Novel Aggregation of *fac(S)*-[Rh(aet)$_3$] by Square-Planar Palladium(II): Crystal Structure of Spontaneously Resolved Rh$^{III}_3$Pd$^{II}_2$ Pentanuclear Complex [Pd{Pd(aet)}{Rh(aet)$_2$}{Rh(aet)$_3$}$_2$]Br$_4$ (aet = 2-Aminoethanethiolate)

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The reaction of *fac(S)*-[Rh(aet)$_3$] (aet = $NH_2CH_2CH_2S^-$) with Pd^{II} gave a novel S-bridged Rh$^{III}_3$Pd$^{II}_2$ pentanuclear complex, [Pd{Pd(aet)}{Rh(aet)$_2$}{Rh(aet)$_3$}$_2$]$^{4+}$ (**1**), of which bromide salt was spontaneously resolved. **1** was converted into [Pd{Pd(aet)}{Rh(aet)($NH_2CH_2CH_2SCH_3$)}{Rh(aet)$_3$}$_2$]$^{5+}$ (**2**) by methylation reaction.

Aggregation of *fac(S)*-[M(aet)$_3$] molecules (M = Co^{III}, Rh^{III}, Ir^{III}; aet = $NH_2CH_2CH_2S^-$) assisted by metal ions has been shown to form a variety of S-bridged polynuclear complexes, retaining the *fac(S)* structure.[1-9] Up to date a number of S-bridged trinuclear [M'{M(aet)$_3$}$_2$]$^{n+}$ (M' = Fe^{III}, Co^{III}, Ni^{II}),[1-3] pentanuclear [M'$_3${M(aet)$_3$}$_2$]$^{n+}$ (M' = Ag^{I}, Hg^{II}),[4,5] and octanuclear [M'$_4$O{M(aet)$_3$}$_4$]$^{6+}$ (M' = Co^{II}, Zn^{II}, Cd^{II}) complexes,[6-8] in which two or four moles of *fac(S)*-[M(aet)$_3$] are linked by metal ions with an octahedral-, linear-, or tetrahedral-type coordination geometry, have been prepared and their stereochemical properties have been clarified. However, no report has appeared on the S-bridged polynuclear complexes composed of *fac(S)*-[M(aet)$_3$] and metal ions with a square-planar geometry. Our previous attempts to incorporate metal ions with a square-planar geometry by reacting *fac(S)*-[M(aet)$_3$] (M = Rh^{III}, Ir^{III}) with Cu^{II} caused the spontaneous reduction to trigonal-planar Cu^{I}, forming S-bridged octanuclear complexes, [Cu$_4${M(aet)$_3$}$_2${M$_2$(aet)$_4$(cysta)}]$^{6+}$ (cysta = cystamine).[10] In this paper, we describe the first aggregation of three moles of *fac(S)*-[Rh(aet)$_3$] by Pd^{II} with a square-planar geometry, which causes the chelate-transfer of one aet ligand from Rh^{III} to Pd^{II} coordination sphere to form an octahedral *cis(N)*-[Rh(N)$_2$(S)$_4$] unit.

To a yellow aqueous suspension of *fac(S)*-[Rh(aet)$_3$] [7b] (0.20 g) was added Na$_2$[PdCl$_4$] (0.12 g), and the mixture was stirred at 70 ℃ for 2 h. The addition of a saturated NaCl solution to the reddish orange solution, followed by cooling in a refrigerator, afforded orange-red needle crystals (**1**Cl$_4$·8H$_2$O, 0.06 g).[11] The chloride salt was converted to the bromide salt by the use of a QAE-Sephadex A-25 column (Br$^-$ form).[11] Spontaneously resolved crystals of the bromide salt (**1**Br$_4$·6H$_2$O), one of which was used for X-ray analysis, were obtained by storing an aqueous solution of the bromide salt in a refrigerator.

X-Ray structural analysis of the bromide salt of **1** revealed the presence of a discrete tetravalent complex cation, four bromide anions, and six water molecules.[12] As shown in Figure 1, the complex cation consists of three Rh and two Pd atoms and nine aet ligands, which is consistent with the plasma emission and elemental analyses.[11] Each of the Rh1 and Rh2 atoms is chelated by three bidentate-*N,S* aet ligands to form an approximately octahedral *fac(S)*-[Rh(aet)$_3$] unit, retaining the structure of the starting mononuclear complex. On the other hand, only two aet ligands chelate to the Rh3 atom, and its remaining two coordination sites are occupied by two S atoms of the aet ligands which chelate to the Rh2 and Pd2 atoms. As a result, the Rh3 atom is coordinated by four S and two N atoms in an approximately octahedral *cis(N)* geometry. The S21, S22, and S23 atoms of the *fac(S)*-Rh2 unit are bound to the Pd1, Pd2, and Rh3 atoms, respectively. This binding mode is the same as that observed for the *fac(S)*-[M(aet)$_3$] units in [M'$_3${M(aet)$_3$}$_2$]$^{n+}$ (M' = Ag^{I}, Hg^{II}) and [M'$_4$O{M(aet)$_3$}$_4$]$^{6+}$ (M' = Co^{II}, Zn^{II}, Cd^{II}).[4-8] On the other hand, the *fac(S)*-Rh1 unit binds to two Pd atoms through three sulfur-bridges, which is the unprecedented binding mode for *fac(S)*-[M(aet)$_3$]. Each Pd atom adopts a distorted square-planar geometry; the Pd1 atom is surrounded by four S atoms from the Rh1, Rh2, and Rh3 units, while one bidentate-*N,S* aet ligand and two S atoms from the Rh1 and Rh2 units complete the square-planar geometry for Pd2. It should be noted that in **1** the three Rh^{III} and two Pd^{II} atoms are linked by eight sulfur-bridges, remaining one non-bridging thiolato S atom (S32).

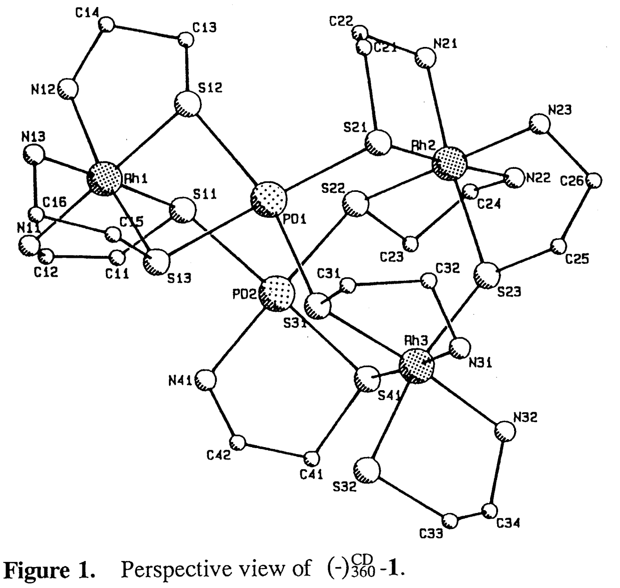

Figure 1. Perspective view of $(-)^{CD}_{360}$-**1**.

Considering the absolute configurations, Δ and Λ, for each of the three octahedral Rh units, eight isomers are possible for **1**. When the reaction solution of *fac(S)*-[Rh(aet)$_3$] and Na$_2$[PdCl$_4$] was chromatographed on an SP-Sephadex C-25 column, only one orange band of **1** was eluted with a 0.4 mol dm^{-3} NaCl solution.[13] Furthermore, **1**Br$_4$ was subject to spontaneous resolution to give two optically active isomers, $(+)^{CD}_{360}$ and $(-)^{CD}_{360}$, which show CD spectra enantiomeric to each other. These results suggest that a pair of enantiomers are selectively formed for **1**. It was determined by the anomalous scattering technique that the Rh1, Rh2, and Rh3 units in $(-)^{CD}_{360}$-**1** have the

Δ, *Λ*, and *Δ* configurations, respectively, as illustrated in Figure 1.[14] Thus, $(+)^{\mathrm{CD}}_{360}$-**1** can be assigned to have the *Λ*(Rh1)*Δ*(Rh2)*Λ*(Rh3) configuration. In the ^{13}C NMR spectrum **1** exhibits 16 methylene carbon signals due to the nine aet ligands in the region of δ 33 – 55, which supports the selective formation of a pair of enantiomers for **1**.[11]

Treatment of an aqueous solution of **1**$Br_4 \cdot 6H_2O$ (0.2 g) with $(CH_3)_2SO_4$ (6 cm^3) at room temperature led a slight solution color change, and from this reaction solution the orange complex (**2**$Br_5 \cdot 11H_2O$) was isolated.[15] The ^{13}C NMR spectrum of **2** exhibits one methyl carbon signal at δ 18.25 besides 16 methylene signals in the region of δ 30 – 55. From this result and elemental analysis, **2** is assignable as $[Pd\{Pd(aet)\}\{Rh(aet)(NH_2CH_2CH_2SCH_3)\}\{Rh(aet)_3\}_2]^{5+}$; that is, methylation on the non-bridging thiolato S atom occurs with retention of the S-bridged pentanuclear structure in **1**. In the ^{1}H NMR spectrum **2** gives one sharp methyl proton signal at δ 2.62, which suggests that the asymmetric thioether donor atom in **2** takes either the *R* or *S* configuration. Molecular model constructions reveal that the *R* configuration is favorable for the *ΔΛΔ* isomer, because there exists a significant non-bonding interaction between the *S*-configurational methyl group and the aet chelate ring of Pd atom.

In the present study, it was found that the novel S-bridged $Rh^{III}_3Pd^{II}_2$ pentanuclear complex (**1**) is produced by the reaction of *fac(S)*-$[Rh(aet)_3]$ with $Na_2[PdCl_4]$ in water at a relatively high temperature. Though *fac(S)*-$[Rh(aet)_3]$ reacted with $Na_2[PdCl_4]$ at room temperature, this reaction did not give any significant amount of **1**; most of the products were found to be adsorbed on the top of the SP-Sephadex C-25 column even by the elution with a saturated NaCl solution. Furthermore, when the complex molecule *fac(S)*-$[Ir(aet)_3]$, which is much robuster than *fac(S)*-$[Rh(aet)_3]$,[3] reacted with $Na_2[PdCl_4]$ in water at 70 ℃, the corresponding S-bridged $Ir^{III}_3Pd^{II}_2$ pentanuclear complex was little formed. Accordingly, it is reasonable to assume that the chelate-transfer of one aet ligand from *fac(S)*-$[Rh(aet)_3]$ to Pd^{II} coordination sphere, accompanied by the S-donation from another *fac(S)*-$[Rh(aet)_3]$, is responsible for the formation of **1**.

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11 Anal. Found for the chloride salt: C, 14.46; H, 4.67; N, 8.30; Rh, 20.5; Pd, 14.0%. Calcd for $[Pd_2Rh_3(C_2H_6NS)_9]Cl_4 \cdot 8H_2O$: C, 14.48; H, 4.73; N, 8.44; Rh, 20.7; Pd, 14.3%. Found for the bromide salt: C, 13.32; H, 4.05; N, 7.68. Calcd for $[Pd_2Rh_3(C_2H_6NS)_9]Br_4 \cdot 6H_2O$: C, 13.22; H, 4.07; N, 7.71%. Visible-UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (logε, mol^{-1} dm^3 cm^{-1})]: 23.3 $(3.8)^{sh}$, 26.7 $(4.1)^{sh}$, 41.32 (4.81), 48.31 (4.79). The sh label denotes a shoulder. CD spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (Δε, mol^{-1} dm^3 cm^{-1})]: 23.26 (+5.09), 27.47 (-25.08), 31.85 (+15.50), 34.82 (-26.49), 40.68 (+107.2), 47.13 (-102.4). ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 33.81, 34.86, 36.19, 37.09, 38.06, 39.27, 39.37, 42.14 for $-CH_2S$ and 48.16, 49.89, 50.06, 50.15, 50.33, 50.73, 53.61, 54.27 for $-CH_2NH_2$.

12 Crystal data for **1**$Br_4 \cdot 6H_2O$: *F. W.* =1634.5, orthorhombic, $P2_12_12_1$ (No. 19), *a* = 14.035(2), *b* = 17.317(2), *c* = 19.792(3) Å, *V* = 4810(1) Å^3, *Z* = 4, *Dc* = 2.26 g cm^{-3}, *R*(*Rw*) = 0.039 (0.044) for 4138 reflections. Selected bond distances (Å) and angles (°): av. Pd1-S = 2.346(4), av. Pd2-S = 2.344(4), Pd-N41 = 2.08(1), av. Rh1-S = 2.313(4), av. Rh1-N = 2.13(1), av. Rh2-S = 2.311(4), av. Rh2-N = 2.13(1), Rh3-S23 = 2.378(3), Rh3-S31 = 2.300(4), Rh3-S32 = 2.355(4), Rh3-S41 = 2.359(4), av. Rh3-N = 2.12(1), S12-Pd1-S13 = 80.2(1), S12-Pd1-S21 = 102.1(1), S13-Pd1-S31 = 84.9(1), S21-Pd1-S31 = 92.0(1), S11-Pd2-S22 = 86.5(1), S11-Pd2-N41 = 93.4(3), S22-Pd2-S41 = 93.4(1), S41-Pd2-N41 = 86.0(3), av. S-Rh1-S = 89.0(1), av. N-Rh1-N = 92.0(5), av. S-Rh2-S = 95.2(1), av. N-Rh2-N = 90.0(5), S31-Rh3-S41 = 93.0(1), S31-Rh3-S32 = 86.6(1), S32-Rh3-S41 = 96.9(1), S23-Rh3-N31 = 95.6(3), S23-Rh3-N32 = 82.1(3), N31-Rh3-N32 = 91.2(4).

13 It was found from this column chromatography that **1** was formed in a 95% yield.

14 Refinement in the enantiomeric parameters gave the values of *R*(*Rw*) = 0.052 (0.057), indicating that the enantiomer selected is correct with greater than 99.5% certainty (W. C. Hamilton, *Acta Crystallogra*, **18**, 502 (1965)).

15 Anal. Found: C, 12.49; H, 4.26; N, 6.79%. Calcd for $[Pd_2Rh_3(C_2H_6NS)_8(C_3H_9NS)]Br_5 \cdot 11H_2O$: C, 12.54; H, 4.38; N, 6.93%. Visible-UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (logε, mol^{-1} dm^3 cm^{-1})]: 21.9 $(3.7)^{sh}$, 25.8 $(4.0)^{sh}$, 31.9 $(4.3)^{sh}$, 40.92 (4.76), 47.39 (4.76). The sh label denotes a shoulder. ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 18.25 for $-SCH_3$, 34.81, 35.16, 37.85, 38.30, 39.44, 39.82, 42.38, 43.88 for $-CH_2S$, and 46.09, 46.51, 47.85, 49.65, 49.99, 50.11, 50.71, 53.32 for $-CH_2NH_2$.