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Novel S-Bridged $Co^{III}Pd^{II}$ Polynuclear Complexes Derived from $[Ni^{II}\{Co^{III}(aet)_2(en)\}_2]Cl_4$ (aet=2-Aminoethanethiolate). Crystal Structures of $[Pd\{Co(aet)_2(en)\}_2]Cl_4$ and $[PdCl_2\{Co(aet)_2(en)\}]Cl$

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The reaction of an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ (**1**), with $Na_2[PdCl_4]$ in a ratio of 1 : 1 gave an S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex, $[Pd\{Co(aet)_2(en)\}_2]Cl_4$ (**2**), while the corresponding 1 : 2 reaction produced an S-bridged $Co^{III}Pd^{II}$ dinuclear complex, $[PdCl_2\{Co(aet)_2(en)\}]Cl$ (**3**). The crystal structures of **2** and **3** were determined by X-ray crystallography: **2**·$6H_2O$ crystallizes in the monoclinic space group $C2/c$ with $a = 14.951(2)$, $b = 19.753(2)$, $c = 12.926(2)$ Å, $\beta = 113.33(1)°$, $V = 3505.4(9)$ Å^3, $Z = 4$, and $R = 0.034$. **3**·$2H_2O$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.282(5)$, $b = 8.497(2)$, $c = 16.139(6)$ Å, $\beta = 115.13(1)°$, $V = 1773(1)$ Å^3, $Z = 4$, and $R = 0.026$. In **2** the Pd^{II} atom is coordinated by four S atoms from two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units, while the Pd^{II} atom in **3** is coordinated by two Cl atoms besides two S atoms from one octahedral C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit. **2** was readily converted to **3** by the reaction with $Na_2[PdCl_4]$, while the conversion of **3** to **2** was achieved by reacting **3** with **1**. **2** and **3** were optically resolved and their electronic absorption and CD spectral behavior is also reported.

It has been recognized that mononuclear Co(III) complexes with thiolato donor atoms can function as S-donating complex-ligands to various metal ions to form S-bridged polynuclear structures.[1—6] In fact, a number of S-bridged polynuclear complexes composed of *fac*(*S*)-[Co(thiolato-*S*)$_3$(amine-*N*)$_3$]-type units have been prepared by reacting $[Co(aet)_3]$ or *fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with metal ions such as Co^{III}, Ni^{II}, and Zn^{II}.[2—5] On the other hand, none of the S-bridged polynuclear complexes composed of *cis*(*S*)-[Co(thiolato-*S*)$_2$(amine-*N*)$_4$]-type units have long been presented, mainly because of the difficulty in isolating this type of mononuclear complex.[7,8] Recently, we found that the reaction of $[Ni(aet)_2]$ with $[CoCl_2(en)_2]^+$ results in a chelate-transfer of aet from Ni^{II} to Co^{III} coordination sphere to give an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ (**1**), in which the central Ni^{II} atom is coordinated by four thiolato S atoms from two octahedral C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units.[9] Furthermore, **1** was found to be convertible to the S-bridged $Co^{III}Cd^{II}$ dinuclear complex, $[CdCl_3[Co(aet)_2(en)\}]$, by a reaction with excess $CdCl_2$, retaining the geometry of the octahedral unit.[10] This fact suggested that other S-bridged polynuclear complexes composed of *cis*(*S*)-$[Co(aet)_2(en)]^+$ units can be prepared, using **1** as a starting complex instead of the mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$. In order to confirm this suggestion and to explore the coordination chemistry of Pd(II) complexes with *cis*(*S*)-[Co(thiolato-*S*)$_2$(amine-*N*)$_4$]-type complex-ligands, we examined the reactivity of **1** toward $[PdCl_4]^{2-}$. As a result, a novel S-bridged $Co^{III}Pd^{II}$ dinuclear complex, besides a $Co^{III}Pd^{II}Co^{III}$ trinuclear complex, was derived from **1**. In this paper we report on the synthesis and stereochemical and spectrochemical properties of these polynuclear complexes, which were characterized by a combination of X-ray diffraction and absorption, CD, and NMR spectra.

Experimental

Preparation of $[Pd\{Co(aet)_2(en)\}_2]Cl_4$ (2). To a solution containing 0.20 g (0.23 mmol) of $[Ni\{Co(aet)_2(en)\}_2]Cl_4·6H_2O$[9b] in 50 cm^3 of water was added a solution containing 0.07 g (0.24 mmol) of $Na_2[PdCl_4]$ in 10 cm^3 of water. The mixture was stirred at 60 °C for 30 min. To the red-brown reaction solution was added 6 cm^3 of a saturated NaCl solution, which was kept in a refrigerator for 3 d. The resulting red-brown fine crystals (**2**·$6H_2O$) were collected by filtration. Yield; 0.15 g (71%). Found: C, 15.99; H, 5.81; N, 12.30; Co, 12.91; Pd, 11.98%. Calcd for $[Pd\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4·6H_2O$: C, 16.03; H, 5.83; N, 12.46; Co, 13.11; Pd, 11.84%. Single crystals suitable for X-ray analysis were obtained by allowing to stand the red-brown reaction solution at room temperature for several days.

Preparation of $[PdCl_2\{Co(aet)_2(en)\}]Cl$ (3). To a solution containing 0.20 g (0.23 mmol) of $[Ni\{Co(aet)_2(en)\}_2]Cl_4·6H_2O$[9b] in 50 cm^3 of water was added a solution containing 0.14 g (0.48 mmol) of $Na_2[PdCl_4]$ in 10 cm^3 of water. The mixture was stirred at 60 °C for 30 min and then a small amount of precipitate was filtered off. To the orange-brown reaction solution was added 6 cm^3 of a saturated NaCl solution, which was kept in a refrigerator for 3 d. The resulting orange-brown fine crystals ($\mathbf{3}\cdot2H_2O$) were collected by filtration. Yield; 0.20 g (82%). Found: C, 13.89; H, 4.44; N, 10.61; Co, 11.40; Pd, 20.98%. Calcd for $[PdCl_2\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]Cl\cdot2H_2O$: C, 13.86; H, 4.65; N, 10.77; Co, 11.33; Pd, 20.46%. Single crystals suitable for X-ray analysis were obtained by recrystallization of the fine crystals at room temperature.

Interconversion of 2 and 3. To a solution containing 0.20 g (0.22 mmol) of $[Pd\{Co(aet)_2(en)\}_2]Cl_4\cdot6H_2O$ ($\mathbf{2}\cdot6H_2O$) in 50 cm^3 of water was added a solution containing 0.07 g (0.24 mmol) of $Na_2[PdCl_4]$ in 10 cm^3 of water. The mixture was stirred at room temperature for 40 min. To the orange-brown reaction solution was added 3 cm^3 of a saturated NaCl solution, which was kept in a refrigerator for 4 d. The resulting orange-brown microcrystals ($\mathbf{3}\cdot2H_2O$) were collected by filtration. Yield; 0.13 g (57%). Found: C, 14.31; H, 4.60; N, 10.98%. Calcd for $[PdCl_2\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]Cl\cdot2H_2O$: C, 13.86; H, 4.65; N, 10.77%.

To a solution containing 0.20 g (0.38 mmol) of $[PdCl_2\{Co(aet)_2(en)\}]Cl\cdot2H_2O$ ($\mathbf{3}\cdot2H_2O$) in 25 cm^3 of water was added a solution containing 0.17 g (0.20 mmol) of $[Ni\{Co(aet)_2(en)\}_2]Cl_4\cdot6H_2O$ in 15 cm^3 of water. The mixture was stirred at room temperature for 1 h, followed by cooling in a refrigerator for 1 d. The resulting red-brown microcrystals ($\mathbf{2}\cdot6H_2O$) were collected by filtration. Yield; 0.27 g (78%). Found: C, 15.89; H, 5.86; N, 12.25%. Calcd for $[Pd\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4\cdot6H_2O$: C, 16.03; H, 5.83; N, 12.46%.

Optical Resolution of 2. To a warm solution containing 1.00 g (1.11 mmol) of $\mathbf{2}\cdot6H_2O$ in 50 cm^3 of water was added a solution containing 1.12 g (1.66 mmol) of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot5H_2O$ dissolved in 25 cm^3 of water. The mixture was allowed to stand in a refrigerator for 2 d and the resulting brown powder ($(+)^{CD}_{520}$ diastereomer, 0.54 g), which showed a positive CD value at 520 nm, was collected by filtration.

To a reddish-brown filtrate, which showed a negative CD value at 520 nm, was added a solution containing 5 cm^3 of a saturated NaCl aqueous solution. When the mixture was stored in a refrigerator for 1 d, racemic crystals of **2** appeared, which were removed by filtration. The remaining filtrate was concentrated to a small volume with a rotary evaporator until dark-red microcrystals appeared. After cooling the concentrated solution in a refrigerator for 1 d, the resulting microcrystals of $(-)^{CD}_{520}$-**2** (0.13 g) were collected by filtration.

To a solution containing 0.54 g of the $(+)^{CD}_{520}$ diastereomer in 50 cm^3 of water was added 5 cm^3 of a saturated NaCl aqueous solution. The mixture was stirred at room temperature for several minutes, followed by cooling in a refrigerator for 1 d. The resulting racemic crystals of **2** were filtered off and the remaining filtrate was concentrated to a small volume until dark red microcrystals appeared. After cooling the concentrated solution in a refrigerator for 1 d, the resulting microcrystals of $(+)^{CD}_{520}$-**2** (0.08 g) were collected by filtration.

The $\Delta\varepsilon$ values for $(-)^{CD}_{520}$-**2** and $(+)^{CD}_{520}$-**2**, which showed CD spectra enantiomeric to each other, were evaluated on the basis of the absorption spectral datum of the racemic salt $\mathbf{2}\cdot6H_2O$.

Optical Resolution of 3. To a warm solution containing 1.00 g (1.92 mmol) of $\mathbf{3}\cdot2H_2O$ in 200 cm^3 of water was added a solution containing 1.39 g (2.06 mmol) of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot5H_2O$ dissolved in a small amount of water. The mixture was allowed to stand in a refrigerator for 2 d and the resulting brown powder ($(+)^{CD}_{520}$ diastereomer, 1.03 g), which showed a positive CD value at 520 nm, was collected by filtration.

To a brown filtrate, which showed a negative CD value at 520 nm, was added 40 cm^3 of a saturated NaCl aqueous solution. When the mixture was stored in a refrigerator for 1 d, a racemic powder of **3** appeared, which was removed by filtration. The remaining filtrate was concentrated to a small volume with a rotary evaporator until a brown powder appeared. This procedure was repeated several times until the optical activity of the filtrate became constant. The last stage of crystalline powder ($(-)^{CD}_{520}$-**3**, 0.01 g) was collected by filtration, after cooling the concentrated solution in a refrigerator for 1 d.

To a solution containing 1.03 g of the $(+)^{CD}_{520}$ diastereomer in 70 cm^3 of water was added 20 cm^3 of a saturated NaCl aqueous solution. The mixture was stirred at room temperature for several minutes, followed by storing in a refrigerator for 1 d. The resulting racemic powder of **3** was filtered off and the remaining filtrate was concentrated to a small volume until a brown powder appeared. This procedure was repeated several times until the optical activity of the filtrate became constant. The last stage of crystalline powder ($(+)^{CD}_{520}$-**3**, 0.01 g) was collected by filtration, after cooling the concentrated solution in a refrigerator for 1 d.

The $\Delta\varepsilon$ values for $(-)^{CD}_{520}$-**3** and $(+)^{CD}_{520}$-**3**, which showed CD spectra enantiomeric to each other, were evaluated on the basis of the absorption spectral datum of the racemic salt $\mathbf{3}\cdot2H_2O$.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer and the CD spectra with a JASCO J-600 spectropolarimeter at room temperature. The 500 MHz ^{13}C NMR spectra were recorded with a BRUKER-AM-500 NMR spectrometer at a prove temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The elemental analyses (C, H, N,) were performed by the Analysis Center of the University of Tsukuba. The concentrations of Co and Pd in the complexes were determined with a Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer.

X-Ray Structure Determination of $\mathbf{2}\cdot6H_2O$. Single-crystal X-ray diffraction experiments for $\mathbf{2}\cdot6H_2O$ were performed on a Rigaku AFC7S diffractometer with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Crystallographic data are summarized in Table 1. Unit-cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the range of $29 < 2\theta < 30°$. The intensity data were collected by the ω–2θ scan mode up to $2\theta = 55°$. The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on ψ scans was also applied. The 2768 independent reflections with $I > 2\sigma(I)$ of the measured 4300 reflections were considered as "observed" and used for structure determination.

The positions of Co, Pd, and S atoms were determined by direct methods and the remaining non-H atom positions were found by successive difference Fourier techniques.[11] The structure was refined by full-matrix least-squares techniques using the teXsan crystallographic software package.[11] The Pd1, Co1, Co2 atoms were constrained to the special positions (0.5, y, 0.25) with the 2 site symmetry. One of three water oxygen atoms was disordered and were best modeled with two positions (O3aw and O3bw) with a site occupancy factor of 0.5. All non-H atoms were refined anisotropically. All H atoms, except for the water H atoms, were located and added to calculations, but their positions were not refined. The maximum peak on the final difference Fourier map corresponded to 0.53 e $Å^{-3}$. The final atomic coordinates for non-H atoms are given in Table 2.[12]

X-Ray Structure Determination of $\mathbf{3}\cdot2H_2O$. Single-crystal X-ray diffraction experiments for $\mathbf{3}\cdot2H_2O$ were performed on an Enraf–Nonius CAD4 diffractometer with a graphite-monochroma-

Table 1. Crystallographic Data[a)] for **2**$\cdot$6H_2O and **3**$\cdot$2H_2O

	2$\cdot$6H_2O	**3**$\cdot$2H_2O
Chem. formula	$C_{12}H_{52}N_8O_6S_4Cl_4Co_2Pd$	$C_6H_{24}N_4O_2S_2Cl_3CoPd$
Fw	899.0	520.1
Cryst. color	Dark brown	Dark red
Cryst. size/mm	0.20 × 0.13 × 0.12	0.32 × 0.18 × 0.08
Space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a/Å	14.951(2)	14.282(5)
b/Å	19.753(2)	8.497(2)
c/Å	12.926(2)	16.139(6)
β/deg	113.33(1)	115.13(1)
V/Å^3	3505.4(9)	1773(1)
Z	4	4
ρ_{calc}/g cm^{-3}	1.70	1.95
μ/cm^{-1}	20.3	26.2
Transm coeff	0.90—1.00	0.88—1.00
$R^{b)}$	0.034	0.026
$R_w$$^{c)}$	0.038	0.029

a) $T=23°C$. b) $R=\sum|(|F_o|-|F_c|)|/\sum(|F_o|)$. c) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) for **2**$\cdot$6H_2O

Atom	x	y	z	B_{eq}[a)]
Pd1	0.5	0.24337(3)	0.25	2.43(1)
Co1	0.5	0.41202(5)	0.25	2.12(2)
Co2	0.5	0.07557(5)	0.25	2.13(2)
S11	0.38714(8)	0.32969(7)	0.2055(1)	2.67(2)
S21	0.61199(8)	0.15705(7)	0.3236(1)	2.72(2)
N11	0.4830(3)	0.4104(2)	0.0903(3)	2.77(9)
N12	0.4022(3)	0.4864(2)	0.2206(4)	2.84(9)
N21	0.5342(3)	0.0774(2)	0.1172(3)	2.92(9)
N22	0.5950(3)	0.0016(2)	0.3208(4)	2.82(9)
C11	0.3462(4)	0.3353(3)	0.0539(4)	3.5(1)
C12	0.4324(4)	0.3500(3)	0.0249(4)	3.5(1)
C13	0.4549(4)	0.5505(3)	0.2623(5)	3.4(1)
C21	0.6720(4)	0.1487(3)	0.2262(5)	3.8(1)
C22	0.5959(4)	0.1345(3)	0.1109(5)	3.8(1)
C23	0.5413(4)	−0.0632(3)	0.3073(5)	3.2(1)
CL1	0.6698(1)	0.47602(9)	0.0598(1)	4.60(4)
CL2	0.66472(9)	0.04855(8)	0.6032(1)	3.86(3)
O1w	0.1357(7)	0.2950(4)	0.1644(9)	13.0(3)
O2w	0.717(1)	0.3207(6)	0.061(2)	23.3(7)
O3aw	0.123(2)	0.251(1)	0.411(2)	22.9(10)
O3bw	0.032(2)	0.243(1)	0.338(3)	19(1)

a) B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

tized Mo $K\alpha$ radiation (λ =0.71073 Å). Unit-cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the range of $15 < 2\theta < 20°$. The intensity data were collected by the ω–2θ scan mode up to $2\theta = 50°$. The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on ψ scans was also applied. The 2772 independent reflections with $F_o > 3\sigma(F_o)$ of the measured 3478 reflections were considered as "observed" and used for a structure determination.

The positions of Co, Pd, and S atoms were determined by direct methods and the remaining non-H atom positions were found by successive difference Fourier techniques.[13)] The structure was refined by full-matrix least-squares techniques using the MOLEN crystallographic software package.[13)] All non-H atoms were refined anisotropically. All H atoms, except for the water H atoms, were located and added to calculations, but their positions were not refined. The maximum peak on the final difference Fourier map corresponded to 0.81 e Å^{-3}. The final atomic coordinates for non-H atoms are given in Table 3.

Results and Discussion

Crystal Structure of [Pd{Co(aet)$_2$(en)}$_2$]Cl$_4$$\cdot$6H$_2$O (2$\cdot$6H$_2$O). X-Ray structural analysis of **2**$\cdot$6H_2O showed the presence of a discrete complex cation, Cl anions, and water molecules. The total number of Cl anions implies that the

Table 3. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) for **3**$\cdot$2H_2O

Atom	x	y	z	B_{eq}[a)]
Pd	0.37877(2)	0.36438(4)	0.72699(2)	2.159(6)
Co	0.27345(4)	0.12039(7)	0.55435(3)	2.02(1)
CL1	0.3828(1)	0.6394(1)	0.73648(7)	3.69(3)
CL2	0.44367(8)	0.3211(2)	0.88561(6)	3.08(2)
S1	0.31341(8)	0.3761(1)	0.57228(6)	2.60(2)
S2	0.36163(8)	0.0994(1)	0.70586(6)	2.43(2)
N1	0.1475(3)	0.1742(4)	0.5716(2)	2.47(7)
N2	0.4043(3)	0.0788(4)	0.5435(2)	2.60(7)
N3	0.1963(3)	0.1324(5)	0.4188(2)	2.59(7)
N4	0.2338(3)	−0.1068(4)	0.5383(2)	2.60(8)
C1	0.1829(4)	0.4477(5)	0.5425(3)	3.2(1)
C2	0.1320(3)	0.3425(6)	0.5868(3)	3.1(1)
C3	0.4841(3)	0.0344(6)	0.7082(3)	3.2(1)
C4	0.4985(3)	0.1074(6)	0.6289(3)	3.1(1)
C5	0.1812(4)	−0.0300(6)	0.3807(3)	3.1(1)
C6	0.1563(3)	−0.1346(6)	0.4433(3)	3.1(1)
CL	0.8546(1)	0.2399(2)	0.83953(8)	4.13(3)
O1w	0.0938(3)	0.2415(4)	0.9903(2)	4.38(9)
O2w	0.2339(5)	0.0852(6)	0.1444(3)	9.0(2)

a) B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

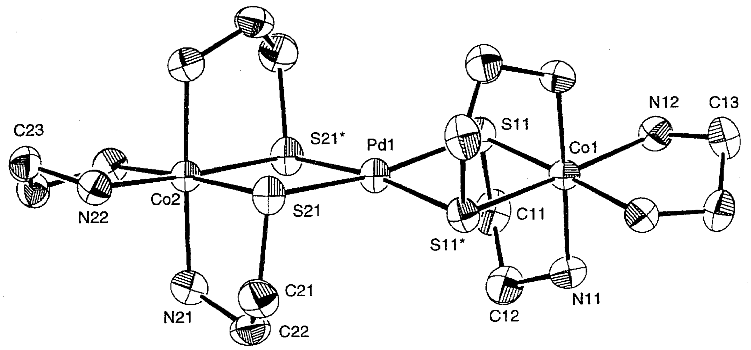

Fig. 1. Perspective views of the complex cation of **2** with the atomic labeling scheme.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **2**·$6H_2O$

	Distances		
Pd1–S11	2.306(1)	Co1–N12	2.001(4)
Pd1–S21	2.314(1)	Co2–S21	2.244(1)
Co1–S11	2.248(1)	Co2–N21	1.977(4)
Co1–N11	1.977(4)	Co2–N22	1.990(4)
	Angles		
S11–Pd1–S11*	84.63(6)	N12–Co1–N12*	85.5(2)
S11–Pd1–S21	170.52(5)	S21–Co2–S21*	88.37(7)
S11–Pd1–S21*	95.93(4)	S21–Co2–N21	87.0(1)
S21–Pd1–S21*	85.07(6)	S21–Co2–N21*	91.4(1)
S11–Co1–S11*	87.33(7)	S21–Co2–N22	93.1(1)
S11–Co1–N11	87.0(1)	S21–Co2–N22*	176.6(1)
S11–Co1–N11*	91.6(1)	N21–Co2–N21*	177.9(3)
S11–Co1–N12	93.7(1)	N21–Co2–N22	91.7(2)
S11–Co1–N12*	176.5(1)	N21–Co2–N22*	89.9(2)
N11–Co1–N11*	178.1(3)	N22–Co2–N22*	85.6(2)
N11–Co1–N12	91.8(2)	Pd1–S11–Co1	94.02(5)
N11–Co1–N12*	89.6(2)	Pd1–S21–Co2	93.28(5)

entire complex cation is tetravalent. A perspective drawing of the entire complex cation of **2** is shown in Fig. 1. The selected bond distances and angles are listed in Table 4.

The entire complex cation of **2** consists of two approximately octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ units and one Pd atom. This is consistent with the plasma emission spectral analysis that gave the value of Co : Pd = 2 : 1. The two thiolato S atoms of each *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit are bound to the central Pd atom to form a linear-type S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear structure. The crystallographic 2-fold axis passing through the Co1, Pd1, and Co2 atoms requires that the three metals are arranged to be exactly linear. The central PdS_4 sphere in **2** is distorted from a square-planar to a tetrahedral geometry, in which the Pd1S11S11* and Pd1S21S21* planes intersect to form a dihedral angle of 14.0°. This is distinct from the square-planar geometry of the central PdS_4 sphere observed in the related S-bridged $Ni^{II}Pd^{II}Ni^{II}$ trinuclear complex, $[Pd\{Ni(L\text{-}N,N,S,S)\}_2]^{2+}$ ($L = {}^-S(CH_2)_2NH(CH_2)_3NH(CH_2)_2S^-$), in which the two thiolato S atoms of each square-planar *cis*(*S*)-[Ni(L-*N*,*N*,*S*,*S*)] unit are bound to the central Pd atom.[14] The S–Pd–S "bite" angles (average 84.85(6)°) in **2** are closer to 90° than those found in $[Pd\{Ni(L\text{-}N,N,S,S)\}_2]^{2+}$ (averaged 79.6(3)°). Moreover, the Co–S–Pd bridging angles in **2** (average 93.65(5)°) approach to the ideal tetrahedral angle of 109°, compared with the Ni–S–Pd bridging angles in $[Pd\{Ni(L\text{-}N,N,S,S)\}_2]^{2+}$ (average 81.3(3)°). Thus, it is considered that the octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit functions as a less strained bidentate-*SS* ligand to the Pd^{II} atom than the square-planar *cis*(*S*)-[Ni(L-*N*,*N*,*S*,*S*)] unit. The Pd–S bond distances in **2** (average 2.310(1) Å) are slightly shorter than those found in the square-planar PdS_4 spheres of $[Pd\{Ni(L\text{-}N,N,S,S)\}_2]^{2+}$ (average 2.338(9) Å) and $[Pd_2\{Ni(aet)_2\}_4]^{4+}$ (averaged 2.336(2) Å),[14,15] presumably due in part to the tetrahedral distortion which decreases the mutual trans influence of the coordinated thiolato S atoms.[7a]

2 ($[Pd\{Co(aet)_2(en)\}_2]Cl_4$) is isostructural with the precursory $Co^{III}Ni^{II}Co^{III}$ complex, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ (**1**), in which the central Ni^{II} atom is bound by two octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ units.[9] The bond distances and angles concerning the *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit in **2** are quite similar to those observed in **1**. However, the S–Pd–S "bite" angles (average 84.85(6)°) in **2** are slightly smaller than the S–Ni–S "bite" angles in **1** (average 86.83(5)°), as a consequence of the Pd–S bond distances which are longer than the Ni–S ones (average 2.204(1) Å). Furthermore, the dihedral angle of the PdS_4 sphere in **2** (14.0°) is smaller than that of the NiS_4 sphere in **1** (16.2°).[9] This is compatible with the fact the Pd^{II} atom prefers a square-planar geometry to a tetrahedral one more strongly than does the Ni^{II} atom.

Considering the absolute configurations (Δ, Λ) and the two geometries (C_1-*cis*(*S*), C_2-*cis*(*S*)) for the two terminal *cis*(*S*)- $[Co(aet)_2(en)]^+$ units,[9b] ten isomers, $\Delta(C_1\text{-}cis(S))\Delta(C_1\text{-}cis(S))$, $\Delta(C_1\text{-}cis(S))\Delta(C_2\text{-}cis(S))$, $\Delta(C_2\text{-}cis(S))\Delta(C_2\text{-}cis(S))$, $\Delta(C_1\text{-}cis(S))\Lambda(C_1\text{-}cis(S))$, $\Delta(C_1\text{-}cis(S))\Lambda(C_2\text{-}cis(S))$, $\Delta(C_2\text{-}cis(S))\Lambda(C_1\text{-}cis(S))$, $\Delta(C_2\text{-}cis(S))\Lambda(C_2\text{-}cis(S))$, $\Lambda(C_1\text{-}cis(S))\Lambda(C_1\text{-}cis(S))$, $\Lambda(C_1\text{-}cis(S))\Lambda(C_2\text{-}cis(S))$, and $\Lambda(C_2\text{-}cis(S))\Lambda(C_2\text{-}cis(S))$, are possible for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$. The isomer of **2** illustrated in Fig. 1 has the Δ configuration and the C_2-*cis*(*S*) geometry for the two *cis*(*S*)-$[Co(aet)_2(en)]^+$ units. Thus, crystal **2** consists of the $\Delta(C_2\text{-}cis(S))\Delta(C_2\text{-}cis(S))$ and $\Lambda(C_2\text{-}cis(S))$ $\Lambda(C_2\text{-}cis(S))$ isomers, which combine to form the racemic compound, as indicated by the space group *C*2/*c* and $Z = 4$. This is consistent with the fact that **2** was optically resolved. All of the chelate rings in **2** have a distinct *gauche* form with the λ conformation for the $\Delta\Delta$ isomer and the δ one for the $\Lambda\Lambda$ isomer. These chiral properties are the same as those observed in **1**.[9)]

Crystal Structure of $[\mathrm{PdCl_2\{Co(aet)_2(en)\}]Cl\cdot 2H_2O}$ ($\mathbf{3}\cdot 2\mathrm{H_2O}$). X-Ray structural analysis of $\mathbf{3}\cdot 2\mathrm{H_2O}$ revealed the presence of a discrete monovalent complex cation, one Cl anion, and two water molecules. A perspective drawing of the entire complex cation of **3** is shown in Fig. 2. The selected bond distances and angles are summarized in Table 5.

The complex cation of **3** consists of one octahedral *cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ unit, two Cl and one Pd atoms, which is consistent with the elemental and plasma emission analyses. The Pd atom is coordinated by two Cl atoms besides two thiolato S atoms from the *cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ unit. Since the coordination geometry of the Pd atom in **3** is approximately square-planar, the tetrahedral distortion observed in **2** may be attributed to the cross-plane interaction between the aet chelate rings of the two *cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ units. In **3** the Cl–Pd–Cl angle (95.60(4)°) is larger than 90°, while the S–Pd–S angle (84.87(4)°) is acute, of which value coincide well with the S–Pd–S "bite" angles in **2**. The Co–S–Pd bridging angles in **3** (average 93.52(4)°) are essentially the same as those found in **2**. However, the averaged Pd–S bond distance in **3** (2.271(1) Å) is 0.04 Å shorter than that in **2**, suggesting that the coordinated Cl atom exerts a structural trans influence weaker than that of the coordinated thiolato S atom. The bond distances and angles concerning the *cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ unit in **3** are in good agreement with those found in **2**.

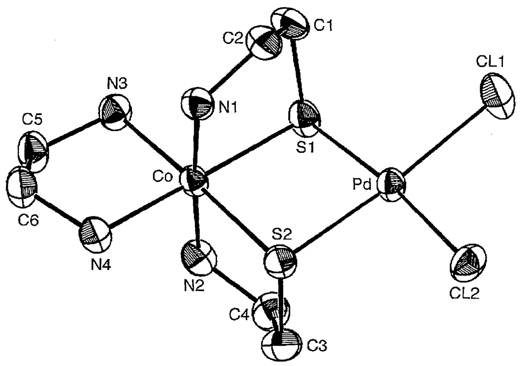

Fig. 2. Perspective view of the complex cation of **3** with the atomic labeling scheme.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{3}\cdot 2\mathrm{H_2O}$

	Distances		
Pd–CL1	2.341(1)	Co–S2	2.232(1)
Pd–CL2	2.352(1)	Co–N1	1.987(4)
Pd–S1	2.266(1)	Co–N2	1.982(4)
Pd–S2	2.275(1)	Co–N3	1.990(3)
Co–S1	2.234(1)	Co–N4	1.997(4)
	Angles		
CL1–Pd–CL2	95.60(4)	S2–Co–N2	88.15(9)
CL1–Pd–S1	90.88(4)	S2–Co–N3	178.2(1)
CL1–Pd–S2	174.83(3)	S2–Co–N4	93.52(9)
CL2–Pd–S1	173.48(4)	N1–Co–N2	175.9(1)
CL2–Pd–S2	88.62(4)	N1–Co–N3	91.7(1)
S1–Pd–S2	84.87(4)	N1–Co–N4	91.0(2)
S1–Co–S2	86.66(4)	N2–Co–N3	90.9(1)
S1–Co–N1	87.4(1)	N2–Co–N4	92.4(2)
S1–Co–N2	89.2(1)	N3–Co–N4	85.0(1)
S1–Co–N3	94.8(1)	Pd–S1–Co	93.62(4)
S1–Co–N4	178.4(1)	Pd–S2–Co	93.42(4)
S2–Co–N1	89.31(9)		

Considering the two absolute configurations and the two geometries for the *cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^+$ unit, four isomers, ($\Delta(C_1$-*cis*(*S*)), $\Delta(C_2$-*cis*(*S*)), $\Lambda(C_1$-*cis*(*S*)), and $\Lambda(C_2$-*cis*(*S*))) are possible for $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^+$. An X-ray analysis indicated that crystal **3** is a racemic compound of a pair of enantiomers, $\Delta(C_2$-*cis*(*S*)) and $\Lambda(C_2$-*cis*(*S*)) (Fig. 2), which is consistent with the fact that **3** was optically resolved. The aet and en chelate rings have a distinct gauche form with the λ conformation for the Δ isomer and the δ one for the Λ isomer.

Synthesis and Properties. The reaction of $[\mathrm{Ni\{Co(aet)_2(en)\}_2]Cl_4}$ (**1**) with 1 molar equiv of $\mathrm{Na_2[PdCl_4]}$ in water under moderate conditions gave $[\mathrm{Pd\{Co(aet)_2(en)\}_2]Cl_4}$ (**2**) in a reasonable yield. This result clearly indicates that the central $\mathrm{Ni^{II}}$ atom in **1** is readily replaced by a $\mathrm{Pd^{II}}$ atom. On the other hand, replacement of the central $\mathrm{Pd^{II}}$ atom in **2** by a $\mathrm{Ni^{II}}$ atom did not occur, even when **2** was treated with excess $\mathrm{NiCl_2\cdot 6H_2O}$. Furthermore, in water **2** exhibited little absorption spectral change with time for a few hours, which is in contrast to the drastic absorption spectral change with time observed for **1**.[9)] Accordingly, it is assumed that the Pd–S bonds in **2** are considerably stronger than the Ni–S bonds in **1**.

When the 1 : 1 reaction solution of **1** and $\mathrm{Na_2[PdCl_4]}$ was chromatographed on an SP-Sephadex C-25 column, only one band for $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$ was eluted with a 0.5 mol dm^{-3} NaCl aqueous solution. Furthermore, the ^{13}C NMR spectrum of **2** in $\mathrm{D_2O}$ gives only three signals ($\delta = 35.47$, $\mathrm{CH_2S}$; 46.52, $\mathrm{CH_2N}$ of en; 55.96, $\mathrm{CH_2N}$ of aet) for the 12 methylene carbons in the complex. Thus, only the racemic isomer of $\Delta(C_2$-*cis*(*S*))$\Delta(C_2$-*cis*(*S*)) and $\Lambda(C_2$-*cis*(*S*))$\Lambda(C_2$-*cis*(*S*)) with a D_2 symmetrical structure was formed for **2**, taking account of the X-ray analytical result. Since **1** is also the racemic isomer of $\Delta(C_2$-*cis*(*S*))$\Delta(C_2$-*cis*(*S*)) and $\Lambda(C_2$-*cis*(*S*))$\Lambda(C_2$-*cis*(*S*)),[9)] it is seen that the metal replacement reaction occurred with retention of the C_2-*cis*(*S*) geometry of the two $[\mathrm{Co(aet)_2(en)}]^+$ units. **2** was optically resolved into the $(-)^{\mathrm{CD}}_{520}$ and $(+)^{\mathrm{CD}}_{520}$ isomers, which show CD spectra enantiomeric to each other. As shown in Fig. 3, the CD spectrum of $(-)^{\mathrm{CD}}_{520}$-**2** in water resembles that of $\Delta\Delta$-$[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ over the whole region.[9)] Thus, the $(-)^{\mathrm{CD}}_{520}$ and $(+)^{\mathrm{CD}}_{520}$ isomers of **2** are assignable to have the $\Delta\Delta$ and $\Lambda\Lambda$ configurations, respectively. For **2** no significant CD spectral change with time was recognized in water for a few hours, in parallel with the absorption spectral behavior. In contrast to the CD spectral similarity, the absorption spectral feature of **2** appears to differ from that of **1** (Fig. 3). That is, **2** gives two intense absorption bands at 30.90 and 35.89×10^3 cm^{-1} (Table 6), while the absorp-

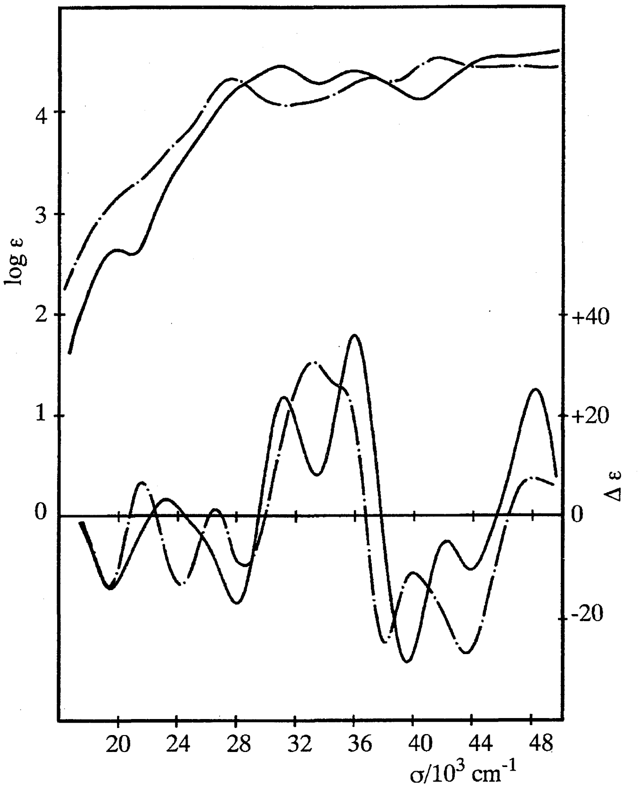

Fig. 3. Electronic absorption and CD spectra of $(-)^{\rm CD}_{520}$-**2** (—) and ΔΔ-**1** (–••–) in H_2O.

tion spectrum of **1** is characterized by three intense bands at 27.70, 37.04, and 41.67×10^3 cm^{-1}.[9] This suggests that the adsorption spectra of **1** and **2** are dominated by the central Ni^{II}S$_4$ or Pd^{II}S$_4$ chromophore, rather than the two terminal *cis*(*S*)-Co^{III}N$_4$S$_2$ ones.

When [Ni{Co(aet)$_2$(en)}$_2$]Cl$_4$ (**1**) was reacted with 2 molar equiv of Na$_2$[PdCl$_4$], the S-bridged Co^{III}Pd^{II} dinuclear complex with one C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ unit, [PdCl$_2${Co(aet)$_2$(en)}]Cl (**3**), was isolated in a high yield. **3** was also obtained by treating [Pd{Co(aet)$_2$(en)}$_2$]Cl$_4$ (**2**) with 1 molar equiv of Na$_2$[PdCl$_4$] even at room temperature. This result indicates that the S-bridged Co^{III}Pd^{II}Co^{III} trinuclear structure in **2** is readily converted to the S-bridged Co^{III}Pd^{II} dinuclear structure in **3** by reacting with an additional Pd^{II} atom. The absorption spectrum of **3** in water is characterized by one intense absorption peak at 34.01×10^3 cm^{-1}, which is accompanied by vague shoulders at lower energy side (Fig. 4 and Table 6). This spectral behavior differs significantly from that of **2**, supporting that the absorption spectrum of **2** is dominated by the central PdS$_4$ chromophore. No significant absorption spectral change with time was noticed for **3** in water for a few hours. Furthermore, in the ^{13}C NMR spectrum **3** gives only three signals ($\delta = 36.99$, CH$_2$S; 46.48, CH$_2$N of en; 54.35, CH$_2$ of aet) for the 6 methylene carbons in the complex. Thus, it is reasonable to consider that the geometry of the C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ unit in **3** observed in crystal is retained in solution.

3 was optically resolved into the $(-)^{\rm CD}_{520}$ and $(+)^{\rm CD}_{520}$ isomers, which show CD spectra enantiomeric to each other. As illustrated in Fig. 4, $(-)^{\rm CD}_{520}$-**3** exhibits a negative and a positive CD bands from the lowest energy side. This CD spectral pattern is the same as that of ΔΔ-**2** and therefore, $(-)^{\rm CD}_{520}$-**3** may be assigned to have the Δ configurational C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ unit. When ΔΔ-**2** was reacted with 1 molar equiv of Na$_2$[PdCl$_4$] at room temperature, the reaction

Table 6. Absorption and CD Spectral Data of $(-)^{\rm CD}_{520}$-[Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$ ($(-)^{\rm CD}_{520}$-**2**) and $(-)^{\rm CD}_{520}$-[PdCl$_2${Co(aet)$_2$(en)}]$^+$ ($(-)^{\rm CD}_{520}$-**3**) in Water

Absorption maxima σ/10^3 cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema σ/10^3 cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
$(-)^{\rm CD}_{520}$-[Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$	
19.91 (2.64)	19.42 (−14.1)
23.7 (3.4)$^{\rm sh}$	23.23 (+3.3)
28.2 (4.2)$^{\rm sh}$	28.03 (−17.1)
30.90 (4.43)	31.17 (+23.5)
35.89 (4.38)	35.95 (+35.6)
45.8 (4.5)$^{\rm sh}$	39.49 (−28.8)
	43.82 (−10.6)
	48.22 (+24.8)
$(-)^{\rm CD}_{520}$-[PdCl$_2${Co(aet)$_2$(en)}]$^+$	
19.5 (2.4)$^{\rm sh}$	19.36 (−6.9)
22.8 (2.9)$^{\rm sh}$	22.91 (+9.1)
29.9 (3.5)$^{\rm sh}$	25.87 (−0.1)
34.01 (4.08)	28.00 (+2.6)
42.7 (4.3)$^{\rm sh}$	32.59 (+20.6)
	37.31 (+2.86)
	41.60 (−5.89)
	46.17 (+6.65)

The sh label denotes a shoulder.

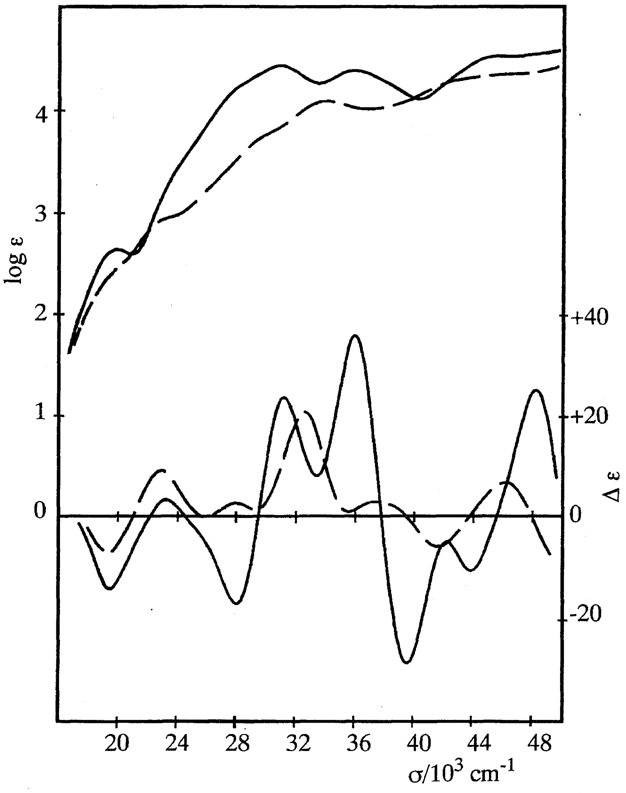

Fig. 4. Electronic absorption and CD spectra of $(-)^{\mathrm{CD}}_{520}$-**2** (—) and $(-)^{\mathrm{CD}}_{520}$-**3** (- - -) in H_2O.

solution showed absorption and CD spectral patterns identical with those of $(-)^{\mathrm{CD}}_{520}$-**3**. Thus, the $(-)^{\mathrm{CD}}_{520}$ isomer of **3** is confidently assigned to the *Δ* isomer, while $(+)^{\mathrm{CD}}_{520}$-**3** is the *Λ* one. Here it should be noted that the CD intensity of this reaction solution was ca. 70% for $(-)^{\mathrm{CD}}_{520}$-*Δ*-**3**. Moreover, the 1 : 1 reaction solution of *ΔΔ*-**2** and $Na_2[PdCl_4]$ at 60 °C showed little CD. These results point out that the conversion reaction of **2** to **3** is accompanied by racemization of the chiral *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit, while the C_2-*cis*(*S*) geometry is retained. Interestingly, it was found that the $Co^{III}Pd^{II}$ dinuclear structure in **3** is easily reverted back to the $Co^{III}Pd^{II}Co^{III}$ trinuclear structure in **2**; treatment of **3** with 0.5 molar equiv of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ (**1**) at room temperature led to the isolation of **2** in a satisfactory yield. The detailed mechanism of this conversion is not clear at present, but it is obvious that **1** acts as a donor of the *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit for the S-bridged polynuclear structure. Accordingly, a variety of S-bridged polynuclear complexes composed of the *cis*(*S*)-$[Co(aet)_2(en)]^+$ units would be available, using **1** as a starting complex in the place of the mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$, which is hardly prepared.⁷⁾

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