First Conversion of a Square-planar [Ni(aet)$_2$] to an Octahedral [Ni(aet)$_2$L] by Forming S-Bridged Structure with Pt(II) (aet = 2-Aminoethanethiolate; L = (H$_2$O)$_2$ or 2,2'-Bipyridine)

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The reaction of [Ni(aet)$_2$] (aet = 2-aminoethanethiolate) with [PtCl$_2$(bpy)] (bpy = 2,2'-bipyridine) in water led to the geometrical conversion of Ni^{II} from square-planar to octahedral, giving a novel S-bridged Pt^{II}Ni^{II} complex, [Pt(bpy)-{Ni(aet)$_2$(H$_2$O)$_2$}]$^{2+}$ (**1**). **1** readily reacted with bpy in water to produce [Pt(bpy){Ni(aet)$_2$(bpy)}]$^{2+}$ (**2**), of which structure was determined by X-ray crystallography.

It has been shown that [M(thiolato-*S*)$_2$(amine-*N*)$_2$]-type complexes (M = Ni^{II}, Pd^{II}) can function as S-donating metalloligands to form S-bridged polynuclear complexes, retaining their square-planar coordination geometries.[1-4] For example, the reaction of [Ni(aet)$_2$] with NiCl$_2$ gave a linear-type S-bridge trinuclear complex, [Ni{Ni(aet)$_2$}$_2$]$^{2+}$, in which each square-planar *cis(S)*-[Ni(aet)$_2$] unit chelates to one Ni^{II} ion.[1] On the other hand, we have recently found that the reactions of [Ni(aet)$_2$] with Na$_2$PdCl$_4$ [4a] or K$_2$PtCl$_4$ [4b] produce pin-wheel-type S-bridged hexanuclear complexes, [M'$_2${Ni(aet)$_2$}$_4$]$^{4+}$ (M' = Pd^{II}, Pt^{II}), in which each square-planar *cis(S)*-[Ni(aet)$_2$] unit spans to two M' ions. From these facts, it is expected that a dinuclear complex [Pt(bpy){Ni(aet)$_2$}]$^{2+}$ or a tetranuclear complex [{Pt(bpy)}$_2${Ni(aet)$_2$}$_2$]$^{4+}$ is formed by the reaction of [Ni(aet)$_2$] with [PtCl$_2$(bpy)]. However, this reaction in water was found to produce a new type of dinuclear complex [Pt(bpy){Ni(aet)$_2$(H$_2$O)$_2$}]$^{2+}$ (**1**), in which the Ni^{II} ion does not have a square-planar coordination geometry but an octahedral geometry. In this paper we describe the synthesis and characterization of **1**, together with the crystal structure of [Pt(bpy){Ni(aet)$_2$(bpy)}]$^{2+}$ (**2**) which was readily formed by reacting **1** with bpy.

To a yellow aqueous suspension of [PtCl$_2$(bpy)] [5] (0.10 g) was added [Ni(aet)$_2$] [1a] (0.05 g), and the mixture was stirred at 50 ℃ for several minutes. The addition of a saturated aqueous NaNO$_3$ solution to the resulting yellow-brown reaction solution, followed by leaving at room temperature afforded yellow-brown crystals (the nitrate salt of **1**, 0.10 g).[6] Treatment of this complex (0.10 g) with bpy (0.024 g) in water at 50 ℃ caused the solution color change from yellow-brown to red-brown in a few minutes, and from this solution red-brown crystals (the nitrate salt of **2**) were isolated (0.08 g).[7]

X-Ray structural analysis of the nitrate salt of **2** revealed the presence of a discrete divalent complex cation, two nitrate anions, and a water molecule.[8] As shown in Figure 1, the complex cation contains one Ni and one Pt atoms, which is consistent with the plasma emission analysis.[7] The Ni atom is coordinated by two aet and one bpy ligands to have an approximately octahedral geometry. Its equatorial coordination sites are occupied by the two aet S and the two bpy N atoms and the axial sites are filled by the two aet N atoms, forming a C$_2$ symmetrical *cis(S)*-[Ni(aet)$_2$(bpy)] unit. The Pt atom has a square-planar geometry as in the case of the starting [PtCl$_2$(bpy)] complex, coordinated by the two bpy N atoms and the two S atoms from the *C$_2$-cis(S)*-[Ni(aet)$_2$(bpy)] unit. The Ni^{II}S$_2$N$_2$ equatorial plane and the Pt^{II}S$_2$N$_2$ plane are essentially coplanar (Figure 1), and therefore there is no interaction between the axial group of the *C$_2$-cis(S)*-[Ni(aet)$_2$(bpy)] unit and the vacant axial site of the Pt atom. The S-Ni-S angle (81.61(5)°) in **2** is very similar to that observed in the square-planar *cis(S)*-[Ni(aet)$_2$] unit of [Ni{Ni(aet)$_2$}$_2$]$^{2+}$ (81.4(2)°).[1b] However, it is noted that the Pt-S-Ni bridging angles (average 95.46(6)°) in **2** approach the ideal tetrahedral angle of 109.5°, compared with the Ni-S-Ni angles (average 77.5(2)°) in [Ni{Ni(aet)$_2$}$_2$]$^{2+}$.[1b] This suggests that the S-bridged structure in **2** with the octahedral *C$_2$-cis(S)* unit is less strained than the structure in [Ni{Ni(aet)$_2$}$_2$]$^{2+}$ with the square-planar *cis(S)* unit. The Ni-S bond distances (average 2.430(2) Å) in **2** are significantly longer than those in the *cis(S)*-[Ni(aet)$_2$] units of [Ni{Ni(aet)$_2$}$_2$]$^{2+}$ (average 2.155(5) Å).[1b] This is in accordance with the fact that the Ni-S distances in six-coordinated Ni^{II} complexes are usually longer than those in four-coordinated Ni^{II} complexes.[9]

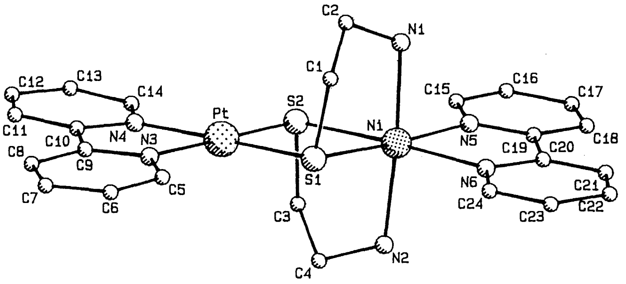
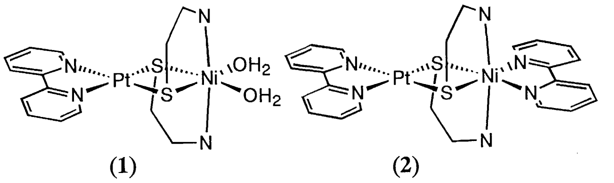


Figure 1. Perspective view of **2**.

The magnetic moment of **2**(NO$_3$)$_2$ is μ_{eff} = 3.13 B. M. at 296 K, which establishes that the octahedral Ni^{II} ion in **2** has a high-spin d^8 electronic configuration. The electronic absorption spectrum of **2** in water is characterized by a near-IR band at 11.82 x 10^3 cm^{-1} with a shoulder at the lower energy side (10.7 x 10^3 cm^{-1}) besides intense near-UV bands at 31.31, 32.85, 33.90, and 40.72 x 10^3 cm^{-1}.[7] A quite similar near-IR absorption band has been observed for an octahedral Ni^{II} mononuclear complex with sulfur donor atoms, which has been assigned as a spin allowed d-d transition ($^3A_{2g} \rightarrow {}^3T_{2g}$).[10]

The elemental and plasma emission analytical data indicate that the formulation of the nitrate salt of **1** is consistent with that of the expected planar-planar dinuclear structure in [Pt(bpy){Ni(aet)$_2$}](NO$_3$)$_2$·2H$_2$O.[6] However, the possibility of this structure is excluded from its magnetic moment (μ_{eff} = 3.23 B. M. at 296 K), which coincides well with that of **2**(NO$_3$)$_2$. The absorption spectral behavior of **1** in water is quite similar to that of **2** over the whole region, showing a near-IR band at 10.64 x 10^3 cm^{-1} with a shoulder at the lower energy side (9.1 x 10^3 cm^{-1}) and intense near-UV bands at 31.31, 32.55, 33.7, and 40.23 x 10^3 cm^{-1}.[6] Furthermore, the molar conductivity of the nitrate salt of **1** in water (228 Ω^{-1} cm^2 mol^{-1}) is in good



(1) (2)

Figure 2. Model structures of **1** and **2**.

agreement with that of the 1:2 electrolyte of $\mathbf{2}(NO_3)_2$ (216 Ω^{-1} cm^2 mol^{-1}). Accordingly, it is reasonable to assume that in water **1** has an S-bridged $Pt^{II}Ni^{II}$dinuclear structure with an octahedral *cis(S)*-[Ni(aet)$_2$(H$_2$O)$_2$] unit, [Pt(bpy){Ni(aet)$_2$(H$_2$O)$_2$}]$^{2+}$. Since the [Ni(aet)$_2$] complex did not react with water nor 2,2'-bipyridine even under severe conditions (ca. 80 ℃ for several hours), it is obvious that the conversion to the octahedral Ni^{II} unit is caused by the formation of the S-bridged structure with the planar Pt^{II}-bpy complex. Three geometries, *C_1-cis(O)*, *C_2-cis(O)*, and *trans(O)*, are possible for the *cis(S)*-[Ni(aet)$_2$(H$_2$O)$_2$] unit. Molecular model examinations reveal that a significant strain on the coordinated sulfur atoms exists in the *C_1-cis(O)* and *trans(O)* geometries, when the Ni^{II} equatorial plane is coplanar with the Pt^{II} one to avoid the axial-axial interaction. Considering these facts and that **1** readily reacts with bpy to form **2**, it is probable that the *cis(S)*-[Ni(aet)$_2$(H$_2$O)$_2$] unit in **1** adopts the *C_2-cis(O)* geometry (Figure 2).

In the IR spectrum (nujol mull suspension), $\mathbf{2}(NO_3)_2$ gives two strong N-O stretching bands at 1324 and 1352 cm^{-1} due to the free NO_3^-. Similar two bands are also observed in the IR spectrum of the nitrate salt of **1** (1317 and 1332 cm^{-1}). However, this complex exhibits additional bands at 1287 and 1404 cm^{-1}, which correspond well with the bands observed for the coordinated monodentato NO_3^-.[11] Thus, in the solid state the nitrate salt of **1** may have the planar-octahedral dinuclear structure in [Pt(bpy){Ni(aet)$_2$(NO$_3$)(H$_2$O)}](NO$_3$)·H$_2$O.

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6 Anal. Found: C, 23.25; H, 3.35; N, 11.64; Ni, 8.13; Pt, 27.01%. Calcd for PtNi(bpy)(aet)$_2$(H$_2$O)$_2$(NO$_3$)$_2$: C, 23.28; H, 3.26; N, 11.57; Ni, 8.50; Pt, 27.48%. Absorption spectrum in H$_2$O [ν_{max}, 10^3 cm^{-1} (ε , mol^{-1} dm^3 cm^{-1})]: 9.1 (9.9)^{sh}, 10.64 (17.69), 17.9 (10.3)^{sh}, 28.3 (24.9 x 10^3)^{sh}, 31.31 (14.60 x 10^3), 32.55 (13.51 x 10^3), 33.7 (11.0 x 10^3)^{sh}, 40.23 (20.46 x 10^3). The sh label denotes a shoulder.

7 Anal. Found: C, 33.30; H, 3.41; N, 12.91; Ni, 6.83; Pt, 22.63%. Calcd for PtNi(bpy)$_2$(aet)$_2$(NO$_3$)$_2$(H$_2$O): C, 33.50; H, 3.51; N, 13.02; Ni, 6.82; Pt, 22.67%. Visible-UV spectrum in H$_2$O [ν_{max}, 10^3 cm^{-1} (ε, mol^{-1} dm^3 cm^{-1})]: 10.7 (17.6)^{sh}, 11.82 (28.02), 28.7 (25.0 x 10^3)^{sh}, 31.31 (15.85 x 10^3), 32.85 (27.44 x 10^3), 33.90 (25.39 x 10^3), 40.72 (30.59 x 10^3).

8 Crystal data for [Pt(bpy){Ni(aet)$_2$(bpy)}](NO$_3$)$_2$·H$_2$O: *F. W.* = 860.5, triclinic, $P\bar{1}$, a = 12.640(3), b = 14.107(4), c = 9.382(2) Å, α = 106.28(1), β = 99.08(2), γ = 65.93(2)°, V = 1464.5(7) Å^3, Z = 2, Dc = 1.95 g cm^{-3}, $R(Rw)$ = 0.028 (0.032) for 5072 reflections. Selected bond distances (Å) and angles (°): Pt-S1 = 2.297(2), Pt-S2 = 2.297(2), Pt-N3 = 2.053(5), Pt-N4 = 2.050(5), Ni-S1 = 2.424(2), Ni-S2 = 2.435(2), Ni-N1 = 2.106(6), Ni-N2 = 2.103(6), Ni-N5 = 2.086(5), Ni-N6 = 2.086(5), S1-Pt-S2 = 87.46(5), N3-Pt-N4 = 79.3(2), S1-Ni-S2 = 81.61(5), S1-Ni-N1 = 85.2(2), S2-Ni-N2 = 85.3(2), N5-Ni-N6 = 78.1(2), Pt-S1-Ni = 95.60(6), Pt-S2-Ni = 95.32(5).

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