Spontaneous Reduction of Gold(III) to Gold(I) That Leads to the Formation of *S*-Bridged $\mathrm{Co^{III}}_2\mathrm{Au^{I}}_2$ Tetranuclear Structure Composed of Unprecedented C_1-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ Units: Synthesis and Characterization of C_2C_2- and C_1C_1-$[\mathrm{Au_2\{Co(aet)_2(en)\}_2}]^{4+}$

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The 1 : 2 reactions of C_2C_2-$[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ (C_2C_2-$[\mathbf{1}]^{4+}$; aet = 2-aminoethanethiolate, en = ethylenediamine) with $\mathrm{Au^I}$ or $\mathrm{Au^{III}}$ in water gave an *S*-bridged $\mathrm{Co^{III}}_2\mathrm{Au^I}_2$ tetranuclear complex, C_2C_2-$[\mathrm{Au^I}_2\mathrm{\{Co(aet)_2(en)\}_2}]^{4+}$ (C_2C_2-$[\mathbf{2}]^{4+}$). On the other hand, the corresponding 1 : 1 reaction with $\mathrm{Au^{III}}$ led to the geometrical isomerization of C_2-*cis(S)*- to C_1-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ unit to produce C_1C_1-$[\mathbf{2}]^{4+}$.

Since the discovery of an *S*-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ trinuclear complex, C_2C_2-$[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ (C_2C_2-$[\mathbf{1}]^{4+}$),[1] considerable progress has been made in the chemistry of *S*-bridged polynuclear complexes composed of *cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units, which can be prepared from C_2C_2-$[\mathbf{1}]^{4+}$ by the metal replacement reactions of the central $\mathrm{Ni^{II}}$ with other metal ions, such as $\mathrm{Pd^{II}}$, $\mathrm{Cd^{II}}$, and $\mathrm{Pt^{II}}$.[2] Two geometrical isomers, C_1-*cis(S)* and C_2-*cis(S)*, are possible for *cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ unit (Figure 1). However, only the C_2-*cis(S)* form has been found in the *S*-bridged polynuclear complexes so far isolated.[2] This is also the case for the analogous *S*-bridged polynuclear complexes composed of *cis(S)*-$[\mathrm{Co(aet)_2(}R\mathrm{\text{-}pn)}]^+$ units (R-pn = (R)-1,2-propanediamine).[3] Thus, the preparation of *S*-bridged polynuclear complexes composed of C_1-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units is very synthetically challenging.

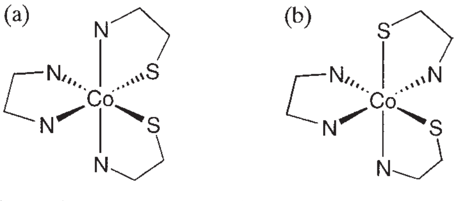

Figure 1. Two geometrical isomers, C_2-*cis(S)* (a) and C_1-*cis(S)* (b), for *cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ unit.

Recently, we have reported that *trans(N)*-$[\mathrm{Co(\text{D-pen-}}N,O,S)_2]^-$ (D-pen = D-penicillaminate), having two thiolato S atoms in a *cis* position, reacts with $\mathrm{Au^I}$ to form an *S*-bridged $\mathrm{Co^{III}}_3\mathrm{Au^I}_3$ metallacycle, $[\mathrm{Au_3\{Co(\text{D-pen-}}N,O,S)_2\}_3]$.[4] Interestingly, the *cis(S)*-type $[\mathrm{Co(\text{D-pen-}}N,O,S)_2]^-$ units in this metallacycle adopt a *trans(O)* geometry, indicating that the geometrical isomerization of *trans(N)* to *trans(O)* was caused by forming the *S*-bridged structure with linear $\mathrm{Au^I}$. Prompted by this result, we carried out the reaction of C_2C_2-$[\mathbf{1}]^{4+}$ with $\mathrm{Au^I}$, anticipating the creation of C_1-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units in an *S*-bridged polynuclear structure. Although this reaction produced a novel $\mathrm{Co^{III}}_2\mathrm{Au^I}_2$ tetranuclear complex (C_2C_2-$[\mathbf{2}]^{4+}$), two *cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units in C_2C_2-$[\mathbf{2}]^{4+}$ were found to adopt the C_2-*cis(S)* form. When C_2C_2-$[\mathbf{1}]^{4+}$ was treated with $\mathrm{Au^{III}}$, however, we found the formation of C_1C_1-$[\mathbf{2}]^{4+}$ composed of C_1-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units. In this paper, we report the synthesis and characterization of C_2C_2-$[\mathbf{2}]^{4+}$ and C_1C_1-$[\mathbf{2}]^{4+}$.

The reaction of an aqueous solution of C_2C_2-$[\mathbf{1}]\mathrm{Cl_4{\cdot}6H_2O}$[1] with 2 molar equiv of $[\mathrm{Au^ICl\{S(CH_2CH_2OH)_2\}}]$[4,5] (60 °C, 20 min) gave a red-brown solution, from which red-brown crystals (C_2C_2-$[\mathbf{2}]\mathrm{Cl_4{\cdot}4.5H_2O}$) were isolated by adding an aqueous solution of NaCl (81% yield).[6] The plasma emission analysis (Co/Au = 1.07) indicated that $[\mathbf{2}]^{4+}$ contains Co and Au atoms in a 1:1 ratio and its elemental analysis is in good agreement with the formula for the 1:1 adduct of $[\mathrm{Co(aet)_2(en)}]^+$ and $\mathrm{Au^I}$.[6] Single-crystal X-ray analysis demonstrated that C_2C_2-$[\mathbf{2}]^{4+}$ is a new class of *S*-bridged $\mathrm{Co^{III}}_2\mathrm{Au^I}_2$ tetranuclear complex, C_2C_2-$[\mathrm{Au_2\{Co(aet)_2(en)\}_2}]^{4+}$, in which two octahedral C_2-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units are linked by two linear $\mathrm{Au^I}$ atoms through four sulfur-bridges (average Co-S = 2.272(4) Å, Au-S = 2.301(3) Å, S-Au-S = 176.9(1)°, S-Co-S = 99.7(1)°) (Figure 2a).[7] The intramolecular Au-Au distance is 2.9640(9) Å, indicating the presence of a bonding interaction between two $\mathrm{Au^I}$ atoms.[8] Furthermore, the two complex-cations are connected through a weak Au···Au interaction (Au2···Au2' = 3.229(1) Å),[8] which forms a dimer of the $\mathrm{Co^{III}}_2\mathrm{Au^I}_2$ tetranuclear structure. Of three isomers ($\Delta\Delta$, $\Lambda\Lambda$, $\Delta\Lambda$) possible for C_2C_2-$[\mathrm{Au_2\{Co(aet)_2(en)\}_2}]^{4+}$, crystal of $[\mathbf{2}]\mathrm{Cl_4}$ consists of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers with a D_2 symmetrical structure (Figure 2a), which combine to form the racemic compound.

A similar reaction of C_2C_2-$[\mathbf{1}]\mathrm{Cl_4{\cdot}6H_2O}$ with 2 molar equiv of $\mathrm{Na[Au^{III}Cl_4]}$ in water also produced dark red crystals of $[\mathbf{2}]\mathrm{Cl_4{\cdot}4.5H_2O}$ (31% yield). When C_2C_2-$[\mathbf{1}]\mathrm{Cl_4{\cdot}6H_2O}$ was treated with 1 molar equiv of $\mathrm{Na[Au^{III}Cl_4]}$ under the same conditions,

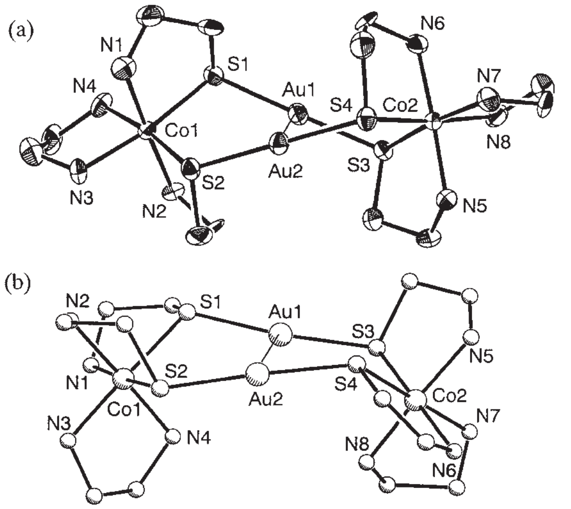

Figure 2. Perspective views of C_2C_2-$[\mathbf{2}]^{4+}$ (a) and C_1C_1-$[\mathbf{2}]^{4+}$ (b). The $\Delta\Delta$ isomers are selected.

however, dark red crystals (C_1C_1-[**2**]Cl$_4$·5H$_2$O) were isolated from the dark red reaction solution by adding an aqueous solution of NaCl (67% yield based on Au).[9] The perchlorate salt of C_1C_1-[**2**]$^{4+}$ was also prepared by adding an aqueous solution of NaClO$_4$ to the reaction solution (86% yield based on Au). The plasma emission (Co/Au $=$ 1.07) and elemental analytical results are consistent with the formula for the *S*-bridged Co$^{III}_2$Au$^I_2$ tetranuclear structure in [Au$^I_2${Co^{III}(aet)$_2$(en)}$_2$]$^{4+}$.[9] However, its electronic absorption spectrum differs significantly from that of C_2C_2-[**2**]$^{4+}$ over the whole region, as illustrated in Figure 3. Moreover, in the ^{13}C NMR spectrum, C_1C_1-[**2**]$^{4+}$ exhibits six main signals, accompanied by another set of minor signals, in the region of δ 36–52, even after its recrystallization.[9] This is in contrast to the fact that only three signals are observed in the ^{13}C NMR spectrum of C_2C_2-[**2**]$^{4+}$ having a D_2 symmetry.[6] From these results, together with the elution behavior in the SP-Sephadex C-25 column,[6,9] it is reasonable to assume that C_1C_1-[**2**]$^{4+}$ is an *S*-bridged Co$^{III}_2$Au$^I_2$ tetranuclear complex containing C_1-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units, C_1C_1-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$. The C_2 symmetrical *S*-bridged Co$^{III}_2$Au$^I_2$ structure, in which two C_1-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units are linked by two linear Au^I ions, was confirmed by X-ray analysis for C_1C_1-[**2**](ClO$_4$)$_4$·4H$_2$O (Figure 2b),[10] although a detailed structural discussion is precluded because of poor crystal quality and positional disorders of one of three complex cations and perchlorate anions in the unit cell. The minor signals observed in the ^{13}C NMR spectrum may be due to the presence of another geometry possible for C_1C_1-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$.[11]

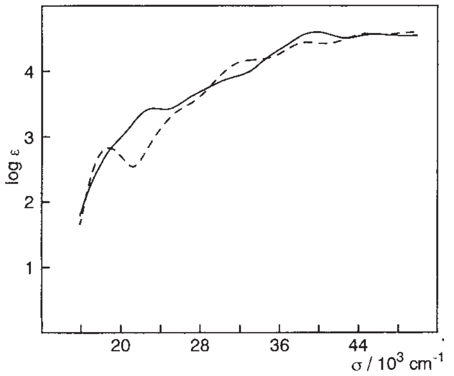

Figure 3. Electronic absorption spectra of C_2C_2-[**2**]$^{4+}$ (—) and C_1C_1-[**2**]$^{4+}$ (- - -) in water.

In summary, it was found that the 1 : 1 reaction of C_2C_2-[Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ with [Au^{III}Cl$_4$]$^-$ is accompanied by the geometrical isomerization of C_2-*cis(S)* to C_1-*cis(S)* to produce C_1C_1-[Au$^I_2${Co(aet)$_2$(en)}$_2$]$^{4+}$, while the corresponding 1 : 2 reaction proceeds with retention of the C_2-*cis(S)* geometry to give C_2C_2-[Au$^I_2${Co(aet)$_2$(en)}$_2$]$^{4+}$. No reducing agents such as free thiols were employed for these reactions. Thus, it is seen that square-planar Au^{III} is spontaneously reduced to linear Au^I by forming an *S*-bridged structure with *cis(S)*-[Co(aet)$_2$(en)]$^+$.[12] The detailed mechanism of these reactions is not clear at present, but it is likely that some redox intermediate is closely related to the stabilization of the unprecedented C_1-*cis(S)* geometry for the 1 : 1 reaction.[13]

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6 Anal. Calcd for C_2C_2-[**2**]Cl$_4$·4.5H$_2$O: C, 12.43; H, 4.26; N, 9.66%. Found: C, 12.14; H, 4.27; N, 9.45%. ^{13}C NMR spectrum in D$_2$O (δ, ppm from DSS): 37.18 (CH$_2$S), 47.54 (CH$_2$NH$_2$ of en), 53.30 (CH$_2$NH$_2$ of aet). When the reaction solution was chromatographed on an SP-Sephadex C-25 column, only one red-brown band containing C_2C_2-[**2**]$^{4+}$ was eluted with a 0.5 mol dm^{-3} aqueous solution of NaCl.

7 Crystal Data for C_2C_2-[**2**]Cl$_4$·4.5H$_2$O: *F. W.* $=$ 1159.4, monoclinic, *C*2/*c*, $a = 26.451(6)$ Å, $b = 13.365(5)$ Å, $c = 21.526(4)$ Å, $\beta = 115.04(1)^\circ$, $V = 6894(2)$ Å^3, $Z = 8$, $D_c = 2.23$ g cm^{-3}, R (R_w) $=$ 0.042 (0.046) for 4327 reflections with $I > 1.9\sigma(I)$.

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9 Anal. Calcd for C_1C_1-[**2**]Cl$_4$·5H$_2$O: C, 12.34; H, 4.31; N, 9.59%. Found: C, 12.30; H, 4.18; N, 9.58%. Calcd for C_1C_1-[**2**](ClO$_4$)$_4$·4H$_2$O: C, 10.24; H, 3.44; N, 7.97%. Found: C, 10.36; H, 3.45; N, 7.97%. ^{13}C NMR spectrum in D$_2$O (δ, ppm from DSS): 36.06, 36.80*, 37.28*, 37.83 (CH$_2$S), 46.20*, 46.52, 48.16, 48.93, 49.58*, 50.96*, 51.88 (CH$_2$NH$_2$). Asterisk denotes a minor peak. When the reaction solution was chromatographed on an SP-Sephadex C-25 column, one dark red band containing C_1C_1-[**2**]$^{4+}$, accompanied by a pale brown band of C_2C_2-[**2**]$^{4+}$, was eluted with a 0.5 mol dm^{-3} aqueous solution of NaCl. The formation ratio was estimated to be $C_1C_1 : C_2C_2 = 20 : 1$.

10 Crystal Data for C_1C_1-[**2**](ClO$_4$)$_4$·4H$_2$O: *F. W.* $=$ 1406.4, monoclinic, *P*2$_1$/*n*, $a = 23.236(2)$ Å, $b = 18.652(2)$ Å, $c = 26.593(2)$ Å, $\beta = 101.367(2)^\circ$, $V = 11299(1)$ Å^3, $Z = 12$, $D_c = 2.48$ g cm^{-3}, $R =$ 0.138 for 14476 reflections with $F > 4.0\sigma(F)$.

11 The structure in Figure 2b possesses an idealized C_2 axis at the center of two Au atoms perpendicular to the Co1–Co2 line. Another geometry, in which an idealized C_2 axis passes through two Au atoms, is possible.

12 It has been shown that *fac(S)*-[M(aet)$_3$] (M $=$ Rh^{III}, Ir^{III}) are oxidized to give dinuclear complexes, [M$_2$(aet)$_4$(cysta)]$^{2+}$ (cysta=NH$_2$CH$_2$CH$_2$-SSCH$_2$CH$_2$NH$_2$), in which two octahedral units are linked by a coordinated disulfide bond.[14] Thus, it is assumed that *cis(S)*-[Co(aet)$_2$(en)]$^+$ acts as a reducing agent for Au^{III}, considering the low yield of C_2C_2-[**2**]$^{4+}$ for the 1 : 2 reaction of C_2C_2-[**1**]$^{4+}$ with [Au^{III}Cl$_4$]$^-$.

13 The most probable intermediate is [Au^I{Co$_2$(aet)$_2$(cysta)(en)$_2$}]$^{5+}$, in which two Co^{III} centers are connected by a coordinated disulfide bond, besides an S-Au-S linkage. Molecular model examinations reveal that in this proposed intermediate there exists a steric repulsion between two C_2-*cis(S)*-units, which is much severer than that between two C_1-*cis(S)*-units.

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