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A New Class of S-Bridged $Co^{III}MCo^{III}$ ($M = Ni^{II}, Pd^{II}$) Trinuclear Complexes with Mixed Aliphatic and Aromatic Thiolate Ligands: Synthesis, Characterization, and Stereochemistry

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Treatments of a mixture of $CoCl_2 \cdot 6H_2O$, HL (Hpyt = 2-pyridinethiol, Hpymt = 2-pyrimidinethiol), and triethylamine with $[Ni(aet)_2]$ (aet = 2-aminoethanethiolate) in methanol led to the isolation of novel S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complexes, $[Ni\{Co(aet)_2(pyt)\}_2]^{2+}$ ($[\mathbf{1}]^{2+}$) and $[Ni\{Co(aet)_2(pymt)\}_2]^{2+}$ ($[\mathbf{2}]^{2+}$), in which a Ni^{II} ion is coordinated by four aet S atoms from two tris(thiolato)-type $[Co(aet)_2(pyt\ or\ pymt)]$ units. The Ni^{II} ion in both $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ was replaced by a Pd^{II} ion through the reaction with $Na_2[PdCl_4]$ in water, giving the corresponding $Co^{III}Pd^{II}Co^{III}$ trinuclear complexes, $[Pd\{Co(aet)_2(pyt)\}_2]^{2+}$ ($[\mathbf{3}]^{2+}$) and $[Pd\{Co(aet)_2(pymt)\}_2]^{2+}$ ($[\mathbf{4}]^{2+}$). The related $Co^{III}Pd^{II}Co^{III}$ trinuclear complexes composed of one $[Co(aet)_2(pyt\ or\ pymt)]$ and one $[Co(aet)_2(en)]^+$ units, $[Pd\{Co(aet)_2(pyt)\}\{Co(aet)_2(en)\}]^{3+}$ ($[\mathbf{5}]^{3+}$) and $[Pd\{Co(aet)_2(pymt)\}\{Co(aet)_2(en)\}]^{3+}$ ($[\mathbf{6}]^{3+}$), were also prepared by the reactions of a 1:1 mixture of $[Ni\{Co(aet)_2(pyt\ or\ pymt)\}_2]^{2+}$ and $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with $Na_2[PdCl_4]$ in water, followed by the column chromatographic separation. The electronic absorption, CD, and NMR spectroscopies indicated that these $Co^{III}MCo^{III}$ trinuclear complexes produce only the *racemic* ($\Delta\Delta/\Lambda\Lambda$) isomer, in which each $[Co(aet)_2(pyt\ or\ pymt)]$ unit adopts a *mer*(*S*) configuration with two aet N atoms at the apical positions. For $[\mathbf{1}]^{2+}$, $[\mathbf{2}]^{2+}$, $[\mathbf{3}]^{2+}$, and $[\mathbf{4}]^{2+}$, another geometrical isomerism of *syn–anti*, which arises from the arrangement of the two terminal pyt or pymt S atoms, was identified.

Thiolate-type ligands tend to form S-bridged polymeric structures, owing to their high nucleophilic character.[1] It has been recognized that the nucleophilic character of aliphatic thiolate ligands is largely retained after coordination to one Co^{III} center, which leads to the formation of relatively stable S-bridged polynuclear structures binding with another metal ion.[2–13] In fact, a number of polynuclear complexes with well-defined S-bridged structures have been prepared by the reactions of *fac*(*S*)-$[Co(aet)_3]$ (aet = 2-aminoethanethiolate) or *fac*(*S*)-$[Co(\text{L-cys-}N,S)_3]^{3-}$ (L-cys = L-cysteinate) with a variety of transition metal ions.[2–9] It has been shown that the constructed chiral structures of these polynuclear complexes are highly dependent on the coordination geometry of metal ions incorporated with the Co^{III} units. For example, the reaction of *fac*(*S*)-$[Co(aet)_3]$ with octahedral Co^{III} gave the *meso* ($\Delta\Lambda$) and *racemic* ($\Delta\Delta/\Lambda\Lambda$) forms of the trinuclear $[Co\{Co(aet)_3\}_2]^{3+}$,[1] while the corresponding reactions with linear Ag^I and tetrahedral Zn^{II} produced only the *racemic* ($\Delta\Delta/\Lambda\Lambda$) form of the pentanuclear $[Ag_3\{Co(aet)_3\}_2]^{3+}$ and the *racemic* ($\Delta\Delta\Delta\Delta/\Lambda\Lambda\Lambda\Lambda$) form of the octanuclear $[Zn_4O\{Co(aet)_3\}_4]^{6+}$, respectively.[6,8] Thus, the polynuclear coordination chemistry of this class has been developed mainly by changing the metal ions used in the reactions.

Our aim has now been directed at expanding the range of the chiral S-bridged polynuclear system by introducing a new class of Co^{III} octahedral units with both chelating aliphatic and aromatic thiolate ligands, which may exhibit unique chemical behavior. The representative chelating aromatic thiolate ligands are 2-pyridinethiolate (pyt) and 2-pyrimidinethiolate (pymt), which have been shown to act as bidentate-*N*,*S* chelators towards a Co^{III} center (Chart 1),[14–16] as in the case of aet. However, none of the Co^{III} complexes with mixed aet and pyt (or pymt), such as $[Co(aet)_2(pyt\ or\ pymt)]$ or $[Co(aet)(pyt\ or\ pymt)_2]$, have appeared in the literatures to date. The preparation of these mixed-type Co^{III} complexes directly from Co^{II}, Haet, and Hpyt (or Hpymt) was not promising, considering the plausible formation of various neutral species with different compositions and geometrical configurations of the form $[Co(aet)_n(pyt\ or\ pymt)_{3-n}]$ ($n = 0$–3), which are hardly separated by column chromatography and/or fractional crystallization. Previously, we have found that the reaction of $[CoCl_2(en)_2]^+$ with $[Ni(aet)_2]$ results in the chelate-transfer of aet from a Ni^{II} to a Co^{III} coordination sphere to afford an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex composed of two *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$.[17] If a similar chelate-transfer reaction is applicable for the Co^{III}-pyt and Co^{III}-pymt systems, it should result in the construction of

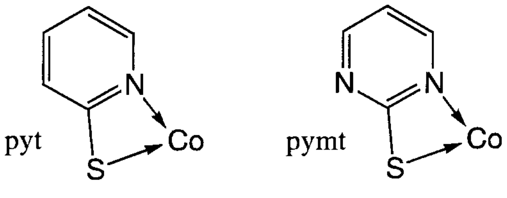
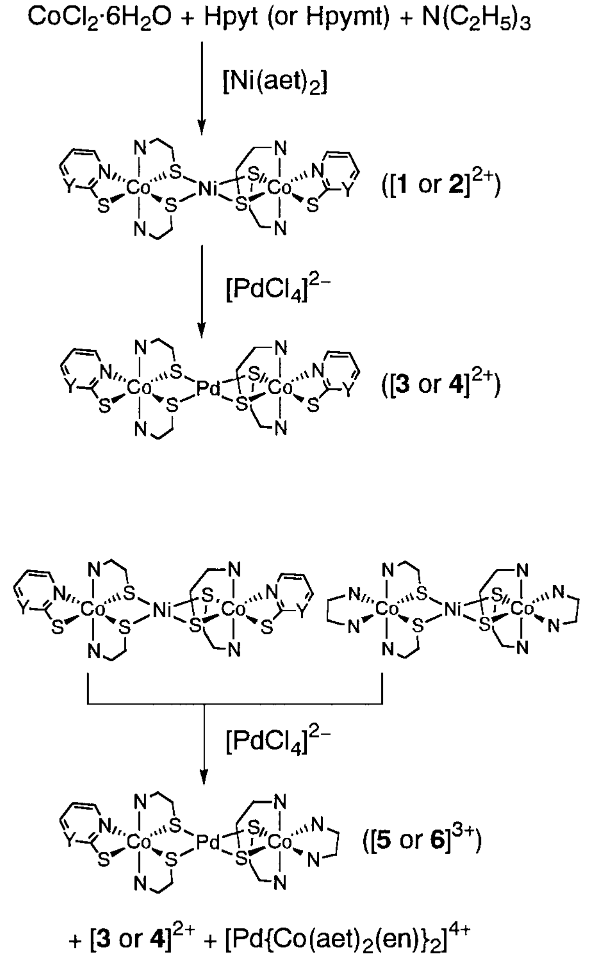


Chart 1.

[Co(aet)$_2$(pyt or pymt)] units in an S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ trinuclear structure. Thus, we investigated the reactions of $\mathrm{Co^{III}}$-pyt or $\mathrm{Co^{III}}$-pymt species with [Ni(aet)$_2$]. Here we report on the synthesis and characterization of [Ni{Co(aet)$_2$(pyt)}$_2$]$^{2+}$ ([**1**]$^{2+}$) and [Ni{Co(aet)$_2$(pymt)}$_2$]$^{2+}$ ([**2**]$^{2+}$) composed of two [Co(aet)$_2$(pyt or pymt)] units, together with those of the corresponding $\mathrm{Co^{III}Pd^{II}Co^{III}}$ complexes which were derived by the metal replacement reactions of [**1** or **2**]$^{2+}$ with $\mathrm{Pd^{II}}$. The related $\mathrm{Co^{III}Pd^{II}Co^{III}}$ complexes composed of both the [Co(aet)$_2$(pyt or pymt)] and [Co(aet)$_2$(en)]$^+$ units, which were successfully prepared by treating a mixture of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ and [**1** or **2**]$^{2+}$ with $\mathrm{Pd^{II}}$, are also presented (Scheme 1).

Experimental

Preparation of Complexes. [Ni{Co(aet)$_2$(pyt)}$_2$]X$_2$ ([1]X$_2$; X = Cl, Br): To a solution containing 0.50 g (2.1 mmol) of $CoCl_2 \cdot 6H_2O$ in 50 cm^3 of methanol was added 0.35 g (3.1 mmol) of Hpyt. The mixture was stirred at room temperature for 10 min to give a green-blue suspension. To this was added dropwise 0.32 g (3.2 mmol) of triethylamine in 5 cm^3 of methanol while stirring, during which time the green-blue suspension turned to a dark brown solution. A 0.45 g (2.1 mmol) sample of [Ni(aet)$_2$]^{1a} was then added to the dark brown solution, and the mixture was stirred at 50 °C for 1 h. After removing insoluble materials by filtration, the brown reaction solution was concentrated to dryness. The residue was dissolved in 50 cm^3 of water, and insoluble materials were again filtered off. To the dark brown filtrate was added 10 cm^3 of a saturated NaCl aqueous solution, followed by refrigeration for 1 day. The deposited brown powder was collected by filtration and washed with acetone. This product was recrystallized from 50 cm^3 of water in a refrigerator by adding 10 cm^3 of a saturated NaCl aqueous solution. The resulting fine needle crystals were collected by filtration and washed with acetone/water (4:1) and then acetone. Yield: 0.45 g (47% based on Co). Anal. Calcd for [**1**]$Cl_2 \cdot 7H_2O$: C, 24.06; H, 5.16; N, 9.35; Co, 13.1; Ni, 6.5%. Found: C, 23.99; H, 4.94; N, 9.46; Co, 13.1; Ni, 6.8%. Molar conductivity in H_2O: 220 Ω^{-1} cm^2 mol^{-1}.



Scheme 1. Synthetic routes of [**1** or **2**]$^{2+}$, [**3** or **4**]$^{2+}$, and [**5** or **6**]$^{3+}$ (Y = CH(pyt) or N(pymt)).

The bromide salt of [**1**]$^{2+}$ was obtained by using a saturated NaBr aqueous solution, instead of a saturated NaCl aqueous solution. Yield: 0.38 g (36% based on Co). Anal. Calcd for [**1**]$Br_2 \cdot 8H_2O$: C, 21.50; H, 4.81; N, 8.36; Co, 11.7; Ni, 5.8%. Found: C, 21.79; H, 4.88; N, 8.44; Co, 12.1; Ni, 5.7%. Molar conductivity in H_2O: 237 Ω^{-1} cm^2 mol^{-1}.

[Ni{Co(aet)$_2$(pymt)}$_2$]Cl$_2$ ([2]Cl$_2$): To a solution containing 0.50 g (2.1 mmol) of $CoCl_2 \cdot 6H_2O$ in 50 cm^3 of methanol was added 0.35 g (3.1 mmol) of Hpyt. The mixture was stirred at room temperature for 10 min to give an orange suspension. To this was added dropwise 0.32 g (3.2 mmol) of triethylamine in 5 cm^3 of methanol while stirring, during which time the orange suspension turned to a dark brown suspension. A 0.45 g (2.1 mmol) sample of [Ni(aet)$_2$]^{1a} was then added to the dark brown suspension, and the mixture was stirred at 50 °C for 1 h. After removing insoluble materials by filtration, the brown reaction solution was concentrated to dryness. The residue was dissolved in 50 cm^3 of water, and insoluble materials were again filtered off. To the dark brown filtrate was added 10 cm^3 of a saturated NaCl aqueous solution, followed by refrigeration for 1 day. The deposited brown powder was collected by filtration and washed with acetone. This product was recrystallized from 50 cm^3 of water in a refrigerator by adding 10 cm^3 of a saturated NaCl aqueous solution. The resulting fine needle crystals were collected by filtration and washed with acetone/water (4:1) and then acetone. Yield: 0.36 g (37% based on Co). Anal. Calcd for [**2**]$Cl_2 \cdot 8H_2O$: C, 20.92; H, 5.05; N, 12.20; Co, 12.8; Ni, 6.4%. Found: C, 20.88; H, 5.12; N, 12.05; Co, 12.4; Ni, 6.8%. Molar conductivity in H_2O: 218 Ω^{-1} cm^2 mol^{-1}.

[Pd{Co(aet)$_2$(pyt)}$_2$]X$_2$ ([3]X$_2$; X = Cl, Br): To a solution containing 0.20 g (0.22 mmol) of [**1**]$Cl_2 \cdot 7H_2O$ in 30 cm^3 of water was added 0.064 g (0.22 mmol) of Na_2[PdCl$_4$] in 10 cm^3 of water. The mixture was stirred at 60 °C for 30 min, during which time the solution color turned from brown to dark green. After filtration, to the dark green reaction solution was added 8 cm^3 of a saturated NaCl aqueous solution, followed by refrigeration for 1 day. The resulting green needle crystals were collected by filtration and washed with acetone/water (4:1) and then acetone. Yield: 0.10 g (47%). Anal. Calcd for [**3**]$Cl_2 \cdot 8H_2O$: C, 22.42; H, 5.02; N, 8.72; Co, 12.2; Pd, 11.0%. Found: C, 22.40; H, 5.01; N, 8.80; Co, 12.3; Pd, 11.3%. Molar conductivity in H_2O: 223 Ω^{-1} cm^2 mol^{-1}.

The bromide salt of [**3**]$^{2+}$ was obtained by using a saturated NaBr aqueous solution, instead of a saturated NaCl aqueous solution. Yield: 0.18 g (78%). Anal. Calcd for [**3**]$Br_2 \cdot 7H_2O$: C, 20.89; H, 4.48; N, 8.12; Co, 11.4; Pd, 10.3%. Found: C, 20.92; H, 4.50; N, 8.21; Co, 11.7; Pd, 9.8%. Molar conductivity in H_2O: 218 Ω^{-1} cm^2 mol^{-1}.

[Pd{Co(aet)$_2$(pymt)}$_2$]Cl$_2$·8H$_2$O ([4]Cl$_2$·8H$_2$O): To a solution containing 0.20 g (0.22 mmol) of [**2**]$Cl_2\cdot 8H_2O$ in 30 cm^3 of water was added 0.064 g (0.22 mmol) of $Na_2[PdCl_4]$ in 10 cm^3 of water. The mixture was stirred at 60 °C for 30 min, during which time the solution color turned from brown to green. After filtration, to the green solution was added 8 cm^3 of a saturated NaCl aqueous solution, followed by refrigeration for 1 day. The resulting green needle crystals were collected by filtration and washed with acetone/water (4:1) and then acetone. Yield: 0.16 g (76%). Anal. Calcd for [**4**]$Cl_2\cdot 8H_2O$: C, 19.89; H, 4.80; N, 11.60; Co, 12.2; Pd, 11.0%. Found: C, 19.67; H, 4.90; N, 11.47; Co, 12.0; Pd, 11.3%. Molar conductivity in H_2O: 212 $\Omega^{-1}\,cm^2\,mol^{-1}$.

Optical Resolution of [3]$^{2+}$ and [4]$^{2+}$: An aqueous solution of [**3**]$Br_2\cdot 7H_2O$ (0.20 g) was chromatographed on an SP-Sephadex C-25 column (Na^+ form, 3.2 cm × 42 cm) using a 0.075 $mol\,dm^{-3}$ aqueous solution of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot 5H_2O$ as an eluent. When the sample was separated into two bands in the column, the eluent was changed to a 0.3 $mol\,dm^{-3}$ aqueous solution of NaBr. Each eluate of the two bands was concentrated to a small volume with a rotary evaporator. The resulting green powder was collected by filtration, washed with cold water, and air-dried. Complex [**4**]$^{2+}$ was also optically resolved by the same column chromatographic method. It was found from the CD spectral measurements that the earlier and the later moving bands for each of [**3**]$^{2+}$ and [**4**]$^{2+}$ contain the $(+)^{CD}_{580}$ and $(-)^{CD}_{580}$ isomers, respectively. Anal. Calcd for $(+)^{CD}_{580}$-[**3**]$Br_2\cdot 6H_2O$: C, 21.26; H, 4.36; N, 8.26%. Found: C, 21.28; H, 4.03; N, 8.34%. Calcd for $(+)^{CD}_{580}$-[**4**]$Br_2\cdot 8H_2O$: C, 18.21; H, 4.39; N, 10.62%. Found: C, 18.09; H, 4.18; N, 10.55%.

[Pd{Co(aet)$_2$(pyt)}{Co(aet)$_2$(en)}]Br$_3\cdot$4H$_2$O ([5]Br$_3\cdot$4H$_2$O): To a solution containing 0.11 g (0.12 mmol) of [**1**]$Cl_2\cdot 7H_2O$ and 0.10 g (0.12 mmol) of $[Ni\{Co(aet)_2(en)\}_2]Cl_4\cdot 6H_2O$[17] in 40 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, during which time the solution color turned from brown to green-brown. The green-brown reaction solution was poured onto an SP-Sephadex C-25 column (Na^+ form, 2.2 cm × 27 cm). After the column had been washed with water, a green A-1 band containing [**3**]$^{2+}$ was eluted with a 0.15 $mol\,dm^{-3}$ aqueous solution of NaBr, and then a brown A-2 band containing [**5**]$^{3+}$ was eluted with a 0.3 $mol\,dm^{-3}$ aqueous solution of NaBr. Finally, a red-brown A-3 band containing $[Pd\{Co(aet)_2(en)\}_2]^{4+}$[14] was eluted with a 0.5 $mol\,dm^{-3}$ aqueous solution of NaCl. The formation ratio of [**3**]$^{2+}$:[**5**]$^{3+}$:$[Pd\{Co(aet)_2(en)\}_2]^{4+}$ for this reaction was estimated to be ca. 1:2:1, based on the volume and absorbance of each eluate. The A-2 eluate containing [**5**]$^{3+}$ was concentrated to a small volume to give a brown powder, which was collected by filtration and washed with ethanol. Yield: 0.087 g (36%). Anal. Calcd for [**5**]$Br_3\cdot 4H_2O$: C, 17.82; H, 4.39; N, 9.70; Co, 11.7; Pd, 10.5%. Found: C, 17.78; H, 4.36; N, 9.76; Co, 11.8; Pd, 10.6%. Molar conductivity in H_2O: 364 $\Omega^{-1}\,cm^2\,mol^{-1}$.

[Pd{Co(aet)$_2$(pymt)}{Co(aet)$_2$(en)}]Br$_3\cdot$4H$_2$O ([6]Br$_3\cdot$4H$_2$O): To a solution containing 0.11 g (0.12 mmol) of [**2**]$Cl_2\cdot 8H_2O$ and 0.10 g (0.12 mmol) of $[Ni\{Co(aet)_2(en)\}_2]Cl_4\cdot 6H_2O$ in 40 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, during which time the solution color turned from brown to green-brown. The green-brown solution was poured onto an SP-Sephadex C-25 column (Na^+ form, 2.2 cm × 27 cm). After the column had been washed with water, a green B-1 band containing [**4**]$^{2+}$ was eluted with a 0.15 $mol\,dm^{-3}$ aqueous solution of NaBr, and then a brown B-2 band containing [**6**]$^{3+}$ was eluted with a 0.3 $mol\,dm^{-3}$ aqueous solution of NaBr. Finally, a red-brown B-3 band containing $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ was eluted with a 0.5 $mol\,dm^{-3}$ aqueous solution of NaBr. The formation ratio of [**4**]$^{2+}$:[**6**]$^{3+}$:$[Pd\{Co(aet)_2(en)\}_2]^{4+}$ for this reaction was estimated to be ca. 1:2:1. The B-2 eluate containing [**6**]$^{3+}$ was concentrated to a small volume with a rotary evaporator to give a brown powder, which was collected by filtration and washed with methanol. Yield: 0.089 g (37%). Anal. Calcd for [**6**]$Br_3\cdot 4H_2O$: C, 16.62; H, 4.28; N, 11.07; Co, 11.6; Pd, 10.5%. Found: C, 16.34; H, 4.16; N, 10.93; Co, 11.7; Pd, 11.2%. Molar conductivity in H_2O: 371 $\Omega^{-1}\,cm^2\,mol^{-1}$.

Attempts to grow crystals suitable for X-ray analyses were unsuccessful for all the new complexes prepared in this study.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 or a JASCO V-530 spectrophotometer, and the CD spectra with a JASCO J-700 spectropolarimeter at room temperature. The ^{13}C NMR spectra were recorded with a JEOL JNM-A500 NMR spectrometer at probe temperature in D_2O. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference. The elemental analyses (C, H, N) were performed at Osaka University. The concentrations of Co, Ni, and Pd in the complexes were determined by plasma emission spectral analyses with a SHIMADZU ICP-1000Ⅲ ICP spectrometer. Molar conductivities of the complexes were measured with a Horiba DS-14 conductivity meter at room temperature.

Results and Discussion

Synthesis and Characterization of Co^{III}Ni^{II}Co^{III} Complexes. Treatment of a methanol solution of $CoCl_2\cdot 6H_2O$ with Hpyt at room temperature, followed by the addition of triethylamine in air gave a dark brown solution. The absorption spectrum of the reaction solution is characterized by an intense UV band at 36.6×10^3 cm^{-1} with broad absorption shoulders on the lower energy side. A similar UV band has been observed for $[Co(pyt)_3]$,[14] suggesting the presence of some cobalt(III)-pyt produced by air oxidation in the dark brown solution. Next, this solution was reacted with a solid sample of $[Ni(aet)_2]$ (in a ratio of Co:aet = 1:2) at 50 °C to produce a brown solution, from which a brown crystalline product of [**1**]X_2 (X = Cl or Br) was isolated. The plasma emission analysis indicated that [**1**]X_2 contains Co and Ni in a ratio of 2:1, and its elemental analytical data are in agreement with the formula for the desired Co^{III}Ni^{II}Co^{III} trinuclear complex, $[Ni\{Co(aet)_2(pyt)\}_2]X_2$. Furthermore, the molar conductivities of [**1**]X_2 in water (220 $\Omega^{-1}\,cm^2\,mol^{-1}$ for [**1**]Cl_2, 237 $\Omega^{-1}\,cm^2\,mol^{-1}$ for [**1**]Br_2) are very close to the value of the related 1:2 electrolyte $[Pd\{Co(aet)_3\}_2]Cl_2$ (234 $\Omega^{-1}\,cm^2\,mol^{-1}$).[9] Figure 1 compares the electronic absorption spectrum of [**1**]$^{2+}$ with that of the S-bridged Co^{III}Ni^{II}Co^{III} trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$,[17] in which two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units are linked by a Ni^{II} ion through four thiolato bridges. The data are summarized in Table 1. Although the absorption intensity of each band for [**1**]$^{2+}$ is usually greater than that of the corresponding band for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, the overall absorption spectral features of [**1**]$^{2+}$ and $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ are similar to each other. In particular, [**1**]$^{2+}$ shows an intense near-UV band at 26.71×10^3 cm^{-1} with a vague shoulder on the lower energy side,

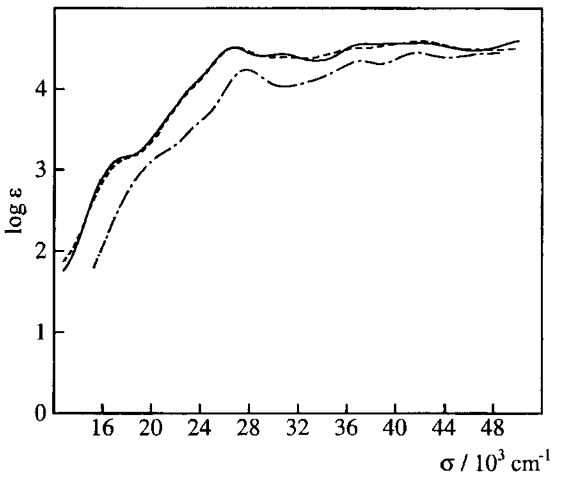


Fig. 1. Electronic absorption spectra of $[\mathbf{1}]^{2+}$ (—), $[\mathbf{2}]^{2+}$ (- - -), and $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ (-••-) in water.

Table 1. Absorption and CD Spectral Data for $[\mathbf{1}]^{2+}$, $[\mathbf{2}]^{2+}$, $[\mathbf{3}]^{2+}$, $[\mathbf{4}]^{2+}$, $[\mathbf{5}]^{3+}$, and $[\mathbf{6}]^{3+}$ in H_2O

Abs max: $\sigma/10^3$ 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})	
$[\mathrm{Ni\{Co(aet)_2(pyt)\}_2}]^{2+}$ ($[\mathbf{1}]^{2+}$)			
18.1	$(3.2)^{\mathrm{sh}}$		
26.71	(4.51)		
30.58	(4.43)		
37.51	(4.56)		
41.95	(4.57)		
$[\mathrm{Ni\{Co(aet)_2(pymt)\}_2}]^{2+}$ ($[\mathbf{2}]^{2+}$)			
18.3	$(3.2)^{\mathrm{sh}}$		
26.88	(4.52)		
30.2	$(4.4)^{\mathrm{sh}}$		
37.0	$(4.5)^{\mathrm{sh}}$		
42.12	(4.60)		
$\Lambda\Lambda$-$[\mathrm{Pd\{Co(aet)_2(pyt)\}_2}]^{2+}$ ($(+)^{\mathrm{CD}}_{580}$-$[\mathbf{3}]^{2+}$)			
16.92	(2.90)	17.29	(+20.4)
27.25	(4.50)	22.40	(−10.0)
30.34	(4.62)	27.29	(−44.8)
37.26	(4.45)	29.59	(−43.7)
43.82	(4.58)	38.68	(+44.5)
		42.46	(+28.3)
		45.56	(−12.5)
		47.56	(−7.4)
$\Lambda\Lambda$-$[\mathrm{Pd\{Co(aet)_2(pymt)\}_2}]^{2+}$ ($(+)^{\mathrm{CD}}_{580}$-$[\mathbf{4}]^{2+}$)			
17.23	(2.91)	17.57	(+24.2)
27.5	$(4.5)^{\mathrm{sh}}$	28.29	(−42.2)
29.87	(4.59)	40.00	(+61.8)
32.0	$(4.6)^{\mathrm{sh}}$	47.39	(−25.1)
43.33	(4.59)		
$[\mathrm{Pd\{Co(aet)_2(en)\}\{Co(aet)_2(pyt)\}}]^{3+}$ ($[\mathbf{5}]^{3+}$)			
17.18	(2.62)		
27.8	$(4.3)^{\mathrm{sh}}$		
30.53	(4.52)		
33.3	$(4.4)^{\mathrm{sh}}$		
45.1	$(4.5)^{\mathrm{sh}}$		
$[\mathrm{Pd\{Co(aet)_2(en)\}\{Co(aet)_2(pymt)\}}]^{3+}$ ($[\mathbf{6}]^{3+}$)			
17.67	(2.66)		
28.2	$(4.4)^{\mathrm{sh}}$		
30.49	(4.51)		
33.69	(4.45)		
45.1	$(4.5)^{\mathrm{sh}}$		

The sh label denotes a shoulder.

which corresponds well with the intense band at 27.70 × 10^3 cm^{-1} due to the Ni(thiolato-S)$_4$ chromophore found in $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$.[17] Taking these facts into consideration, an S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ trinuclear structure in $[\mathrm{Ni\{Co(aet)_2(pyt)\}_2}]^{2+}$, in which a $\mathrm{Ni^{II}}$ ion is coordinated by four thiolato S atoms from two [Co(aet)$_2$(pyt)] units, can be assigned to $[\mathbf{1}]^{2+}$.

A similar reaction using $\mathrm{CoCl_2 \cdot 6H_2O}$, Hpymt, triethylamine, and [Ni(aet)$_2$] in methanol also produced a brown solution, from which a brown crystalline product of $[\mathbf{2}]\mathrm{Cl_2}$ was isolated. As shown in Fig. 1, the absorption spectrum of $[\mathbf{2}]^{2+}$ is very similar to that of $[\mathbf{1}]^{2+}$ over the observed region, giving a characteristic intense near-UV band at almost the same position (26.88 × 10^3 cm^{-1}) as the near-UV band for $[\mathbf{1}]^{2+}$. From this spectral behavior, together with the elemental and plasma emission analyses and the molar conductivity in water (218 Ω^{-1} cm^2 mol^{-1}), $[\mathbf{2}]^{2+}$ is assigned to the corresponding S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ complex composed of two [Co(aet)$_2$(pymt)] units, $[\mathrm{Ni\{Co(aet)_2(pymt)\}_2}]^{2+}$.

In the 500 MHz ^{13}C NMR spectra $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ show five pyt or four pymt aromatic carbon signals at a lower magnetic field, besides two $\mathrm{SCH_2}$ and two $\mathrm{NCH_2}$ aet methylene carbon signals at a higher magnetic field (Table 2), which is expected for the $\mathrm{Co^{III}Ni^{II}Co^{III}}$ structure in $[\mathrm{Ni\{Co(aet)_2(pyt\ or\ pymt)\}_2}]^{2+}$. The chemical shifts of $\mathrm{SCH_2}$ and $\mathrm{NCH_2}$ methylene carbon signals for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ are quite comparable to the values observed for $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ (δ 34.76 for $\mathrm{SCH_2}$ and δ 56.00 for $\mathrm{NCH_2}$ of aet).[17] This suggests that in $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ each [Co(aet)$_2$(pyt or pymt)] unit binds with the central $\mathrm{Ni^{II}}$ ion through two aet S atoms, rather than through one aet S and one pyt or pymt S atoms, which can be rationalized by the weaker nucleophilicity of aromatic thiolato donors compared with the aliphatic thiolato donors. Three geometrical configurations, *mer*(S)•*trans*(N_{aet}), *mer*(S)•*cis*-(N_{aet}), and *fac*(S)•*cis*(N_{aet}), are possible for the [Co(aet)$_2$(pyt or pymt)] unit chelating to the $\mathrm{Ni^{II}}$ ion through two aet S atoms (Fig. 2). It has been shown that in all of the S-bridged $\mathrm{Co^{III}MCo^{III}}$ (M = $\mathrm{Ni^{II}}$, $\mathrm{Pd^{II}}$, $\mathrm{Pt^{II}}$) trinuclear complexes, $[\mathrm{M\{Co(aet)_2(en)\}_2}]^{4+}$ and [M{Co(D-penicillaminato-N,O,S)$_2$}{Co(aet)$_2$(en)}]$^{2+}$, the *cis*(S)-[Co(aet)$_2$(en)]$^+$ units commonly adopt the C_2-*cis*(S) configuration having two aet N atoms *trans* to each other, because of the steric requirement.[17–20] Thus, it is likely that the two [Co(aet)$_2$(pyt or pymt)] units in $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ have the *mer*(S)•*trans*(N_{aet}) configuration, with the pyt or pymt ligand occupying the coordination site of the en ligand in the C_2-*cis*(S)-[Co(aet)$_2$(en)]$^+$ unit. It is noticed that each of the two $\mathrm{SCH_2}$ signals for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, beside one aromatic carbon signal for $[\mathbf{1}]^{2+}$, splits into two (Table 2), which suggests of the presence of two isomers. In addition to the *meso–racemic* ($\Delta\Lambda$–$\Delta\Delta/\Lambda\Lambda$) isomerism, another isomerism of *syn–anti* is possible for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, which arises from the relative configuration of the two non-bridging pyt or pymt S atoms (Fig. 3). The most probable isomers for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ are *racemic-syn* and *racemic-anti*, considering the fact

Table 2. ^{13}C NMR Spectral Data of $\mathrm{Co^{III}Ni^{II}Co^{III}}$ and $\mathrm{Co^{III}Pd^{II}Co^{III}}$ Trinuclear Complexes in D_2O (Chemical Shift/ppm from DSS)

Complex	CH_2S (aet)				CH_2N (en)	CH_2N (aet)			pyt or pymt				
$[\mathbf{1}]^{2+}$	34.08 34.35	35.27 35.55				55.55	56.75		121.63	130.21	140.55	149.79 149.85	178.55
$[\mathbf{2}]^{2+}$	34.25 34.53	35.60 35.90				55.46	56.61		118.83		159.27	161.51	185.55
$[\mathbf{3}]^{2+}$	34.80 35.11	36.18 36.51				55.86	57.19		121.62	130.25	140.62	149.69 149.74	178.49
$[\mathbf{4}]^{2+}$	34.98 35.30	36.54 36.88				55.79	57.04		118.86		159.10 159.16	161.60	185.47
$[\mathbf{5}]^{3+}$	35.09	35.37	35.68	36.46	46.63	55.92	56.09	57.73	121.70	130.29	140.67	149.80	178.48
$[\mathbf{6}]^{3+}$	35.20	35.39	35.73	36.75	46.61	55.80	56.10	57.06	118.86		159.17	161.59	185.49

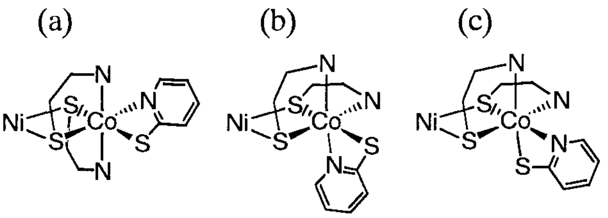


Fig. 2. Three geometries possible for the $[Co(aet)_2(pyt)]$ unit bound to $\mathrm{Ni^{II}}$ through two aet S atoms, *mer*(*S*)•*trans*(N_{aet}) (a), *mer*(*S*)•*cis*(N_{aet}) (b), and *fac*(*S*)•*cis*(N_{aet}) (c).

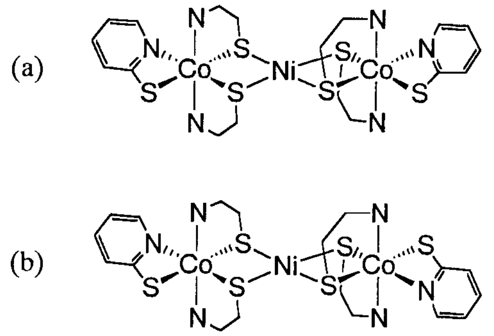


Fig. 3. The *syn* (a) and *anti* (b) isomers of $[\mathbf{1}]^{2+}$.

that only the thermodynamically stable *racemic* isomer is formed for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$,[17] and with the fact that the *meso* and *racemic* isomers isolated for $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ exhibit CH_2S ^{13}C NMR signals well separated from each other (δ 36.37 for *racemic* and δ 37.39 for *meso*).[20] Further assignment of the two isomers for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ based on the separation and/or optical resolution with the use of SP-Sephadex C-25 column chromatography could not be made, due to decomposition in the column.

Synthesis and Characterization of $\mathrm{Co^{III}Pd^{II}Co^{III}}$ Complexes. Treatments of aqueous solutions of $[\mathbf{1}]Cl_2$ and $[\mathbf{2}]Cl_2$ with equimolar $Na_2[PdCl_4]$ at 60 °C gave dark green solutions, from which green crystalline products of $[\mathbf{3}]X_2$ (X = Cl, Br) and $[\mathbf{4}]Cl_2$ were isolated, respectively. The elemental and plasma emission analyses of $[\mathbf{3}]X_2$ and $[\mathbf{4}]Cl_2$ are in agreement with the formulas for the $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complexes, $[Pd\{Co(aet)_2(pyt)\}_2]X_2$ and $[Pd\{Co(aet)_2(pymt)\}_2]Cl_2$, respectively, and their molar conductivities in water are compatible with the 1:2 electrolytes (223 $\Omega^{-1}\,cm^2\,mol^{-1}$ for $[\mathbf{3}]Cl_2$, 218 $\Omega^{-1}\,cm^2\,mol^{-1}$ for $[\mathbf{3}]Br_2$, 212 $\Omega^{-1}\,cm^2\,mol^{-1}$ for $[\mathbf{4}]Cl_2$). As shown in Fig. 4, the absorption spectra of $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ are characterized by a well-defined visible band at ca. 17×10^3 cm^{-1} and three intense absorption bands in the region of ca. 25–35 $\times 10^3$ cm^{-1}. This absorption characteristic is also observed for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$,[18] although each absorption band for $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ is located at lower energy and with lower intensity, compared with the corresponding absorption band for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$. From these results, $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ can be assigned to the S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complexes, $[Pd\{Co(aet)_2(pyt)\}_2]^{2+}$ and $[Pd\{Co(aet)_2(pymt)\}_2]^{2+}$, respectively, in which a $\mathrm{Pd^{II}}$ ion is coordinated by four thiolato S atoms from two terminal $[Co(aet)_2(\text{pyt or pymt})]$ units.

The ^{13}C NMR spectra of $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ in D_2O are quite similar to those of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, respectively, having five pyt or four pymt aromatic carbon signals at a lower magnetic field and four aet methylene carbon signals at a higher magnetic field (Table 2). Each aromatic carbon signal for $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ is located at almost the same position as the corresponding signal for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, while each methylene carbon signal for $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ shifts slightly to a lower magnetic field than the corresponding signal for $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, respectively. This result indicates that the two $[Co(aet)_2(\text{pyt or pymt})]$ units in $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ bind with the central $\mathrm{Pd^{II}}$ ion through two aet S atoms to have the *mer*(*S*)•*trans*(N_{aet}) configuration, like the $[Co(aet)_2(\text{pyt or pymt})]$ units in the starting $\mathrm{Co^{III}Ni^{II}Co^{III}}$ complexes ($[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$). Complexes $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ also show the splitting of two SCH_2 signals, besides one aromatic carbon signal, as in the case of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$, indicating the presence of two isomers. When an aqueous solution of $[\mathbf{3}\text{ or }\mathbf{4}]^{2+}$ was chromatographed on an SP-Sephadex C-25 column, only one band was eluted with a 0.15 mol dm^{-3} NaCl aqueous solution. On the other hand, the adsorbed band for $[\mathbf{3}\text{ or }\mathbf{4}]^{2+}$ was separated into two optically active bands, $(+)^{\mathrm{CD}}_{580}$ and $(-)^{\mathrm{CD}}_{580}$, on eluting with a 0.075 mol dm^{-3} $Na_2[Sb_2(R,R\text{-tartrato})_2]$ aqueous solution. Since the $(+)^{\mathrm{CD}}_{580}$ and $(-)^{\mathrm{CD}}_{580}$ eluates show CD spectra enantiomeric to each other, it is confirmed that $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ are the *racemic* compound. Accordingly, each of $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ can be as-

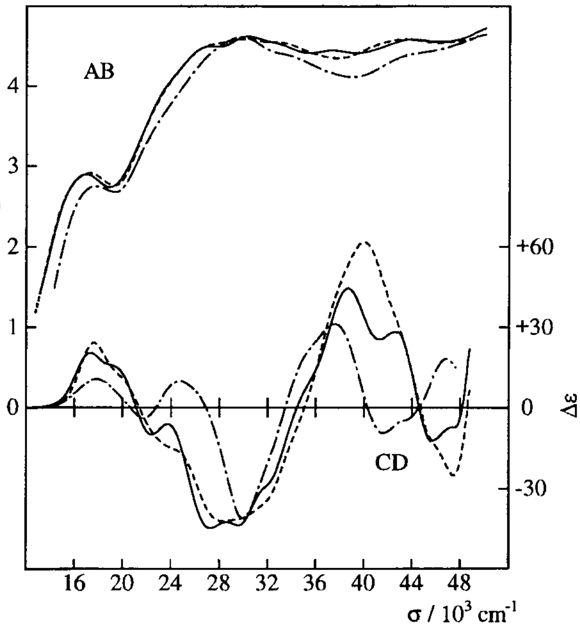


Fig. 4. Electronic absorption and CD spectra of $(+)^{\rm CD}_{580}$-[**3**]$^{2+}$ (—), $(+)^{\rm CD}_{580}$-[**4**]$^{2+}$ (- - -), and ΛΛ-[Pd{Co(aet)$_3$}$_2$]$^{2+}$ (-••-) in water.

signed to a mixture of C_2 symmetrical *racemic-syn* and *racemic-anti* isomers, which is consistent with the assignment of the two isomers proposed for [**1**]$^{2+}$ and [**2**]$^{2+}$. Unfortunately, attempts to separate the *racemic-syn* and *racemic-anti* isomers by column chromatography or fractional crystallization were unsuccessful. This can be explained by the similarities in their chemical properties, as shown by the NMR spectral behavior. The CD spectra of $(+)^{\rm CD}_{580}$-[**3**]$^{2+}$ and $(+)^{\rm CD}_{580}$-[**4**]$^{2+}$ resemble each other over the whole region, and their CD spectral patterns correspond with that of ΛΛ-[Pd{Co(aet)$_3$}$_2$]$^{2+}$ (Fig. 4).[9] This indicates that the $(+)^{\rm CD}_{580}$- and $(-)^{\rm CD}_{580}$ isomers for [**3**]$^{2+}$ and [**4**]$^{2+}$ have the ΛΛ and ΔΔ configurations, respectively.

Synthesis and Characterization of Mixed-Type $\mathrm{Co^{III}Pd^{II}Co^{III}}$ Complexes. The reaction of a 1:1 mixture of [**1**]Cl$_2$ and [Ni{Co(aet)$_2$(en)}$_2$]Cl$_4$ with Na$_2$[PdCl$_4$] was carried out in water, with the expectation of forming unique S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complexes consisting of both the tris(thiolato)-type [Co(aet)$_2$(pyt)] and the bis(thiolato)-type [Co(aet)$_2$(en)]$^{+}$ units. When the reaction solution was chromatographed onto an SP-Sephadex C-25 column, dark-green (A-1), brown (A-2), and red-brown (A-3) bands were eluted with 0.15 mol dm^{-3}, 0.30 mol dm^{-3}, and 0.50 mol dm^{-3} aqueous solutions of NaBr, respectively. It was found from the absorption spectral measurements that the A-1 and the A-3 eluates contain the divalent [Pd{Co(aet)$_2$(pyt)}$_2$]$^{2+}$ ([**3**]$^{2+}$) and the tetravalent [Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$,[18] respectively. The A-2 eluate showing a novel absorption spectrum was concentrated to a small volume to isolate a brown powder of [**5**]Br$_3$. A similar reaction using [**2**]Cl$_2$, instead of [**1**]Cl$_2$, led to the formation of [**6**]$^{3+}$, besides [Pd{Co(aet)$_2$(pymt)}$_2$]$^{2+}$ ([**4**]$^{2+}$) and [Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$. The elemental and plasma emission analyses of [**5**]Br$_3$ and [**6**]Br$_3$ are in good agreement with the formulas for the mixed-type $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complexes, [Pd{Co(aet)$_2$(pyt)}{Co(aet)$_2$(en)}]Br$_3$ and [Pd{Co(aet)$_2$(pymt)}{Co(aet)$_2$(en)}]Br$_3$, respectively. Furthermore, the molar conductivity measurements (364 Ω^{-1} cm^2 mol^{-1} for [**5**]Br$_3$, 371 Ω^{-1} cm^2 mol^{-1} for [**6**]Br$_3$) suggest that [**5**]$^{3+}$ and [**6**]$^{3+}$ are the trivalent species.

As illustrated in Fig. 5, the electronic absorption spectra of [**5**]$^{3+}$ and [**6**]$^{3+}$ are quite similar to each other, showing a visible absorption band at ca. 17.5 × 10^3 cm^{-1} and intense near-UV bands at ca. 28 × 10^3, 30.5 × 10^3, and 33.5 × 10^3 cm^{-1}. The overall absorption spectral behavior of [**5** or **6**]$^{3+}$ is just between the spectra of [**3** or **4**]$^{2+}$ and [Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$. Moreover, the ^{13}C NMR spectrum of [**5** or **6**]$^{3+}$ shows en methylene and pyt or pymt aromatic carbon signals, besides aet methylene carbon signals, which correspond with the signals observed for [**3** or **4**]$^{2+}$ and [Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$ (Table 2). From these results, it is assigned that [**5**]$^{3+}$ and [**6**]$^{3+}$ are the mixed-type S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complexes, [Pd{Co(aet)$_2$(en)}{Co(aet)$_2$(pyt)}]$^{3+}$ and [Pd{Co(aet)$_2$(en)}{Co(aet)$_2$(pymt)}]$^{3+}$, respectively, in which two types of $\mathrm{Co^{III}}$ octahedral units, *mer*(*S*)•*trans*($N_{\rm aet}$)-[Co(aet)$_2$(pyt or pymt)] and C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^{+}$, are linked by a $\mathrm{Pd^{II}}$ ion.

The number of the ^{13}C NMR signals implies the formation of only one geometrical isomer for [**5**]$^{3+}$ and [**6**]$^{3+}$, taking into account that the *syn–anti* isomerism does not exist in this mixed-type S-bridged structure and that its idealized symmetry is C_1. Preliminary experiments showed that [**5**]$^{3+}$ and [**6**]$^{3+}$ are partially resolved into two optically active isomers by the SP-Sephadex C-25 column chromatography with use of [Sb$_2$(*R*,*R*-tartrato)$_2$]$^{2-}$ as the eluent, which exhibit CD spectra enantiomeric to each other. Accordingly, it is concluded that [**5**]$^{3+}$ and [**6**]$^{3+}$ selectively form the *racemic* (ΔΔ/ΛΛ) isomer, which is compatible with the structural assignment for [**1**]$^{2+}$, [**2**]$^{2+}$, [**3**]$^{2+}$, and [**4**]$^{2+}$.

Concluding Remarks

In this study, the C_2 symmetrical S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ trinuclear complexes composed of two octahedral *mer*(*S*)•*trans*($N_{\rm aet}$)-[Co(aet)$_2$(pyt or pymt)] units, [Ni{Co(aet)$_2$(pyt or pymt)}$_2$]$^{2+}$ ([**1** or **2**]$^{2+}$), were successfully prepared by utilizing the chelate-transfer reaction of aet from $\mathrm{Ni^{II}}$ to $\mathrm{Co^{III}}$. As far as we know, these are the first examples of $\mathrm{Co^{III}}$ species containing both aliphatic and aromatic thiolato donors. The preparative method employed for [**1** or **2**]$^{2+}$ is similar to that used for [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$,[17] but is of greater advantage. That is, [**1**]$^{2+}$ and [**2**]$^{2+}$ were obtained "directly" from CoCl$_2$•6H$_2$O, pyt or pymt, and [Ni(aet)$_2$] in air with satisfactory yields (ca. 40–50%), while [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ was prepared by the reaction of the "isolated" [CoCl$_2$(en)$_2$]Cl with [Ni(aet)$_2$] in a poor yield (ca. 10%). Thus, this improved method could be applicable for the preparation of novel S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ trinuclear complexes containing a variety of functional chelating ligands in place of pyt or pymt. It was found that the central $\mathrm{Ni^{II}}$ ion in [**1** or **2**]$^{2+}$ is readily replaced by a $\mathrm{Pd^{II}}$ ion to form the corresponding $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complexes, [Pd{Co(aet)$_2$(pyt or pymt)}$_2$]$^{2+}$ ([**3** or **4**]$^{2+}$). The ^{13}C NMR spectroscopy indicated that these trinuclear complexes commonly afford two isomers, which are assigned as *racemic-syn* and *racemic-anti*, based on the optical resolution

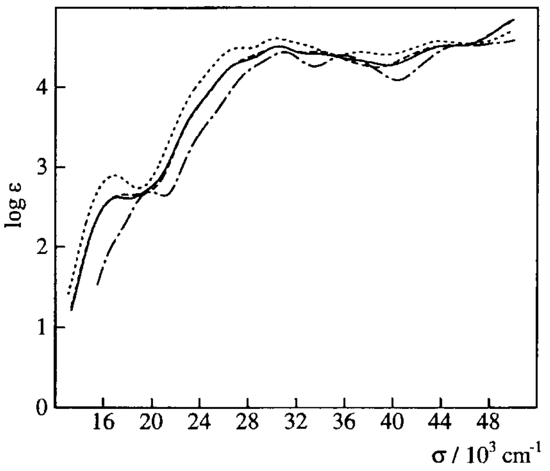


Fig. 5. Electronic absorption spectra of $[\mathbf{3}]^{2+}$ (···), $[\mathbf{5}]^{3+}$ (—), $[\mathbf{6}]^{3+}$ (- - -), and $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$ (-••-) in water.

of $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$. This assignment was confirmed by the selective formation of the *racemic* isomer for the C_1 symmetrical mixed-type trinuclear complexes, $[\mathrm{Pd\{Co(aet)_2(en)\}\{Co(aet)_2(pyt\ or\ pymt)\}}]^{3+}$ ($[\mathbf{5}$ or $\mathbf{6}]^{3+}$), which were prepared from $[\mathrm{Ni\{Co(aet)_2(pyt\ or\ pymt)\}_2}]^{2+}$ ($[\mathbf{1}$ or $\mathbf{2}]^{2+}$), $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$, and $[\mathrm{PdCl_4}]^{2-}$. Recently, we showed that only the *racemic-syn* isomer is formed for the related $\mathrm{Co^{III}Pd^{II}Co^{III}}$ complex composed of two *mer*(*S*)-$[\mathrm{Co(aet)_3}]$ units, $[\mathrm{Pd\{Co(aet)_3\}_2}]^{2+}$.[9] Thus, the electronic nature of the terminal non-bridging bidentate-*N*,*S* ligands seems to affect the relative stability of the *syn* isomer versus the *anti* isomer. Finally, it should be noted that the present trinuclear complexes possess aromatic thiolato groups at the terminal, which could still be available for bridging. It has been reported that S-bridged polynuclear structures formed by aromatic thiolate ligands are significantly different from those constructed with aliphatic thiolate ligands with respect to M–S bond distances and M–S–M bridging angles.[21–27] Accordingly, the novel construction of *mer*(*S*)-$[\mathrm{Co(aet)_2(pyt\ or\ pymt)}]$ units in the S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ structure performed in this study, together with the conversion to the $\mathrm{Co^{III}Pd^{II}Co^{III}}$ structure by a facile metal replacement reaction, would open the way to the creation of a new class of metallo-aggregates based on chiral thiolato $\mathrm{Co^{III}}$ octahedrons.

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