Enantioselective Aggregation of Cobalt(III) Octahedrons in a One-Dimensional S-Bridged $Co^{III}Ag^{I}$ Array That Leads to Spontaneous Resolution

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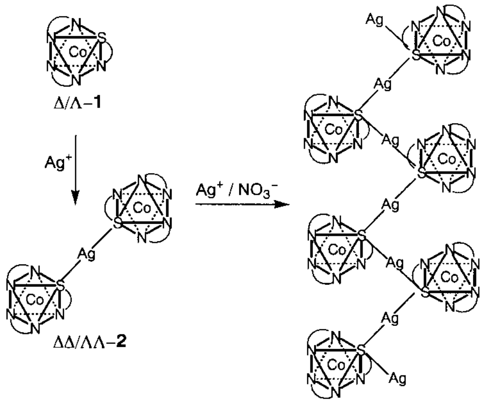
The reaction of $[Co(aet)(en)_2](NO_3)_2$ (**1**$(NO_3)_2$; aet = 2-aminoethanethiolate; en = ethylenediamine) with $AgNO_3$ in water produced a novel S-bridged $Co^{III}Ag^{I}$ chain complex-polymer, $[Ag\{Co(aet)(en)_2\}](NO_3)_3$ (**3**$(NO_3)_3$), by way of a $Co^{III}Ag^{I}Co^{III}$ trinuclear complex, $[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$ (**2**$(NO_3)_5$). The crystal structure of **3**$(NO_3)_3$, which crystallizes as a conglomerate, was determined by X-ray crystallography.

In 1979 Heeg et al. reported that the mono(thiolato)-type Co^{III} complexes, $[Co(aet)(en)_2]^{2+}$ (**1**) and $[Co(tga)(en)_2]^{+}$ (tga = mercaptoacetate), readily form 1:1 and 2:1 adducts with Ag^{I} or Hg^{II} in water.[1] Only the 2:1 adducts with Ag^{I} that were isolated as solid samples have been characterized to have an S-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear structure in $[Ag\{Co(aet\ or\ tga)(en)_2\}_2]^{5+\ or\ 3+}$.[1,2] No further reports concerning these adducts have appeared to date, despite intensive interest concerning the structures and chiral properties of S-bridged polynuclear complexes constructed by the aggregation of octahedral thiolato metal complexes.[3] We, therefore, thought it worthwhile to reexamine this fundamental system, in order to find key factors to control the aggregation of thiolato complexes around metal ions. Here we report that the 1:1 adduct of $[Co(aet)(en)_2](NO_3)_2$ (**1**$(NO_3)_2$) and $AgNO_3$, which is obtained by way of the 2:1 adduct $[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$ (**2**$(NO_3)_5$), does not take a $Co^{III}Ag^{I}$ dinuclear structure but a one-dimensional chain structure in $[Ag\{Co(aet)(en)_2\}](NO_3)_3$ (**3**$(NO_3)_3$) in solid state (Scheme 1). The fascinating stereochemical behavior of **3**, together with the significance of the counter anion for the aggregation of thiolato complexes around Ag^{I} ion is also reported.



Scheme 1.

Treatment of a dark-brown aqueous solution of **1**$(NO_3)_2$[4] with $AgNO_3$ in a ratio of 2:1 at room temperature gave a dark-red solution, from which a red crystalline powder (**2**$(NO_3)_5 \cdot 4H_2O$) was isolated by adding an aqueous solution of $NaNO_3$.[5] The elemental and plasma emission analyses of this red product are in good agreement with the formula for an S-bridged $Co^{III}Ag^{I}Co^{III}$ complex, $[Ag\{Co(aet)(en)_2\}_2](NO_3)_5 \cdot 4H_2O$. The molecular structure of **2** was determined by X-ray analysis for its ClO_4^- salt,[6] which was prepared by adding an aqueous solution of $NaClO_4$ to the aqueous solution of **2**$(NO_3)_5 \cdot 4H_2O$.[7] As pointed out by Heeg,[1] in **2** one Ag atom is coordinated by two S atoms from two octahedral $[Co(aet)(en)_2]^+$ units to form an S-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear structure. The S–Ag–S angle (164.50(8)°) is significantly deviated from 180°, which is inferred by three weak interactions between Ag^{I} ion and ClO_4^- anions (Ag---O = 2.884(9) Å, 2.884(9) Å, and 3.01(1) Å). Considering the chiral configurations (Δ and Λ) for the two $[Co(aet)(en)_2]^{2+}$ units, three isomers (ΔΔ, ΛΛ, and ΔΛ) are possible for **2**. Crystal **2** consists of ΔΔ and ΛΛ isomers, which combine to form a racemic compound.

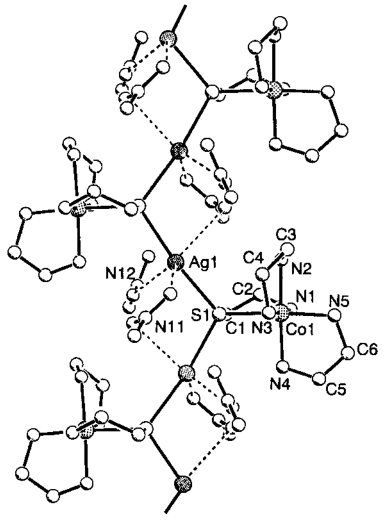


Figure 1. A perspective view for Λ-**3**$(NO_3)_3$ with the atomic labeling scheme. One of nitrate anions, which does not contact with Ag atom, besides H atoms, is omitted for clarity.

When an aqueous solution of **2**$(NO_3)_5$ was treated with ca. 1 molar equiv of $AgNO_3$ at room temperature, the first d–d absorption band at 20.33×10^3 cm^{-1} characteristic for **2**[5] shifted slightly to the lower energy side, from which a pink powder (**3**$(NO_3)_3 \cdot H_2O$) was isolated by adding an aqueous solution of $NaNO_3$.[8] This product was also obtained directly from the 1:1 reaction of **1**$(NO_3)_2$ with $AgNO_3$ in water at room temperature. The plasma emission analysis indicated that **3** contains Co and Ag atoms in a ratio of 1:1, and the elemental analysis is consistent with the 1:1 stoichiometry of $[Co(aet)(en)_2](NO_3)_2 \cdot AgNO_3 \cdot H_2O$. X-ray analysis of a single crystal of **3**$(NO_3)_3 \cdot H_2O$,[9] which was prepared by slow evaporation of an aqueous solution of the pink powder at room temperature, demonstrated that **3** is not a discrete S-bridged $Co^{III}Ag^{I}$ dinuclear complex, but an unprecedented one-dimensional $Co^{III}Ag^{I}$ chain complex-polymer. As shown in Figure 1, the S atom in each octahedral $[Co(aet)(en)_2]^{2+}$ unit is bound to two Ag^{I} ions to form a μ_3-thiolato structure, such that the chain of $[Ag\{Co(aet)(en)_2\}]^{3+}$ zigzags in the direction parallel to the *c* axis having the S–Ag–S angle of 173.14(6)°. In **3** the Ag–S bond distances (2.546(2) Å and 2.532(2) Å) are considerably longer than the Ag–S distance (2.400(1) Å) observed in **2**. Since the Co–S distance in **3** (2.287(2) Å) is similar to that in **2** (2.259(2) Å), the much longer Ag–S distances in **3** are ascribed mainly to the bonding interaction of NO_3^- anions with Ag^{I} ion (Ag---O = 2.657(6) Å, 2.725(7) Å, and 2.924(7) Å), which could diminish the electrophilicity of Ag^{I} atom toward the S atom in $[Co(aet)(en)_2]^{2+}$, rather than the coordination of μ_3-thiolato S atoms in **3**.[10] Here it should be noted that in **3** the same configurational $[Co(aet)(en)_2]^{2+}$ units are linked by Ag^{I} ions to form a chiral $Co^{III}Ag^{I}$ chain. Furthermore, **3**$(NO_3)_3\cdot H_2O$ is subject to spontaneous resolution to give a conglomerate,[11] which implies that one crystal of **3**$(NO_3)_3\cdot H_2O$ is composed of the same configurational $Co^{III}Ag^{I}$ chains (Figure 2). For the crystal used for X-ray analysis, the absolute configuration for each $[Co(aet)(en)_2]^{2+}$ unit was determined to be Λ from the Flack parameters, which were calculated for each configuration.[12]

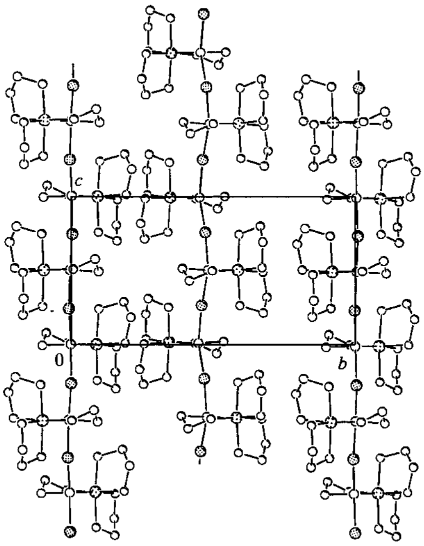


Figure 2. A perspective view for Λ-**3**$(NO_3)_3$ along the *a* direction, showing the packing of the chain units in the crystal. Nitrate anions, besides H atoms, are omitted for clarity.

In contrast to the 1:1 reaction of **2**$(NO_3)_5$ with $AgNO_3$, the corresponding 1:1 reaction using **2**$(ClO_4)_5$ and $AgClO_4$ in water did not produce **3**; only **2**$(ClO_4)_5\cdot 2H_2O$ was precipitated from the dark red reaction solution. This was also the case for the 1:1 reaction of **2**$(BF_4)_5$ with $AgBF_4$ in water.[13] It is considered that neither ClO_4^- nor BF_4^- anion contacts with Ag^{I} ions as closely as does the NO_3^- anion, because of the non-planar geometry and the lower nucleophilic character. Thus, the chain structure in **3** is stabilized by the close contact of NO_3^- anions with Ag^{I} ion, which weakens the electrophilicity of Ag^{I} ion, so as to permit two Ag^{I} ions to bind to one thiolato S atom in $[Co(aet)(en)_2]^{2+}$.

In summary, it was demonstrated in this study that treatment of the mononuclear complex **1**$(NO_3)_2$ with $AgNO_3$ gives an unexpected one-dimensional $Co^{III}Ag^{I}$ chain complex-polymer **3**$(NO_3)_3$, besides the S-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear complex **2**$(NO_3)_5$. The chain structure in **3** was found to be stabilized by the close contact of NO_3^- anions with Ag^{I} ions, which diminishes the electrophilicity of Ag^{I} ion toward the thiolato S atom in $[Co(aet)(en)_2]^{2+}$. While **3** is no other than the aggregate of the mononuclear complex **1**, **3** can be regarded as resulting from the aggregation of the S-bridged trinuclear complex **2** assisted by additional Ag^{I} ion. Thus, a variety of aggregates based on S-bridged polynuclear complexes could be constructed by controlling the nuleophilicity of μ_2-thiolato S atoms and/or the electrophilicity of bridging metal ions. The chain structure in **3**$(NO_3)_3$ was found to isolate the chiral configurations (Δ and Λ) of $[Co(aet)(en)_2]^{2+}$, giving Δ-$Co^{III}Ag^{I}$ and Λ-$Co^{III}Ag^{I}$ enantiomeric chains, which separate from one another as homochiral crystals. Since the mononuclear complex Δ/Λ-**1** and the trinuclear complex ΔΔ/ΛΛ-**2** are racemates, it is considered that the high organization of the octahedral mono(thiolato) Co^{III} units in a one-dimensional chain array leads to a rare example of spontaneous resolution.[14]

References and Notes

1 M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 2036 (1979).

2 M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **19**, 554 (1980).

3 T. Konno and K. Okamoto, *Inorg. Chem.*, **36**, 1403 (1997); T. Konno, T. Machida, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **71**, 175 (1998); K. Okamoto, C. Sasaki, Y. Yamada, and T. Konno, *Bull. Chem. Soc. Jpn.*, **72**, 1685 (1999); K. Tokuda, K. Okamoto, and T. Konno, *Inorg. Chem.*, **39**, 333 (2000); T. Konno, M. Hattori, T. Yoshimura, and M. Hirotsu, *Chem. Lett.*, **2000**, 853.

4 L. E. Asher and E. Deutsch, *Inorg. Chem.*, **12**, 1774 (1973); D. L. Nosco and E. Deutsch, *Inorg. Synth.*, **21**, 19 (1982).

5 Yield: 93%. Anal. Calcd for **2**$(NO_3)_5\cdot 4H_2O$: C, 14.41; H, 5.24; N, 21.00; Co, 11.78; Ag, 10.78%. Found: C, 14.49; H, 5.10; N, 21.08; Co, 11.71; Ag, 11.01%. Visible–UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 20.37 (2.48), 27.5 (2.8 sh), 35.19 (4.42).

6 Crystal Data for **2**$(ClO_4)_5\cdot 2H_2O$: FW 1151.7, monoclinic, *C*2/*c*, a = 15.820(3) Å, b = 8.943(3) Å, c = 27.592(3) Å, β = 97.16(1)°, V = 3873(1) $Å^3$, Z = 4, D_c = 1.98 g cm^{-3}, R (R_w) = 0.051 (0.053) for 3230 reflections with $I > 2.0\sigma(I)$.

7 Yield: 86%. Anal. Calcd for **2**$(ClO_4)_5\cdot 2H_2O$: C, 12.51; H,4.20; N,12.16%. Found: C, 12.44; H, 4.24; N, 12.08%.

8 Anal. Calcd for **3**$(NO_3)_3\cdot H_2O$: C, 12.71; H, 4.27; N, 19.76; Co, 10.39; Ag, 19.02%. Found: C, 12.71; H, 4.30; N, 19.68; Co, 10.49; Ag, 18.72%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 20.24 (2.22), 27.7 (2.6 sh), 35.01 (4.13).

9 Crystal data for Λ-**3**$(NO_3)_3\cdot H_2O$, FW 567.2, orthorhombic, $P2_12_12_1$, a = 13.852(2) Å, b = 15.746(1) Å, c = 8.135(2) Å, V = 1774.3(4) $Å^3$, Z = 4, D_c = 2.12 g cm^{-3}, R (R_w) = 0.033 (0.033) for 1902 reflections with $I > 2.0\sigma(I)$.

10 It has been shown that in $[Ag_5\{Rh(aet)_3\}_4]^{5+}$ the averaged Ag–S(μ_3) bond distance is only ca. 0.05 Å longer than the averaged Ag–S(μ_2) distance, while there is a marked difference in the averaged Ag–S bond distances (ca. 0.14 Å) between the two-coordinated and three-coordinated Ag atoms. T. Konno and K. Okamoto, *Inorg. Chem.*, **36**, 1403 (1997).

11 Each crystal that was picked up from the bulk showed a positive or negative CD sign at 280 nm. Since the 1:1 reaction of Λ-**1** with Ag^+ gave $(-)^{CD}_{280}$-**3**, it is reasonable to assign that the $(-)^{CD}_{280}$ and $(+)^{CD}_{280}$ isomers have the Λ- and Δ-$[Co(aet)(en)_2]^{2+}$structures, respectively.

12 H. D. Flack, *Acta Crystallogr., Sect. A*, **39**, 876 (1983); H. D. Flack and G. Bernandinello, *Acta Crystallogr., Sect. A*, **41**, 500 (1985). Flack parameters refined for the Λ and Δ structures give the values 0.07(6) and 0.93(6), respectively, suggesting that the former is the correct choice.

13 Anal. Calcd for **2**$(BF_4)_5\cdot 4H_2O$: C, 12.82; H, 4.66; N, 12.46; Co, 10.48; Ag, 9.59%. Found: C, 12.68; H, 4.84; N, 12.22; Co, 10.72; Ag, 9.72%.

14 J. Jacques, A. Collet, and S. H. Wilen, in "Enantiomers, Racemates and Resolutions," John Wiley & Sons Ltd., New York (1981).