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Bull. Chem. Soc. Jpn., 72, 1685—1696 (1999) 1685

Headline Articles

Stereoselectivity for S-Bridged Polynuclear Transition Metal Complexes Formed by Aggregation of Octahedral Complexes to Square-Planar Palladium(II)

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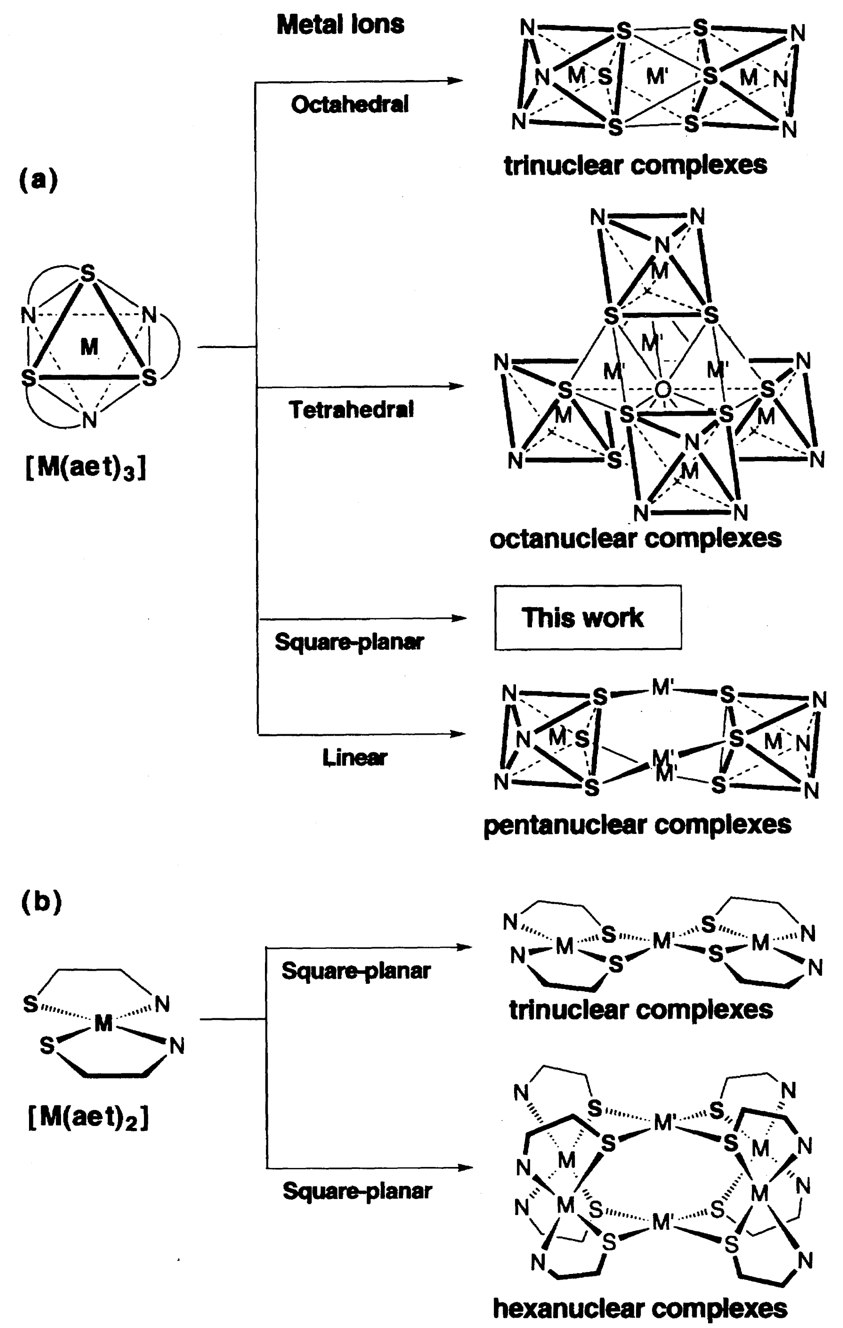
(Received December 1, 1998)

Novel pentanuclear complexes, $[Pd\{Pd(aet)\}\{M(aet)_2\}\{M(aet)_3\}_2]^{4+}$ (M = Rh (**1**); Ir (**2**); aet = 2-aminoethanethiolate) and $[Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ (**4**), were prepared by the reactions of *fac*(*S*)-$[M'(aet)_3]$ (M′ = M, Co) with $Na_2[PdCl_4]$. Molecular structures for **1**, **2** and **4** were determined by X-ray diffraction. In **1** and **2**, two Pd atoms forming the parallel planes are spanned by the aggregation of two octahedral *fac*(*S*)-$[M(aet)_3]$ units and *cis*(*N*)-$[M(S)_2(aet)_2]$ unit. In these complexes, one of the aet ligands in the starting *fac*(*S*)-$[M(aet)_3]$ transfers from the M (= Rh, Ir) atom to the Pd one. Two Pd atoms in **4** are bridged by two *fac*(*S*)-$[Co(aet)_3]$ units and *cis*(*S*)-$[Pd(aet)_2]$ unit. In this complex, two aet ligands transfer to the Pd one. The methylation reaction for one non-bridging S atom in **1** gave the corresponding complex $[Pd\{Pd(aet)\}\{Rh(aet)(smaet\}\{Rh(aet)_3\}_2]^{5+}$ (**3**; smaet = S-methyl-2-aminoethanethiolate), whose structure was also determined by X-ray diffraction. For all of the complexes, the chiral configurations are selectively regulated owing to the octahedral units (Δ or Λ) and the bridging sulfur atoms (*R* or *S*), and they are characterized on the basis of the electronic absorption, circular dichroism (CD) and ^{13}C NMR spectral behavior. The binding modes of the octahedral units in **1**, **2**, and **4** are also discussed in relation to their stereochemical behavior.

The octahedral complexes, *fac*(*S*)-$[M(aet)_3]$ (M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III}; aet = $NH_2CH_2CH_2S^-$), can be regarded as building blocks for the selective constructions of the S-bridged polynuclear complexes (Scheme 1). Since the structures of these polynuclear complexes are highly dependent on the coordination geometry of the reacting metal ions, a number of S-bridged complexes of trinuclear $[M'\{M(aet)_3\}_2]^{n+}$ (M′ = Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}),[1—4] octanuclear $[\{M(aet)_3\}_4M'_4O]^{6+}$ (M′ = Co^{II}, Zn^{II}, Cd^{II}, Hg^{II}),[7—10] and pentanuclear $[\{M(aet)_3\}_2M'_3]^{n+}$ (M′ = Ag^{I}, Hg^{II}),[5,6)] in which *fac*(*S*)-$[M(aet)_3]$ are linked by metal ions with an octahedral, tetrahedral, or linear type coordination geometry, have been investigated and some their properties have been clarified up to now (Scheme 1(a)). In such polynuclear complexes, the binding modes of the trinuclear complexes differ from those of the pentanuclear and octanuclear complexes, that is, three sulfur atoms in the former trinuclear complexes coordinate to the same M′ ion but those in the latter complexes do to three different M′ ions. The $[Co(aet)_2(en)]$ units in the linear-type trinuclear complexes $[\{Co(aet)_2(en)\}_2M']^{n+}$ (M′ = Ni^{II}, Pd^{II}) have two bridging sites and coordinate to the same M′ ions with the square-planar geometry.[11] Similarly, $[M(aet)_2]$ (M = Ni^{II}, Pd^{II}) have readily coordinated to one divalent metal ion to give S-bridged trinuclear complexes (Scheme 1(b)).[1a,12] In recent work, we reported that the reactions of $[M(aet)_2]$ with Pd(II) ion have produced hexanuclear complexes $[Pd_2\{M(aet)_2\}_4]^{4+}$ (Scheme 1(b)).[13] In these complexes, four *cis*(*S*)-$[M(aet)_2]$ units are aggregated around two Pd(II) planes, which are parallel to each other and have square-planar PdS_4 units, and two different Pd(II) atoms are bridged by the four units. A similar complex with the parallel planes was observed for the tetranuclear Pd(II) complex with L-cysteine (L-H_2cys), although it was randomly aggregated.[14] The aggregations of the octahedral complexes to the square-planar metal ions with the parallel planes are of interest in relation to the stereochemistry of the polynuclear complexes or the interactions between the parallel metals. However, there is no report of the S-bridged polynuclear complexes composed with the aggregation of *fac*(*S*)-$[M(aet)_3]$ to metal ions with a square-planar geometry. The reaction of Cu(II) ion with *fac*(*S*)-$[M(aet)_3]$ (M = Rh^{III}, Ir^{III}) produced the S-bridged octanuclear complexes, $[Cu_4\{M(aet)_3\}_2\{M_2(aet)_4(cysta)\}]^{6+}$ (cysta = cystamine), but it has caused the spontaneous reduction to trigonal-planar Cu(I) ion.[15] During the course of our synthetic investigation of such aggregations, we have found a fairly



Scheme 1.

stable pentanuclear complex, $[Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2]^{4+}$ (**1**), by the reaction of *fac*(*S*)-$[Rh(aet)_3]$ with the Pd(II) ion. A partial report on **1** has been published as a preliminary communication.[16] We report here the complete description of the synthesis, characterization, and some properties of **1**, the complex $[Pd\{Pd(aet)\}\{Rh(aet)(smaet)\}\{Rh(aet)_3\}_2]^{5+}$ (**3**; smaet = S-methyl-2-aminoethanethiolate) methylated on one non-bridging S atom in **1**, and the novel S-bridged polynuclear complexes (**2** and **4**) which will be formed by the aggregations of *fac*(*S*)-$[M(aet)_3]$ (M = Ir^{III} (**2**); Co^{III} (**4**)) to the Pd(II) ions. The spectrochemical and stereochemical properties of all of the complexes are discussed on the basis on the X-ray diffraction studies, and the electronic absorption, circular dichroism (CD), ^{13}C NMR and IR spectral behavior.

Experimental

Materials. $RhCl_3 \cdot nH_2O$ was purchased from N. E. Chemcat Co., Ltd. $IrCl_3$ was purchased from Rare Metallic Co., Ltd. $Na_2[Sb_2(d\text{-tartrato})_2] \cdot 5H_2O$ was prepared from Sb_2O_3 and $Na(d\text{-}H_3\text{tartrate}) \cdot H_2O$. The other reagents were purchased from Tokyo Kasei Kogyo Co., Ltd., Wako Pure Chemical Ind., Ltd., Kanto Chemical Co., Inc., and Aldrich Chemical Co., Inc. All chemicals were of reagent grade and were used without further purification.

Preparation of Mononuclear Complexes. *fac*(*S*)-$[Co(aet)_3]$,[1b] *fac*(*S*)-$[Rh(aet)_3]$,[2c,9a,17] and *fac*(*S*)-$[Ir(aet)_3]$[2c,3] were prepared by the methods in the literatures.

$[Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2]^{4+}$ (1). To a yellow aqueous suspension containing 0.20 g (0.62 mmol) of *fac*(*S*)-

[Rh(aet)$_3$] in 7 cm^3 of water was added 0.12 g (0.40 mmol) of Na$_2$[PdCl$_4$]. The mixture was stirred at 70 °C for 2 h, whereupon it became a red solution. After unreacted materials were removed by filtration, the filtrate was concentrated to a small volume with a rotary evaporator. The saturated NaCl solution was added to the solution, followed by cooling in a refrigerator. The resulting orange-red needle crystals (**1**Cl$_4$·8H$_2$O) were collected by filtration (0.06 g). The yield in the solution was about 95%, which was calculated by the absorbance for the eluate of the SP-Sephadex C-25 column. Found: C, 14.46; H, 4.67; N, 8.30; Rh, 20.5; Pd, 14.0%. Calcd for [Pd{Pd(aet)}{Rh(aet)$_2$}{Rh(aet)$_3$}$_2$]Cl$_4$·8H$_2$O = C$_{18}$H$_{70}$N$_9$S$_9$O$_8$Rh$_3$Pd$_2$Cl$_4$: C, 14.48; H, 4.73; N, 8.44; Rh, 20.7; Pd, 14.3%.

1Cl$_4$·8H$_2$O was dissolved in a small amount of water, and converted to the bromide salt by the use of a QAE-Sephadex A-25 column (Br$^-$ form, 3 cm×25 cm) eluting with water. The eluate was concentrated with a rotary evaporator to a small volume, and kept in a refrigerator for 1 d. The resulting dark red rod crystals (**1**Br$_4$·6H$_2$O) were collected by filtration. One of them, which were spontaneously resolved, was used for X-ray structure analysis. Each of the spontaneously resolved crystals was dissolved and its solution showed the positive and negative signs of the major CD component near 360 nm, $(+)^{\mathrm{CD}}_{360}$ and $(-)^{\mathrm{CD}}_{360}$ was collected into the quartz cells, respectively. The $\Delta\varepsilon$ values of the solution containing the $(-)^{\mathrm{CD}}_{360}$ isomer were evaluated on the basis of the absorption spectral data of **1**Cl$_4$·8H$_2$O. Found: C, 13.32; H, 4.05; N, 7.68: Rh, 18.5; Pd, 12.8%. Calcd for **1**Br$_4$·6H$_2$O: C, 13.22; H, 4.07; N, 7.71; Rh, 18.9; Pd, 13.0%.

[Pd{Pd(aet)}{Ir(aet)$_2$}{Ir(aet)$_3$}$_2$]$^{4+}$ (2). To an off-white suspension containing 0.50 g (1.19 mmol) of *fac*(*S*)-[Ir(aet)$_3$] in 60 cm^3 of water was added 0.24 g (0.80 mmol) of Na$_2$[PdCl$_4$]. The mixture was stirred at 80 °C for 3 d under a nitrogen atmosphere, whereupon it became a dark brown solution. After unreacted materials were removed by filtration, the filtrate was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm×25 cm). The main band containing the desired complex was eluted. The eluate was concentrated with a rotary evaporator until NaCl appeared and the deposited NaCl was filtered off. After the filtrate was cooled in a refrigerator, the resulting dark red crystals (**2**Cl$_4$·7.5H$_2$O) were collected by filtration. One of them was used for X-ray structure analysis. Yield 56% (calculated by the same method as in **1**). Found: C, 12.30; H, 4.03; N, 7.12%. Calcd for [Pd{Pd(aet)}{Ir(aet)$_2$}{Ir(aet)$_3$}$_2$]Cl$_4$·7.5H$_2$O = C$_{18}$H$_{69}$N$_9$S$_9$O$_{7.5}$Ir$_3$Pd$_2$Cl$_4$: C, 12.34; H, 3.97; N, 7.20%.

To a dark red solution of **2**Cl$_4$·7.5H$_2$O in a small amount of water was added saturated NaBr solution. After the filtrate was cooled in a refrigerator, the resulting dark red crystals (**2**Br$_4$·8H$_2$O) were collected by filtration. Found: C, 11.03; H, 3.61; N, 6.23; Ir, 29.54; Pd, 11.12%. Calcd for **2**Br$_4$·8H$_2$O: C, 11.15; H, 3.64; N, 6.50; Ir, 29.75; Pd, 10.98%.

An aqueous solution of **2**Cl$_4$·7.5H$_2$O was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 1 cm×50 cm), and it was eluted with a 0.25 mol dm^{-3} Na$_2$[Sb$_2$(*d*-tart)$_2$]·5H$_2$O aqueous solution. One dark red band was partially separated into two optical isomers. The first and the last fractions of the eluate showed the positive and negative signs of the major CD component near 370 nm, $(+)^{\mathrm{CD}}_{370}$ and $(-)^{\mathrm{CD}}_{370}$, respectively. The $\Delta\varepsilon$ values of each eluate containing the $(+)^{\mathrm{CD}}_{370}$ and $(-)^{\mathrm{CD}}_{370}$ isomers were evaluated on the basis of the absorption spectral data of **2**Cl$_4$·7.5H$_2$O.

[Pd{Pd(aet)}{Rh(aet)(smaet)}{Rh(aet)$_3$}$_2$]$^{5+}$ (3). To a solution containing 0.11 g (0.074 mmol) of **1**Cl$_4$·8H$_2$O, which was racemate, in 10 cm^3 of water was added 6 cm^3 of dimethyl sulfate. When the mixture was stirred at room temperature for 10 min and kept for 1 d, it separated into two layers. The orange-red upper layer was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm×25 cm). The reaction solution was made acidic with dimethyl sulfate; therefore, a column of SP-Sephadex C-25 should be swept by a sufficient quantity of water before eluting with NaCl solution in order to make the acidity low. When the adsorbed band was eluted with 1 mol dm^{-3} NaCl solution, only one band was eluted. The eluate was concentrated with a rotary evaporator until NaCl appeared and the deposited NaCl was filtered off. After the filtrate was cooled in a refrigerator, the resulting orange rod crystals (**3**Cl$_5$·10H$_2$O) were collected by filtration. One of them was used for X-ray structure analysis. Found: C, 14.27; H, 5.05; N, 7.79%. Calcd for [Pd{Pd(aet)}{Rh(aet)(smaet)}{Rh(aet)$_3$}$_2$]Cl$_5$·10H$_2$O = C$_{19}$H$_{77}$N$_9$S$_9$O$_{10}$Rh$_3$Pd$_2$Cl$_5$: C, 14.45; H, 4.91; N, 7.98%.

To a solution containing 0.22 g (0.14 mmol) of **1**Br$_4$·6H$_2$O in 20 cm^3 of water was added 20 cm^3 of dimethyl sulfate. When the mixture was stirred at room temperature for 20 min and kept for 1 d, it separated into two layers. The orange-red upper layer was poured onto a column of QAE-Sephadex A-25 (Br$^-$ form, 3 cm×25 cm), and the column was eluted with water. The eluate was concentrated with a rotary evaporator to a small volume, and it was kept in a refrigerator. The resulting orange crystals (**3**Br$_5$·11H$_2$O) were collected by filtration. Yield 86% (calculated by the same method as in **1**). Found: C, 12.49; H, 4.26; N, 6.79; Rh, 17.0; Pd, 11.2%. Calcd for [Pd{Pd(aet)}{Rh(aet)(smaet)}{Rh(aet)$_3$}$_2$]Br$_5$·11H$_2$O = C$_{19}$H$_{79}$N$_9$S$_9$O$_{11}$Rh$_3$Pd$_2$Br$_5$: C, 12.54; H, 4.38; N, 6.93; Rh, 17.0; Pd, 11.7%.

An aqueous solution of **3**Cl$_5$·10H$_2$O was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 1 cm×50 cm), and eluted with a 0.25 mol dm^{-3} Na$_2$[Sb$_2$(*d*-tart)$_2$]·5H$_2$O aqueous solution. The orange-red band was partially separated to two optical isomers. The first and the last fractions of the eluate showed the negative and positive signs of the major CD component near 370 nm, $(-)^{\mathrm{CD}}_{370}$ and $(+)^{\mathrm{CD}}_{370}$, respectively. The $\Delta\varepsilon$ values of each eluate containing the $(-)^{\mathrm{CD}}_{370}$ and $(+)^{\mathrm{CD}}_{370}$ isomers were evaluated on the basis of the absorption spectral data of **3**Cl$_5$·10H$_2$O.

[Pd$_2${Pd(aet)$_2$}{Co(aet)$_3$}$_2$]$^{4+}$ (4). To a green-blue suspension containing 0.21 g (0.71 mmol) of *fac*(*S*)-[Co(aet)$_3$] in 30 cm^3 of water was added 0.24 g (0.80 mmol) of Na$_2$[PdCl$_4$]. The mixture was stirred at 35 °C for 3 d, whereupon it became a dark brown solution. After we removed unreacted materials and yellow powder ([Pd(aet)$_2$]) by filtration, the filtrate was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm×25 cm). Four bands, brown (F-1), brownish green (F-2), black (F-3), and dark brown (F-4) bands, were eluted in this order. The bands F-1 and F-2 were eluted with a 0.3 mol dm^{-3} NaCl solution, and their eluates showed the absorption spectra identical with *meso*- and *rac*-[Co{Co(aet)$_3$}$_2$]$^{3+}$, respectively.[1b,18] The eluate F-4 was so little that its structure was not determined. The main eluate F-3 was eluted with a 0.5 mol dm^{-3} NaCl solution, and concentrated with a rotary evaporator until NaCl appeared. The deposited NaCl was filtered off. After cooling in a refrigerator, the resulting black crystals (**4**Cl$_4$·5.5H$_2$O) were collected by filtration. Yield 35% (calculated by the same method as in **1**). Found: C, 14.81; H, 4.43; N, 8.47; Co, 8.53; Pd, 25.31%. Calcd for [Pd$_2${Pd(aet)$_2$}{Co(aet)$_3$}$_2$]Cl$_4$·5.5H$_2$O = C$_{16}$H$_{59}$N$_8$S$_8$O$_{5.5}$Co$_2$Pd$_3$Cl$_4$: C, 14.93; H, 4.62; N, 8.71; Co, 9.15; Pd, 24.80%.

An aqueous solution of **4**Cl$_4$·5.5H$_2$O was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm×25 cm), and it was eluted with a 0.25 mol dm^{-3} Na$_2$[Sb$_2$(*d*-tart)$_2$]·5H$_2$O aqueous solution.

One black band was partially separated into two optical isomers. The first and the last fractions of the eluate showed the positive and negative signs of the major CD component near 360 nm, $(+)^{\mathrm{CD}}_{360}$ and $(-)^{\mathrm{CD}}_{360}$, respectively. The $\Delta\varepsilon$ values of each eluate containing the $(+)^{\mathrm{CD}}_{360}$ and $(-)^{\mathrm{CD}}_{360}$ isomers were evaluated on the basis of the absorption spectral data of $\mathbf{4}Cl_4\cdot 5.5H_2O$.

Measurements. The electronic absorption spectra were recorded with a JASCO V-560 spectrophotometer, and the CD spectra with a JASCO J-600 spectropolarimeter. The measurements were carried out in aqueous solutions at room temperature. The concentrations of the Pd, Rh, Ir, Co, and Pt atoms in the complexes were determined with NIPPON Jarrel-Ash ICPA-575 ICP spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AM-500 NMR spectrometers at a probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The molar conductances of the complexes were measured with a Horiba conductivity meter DS-14 in aqueous solution at room temperature. The infrared spectra were recorded as a KBr disk with a JASCO FT/IR-550 spectrometer. The elemental analyses (C, H, N) were done by the Analysis Center of the University of Tsukuba. Molecular mechanics (MM2) calculations were performed by a Macintosh computer using the CAChe program package.[19]

Crystallography. Single crystals of $(-)^{\mathrm{CD}}_{360}$-$\mathbf{1}Br_4\cdot 6H_2O$ and $\mathbf{3}Cl_5\cdot 10H_2O$ were used for data collection on an Enraf Nonius CAD4 diffractometer, and those of $\mathbf{2}Cl_4\cdot 7.5H_2O$ and $\mathbf{4}Cl_4\cdot 5.5H_2O$ were used on a Rigaku RASA-7S diffractometer with graphite monochromated Mo $K\alpha$ radiation. Each of the unit-cell parameters was determined by least-squares refinement of 25 reflections. The experimental parameters are listed in Table 1. The intensity data were collected by the ω–2θ scan technique. 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 $I_o > 1.5\sigma(I_o)$ were used for structure determinations.

The positions of most non-hydrogen atoms were located by the direct method.[20] 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 for the non-hydrogen atoms in each complex. The hydrogen atoms were fixed by the geometrical and thermal constrains (C–H = N–H = 0.95 Å, $U = 1.3\ U$(C or N)). The occupancy factors (occ) for some water molecules are listed in the deposited Tables S2—S4.[21] The parameters for the $\Delta\Lambda\Delta$ configuration of the complex $(-)^{\mathrm{CD}}_{360}$-$\mathbf{1}Br_4\cdot 6H_2O$ converged to $R = 0.063$ and $R_w = 0.071$, and those for the enantiomeric $\Lambda\Delta\Lambda$ configuration did to $R = 0.072$ and $R_w = 0.083$. These facts indicate that the former is probably the correct choice, namely the $(-)^{\mathrm{CD}}_{360}$-$\mathbf{1}Br_4\cdot 6H_2O$ isomer has the $\Delta\Lambda\Delta$ configuration (Fig. 1). All the calculations were performed on an

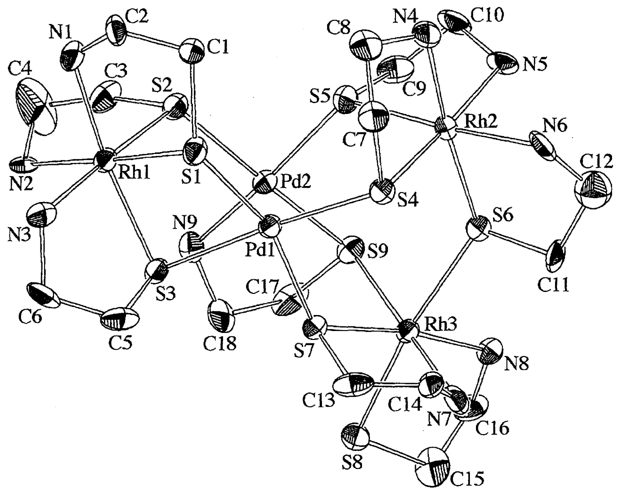


Fig. 1. Perspective view of $[Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2]^{4+}$ (**1**) with the atomic labeling scheme.

Table 1. Crystallographic Data

	$\mathbf{1}Br_4\cdot 6H_2O$	$\mathbf{2}Cl_4\cdot 7.5H_2O$	$\mathbf{3}Cl_5\cdot 10H_2O$	$\mathbf{4}Cl_4\cdot 5.5H_2O$
Formula	$C_{18}H_{66}N_9S_9O_6Br_4Rh_3Pd_2$	$C_{18}H_{69}N_9S_9O_{7.5}Cl_4Ir_3Pd_2$	$C_{19}H_{74}N_9S_9O_{10}Cl_5Rh_3Pd_2$	$C_{16}H_{59}N_8S_8O_{5.5}Cl_4Co_2Pd_3$
Fw	1634.45	1751.61	1576.17	1287.05
Cryst dimens/mm	0.48 × 0.25 × 0.08	0.30 × 0.28 × 0.15	0.33 × 0.18 × 0.07	0.35 × 0.25 × 0.18
Color	Red	Dark-red	Orange	Black
Space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	14.035(2)	13.845(3)	13.107(5)	13.500(2)
b/Å	17.317(2)	21.490(5)	27.456(5)	14.893(3)
c/Å	19.792(3)	16.409(4)	15.822(7)	12.087(2)
α/deg				108.40(1)
β/deg		100.50(2)	106.23(2)	108.70(1)
γ/deg				84.79(1)
V/Å^3	4810(1)	4800(1)	5466(3)	2184(6)
Z	4	4	4	2
μ/cm^{-1}	55.05	97.06	21.66	26.22
Transm factor	0.69—1.00	0.37—1.00	0.82—1.00	0.81—1.00
2θ range/°	0—50	0—55	0—50	0—55
No. of reflcns measd	4732	11803	10234	10482
No. of reflcns used	4098	8922	7387	8593
No. of variables used	431	478	488	434
D_{calcd}/g cm^{-3}	2.257	2.424	1.915	1.957
R (R_w)	0.063 (0.071)	0.032 (0.046)	0.058 (0.076)	0.034 (0.060)
GOF	1.71	1.17	1.56	1.68

Indigo II computer using the crystallographic package teXan.[20] The final atomic positional parameters are deposited in Tables S1—S4.[21]

Results and Discussion

Syntheses and Stereochemistry. The perspective drawings of the complex cations, **1**—**4**, and the polyhedral representations are illustrated in Figs. 1, 2, 3, 4, and 5, and their selected bond distances and angles are listed in Tables 2 and 3. As shown in Figs. 1, 2, and 5, **1** and **2** contain three M (Rh (**1**); Ir (**2**)) and two Pd atoms to form the pentanuclear complexes, $[\mathrm{Pd\{Pd(aet)\}\{M(aet)_2\}\{M(aet)_3\}_2}]^{4+}$. This is consistent with the plasma emission spectral analysis, which gave a value of M : Pd = 3 : 2. The Pd(1) atom in **1** and **2** is surrounded by four S atoms from the M(1), M(2), and M(3) units, while one bidentate aet ligand and two S atoms from M(1) and M(2) units complete the square-planar geometry for the Pd(2) atom. In the two square-planar Pd planes in **1**

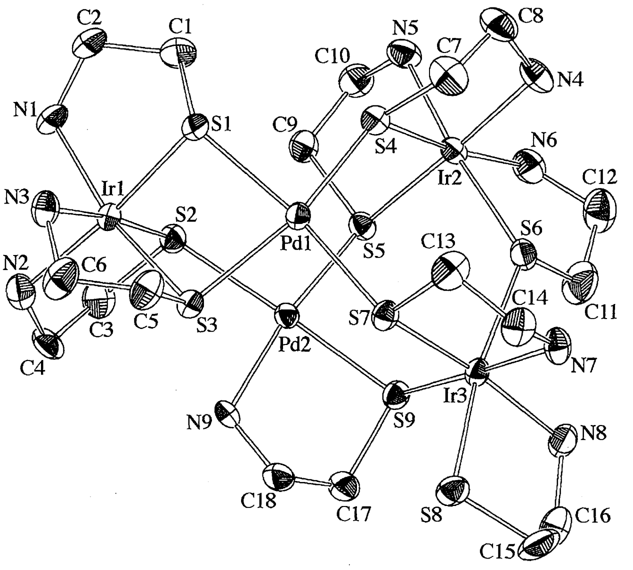


Fig. 2. Perspective view of $[\mathrm{Pd\{Pd(aet)\}\{Ir(aet)_2\}\{Ir(aet)_3\}_2}]^{4+}$ (**2**) with the atomic labeling scheme.

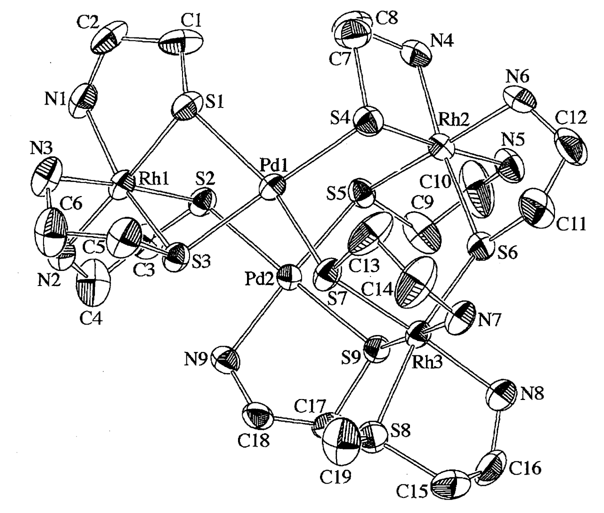


Fig. 3. Perspective view of $[\mathrm{Pd\{Pd(aet)\}\{Rh(aet)(smaet)\}\{Rh(aet)_3\}_2}]^{5+}$ (**3**) with the atomic labeling scheme.

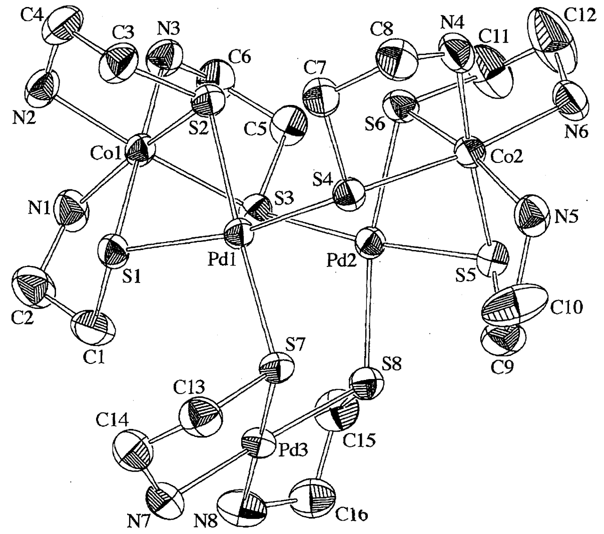


Fig. 4. Perspective view of $[\mathrm{Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2}]^{4+}$ (**4**) with the atomic labeling scheme.

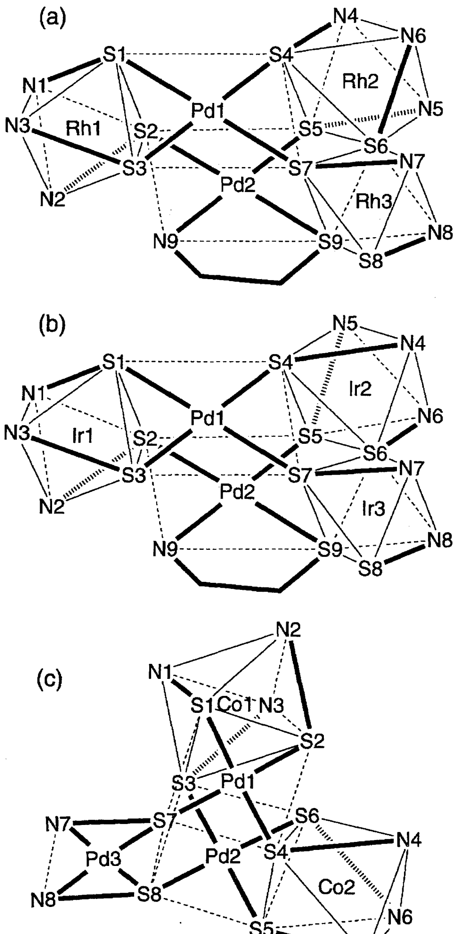


Fig. 5. Polyhedral representations of $[\mathrm{Pd\{Pd(aet)\}\{M(aet)_2\}\{M(aet)_3\}_2}]^{4+}$ M = Rh (a; $\Delta\Lambda\Delta$ isomer) and Ir (b; $\Delta\Delta\Delta$ isomer), and $[\mathrm{Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2}]^{4+}$ (c; $\Lambda\Lambda$ isomer); the chemical bonds and chelate rings denote thick solid or dotted lines.

Table 2. Selected Bond Distances (Å) and Angles (°) of **1**$Br_4 \cdot 6H_2O$, **2**$Cl_4 \cdot 7.5H_2O$, and **3**$Cl_5 \cdot 10H_2O$

	1: M = Rh	**2**: M = Ir	**3**: M = Rh		**1**: M = Rh	**2**: M = Ir	**3**: M = Rh
Pd(1)–Pd(2)	3.050(2)	3.1534(7)	3.0887(9)	S(1)–M(1)–S(2)	92.7(2)	97.28(6)	93.34(10)
Pd(1)–S(1)	2.363(5)	2.338(2)	2.344(3)	S(1)–M(1)–S(3)	83.1(2)	81.64(6)	81.75(9)
Pd(1)–S(3)	2.382(5)	2.424(2)	2.369(3)	S(2)–M(1)–S(3)	91.3(2)	92.63(6)	92.58(9)
Pd(1)–S(4)	2.321(5)	2.320(2)	2.315(3)	S(1)–M(1)–N(1)	86.7(5)	85.6(2)	85.7(3)
Pd(1)–S(7)	2.310(5)	2.330(2)	2.334(3)	S(1)–M(1)–N(2)	178.1(4)	174.5(2)	178.0(2)
Pd(2)–S(2)	2.395(5)	2.360(2)	2.374(3)	S(2)–M(1)–N(2)	86.1(5)	84.7(2)	85.9(2)
Pd(2)–S(5)	2.295(5)	2.322(2)	2.294(3)	S(2)–M(1)–N(3)	176.6(5)	174.1(2)	176.0(3)
Pd(2)–S(9)	2.326(5)	2.326(2)	2.317(2)	S(3)–M(1)–N(1)	169.8(5)	167.3(2)	167.4(3)
Pd(2)–N(9)	2.07(2)	2.089(6)	2.088(7)	S(3)–M(1)–N(3)	85.9(4)	86.1(2)	86.3(3)
M(1)–S(1)	2.297(5)	2.303(2)	2.298(3)	S(4)–M(2)–S(5)	94.2(2)	95.08(6)	96.26(9)
M(1)–S(2)	2.344(5)	2.346(2)	2.334(3)	S(4)–M(2)–S(6)	94.8(2)	99.06(6)	94.61(9)
M(1)–S(3)	2.291(5)	2.334(2)	2.313(2)	S(5)–M(2)–S(6)	96.0(2)	96.71(6)	98.97(9)
M(1)–N(1)	2.12(2)	2.128(6)	2.125(8)	S(4)–M(2)–N(4)	86.3(5)	84.9(2)	87.5(3)
M(1)–N(2)	2.10(2)	2.133(7)	2.103(8)	S(4)–M(2)–N(5)	176.1(4)	88.3(2)	177.1(2)
M(1)–N(3)	2.13(2)	2.117(6)	2.092(9)	S(4)–M(2)–N(6)	89.6(5)	174.2(2)	88.5(2)
M(2)–S(4)	2.309(5)	2.307(2)	2.315(3)	S(5)–M(2)–N(4)	89.7(5)	176.7(2)	86.2(2)
M(2)–S(5)	2.321(5)	2.316(2)	2.314(2)	S(5)–M(2)–N(5)	85.5(5)	85.7(2)	84.8(2)
M(2)–S(6)	2.295(5)	2.329(2)	2.327(3)	S(5)–M(2)–N(6)	175.6(5)	88.6(2)	173.4(2)
M(2)–N(4)	2.13(2)	2.130(6)	2.092(8)	S(6)–M(2)–N(4)	174.1(5)	86.6(2)	174.2(2)
M(2)–N(5)	2.10(1)	2.129(6)	2.117(8)	S(6)–M(2)–N(5)	89.1(4)	172.0(2)	87.8(3)
M(2)–N(6)	2.14(2)	2.122(6)	2.114(8)	S(6)–M(2)–N(6)	85.7(6)	85.0(2)	85.1(2)
M(3)–S(6)	2.378(5)	2.369(2)	2.372(3)	S(6)–M(3)–S(7)	104.9(2)	96.47(6)	101.08(9)
M(3)–S(7)	2.306(5)	2.321(2)	2.320(3)	S(6)–M(3)–S(8)	168.1(2)	170.01(6)	166.8(1)
M(3)–S(8)	2.352(5)	2.361(2)	2.347(3)	S(6)–M(3)–S(9)	82.6(2)	91.73(6)	83.14(9)
M(3)–S(9)	2.358(5)	2.331(2)	2.374(3)	S(7)–M(3)–S(8)	86.9(2)	86.85(6)	91.6(1)
M(3)–N(7)	2.11(2)	2.127(6)	2.117(9)	S(7)–M(3)–S(9)	92.7(2)	97.28(6)	97.27(9)
M(3)–N(8)	2.10(1)	2.126(6)	2.109(8)	S(8)–M(3)–S(9)	96.7(2)	97.21(7)	91.61(9)
				S(7)–M(3)–N(7)	84.3(5)	84.9(2)	84.4(2)
S(1)–Pd(1)–S(3)	79.8(2)	79.03(6)	79.63(9)	S(7)–M(3)–N(8)	171.5(4)	170.5(2)	172.9(2)
S(1)–Pd(1)–S(4)	102.1(2)	89.93(7)	102.61(10)	S(8)–M(3)–N(8)	85.4(4)	84.0(2)	83.3(2)
S(1)–Pd(1)–S(7)	161.0(2)	161.49(7)	156.64(10)	S(9)–M(3)–N(7)	176.2(5)	175.4(2)	176.6(2)
S(3)–Pd(1)–S(4)	175.8(2)	161.94(6)	177.55(9)	Pd(1)–S(1)–M(1)	91.1(2)	92.00(6)	91.76(9)
S(3)–Pd(1)–S(7)	85.3(2)	90.54(6)	86.79(9)	Pd(2)–S(2)–M(1)	116.3(2)	115.82(7)	112.44(10)
S(4)–Pd(1)–S(7)	92.1(2)	103.64(6)	91.41(10)	Pd(1)–S(3)–M(1)	90.7(2)	89.09(6)	90.77(9)
S(2)–Pd(2)–S(5)	86.4(2)	94.72(6)	85.68(9)	Pd(1)–S(4)–M(2)	113.7(2)	119.56(8)	113.2(1)
S(2)–Pd(2)–S(9)	175.6(2)	176.46(6)	177.25(8)	Pd(2)–S(5)–M(2)	125.2(2)	121.07(7)	123.6(1)
S(2)–Pd(2)–N(9)	93.5(5)	92.9(2)	94.9(2)	M(2)–S(6)–M(3)	127.8(2)	129.64(7)	128.4(1)
S(5)–Pd(2)–S(9)	93.6(2)	85.85(6)	92.26(9)	Pd(1)–S(7)–M(3)	127.1(2)	127.08(7)	124.7(1)
S(5)–Pd(2)–N(9)	171.9(5)	166.0(2)	170.4(2)	Pd(2)–S(9)–M(3)	110.0(2)	112.95(7)	114.47(10)
S(9)–Pd(2)–N(9)	85.8(5)	85.8(2)	86.9(2)				

and **2**, their least-square planes are almost parallel, that is, their dihedral angles are 8.4° for **1** and 11.7° for **2**. Each of the M(1) and M(2) atoms is an approximately octahedral *fac*(*S*)-[M(aet)$_3$] unit, retaining the structure of the starting mononuclear complex. All of the S atoms in the M(1) unit are used as bridging atoms for the Pd(1) and Pd(2) atoms; that is, the Pd(1) atom through two S atoms (S(1) and S(3)) and the Pd(2) atom through one S(2) atom. This indicates the unprecedented binding modes for the *fac*(*S*)-[M(aet)$_3$] units. Two S (S(4) and S(5)) atoms in the M(2) unit also bridge between the Pd(1) and Pd(2) atoms, but a third S atom coordinates to the M(3) atom. Therefore, three S atoms of the M(2) unit are bound to three different metal atoms (Pd(1), Pd(2) and Rh(3)). This binding mode is similar to those observed for the *fac*(*S*)-[M(aet)$_3$] units in $[\{M(aet)_3\}_2M'_3]^{n+}$ (M′ = Ag^{I}, Hg^{II})[5,6] and $[\{M(aet)_3\}_4M'_4O]^{6+}$ (M′ = Co^{II}, Zn^{II}, Cd^{II}, Hg^{II}).[7—10] In the M(3) unit, only two aet ligands chelate the M(3) atom and two remaining coordination sites are occupied by two S atoms of the aet ligands coordinated to the M(2) and Pd(2) atoms, giving an approximately octahedral *cis*(*N*) geometry around the M(3) atom. This means that one of the aet ligands in the starting *fac*(*S*)-[M(aet)$_3$] transfers from the M(3) atom to the Pd one. This is the first example of the transfer of the aet ligands from the *fac*(*S*)-[M(aet)$_3$] units to the other metals.[1—10] These facts also indicate that the environments of the three M units differ from one another. The structure of **3** is quite similar to that of the starting pentanuclear complex **1** except for the methyl group (Figs. 1 and 3, and Table 2). In the crystal of **3**, the two least-square planes for two Pd atoms also are almost parallel (the dihedral angle, 10.5°), and three mononuclear octahedral units are aggregated around them (Figs. 3 and 5).

The structure of **4**, which was obtained by reaction similar to **1** and **2**, is significantly different from those of **1** and

Table 3. Selected Bond Distances (Å) and Angles (°) of **4**Cl$_4$·5.5H$_2$O)

Pd(1)–Pd(2)	2.9830(4)	Pd(1)–S(1)	2.329(1)
Pd(1)–S(2)	2.349(1)	Pd(1)–S(4)	2.341(1)
Pd(1)–S(7)	2.346(1)	Pd(2)–S(3)	2.362(1)
Pd(2)–S(5)	2.302(1)	Pd(2)–S(6)	2.375(1)
Pd(2)–S(8)	2.337(1)	Pd(3)–S(7)	2.272(1)
Pd(3)–S(8)	2.266(1)	Pd(3)–N(7)	2.077(4)
Pd(3)–N(8)	2.093(5)	Co(1)–S(1)	2.235(1)
Co(1)–S(2)	2.236(1)	Co(1)–S(3)	2.319(1)
Co(1)–N(1)	2.011(4)	Co(1)–N(2)	1.995(4)
Co(1)–N(3)	2.004(4)	Co(2)–S(4)	2.305(1)
Co(2)–S(5)	2.217(1)	Co(2)–S(6)	2.239(1)
Co(2)–N(4)	1.995(4)	Co(2)–N(5)	2.006(4)
Co(2)–N(6)	1.993(4)		
S(1)–Pd(1)–S(2)	77.48(4)	S(1)–Pd(1)–S(4)	167.38(4)
S(1)–Pd(1)–S(7)	102.79(4)	S(2)–Pd(1)–S(4)	95.12(4)
S(2)–Pd(1)–S(7)	174.33(4)	S(4)–Pd(1)–S(7)	85.60(4)
S(3)–Pd(2)–S(5)	171.62(4)	S(3)–Pd(2)–S(6)	96.51(4)
S(3)–Pd(2)–S(8)	96.35(4)	S(5)–Pd(2)–S(6)	78.25(4)
S(5)–Pd(2)–S(8)	88.94(4)	S(6)–Pd(2)–S(8)	167.14(4)
S(7)–Pd(3)–N(7)	86.6(1)	S(7)–Pd(3)–N(8)	178.3(1)
S(8)–Pd(3)–N(7)	176.5(1)	S(8)–Pd(3)–N(8)	86.6(1)
S(1)–Co(1)–S(2)	81.81(5)	S(1)–Co(1)–S(3)	94.66(4)
S(2)–Co(1)–S(3)	92.75(4)	S(1)–Co(1)–N(1)	87.4(1)
S(1)–Co(1)–N(3)	179.1(1)	S(2)–Co(1)–N(1)	169.2(1)
S(2)–Co(1)–N(2)	88.0(1)	S(3)–Co(1)–N(2)	174.2(1)
S(3)–Co(1)–N(3)	85.5(1)	S(4)–Co(2)–S(5)	98.80(5)
S(4)–Co(2)–S(6)	90.33(4)	S(5)–Co(2)–S(6)	82.97(5)
S(4)–Co(2)–N(4)	85.2(1)	S(4)–Co(2)–N(6)	172.4(1)
S(5)–Co(2)–N(4)	176.0(1)	S(5)–Co(2)–N(5)	84.9(1)
S(6)–Co(2)–N(5)	167.6(1)	S(6)–Co(2)–N(6)	88.5(1)
Pd(1)–S(1)–Co(1)	91.59(4)	Pd(1)–S(2)–Co(1)	91.06(4)
Pd(2)–S(3)–Co(1)	122.35(5)	Pd(1)–S(4)–Co(2)	120.53(5)
Pd(2)–S(5)–Co(2)	92.69(4)	Pd(2)–S(6)–Co(2)	90.20(4)
Pd(1)–S(7)–Pd(3)	106.53(4)	Pd(2)–S(8)–Pd(3)	112.33(5)

2. As shown in Figs. 4 and 5, **4** takes also an S-bridged pentanuclear structure, but consists of two octahedral Co and three square-planar Pd atoms. Both the Pd(1) and the Pd(2) atoms are surrounded by four S atoms from the Co(1), Co(2), and Pd(3) units, and their least-square planes are almost parallel (the dihedral angle is 11.4°). The binding modes of the approximately octahedral Co(1) and Co(2) units for the parallel Pd planes are the same as those observed for the M(1) units in **1** and **2**, namely, the two Pd atoms are bound through all three S atoms in each of the Co(1) and Co(2) units. The remaining coordination sites on the Pd(1) and Pd(2) atoms are occupied by two S atoms in the Pd(3) unit, which is surrounded by two aet ligands with *cis*(*S*) geometry, *cis*(*S*)-[Pd(aet)$_2$]. This suggests that two aet ligands transfer from the starting *fac*(*S*)-[Co(aet)$_3$] to the Pd atom.

The reaction of *fac*(*S*)-[M(aet)$_3$] (M = Rh (**1**); Ir (**2**)) with Na$_2$[PdCl$_4$] was performed by the molar ratio of M : Pd = 3 : 2 in water to give novel pentanuclear S-bridged complexes, [Pd{Pd(aet)}{M(aet)$_2$}{M(aet)$_3$}$_2$]$^{4+}$. As shown in the crystal system (Table 1), **1** exists as the spontaneously resolved materials to give two optically active isomers (vide infra), $(-)^{\mathrm{CD}}_{360}$-$\Delta\Lambda\Delta$-**1** and $(+)^{\mathrm{CD}}_{360}$-$\Lambda\Delta\Lambda$-**1**, in which $\Delta\Lambda\Delta$ and $\Lambda\Delta\Lambda$ denote the absolute configurations for the M(1), M(2), and M(3) units, since the octahedral M units can take the Δ and Λ configurations. These suggest that a pair of enantiomer in many isomers is selectively formed for **1**. Similarly, a pair of enantiomer of the $\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda$ configurations is selectively formed for **2** in the crystal. Taking both of these structures and molecular model constructions into consideration, it is indicated in **1** and **2** that the S(6) atom in the M(2) unit exists the opposite direction to the M(1) unit and the M(2) unit can take both of the Δ and Λ configurations, when the M(1) unit takes the Δ (or Λ) configuration (Fig. 5). In this situation, the M(3) unit has to take the Δ (or Λ) configuration, since the N(9) atom can transfer from the M(3) unit to the Pd(2) atom, because the N(9) atom in the Λ configuration could not transfer to the Pd(2) atom (Figs. 1, 2, and 5). This coincides well with the results that only $\Delta\Lambda\Delta$ and $\Delta\Delta\Delta$ (or its enantiomers) isomers in the pentanuclear complexes have been obtained in many isomers for **1** and **2**. The MM2 calculations of these optical isomers indicate that the stability orders of the isomers are the $\Delta\Lambda\Delta$ (or $\Lambda\Delta\Lambda$) and $\Delta\Delta\Delta$ (or $\Lambda\Lambda\Lambda$) configurations of the M(1), M(2), and M(3) units for **1** and **2** (343 and 411×10^3 J mol^{-1} for **1**; 347 and 411×10^3 J mol^{-1} for **2**, respectively). This MM2 calculation, accordingly, is consistent with the formation of **1**. In **2**, the $\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda$ configurations are formed in the crystal, but they are relatively low yield. Taking accounts of the result of the second stable pair by the MM2 calculations and the selective formation of **1**, it is reasonable to assume that the isolation of the $\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda$ isomers in **2** depends on the solubility and/or packing modes of the isomers in the crystal. When the *fac*(*S*)-[Ir(aet)$_3$] molecule, which is more stable than *fac*(*S*)-[Rh(aet)$_3$],[3] was allowed to react with Na$_2$[PdCl$_4$] under the same preparation condition as **1**, little **2** was formed. This indicates that the formation of **2** requires more severe conditions than that of **1** in order to ligand-transfer one aet ligand from *fac*(*S*)-[M(aet)$_3$] to the Pd(II) coordination sphere. This consideration is supported by the stability of mononuclear complexes (*fac*(*S*)-[Co(aet)$_3$] < *fac*(*S*)-[Rh(aet)$_3$] ≪ *fac*(*S*)-[Ir(aet)$_3$]), as investigated in the previous paper.[2,3]

In complex **1**, one thiolato S atom in the Rh(3) unit coordinates only to the Pd atom, and the chemical modification of the non-bridging S atom is performed with dimethyl sulfate, which is strongly acidic. This reaction proceeds with retention of the structure. This complex can also be prepared with methyl iodide, which is neutral, instead of dimethyl sulfate, as a methylation agent. This suggests that the methylation in **1** is not affected by the acidity and that the pentanuclear complex is fairly stable under these conditions.

Although **4** was obtained by reactions similar to those for **1** and **2**, its structure differs significantly from those of **1** and **2**. In addition to two *fac*(*S*)-[Co(aet)$_3$] units, the parallel Pd(II) planes are bridged by the *fac*(*S*)-[Pd(aet)$_2$] unit, accompanied by the replacement of the aet ligands from the starting *fac*(*S*)-[Co(aet)$_3$] to the Pd(II) atom, giving [Pd$_2${Pd(aet)$_2$}{Co(aet)$_3$}$_2$]$^{4+}$ (Figs. 4 and 5). This formation mechanism for **4** is different from those for **1** and **2**. When the MM2 calculation was achieved for the optical isomers of **4**, it is indicated that the most stable isomer is the $\Lambda\Lambda_{\mathrm{SR}}$ (or $\Delta\Delta_{\mathrm{RS}}$) form ($273\times10^3$ J mol^{-1}; the others 325—425×10^3 J mol^{-1}) in the configurational chirality (Λ and Δ) of the *fac*(*S*)-[Co(aet)$_3$] units and the asymmetric sulfur atoms (*S* and *R*) of the *cis*(*S*)-[Pd(aet)$_2$] units (Fig. 5). This is good agreement with the results that the $\Lambda\Lambda_{\mathrm{SR}}$ (or $\Delta\Delta_{\mathrm{RS}}$) isomer in **4** is selectively formed. In order to form a pentanuclear complex which corresponds to **1** and **2**, the reaction of *fac*(*S*)-[Co(aet)$_3$] with Pd(II) ion was firstly attempted by the molar ratio of Co : Pd = 3 : 2 in water under mild conditions. However, the reaction products involve fairly large amounts of *meso*- and *rac*-[Co{Co(aet)$_3$}$_2$]$^{3+}$,[1b,18] which is exhibited by the use of the column chromatographic separations. The attempts to obtain the main product **4** were tried by some syntheses under several conditions, and it was achieved by the ratio of Co : Pd = 1 : 1. These facts seem to indicate that the stability of the *fac*(*S*)-[M(aet)$_3$] (M = Co$^{\mathrm{III}}$, Rh$^{\mathrm{III}}$, Ir$^{\mathrm{III}}$) units depend on the formation of the S-bridged polynuclear complexes with the parallel Pd(II) geometry spanned by the aggregation of the complexes.

Characterizations. The ^{13}C NMR chemical shifts of [Pd{Pd(aet)}{M(aet)$_2$}{M(aet)$_3$}$_2$]$^{4+}$ (M = Rh (**1**); Ir (**2**)) exhibit sixteen resonance lines for **1** and fifteen ones for **2** due to the eighteen methylene carbon atoms of the aet ligand (Fig. 6 and Table 4). They are divided into two kinds of groups, that is, eight resonance lines (δ = 32—42) at the higher field and the remaining signals (δ = 48—55) at the lower field. A similar trend was also observed for the polynuclear complexes with *fac*(*S*)-[M(aet)$_3$] units. The signals at higher field are due to the carbon atoms adjacent to the sulfur atoms and the signals at the lower field are due to those to the amino group.[3,8,9,22] Taking account of these ^{13}C NMR spectral behavior, in addition to the molar conductivity and the electronic absorption and CD spectral behavior, [Pd{Pd(aet)}{M(aet)$_2$}{M(aet)$_3$}$_2$]$^{4+}$ seems to be fairly stable in solution, and the pentanuclear structures observed in crystals are retained in solution. The chemical shifts of the –CH$_2$–S– carbon atoms in **2** appear at lower field than those of the corresponding carbons in **1**, while the –CH$_2$–NH$_2$– carbon atoms in **2** are higher field than those in **1**. A similar tendency was observed for the dinuclear complexes [M$_2$(aet)$_4$(cysta)]$^{2+}$ (M = Ir$^{\mathrm{III}}$, Rh$^{\mathrm{III}}$; cysta = cystamine),[22] depending on the bond strength around the metal ions.

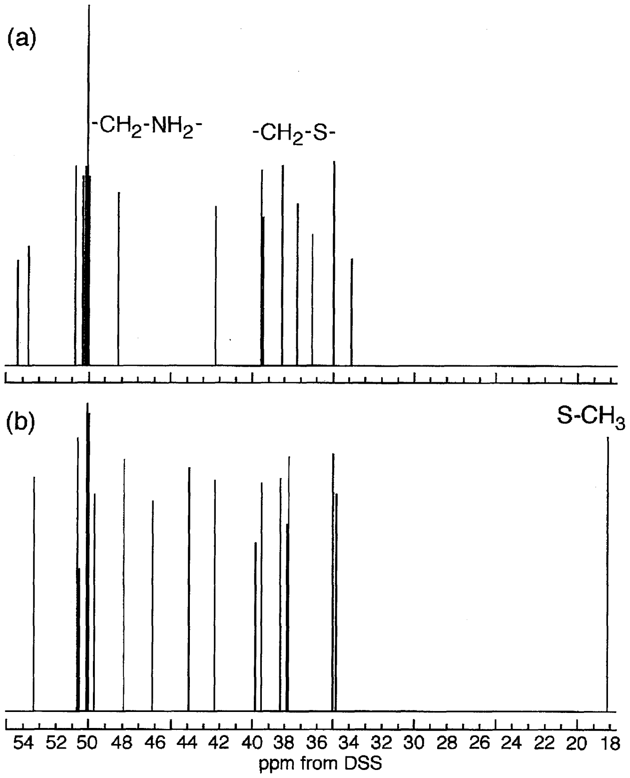


Fig. 6. ^{13}C NMR spectra of (a) [Pd{Pd(aet)}{Rh(aet)$_2$}{Rh(aet)$_3$}$_2$]$^{4+}$ and (b) [Pd{Pd(aet)}{Rh(aet)(smaet)}{Rh(aet)$_3$}$_2$]$^{5+}$.

The ^{13}C NMR spectrum of **3** with thioether type smaet ligand was divided into three groups (Fig. 6 and Table 3); two groups are shown in similar regions (δ = 34—44 for –CH$_2$S–; δ = 46—54 for –CH$_2$NH$_2$–) to those of **1** and **2**. The third group of **3** shows only one signal at δ = 18.18 due to methyl group, and further the ^{1}H NMR spectrum exhibits only one sharp signal at δ = 2.61 due to the S-methyl

Table 4. ^{13}C NMR Chemical Shifts[a)] of Complexes

	–S–CH$_3$	–CH$_2$–S–	–CH$_2$–NH$_2$–
[Pd{Pd(aet)}{Rh(aet)$_2$}{Rh(aet)$_3$}$_2$]$^{4+}$ (**1**)		33.81 34.86 36.19 37.09 38.06 39.27 39.37 42.14	48.16 49.89 50.06 50.15 50.33 50.73 53.61 54.27
[Pd{Pd(aet)}{Ir(aet)$_2$}{Ir(aet)$_3$}$_2$]$^{4+}$ (**2**)		32.57 34.54 36.22 37.54 37.91 40.04 41.40	49.26 50.88 51.47 51.86 52.05 52.79 53.51 54.78
[Pd{Pd(aet)}{Rh(aet)(smaet)}{Rh(aet)$_3$}$_2$]$^{5+}$ (**3**)	18.18	34.77 35.03 37.75 37.82 38.24 39.41 39.77 42.31 43.88	46.10 47.85 49.66 49.99 50.11 50.61 50.70 53.30
[{Rh(aet)$_3$}Zn$_4$O]$^{6+}$ [b)]		33.86	51.20
[{Ir(aet)$_3$}Zn$_4$O]$^{6+}$ [c)]		33.36	52.69

a) In ppm from DSS. b) Ref. 9a. c) Ref. 10b.

protons. A similar S-methyl signal was observed for those (δ = 2.23, 2.22, and 2.18) of [Co(S-methyl-L-penicillaminato)(diethylenetriamine)]$^{2+}$, in which the S-methyl groups take the selective direction.[23] Such NMR spectral behavior suggests that the pentanuclear structure of **3**, which takes the R configuration for the $\Delta\Lambda\Delta$ (or S for $\Lambda\Delta\Lambda$) isomer in the crystalline state, is also retained in solution (Fig. 3), and the methylation reaction of **1** is selectively proceeded with retention of its structure. This is consistent with the molecular model examinations that a significant non-bonding interaction between the S-bonded methyl group and the aet chelate ring in the Pd(2) unit exist for the S configuration of the $\Delta\Lambda\Delta$ (or *R* for $\Lambda\Delta\Lambda$) isomer, but no such interaction is exhibited for its *R* (or *S*) configuration.

As illustrated in Fig. 7, the absorption spectra of the pentanuclear Rh complexes (**1** and **3**) are characterized by two intense bands at about 41 and 48×10^3 cm^{-1}, accompanied by more complicated intense bands in the visible and near-UV region of the lower energy side. The absorption pattern of **2** is similar to those of **1** and **3**, although the band (shoulder at 47.9×10^3 cm^{-1}) in **2** is shifted to higher energy side than those in **1** and **3**. These intense bands correspond well to the sulfur-to-metal charge transfer (CT) bands, since a similar tendency was observed for *fac*(*S*)-[M(aet)$_3$], *fac*(*S*)-[M(L-cys)$_3$]$^{3-}$, and [(M(aet)$_3$)$_4$Zn$_4$O]$^{6+}$.[7—10,22] As the pentanuclear complexes seem to exhibit two spin-allowed d–d transition bands similar to the corresponding mononuclear and polynuclear complexes (Table 5), they have only a little absorption band depending on the octahedral Rh or Ir units in the visible region (lower energy than 24×10^3 cm^{-1} for Rh; 30×10^3 cm^{-1} for Ir). Taking these facts into consideration, the visible absorption bands in the lower energy side can be assigned as arising from the two square-planar Pd(II) chromophores. Over the whole region, the $(+)^{\mathrm{CD}}_{360}$-**1** isomer shows the enantiomeric CD spectra to that of the $(-)^{\mathrm{CD}}_{360}$-**1** one, whose absolute configuration was determined to the $\Delta\Lambda\Delta$ form by the X-ray structure analysis (Table 5). Thus, the $(+)^{\mathrm{CD}}_{360}$-**1** isomer can be assigned to have the Λ(Rh(1)) Δ(Rh(2)) Λ(Rh(3)) configuration. In the visible region, further, the $(-)^{\mathrm{CD}}_{370}$-**2** isomer shows similar CD bands to those for the $\Delta\Lambda\Delta$-$(-)^{\mathrm{CD}}_{360}$-**1** isomer (Table 5). If the CD contributions for the Pd(II) chromophore are additive and mainly depend on the configurations of the octahedral units, it will be assigned that $(-)^{\mathrm{CD}}_{370}$-**2** takes the $\Delta\Lambda\Delta$ configuration.

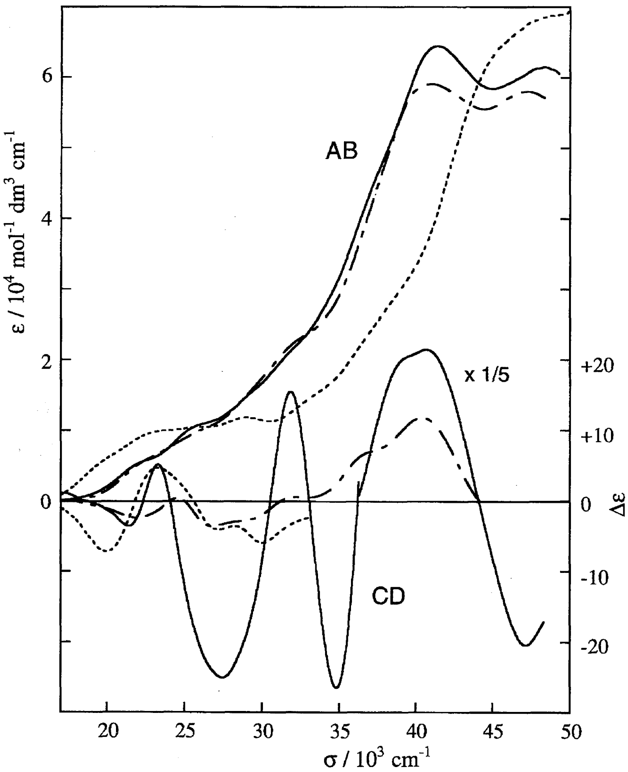


Fig. 7. Absorption and CD spectra of [Pd{Pd(aet)}{M(aet)$_2$}{M(aet)$_3$}$_2$]$^{4+}$; M = Rh (**1**, $(-)^{\mathrm{CD}}_{360}$-$\Delta\Lambda\Delta$ isomer; ——) and Ir (**2**, $(-)^{\mathrm{CD}}_{370}$-$\Delta\Lambda\Delta$ isomer; - - - - - -), and $(-)^{\mathrm{CD}}_{370}$-$\Delta\Lambda\Delta$-[Pd{Pd(aet)}{Rh(aet)(smaet}{Rh(aet)$_3$}$_2$]$^{5+}$ (**3**; – · –).

Although the structure of **3** is similar to **1** except for one thiolato S atom, the sulfur-to-metal CT band of **3** shifts to lower energy side and the intensity is weaker than that of **1** (Fig. 7 and Table 5). Further, the CD spectral patterns of $(-)^{\mathrm{CD}}_{370}$-**3** are similar to those of $\Delta\Lambda\Delta$-**1**, although each CD band of **3** is more ambiguous and weaker than those of **1**. These facts indicate that $(-)^{\mathrm{CD}}_{370}$-**3** takes the $\Delta\Lambda\Delta$ configuration, and the electronic absorption and CD spectral behaviors are significantly affected by the methylation. Namely, one thiolato S atom in the pentanuclear complexes gives the significant contribution to the spectrochemical behavior, although a similar spectral behavior was observed for the mononuclear complex, [Co(L-penicillaminato)(triammine)]$^{+}$, and its methylated complex.[23]

By similar discussion for the absorption and CD spectra of the $(-)^{\mathrm{CD}}_{360}$-**4** isomer to those for **1** and **2**, the $(-)^{\mathrm{CD}}_{360}$-**4** isomer can be assigned to the $\Lambda\Lambda$ configuration.[24] The absorption and CD spectra of the $(-)^{\mathrm{CD}}_{360}$-**4** isomer are not changed in water at least over several days, indicating that this complex is fairly stable in solution.

Details of Structures. X-Ray structural analyses for the complexes **1**—**4** revealed the presence of a discrete complex cation, four (**1**, **2**, and **4**) or five (**3**) counter anions and some water molecules. These suggest that the complex cations are tetravalent, [Pd{Pd(aet)}{M(aet)$_2$}{M(aet)$_3$}$_2$]$^{4+}$ (M = Rh (**1**); Ir (**2**)), and [Pd$_2${Pd(aet)$_2$}{Co(aet)$_3$}$_2$]$^{4+}$ (**4**) or pentavalent [Pd{Pd(aet)}{Rh(aet)(smaet}{Rh(aet)$_3$}$_2$]$^{5+}$ (**3**); these are supported by the elemental analyses and the fact, for example, that the molar conductivity of **1**Br$_4$·6H$_2$O in water gave the value of 491 S cm^2 mol^{-1}, which is similar to the value of the known tetravalent complex cations, [Pd$_2${Ni(aet)$_2$}$_4$]Br$_4$·6H$_2$O (532 S cm^2 mol^{-1}) and [Pd$_2${Ni(aet)$_2$}$_4$]Br$_4$·6H$_2$O (540 S cm^2 mol^{-1}).[13]

As listed in Tables 2 and 3, the bond distances and angles in the octahedral units in **1**—**4** are close to the values observed for those in the polynuclear complexes with the corresponding octahedral units.[1—10,22] However, they are significantly influenced by the binding modes around the Pd atoms. The S(1)–M(1)–S(2) and S(2)–M(1)–S(3) angles (ca. 91—94°) spanned to the Pd(1) and Pd(2) atoms are larger

Table 5. Absorption and CD Spectral Data

Complex	Absorption maxima $\sigma/10^3\ \mathrm{cm^{-1}}$ $(\varepsilon/\mathrm{mol^{-1}\,dm^3\,cm^{-1}})$	CD extrema $\sigma/10^3\ \mathrm{cm^{-1}}$ $(\Delta\varepsilon/\mathrm{mol^{-1}\,dm^3\,cm^{-1}})$
$\Delta\Lambda\Delta$-$(-)^{\mathrm{CD}}_{360}$-$[\mathrm{Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2}]^{4+}$ (**1**)	21.9 (5180 sh[a)])	21.39 (−3.63)
	26.1 (10860 sh)	23.26 (+5.09)
	32.1 (21700 sh)	27.47 (−25.08)
	41.32 (64420)	31.85 (+15.50)
	48.31 (61460)	34.82 (−26.49)
		40.68 (+107.2)
		47.03 (−102.4)
$\Delta\Delta\Delta$-$(-)^{\mathrm{CD}}_{370}$-$[\mathrm{Pd\{Pd(aet)\}\{Ir(aet)_2\}\{Ir(aet)_3\}_2}]^{4+}$ (**2**)	20.0 (5980 sh)	19.92 (−7.18)
	23.5 (9900 sh)	23.21 (+4.65)
	25.9 (10470 sh)	27.19 (−4.09)
	28.97 (11820)	30.03 (−5.97)
	33.2 (14710 sh)	
	36.4 (22070 sh)	
	47.9 (68180 sh)	
$\Delta\Lambda\Delta$-$(-)^{\mathrm{CD}}_{370}$-$[\mathrm{Pd\{Pd(aet)\}\{Rh(aet)(smaet)\}\{Rh(aet)_3\}_2}]^{4+}$ (**3**)	21.9 (4970 sh)	21.89 (−2.48)
	25.8 (9730 sh)	24.55 (+0.34)
	31.9 (22140 sh)	26.78 (−3.62)
	41.05 (59050)	29.02 (−2.79 sh)
	47.21 (57970)	32.26 (+0.53 sh)
		36.31 (+6.19 sh)
		40.42 (+11.79)
$\Lambda\Lambda$-$(-)^{\mathrm{CD}}_{360}$-$[\mathrm{Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2}]^{4+}$ (**4**)	17.3 (520 sh)	16.99 (+6.52)
	20.7 (3510 sh)	20.62 (−19.23)
	23.3 (6130 sh)	23.42 (−16.61 sh)
	28.2 (13920 sh)	28.07 (+24.60)
	31.3 (26150 sh)	31.19 (+4.60)
	33.5 (30930 sh)	33.31 (+14.26)
	35.9 (36780 sh)	35.82 (−4.53)
	37.9 (39950 sh)	37.82 (+11.75)
	40.49 (43710)	39.81 (−1.65 sh)
	44.1 (39700 sh)	44.76 (−39.46)

a) The sh label denotes a shoulder.

than the S(1)–M(1)–S(3) angle (ca. 81—83°) coordinated to the same Pd(1) atom (Table 2). This is consistent with the fact that the M(1)–S(2) distance is larger than the M(1)–S(1) and M(1)–S(3) ones. A similar trend was also observed for the distances and angles around the two octahedral Co units in **4** atom, taking a similar binding mode (Fig. 5 and Table 3). The S(6)–M(3)–S(8) angles (ca. 167—170°) in **1**—**3** are significantly deviated from the regular angle 180°, which will be related to the deviations (ca. 157—162°) for the S(1)–Pd(1)–S(7) angles (Table 2). These seem to indicate that the aggregation of the M(3) unit to the Pd planes has considerable steric hindrance. The relations between the Rh(3)–S(6) and Rh(3)–S(8) distances in **1** and **3** are similar to each other. This suggests that there is no significant trans influence due to the thiolate and methylation groups in the present pentanuclear complexes, which would be in contrast to the fact that the thiolate group shows a fairly large trans influence in the mononuclear complexes.[25]

The Pd–S distances of the parallel planes in **1**—**4** are in good agreement with those (av. 2.336(2) Å) found in the hexanuclear complexes, $[\mathrm{Pd_2\{Ni(aet)_2\}_4}]^{4+}$.[13] However, the Pd(3)–S (av. 2.269(1) Å) distances in **4** are ca. 0.07 Å shorter than that (av. 2.343(1) Å) of central $\mathrm{PdS_4}$ units, which coincides well with those (av. 2.2801(9) Å) of the tetranuclear complexes $[\mathrm{Pd_4Cl_4(L\text{-}Hcys)_4}]$.[14] These facts may depend on the coordination geometry around two Pd atoms. The Pd–Pd distances (3.050(2) for **1**; 3.1534(7) for **2**; 3.0887(9) for **3**; (2.9830(4) Å for **4**) are similar to those in $[\mathrm{Pd_2\{Ni(aet)_2\}_4}]^{4+}$ (3.0240(7) Å),[13] $[\mathrm{Pd_2\{Pd(aet)_2\}_4}]^{4+}$ (3.1886(6) Å),[13] and $[\mathrm{Pd_4Cl_4(L\text{-}Hcys)_4}]$ (3.2210(7) Å),[14] although the distances in **1** to **4** increase somewhat in order of the complexes with the Co, Rh, and Ir units. However, their distances are considerably longer than those (2.55—2.75 Å) found in [Pd(bridge)$_4$Pd]-type complexes.[26] Accordingly, these facts seem to indicate that there is no Pd–Pd bond in the present pentanuclear complexes, and that their distances depend on the bridging complex units.

Taking accounts of the absolute configurations for each of the octahedral units (Δ and Λ) and the asymmetric sulfur atoms (*R* and *S*), many isomers are possible for **1**—**4**. It was determined by the anomalous scattering technique that the Rh(1), Rh(2), and Rh(3) units in the spontaneously resolved $(-)^{\mathrm{CD}}_{360}$-**1** isomer have the Δ, Λ, and Δ configurations, respectively, as shown in Figs. 1 and 5. All of the bridging sulfur atoms in the Rh(1) and Rh(2) units are fixed to the S configurations for the Δ unit and to the *R* configurations for the Λ unit, while two bridging S(7) and S(9) atoms in the Rh(3) unit are also fixed to the reversed configuration to the Rh(1) and Rh(2) units, that is, the *R* configuration is fixed for the Δ unit (Figs. 1 and 5). The absolute configuration around the Ir(2) unit in **2** differs from that the corresponding Rh(2) unit in **1**, although the other configurations are quite similar to each other (Figs. 1, 2, and 5). Namely, **2** is formed as a pair of enantiomers of the $\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda$ configurations as shown in the crystal system $P2_1/c$ (Table 1). All of the bridging sulfur atoms in **2** are also fixed to the same selective configurations as in the case of **1**, although their notations are reversed because the atomic number of the Ir atom is larger than that of the Pd atom (the S configurations for the Δ unit and the *R* configurations for the Λ unit). For **3**, a pair of enantiomers, in which the Rh(1), Rh(2), and Rh(3) units have the $\Delta\Lambda\Delta$ or $\Lambda\Delta\Lambda$ configuration, are selectively formed as well as those in **1** (Figs. 1 and 3). All of the bridging sulfur atoms in **3** are also fixed to the same configurations as those in **1**. When **3** is the $\Delta\Lambda\Delta$ isomer, furthermore, the methylated S(8) atom in the Rh(3) unit is regulated to the *R* (or *S* for the $\Lambda\Delta\Lambda$ isomer) configuration as shown in Fig. 3. **4** is formed as the racemic compound in the crystal, having the $\Delta\Delta$ and $\Lambda\Lambda$ configurations for the two *fac*(*S*)-[Co(aet)$_3$] units (Figs. 4 and 5). When the Co(1) and Co(2) units in **4** take the $\Lambda\Lambda$ configuration, the S(7) and S(8) atoms on the Rh(3) unit are also regulated to the *S* and *R* configurations (or *R* and *S* configurations for the $\Delta\Delta$ isomer).

This work was supported by a Grant-in-Aid for Scientific Research No. 10149206 from the Ministry of Education, Science, Sports and Culture.

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