Novel S-Bridged Tetranuclear Cobalt(III) Complexes with 2-Aminoethanethiolate Formed by Ligand Transfer from Nickel(II) to Cobalt(III)

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The reaction of $[CoCl(NH_3)_5]^{2+}$ with $[Ni(aet)_2]$ (aet = 2-aminoethanethiolate) in water gave two pairs of racemic isomers of a novel S-bridged tetracobalt(III) complex, $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$, in which four chiral cobalt atoms are linked by one double and two triple sulfur-bridges to have a boat-type metal array.

The stereochemistry and spectrochemistry of the S-bridged polynuclear complexes composed of *fac(S)*-[M(aminothiolato-*N,S*)$_3$]-type (M = Co^{III}, Rh^{III}, Ir^{III}) units have received considerable attention during past three decades.[1-4] Of these complexes, the best known is the linear-type S-bridged tricobalt(III) complexes with 2-aminoethanethiolate (aet = $NH_2CH_2CH_2S^-$), $[Co\{Co(aet)_3\}_2]^{3+}$ (**1**),[1] and the chemistry of the S-bridged polynuclear complexes of this class has largely been developed based on the properties of **1**.[2,3] **1** has easily been prepared by reacting *fac(S)*-[Co(aet)$_3$] with Co^{2+} or $[CoBr(NH_3)_5]^{2+}$,[1a] and furthermore it has been shown that the reactions of *fac(S)*-[Co(aet)$_3$] with reducing metal ions such as Cr^{2+} and Fe^{2+} or oxidizing metal ions such as Ce^{4+} and $[VO(SO_4)]$ cause the rearrangement of aet to form **1**.[2a,b] These facts pointed out that **1** is the stable end product of these reactions, and no other S-bridged polynuclear complexes composed of Co^{III} and aet have been discovered. In this letter, we wish to report that the reaction of $[CoCl(NH_3)_5]^{2+}$ with $[Ni(aet)_2]$ in water leads to the transfer of coordinated aet from Ni^{II} to Co^{III} to give two pairs of racemic isomers (**2a** and **2b**) of a novel S-bridged polynuclear complex, $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$, which contains four chiral Co^{III} centers.

Treatment of a green aqueous suspension of $[Ni(aet)_2]$[5] (2.0 g) with $[CoCl(NH_3)_5]Cl_2$ (2.4 g) at room temperature gave a black solution after several hours. The addition of a saturated aqueous solution of $NaNO_3$ to this reaction solution, followed by cooling in a refrigerator, gave black crystals of **2a**$(NO_3)_4$ (0.44 g).[6]

X-Ray structural analysis for **2a**$(NO_3)_4$ revealed the presence of a discrete tetravalent complex cation, four nitrate anions, and two water molecules.[7] As shown in Figure 1, the complex cation consists of four cobalt atoms and eight aet ligands, which is consistent with the elemental and plasma emission spectral analyses.[6] Each of the outer cobalt atoms is chelated by three aet ligands to form an approximately octahedral *fac(S)*-[Co(aet)$_3$] unit. On the other hand, the inner cobalt atoms, each of which is chelated by one aet ligand, are linked to each other by a double sulfur-bridge to form a $[Co_2(aet)_2]^{4+}$ moiety. To this $[Co_2(aet)_2]^{4+}$ moiety each of the two *fac(S)*-[Co(aet)$_3$] units is bound by a triple sulfur-bridge, completing the S-bridged tetranuclear structure with a boat-type metal array (Co1-Co2-Co4 = 136.03(4)°, Co3-Co1-Co2 = 136.29(4)°, Co1-Co2 = 3.351(1) Å, Co1-Co3 = 2.929(1) Å, Co2-Co4 = 2.932(1) Å). The Co-S (2.206(2) Å ~ 2.325(2) Å) and Co-N (1.988(6) Å ~ 2.020(6) Å) bond distances are within the approximate ranges observed for the S-bridged polynuclear Co(III) complexes with aet.[1c,3g-i,8]

Ten isomers[9] are possible for $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$, considering the absolute configurations of the outer (Δ and Λ configurations due to the skew pair of chelate rings) and the inner (*R* and *S* configurations[10] due to the arrangement of the ligating atoms) Co^{III} chiral centers. A crystal of **2a** consists of the $\Delta SS\Delta$ and $\Lambda RR\Lambda$ isomers (Figures 1 and 2a), which combine to form the racemic compound. This is consistent with the fact that **2a** was optically resolved with use of $[Sb_2(R,R\text{-tartrato})_2]^{2-}$ as the resolving agent, showing CD extrema with opposite signs at 331 and 282 nm. All the aet chelate rings of the two *fac(S)*-[Co(aet)$_3$] units have a distinct *gauche* form with the λ conformation in the $\Delta SS\Delta$ isomer (Figure 1). On the other hand, the two aet chelate rings of the $[Co_2(aet)_2]^{4+}$ moiety possess the δ and λ conformations, which avoid the non-bonding interaction between these chelate rings. The ^{13}C NMR spectrum of **2a** in D_2O exhibits four -CH_2S and four -CH_2NH_2 methylene carbon signals for the eight aet ligands.[6] Furthermore, the absorption spectrum of **2a** in water, which is characterized by the three intense bands at 454, 335, and 260 nm,[6] changes little at least for several hours. The above spectral behavior implies that the quasi-C_2 symmetrical S-bridged tetranuclear structure observed in crystal is retained in solution.

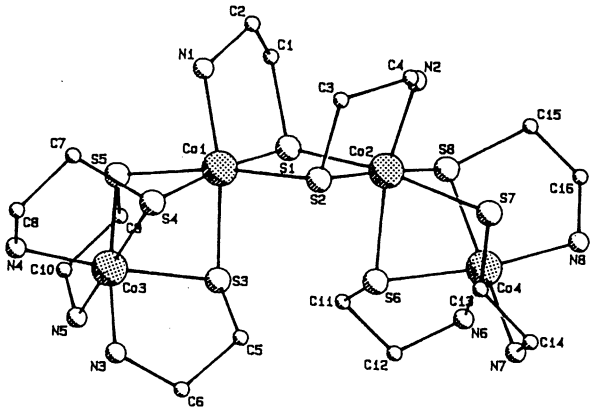

Figure 1. Perspective view of **2a** (the $\Delta SS\Delta$ isomer).

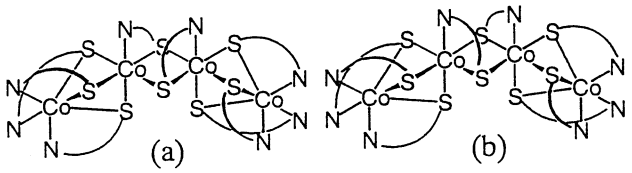

Figure 2. Model structures of the $\Delta SS\Delta$ isomer of **2a** (a) and the $\Delta RR\Delta$ isomer of **2b** (b).

The cation exchange column chromatography (SP-Sephadex C-25) showed the presence of **2b** besides **2a** in the reaction solution (ca. **2a**:**2b** = 4:1). The elemental and plasma emission analytical values of **2b**, which was isolated as the nitrate salt from the eluate of the column chromatography, are in good agreement with those of **2a**.[11] Moreover, the absorption spectrum of **2b** is very similar to that of **2a** over the whole region, giving three intense bands at 454, 368, and 260 nm.[11] These facts indicate that **2b** is another isomer for $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$. **2b** was optically resolved into two enantiomers which show CD extrema with opposite signs at 371 and 267 nm, and its ^{13}C NMR spectrum gives eight carbon signals as does **2a**.[11] Accordingly, **2b** is assigned to *ΔRRΔ/ΛSSΛ*-$[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ having a quasi-C_2 symmetrical S-bridged tetranuclear structure (Figure 2b).[9]

In the present work, it was found that the novel S-bridged tetracobalt(III) complex, $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ (**2**), is produced by reacting $[CoCl(NH_3)_5]^{2+}$ with $[Ni(aet)_2]$ under a moderate condition. On the other hand, the well-known S-bridged tricobalt(III) complex, $[Co\{Co(aet)_3\}_2]^{3+}$ (**1**), was little formed in this reaction. Since the direct reaction of $[CoCl(NH_3)_5]^{2+}$ with aet under the same conditions produced only **1** as the S-bridged polynuclear complex, it is obvious that Ni^{II} ion plays a significant role in the formation of **2**. However, the addition of $NiCl_2$ to this reaction formed only a trace amount of **2** besides the main product of **1**. These facts suggest that **2** is formed by way of some intermediate having a Ni^{II}-SR-Co^{III} μ_2-thiolato structure. Of ten isomers possible for **2**,[9] *ΔSSΔ/ΛRRΛ* (**2a**) and *ΔRRΔ/ΛSSΛ* (**2b**) are formed. To our knowledge, this is the first example of the formation of two pairs of racemic isomers for the S-bridged polynuclear complexes with aminothiolate ligands; one racemic and/or meso isomers have been formed for all other known S-bridged complexes.[1-4,8] It should be noted that the *ΔSSΔ* or *ΛRRΛ* isomer of **2a** and the *ΔRRΔ* or *ΛSSΛ* isomer of **2b** are a pair of diastereomers, which can be discriminated by the chirality at Co^{III} centers. Thus, detailed analysis of the spectroscopic data of **2a** and **2b** would serve significantly to elucidate the relationship between the absolute configuration and circular dichroism, which has not been established for the S-bridged polynuclear system.

References and Notes

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6 Anal. Found: C, 16.91; H, 4.80; N, 14.95; Co, 20.60%. Calcd for $[Co_4(C_2H_6NS)_8](NO_3)_4{\cdot}2H_2O$: C, 17.02; H, 4.64; N, 14.89; Co, 20.88%. Visible-UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (ε, 10^3 mol^{-1} dm^3 cm^{-1})]: 22.0 (13.7)^{sh}, 29.85 (20.06), 38.46 (43.09). The sh label denotes a shoulder. ^{13}C NMR spectrum in D_2O (ppm from DSS): δ 30.70, 33.20, 33.81, and 37.69 for -CH_2S and δ 48.82, 49.27, 49.37, and 51.05 for -CH_2NH_2.

7 Crystal data for $[Co_4(C_2H_6NS)_8](NO_3)_4{\cdot}2H_2O$: *F. W.* = 1128.9, triclinic, $P\bar{1}$, a = 13.585(3), b = 15.132(3), c = 10.699(2) Å, α = 101.45(1), β = 104.78(1), γ = 95.89(1)°, V = 2056.6(8) Å^3, Z = 2, Dc = 1.82 g cm^{-3}, $R(Rw)$ = 0.045 (0.051) for 5353 reflections.

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9 The possible isomers are *ΔSSΔ* and *ΛRRΛ* (racemic, C_2-symmetry), *ΔRRΔ* and *ΛSSΛ* (racemic, C_2-symmetry), *ΔSSΛ* and *ΔRRΛ* (racemic, C_1-symmetry), *ΔSRΔ* and *ΛSRΛ* (racemic, C_1-symmetry), *ΔSRΛ* (meso), and *ΔRSΛ* (meso).

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11 Anal. Found: C, 17.06; H, 4.66; N, 14.60; Co, 20.68%. Calcd for $[Co_4(C_2H_6NS)_8](NO_3)_4{\cdot}2H_2O$: C, 17.02; H, 4.64; N, 14.89; Co, 20.88%. Visible-UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (ε, 10^3 mol^{-1} dm^3 cm^{-1})]: 22.0 (12.0)^{sh}, 27.17 (20.50), 38.46 (39.60). The sh label denotes a shoulder. ^{13}C NMR spectrum in D_2O (ppm from DSS): δ 29.75, 32.74, 33.16, and 37.77 for -CH_2S and δ 49.14, 49.21, 49.65, and 52.76 for -CH_2NH_2.