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Precise Investigation of the Axial Ligand Substitution Mechanism on a Hydrogenphosphato-Bridged Lantern-Type Platinum(III) Binuclear Complex in Acidic Aqueous Solution

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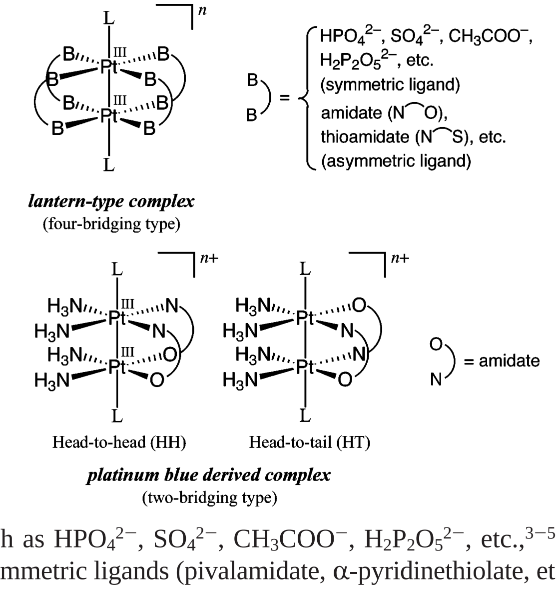
Detailed equilibrium and kinetic studies on axial water ligand substitution reactions of the "lantern-type" platinum(III) binuclear complex, $[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]^{2-}$, with halide and pseudo-halide ions ($X^- = Cl^-$, Br^-, and SCN^-) were carried out in acidic aqueous solution at 25 °C with $I = 1.0$ M. The diaqua Pt(III) dimer complex is in acid dissociation equilibrium in aqueous solution with $-\log K_{h1} = 2.69 \pm 0.04$. The consecutive formation constants of the aquahalo complex (K_1^X) and the dihalo complex (K_2^X) were determined spectrophotometrically to be $\log K_1^{Cl} = 2.36 \pm 0.01$ and $\log K_2^{Cl} = 1.47 \pm 0.01$ for the reaction with Cl^- and $\log K_1^{Br} = 2.90 \pm 0.04$ and $\log K_2^{Br} = 2.28 \pm 0.01$ for the reaction with Br^-, respectively. In the kinetic measurements carried out under the pseudo-first-order conditions with a large excess concentration of halide ion compared to that of Pt(III) dimer ($C_{X^-} \gg C_{Pt}$), all of the reactions proceeded via a one-step first-order reaction, which is a contrast to the consecutive two-step reaction for the amidato-bridged platinum(III) binuclear complexes. The conditional first-order rate constant (k_{obs}) depended on C_{X^-} as well as the acidity of the solution. From kinetic analyses, the rate-limiting step was determined to be the first substitution process that forms the monohalo species, which is in rapid equilibrium with the dihalo complex. The reaction with 4-penten-1-ol was also kinetically investigated to examine the reactivity of the lantern complex with olefin compounds.

Introduction

Platinum(III) binuclear complexes having a Pt−Pt bond in a rare oxidation state are classified into three groups, according to the number of bridging ligands:[1] (1) "lantern-type" complexes having four bridging ligands, (2) amidato-bridged complexes having two bridging ligands derived from so-called "platinum blues",[1,2] and (3) diplatinum(III) complexes with no bridging ligand (very rare). Several lantern-type complexes (Chart 1) with symmetric bridging ligands, such as HPO_4^{2-}, SO_4^{2-}, CH_3COO^-, $H_2P_2O_5^{2-}$, etc.,[3−5] and asymmetric ligands (pivalamidate, α-pyridinethiolate, etc.[6,7])

Chart 1



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have been synthesized and characterized by X-ray crystallographic and spectroscopic analyses to date. The amidato-bridged complexes (Chart 1) which were developed in the 1980s, in particular, have been widely examined as a new type of platinum(III) compound and a possible catalyst for the oxidation of olefin compounds.[8−11]

Recently, we determined the reaction mechanism of the head-to-head (HH) and head-to-tail (HT) type amidato-bridged *cis*-diammineplatinum(III) binuclear complexes, HH- and HT-$[Pt_2(NH_3)_4(\mu\text{-amidato})_2(OH_2)_2]^{4+}$ (amidato = α-pyridonato, α-pyrrolidonato, or pivalamidato), with halide ions[12,13] and some olefins.[14,15] All of the HH and HT complexes react with halide ions in a consecutive two-step reaction, via the formation of a monohalo species (step 1) and then a dihalo species (step 2), under pseudo-first-order conditions with a large excess concentration of the halide ion compared to that of the Pt(III) dimer complex ($C_{X^-} \gg C_{Pt}$). In step 1, there are two parallel reaction pathways for each system. The first pathway is simple ligand substitution of the diaqua complex, and the second pathway involves water ligand substitution on the aquahydroxo complex which is produced by deprotonation of the original complex. In step 2, there are three reaction pathways depending on the nature of the halide ion as well as the bridging ligand: (a) simple ligand substitution for the reactions of the HH α-pyrrolidonato-bridged and HH pivalamidato-bridged complexes with Cl^-, (b) the path via a coordinatively unsaturated intermediate produced by the dissociation of the H_2O molecule along with simple substitution for the reactions of the HH and HT α-pyridonato-bridged complex with Br^- and of the HH α-pyrrolidonato-bridged complex with Br^-, and (c) two parallel pathways involving ligand substitution on the aquahalo complex and on the halohydroxo complex similar to that in step 1 for the reactions of the HT α-pyridonato-bridged complex with Cl^- and of the HH pivalamidato-bridged complex with Br^-.[12,13] These mechanistic studies provided the first detailed information concerning the reactivity of Pt(III) binuclear complexes.

There are two reports of kinetic and mechanistic studies concerning axial water ligand substitution reaction between lantern-type Pt(III) binuclear complexes and halide ions to the best of our knowledge.[16,17] El-Mehdawi et al.[16] reported the ligand substitution kinetics for the hydrogenphosphato-bridged platinum(III) binuclear complex $[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]^{2-}$ with halide ions ($X^- = Cl^-$ and Br^-) in acidic aqueous solution (pH = 3), and they concluded that the reaction proceeds through a consecutive two-step reaction. On the other hand, Camadanli et al.[17] recently reported that only a one-step reaction was observed for this system under similar reaction conditions and that the reaction rate depended on the concentration of the ligand as well as the acidity of the solution. However, the kinetic analyses were insufficient because the acid dissociation constant of the original diaqua platinum(III) binuclear complex, which is the most fundamental quantity, was not considered in the analyses. Thus, further mechanistic studies for the lantern-type complexes were needed.

In this study, we present detailed equilibrium and kinetic studies on axial ligand substitution reactions of $[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]^{2-}$ with halide and pseudo-halide ions ($X^- = Cl^-$, Br^-, and SCN^-) in acidic aqueous solution and precisely analyze the results on the basis of the knowledge obtained in our previous kinetic studies.[12−15] Additionally, the reaction with 4-penten-1-ol was also kinetically investigated to understand the differences in the reactivity with olefins between the lantern-type complexes and the amidato-bridged complexes.[14,15]

Experimental Section

Reagents. $K_2[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]$ was prepared by the reported method.[18] High purity reagents (99.99+%) of sodium chloride, sodium bromide, and sodium thiocyanate were purchased from Aldrich and were used without further purification. 4-Penten-1-ol was purified by distillation under reduced pressure. Sodium perchlorate was prepared and purified according to the literature.[19] Perchloric acid (60% UGR for trace analysis, Kanto Chemical Co.

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Inc.) was used without further purification. The sample solutions were prepared using twice distilled water for the spectrophotometric measurements and D_2O (99.9 atom %, Isotec) for the NMR measurements.

Spectroscopic and Kinetic Measurements. ^{31}P NMR measurements were carried out using a Bruker Avance 400 spectrometer and referenced to 85% H_3PO_4. The solutions for the NMR experiments were prepared by converting the potassium salt of the complex into the sodium salt in a $DClO_4-D_2O$ solution (0.1 M).[20] Spectrophotometric measurements were carried out using a Shimadzu UV2450 spectrophotometer, and the temperature of the sample solution was kept at 25.0 ± 0.1 °C with a thermostat. The ionic strength of the solutions was adjusted to $I = 1.0$ M with perchloric acid and sodium perchlorate. For equilibrium experiments, the acid dissociation constant ($-\log K_{h1}$) of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ and the equilibrium constants ($\log K_1^X$, $\log K_2^X$) were determined by analyzing the UV−vis spectra with SPECFIT.[21] For kinetic measurements, a Hi-Tech SFA-20 rapid kinetics accessory mounted on a UV-2450 was used for mixing the solutions for the reaction with X^-, and a Unisoku USP500 rapid scan/stopped-flow spectrophotometer was used for monitoring the reaction with 4-penten-1-ol (L). Kinetic measurements were carried out under pseudo-first-order conditions with a large excess concentration of ligand (X^- or L) compared to that of the platinum(III) complex ($C_{X^-} \gg C_{Pt}$ or $C_L \gg C_{Pt}$). The conditional pseudo-first-order rate constants (k_{obs}) for the reaction with X^- were obtained by single-exponential analysis of the absorbance change with time at more than two different wavelengths (264 and 297 nm for the reaction with Cl^-; 240, 285, and 341 nm for the reaction with Br^-; and 240, 313, and 380 nm for the reaction with SCN^-). The values of k_{obs} for the reaction with 4-penten-1-ol were obtained from the absorbance change at 270 nm with time. A nonlinear least-squares fit was used to analyze the dependence of k_{obs} on the concentration of excess ligand, as well as the acidity of the solution.

Results and Discussion

Equilibrium Analyses. According to our previous study on the axial ligand substitution reactions involving amidato-bridged *cis*-diammineplatinum(III) binuclear complexes HH- and HT-$[(H_2O)Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2(OH_2)]^{4+}$, all of the diaqua Pt(III) dimers were found to be in an acid dissociation equilibrium in acidic aqueous solution.[12−15] So, we attempted to determine the acid dissociation constant of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ by addition of an acid ($HClO_4$) or a base (NaOH) to the sample solution. From the UV−vis spectra of the dimer at various $[H^+]$ (Figure S1), it was found that the diaqua complex in this study was also in an acid dissociation equilibrium with the aquahydroxo complex, $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH)]^{3-}$. The spectrophotometric titration results were analyzed by using SPECFIT,[21] and the acid dissociation constant (K_{h1}) was determined to be $-\log K_{h1} = 2.69 \pm 0.04$ at $I = 1.0$ M and 25 °C. The value of K_{h1} indicates that ca. 67% of the aquahydroxo complex exists under the experimental conditions used by El-Mehdawi et al.,[16] which leads to inaccurate estimates of the formation constants of the monohalo and dihalo complexes (vide infra).

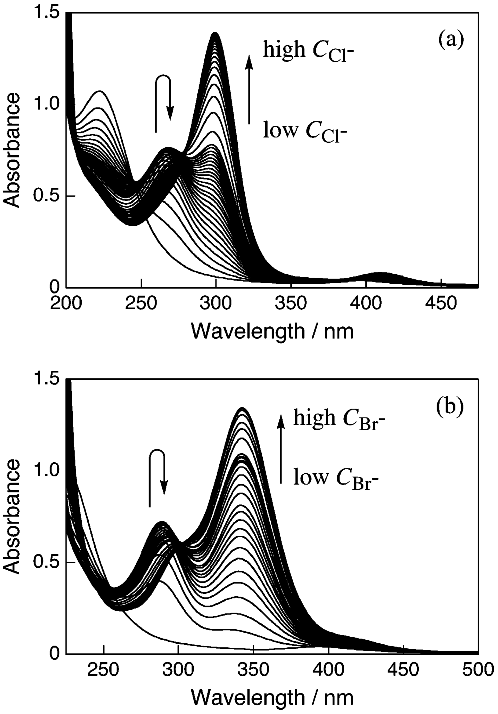

Figure 1. UV−vis spectra of the hydrogenphosphato-bridged lantern-type platinum(III) binuclear complex in acidic aqueous solution with different C_{X^-} values at $I = 1.0$ M and 25.0 °C. Reaction with Cl^- (a: $C_{Cl^-} = 0-0.31$ M) and with Br^- (b: $C_{Br^-} = 0-0.12$ M). $C_{Pt} = 5.1 \times 10^{-4}$ M, and $[H^+] = 0.10$ M.

The UV−vis spectra of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ at various concentrations of halide ion (C_{X^-}) in acidic aqueous solution (pH = 1.0) at $I = 1.0$ M are shown in Figure 1. Two independent isosbestic points were observed as C_{X^-} increased, indicating stepwise substitution reactions. From simultaneous analyses of the UV−vis spectra in Figure 1 using SPECFIT,[21] the first equilibrium corresponds to the formation of the aquahalo complex (eq 1) and the second to that of the dihalo complex (eq 2). The absorption bands of each species obtained by analyses were consistent with those previously reported (Table S1). The formation constants of the monohalo (K_1^X) and dihalo complexes (K_2^X) at 25 °C are listed in Table 1. All of the values of K_1^X and K_2^X are

$$[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-} + X^- \overset{K_1^X}{\rightleftarrows} [XPt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{3-} + H_2O \quad (1)$$

$$[XPt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{3-} + X^- \overset{K_2^X}{\rightleftarrows} [XPt(\mu\text{-}HPO_4)_4PtX]^{4-} + H_2O \quad (2)$$

different from those reported by El-Mehdawi et al.[16] because they determined the conditional values, which are constant only at a given pH, whereas our values are not conditional ones. The difference arises based on whether the acid dissociation of the diaqua complex is considered. The formation constants for the reaction with the thiocyanate ion,

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(19) Funahashi, S.; Haraguchi, K.; Tanaka, M. *Inorg. Chem.* **1977**, *16*, 1349−1353.

(20) The potassium salt of the Pt(III) complex was suspended in a $DClO_4-D_2O$ solution (0.1 M), and then, sodium perchlorate was added in small portions to afford the corresponding sodium salt in solution. The concentration of the Pt(III) complex was determined by spectrophotometric analysis.

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Table 1. Equilibrium Constants for the Reaction of the Hydrogenphosphato-Bridged Lantern-Type Platinum(III) Binuclear Complex with Halide Ions (X^-) Determined Spectrophotometrically at $I = 1.0$ M and 25 °C

bridging ligand	ligand (X^-)	$\log K_1^X$	$\log K_2^X$	$-\log K_{h1}$
Lantern-Type Dimer Complex System (This Work)				
hydrogenphosphate	Cl^-	2.36 ± 0.01 1.3^a	1.47 ± 0.01 1.0^a	2.69 ± 0.04
	Br^-	2.90 ± 0.04 1.3^a	2.28 ± 0.01 1.3^a	
HT-Amidato-Bridged Dimer Complex System[b]				
α-pyridonate[c]	Cl^-	5.27 ± 0.02	3.83 ± 0.01	1.98 ± 0.01
	Br^-	5.53 ± 0.03	4.44 ± 0.02	
HH-Amidato-Bridged Dimer Complex System[b]				
α-pyridonate[d]	Cl^-	5.93 ± 0.02	3.71 ± 0.01	1.71 ± 0.03
	Br^-	6.20 ± 0.05	4.55 ± 0.01	
α-pyrrolidonate[e]	Cl^-	5.61 ± 0.03	3.73 ± 0.01	1.74 ± 0.08^f
	Br^-	5.50 ± 0.03^g	4.68 ± 0.01	
pivalamidate[e]	Cl^-	5.04 ± 0.04	3.21 ± 0.01	2.88 ± 0.01
	Br^-	5.93 ± 0.01	3.91 ± 0.01	

[a] Reference 16. [b] Determined at $I = 2.0$ M and 25 °C.[12,13] [c] Reference 12. [d] Reference 13a. [e] Reference 13b. [f] This was determined by our group again, and the corrected value was obtained. [g] The unconditional value was recalculated according to $K_1^{Br} = K_1^{Br\prime}(1 + K_{h1}/[H^+])/(1 + K_{h2}/[H^+]) \approx K_1^{Br\prime}(1 + K_{h1}/[H^+])$, by using the conditional value of $\log K_1^{Br\prime} = 5.48 \pm 0.02$ at $[H^+] = 0.401$ M (see ref 13b) and $-\log K_{h1} = 1.74 \pm 0.08$.

however, could not be determined because the complex(es) decomposed.

The equilibrium constants for the reaction of the lantern-type complex determined in this study are smaller than those for the HH and HT amidato-bridged complexes (Table 1); in particular, the K_1^X values for the lantern dimer ($\log K_1^{Cl} = 2.36$ and $\log K_1^{Br} = 2.90$) are ~3 orders of magnitude smaller than those for the amidato-bridged dimers ($\log K_1^{Cl} = 5.04-5.93$ and $\log K_1^{Br} = 5.53-6.20$). This means that the monohalo complexes in the amidato-bridged complex systems are more stable than those in the HPO_4^{2-}-bridged lantern-type complex systems. The difference in stabilization of the monosubstituted species would be responsible for the difference in the substitution reaction mechanisms for the lantern-type and the amidato-bridged complexes (see discussion of the reaction mechanism).

Kinetic Studies on the Axial Ligand Substitution Reactions of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ with Halide and Pseudohalide Ions. Previously, two research groups performed the kinetic measurements on the axial water ligand substitution of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ with halide ions and pseudo-halide ion (eq 3) in acidic aqueous solution under pseudo-first-order conditions ($C_{X^-} \gg C_{Pt}$).[16,17] However, the

$$[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-} \overset{\text{step 1}}{\xrightleftharpoons{+X^-}} [XPt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{3-} + H_2O \overset{\text{step 2}}{\xrightleftharpoons{+X^-}} [XPt(\mu\text{-}HPO_4)_4PtX]^{4-} + 2H_2O \quad (3)$$

obtained results were inconsistent with each other. El-Mehdawi et al. concluded that the reaction proceeds successively in two steps (eq 3),[16] while Camadanli et al. analyzed it as a one-step reaction.[17] The former group did not examine the effect of acidity on the reaction rate, and the latter used a "log−log" plot analysis, i.e., the plots of the logarithms of the conditional first-order rate constants vs the logarithms of the concentration of excess reagents, which gives no meaningful mechanistic information for the present complicated system.[22] Additionally, no reactive species were specified. Thus, we have reinvestigated this system under similar conditions.

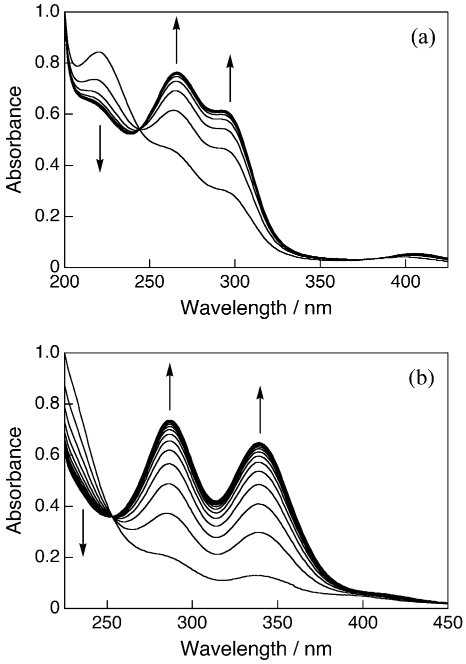

Figure 2. Time-resolved UV−vis spectra for the reaction of the hydrogenphosphato-bridged lantern-type platinum(III) binuclear complex with Cl^- (a) and Br^- (b) in acidic aqueous solution at $I = 1.0$ M and 25.0 °C. (a) $C_{Cl^-} = 2.04 \times 10^{-2}$ M, and (b) $C_{Br^-} = 4.95 \times 10^{-3}$ M. Taken every 40 s, $C_{Pt} = 5.1 \times 10^{-5}$ M, and $[H^+] = 1.35 \times 10^{-2}$ M.

A single isosbestic point was observed in the time-resolved UV−vis spectra for both reaction systems involving halide ions (Cl^- and Br^-), as shown in Figure 2. The absorption band assigned to the dihalo complex simultaneously increased with that of the monohalo complex (Figure 2), indicating that both complexes are in rapid equilibrium. The kinetic traces were first-order over at least 5 half-lives, and then, the rate equation is expressed as eq 4,

$$\frac{d[Pt_2X]}{dt} = k_{obs}[Pt_2X] \left(= \frac{d[Pt_2X_2]}{dt} = k_{obs}[Pt_2X_2] \right) \quad (4)$$

where k_{obs} is the observed (conditional) pseudo-first-order rate constant and Pt_2X and Pt_2X_2 denote the monohalo and dihalo complexes, respectively. The values of k_{obs} determined at different wavelengths were the same within experimental error (Table S2). Furthermore, time-resolved ^{31}P NMR measurements with C_{X^-} ca. 2 or 3 times greater than C_{Pt} showed that, as the signal assigned to the diaqua complex ($\delta = 22$ ppm) decreased, the signals assigned to the aquahalo ($\delta = 24$ and 25 ppm for the aquachloro and aquabromo species, respectively) and the dihalo complexes ($\delta = 27$ and 30 ppm for the dichloro and dibromo species, respectively)

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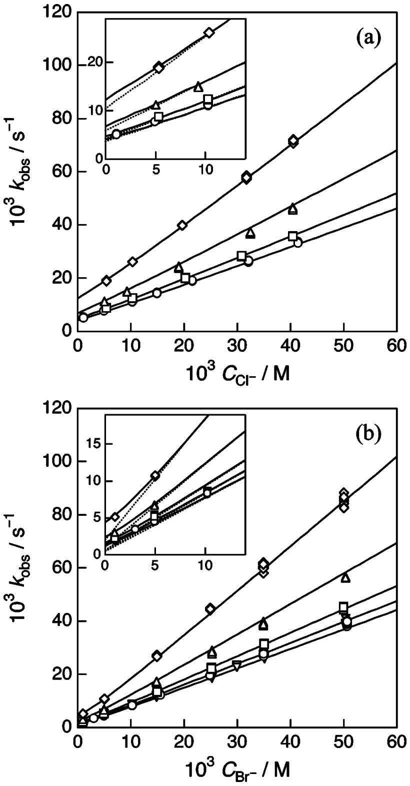
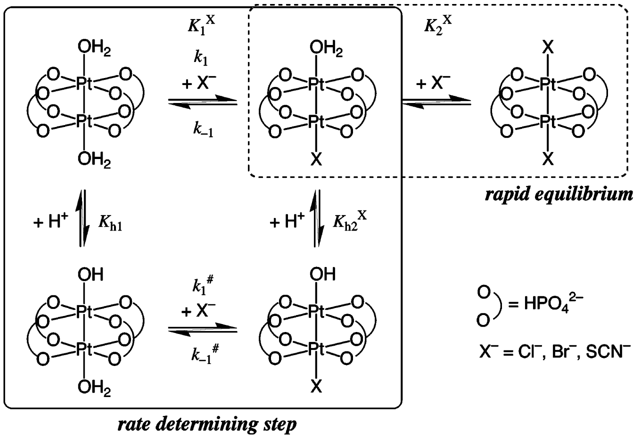


Figure 3. Dependence of the conditional pseudo-first-order rate constants (k_{obs}) on the concentration of excess halide ions (C_{X^-}) under various acidic conditions for the reaction of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ with chloride (a) and bromide (b) ions at $I = 1.0$ M and 25.0 °C. $C_{Pt} = (4.7-5.9) \times 10^{-5}$ M. $[H^+] = 3.47 \times 10^{-3}$ (◇), 6.92×10^{-3} (△), 1.10×10^{-2} (□), 1.35×10^{-2} (○), and 1.55×10^{-2} M (▽). The inset in each figure is a magnified figure of data around the intercept: the solid lines show the best-fit curves according to eq 5, which deviate from straight lines (dotted lines) at low C_{X^-}.

increased simultaneously for both systems (Figure S2). These findings also indicate that the ligand substitution reaction involving $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH)_2]^{2-}$ proceeds in one step and that the monohalo species is in rapid equilibrium with the dihalo species.

The rate constants (k_{obs}) depended on the concentration of the excess halide ion (C_{X^-}: $X^- = Cl^-$ and Br^-), as well as on the acidity of the solution; a large k_{obs} value was obtained at high C_{X^-} as well as at low $[H^+]$ (Figure 3). The dependence of k_{obs} on the acidity (Figure 3) indicates that the aquahydroxo complex also reacts with halide ion to give the halohydroxo complex $[XPt(\mu\text{-}HPO_4)_4Pt(OH)]^{4-}$, which was observed in our previous systems.[12-15] On the other hand, the values of k_{obs} deviate significantly from a straight line at low C_{X^-} (Figure 3, inset) because of the rapid equilibrium between the monohalo and dihalo complexes, as mentioned below. The reaction mechanism is proposed as shown in Scheme 1. (i) The reaction occurs in one step, in which the rate-determining step corresponds to the formation of the monosubstituted species, (ii) the rate-determining step consists of two parallel reaction pathways, where both the diaqua and the aquahydroxo complexes, which were in an acid dissociation equilibrium, react with X^-, and (iii) the disubstituted complex forms via a rapid equilibrium with the monosubstituted species. This mechanism is essentially the same as the one for the complex formation reactions of the various metal ions with monodentate ligands.[23]

Scheme 1. Axial Water Ligand Substitution Mechanism of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ with X^- (Cl^-, Br^-, and SCN^-) in Acidic Aqueous Solution



On the basis of the proposed mechanism (Scheme 1), k_{obs} is expressed as eq 5.[24]

$$k_{obs} = \frac{k_1 + \dfrac{k_1^\# K_{h1}}{[H^+]}}{1 + \dfrac{K_{h1}}{[H^+]}} C_{X^-} + \frac{k_{-1} + \dfrac{k_{-1}^\# K_{h2}^X}{[H^+]}}{1 + \dfrac{K_{h2}^X}{[H^+]} + K_2^X C_{X^-}} \approx \frac{k_1 + \dfrac{k_1^\# K_{h1}}{[H^+]}}{1 + \dfrac{K_{h1}}{[H^+]}} C_{X^-} + \frac{k_{-1} + \dfrac{k_{-1}^\# K_{h2}^X}{[H^+]}}{1 + K_2^X C_{X^-}} \qquad (5)$$

The simplification in eq 5 is reasonable under our experimental conditions ($[H^+] \gg K_{h2}^X$), since $K_{h2}^X \ll K_{h1}$.[12-15] The best-fit curves in Figure 3 (solid lines) were determined by applying a nonlinear least-squares fitting of eq 5 and are consistent with the experimental data, even at low C_{X^-}. The values of the rate constants in eq 5 are summarized in Table 2.

The kinetics for the reaction with SCN^- were somewhat different from those with the halide ions. The UV−vis spectral changes (Figure S3) were similar to those observed for the halide ions (Figure 2), indicating that the substitution reaction occurs in one step. On the other hand, the dependence of k_{obs} on C_{SCN^-} was linear even at low C_{SCN^-}, and the dependence of k_{obs} on $[H^+]$ was similar to that for the reaction with the halide ions (Figure S4). These effects on k_{obs} are attributed to negligible contributions from the reverse reactions (the k_{-1} and $k_{-1}^\#$ values are negligibly small), as shown by the plots with zero intercepts (Figure S4). Therefore, eq 5 is simplified to eq 6,

$$k_{obs} = \frac{k_1 + \dfrac{k_1^\# K_{h1}}{[H^+]}}{1 + \dfrac{K_{h1}}{[H^+]}} C_{SCN^-} \equiv k_{f(SCN)} C_{SCN^-} \qquad (6)$$

Table 2. Rate Constants for the Reaction of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ with Halide and Pseudohalide Ions (X^-) and 4-Penten-1-ol (L) at $I = 1.0$ M and 25.0 °C

ligand	k_1 (M^{-1} s^{-1})	$k_1^{\#}K_{h1}$ (s^{-1})	$k_1^{\#}$ (M^{-1} s^{-1})	k_{-1}[a] (s^{-1})	$k_{-1}^{\#}K_{h2}^{X}$ (s^{-1})
Cl^- [b]	0.272 ± 0.007 0.136[d]	$(7.92 \pm 0.06) \times 10^{-3}$	3.9 ± 0.2 2.0[d]	$(1.2 \pm 0.2) \times 10^{-3}$	$(3.9 \pm 0.1) \times 10^{-5}$
Br^- [b]	0.297 ± 0.006 0.149[d]	$(8.29 \pm 0.05) \times 10^{-3}$	4.1 ± 0.2 2.1[d]	$(3.7 \pm 0.4) \times 10^{-4}$	$(1.4 \pm 0.2) \times 10^{-6}$
SCN^- [c]	1.19 ± 0.02 0.60[d]	$(1.12 \pm 0.01) \times 10^{-2}$	5.5 ± 0.1 2.8[d]		
L	0.41 ± 0.02 0.21[d]	$(8.25 \pm 0.08) \times 10^{-3}$	4.0 ± 0.1 2.0[d]		

[a] Determined by using $k_{-1} = k_1/K_1^{X}$. [b] Analyzed according to eq 5. [c] Analyzed according to eq 6. [d] The statistical factor was taken into account, as X^- can replace both aqua ligands with an equal probability.

where $k_{f(SCN)}$ denotes the slope from the k_{obs} vs C_{SCN^-} plots (Figure S4), and then,

$$\left(1 + \frac{K_{h1}}{[H^+]}\right)k_{f(SCN)} = k_1 + \frac{k_1^{\#}K_{h1}}{[H^+]} \qquad (7)$$

The plot of $(1 + K_{h1}/[H^+])k_{f(SCN)}$ against $[H^+]^{1-}$ (Figure S5) was linear, indicating that the assumption mentioned above is valid. The rate constants (k_1 and $k_1^{\#}$) in eq 6 obtained from the graph of eq 7 (the slope and the intercept in Figure S5) are summarized in Table 2. The negligible reverse reactions in kinetic analysis suggest a higher coordination ability of SCN^- compared to those of Cl^- and Br^-.

Reaction of $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ with 4-Penten-1-ol. Although the amidato-bridged dimer complexes react with olefin compounds, such as *p*-styrenesulfonate, 4-penten-1-ol, etc.,[10,14,15] the $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$ complex only reacts with 4-penten-1-ol in acidic aqueous solution. Therefore, the kinetic measurements for the reaction with 4-penten-1-ol (L) were conducted under conditions similar to those for the reactions with X^- ($C_L \gg C_{Pt}$ at $I = 1.0$ M and 25.0 °C). The product of this reaction system was the same as the one observed for the corresponding reactions of the amidato-bridged complexes, as confirmed by ^1H NMR spectroscopy (Figure S6). Absorbance changes at 270 nm (Figure S7) were first-order within at least 4 half-lives. The dependence of k_{obs} for this reaction on C_L and on $[H^+]$ (Figure S8) was similar to that for the reaction with SCN^-, and k_{obs} linearly depended on C_L with zero intercept at a given $[H^+]$, indicating that only the first ligand substitution process was observed. Therefore, k_{obs} is expressed as eq 6′ (which is essentially the same as eq 6). Just like the reaction with

$$k_{obs} = \frac{k_1 + \dfrac{k_1^{\#}K_{h1}}{[H^+]}}{1 + \dfrac{K_{h1}}{[H^+]}}C_L \equiv k_{f(L)}C_L$$

$$\text{(for the reaction with 4-penten-1-ol)} \quad (6')$$

SCN^-, the plot of $(1 + K_{h1}/[H^+])k_{f(L)}$ vs $[H^+]^{1-}$ (Figure S9) was linear, and the rate constants (k_1 and $k_1^{\#}$) were obtained (Table 2) by using a method similar to that for the reaction with SCN^-. The reaction mechanism of the lantern complex with 4-penten-1-ol (L) in acidic aqueous solution is similar to that of the SCN^- system (Scheme S1), based on the results from the halide systems in this study and our previous studies on the reaction of the amidato-bridged Pt(III) binuclear complexes with L.[14,15]

Comparison of the Reaction Mechanisms for the Lantern-Type Complex and the Amidato-Bridged Complexes. The main difference in the ligand substitution reaction mechanisms for the amidato-bridged (two-bridged type) dimer complexes and the HPO_4^{2-}-bridged lantern-type (four-bridged) complex is the number of reaction steps: a consecutive two-step reaction was observed for the former[12−15] and a one-step reaction for the latter. The contrastive kinetics indicate that the monosubstituted amidato-bridged species is more stable than the lantern-type species(Table 1). This finding can be explained by the higher flexibility of the two-bridged structure compared to that of the four-bridged structure; that is, a suitable structural change to stabilize the complex is possible in the two-bridged complexes by flexibly changing the tilt angle and the Pt−Pt, $Pt-L^1$, and $Pt-L^2$ bond lengths. In fact, in the crystal structures of the HH- and HT-$[L^1-Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2-L^2]^{n+}$ (amidato = α-pyridonato, α-pyrrolidonato, and pivalamidato; L^1, L^2 = halide, NO_3^-, NO_2^-, $CH_3COCH_2^-$, etc.), the two adjacent equatorial planes are tilted (the tilt angle, τ, ∼20−30°).[8−11,25−27] On the other hand, in the lantern-type complexes, all of the equatorial sites are coordinated tightly by the bridging ligands, and so, the structure is more rigid ($\tau = 0°$) around the Pt−Pt bond.[28] Furthermore, the electrons in the amidato-bridged complexes are more easily localized to

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Table 3. First Water Ligand Substitution Rate Constants (k_1) of Various Platinum Complexes with Halide and Pseudohalide Ions (X^-)

complex	ligand (X^-)	k_1 ($M^{-1}\ s^{-1}$)
$[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]^{2-}$ [a]	Cl^-	0.136[e]
	Br^-	0.149[e]
	SCN^-	0.60[e]
HT-$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2(H_2O)_2]^{4+}$ [b]	Cl^-	1.2×10^3 [e]
	Br^-	3.3×10^3 [e]
HH-$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2(H_2O)_2]^{4+}$ [c]	Cl^-	3.1×10^3
	Br^-	7.2×10^3
HH-$[Pt_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrrolidonato})_2(H_2O)_2]^{4+}$ [c]	Cl^-	3.20×10^3 [f]
	Br^-	5.5×10^2 [f]
HH-$[Pt_2(NH_3)_4(\mu\text{-pivalamidato})_2(H_2O)_2]^{4+}$ [c]	Cl^-	1.12×10^3
	Br^-	1.12×10^3
$[Pt(OH_2)_4]^{2+}$ [d]	Cl^-	6.7×10^{-3} [e]
	Br^-	5.3×10^{-2} [e]
	SCN^-	0.32[e]

[a] This work at $I = 1.0$ M ($HClO_4-NaClO_4$) and 25 °C. [b] Reference 12 at $I = 2.0$ M ($HClO_4-NaClO_4$) and 25 °C. [c] Reference 13 at $I = 2.0$ M ($HClO_4-NaClO_4$) and 25 °C. [d] Reference 34 at $I = 1.0$ M ($HClO_4-NaClO_4$) and 25 °C. [e] The statistical factor was taken into account. [f] Determined by reanalyzing the kinetic data using $-\log K_{h1} = 1.74$ (Table 1).

give a Pt(IV)−Pt(II) complex, $[L^1-Pt^{IV}(NH_3)_2(\mu\text{-amidato})_2Pt^{II}(NH_3)_2-L^2]^{n+}$,[10,12−15] which would be shown by the chemical shifts in the ^{195}Pt NMR spectra. ^{195}Pt NMR signals of $[XPt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{3-}$ are observed at $\delta_{Pt} = 1713$ and 1886 ppm (the difference of the two signals, $\Delta\delta_{Pt-Pt} = 173$ ppm) for $X^- = Cl^-$ and at $\delta_{Pt} = 1550$ and 1973 ppm ($\Delta\delta_{Pt-Pt} = 423$ ppm) for $X^- = Br^-$,[18,29] while the HT-$[XPt(NH_3)_2(\mu\text{-}\alpha\text{-pyridonato})_2Pt(NH_3)_2(OH_2)]^{3+}$ complexes have peaks at $\delta_{Pt} = -652$ and -102 ppm ($\Delta\delta_{Pt-Pt} = 550$ ppm) for $X^- = Cl^-$ and at $\delta_{Pt} = 20$ and -900 ppm ($\Delta\delta_{Pt-Pt} = 920$ ppm) for $X^- = Br^-$,[30] respectively. The larger $\Delta\delta_{Pt-Pt}$ for the amidato-bridged complex suggests the Pt−Pt bond is more polarized to afford a mixed valence Pt(IV)−Pt(II) complex. This polarizability would be important for stabilizing the monosubstituted species of platinum(III) binuclear complexes.[12−15] Therefore, the difference in the mechanisms for these reaction systems is attributable to the degree of polarizability of the Pt(III) dimer, and the polarized Pt−Pt bond in the amidato-bridged complexes is caused by the flexibility around the metal−metal bond of the tilted two-bridged structure.

The values of k_1 obtained for the HPO_4-bridged lantern complex are ~10^4 times smaller than those for the amidato-bridged complexes (Table 3). The slow substitution reaction rate for the lantern Pt(III) binuclear complex can be explained by the following: (i) the negatively charged diaqua lantern dimer (−2) interacts unfavorably with the negatively charged ligand X^-, whereas the positively charged diaqua amidato-bridged dimer (+4) interacts much more favorably with X^-, and (ii) the low electron density of Pt(III) in the lantern-type complexes, for which the ^{195}Pt NMR chemical shifts are close to those of Pt(IV),[31,32] is the reason that these Pt(III) complexes are quite inert. Therefore, to understand the reactivity of the platinum(III) binuclear complexes, both the electron localization on the Pt−Pt bond and the electron density of the Pt centers depending on the nature of the equatorial (bridging) ligand must be considered.

The low reactivity of the HPO_4^{2-}-bridged lantern-type complex with olefins (i.e., it only reacts slowly with 4-penten-1-ol in acidic aqueous solution) can also be explained by the charge effect between the complex and the olefin ligand, the inert nature of Pt(III) center of the lantern complex, and the nucleophilicity and the steric hindrance of the olefin ligands, as observed in the kinetic studies on the reaction of the amidato-bridged complexes with olefins.[14,15] It should be noted that the lantern-type organoplatinum(III) product is formed in a one-step reaction; the first ligand substitution process, which is rate-determining, is followed by faster reactions involving $\pi-\sigma$ conversion. The fast $\pi-\sigma$ conversion process is much the same as that for the reactions of the HH- and HT-amidato-bridged complexes with olefins.[14,15] In other words, the conversion from a π complex to a σ complex for the reaction of Pt(III) binuclear complexes with olefins is not a slow process. Thus, the initial axial ligand substitution process is one of the most important processes for the catalytic oxidation of olefins using Pt(III) compounds.

The k_1 values for each Pt(III) complex system in Table 3 vary little with the nature of X^-; the values are on the order of ~$10^{-1}\ M^{-1}\ s^{-1}$ for the reaction involving the HPO_4^{2-}-bridged lantern dimer, while they are on the order of ~$10^3\ M^{-1}\ s^{-1}$ for the amidato-bridged dimers. On the other hand, a drastic change in k_1 with different X^- was observed for the substitution reaction on $[Pt(OH_2)_4]^{2+}$ (Table 3), indicating an associative interchange (I_a) mechanism.[33,34] Therefore, the intimate mechanism of the first axial water ligand substitution (k_1 path) for both types of Pt(III) binuclear complexes would be dissociative interchange (I_d), which is due to the filled dπ orbital of the d^7 Pt(III) centers.[22,35]

Conclusions. The present reinvestigation of the previously reported kinetic studies[16,17] showed that the axial water substitution reaction of the lantern-type complex, $[(H_2O)Pt(\mu\text{-}HPO_4)_4Pt(OH_2)]^{2-}$, with halide and pseudo-halide ions proceeds via one-step reaction kinetics, which is in contrast to the two-step reaction kinetics determined for the amidato-bridged Pt(III) binuclear complexes. The rate-determining step is the formation of the monosubstituted species, during which both the diaqua and aquahydroxo complexes in the acid equilibrium react with X^- (parallel reaction pathways). The disubstituted complex forms via a rapid equilibrium with the monosubstituted species.

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Supporting Information Available: Absorption spectral data (Table S1), observed rate constants (Table S2), spectrophotometric pH titration results (Figure S1), ^{31}P NMR spectra (Figure S2), kinetic data for the reaction with SCN^- and 4-penten-1-ol (L) (Figures S3−S5 and Figures S6−S9, respectively), and reaction mechanism with L (Scheme S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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