A New Class of S-Bridged Hexanuclear Complexes with Amino Thiolate Ligands. Formation and Structural Characterization of $[Pd^{II}_2\{Ni^{II}(aet)_2\}_x\{Pd^{II}(aet)_2\}_{4-x}]Br_4$ (x = 0–4; aet = 2-Aminoethanethiolate)

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The reactions of $[M(aet)_2]$ with Pd^{II} in water, followed by the addition of NaBr, gave a new class of S-bridged hexanuclear complexes $[Pd_2\{M(aet)_2\}_4]Br_4{\cdot}6H_2O$ (aet = aminoethanethiolate; M = Ni^{II} (**1**), Pd^{II} (**2**)). The same reaction of $[Pd(aet)_2]$ with Ni^{II} led to the formation of a mixture of S-bridged hexanuclear complexes $[Pd_2\{Ni(aet)_2\}_x\{Pd(aet)_2\}_{4-x}]Br_4{\cdot}6H_2O$ (x = 0–4) (**3**), which implies that the didentate-N,S ligand aet readily transfers from the Pd^{II} to the Ni^{II} coordination sphere. The crystal structures of **1**–**3** were determined by X-ray crystallography: $[Ni_4Pd_2(C_2H_6NS)_8]Br_4{\cdot}6H_2O$ (**1**), triclinic, $P\bar{1}$, a = 11.094(3) Å, b = 11.198(3) Å, c = 10.937(4) Å, α = 101.00(2)°, β = 117.18(1)°, γ = 71.40(3)°, V = 1143.9(7) Å^3, Z = 1, and R = 0.048; $[Pd_6(C_2H_6NS)_8]Br_4{\cdot}6H_2O$ (**2**), triclinic, $P\bar{1}$, a = 11.212(3) Å, b = 11.278(3) Å, c = 10.951(4) Å, α = 101.78(2)°, β = 116.78(2)°, γ = 71.21(3)°, V = 1168.8(7) Å^3, Z = 1, and R = 0.033; $[Ni_2Pd_4(C_2H_6NS)_8]Br_4{\cdot}6H_2O$ (**3**), triclinic, $P\bar{1}$, a = 11.170(4) Å, b = 11.240(3) Å, c = 10.963(4) Å, α = 100.85(2)°, β = 117.02(1)°, γ = 71.30(3)°, V = 1160.0(7) Å^3, Z = 1, and R = 0.046. In these complexes, two Pd^{II} ions are spanned by four *cis*(*S*)-$[Ni(aet)_2]$ and/or *cis*(*S*)-$[Pd(aet)_2]$ units, forming an C_{4h} symmetrical S-bridged hexanuclear structure composed of six square planes. The electronic absorption and ^{13}C NMR spectral behavior of these complexes is also reported.

Introduction

Coordinated thiolato sulfur atoms tend to make bridges with a variety of metal ions, and considerable attention has been focused on the S-bridged polynuclear structure derived from [M(thiolato-*S*)$_2$(amine-*N*)$_2$]-type (M = Ni^{II}, Pd^{II}) mononuclear complexes.[1–16] It has been recognized that $[M(aet)_2]$ compounds (aet = 2-aminoethanethiolate, $NH_2CH_2CH_2S^-$) readily react with divalent metal ions M′ such as Ni^{II}, Pd^{II}, Pt^{II}, and Cd^{II} to give S-bridged polynuclear complexes.[1–4] An S-bridged trinuclear structure, $[M'\{M(aet)_2\}_2]^{2+}$, in which M′ is coordinated by four sulfur atoms from two *cis*(*S*)-$[M(aet)_2]$ units, has been proposed for these complexes, and this structure has been confirmed by single-crystal X-ray analysis for M, M′ = Ni^{II}.[3] Analogous S-bridged $Ni^{II}Ni^{II}Ni^{II}$ and $Ni^{II}Pd^{II}Ni^{II}$ trinuclear complexes with other amino thiolate ligands have been prepared,[5–11] some of which have been structurally characterized.[7–10] In view of these facts, it has long been believed that all the reaction products of $[M(aet)_2]$ and divalent metal ions M′ are the S-bridged trinuclear complexes $[M'\{M(aet)_2\}_2]^{2+}$. Here we report that the facile reactions of $[Ni(aet)_2]$ with Pd^{2+}, $[Pd(aet)_2]$ with Pd^{2+}, and $[Pd(aet)_2]$ with Ni^{2+} in water produce a new class of S-bridged hexanuclear complexes having a C_{4h} symmetry $[Pd_2\{Ni(aet)_2\}_x\{Pd(aet)_2\}_{4-x}]^{4+}$ (x = 0–4), in which two Pd^{II} ions are spanned by four *cis*(*S*)-$[Ni(aet)_2]$ and/or *cis*(*S*)-$[Pd(aet)_2]$ units.[17]

Experimental Section

Preparation of Complexes. $[Pd_2\{Ni(aet)_2\}_4]Br_4{\cdot}6H_2O$ (1). To a green suspension containing 0.5 g (2.4 mmol) of $[Ni(aet)_2]$ [1] in 50 cm^3 of water was added 0.35 g (1.2 mmol) of Na_2PdCl_4 (0.35 g, 1.2 mmol). The mixture was stirred at 40 °C for 2 h, which gave a deep red solution. After the mixture was allowed to stand at room temperature overnight, 2.5 g of NaBr was added in 5 cm^3 of water. The resulting fine red crystals (**1**) were collected by filtration and washed with methanol–ethanol (1:1). Yield: 74%. Anal. Found: C, 12.96; H, 4.10; N, 7.44, Ni, 15.83; Pd, 14.67. Calcd for $[Ni_4Pd_2(C_2H_6NS)_8]Br_4{\cdot}6H_2O$: C, 12.95; H, 4.07; N, 7.55; Ni, 15.81; Pd, 14.34. Visible–UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (ϵ, 10^3 mol^{-1} dm^3 cm^{-1})]: 25.64 (5.73), 33.56 (14.59), 37.45 (20.18), 45.0 (25.0, sh). The sh label denotes a shoulder. ^{13}C NMR in D_2O (500 MHz, ppm from DSS): δ 37.58 ($-CH_2S$), 49.85 ($-CH_2NH_2$). Molar conductivity in H_2O: 532 Ω^{-1} cm^2 mol^{-1}. Red crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution of **1** at room temperature.

$[Pd_2\{Pd(aet)_2\}_4]Br_4{\cdot}6H_2O$ (2). This complex was prepared by the same procedure for **1**, using $[Pd(aet)_2]$ [1] (2.4 mmol) instead of $[Ni(aet)_2]$ (2.4 mmol). Yield: 80%. Anal. Found: C, 11.28; H, 3.45; N, 6.48, Pd, 38.28. Calcd for $[Pd_6(C_2H_6NS)_8]Br_4{\cdot}6H_2O$: C, 11.47; H, 3.61; N, 6.69; Pd, 38.11. Visible–UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (ϵ, 10^3 mol^{-1} dm^3 cm^{-1})]: 30.21 (14.10), 41.49 (26.27), 45.05 (28.73). ^{13}C NMR in D_2O (500 MHz, ppm from DSS): δ 38.54 ($-CH_2S$), 51.60 ($-CH_2NH_2$). Molar conductivity in H_2O: 540 Ω^{-1} cm^2 mol^{-1}. Yellow crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution of **2** at room temperature.

$[Pd_2\{Ni(aet)_2\}_x\{Pd(aet)_2\}_{4-x}]Br_4{\cdot}6H_2O$ (x = 0–4) (3). A mixture of hexanuclear complexes was prepared by the same procedure for **1**, using $[Pd(aet)_2]$ (2.4 mmol) and $NiCl_2{\cdot}6H_2O$ (1.2 mmol) instead of $[Ni(aet)_2]$ (2.4 mmol) and Na_2PdCl_4 (1.2 mmol). Yield: 79%. Anal. Found: C, 12.00; H, 3.70; N, 6.85, Ni, 7.02; Pd, 27.19. Calcd for $[Ni_2Pd_4(C_2H_6NS)_8]Br_4{\cdot}6H_2O$: C, 12.16; H, 3.83; N, 7.09; Ni, 7.43; Pd, 26.94. Visible–UV spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (ϵ, 10^3 mol^{-1} dm^3

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(17) After submission of this paper, Stephan and co-workers reported an S-bridged Pd^{II}_6 complex $[Pd_2\{Pd(PhCH_2SCH_2CH_2S)_2\}_4]^{4+}$,[18] of which structure is very similar to that of $[Pd_2\{Pd(NH_2CH_2CH_2S)_2\}_4]^{4+}$ presented here.

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Table 1. Crystallographic Data[a] for **1–3**

	1	**2**	**3**
chem formula	$C_{16}H_{60}N_8O_6S_8Ni_4Br_4Pd_2$	$C_{16}H_{60}N_8O_6S_8Br_4Pd_6$	$C_{16}H_{60}N_8O_6S_8Ni_2Br_4Pd_4$
fw	1484.5	1675.4	1579.9
cryst color	red	yellow	orange
cryst size, mm	0.10 × 0.15 × 0.15	0.15 × 0.20 × 0.20	0.13 × 0.15 × 0.38
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	11.094(3)	11.212(3)	11.170(4)
b, Å	11.198(3)	11.278(3)	11.240(3)
c, Å	10.937(4)	10.951(4)	10.963(4)
α, deg	101.00(2)	101.78(2)	100.85(2)
β, deg	117.18(1)	116.78(2)	117.02(1)
γ, deg	71.40(3)	71.21(3)	71.30(3)
V, Å^3	1143.9(7)	1168.8(7)	1160.0(7)
Z	1	1	1
ρ_{calc}, g cm^{-3}	2.15	2.37	2.26
μ, cm^{-1}	62.4	59.9	60.9
transm coeff	0.781–1.000	0.806–0.999	0.714–0.998
R[b]	0.048	0.033	0.046
R_w[c]	0.051	0.040	0.053

[a] $T = 23$ °C; λ(Mo Kα) = 0.710 73 Å. [b] $R = \sum(|F_o| - |F_c|)|/\sum(|F_o|)$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

cm^{-1})]: 27.2 (6.0 sh), 33.00 (13.41), 40.32 (23.66), 45.05 (26.14). The sh label denotes a shoulder. Molar conductivity in H_2O: 527 Ω^{-1} cm^2 mol^{-1}. Orange crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution of **3** at room temperature.

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

X-ray Structure Determination. Single-crystal X-ray diffraction experiments were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Crystallographic data are summarized in Table 1. Unit cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the range of $15 < 2\theta < 20°$. The intensity data were collected by the ω–2θ scan mode up to $2\theta = 52°$. The intensities were corrected for Lorentz and polarization. Empirical absorption corrections based on a series of ψ scans were also applied. The 4095, 4269, and 4147 independent reflections with $F_o > 3\sigma(F_o)$ of the measured 4748, 4854, and 4823 reflections were considered as "observed" and used for structure determinations of **1–3**, respectively. The structures were solved by direct method and difference Fourier techniques and refined by full-matrix least squares using anisotropic thermal parameters for non-hydrogen atoms.[19] Hydrogen atoms were not included in the calculation. For **3**, the mixed Ni/Pd sites (0.5 Ni + 0.5 Pd) atoms (M2 and M3) were refined as Pd atoms with a site occupancy factor of 0.804. Non-hydrogen atom coordinates for the complex cations are listed in Tables 2–4.

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Complex Cation of **1**

atom	x	y	z	B_{eq}[a]
Pd	0.12685(5)	0.05255(4)	0.57238(5)	1.79(1)
Ni1	−0.13668(8)	0.19689(8)	0.70392(8)	1.83(2)
Ni2	−0.14899(8)	0.22104(8)	0.27302(8)	1.90(2)
S1	0.0058(2)	0.2427(2)	0.6435(2)	2.36(4)
S2	0.2587(2)	−0.1360(2)	0.5083(2)	2.36(4)
S3	0.0771(2)	0.1400(2)	0.3717(2)	2.34(4)
S4	0.1795(2)	−0.0330(2)	0.7753(2)	2.20(4)
N1	−0.0334(6)	0.2604(7)	0.8920(6)	3.2(2)
N2	0.2715(7)	−0.1667(7)	0.2450(7)	3.6(2)
N3	−0.1165(8)	0.3881(6)	0.3107(9)	4.5(2)
N4	0.3531(7)	−0.2896(6)	0.8260(7)	3.5(2)
C1	0.1306(7)	0.2865(7)	0.8167(8)	2.9(2)
C2	0.0448(8)	0.3502(7)	0.8980(8)	3.1(2)
C3	0.3891(7)	−0.0891(8)	0.4803(8)	3.1(2)
C4	0.4127(8)	−0.1752(8)	0.3645(8)	3.5(2)
C5	0.1368(8)	0.2837(7)	0.4268(8)	3.3(2)
C6	0.0251(8)	0.3834(7)	0.3227(9)	3.9(2)
C7	0.3715(7)	−0.0724(7)	0.8639(8)	3.2(2)
C8	0.4203(8)	−0.1966(8)	0.9332(8)	3.6(2)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)(B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Results and Discussion

X-ray structural analysis for each of **1–3** revealed the presence of a discrete tetravalent complex cation, four bromide anions, and six water molecules. A perspective drawing of the entire complex cation of **1** is given in Figure 1. The selected bond distances and angles for **1–3** are listed in Tables 5–7.

The entire complex cation of **1**, which has a crystallographically imposed inversion center, consists of four square-planar *cis*(*S*)-[Ni(aet)$_2$] units and two palladium atoms. This is consistent with the plasma emission spectral analysis which gave the value of Ni:Pd = 2:1. The two sulfur atoms in each of four *cis*(*S*)-[Ni(aet)$_2$] units bind to two palladium atoms such that each palladium atom is situated in a square-planar environment. As a result, the two PdS_4 square planes face each other, connected by the four perpendicular NiN_2S_2 square planes. This is in contrast to the case where the two sulfur atoms of *cis*(*S*)-[Ni(aet)$_2$] coordinate to one Ni^{II} to form a linear-type Ni^{II}Ni^{II}Ni^{II} trinuclear complex, [Ni{Ni(aet)$_2$}$_2$]$^{2+}$.[1,3] Two absolute configurations, *R* and *S*, are possible for each of eight bridging sulfur atoms in **1**. The two sulfur atoms in each *cis*(*S*)-[Ni(aet)$_2$] unit take the *R* and *S* configurations with the δ and λ conformational aet chelate rings, respectively. In addition, the four sulfur atoms in each PdS_4 plane are required to have the same absolute configuration, completing a pinwheel-like S-bridged hexanuclear structure with a C_{4h} symmetry. A pinwheel-like S-Bridged structure composed of three *cis*(*S*)-[Ni(thiolato)$_2$(amine)$_2$]-type units has been observed in [Zn$_2$Cl$_2${Ni(BME-DACO)}$_3$]$^{2+}$,[14] where each of two Zn^{II} ions is tetrahedrally coordinated by three sulfur atoms from three [Ni(BME-DACO)] units and one chlorine atom.

The cis angles of S–Ni–S (average 90.56(8)°) and S–Pd–S (average 90.0(7)°) are virtually right angles, and the bridging Ni–S–Pd angles (average 108.2(1)°) are close to the ideal tetrahedral angle of 109.5° in **1** (Table 5). On the other hand, in [Ni{Ni(aet)$_2$}$_2$]$^{2+}$ the cis S–Ni–S angles subtended at the terminal (84.0(2)°) and the central nickel atoms (81.4(2) and 98.6(2)°) are significantly deviated from 90° and the bridging Ni–S–Ni angles (77.5(2) and 77.5(2)°) are unusually acute.[3] A similar trend has been observed for the related Ni^{II}Pd^{II}Ni^{II} trinuclear complex [Pd{Ni(S(CH$_2$)$_2$NH(CH$_2$)$_3$NH(CH$_2$)$_2$S)}$_2$]$^{2+}$ (S–Ni–S = 86.6(4)°, S–Pd–S = 79.6(3) and 100.4(3)°, Ni–S–Pd = 81.2(3)°).[7] Therefore, it is considered that the present S-bridged hexanuclear structure in [Pd$_2${Ni(aet)$_2$}$_4$]$^{4+}$ is much less strained than the related S-bridged trinuclear structure. The Ni–S (average 2.181(3) Å) and Pd–S (average 2.336(2) Å) bond distances in **1** agree with those in [Pd{Ni(S(CH$_2$)$_2$NH(CH$_2$)$_3$-

Table 3. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Complex Cation of **2**

atom	x	y	z	B_{eq}[a]
Pd1	0.13220(4)	0.05408(4)	0.57519(4)	1.422(9)
Pd2	−0.13748(4)	0.19737(4)	0.70388(4)	1.743(9)
Pd3	−0.14841(4)	0.22178(4)	0.27324(5)	1.752(9)
S1	0.0125(1)	0.2441(1)	0.6451(2)	1.93(3)
S2	0.2642(1)	−0.1338(1)	0.5141(2)	1.88(3)
S3	0.0849(1)	0.1393(1)	0.3747(1)	1.89(3)
S4	0.1839(1)	−0.0288(1)	0.7784(1)	1.83(3)
N1	−0.0282(6)	0.2647(6)	0.9020(5)	2.7(1)
N2	0.2837(5)	−0.1672(6)	0.2446(6)	3.0(1)
N3	−0.1081(6)	0.3967(6)	0.3144(8)	4.1(2)
N4	0.3639(6)	−0.2911(6)	0.8321(7)	3.1(2)
C1	0.1329(6)	0.2846(6)	0.8183(7)	2.5(1)
C2	0.0484(7)	0.3515(6)	0.9003(7)	2.7(2)
C3	0.3898(6)	−0.0870(7)	0.4815(7)	2.6(1)
C4	0.4186(6)	−0.1755(7)	0.3669(8)	3.1(2)
C5	0.1396(7)	0.2845(6)	0.4263(7)	2.7(2)
C6	0.0329(7)	0.3829(7)	0.3233(8)	3.5(2)
C7	0.3720(6)	−0.0729(7)	0.8636(7)	2.8(2)
C8	0.4233(7)	−0.1964(7)	0.9353(7)	3.0(2)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)(B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 4. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Complex Cation of **3**

atom	x	y	z	B_{eq}[a]
Pd1	0.12995(5)	0.05333(5)	0.57403(5)	1.39(1)
M2	−0.13745(6)	0.19787(6)	0.70362(6)	1.33(1)
M3	−0.14837(7)	0.22143(6)	0.27309(7)	1.64(1)
S1	0.0107(2)	0.2437(2)	0.6445(2)	1.97(4)
S2	0.2624(2)	−0.1348(2)	0.5123(2)	1.93(4)
S3	0.0812(2)	0.1396(2)	0.3735(2)	1.99(4)
S4	0.1821(2)	−0.0308(2)	0.7768(2)	1.87(4)
N1	−0.0292(7)	0.2638(7)	0.8983(7)	2.9(2)
N2	0.2798(7)	−0.1679(7)	0.2446(7)	3.2(2)
N3	−0.1112(9)	0.3931(8)	0.313(1)	4.5(3)
N4	0.3576(8)	−0.2897(7)	0.8293(9)	3.3(2)
C1	0.1341(8)	0.2839(8)	0.8158(9)	2.6(2)
C2	0.0492(9)	0.3513(8)	0.9007(9)	2.8(2)
C3	0.3903(8)	−0.0877(8)	0.4833(9)	2.7(2)
C4	0.4176(9)	−0.1752(9)	0.368(1)	3.3(2)
C5	0.1387(9)	0.2836(8)	0.4260(9)	2.9(2)
C6	0.030(1)	0.3830(8)	0.324(1)	3.7(2)
C7	0.3718(9)	−0.0733(8)	0.865(1)	2.9(2)
C8	0.4217(9)	−0.1969(9)	0.935(1)	3.2(2)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)(B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

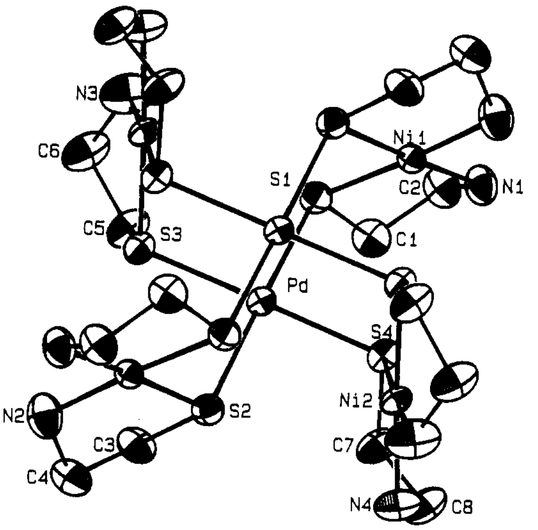

Figure 1. ORTEP view of the complex cation of **1** ($[Pd_2\{Ni(aet)_2\}_4]^{4+}$) with the atomic labeling scheme (50% probability thermal ellipsoids).

Table 5. Selected Bond Distances (Å) and Angles (deg) for **1**

Distances			
Pd–S1	2.332(2)	Ni1–N1	1.964(6)
Pd–S2	2.343(2)	Ni1–N2	1.955(9)
Pd–S3	2.334(2)	Ni2–S3	2.175(2)
Pd–S4	2.335(2)	Ni2–S4	2.167(2)
Ni1–S1	2.190(3)	Ni2–N3	1.949(8)
Ni1–S2	2.190(2)	Ni2–N4	1.964(6)
Angles			
S1–Pd–S2	177.22(6)	N1–Ni1–N2	91.5(3)
S1–Pd–S3	90.87(7)	S3–Ni2–S4	89.77(7)
S1–Pd–S4	88.89(7)	S3–Ni2–N3	88.9(2)
S2–Pd–S3	89.68(7)	S3–Ni2–N4	176.7(2)
S2–Pd–S4	90.51(6)	S4–Ni2–N3	177.2(3)
S3–Pd–S4	179.01(7)	S4–Ni2–N4	88.8(2)
S1–Ni1–S2	91.35(8)	N3–Ni2–N4	92.4(3)
S1–Ni1–N1	88.5(3)	Pd–S1–Ni1	106.69(8)
S1–Ni1–N2	176.4(2)	Pd–S2–Ni1	110.19(6)
S2–Ni1–N1	177.0(2)	Pd–S3–Ni2	107.1(1)
S2–Ni1–N2	88.5(2)	Pd–S4–Ni2	108.87(7)

Table 6. Selected Bond Distances (Å) and Angles (deg) for **2**

Distances			
Pd1–S1	2.332(1)	Pd2–N1	2.091(5)
Pd1–S2	2.339(1)	Pd2–N2	2.095(8)
Pd1–S3	2.332(2)	Pd3–S3	2.267(1)
Pd1–S4	2.330(2)	Pd3–S4	2.260(2)
Pd2–S1	2.279(2)	Pd3–N3	2.087(7)
Pd2–S2	2.278(1)	Pd3–N4	2.095(5)
Angles			
S1–Pd1–S2	176.67(5)	N1–Pd2–N2	93.0(3)
S1–Pd1–S3	90.99(6)	S3–Pd3–S4	91.55(5)
S1–Pd1–S4	88.79(6)	S3–Pd3–N3	86.6(2)
S2–Pd1–S3	89.75(6)	S3–Pd3–N4	176.3(2)
S2–Pd1–S4	90.39(6)	S4–Pd3–N3	176.5(3)
S3–Pd1–S4	178.62(6)	S4–Pd3–N4	86.4(2)
S1–Pd2–S2	93.51(6)	N3–Pd3–N4	95.3(2)
S1–Pd2–N1	86.7(2)	Pd1–S1–Pd2	106.09(7)
S1–Pd2–N2	176.0(2)	Pd1–S2–Pd2	109.39(5)
S2–Pd2–N1	177.1(1)	Pd1–S3–Pd3	106.27(8)
S2–Pd2–N2	86.6(1)	Pd1–S4–Pd3	107.84(6)

$NH(CH_2)_2S)\}_2]^{2+}$ (average Ni–S = 2.182(11) Å and Pd–S = 2.338(9) Å).[7] The Pd···Pd distance (3.0240(7) Å), which is the longest among those (2.55–2.75 Å) found in [Pd(bridge)$_4$Pd]-type complexes,[20–25] indicates the absence of a Pd–Pd dative bond.

The complex cation of **2** ($[Pd_2\{Pd(aet)_2\}_4]^{4+}$) is isostructural with the complex cation of **1**, consisting of four *cis*(*S*)-[Pd(aet)$_2$] units and two Pd^{II} (Tables 1 and 3). The bond distances and angles in **2** (Table 6) are similar to those observed in **1**. However, it is noted that the Pd···Pd distance in **2** (3.1886(6) Å) is ca. 0.17 Å longer than that in **1**, owing to the longer Pd–S bonds (average 2.271(3) Å) and the larger S–Pd–S angles (average 92.53(6)°) in the *cis*(*S*)-[Pd(aet)$_2$] units of **2**, compared with the Ni–S bonds (average 2.181(3) Å) and the S–Ni–S angles (average 90.56(8)°) in the *cis*(*S*)-[Ni(aet)$_2$] units of **1**. A very closely related hexapalladium(II) complex, $[Pd_2\{Pd(PhCH_2SCH_2CH_2S)_2\}_4]^{4+}$, which consists of four $[Pd(PhCH_2SCH_2CH_2S)_2]$ units and two Pd^{II} ions, has been reported after submission of this paper.[18] The overall S-bridged structure of $[Pd_2\{Pd(PhCH_2SCH_2CH_2S)_2\}_4]^{4+}$ resembles that of **2**. In particular, the bond distances and angles

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Table 7. Selected Bond Distances (Å) and Angles (deg) for 3

	Distances		
Pd1–S1	2.331(2)	M2–N1	2.049(6)
Pd1–S2	2.341(2)	M2–N2	2.05(1)
Pd1–S3	2.334(2)	M3–S3	2.222(2)
Pd1–S4	2.332(2)	M3–S4	2.219(2)
M2–S1	2.252(3)	M3–N3	2.029(9)
M2–S2	2.248(2)	M3–N4	2.025(7)
	Angles		
S1–Pd1–S2	176.53(7)	N1–M2–N2	92.5(3)
S1–Pd1–S3	90.84(7)	S3–M3–S4	90.85(7)
S1–Pd1–S4	88.90(7)	S3–M3–N3	87.5(2)
S2–Pd1–S3	89.81(7)	S3–M3–N4	176.4(3)
S2–Pd1–S4	90.39(7)	S4–M3–N3	176.9(4)
S3–Pd1–S4	178.85(7)	S4–M3–N4	87.2(2)
S1–M2–S2	92.65(8)	N3–M3–N4	94.2(3)
S1–M2–N1	87.2(3)	Pd1–S1–M2	106.31(9)
S1–M2–N2	176.3(2)	Pd1–S2–M2	109.71(6)
S2–M2–N1	177.3(2)	Pd1–S3–M3	106.8(1)
S2–M2–N2	87.5(2)	Pd1–S4–M3	108.35(7)

around the central palladium atoms (average Pd–S = 2.335(5) Å and cis S–Pd–S = 89.9(1)°) are quite similar to those observed in **2**. The Pd–S(thiolato) distances (average 2.304(4) Å) in the [Pd($PhCH_2SCH_2CH_2S$)$_2$] units are slightly longer than those in the [Pd(aet)$_2$] units of **2**.

As illustrated in Figure 2, the electronic absorption spectrum for each of **1** and **2** in water is characterized by three intense absorption bands (25.64 × 10^3, 33.56 × 10^3, and 37.45 × 10^3 cm^{-1} for **1** and 30.21 × 10^3, 41.49 × 10^3, and 45.05 × 10^3 cm^{-1} for **2**). Each band for **2** is located at higher energy than the corresponding band for **1**, suggesting that the absorption spectra of these complexes are dominated by the four *cis*(*S*)-MN_2S_2 (M = Ni^{II}, Pd^{II}) chromophores, rather than the two Pd^{II}S$_4$ ones. No significant absorption spectral changes were recognized for **1** and **2** at least for several hours. Furthermore, the addition of excess Cd^{2+} to the aqueous solution of **1** or **2** causes little absorption spectral change, which is in contrast to the case where the central Ni^{II} is quantitatively displaced by Cd^{II} in water for [Ni{Ni(aet)$_2$}$_2$]$^{2+}$.[4] In the ^{13}C NMR spectra **1** and **2** exhibit only two signals due to two kinds of methylene carbon atoms for the eight aet ligands (Figure 3). These results indicate that **1** and **2** are fairly stable in solution, retaining the C_{4h} symmetrical S-bridged hexanuclear structure observed in the crystal.

The ^{13}C NMR spectrum of **3**, which contains Ni and Pd atoms in a ratio of 1:2, shows two clusters of methylene carbon signals at ca. δ 38 and 50, including four signals observed for **1** and **2** (Figure 3). The absorption spectrum of **3** behaves like a 1:1 mixture of **1** and **2** (Figure 2), although **3** is fairly stable in water as in the case of **1** and **2**. X-ray analysis revealed that **3** is isostructural with **1** and **2**, consisting of four *cis*(*S*)-[M(aet)$_2$] units and two M′ (Pd1) atoms (Tables 1 and 4). As listed in Table 7, the M–S bond distances (average 2.235(3) Å) are intermediate between the Ni–S distances (average 2.181(3) Å) in the *cis*(*S*)-[Ni(aet)$_2$] units of **1** and the Pd–S distances (average 2.271(3) Å) in the *cis*(*S*)-[Pd(aet)$_2$] units of **2**, while the M′ (Pd1)–S bond distances (average 2.335(2) Å) are essentially the same as the Pd–S distances in **1** (average 2.336(2) Å) and **2** (average 2.333(2) Å). Taking these facts into consideration, **3** is assignable as a mixture of S-bridged hexanuclear complexes [Pd$_2${Ni(aet)$_2$}$_x${Pd(aet)$_2$}$_{4-x}$]$^{4+}$ (x = 0–4), in which each of two Pd^{II} ions is coordinated by four sulfur atoms from the four *cis*(*S*)-[Ni(aet)$_2$] and/or *cis*(*S*)-[Pd(aet)$_2$] units.

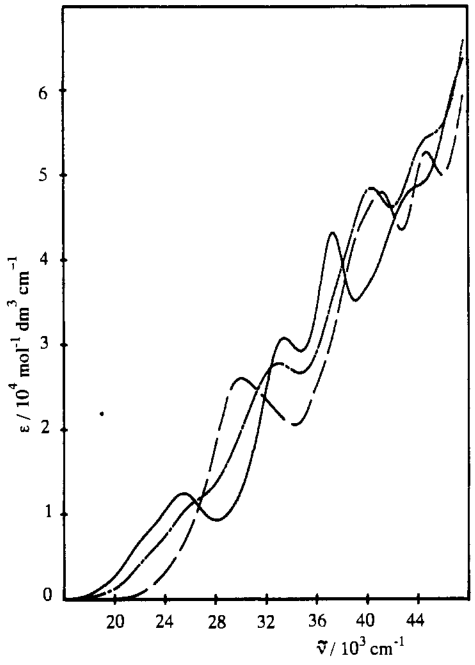

Figure 2. Electronic absorption spectra for **1** (—), **2** (– –), and **3** (– · · –) in H_2O.

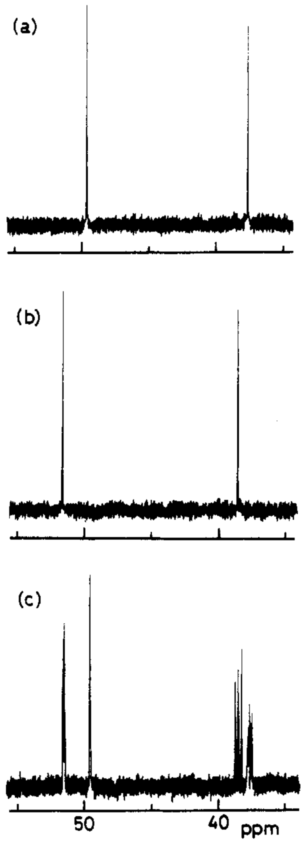

Figure 3. ^{13}C NMR spectra of **1** (a), **2** (b), and **3** (c) in D_2O (ppm from DSS).

Concluding Remarks

In the present study, it was found that the reactions of [Ni(aet)$_2$] or [Pd(aet)$_2$] with Pd^{II} produce the pinwheel-like S-bridged hexanuclear complexes [Pd$_2${M(aet)$_2$}$_4$]$^{4+}$ (M = Ni^{II} (**1**), Pd^{II} (**2**)). This S-bridged polynuclear structure composed of six square planes is stable in solution and may be regarded as a dimer of the trinuclear structure in [Pd{M(aet)$_2$}$_2$]$^{2+}$. An analogous hexanuclear complex [Ni$_2${Pd(aet)$_2$}$_4$]$^{4+}$ is expected to be formed by reacting [Pd(aet)$_2$] with Ni^{II}. However, this reaction was found to give a mixture of S-bridged hexanuclear complexes [Pd$_2${Ni(aet)$_2$}$_x${Pd(aet)$_2$}$_{4-x}$]$^{4+}$ (**3**). This result obviously implies that the didentate-N,S ligand aet readily transfers from the Pd^{II} to the Ni^{II} coordination sphere.

Supplementary Material Available: Tables SI–SXII, listing atomic coordinates and equivalent isotropic thermal parameters, complete bond distances and angles, and anisotropic thermal parameters for **1**–**3** (20 pages). Ordering information is given on any current masthead page.