Novel Aggregation of Bis(thiolato)-type Cobalt(III) Octahedra Assisted by Silver(I) Ions: Structural Interconversion by Counter Anions

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The reaction of $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ (aet = 2-aminoethanethiolate) with $\mathrm{Ag^I}$ in the presence of $\mathrm{ClO_4}^-$ and $\mathrm{NO_3}^-$ anions gave a S-bridged $\mathrm{Co^{III}{}_4Ag^I{}_4}$ octanuclear and a $(\mathrm{Co^{III}{}_2Ag^I{}_3})_n$ polymeric complexes, respectively, which are interconvertible with each other by changing the counter anions.

The construction of metal-based molecular aggregates is of current great interest not only in the field of supramolecular chemistry but also in the field of coordination chemistry.[1] Typical synthetic routes to create metalloaggregates are the metal-directed self-assembly of multidentate organic compounds that connect two or more metal centers. However, this approach often encounters the difficulty in the creation of heterometallic systems, as well as the difficulty in the control and modification of their overall structures. An alternative approach that could overcome these difficulties is the use of metal complexes as building blocks, which contain potential donor sites for second metal centers. It has been recognized that coordinated thiolato groups possess high Lewis basicity to bind with a variety of transition-metal ions, and thus, we have been studying the aggregation of thiolato complex-units assisted by transition-metal ions.[2,3] Recently, we have found that the central $\mathrm{Ni^{II}}$ ion in $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ ($[\mathbf{1}]^{4+}$), which is composed of two C_2-*cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ units,[4] is replaced by two linear $\mathrm{Au^I}$ ions to produce a S-bridged $\mathrm{Co^{III}{}_2Au^I{}_2}$ tetranuclear complex, $[\mathrm{Au_2\{Co(aet)_2(en)\}_2}]^{4+}$.[5] In this $\mathrm{Co^{III}{}_2Au^I{}_2}$ structure, the S–Co–S angle (99.7(1) Å) in each $[\mathrm{Co(aet)_2(en)}]^+$ unit is significantly deviated from the ideal right angle so as to form an intramolecular bonding interaction between two $\mathrm{Au^I}$ ions (Au–Au = 2.9640(9) Å). Since Ag···Ag interaction is commonly weaker than Au···Au interaction,[6] it is interesting to clarify whether an analogous S-bridged $\mathrm{Co^{III}{}_2Ag^I{}_2}$ tetranuclear complex is formed by the reaction of $[\mathbf{1}]^{4+}$ with $\mathrm{Ag^I}$. Here, we report that this reaction affords a new class of S-bridged polynuclear and polymeric structures, which can be controlled by counter anions employed.

Treatment of a dark-brown aqueous solution of $[\mathbf{1}](\mathrm{ClO_4})_4\cdot 2\mathrm{H_2O}$[7] with $\mathrm{AgClO_4}$ (60 °C, 20 min) in a 1:2 ratio gave a red-brown solution, from which almost black crystals ($[\mathbf{2}](\mathrm{ClO_4})_8\cdot 7\mathrm{H_2O}$) were isolated.[8] Complex $[\mathbf{2}](\mathrm{ClO_4})_8$ is easily soluble in water, and its absorption spectrum differs significantly from that of $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$.[4] This suggests that the $\mathrm{Ni^{II}}$ ion in $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ is replaced by $\mathrm{Ag^I}$, like the corresponding reaction with $\mathrm{Au^I}$.[5] The elemental and plasma emission analyses of $[\mathbf{2}](\mathrm{ClO_4})_8$ are in agreement with the formula for an expected 2:2 adduct $[\mathrm{Ag_2\{Co(aet)_2(en)\}_2}](\mathrm{ClO_4})_4$. However, X-ray analysis revealed that $[\mathbf{2}](\mathrm{ClO_4})_8$ contains $[\mathrm{Co(aet)_2(en)}]^+$, $\mathrm{Ag^+}$, and $\mathrm{ClO_4}^-$ in a 4:4:8 ratio.[8] As shown in Figure 1a, the complex cation $[\mathbf{2}]^{8+}$ consists of four C_2-*cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ units that are spanned by four $\mathrm{Ag^I}$ atoms to form a S-bridged $\mathrm{Co^{III}{}_4Ag^I{}_4}$ cyclic structure (av. Ag–S = 2.404(2) Å, S–Ag–S = 167.73(9)°). The S–Co–S angles (av. 92.28(8)°) of the $[\mathrm{Co(aet)_2(en)}]^+$ units in $[\mathbf{2}]^{8+}$ are close to 90°, indicating that the linkage of C_2-*cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ units in this octanuclear structure requires little strain about each Co center, unlike the case for $[\mathrm{Au_2\{Co(aet)_2(en)\}_2}]^{4+}$.[5] The chiral configurations of the four $[\mathrm{Co(aet)_2(en)}]^+$ units in $[\mathbf{2}]^{8+}$ are Δ, Δ, Λ, and Λ, which combine to form a meso compound. It should be noted that the $\mathrm{Co^{III}{}_4Ag^I{}_4}$ complex cations $[\mathbf{2}]^{8+}$ are connected with one another through a mutual weak Ag···S interaction (Ag2–S2 = 3.070(2) Å) to afford a 1D chain-like structure (Figure 1b).

Similar treatment of $[\mathbf{1}](\mathrm{NO_3})_4\cdot\mathrm{H_2O}$[7] with $\mathrm{AgNO_3}$ in a 1:2 ratio also gave red-brown crystals ($[\mathbf{3}](\mathrm{NO_3})_5\cdot\mathrm{H_2O}$), which are poorly soluble in water.[9] The plasma emission spectral analysis implies that $[\mathbf{3}](\mathrm{NO_3})_5$ contains Co and Ag atoms in a 2:3 ratio, rather than a 2:2 ratio. Furthermore, the elemental analysis of $[\mathbf{3}](\mathrm{NO_3})_5$ is in agreement with the formula for a 2:3 adduct $[\mathrm{Ag_3\{Co(aet)_2(en)\}_2}](\mathrm{NO_3})_5$. The crystal structure of $[\mathbf{3}](\mathrm{NO_3})_5$ that contains $[\mathrm{Co(aet)_2(en)}]^+$, $\mathrm{Ag^+}$, and $\mathrm{NO_3}^-$ in a 2:3:5 ratio was established by X-ray crystallography.[9] As shown in Figure 2a, the complex cation $[\mathbf{3}]^{5+}$ has a $\mathrm{Co^{III}{}_2Ag^I{}_2}$ tetranuclear structure, in which two C_2-*cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ units are con-

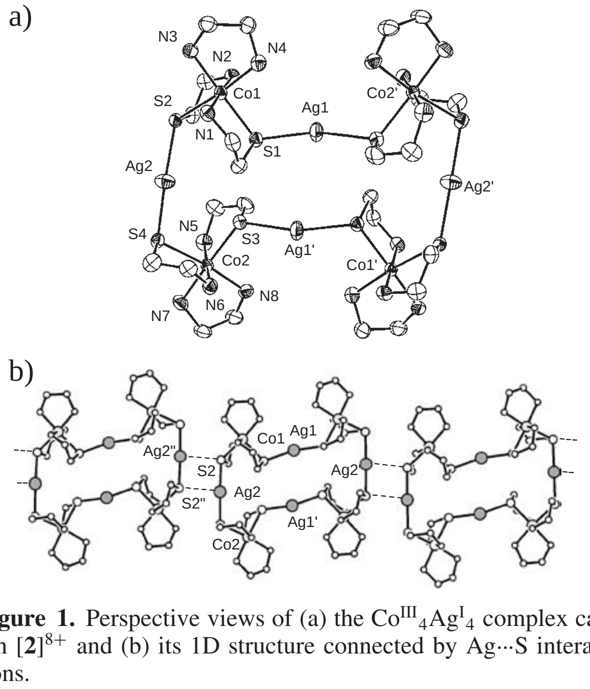

Figure 1. Perspective views of (a) the $\mathrm{Co^{III}{}_4Ag^I{}_4}$ complex cation $[\mathbf{2}]^{8+}$ and (b) its 1D structure connected by Ag···S interactions.

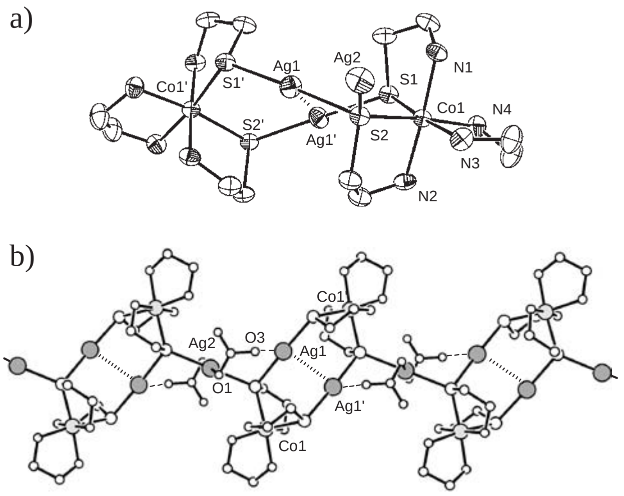

Figure 2. Perspective views of (a) the $Co^{III}_2Ag^I_3$ pentanuclear unit of $[\mathbf{3}]^{5+}$ and (b) its 1D structure connected by Ag–S bonds (nitrate anions closely contacted with Ag^I are included).

nected by two linear Ag^I atoms (av. $Ag1–S = 2.396(2)$ Å, $S–Ag1–S = 177.24(4)^\circ$). The coordination geometry about each Co atom is roughly octahedral, but the S1–Co–S2 angle ($97.51(6)^\circ$) is appreciably expanded from 90°. The Ag–Ag distance is 3.0940(6) Å, which is suggestive of the presence of a weak interaction between two Ag^I ions.[10] This S-bridged $Co^{III}_2Ag^I_2$ structure corresponds well with the $Co^{III}_2Au^I_2$ structure in $[Au_2\{Co(aet)_2(en)\}_2]^{4+}$.[5] However, an additional Ag^I atom (Ag2) is bound to a S atom (S2), which links the $Co^{III}_2Ag^I_2$ tetranuclear units to form a 1D $(Co^{III}_2Ag^I_3)_n$ chain structure ($Ag2–S2 = 2.4837(9)$ Å, $S2–Ag2–S2' = 180.0^\circ$) (Figure 2b). Of note is the close contact of two NO_3^- anions with each linking Ag^I atom ($Ag2–O1 = 2.646(6)$ Å).[11] These anions also contact with adjacent Ag^I atoms of the tetranuclear units ($Ag1–O3 = 2.911(7)$ Å), which appears to sustain the 1D polymeric structure. In $[\mathbf{3}]^{5+}$, the two $[Co(aet)_2(en)]^+$ units of each $Co^{III}_2Ag^I_2$ moiety have the same chiral configuration to give ΔΔ and ΛΛ forms, which are alternately linked by Ag^I atoms to construct a meso structure.

A remarkable feature of this $Co^{III}Ag^I$ system is that the $Co^{III}_4Ag^I_4$ octanuclear structure in $[\mathbf{2}]^{8+}$ and the $(Co^{III}_2Ag^I_3)_n$ polymeric structure in $[\mathbf{3}]^{5+}$ are interconvertible with each other by changing the counter anions. That is, treatment of the isolated $[\mathbf{2}](ClO_4)_8$ with excess $NaNO_3$ in water gave $[\mathbf{3}](NO_3)_{4.5}(ClO_4)_{0.5}$, while $[\mathbf{3}](NO_3)_5$ was converted to $[\mathbf{2}](ClO_4)_8$ by treating with excess $NaClO_4$.[12] As mentioned above, $[\mathbf{3}]^{5+}$ containing Co^{III} and Ag^I in a 2:3 ratio was obtained from the 1:2 reaction of $[\mathbf{1}](NO_3)_4$ with $AgNO_3$ (Co:Ag = 2:2). In addition, attempts to prepare $[\mathbf{3}]^{5+}$ by reacting $[\mathbf{1}](ClO_4)_4$ with $AgClO_4$ in a 1:3 ratio were unsuccessful; only $[\mathbf{2}](ClO_4)_8$ was isolated. These results clearly indicate that the coexisting counter anions, rather than the reaction stoichiometries, play a crucial role in determining the S-bridged structures constructed from C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ and Ag^I.

In summary, the metal replacement reaction of $[\mathbf{1}]^{4+}$ was applied for the generation of novel S-bridged structures consisting of bis(thiolato)-type Co^{III} units and Ag^I ions, which are highly dependent on the counter anions. Interestingly, the formation of a $Co^{III}_2Ag^I_2$ complex analogous to $[Au_2\{Co(aet)_2(en)\}_2]^{4+}$ was not noticed for the present reactions. This is most likely ascribed to the weakness of Ag···Ag interaction, which can not make up for the disadvantage due to the distortion around Co^{III} centers existed in the S-bridged tetranuclear structure, leading to the cyclic $Co^{III}_4Ag^I_4$ structure composed of less strained $[Co(aet)_2(en)]^+$ units or the 1D $(Co^{III}_2Ag^I_3)_n$ structure stabilized by the short contact between Ag^I and NO_3^-. Accordingly, this study points out that the overall S-bridged structures could be controlled by the slight modification of the degree of metal–metal and metal–anion interactions.

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References and Notes

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7 The ClO_4^- and NO_3^- salts of $[\mathbf{1}]^{4+}$ were prepared by the metathesis of the Cl^- salt[4] with $NaClO_4$ and $NaNO_3$, respectively. Calcd for $[\mathbf{1}](ClO_4)_4 \cdot 2H_2O$: C, 13.92; H, 4.28; N, 10.82%. Found: C, 13.64; H, 4.11; N, 10.53%. Calcd for $[\mathbf{1}](NO_3)_4 \cdot H_2O$: C, 16.62; H, 4.88; N, 19.38%. Found: C, 16.48; H, 4.90; N, 19.21%.

8 Calcd for $[\mathbf{2}](ClO_4)_8 \cdot 7H_2O$: C, 11.82; H, 3.89; N, 9.19%. Found: C, 11.66; H, 3.96; N, 8.90%. Yield: 68%. UV–vis spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\log \varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 23.25 (3.45), 31.98 $(4.3)^{sh}$, 37.97 (4.97). Crystal data for $[\mathbf{2}](ClO_4)_8 \cdot 7H_2O$: fw 2438.40, triclinic, $P\bar{1}$, $a = 12.751(3)$, $b = 16.982(3)$, $c = 9.711(2)$ Å, $\alpha = 96.01(1)$, $\beta = 104.77(2)$, $\gamma = 75.38(2)^\circ$, $V = 1965.6(6)$ Å^3, $Z = 1$, $D_{calcd} = 2.060\,g/cm^3$, $R_1 = 0.054$ ($I > 2.0\sigma(I)$), $wR_2 = 0.147$ (all data).

9 Calcd for $[\mathbf{3}](NO_3)_5 \cdot H_2O$: C, 12.07; H, 3.54; N, 15.25%. Found: C, 12.03; H, 3.59; N, 15.20%. Yield: 43%. UV–vis spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\log \varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 23.26 (3.12), 32.3 $(4.0)^{sh}$, 37.97 (4.60). This complex was also obtained in a higher yield (85%) by the 1:2.5 reaction. Crystal data for $[\mathbf{3}](NO_3)_5 \cdot H_2O$: fw 1194.25, monoclinic, $C2/c$, $a = 23.532(4)$, $b = 11.907(3)$, $c = 14.797(3)$ Å, $\beta = 123.08(1)^\circ$, $V = 3473(1)$ Å^3, $Z = 4$, $D_{calcd} = 2.283\,g/cm^3$, $R_1 = 0.041$ ($I > 2.0\sigma(I)$), $wR_2 = 0.132$ (all data).

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11 Another NO_3^- anion also contacts with two Ag^I atoms so as to sustain the 1D structure ($Ag–O = 2.907(4)$ Å and 2.919(7) Å). Unlike ClO_4^- anions, planar and higher nucleophilic NO_3^- anions can form short contacts with Ag^I atoms, which diminishes the electrophilicity of Ag^I atoms so as to permit a thiolato group in each $[Co(aet)_2(en)]^+$ unit to bind with two Ag^I atoms. T. Konno, T. Yoshimura, G. Masuyama, M. Hirotsu, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2185.

12 The conversion of $[\mathbf{2}]^{8+}$ to $[\mathbf{3}]^{5+}$ was effectively carried out by adding a small amount of $AgNO_3$. Calcd for $[\mathbf{3}](NO_3)_{4.5}(ClO_4)_{0.5}$: C, 12.06; H, 3.37; N, 14.65%. Found: C, 12.02; H, 3.42; N, 14.47%. Yield: 51%. Calcd for $[\mathbf{2}](ClO_4)_8$: C, 11.82; H, 3.89; N, 9.19%. Found: C, 11.62; H, 4.07; N, 8.94%. Yield: 78%.

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