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Optically Active S-Bridged $Co^{III}Pd^{II}$ Polynuclear Complexes Derived from $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ (aet = 2-Aminoethanethiolate, *R*-pn = (*R*)-1,2-Propanediamine)

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The substitution reaction of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ with equimolar $Na_2[PdCl_4]$ in water gave selectively an optically active trinuclear complex, $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ (**1**). On the other hand, an optically active dinuclear complex, Δ-$[PdCl_2\{Co(aet)_2(R\text{-}pn)\}]^{+}$ (**2**), was also obtained by a two-molar equivalent addition of $Na_2[PdCl_4]$ under the same reaction condition. Similarly, the reaction of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ with two molar equivalent $[Pd(NO_3)_2(bpy)]$ produced an optically active dinuclear complex, Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ (**3**). The crystal structures of complexes **1**, **2**, and **3** were determined by X-ray crystallography. Each of the Co atoms in **1**, **2**, and **3** is coordinated by two aet and one *R*-pn ligands to take an approximately octahedral geometry. The Pd atom in **1** is coordinated by four S atoms from two *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units. The Pd atom in **2** is ligated by two S atoms from one *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ unit and two Cl atoms, while the Pd atom in **3** is coordinated by two S atoms from one *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ unit and two N atoms in bpy. All of the Pd atoms in **1**, **2**, and **3** take an almost square-planar geometry. These complexes are also characterized on the basis of the electronic absorption, CD, and ^{13}C NMR spectra. The interconversions of the trinuclear and dinuclear complexes obtained in this work are discussed.

The mononuclear complexes with aminothiolate ligands, such as 2-aminoethanethiolate (aet) and L-cysteinate (L-cys), are of very important classes of building-blocks for constructing S-bridged polynuclear structures, because of their high abilities for binding other metal ions or complexes.[1—16] For instance, *fac*(*S*)-$[M(aet)_3]$ (M = Cr^{III}, Co^{III}, Rh^{III}, or Ir^{III}) has three effective S atoms for bridging, and reacts with various metal ions to form S-bridged polynuclear complexes including octahedral $[M(aet)_3]$ units.[1—9] Further, $[M'(aet)_2]$ (M′ = Ni^{II} or Pd^{II}) has two effective S atoms for bridging, and reacts with various metal ions to form S-bridged polynuclear complexes including square-planar $[M'(aet)_2]$ units.[10—14] On the contrary to a number of polynuclear complexes with such S-donating metalloligands,[1—16] little has been known concerning the polynuclear structures, including octahedral units with two aet ligands, because of a difficulty to synthesize such units. Recently, it has been shown that the central Ni^{2+} ion in the S-bridged trinuclear complex $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (en = ethylenediamine) is readily substituted by the other metal ions or complexes, and that the octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ units can be regarded as a metalloligand with two donating S-atoms.[9,17—19] These facts suggest that S-bridged polynuclear complexes can be obtained by substitution reactions of $[Ni\{M''(aet)_2(diamine)\}_2]^{4+}$ (M″ = Co^{III}, Rh^{III}, or Ir^{III}) with other metal ions or complexes. We have recently reported that the trinuclear complex $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ (pn = 1,2 − propanediamine) has been stereoselectively obtained by the reaction of $[Ni(aet)_2]$ with an optically active $[CoCl_2(R\text{-}pn)_2]^+$.[20] It is expected that, accordingly, the substitution reactions of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ with other ions or complexes stereoselectively produce optically active polynuclear complexes including Δ-*cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units. Furthermore, the use of the optically active (*R*)-pn ligand would make it possible to clarify the absolute cofigurations of the resulting complexes and the stereochemistry in the reactions. In the present paper, we report on the syntheses, structures and characterizations of the optically active S-bridged $Co^{III}Pd^{II}$ polynuclear complexes, $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$, Δ-$[PdCl_2\{Co(aet)_2(R\text{-}pn)\}]^+$, and Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ (bpy = 2,2′-bipyridine). The possibilities for interconversions between $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ and Δ-$[PdCl_2\{Co(aet)_2(R\text{-}pn)\}]^+$, and that between Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ and $[PdCl_2\{Co(aet)_2(R\text{-}pn)\}]^+$ are also discussed.

Experimental

Materials. 2-Aminoethanethiol hydrochloride was purchased from Tokyo Chemical Co., Ltd. Sodium tetrachloropalladate(II), cobalt(II) chloride hexahydrate, 1,2-propanediamine, and the other reagents were purchased from Wako Pure Chemical Ind. Co., Ltd. All of the chemicals were of reagent grade and used without further purification.

Preparation of Complexes. $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ (1). To a solution containing 0.26 g (0.25 mmol) of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2](ClO_4)_4\cdot H_2O$ in 50 cm^3 of water was added a solution containing 0.07 g (0.25 mmol) of $Na_2[PdCl_4]$ in 10 cm^3 of water.[20] After the mixture was stirred at 55 °C for 1 h, 50 cm^3 of a saturated $NaClO_4$ solution was added to the resulting reddish-brown solution. The mixture was allowed to stand at 4 °C for several days, and the resulting reddish-brown fine crystals were collected by filtration. The crystals were purified by recrystallization from a small amount of water. A well-formed crystal of **1**$(ClO_4)_4\cdot0.5H_2O$ was used for the X-ray structural analysis. Yield: 0.20 g (74%). Calcd for $[Pd\{Co(aet)_2(R\text{-pn})\}_2](ClO_4)_4\cdot0.5H_2O$ = $C_{14}H_{45}N_8O_{16.5}S_4Cl_4Co_2Pd$: C, 15.51; H, 4.18; N, 10.34%. Found: C, 15.25; H, 4.29; N, 10.08%.

Δ-$[PdCl_2\{Co(aet)_2(R\text{-pn})\}]^+$ (2). To a solution containing 0.26 g (0.25 mmol) of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-pn})\}_2](ClO_4)_4\cdot H_2O$ in 50 cm^3 of water was added a solution containing 0.15 g (0.50 mmol) of $Na_2[PdCl_4]$ in 10 cm^3 of water.[20] After the mixture was stirred at 55 °C for 1 h, 10 cm^3 of a saturated NaCl solution was added to the resulting reddish-brown solution. The mixture was allowed to stand at 4 °C for several days, and the resulting reddish-brown fine crystals were collected by filtration. The crystals were purified by recrystallization from a small amount of water. A well-formed crystal of **2**$Cl\cdot2H_2O$ was used for the X-ray structural analysis. Yield: 0.22 g (81%). Calcd for $[PdCl_2\{Co(aet)_2(R\text{-pn})\}]Cl\cdot2H_2O$ = $C_7H_{26}N_4O_2S_2Cl_3CoPd$: C, 15.74; H, 4.91; N, 10.49%. Found: C, 15.70; H, 4.94; N, 10.38%.

Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-pn})\}]^+$ (3). To a solution containing 0.26 g (0.25 mmol) of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-pn})\}_2](ClO_4)_4\cdot H_2O$ in 50 cm^3 of water was added 0.20 g (0.50 mmol) of $[Pd(NO_3)_2(bpy)]$.[20,21] After the mixture was stirred at 55 °C for 1 h, 50 cm^3 of a saturated $NaClO_4$ solution was added to the resulting reddish-brown solution. The mixture was allowed to stand at 4 °C for several days, and the resulting reddish-brown fine crystals were collected by filtration. The crystals were purified by recrystallization from a small amount of water. A well-formed crystal of **3**$(ClO_4)_3$ was used for the X-ray structural analysis. Yield: 0.35 g (83%). Calcd for $[Pd(bpy)\{Co(aet)_2(R\text{-pn})\}](ClO_4)_3$ = $C_{17}H_{30}N_6O_{12}S_2Cl_3CoPd$: C, 24.13; H, 3.57; N, 9.93%. Found: C, 23.93; H, 3.62; N, 9.81%.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest V-560 spectrophotometer, and the CD spectra with a JASCO J-600 spectropolarimeter. All of the measurements were carried out in aqueous solutions at room temperature. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer in D_2O. The sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. The elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba.

Crystallography. The unit-cell parameters and intensity data for **1**$(ClO_4)_4\cdot0.5H_2O$, **2**$Cl\cdot2H_2O$, and **3**$(ClO_4)_3$ were used for data collection on a Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-square refinement of 25 reflections ($5° < \theta < 15°$). The crystal data and experimental parameters are listed in Table 1. The intensity data were collected by the ω–2θ scan technique, and the intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of Ψ scans was applied. The independent reflections with $I_0 > 2\sigma(I_0)$ were used for structure determinations. The positions of the Co, Pd, and other non-H atoms were determined by a direct method. The difference Fourier maps based on these atomic positions revealed some remaining non-hydrogen atoms. The structures were refined by a full-matrix least-squares refinement on F of the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms in **1**$(ClO_4)_4\cdot0.5H_2O$, **2**$Cl\cdot2H_2O$, and **3**$(ClO_4)_3$. The hydrogen atoms on the ligands were fixed by the geometrical and thermal constrains (C–H = N–H = 0.95 Å and $U = 1.3U$(C, N)). For the $[Co(aet)_2(R\text{-pn})]^+$ units in $(-)^{\rm CD}_{500}$-$[Pd\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ (**1**), $(-)^{\rm CD}_{500}$-$[PdCl_2\{Co(aet)_2(R\text{-pn})\}]^{4+}$ (**2**), and $(-)^{\rm CD}_{500}$-$[Pd(bpy)\{Co(aet)_2(R\text{-pn})\}]^+$ (**3**), Δ and Λ configurations are possible. The asymmetric carbon atom of 1,2-propanediamine in the Δ configuration shows the R configuration, which is expected for the used ligand. However, the asymmetric carbon atom of 1,2-propanediamine in the Λ configuration exhibits S configuration. It was thus assumed that the former is most likely to be the correct choice; namely, all of the *cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ units in $(-)^{\rm CD}_{500}$ complex

Table 1. Crystal Data of $[Pd\{Co(aet)_2(R\text{-pn})\}_2](ClO_4)_4\cdot0.5H_2O$ (**1**$(ClO_4)_4\cdot0.5H_2O$), $[PdCl_2\{Co(aet)_2(R\text{-pn})\}]Cl\cdot2H_2O$ (**2** $Cl\cdot2H_2O$), and $[Pd(bpy)\{Co(aet)_2(R\text{-pn})\}](ClO_4)_3$ (**3**$(ClO_4)_3$)

	1	2	3
Formula	$C_{14}H_{45}N_8O_{16.5}S_4Cl_4Co_2Pd$	$C_7H_{26}N_4O_2S_2Cl_3CoPd$	$C_{17}H_{30}N_6O_{12}S_2Cl_3CoPd$
Fw	1083.87	534.12	846.27
Cryst dimens/mm	0.50 × 0.45 × 0.40	0.23 × 0.20 × 0.10	0.45 × 0.30 × 0.25
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	13.762(6)	9.079(2)	14.133(4)
b/Å	30.442(4)	24.341(4)	16.955(4)
c/Å	9.349(4)	8.627(3)	12.870(3)
V/Å^3	3916(1)	1906.5(8)	3083(1)
Z	4	4	4
$D_{\rm calcd}$/g cm^{-3}	1.838	1.861	1.823
μ/cm^{-1}	18.49	24.57	15.81
Transm factor	0.74—0.99	0.75—1.00	0.88—1.00
Scan type	ω–2θ	ω–2θ	ω–2θ
2θrange/deg	55.1	55.0	55.0
No. of reflcns measd	5028	2518	3948
No. of reflcns used	2946	1607	3117
No. of variables used	452	182	380
R (R_w)	0.079 (0.110)	0.043 (0.054)	0.054 (0.068)
GOF	1.93	1.21	1.68
Flack parameter	0.00(5)	−0.04(5)	−0.05(5)

cations with the Δ configuration. In fact, the Flack parameters give values of 0.00(5) for **1**, − 0.04(5) for **2**, and − 0.05(5) for **3**,[12] when the refinements were carried out using a set of parameters containing the Δ configuration of the *cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ units. On the other hand, the refinements using the enantiomeric atomic parameters (the Λ configuration) resulted in Flack parameters of 1.02(5) for **1**, 1.04(5) for **2**, and 1.00(5) for **3**. All of the calculations were performed on an Indigo II computer using teXsan.[22] The final atomic positional parameters are deposited in Tables S1—S9.[23] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 145153-145155.

Results and Discussion

Syntheses. The substitution reaction of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ with an equimolar $Na_2[PdCl_4]$ in water selectively gave an optically active trinuclear complex, $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ (**1**). On the other hand, an optically active dinuclear complex, Δ-$[PdCl_2\{Co(aet)_2(R\text{-pn})\}]^+$ (**2**), was also formed by a two-molar equivalent addition of $Na_2[PdCl_4]$ under the same reaction condition. Further, the reaction of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ with a two-molar equivalent $[Pd(NO_3)_2(bpy)]$ produced an optically active dinuclear complex, Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-pn})\}]^{3+}$ (**3**). These facts indicate that the central Ni atom in $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ is readily replaced by a Pd atom or its complexes, during which the octahedral Δ-*cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ unit retains its absolute configuration. The trinuclear complex **1** was also obtained by the equimolar addition of $[Ni\{Co(aet)_2(R\text{-pn})\}_2](ClO_4)_4{\cdot}H_2O$ to $\mathbf{2}Cl{\cdot}2H_2O$ in aqueous solution. However, the central Pd atom in **1** was not replaced by a Ni atom, even when **1** was treated with excess $Ni(ClO_4)_2{\cdot}6H_2O$ in aqueous solution. It can therefore be regarded that the Pd–S bonds in **1** are significantly stronger than the Ni–S bonds in $[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$. On the other hand, the dinuclear complex **2** was also formed by the equimolar addition of $Na_2[PdCl_4]$ to $\mathbf{1}(ClO_4)_4{\cdot}0.5H_2O$, and **3** was formed by the equimolar addition of bpy to $\mathbf{2}Cl{\cdot}2H_2O$. This implies that two Cl atoms in **2** are also readily substituted by other ligands. Furthermore, all of the octahedral *cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ units in these complexes take the Δ configuration, as expected from the fact that the starting complex, $[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$, is of the $\Delta\Delta$ configuration.[20] This implies that the substitution reactions of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ with metal ions or their complexes can stereoselectively produce optically active polynuclear complexes including Δ-*cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ units.

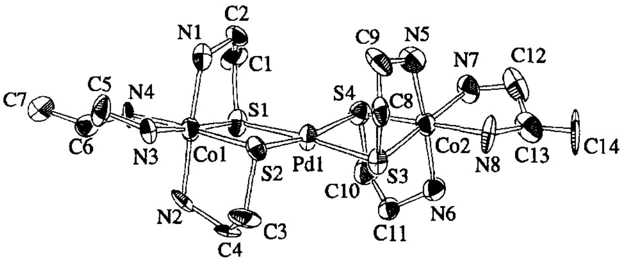

Fig. 1. Perspective view of $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ (**1**) with the atomic labeling scheme.

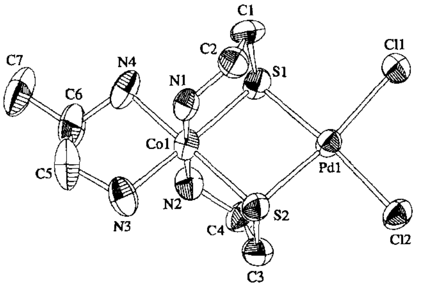

Fig. 2. Perspective view of Δ-$[PdCl_2\{Co(aet)_2(R\text{-pn})\}]^+$ (**2**) with the atomic labeling scheme.

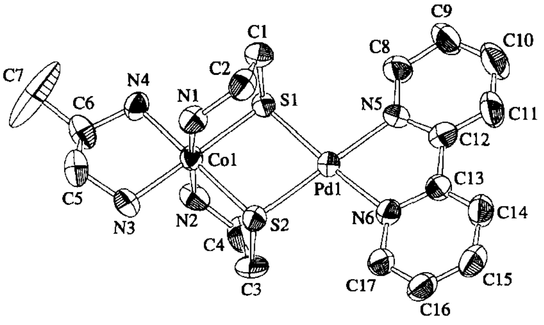

Fig. 3. Perspective view of Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-pn})\}]^{3+}$ (**3**) with the atomic labeling scheme.

Crystal Structures. Perspective drawings of the complex cations of **1**, **2**, and **3** are shown in Figs. 1, 2, and 3, and the selected bond distances and angles are listed in Tables 2, 3, and 4. The complex cation **1** consists of two Co atoms and one Pd atom and exhibits quite similar trinuclear structures to $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ and $[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$;[19,20] namely, each Co atom has an approximately octahedral geometry forming an asymmetrical *cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ unit. This means that only the central Ni atom of the starting material is replaced by the Pd atom. The Co(III) equatorial plane and the PdS_4 plane in **1** are essentially coplanar (dihedral angles; av. 12.22°), as in the case of $[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ (dihedral angles; av. 11.1°). The central PdS_4 sphere in **1** is somewhat distorted from a square-planar to a tetrahedral geometry, in which the PdS_1S_2 and PdS_3S_4 planes intersect to form a dihedral angle of 12.38°, but is less distorted than that of $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ (dihedral angle; 14.0°),[19] $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (dihedral angle; 16.2°),[17] and $[Ni\{Co(aet)_2(R\text{-pn})\}_2]^{4+}$ (dihedral angle; 13.94°).[20] Contrary to **1**, each of the complex cations **2** and **3** contains one Co atom and one Pd atom to form a dinuclear structure (Figs. 2 and 3). The Pd atom in **2** is coordinated by two Cl atoms besides two thiolato S atoms from the *cis*(*S*)-$[Co(aet)_2(R\text{-pn})]^+$ unit. On the other hand, the Pd atom in **3** is coordinated by two N atoms of the bpy skeleton, instead of the Cl atoms. The Co(III) equatorial plane and the $PdCl_2S_2$ plane in **2** (5.12°) or the PdN_2S_2 plane in **3** (dihedral angle; av. 5.68°) are essentially coplanar, which are significantly less than that in **1**. Although the Pd atoms in **2** and **3** take an almost square-planar geometry, the $PdCl_2S_2$ or PdN_2S_2 sphere is somewhat

Table 2. Selected Bond Distances (Å) and Angles (deg) of $[Pd\{Co(aet)_2(R\text{-}pn)\}_2](ClO_4)_4\cdot0.5H_2O$ ($\mathbf{1}(ClO_4)_4\cdot0.5H_2O$)

Pd(1)–S(1)	2.329(5)	Pd(1)–S(2)	2.318(5)
Pd(1)–S(3)	2.326(5)	Pd(1)–S(4)	2.312(5)
Co(1)–S(1)	2.235(5)	Co(1)–S(2)	2.233(5)
Co(1)–N(1)	2.03(1)	Co(1)–N(2)	1.97(1)
Co(1)–N(3)	2.01(1)	Co(1)–N(4)	1.99(1)
Co(2)–S(3)	2.243(5)	Co(2)–S(4)	2.251(6)
Co(2)–N(5)	2.03(2)	Co(2)–N(6)	1.99(2)
Co(2)–N(7)	2.00(1)	Co(2)–N(8)	2.02(2)
S(1)–Pd(1)–S(2)	84.3(2)	S(1)–Pd(1)–S(3)	174.5(2)
S(1)–Pd(1)–S(4)	95.9(2)	S(2)–Pd(1)–S(3)	96.2(2)
S(2)–Pd(1)–S(4)	169.5(2)	S(3)–Pd(1)–S(4)	84.6(2)
S(1)–Co(1)–S(2)	88.5(2)	S(1)–Co(1)–N(1)	87.8(4)
S(1)–Co(1)–N(2)	89.0(5)	S(1)–Co(1)–N(3)	176.8(5)
S(1)–Co(1)–N(4)	95.9(5)	S(2)–Co(1)–N(1)	89.7(5)
S(2)–Co(1)–N(2)	88.1(5)	S(2)–Co(1)–N(3)	91.8(5)
S(2)–Co(1)–N(4)	175.6(5)	N(1)–Co(1)–N(2)	176.2(6)
N(1)–Co(1)–N(3)	89.1(6)	N(1)–Co(1)–N(4)	91.1(6)
N(2)–Co(1)–N(3)	94.2(6)	N(2)–Co(1)–N(4)	91.3(6)
N(3)–Co(1)–N(4)	83.9(6)	S(3)–Co(2)–S(4)	88.0(2)
S(3)–Co(2)–N(5)	87.6(5)	S(3)–Co(2)–N(6)	90.9(5)
S(3)–Co(2)–N(7)	176.0(5)	S(3)–Co(2)–N(8)	96.7(5)
S(4)–Co(2)–N(5)	90.2(6)	S(4)–Co(2)–N(6)	86.7(5)
S(4)–Co(2)–N(7)	93.2(6)	S(4)–Co(2)–N(8)	174.8(5)
N(5)–Co(2)–N(6)	176.6(7)	N(5)–Co(2)–N(7)	88.5(7)
N(5)–Co(2)–N(8)	92.2(7)	N(6)–Co(2)–N(7)	93.0(7)
N(6)–Co(2)–N(8)	91.0(7)	N(7)–Co(2)–N(8)	82.3(7)
Pd(1)–S(1)–Co(1)	93.4(2)	Pd(1)–S(2)–Co(1)	93.7(2)
Pd(1)–S(3)–Co(2)	93.0(2)	Pd(1)–S(4)–Co(2)	93.1(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) of $[PdCl_2\{Co(aet)_2(R\text{-}pn)\}]Cl\cdot2H_2O$ ($\mathbf{2}\ Cl\cdot2H_2O$)

Pd(1)–Cl(1)	2.348(3)	Pd(1)–Cl(2)	2.359(2)
Pd(1)–S(1)	2.269(2)	Pd(1)–S(2)	2.278(3)
Co(1)–S(1)	2.219(3)	Co(1)–S(2)	2.252(2)
Co(1)–N(1)	1.981(8)	Co(1)–N(2)	1.965(8)
Co(1)–N(3)	1.982(8)	Co(1)–N(4)	2.013(7)
Cl(1)–Pd(1)–Cl(2)	95.30(9)	Cl(1)–Pd(1)–S(1)	90.11(10)
Cl(1)–Pd(1)–S(2)	173.52(9)	Cl(2)–Pd(1)–S(1)	172.39(10)
Cl(2)–Pd(1)–S(2)	90.73(9)	S(1)–Pd(1)–S(2)	84.11(9)
S(1)–Co(1)–S(2)	85.86(10)	S(1)–Co(1)–N(1)	87.3(2)
S(1)–Co(1)–N(2)	91.2(2)	S(1)–Co(1)–N(3)	177.6(3)
S(1)–Co(1)–N(4)	93.5(3)	S(2)–Co(1)–N(1)	91.4(2)
S(2)–Co(1)–N(2)	87.2(2)	S(2)–Co(1)–N(3)	94.0(3)
S(2)–Co(1)–N(4)	176.6(2)	N(1)–Co(1)–N(2)	178.0(3)
N(1)–Co(1)–N(3)	90.3(3)	N(1)–Co(1)–N(4)	91.9(3)
N(2)–Co(1)–N(3)	91.2(3)	N(2)–Co(1)–N(4)	89.5(3)
N(3)–Co(1)–N(4)	86.8(4)	Pd(1)–S(1)–Co(1)	95.5(1)
Pd(1)–S(2)–Co(1)	94.33(10)		

distorted to a tetrahedral geometry ($PdCl_1Cl_2$ and PdS_1S_2 planes: 6.11°, PdN_5N_6 and PdS_1S_2 planes: 4.52°). These distortions around the Pd atoms in **2** and **3** are of lesser extent compared with that in **1**. These may be attributed to the cross-plane interaction between the aet chelate rings of the two *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units in **1**.

Table 4. Selected Bond Distances (Å) and Angles (deg) of $[Pd(bpy)\{Co(aet)_2(R\text{-}pn)\}](ClO_4)_3$ ($\mathbf{3}(ClO_4)_3$)

Pd(1)–S(1)	2.291(2)	Pd(1)–S(2)	2.288(2)
Pd(1)–N(5)	2.035(7)	Pd(1)–N(6)	2.043(7)
Co(1)–S(1)	2.247(2)	Co(1)–S(2)	2.240(2)
Co(1)–N(1)	1.975(7)	Co(1)–N(2)	1.977(7)
Co(1)–N(3)	2.002(7)	Co(1)–N(4)	1.970(7)
S(1)–Pd(1)–S(2)	83.15(8)	S(1)–Pd(1)–N(5)	98.4(2)
S(1)–Pd(1)–N(6)	175.2(2)	S(2)–Pd(1)–N(5)	177.7(2)
S(2)–Pd(1)–N(6)	98.7(2)	N(5)–Pd(1)–N(6)	79.5(3)
S(1)–Co(1)–S(2)	85.25(8)	S(1)–Co(1)–N(1)	88.0(2)
S(1)–Co(1)–N(2)	90.3(2)	S(1)–Co(1)–N(3)	177.7(2)
S(1)–Co(1)–N(4)	94.6(2)	S(2)–Co(1)–N(1)	89.5(2)
S(2)–Co(1)–N(2)	87.5(2)	S(2)–Co(1)–N(3)	95.4(2)
S(2)–Co(1)–N(4)	177.2(2)	N(1)–Co(1)–N(2)	176.6(3)
N(1)–Co(1)–N(3)	89.8(3)	N(1)–Co(1)–N(4)	93.3(3)
N(2)–Co(1)–N(3)	92.0(3)	N(2)–Co(1)–N(4)	89.7(3)
N(3)–Co(1)–N(4)	84.9(3)	Pd(1)–S(1)–Co(1)	95.58(8)
Pd(1)–S(2)–Co(1)	95.87(9)		

All of the complexes with *R*-pn ligands selectively gave only optically active isomers. Taking the absolute configurations (Δ and Λ) of the *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units into consideration, three isomers ($\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$) are possible for **1**, and two isomers (Δ and Λ) are possible for **2** and **3**. The X-ray structural analyses and column chromatography indicate, however, that all of the crystals of the *R*-pn complex consist of only the optically active isomers with Δ-*cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units to show negative CD signs at 500 nm in solution. Accordingly, it is concluded that the absolute configuration of the starting optically active complex, $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$, can be retained during the reactions. Furthermore, all of the two aet and one *R*-pn chelate rings in each *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ unit in **1**, **2**, and **3** take λ conformations. These may be attributed to the fact that the methyl groups of the *R*-pn ligands take equatorial configurations.[24] Further, two geometrical isomers, *cis* and *trans*, are possible for the methyl groups in **1**. It is noted that the methyl groups of two *R*-pn ligands are situated in the *trans* position with respect to the C_2 axis passing through the central Pd atom, as in the case of $\Delta\Delta$-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$, although the reason is not understood at the present.

Characterization. As shown in Fig. 4 and Table 5, the ^{13}C NMR spectrum of $\Delta\Delta$-$[Pd\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ (**1**) in D_2O exhibits six signals at δ = 19.46, 35.39, 35.50, 52.24, 55.99, and 56.02. Among these signals, the signals at δ = 35.39 and 35.50 are due to the carbon atoms of $-CH_2S$ groups, and the signal at δ = 55.99 to $-CH_2N$ groups in aet.[6,8,9,17,20] Further, the signals at δ = 19.46, 52.24, and 56.02 are assigned to the carbon atoms of $-CH_3$, $-CH_2N$, and $-CH$ groups in *R*-pn, respectively.[20] Similarly to the case of **1**, each of Δ-$[PdCl_2\{Co(aet)_2(R\text{-}pn)\}]^+$ (**2**) and Δ-$[Pd(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ (**3**) shows six signals due to the carbon atoms of aet and *R*-pn ligands in the region of 10—60 ppm. These imply that two aet and one *R*-pn ligands in each of the *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units in **1**, **2**, and **3** indicate

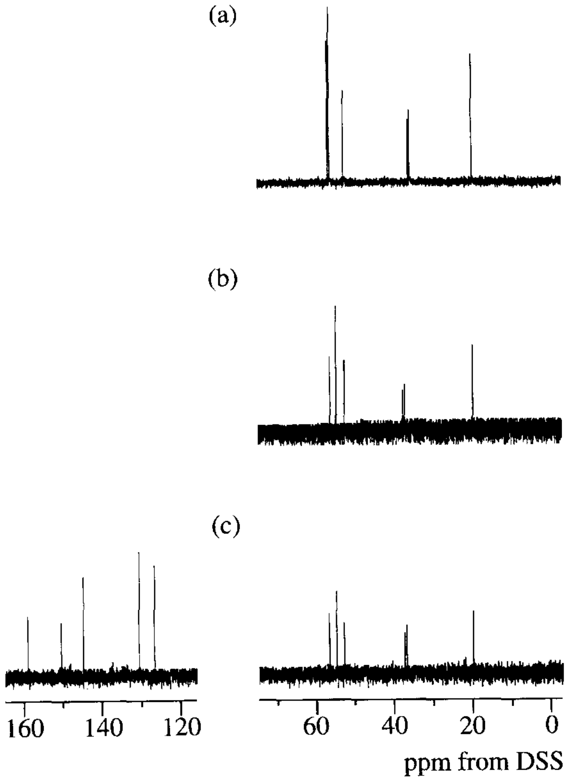

Fig. 4. ^{13}C NMR spectra of (a) $\Delta\Delta$-[Pd{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$ (**1**), (b) Δ-[PdCl$_2${Co(aet)$_2$(R-pn)}]$^+$ (**2**), and (c) Δ-[Pd(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (**3**) in D$_2$O.

the C_1 symmetry. In the case of **3**, furthermore, the additional five signals due to the carbon atoms of the bpy ligand, which appeared at an almost identical field with those of the other complexes containing bpy ligands,[9] are observed. Reflecting slight differences in the structures of the terminal Co(III) units, the signals due to the aet and R-pn ligands in **1**, **2**, and **3** are located at different fields from each other. No other peaks were found in the spectra of **1**, **2**, and **3** for periods exceeding 1 week. These facts indicate that these optically active complexes are relatively stable in solution, and retain their structures, which are expected to be almost the same as those in the crystalline state.

The electronic absorption and CD spectra of **1**, **2**, and **3** are shown in Fig. 5, and the data are summarized in Table 6. The absorption spectral pattern of $(-)^{\mathrm{CD}}_{500}$-**1** isomer is almost identical with that of [Ni{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$.[20] Namely, the Pd complex shows three intense charge-transfer (CT) bands at 27.9, 35.84, and 45.45×10^3 cm^{-1}, two d–d bands due to the Co^{3+} ion at 20.00 and 24.2×10^3 cm^{-1}, and one d–d band due to the Pd^{2+} ion at 30.86×10^3 cm^{-1}. Among the above CT bands, the band at 45.45×10^3 cm^{-1} of the Pd complex is located at a higher energy side than the corresponding band of the Ni complex.[20] This indicates that the band at 45.45×10^3 cm^{-1} is assigned as the CT transition from the bridging S atom to the Pd atom. Furthermore, the $(-)^{\mathrm{CD}}_{500}$-**1** isomer, whose absolute configuration is $\Delta\Delta$, exhibits similar

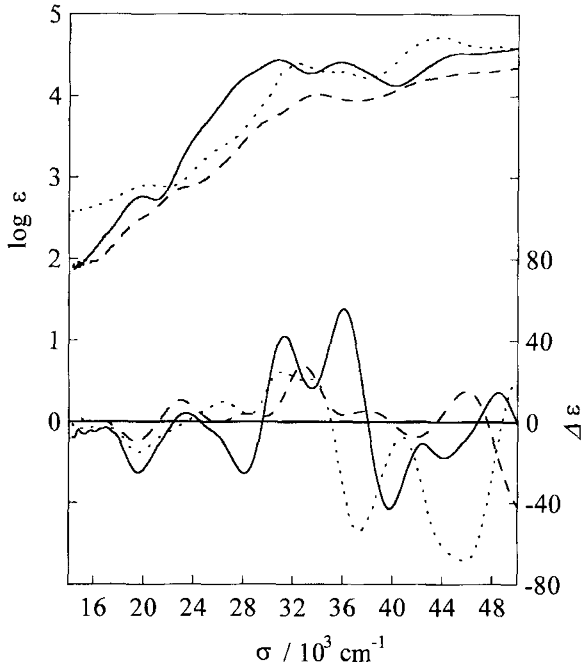

Fig. 5. Electronic absorption and CD spectra of $\Delta\Delta$-[Pd{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$ (**1**) (———), Δ-[PdCl$_2${Co(aet)$_2$(R-pn)}]$^+$ (**2**) (- - - - -), and Δ-[Pd(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (**3**) (········) in H$_2$O.

Table 5. ^{13}C NMR Chemical Shifts[a)] of $\Delta\Delta$-[Pd{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$ (**1**), Δ-[PdCl$_2${Co(aet)$_2$(R-pn)}]$^+$ (**2**), and Δ-[Pd(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (**3**)

	$\Delta\Delta$-[Pd{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$ (**1**)	Δ-[PdCl$_2${Co(aet)$_2$(R-pn)}]$^+$ (**2**)	Δ-[Pd(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (**3**)
–CH$_2$S (aet)	35.39	36.68	36.47
	35.50	37.01	36.58
–CH$_2$N (aet)	55.99	54.30	54.57
–CHN (pn)	56.02	55.99	56.46
–CH$_2$N (pn)	52.24	52.22	52.58
–CH$_3$ (pn)	19.46	19.52	19.63
Aromatic carbons (bpy)			126.53
			130.42
			144.52
			150.21
			158.64

a) In ppm from DSS.

Table 6. Absorption and CD Spectral Data of $\Delta\Delta$-[Pd{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ (**1**), Δ-[PdCl$_2${Co(aet)$_2$(*R*-pn)}]$^{+}$ (**2**), and Δ-[Pd(bpy){Co(aet)$_2$(*R*-pn)}]$^{3+}$ (**3**)

Absorption maxima $\sigma/10^3$ cm^{-1}	(log ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1}	($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
$\Delta\Delta$-[Pd{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ (**1**)			
20.00	(2.76)	19.53	(−25.40)
24.2	(2.9)$^{\rm sh}$	23.36	(+3.99)
27.9	(4.2)$^{\rm sh}$	28.09	(−25.67)
30.86	(4.44)	31.25	(+41.98)
35.84	(4.41)	36.10	(+55.08)
45.45	(4.52)	39.68	(−42.95)
		44.05	(−17.83)
		48.54	(+14.30)
Δ-[PdCl$_2${Co(aet)$_2$(*R*-pn)}]$^{+}$ (**2**)			
18.6	(2.3)$^{\rm sh}$	19.46	(−9.85)
23.0	(2.9)$^{\rm sh}$	22.99	(+10.29)
29.7	(3.7)$^{\rm sh}$	26.04	(−0.45)
33.89	(4.02)	28.25	(+3.77)
45.0	(4.3)$^{\rm sh}$	32.79	(+27.43)
		37.88	(+5.37)
		41.84	(−7.70)
		45.87	(+14.96)
Δ-[Pd(bpy){Co(aet)$_2$(*R*-pn)}]$^{3+}$ (**3**)			
20.28	(2.90)	19.61	(−15.17)
26.1	(3.4)$^{\rm sh}$	26.38	(+9.52)
29.6	(3.9)$^{\rm sh}$	31.06	(+24.25)
32.36	(4.40)	33.44	(+20.72)
35.71	(4.29)	37.31	(−53.78)
43.86	(4.72)	45.87	(−68.50)

absorption and CD bands over the whole region to the case of (−)$^{\rm CD}_{520}$-[Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$.[19] This supports the results of the assignment of the optically active en complex, which are determined from the empirical relationship between the absolute configuration and the CD spectral sign in the first d–d absorption regions.[25] Similar trends are also observed for **2** and **3**. The absorption spectrum of **2** is characterized by one intense peak at 33.89×10^3 cm^{-1} and four shoulders around 18.6, 23.0, 29.7, and 45.0×10^3 cm^{-1}. On the other hand, **3** shows 20.28, 26.1, 29.6, 32.36, 35.71, and 43.86×10^3 cm^{-1}. Thus, the spectral behaviors of **1**, **2**, and **3** are significantly different from each other, especially for those related on the chromophores around Pd atoms. Similarly to the case of (−)$^{\rm CD}_{500}$-**1** isomer, each of the (−)$^{\rm CD}_{500}$-**2** and (−)$^{\rm CD}_{500}$-**3** isomers exhibits negative and positive CD bands from the lowest energy side. This indicates that both of the (−)$^{\rm CD}_{500}$-**2** and (−)$^{\rm CD}_{500}$-**3** isomers have Δ-configuration for *cis*(*S*)-[Co(aet)$_2$(*R*-pn)]$^+$ units, as in the case of the (−)$^{\rm CD}_{500}$-**1** isomer. Reflecting the concordance between the absolute configurations around the octahedral Co(III) units of **1**, **2**, and **3**, it is expected that the CD spectral behaviors in the S–Co–CT band regions are also identical with each other. Influenced by the Pd atoms and/or coordinated atoms to the Pd atoms, however, the behaviors are rather different from each other. It is therefore concluded that the absorption and CD spectral behaviors of such types of $Co^{III}Pd^{II}$ polynuclear complexes are largely dependent on the square-planar Pd(II) units as well as the octahedral Co(III) units.

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