometry with metal ions and the choice of counter anions of supramolecules.

References and Notes

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6 Anal. Calcd for $[\mathbf{1}](ClO_4)_3 \cdot 4H_2O$: C, 15.64; H, 4.69; N, 13.01; Co, 10.96; Ag, 10.04%. Found: C, 15.72; H, 4.70; N, 12.90; Co, 11.02; Ag, 9.71%. Visible-UV spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\log \varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 19.98 (2.46), 28.3 (2.9 sh), 34.92 (4.35). The sh label denotes a shoulder. CD spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\Delta\varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 19.40 (−5.56), 24.60 (+4.77), 34.84 (−6.70), 47.39 (+37.0). This complex was also produced even when Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$(ClO_4)_2 \cdot H_2O$ was treated with $AgClO_4$ in a 3 : 1 ratio.

7 Crystal Data for $(\Delta_L)_2$-$[\mathbf{1}](ClO_4)_3 \cdot 4H_2O$: fw = 1074.8 ($C_{14}H_{50}AgCl_3Co_2N_{10}O_{20}S_2$), monoclinic, $C2$, $a = 15.497(7)$ Å, $b = 9.412(1)$ Å, $c = 25.872(2)$ Å, $\beta = 95.40(2)^\circ$, $V = 3760(2)$ Å^3, $Z = 4$, $D_c = 1.90\,g\,cm^{-3}$, $R(R_w) = 0.057(0.067)$ for 3976 reflections with $I > 2.0\sigma(I)$.

8 Anal. Calcd for $[\mathbf{2}](NO_3)_4(ClO_4) \cdot 3H_2O$: C, 17.67; H, 4.87; N, 18.65; Co, 12.39; Ag, 7.56%. Found: C, 17.61; H, 4.64; N, 18.47; Co, 12.64; Ag, 7.39%. Visible-UV spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\log \varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 20.04 (2.61), 26.85 (3.0 sh), 35.06 (4.54). The sh label denotes a shoulder. CD spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\Delta\varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 19.34 (−8.88), 24.51 (+7.09), 35.24 (−11.28), 47.44 (+60.0).

9 Crystal data for $(\Delta_L)_3$-$[\mathbf{2}](NO_3)_4(ClO_4) \cdot 3H_2O$, fw = 475.1 ($C_7H_{23}Ag_{1/3}Cl_{1/3}CoN_{19/3}Na_{1/3}O_{25/3}S$), hexagonal, $P6_3$, $a = 13.864(2)$ Å, $c = 15.023(2)$ Å, $V = 2500.8(8)$ Å^3, $Z = 6$, $D_c = 1.89\,g\,cm^{-3}$, $R(R_w) = 0.036(0.038)$ for 1758 reflections with $I > 2.0\sigma(I)$.

10 Recently, discrete chiral octanuclear complexes consisting of three kinds of metal ions (Co^{III}, Pd^{II}, and Ag^I or Au^I) have been reported. T. Konno, Y. Chikamoto, K. Okamoto, T. Yamaguchi, T. Ito, and M. Hirotsu, *Angew. Chem., Int. Ed.*, **39**, 4098 (2000).

11 In the Cambridge Structural Database, we found only one example; a discrete thiolato bridged $Rh^{III}_4Ag^I_5$ nonanuclear complex $[Ag_5\{Rh(aet)_3\}_4]^{5+}$, containing both two-coordinated and three-coordinated Ag^I ions. T. Konno and K. Okamoto, *Inorg. Chem.*, **36**, 1403 (1997).