DOI: 10.1002/ejic.200500954

^{195}Pt NMR Spectra of Head-to-Head and Head-to-Tail Amidato-Bridged Platinum(III) Dinuclear Complexes

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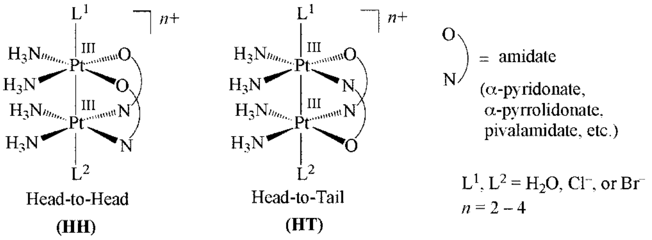
Keywords: Platinum / ^{195}Pt NMR / α-Pyridone / α-Pyrrolidone / Pivalamide / NMR spectroscopy

^{195}Pt chemical shifts and $^{1}J_{\text{Pt–Pt}}$ coupling constants were measured for a series of head-to-head (HH) and head-to-tail (HT) amidato-bridged *cis*-diammineplatinum(III) dinuclear complexes involved in the axial water substitution reactions with halide ions (X^- = Cl^-, Br^-): HH-$[Pt_2(NH_3)_4(\mu\text{-amidato})_2L^1L^2]^{n+}$ ≡ $[L^1\text{–}Pt(N_2O_2)\text{–}Pt(N_4)\text{–}L^2]^{n+}$ (amidato = α-pyridonato, α-pyrrolidonato, and pivalamidato) and HT-$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2L^1L^2]^{n+}$ ≡ $[L^1\text{–}Pt(N_3O)\text{–}Pt(N_3O)\text{–}L^2]^{n+}$; the diaqua ($L^1$, L^2 = H_2O, n = 4), the aquahalo (L^1 = X^-, L^2 = H_2O, n = 3), and the dihalo complexes (L^1, L^2 = X^-, n = 2). The ^{195}Pt NMR spectroscopic data were considered in relation to the lability in the axial ligand substitution reaction and the electron distribution along the Pt–Pt bond. The NMR spectroscopic data suggested different electron distributions along the Pt–Pt bonds in all the HH dimers and in the HT aquahalo dimers, such as $[L^1\text{–}Pt^{IV}(N_2O_2)\text{–}Pt^{II}(N_4)\text{–}L^2]^{n+}$ and $[X\text{–}Pt^{IV}(N_3O)\text{–}Pt^{II}(N_3O)\text{–}OH_2]^{3+}$, respectively. Relative shifts of the ^{195}Pt NMR signals for each substitution step indicate that the replacement of the axial water ligand by X^- affects more effectively the electron density of the opposite Pt atom than that of the substituted one.

Introduction

Head-to-head (HH) and head-to-tail (HT) amidato-bridged platinum(III) dinuclear complexes having a metal–metal bond between the two d^7 platinum atoms have two inorganic axial ligands, and the substitution reactions at the axial sites are well known synthetically[1–3] and kinetically.[4–8]

The two platinum atoms in the HH complex are not equivalent, that is, one is coordinated by two amidate oxygen atoms and two ammine nitrogen atoms $[Pt(N_2O_2)]$, whereas the other is coordinated by four nitrogen atoms $[Pt(N_4)]$. On the other hand, the HT complex has two equivalent Pt atoms $[Pt(N_3O)]$.



The axial ligand substitution with halide ion (X^- = Cl^-, Br^-) on both the HH and HT diaqua Pt^{III} complexes occurs consecutively in two steps [Equations (1) and (2)].[4–6]

$$[(H_2O)Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2(OH_2)]^{4+} + X^- \xrightleftharpoons{\text{step 1}} [(H_2O)Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2(X)]^{3+} + H_2O \quad (1)$$

$$[(H_2O)Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2(X)]^{3+} + X^- \xrightleftharpoons{\text{step 2}} [(X)Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2(X)]^{2+} + H_2O \quad (2)$$

In step 1 [Equation (1)] for the reaction of the diaqua Pt^{III} dinuclear complexes, deprotonation of the aqua ligands occurs preferentially on the $Pt(N_4)$ atom and substitution occurs on the $Pt(N_2O_2)$ atom in HH diaqua Pt^{III} complexes, whereas deprotonation occurs on one of the two equivalent $Pt(N_3O)$ atoms and substitution occurs on the other $Pt(N_3O)$ atom in HT diaqua Pt^{III} complexes. There are two parallel reaction paths in step 1 for both HH and

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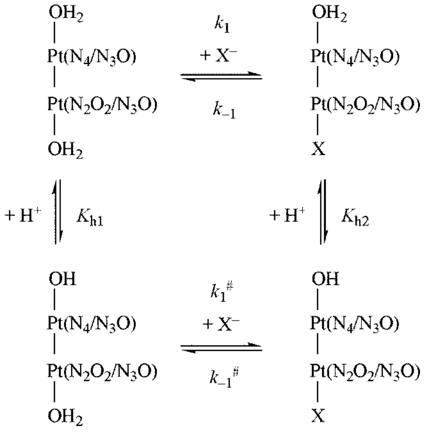
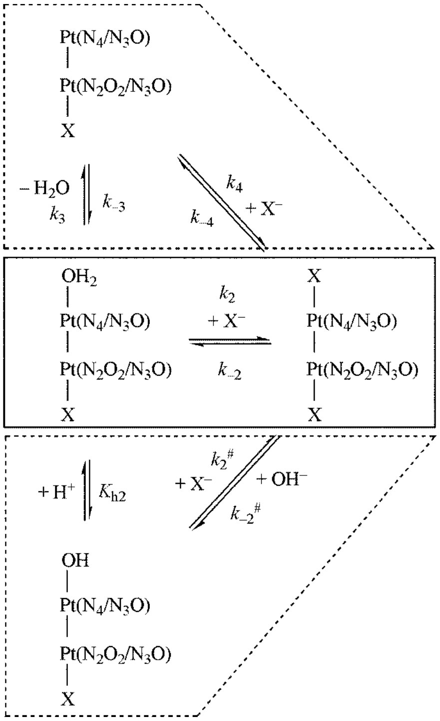
HT complexes (k_1 and $k_1^{\#}$ in Scheme 1), because the diaqua complex exists in equilibrium with the aquahydroxo complex, and both complexes undergo substitution with X^-.[4–8] In step 2 [Equation (2)], there are three possible pathways (Scheme 2), and step 2 proceeds by either one or two paths of the three, depending on the axial ligand (X^-). One of the three paths is the direct substitution path (**A**), the second path (**B**) is by dissociation of the water molecule on the $Pt(N_4)$ atom or on the $Pt(N_3O)$ atom, and the third (**C**) is the unusual path of OH^- replacement.[4–6] The substitution lability of the second step is influenced strongly by the first halide ligand on the opposite axial site, which is explained as follows: the extent of the charge localization in the Pt–Pt bond in the dinuclear complex {the contribution of $[X–Pt^{IV}(NH_3)_2(\mu\text{-amidato})_2Pt^{II}(NH_3)_2–OH_2]^{3+}$ as compared to $[X–Pt^{III}(NH_3)_2(\mu\text{-amidato})_2Pt^{III}(NH_3)_2–OH_2]^{3+}$} depends largely on the electron-donating ability of the first substituted ligand (X^-), which is reflected in the reaction mechanisms examined so far for several amidato-bridged Pt^{III} dinuclear complexes. The different extent of the Pt–Pt bond polarization leads to variations of the substitution lability and coordination stability of the axial aqua ligand, thus affecting the substitution reaction mechanism. When X^- is less electron-donating, paths **A** and **C** or only path **A** take place in the reactions of the HT α-pyridonato-bridged and HH α-pyrrolidonato-bridged complexes, whereas paths **A** and **B** are preferred in these complexes when X^- is more electron-donating, though paths **A** and **B** are preferred irrespective of X^- in the reaction of the HH α-pyridonato-bridged complex.[4–6] In contrast, however, paths **A** and **C** are involved in the reaction of the HH pivalamidato-bridged complex for more electron-donating X^- (Scheme 2 and Table 1).[6]



Scheme 1. Reaction paths in step 1 for the reaction of the HH and HT amidato-bridged Pt^{III} dimer with X^- ($X^- = Cl^-$ or Br^-).



Scheme 2. Three possible reaction paths in step 2 for the reaction of the HH and HT amidato-bridged Pt^{III} dimer with X^- (= Cl^- or Br^-).

Table 1. Reaction paths in step 2 (**A**, **B**, and **C** in Scheme 2) for the reactions of HH and HT Pt^{III} dimers with halide ions.[a]

Pt^{III} dimer	$X^- = Cl^-$	$X^- = Br^-$
α-Pyridonato-bridged HH	**A** and **B**	**A** and **B**
α-Pyrrolidonato-bridged HH	**A**	**A** and **B**
Pivalamidato-bridged HH	**A**	**A** and **C**
α-Pyridonato-bridged HT	**A** and **C**	**A** and **B**

[a] Refs.[4–6]

In this paper we present the systematic ^{195}Pt NMR spectroscopic data for a series of the HH and HT amidato-bridged *cis*-diammineplatinum(III) dinuclear complexes involved in the axial water substitution reactions with halide ions ($X^- = Cl^-$, Br^-): HH-$[Pt_2(NH_3)_4(\mu\text{-amidato})_2L^1L^2]^{n+}$ (amidato = α-pyridonato, α-pyrrolidonato, and pivalamidato) and HT-$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2L^1L^2]^{n+}$; the diaqua ($L^1$, $L^2 = H_2O$, $n = 4$), the aquahalo ($L^1 = X^-$, $L^2 = H_2O$, $n = 3$), and the dihalo complexes (L^1, $L^2 = X^-$, $n = 2$). The electron localization and consequently the axial ligand substitution must be reflected in the ^{195}Pt NMR spectroscopic data. The exceptional reactivity observed for the second step (step 2) of the HH pivalamidato-bridged Pt^{III} dinuclear complex (Scheme 2 and Table 1) may be reflected in and related to the chemical shift and the Pt–Pt coupling constant of the ^{195}Pt NMR spectra.

Results and Discussion

Assignment of ^{195}Pt NMR Signals

Figure 1 shows the ^{195}Pt NMR spectra of the HH diaqua complex bridged by α-pyridonate {the HH-$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2(OH_2)_2]^{4+}$ complex}. A set of two signals at higher and lower fields both with a couple of satellite signals due to Pt–Pt coupling was successfully assigned to $Pt(N_4)$ and $Pt(N_2O_2)$, respectively, based on the multiplicity of the lines [9 for $Pt(N_4)$ and 5 for $Pt(N_2O_2)$ because of ^{195}Pt–^{14}N coupling]. Similar assignable signals were observed for all the other HH α-pyridonato-bridged Pt^{III} dimers, that is, the aquachloro (Figure 2), aquabromo (Figure S1), dichloro (Figure S2), and dibromo complexes (Figure S3). The signal of the $Pt(N_2O_2)$ moiety of all the HH α-pyridonato-bridged Pt^{III} dimers is always observed at a lower field, and the $Pt(N_4)$ signal at a higher field. For the HH α-pyrrolidonato-bridged and the pivalamidato-bridged complex systems, the signal assignments similar to those of α-pyridonato-bridged dimers are applied to the aquahalo and dihalo complexes. The ^{195}Pt NMR signals for the α-pyrrolidonato-bridged and the pivalamidato-bridged HH diaqua complexes could not be assigned; the Pt–Pt coupling was observed with no distinguishable Pt–N couplings such as those mentioned above (Figures S12 and S13). Therefore, the assignment for these diaqua dimers was performed according to the result of the HH α-pyridonato-bridged diaqua complex. The ^{195}Pt chemical shifts (δ_{Pt}) and Pt–Pt coupling constants ($^1J_{Pt-Pt}$) for the present HH amidato-bridged Pt^{III} dinuclear complexes are summarized in Table 2.

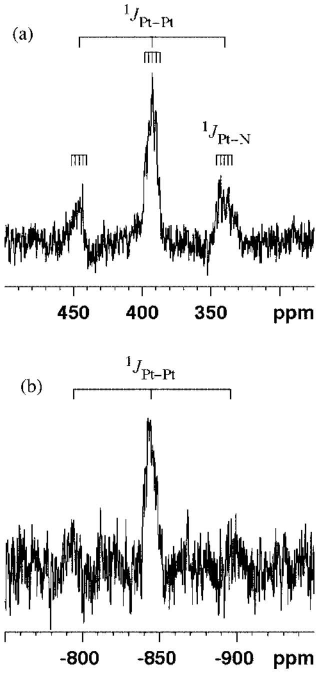


Figure 1. ^{195}Pt NMR signals of the $Pt(N_2O_2)$ (a) and the $Pt(N_4)$ (b) moieties in the HH α-pyridonato-bridged diaqua dimer in $DClO_4$ (1.2 M)/D_2O.

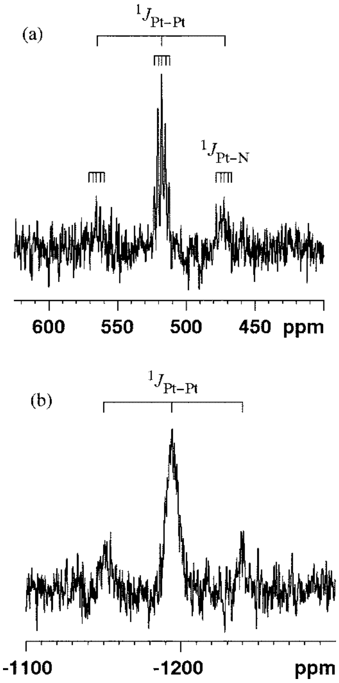


Figure 2. ^{195}Pt NMR signals of the $Pt(N_2O_2)$ (a) and the $Pt(N_4)$ (b) moieties in the HH α-pyridonato-bridged aquachloro dimer in $DClO_4$ (1.2 M)/D_2O.

The HT α-pyridonato-bridged Pt^{III} dimer complexes with the same axial ligands (the diaqua, dichloro, and dibromo dimers) showed a single ^{195}Pt NMR signal (Figure S14), as the two platinum atoms are equivalent: $[L^1–Pt(N_3O)–Pt(N_3O)–L^2]^{n+}$ where $L^1 = L^2$. On the other hand, the HT aquahalo complexes afforded two different ^{195}Pt signals (Figures S15 and S16) that have similar Pt–Pt (a couple of satellite) and Pt–N couplings [a multiplicity of 7 due to $Pt(N_3O)$ moieties] to those of the HH complexes. Therefore, the assignment of these HT aquahalo dimers was done based on the results of the corresponding HH amidato-bridged Pt^{III} aquahalo complexes; a lower-field signal was assigned to $X–Pt(N_3O)$, while a higher-field signal was assigned to $Pt(N_3O)–OH_2$. In Table 2 the δ_{Pt} and $^1J_{Pt-Pt}$ values obtained for the HT α-pyridonato-bridged Pt^{III} dimers are also listed.

The ^{195}Pt NMR spectra of the HH and HT amidato-bridged Pt^{III} aquahydroxo complexes could not be measured because of the gradual decomposition of the complexes in less acidic aqueous solution for a prolonged measuring time (> ca. 8 h).

In general, the ^{195}Pt chemical shifts of Pt^{IV} complexes tend to be at lower fields than those of Pt^{II} complexes (Table S1).[9,10] Therefore, the HH amidato-bridged Pt^{III} dimer seems to be polarized close to $[L^1–Pt^{IV}(N_2O_2)–Pt^{II}(N_4)–L^2]^{n+}$ (L^1, L^2 = H_2O, Cl^-, or Br^-). Our previous studies on the reaction of the diaqua complex, $[H_2O–Pt^{IV}(N_2O_2)–Pt^{II}(N_4)–OH_2]^{4+}$, with X^- showed that the first substitution always occurs at the $Pt^{IV}(N_2O_2)$ atom and the acid dissociation occurs preferentially at the axial H_2O ligand of the $Pt^{II}(N_4)$ atom.[5,6] It is known that Pt^{II} complexes are usually inert for substitution, and Pt^{IV} complexes are even more inert.[11] In the HH amidato-bridged Pt^{III} dimer, however, the axial site of the $Pt(N_2O_2)$ atom having Pt^{IV} character is more substitution-active than that of the $Pt(N_4)$ atom having Pt^{II} character, which suggests that both the $Pt(N_2O_2)$ and the $Pt(N_4)$ atoms still have a Pt^{III} character to a substantial extent in the polarized Pt^{III} complexes. In all these complexes, deprotonation occurs preferentially at the $H_2O–Pt^{II}(N_4)$ moiety having a shorter $Pt–OH_2$ bond, whereas the first substitution occurs at the $Pt^{IV}(N_2O_2)$ atom having a longer $Pt–OH_2$ bond.

Table 2. ^{195}Pt NMR chemical shifts of the head-to-head (HH) and head-to-tail (HT) amidato-bridged Pt^{III} dinuclear complexes and the lantern-type complexes.[a]

Type	Bridging ligand	L^1–Pt–Pt–L^2	δ_{Pt} [ppm] (assignment)		$\Delta\delta$ (δ_{center}) [ppm]	$^1J_{Pt-Pt}$ [Hz]	Path in step 2
HH	α-pyridonate	H_2O/H_2O	393 [$Pt(N_2O_2)$]	–844 [$Pt(N_4)$]	1237 (–226)	8886	
		Cl^-/Cl^-	129 [$Pt(N_2O_2)$]	–948 [$Pt(N_4)$]	1077 (–410)	6636	
		Br^-/Br^-	–32 [$Pt(N_2O_2)$]	–988 [$Pt(N_4)$]	956 (–510)	6306	
		Cl^-/H_2O	518 [$Pt(N_2O_2)$]	–1194 [$Pt(N_4)$]	1712 (–338)	7774	**A + B**
		Br^-/H_2O	643 [$Pt(N_2O_2)$]	–1391 [$Pt(N_4)$]	2034 (–374)	7574	**A + B**
	α-pyrrolidonate	H_2O/H_2O	266[b]	–889[b]	1155 (–312)	9482	
		Cl^-/Cl^-	3 [$Pt(N_2O_2)$]	–1081 [$Pt(N_4)$]	1084 (–539)	7132	
		Br^-/Br^-	–140 [$Pt(N_2O_2)$]	–1195 [$Pt(N_4)$]	1055 (–668)	6682	
		Cl^-/H_2O	328 [$Pt(N_2O_2)$]	–1288 [$Pt(N_4)$]	1616 (–480)	8096	**A**
		Br^-/H_2O	439 [$Pt(N_2O_2)$]	–1545 [$Pt(N_4)$]	1984 (–553)	7940	**A + B**
	pivalamidate	H_2O/H_2O	222[b]	–989[b]	1212 (–384)	9262	
		Cl^-/Cl^-	8 [$Pt(N_2O_2)$]	–1190 [$Pt(N_4)$]	1198 (–591)	7216	
		Br^-/Br^-	–108 [$Pt(N_2O_2)$]	–1327 [$Pt(N_4)$]	1219 (–718)	6902	
		Cl^-/H_2O	284 [$Pt(N_2O_2)$]	–1383 [$Pt(N_4)$]	1667 (–550)	8234	**A**
		Br^-/H_2O	394 [$Pt(N_2O_2)$]	–1672 [$Pt(N_4)$]	2066 (–639)	8086	**A + C**
HT	α-pyridonate	H_2O/H_2O	–265		0 (–265)		
		Cl^-/Cl^-	–433		0 (–433)		
		Br^-/Br^-	–529		0 (–529)		
		Cl^-/H_2O	–102 (Pt–Cl)[c]	–652 (Pt–OH_2)[c]	550 (–377)	7564	**A + C**
		Br^-/H_2O	20 (Pt–Br)[c]	–900 (Pt–OH_2)[c]	920 (–440)	7260	**A + B**
Lantern[d]	hydrogenphosphate	H_2O/H_2O	1796		0 (1796)		
		Cl^-/Cl^-	1822		0 (1822)		
		Br^-/Br^-	1744		0 (1744)		
		Cl^-/H_2O	1713 (Pt–Cl)	1886 (Pt–OH_2)	173 (1800)	5342	
		Br^-/H_2O	1550 (Pt–Br)	1973 (Pt–OH_2)	423 (1761)	5349	
	sulfate	H_2O/H_2O	1756		0 (1756)		
		Cl^-/Cl^-	1720		0 (1720)		
		Br^-/Br^-	1592		0 (1592)		
		Cl^-/H_2O	1638 (Pt–Cl)	1809 (Pt–OH_2)	170 (1724)	3464	
		Br^-/H_2O	1440 (Pt–Br)	1866 (Pt–OH_2)	427 (1653)	3472	

[a] Relative to aqueous H_2PtCl_6 (δ = 0 ppm) or K_2PtCl_4 (δ = –1622 ppm) as external references. [b] The signals could not be assigned experimentally. [c] The assignments are performed based on the trends of the chemical shift change in the HH complex systems. [d] Refs.[15,16]

^{195}Pt Chemical Shifts and $^1J_{Pt-Pt}$ Coupling Constants

Variations of the ^{195}Pt chemical shift for the diaqua, dichloro, and dibromo complexes of HH-[L^1–$Pt(N_2O_2)$–$Pt(N_4)$–L^2]$^{n+}$ and HT-[L^1–$Pt(N_3O)$–$Pt(N_3O)$–L^2]$^{n+}$ (L^1 = L^2) are shown in Figure 3. For the HH diaqua and dihalo complexes, both of the $Pt(N_2O_2)$ and the $Pt(N_4)$ signals shift to higher field, when both of the axial aqua ligands are changed to Cl^- and Br^-, though the $\Delta\delta$ (= $\delta_{Pt(N_2O_2)} - \delta_{Pt(N_4)}$) values are almost constant (Table 2). A similar tendency is observed for the chemical shift of the $Pt(N_3O)$ signal in the HT complex. On the other hand, when only the aqua ligand on the $Pt(N_2O_2)$ atom in the HH diaqua dimer is changed to Cl^- and Br^-, the $Pt(N_2O_2)$ signals shift to much lower fields and the $Pt(N_4)$ signals shift to much higher fields, compared to those of the diaqua, dichloro (Figure 4a), and dibromo complexes (Figure 4b). The X–$Pt(N_3O)$ and H_2O–$Pt(N_3O)$ signals of the HT dimer shift similarly (Figure 4). These indicate that the Pt–Pt bonds in the monosubstituted (aquahalo) complexes are more polarized as X–$Pt^{IV}(N_2O_2/N_3O)$–$Pt^{II}(N_4/N_3O)$–OH_2, compared to those of the Pt^{III} dimer complexes having the same axial ligands (the diaqua and dihalo complexes).

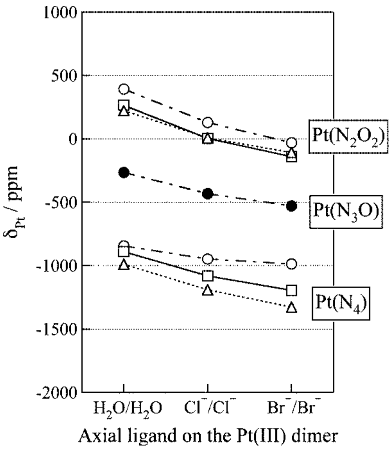


Figure 3. Dependence of δ_{Pt} on the axial ligands in the diaqua, dichloro, and dibromo complexes of the HH α-pyridonato-bridged (○), α-pyrrolidonato-bridged (□), and pivalamidato-bridged (Δ) dimers [$Pt(N_2O_2)$ and $Pt(N_4)$] and the HT α-pyridonato-bridged (●) dimer [$Pt(N_3O)$].

Variation of the Pt–Pt coupling constants with the axial ligands is depicted in Figure 5. The coupling constants in each HH dimer system tend to decrease in the order: H_2O–$Pt(N_2O_2)$–$Pt(N_4)$–OH_2 > Cl–$Pt(N_2O_2)$–$Pt(N_4)$–OH_2 > Br–$Pt(N_2O_2)$–$Pt(N_4)$–OH_2 > Cl–$Pt(N_2O_2)$–$Pt(N_4)$–Cl > Br–$Pt(N_2O_2)$–$Pt(N_4)$–Br. In all of the HH aquahalo and dihalo complexes, the coupling constants decrease in the order: pivalamidato-bridged dimer > α-pyrrolidonato-bridged di-

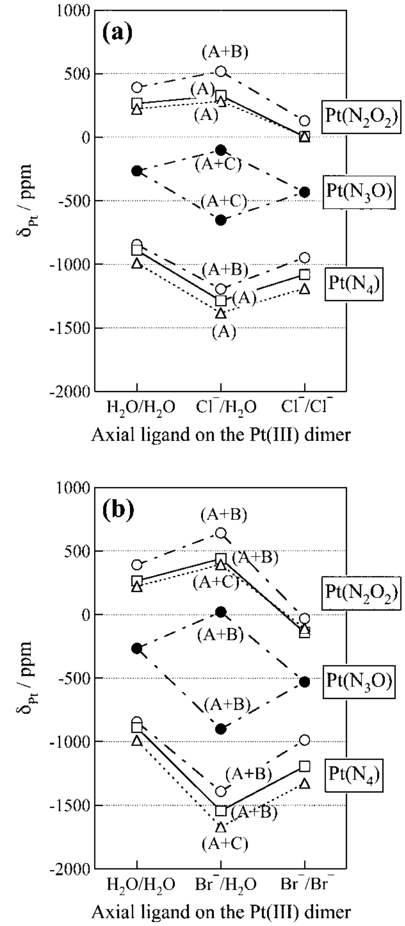


Figure 4. Dependence of δ_{Pt} on the axial ligands in the diaqua, aquahalo, and dihalo complexes for the reaction systems with Cl^- (a) and Br^- (b); HH α-pyridonato-bridged (○), α-pyrrolidonato-bridged (□), and pivalamidato-bridged (Δ) dimers [$Pt(N_2O_2)$ and $Pt(N_4)$] and HT α-pyridonato-bridged (●) dimer [$Pt(N_3O)$].

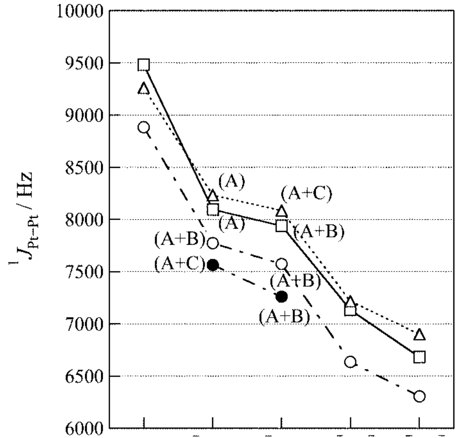


Figure 5. Dependence of $^1J_{Pt-Pt}$ on the axial ligands in the HH α-pyridonato-bridged (○), α-pyrrolidonato-bridged (□), and pivalamidato-bridged (Δ) dimers and the HT α-pyridonato-bridged (●) dimer.

mer > α-pyridonato-bridged dimer, but for the HH diaqua complexes the order is different, that is, the coupling constant of the pivalamidato-bridged dimer is smaller than that of the α-pyrrolidanato-bridged dimer.

^{195}Pt NMR Spectroscopic Data and Ligand Substitution Mechanism

Both of the ^{195}Pt NMR chemical shifts and the Pt–Pt coupling constants should be taken into account to understand the electronic structure of the Pt–Pt bonds and the mechanism of the axial substitution reactions. The deprotonation and the substitution lability of the diaqua dimers mentioned earlier in this paper suggest that the L^2–$Pt(N_4)$ bond having a higher-field chemical shift would be stronger and less labile than the L^1–$Pt(N_2O_2)$ bond having a lower-field shift in each complex, that is, the diaqua, aquahalo, and dihalo complexes. In other words, the Pt atom having the stronger axial Pt–L bond would give the higher-field chemical shift in the present HH amidato-bridged dimer complexes. Thus, both of the L^1–$Pt(N_2O_2)$ and the L^2–$Pt(N_4)$ bonds become stronger in the order: diaqua dimer < dichloro dimer < dibromo dimer. On the other hand, the Pt–Pt bond becomes weaker in the same order, based on the Pt–Pt coupling constants in Figure 5.

In the aquachloro complexes {$[Cl–Pt(N_2O_2)–Pt(N_4)–OH_2]^{3+}$}, all of the axial bonds, Cl–$Pt(N_2O_2)$, Pt–Pt, and $Pt(N_4)$–OH_2 bonds, would be strengthened in the order: α-pyridonato-bridged dimer < α-pyrrolidonato-bridged dimer < pivalamidato-bridged dimer, as the resonance fields (opposite order in the chemical shifts) and the coupling constants increase in the same order (Figure 4a and Figure 5). The same is true for a series of aquabromo dimers (Figure 4b and Figure 5). These orders of the axial bond strengths in the aquahalo dimers explain the variation of the axial water substitution mechanism in step 2 (Scheme 2) among the HH dimer systems. (1) For the HH dimer + Cl^- systems, the reaction of the HH α-pyridonato-bridged aquachloro dimer proceeds through paths **A** and **B**, while the reactions of the α-pyrrolidonato-bridged and the pivalamidato-bridged aquachloro dimers proceed only by path **A**, because the H_2O–$Pt(N_4)$ bond in the former dimer is relatively weak compared to that of the latter. (2) For the HH dimer + Br^- systems, both of the α-pyridonato-bridged and α-pyrrolidonato-bridged aquabromo dimers prefer paths **A** and **B**, because of the weaker H_2O–$Pt(N_4)$ bonds. In contrast, however, the pivalamidato-bridged dimer reacts with Br^- by paths **A** and **C** in step 2. The exceptional behavior would be because deprotonation of the H_2O ligand at the $Pt(N_4)$ atom is easier owing to the stronger H_2O–$Pt(N_4)$ bond. This is strongly supported by the highest field in the chemical shifts and the coupling constant of the pivalamidato-bridged aquabromo dimer among the present HH dimer + Br^- systems (Figures 4b and 5).

The pK_a values of the diaqua complexes are reported to be 1.71, 1.74, and 2.88 for the α-pyridonato-bridged dimer, the α-pyrrolidonato-bridged dimer, and the pivalamidato-bridged dimer, respectively,[6,12] which is the opposite of the result expected from the chemical shift data of these diaqua complexes. The $^1J_{\mathrm{Pt-Pt}}$ values of the diaqua dimers, which would involve the effects of all of the axial bonds as well as of the equatorial (bridging) ligands, decrease in the order: α-pyrrolidonato-bridged dimer > pivalamidato-bridged dimer > α-pyridonato-bridged dimer (Figure 4). These differences would be explained by: the chemical shifts and the coupling constants reflect the electronic distributions around the Pt atoms in the $H_2O–Pt(N_2O_2)–Pt(N_4)–OH_2$ moiety, while pK_a reflects the Pt–OH_2 bond strength. It seems that the effects of both the bridging ligands and the axial ligands are important in determining the substitution reaction path.

The exceptional reactivity of the HH pivalamidato-bridged Pt^{III} dinuclear complex (Scheme 2 and Table 1), as mentioned above, could not be explicitly reflected in the chemical shift and coupling constant of the ^{195}Pt NMR spectroscopy. This may suggest that not only electronic effects that are reflected in the NMR spectroscopic data but also (dynamic) steric effects due to bridging ligands, complementary ligands, solvent, etc. contribute significantly and complicatedly to the determination of the ligand substitution mechanism for the present systems. That is, the ^{195}Pt NMR spectroscopic data would be reproduced by detailed DFT calculations including solvent effect, relativistic effect, etc.,[13] but the calculations do not serve the ligand substitution mechanism.

Comparison Between the Amidato-Bridged Pt^{III} Dinuclear Complexes and the Lantern-Type Pt^{III} Dinuclear Complexes

In Table 2, the ^{195}Pt chemical shifts of the lantern-type complexes are at much lower field than those of the amidato-bridged complexes, and the $\Delta\delta$ values of the aquahalo lantern-type complexes are much smaller than those of the amidato-bridged aquahalo dimers, that is, much less electron localization occurs in the lantern-type complexes, suggesting that the reactivities of the two-type complexes are different. Indeed, the axial ligand substitution occurs in two steps in the present amidato-bridged complexes, whereas it is one step in the hydrogenphosphato-bridged lantern-type complex.[14] In the amidato-bridged diaqua complexes, the two Pt centers behave differently and independently, because the electron distribution along the Pt–Pt bond of the intermediate (the aquahalo complex) after step 1 of the amidato-bridged complexes is very different from that of the original diaqua complex. This fact and the ^{195}Pt NMR spectroscopic data again support the higher flexibility of the Pt–Pt bond in the amidato-bridged complexes compared to those of the lantern-type complexes, as mentioned in the previous report.[14] In Table 2, two opposite assignments of ^{195}Pt NMR for the same complex, $[(L)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{n-}$ (L = Cl^-, Br^-, SCN^-, NO_2^-, CN^-, NH_3, etc.) are reported by Appleton et al.: (a) a higher field is assigned to Pt–L and a lower field to Pt–OH_2 for L = Cl^-, Br^-, and SCN^-, and (b) a lower field is assigned to Pt–L and a higher field to Pt–OH_2 for L = NO_2^-, CN^-, and NH_3.[15,16] All of the assignments of the aquahalo amidato-bridged complexes, which are based on the Pt–N coupling pattern of HH α-pyridonato-bridged complexes, are consistent with assignment (b). Table 2 and Figure 4 show that axial ligand substitution has much more influence on the opposite Pt atom $[Pt(N_4)]$ than the Pt atom directly coordinated with X^- $[Pt(N_2O_2)]$.

Conclusions

^{195}Pt NMR spectroscopic data (the chemical shifts and Pt–Pt coupling constants) were systematically obtained for a series of HH and HT bis(amidato-bridged) platinum(III) dinuclear complexes existing in the axial water ligand substitution reactions with Cl^- and Br^-. Polarization of the Pt–Pt bond is observed in the ^{195}Pt NMR spectra for the HH amidato-bridged diaqua Pt^{III} dinuclear complex similarly to the HH aquahalo Pt^{III} complexes, that is, the Pt–Pt bond is polarized approximately to $[H_2O–Pt^{IV}(N_2O_2)–Pt^{II}(N_4)–OH_2]^{4+}$. The first substitution of H_2O on the $Pt^{IV}(N_2O_2)$ atom with X^- enhances the electron localization to form the more polarized aquahalo complex having very different axial Pt–OH_2 bond lengths from that of the original diaqua complex. More pronounced electron localization was observed for the HT complex. The second substitution of the H_2O ligand on the $Pt^{II}(N_4)$ atom in $[X–Pt^{IV}(N_2O_2)–Pt^{II}(N_4)–OH_2]^{3+}$ with X^- reduces the electron polarization to an extent similar to the diaqua complex.

Experimental Section

Materials: *cis*-$[Pt(NH_3)_2Cl_2]$ was prepared from $K_2[PtCl_4]$ (Tanaka Kikinzoku Kogyo K. K., Tokyo) according to Dhara's method.[17] α-Pyridone (97+%, Wako Pure Chemical Industries Ltd., Osaka) was recrystallized twice from water. Reagent grade α-pyrrolidone (Kanto Chemical Co. Inc., Tokyo) was purified once by vacuum distillation. Pivalamide (98%, Kanto) was recrystallized twice from water. HT-$[(NO_3)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_2\cdot 0.5H_2O$ (HT α-pyridonato-bridged dimer), HH-$[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_3\cdot 2H_2O$ (HH α-pyridonato-bridged dimer), HH-$[(H_2O)Pt(NH_3)_2(\mu\text{-}C_4H_6NO)_2Pt(NH_3)_2(H_2O)](NO_3)_4\cdot 2H_2O$ (HH α-pyrrolidonato-bridged dimer), and HH-$[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_{10}NO)_2Pt(NH_3)_2(H_2O)](NO_3)_4\cdot 2H_2O$ (HH pivalamidato-bridged dimer) were prepared according to the literature.[18–21] Sodium chloride (99.99%, Aldrich) and sodium bromide (99.99%, Aldrich) were used without further purification. The NMR sample solution was prepared by using D_2O (99.9 atom-%, Isotec) and [D]perchloric acid (68 wt.-% in D_2O, Aldrich).

Measurements: The ^{195}Pt NMR spectra were recorded with a Bruker Avance 400 spectrometer operating at 85.9 MHz at ambient temperature (20 ± 2 °C). The chemical shift was referenced to H_2PtCl_6 (δ = 0 ppm) or K_2PtCl_4 (δ = –1622 ppm) as external standards. The sample solution was prepared by using an acidic D_2O solution ($DClO_4/D_2O$) to suppress deprotonation of the diaqua complexes; acid dissociation constants: $-\log K_{h1}$ = 1.98 (HT α-pyridonato-bridged dimer),[4] 1.71 (HH α-pyridonato-bridged dimer),[5] 1.74 (HH α-pyrrolidonato-bridged dimer),[6,12] and 2.88 (HH pivalamidato-bridged dimer).[6] The concentration of the platinum(III) dimer (C_{Pt}) was adjusted to appropriately 5–40 mM according to the solubility of each compound in D_2O. The concentration of halide ion (C_X) in the monohalo and dihalo complex solutions was adjusted considering each equilibrium constant (K_1^X, K_2^X); $\log K_1^{Cl} = 5.27$ and $\log K_2^{Cl} = 3.83$ (HT α-pyridonato-bridged dimer + Cl^-),[4] $\log K_1^{Br} = 5.53$ and $\log K_2^{Br} = 4.44$ (HT α-pyridonato-bridged dimer + Br^-),[4] $\log K_1^{Cl} = 5.93$ and $\log K_2^{Cl} = 3.71$ (HH α-pyridonato-bridged dimer + Cl^-),[5] $\log K_1^{Br} = 6.20$ and $\log K_2^{Br} = 4.55$ (HH α-pyridonato-bridged dimer + Br^-),[5] $\log K_1^{Cl} = 5.61$ and $\log K_2^{Cl} = 3.73$ (HH α-pyrrolidonato-bridged dimer + Cl^-),[6] $\log K_1^{Br} = 5.50$ and $\log K_2^{Br} = 4.68$ (HH α-pyrrolidonato-bridged dimer + Br^-),[6] $\log K_1^{Cl} = 5.04$ and $\log K_2^{Cl} = 3.21$ (HH pivalamidato-bridged dimer + Cl^-),[6] and $\log K_1^{Br} = 5.93$ and $\log K_2^{Br} = 3.91$ (HH pivalamidato-bridged dimer + Br^-).[6]

Supporting Information (see footnote on the first page of this article): Pt^{195} NMR chemical shifts of Pt^{IV} and Pt^{II} complexes (Table S1) and ^{195}Pt NMR spectra of all the other HH and HT Pt^{III} dimers measured in this study except for the spectra shown in Figures 1 and 2 (Figures S1–S16).

Acknowledgments

We wish to express our thanks for financial supports from the 21COE "Practical Nano-Chemistry" project from MEXT, Japan and from the Waseda University Grant for Special Research Projects (2004A-131).

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[1] K. Matsumoto, M. Ochiai, *Coord. Chem. Rev.* **2002**, *231*, 229–238, and references therein.
[2] K. Matsumoto, K. Sakai, *Adv. Inorg. Chem.* **2000**, *49*, 375–427, and references therein.
[3] B. Lippert, *Coord. Chem. Rev.* **1999**, *182*, 263–295, and references therein.
[4] N. Saeki, Y. Hirano, Y. Sasamoto, I. Sato, T. Toshida, S. Ito, N. Nakamura, K. Ishihara, K. Matsumoto, *Eur. J. Inorg. Chem.* **2001**, 2081–2088.
[5] N. Saeki, Y. Hirano, Y. Sasamoto, I. Sato, T. Toshida, S. Ito, N. Nakamura, K. Ishihara, K. Matsumoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 861–868.
[6] K. Shimazaki, H. Sekiya, H. Inoue, N. Saeki, N. Nakamura, K. Ishihara, K. Matsumoto, *Eur. J. Inorg. Chem.* **2003**, 1785–1793.
[7] N. Saeki, N. Nakamura, T. Ishibashi, M. Arime, H. Sekiya, K. Ishihara, K. Matsumoto, *J. Am. Chem. Soc.* **2003**, *125*, 3605–3616.
[8] M. Arime, K. Ishihara, K. Matsumoto, *Inorg. Chem.* **2004**, *43*, 309–316.
[9] R. J. Goodfellow in *Multinuclear NMR* (Ed.: J. Mason), Plenum Press, New York, **1987**.
[10] *Studies in Inorganic Chemistry*, vol. 13 ("Transition Metal Nuclear Magnetic Resonance") (Ed.: P. S. Pregosin), Elsevier, Amsterdam, **1991**.
[11] F. A. Cotton, R. G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., John Wiley & Sons, New York, **1988**.
[12] The acid dissociation constant for the HH α-pyrrolidonato-bridged dimer was redetermined at $I = 2.0$ M and 25 °C by spectrophotometry.
[13] K. Matsumoto, S. Arai, M. Ochiai, W. Chen, A. Nakata, H. Nakai, S. Kinoshita, *Inorg. Chem.* **2005**, *44*, 8552–8560.
[14] S. Iwatsuki, C. Mizushima, N. Morimoto, S. Muranaka, K. Ishihara, K. Matsumoto, *Inorg. Chem.* **2005**, *44*, 8097–8104.
[15] T. G. Appleton, J. R. Hall, D. W. Neale, *Inorg. Chim. Acta* **1985**, *104*, 19–31.
[16] T. G. Appleton, J. R. Hall, D. W. Neale, S. F. Ralph, *Inorg. Chim. Acta* **1983**, *77*, L149–L151.
[17] S. C. Dhara, *Indian J. Chem.* **1970**, *8*, 193–194.
[18] K. Matsumoto, Y. Nakai, J. Matsunami, K. Mizuno, T. Abe, R. Somazawa, J. Kinoshita, H. Shimura, *J. Am. Chem. Soc.* **1998**, *120*, 2900–2907.
[19] L. S. Hollis, S. J. Lippard, *Inorg. Chem.* **1983**, *22*, 2605–2614.
[20] K. Sakai, K. Matsumoto, *J. Am. Chem. Soc.* **1989**, *111*, 3074–3075.
[21] K. Sakai, K. Matsumoto, *J. Mol. Catal.* **1991**, *67*, 7–18.

Received: October 28, 2005