Review

Kinetics and mechanisms of the axial ligand substitution reactions of platinum(III) binuclear complexes with halide ions

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Abstract

The axial water ligand substitution reaction on the head-to-head (HH) and head-to-tail (HT) amidato-bridged \textit{cis}-diammineplatinum(III) binuclear complexes, HH- and HT-[Pt\textsubscript{2}(NH\textsubscript{3})\textsubscript{4}(\textit{\textmu}-amidato)\textsubscript{2}(OH\textsubscript{2})\textsubscript{2}]\textsuperscript{4+} (amidato = \textit{\alpha}-pyridonato, \textit{\alpha}-pyrrolidonato, or pivalamidato), with halide ions (X\textsuperscript{−} (Cl\textsuperscript{−}, Br\textsuperscript{−})) in acidic aqueous solution reveals a consecutive 2-step kinetics under the pseudo first-order conditions of a large excess concentration of halide ion relative to that of the complex \((C_X \gg C_{Pt})\), corresponding to formation of the monohalo (step 1) and the dihalo complexes (step 2). The first substitution step of all the HH and HT diaqua dimers consists of two parallel reaction pathways: one is the simple substitution path of one of the coordinated aqua ligands with X\textsuperscript{−}, and the other is the replacement in the aquahydroxo complex which is the conjugate base of the diaqua dimer. In step 2, there are three reaction pathway patterns: the direct substitution path, the path via a coordinatively unsaturated intermediate, and the unusual path of OH\textsuperscript{−} replacement. Step 2 proceeds via either one or two paths of the three depending on the nature of the halide ion as well as the bridging ligand. On the other hand, the substitution reaction of the hydrogenphosphato-bridged lantern-type complex, [Pt\textsubscript{2}(\text{	extmu-HPO}_4)\textsubscript{4}(OH\textsubscript{2})\textsubscript{2}]\textsuperscript{2−} proceeds in 1-step at \((C_X \gg C_{Pt})\), in which the first aqua ligand substitution to form the monohalo species is rate-determining and the monohalo species is in rapid equilibrium with the dihalo complex. The rate-determining step consists of parallel pathways similar to step 1 in the amidato-bridged complex systems.

Keywords: Platinum(III); Ligand substitution; Equilibrium; Kinetics; Mechanism

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1. Introduction

Platinum(III) has been known as a rare oxidation state in platinum chemistry. A substantial number of platinum(III)-involved oligo-nuclear complexes having Pt(III)–Pt(III)/(II) or Pt(III)–other-metal bonds has been widely investigated to date because their metal–metal interactions are expected to induce novel chemical and/or physical properties, e.g., effective and selective catalysts for organic compounds. The kinetic analyses provide the first detailed information concerning the reactivity of Pt(III) binuclear complexes.

2. Equilibrium and kinetic studies on the axial water ligand substitution reaction of the amidato-bridged cis-diammineplatinum(III) binuclear complexes with halide ions in acidic aqueous solution

2.1. Equilibrium analyses

X-ray crystallographic analyses of HH and HT cis-pyrrolidonato-bridged cis-diammineplatinum(III) binuclear complexes indicate that one or two nitrate ions cap axial positions as HH-[H2O]3Pt(NH3)2[(μ-κ-pyrrolidonato)2Pt(NH3)2(NO3)]c2H2O and HT-[NO3]2Pt(NH3)2[(μ-κ-pyrrolidonato)2Pt(NH3)2](NO3)3·0.5H2O in solid state, respectively [33]. On dissolution of these complexes into acidic aqueous solution, all the axial nitrate ions are completely replaced by H2O or OH−, since no spectral change was observed when sodium nitrate was added up to 0.020 M (mol dm−3) to the aqueous solutions of the dimers (5.0 × 10−3 M). Therefore, observed are the reactions of the diaqua complexes with halide ions in these studies (Scheme 1). Similar observations were found in the analogous complexes with the κ-pyrrolidonato- or pivalamidato-bridging ligand. To clarify the detailed reaction mechanisms, it is essential to determine the equilibrium constants for the axial water ligand substitution reaction with halide ions as well as the acid dissociation constants of the diaqua complexes.

2.1.1. Acid dissociation constants of the diaqua complexes

When the acidity of the solution was varied, isosbestic points were observed in the UV spectral change for all the amidato-bridged dimers as shown in Fig. 1. The spectral change is pH-dependent and -reversible, as expected for deprotonation of one of the coordinated axial water molecules shown in Eq. (1).

\[
K_{\text{d}} = \frac{[\text{Pt}_2(\text{NH}_3)_4(\text{μ-amidato})_2(\text{OH}_2)_2]}{[\text{Pt}_2(\text{NH}_3)_4(\text{μ-amidato})_2]} + \text{H}^+ \quad (1)
\]
The apparent molar absorption coefficient ε is expressed as 
\[ \varepsilon = (\varepsilon_1 + \varepsilon_2 K_{a1}/[H^+])(1 + K_{a1}/[H^+]), \]
where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the molar absorption coefficients of the undissociated (diaqua) \([\text{Pt}(\text{NH}_3)_2(\mu\text{-amidato})_2(\text{OH}_2)]^{2+}\) and deprotonated (aquahydroxo) \([\text{Pt}(\text{NH}_3)_2(\mu\text{-amidato})_2(\text{OH}_2)(\text{OH})]^{3+}\) dimers, respectively, and the \( K_{a1} \) in Eq. (1) is the first acid dissociation constant of a diaqua Pt(III) dimer complex. The \( \varepsilon \) values at more than five different wavelengths were analyzed simultaneously as a function of [H\(^+\)] by using a nonlinear least-squares fitting method. The obtained p\( K_{a1} \) (= -log \( K_{a1} \)) values at \( I = 2.0 \) M and \( 25^\circ C \) are listed in Table 1.

Deprotonation occurs to either one of the two equivalent water molecules in the HT \( \alpha \)-pyridonato-bridged dimer. The value of \( K_{a1} \) for the present HT dimer (p\( K_{a1} = 1.98 \)) is more than one order of magnitude larger than that of the 1-methyluracilato-bridged HT dimer [34]: p\( K_{a1} = 3.49 \).

The difference can be explained by the less-donating \( \alpha \)-pyridonate coordination, compared to methyluracilato. Because of the weaker donation, the Pt(III) atom in the \( \alpha \)-pyridonato-bridged complex would be more electron withdrawing.

In the case of the HH dimers, which have nonequivalent Pt(III) centers, Pt(\( N_2\text{O}_2 \)) and Pt(\( N_4 \)), on the equatorial plane, proton dissociates from the axial aqua ligand bound to the Pt(\( N_4 \)) center as will be mentioned in the next section. That is, the axial water molecule on the Pt(\( N_4 \)) is a stronger Brønsted acid than that on the Pt(\( N_2\text{O}_2 \)). Both of the HH \( \alpha \)-pyridonato-bridged diaqua dimer (p\( K_{a1} = 1.71 \)) and the HH \( \alpha \)-pyrrolidonato-bridged dimer (1.74) have higher acidity than that of the pivalamidamidato-bridged dimer (2.88). The higher acidity of the former complexes can be explained by the less electron donating ability of \( \alpha \)-pyridonate and \( \alpha \)-pyrrolidonate compared to pivalamidate. Thus, the Pt(III) atom in the \( \alpha \)-pyridonato-bridged complex as well as the \( \alpha \)-pyrrolidonato-bridged one would be more electron-withdrawing.

### 2.1.2. Consecutive formation constants of the monohalo and dihalo complexes

Fig. 2 shows the absorption spectra of a sufficiently acidic aqueous solution of the HH \( \alpha \)-pyridonato-bridged Pt(III) dimer complex measured at various halide ion concentration (C\( _{X^-} \)). Similar changes were found for all the HH and HT dimer complexes. The absorption spectrum of the HH \( \alpha \)-pyridonato-bridged Pt(III) dimer complex changes with two distinct isosbestic points as C\( _{X^-} \) increases (Fig. 2). Plot of the absorbance at the isosbestic point in the longer wavelength (e.g., 273 and 303 nm in Fig. 2) against C\( _{X^-} \)/C\( _{Pt} \) shows a clear inflection point at C\( _{X^-} \)/C\( _{Pt} = 1 \), however, another inflection point corresponding to C\( _{X^-} \)/C\( _{Pt} = 2 \) is unclear, probably because of the smaller formation constant of the dihalo complex. These observations correspond to the following equations (Eqs. (2) and (3)), for the consecutive formation of the monohalo and dihalo complexes. The equilibria in Eqs. (2) and (3) are also supported by the \( ^1\text{H NMR} \) spectral change with C\( _{X^-} \) change, that is, the HH diaqua complex forms only one monohalo complex, from which the dihalo complex forms when C\( _{X^-} \) increases. The same is true for the HT diaqua complex [27,28]. In Table 2 are listed the consecutive formation constants (\( K_1^X \) and \( K_2^X \)) obtained by simultaneously analyzing all the UV–Vis spectra at \( I = 2.0 \) and 25°C.

\[
\text{[Pt}_2(\text{NH}_3)_4(\mu\text{-amidato})_2(\text{OH}_2)]^{2+} + \text{X}^- \leftrightarrow \text{[Pt}_2(\text{NH}_3)_4(\mu\text{-amidato})_2(\text{OH}_2)\text{X}]^{3+} + \text{H}_2\text{O},
\]

or

\[
\text{[Pt}_2(\text{NH}_3)_4(\mu\text{-amidato})_2(\text{OH}_2)\text{X}]^{3+} + \text{X}^- \leftrightarrow \text{[Pt}_2(\text{NH}_3)_4(\mu\text{-amidato})_2(\text{OH}_2)\text{X}_2]^{4+} + \text{H}_2\text{O}.
\]

For the HT \( \alpha \)-pyridonato-bridged dimer having two equivalent Pt(\( N_3\text{O}_2 \))/OH\(_2 \) centers, which is also shown by almost the same Pt(\( N_3\text{O}_2 \))/L bond lengths in solid state (\( \text{NO}_3^- \) or NO\(_2^- \) in Table 3, 1st and 2nd entries) [33,35], the experimental data were consistently and reasonably...
analyzed by postulating that the deprotonation and substitution reactions occur to the different Pt sites. That is, the first substitution in HT diaqua dimer occurs to one of the two equivalent axial Pt(N3O) sites, while deprotonation occurs from the water molecule on the other Pt(N3O) site.

For the reactions of HH dimers with X–/C0, the first substitution occurs selectively to one of the two nonequivalent Pt centers, Pt(N4) or Pt(N2O2), as shown by the 1H NMR spectral change with $C_X/C_0$ change, as mentioned above. It should first be considered whether the deprotonation (Eq. (1)) and the first substitution reactions with halide (Eq. (2)) occur to the same or opposite axial sites of the Pt(III) dimer. By considering crystal structures on the related HH and HT dimers (Table 3), it is clearly indicated that the axial position of the Pt(N2O2) in the HH complexes is always occupied by a ligand with a stronger trans influence[33,36–40]. Furthermore, some of the HH pivalamidato-bridged organopaltinum(III) dimers, in which an alkenyl or a ketonyl group with much strong trans influence binds to the Pt(N2O2) moiety, have no ligand at opposite Pt(N4) axial site [23,34,41–43]. This suggests that the axially substituted group on the Pt(N2O2) is more stable than that on the Pt(N4). In other words, the mono-substitution product from the diaqua complex is more stable on the axial site of the Pt(N2O2) than that of the Pt(N4). Therefore, the first halide substitution occurs exclusively to the Pt(N2O2) in the reaction of the HH diaqua dimer. In the HH $\alpha$-pyrrolidonato-bridged complexes having axial ligands Cl–/C0 or NO3–/C0 at the Pt(N2O2) (Table 3, 4th and 5th entries), the Pt(N4)–L2 bond lengths are shorter than the L1–Pt(N2O2) [44]. This suggests that the Pt(N4)–OH2 bond in the diaqua dimer, formed when nitrate salt of the HH dimers is dissolved in water, would be shorter than the

Table 1

Acid dissociation constants of platinum(III) binuclear complexes determined spectrophotometrically at 25 °C

| Type                  | Bridging ligand          | $pK_{1H}$ | Ionic strengtha |
|-----------------------|--------------------------|-----------|-----------------|
| $[\text{Pt}_2(\text{NH}_3)_4(\text{bridging ligand})_2(\text{H}_2\text{O})_2]^{4+}$ | x-Pyridonateb             | 1.98±0.01 | I = 2.0 M       |
| Head-to-tail (HT)     | 1-Methyluracilatec       | 3.49      |                 |
| $[\text{Pt}_2(\text{bridging ligand})_4(\text{H}_2\text{O})_2]^{2–}$ | Hydrogenphosphateg       | 2.69±0.04 | I = 1.0 M       |
| Lantern               | Sulfateh                 | 4.3       | I = 1.0 M       |

aAdjusted with sodium perchlorate and perchloric acid.
bRef. [27].
cRef. [34].
dRef. [28].
eRef. [29].
fDetermined by our group again [32].
gRef. [32].
hUnpublished result.

Fig. 2. The UV–Vis spectra of the HH-[Pt2(NH3)4(μ-x-pyridonato)2(OH2)2]4+ complex in acidic aqueous solutions ([H+]=1.27 M) at various concentrations of chloride ion (a) and bromide ion (b) at $I = 2.0$ M and $25\degree$ C. (a) $C_{Pt} = 2.34 \times 10^{-5}$ M and $C_{Cl\text{–}} = 0–1.35 \times 10^{-2}$ M, (b) $C_{Pt} = 2.48 \times 10^{-5}$ M and $C_{Br\text{–}} = 0–8.0 \times 10^{-2}$ M.
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2.2. Kinetic analyses: two-step kinetics for the formation of the monohalo and dihalo complexes

Kinetic measurements of the axial ligand substitution reactions were carried out by using pseudo first-order conditions. At a large excess concentration of the platinum(II) dimer complex (C\textsubscript{Pt}) over halide ion (C\textsubscript{X}), the reactions were first order and monophasic, i.e., only the first substitution process (Eq. (2)) is observed. On the other hand, under the condition of C\textsubscript{X} \gg C\textsubscript{Pt}, the kinetic traces are biphasic, and are expressed as \( A_t = A_\infty + x \exp(-k_{\text{obs1}}t) + \beta \exp(-k_{\text{obs2}}t) \), where \( A_t \) and \( A_\infty \) are the absorbances at time \( t \) and \( \infty \), respectively, and \( x \) and \( \beta \) are composite parameters [45]. The UV–Vis spectral changes of the biphasic reactions (Fig. 3) show that the absorption bands of the monohalo complex increase in the first step (step 1), and those of the dihalo complex increase in the second step (step 2), successively, indicating consecutive two-step formation reactions of the monohalo and dihalo complexes (Eq. (4)).

\[
\begin{align*}
\text{[Pt}_2(\text{NH}_3)_4(\mu-\text{amidato})_2(\text{OH}_2)_2]^{4+} & \quad \text{[step 1]} \\
+ X^- & \quad \rightarrow \quad \text{[Pt}_2(\text{NH}_3)_4(\mu-\text{amidato})_2(\text{OH}_2)X]^{3+} + \text{H}_2\text{O} \\
+ X^- & \quad \rightarrow \quad \text{[Pt}_2(\text{NH}_3)_4(\mu-\text{amidato})_2 \cdot 2]^{2+} + 2\text{H}_2\text{O} \quad \text{(4)}
\end{align*}
\]

2.2.1. Kinetics for the formation of the monohalo complexes

The formation rate of the monohalo complex (Pt\textsubscript{2}X) is given by Eq. (5), where [Pt\textsubscript{2}] and [X\textsuperscript{-}] are the concentrations of the unreacted Pt(III) dimer and the free halide ion,

\[
\begin{align*}
\text{d[Pt}_2X]/\text{dt} = k_{\text{obs1}}[\text{Pt}_2] & \quad \text{(at C}_X \gg \text{C}_\text{Pt}) \\
= k_{\text{obs1}}'X^- & \quad \text{(at C}_\text{Pt} \gg C_X^-)
\end{align*}
\]

respectively. The conditional first-order rate constant, \( k_{\text{obs1}} \) (or \( k_{\text{obs1}}' \)), was found to involve the halide ion concentration and [H\textsuperscript{+}] under the conditions of \( C_X \gg C_{\text{Pt}} \) (or, \( k_{\text{obs1}} \) involves the dimer concentration and [H\textsuperscript{+}] at \( C_{\text{Pt}} \gg C_X^- \)).

As shown in Fig. 4, a large \( k_{\text{obs1}} \) (or \( k_{\text{obs1}}' \)) value is obtained at high \( C_X^- \) (or \( C_{\text{Pt}} \)) as well as at low [H\textsuperscript{+}]. The effect of the acidity on \( k_{\text{obs1}} \) (or \( k_{\text{obs1}}' \)) indicates that the aquahydroxo complex, formed by acid dissociation of the diaqua complex, also reacts with halide ion. Thus, the reaction mechanism for step 1 consists of two parallel reaction pathways of the diaqua and aquahydroxo complexes as shown in Scheme 2. As discussed earlier in this review, the first aqua ligand substitution in the HH complex systems occurs at the axial site of the Pt(N\textsubscript{2}O\textsubscript{2}) moiety, while the acid dissociation at the opposite Pt(N\textsubscript{4}) site (Scheme 2).

In the present mechanism (Scheme 2), \( k_{\text{obs1}} \) (or \( k_{\text{obs1}}' \)) is expressed as Eq. (6), since the contribution of the reverse reactions is negligible, i.e., zero intercept in Fig. 4. The fitted lines in Fig. 4 obtained by nonlinear least-squares analysis of Eq. (6) are consistent with the experimental data. The obtained values of \( k_1 \) and \( k_1' \) for each reaction system are listed in Table 4.

\[
k_{\text{obs1}} = \frac{k_1 + (k_1'K_{H\text{I}}/[H\textsuperscript{+}])}{1 + (K_{H\text{I}}/[H\textsuperscript{+}])} C_X^- \quad \text{or} \quad C_{\text{Pt}}. \quad \text{(6)}
\]
2.2.2. Kinetics for the formation of the dihalo complexes

Under the conditions of \( C_{X^-} \gg C_{Pt} \), the faster step (step 1) and the slower step (step 2) were observed for all the present amidato-bridged complex systems. Furthermore, the reactions of some of the diaqua complexes with olefins proceed with similar rate constants \( k_1 \) for each bridging ligand system, and the \( k_1 \) values are in the order of \( \sim 10^3 \) for all the present amidato-bridged complex systems. These results suggest that the first ligand substitution of the diaqua complex \( (k_1\text{ path}) \) proceeds via a dissociative interchange mechanism \((I_d)\) \cite{46}.

### Scheme 2.

There is no significant difference between the \( k_1 \) values for the reactions with \( Cl^- \) and \( Br^- \) for each bridging ligand system, and the \( k_1 \) values are in the order of \( \sim 10^3 \) for all the present amidato-bridged complex systems. Furthermore, the reactions of some of the diaqua complexes with olefins proceed with similar rate constants \( (k_1 = 10^{-2} - 10^{-3} \text{ M}^{-1} \text{ s}^{-1}) \) \cite{30,31}. These results suggest that the first ligand substitution of the diaqua complex \( (k_1\text{ path}) \) proceeds via a dissociative interchange mechanism \((I_d)\) \cite{46}.

#### 2.2. Kinetics for the formation of the dihalo complexes

The dependence (A) shows a simple substitution path from the aquahalo complex to the dihalo complex (Scheme 3), and the \( k_{obs2} \) is expressed as Eq. (8). For the reaction of the HH \( \alpha \)-pyrrolidonato-bridged dimer with \( Cl^- \), the best fit line obtained with Eq. (8) reveals that the reverse reaction is negligible \((k_{-2} = 0)\). The rate constants in Eq. (8) are listed in Table 4.

\[
k_{obs2} = k_2 C_{X^-} + k_{-2}.
\]  

(8)

For the dependence (B), \( k_{obs2} \) increases linearly with \( C_{X^-} \) at lower \( C_{X^-} \), and at higher \( C_{X^-} \) also increases linearly, but with a different slope as shown in Fig. 5b. Considering trans effect through the Pt–Pt bond, step 2 would proceed also through a dissociative path via a coordinatively unsaturated complex as depicted in Scheme 4. It is also notable that \( k_{obs2} \) is almost independent of \( [H^+] \). If the steady-state approximation is applied to the monohalo dimer without an axial ligand at the opposite site in Scheme 4, Eq. (9) is obtained. In this case, the best fit curve reveals that the reverse reactions of \( k_2 \) and \( k_4 (k_{-2} \text{ and } k_{-4}) \) are negligible \((k_{-2} \text{, } k_{-4} = 0)\). The rate constants obtained by applying nonlinear least-squares fitting of Eq. (9) are also listed in Table 4.

\[
k_{obs2} = k_2 C_{X^-} + \frac{k_2 k_4 C_{X^-}}{k_{-3} + k_4 C_{X^-}} = k_2 C_{X^-} + \frac{k_3 C_{X^-}}{k_{-3} / k_4 + C_{X^-}}.
\]  

(9)

In the case of dependence (C), it is obvious from Fig. 5c that \( k_{obs2} \) varies with \( C_{X^-} \) and \( [H^+] \) in the same way as in Fig. 4. In addition, the intercept in Fig. 5c is not zero, therefore the reverse reaction should be considered. In this way, the reaction paths in Scheme 5 are possible, for which Eq. (10) is derived.

\[
k_{obs2} = \frac{k_2 + (k_{1/2} K_{h2} / [H^+]^2) C_{X^-} + k_{-2} + k_{3/2} K_{W} / [H^+]^2)}{1 + (k_{1/2} / [H^+]^2)} C_{X^-} + k_{-2}.
\]  

(10)

The simplification in Eq. (10) is reasonable under the experimental conditions \([H^+] > 0.1 \text{ M}) \cite{29}. In Scheme 5, the \( k_2 \) path must be included in case (C), which is unusual, though, considering the usual inertness of \( OH^- \) in \( M(H_2O)_n(OH)^{(n-1)}^- \).

Schemes 2–5 are unified into Scheme 6. The trans-influence and/or the trans-effect through the Pt–Pt bond seems to determine the reaction paths in step 2 (Scheme 6). For example, the mechanistic difference between the \( \alpha \)-pyridonato-bridged HH and HT binuclear complexes is interpreted as follows: the difference between the HT \( \alpha \)-pyridonato-bridged complex + \( Cl^- \) and the HT complex + \( Br^- \) systems can be reasonably explained by the relative electron donor ability of \( Cl^- \) and \( Br^- \). Because the more electron donating \( Br^- \) facilitates dissociation of...
the axial aqua ligand from the opposite Pt atom, the coordinatively unsaturated intermediate is involved in the mechanism. The charge localization through the Pt–Pt bond would be more pronounced in the HH aquahalo dimer than in the HT aquahalo dimer, since the two Pt atoms are not equivalent, i.e., the HH aquahalo dimer has more Pt(N4)–Pt(N2O2)–X polarized character of Pt–Pt bond than the HT aquahalo dimer, and because of this fact mechanism C is shifted to the dissociative mechanism B on going from HT to HH dimer in Scheme 6. However, the reaction paths for the pivalamidato-bridged systems can not be explained in a similar way. Probably both a bridging ligand and an axial ligand X− affect the mechanism. Exceptional observation for the pivalamidato-bridged complex systems is also found in pKb1; the pKb1 value of the HH pivalamidato-bridged complex is higher than the other HH diaqua complexes as mentioned earlier. Thus, in the HH amidato-bridged Pt(III) binuclear complexes, trans-labilizing effect of the coordinated X− in the monohalo species as well as the electron donating ability of the bridging ligand would be responsible for determining the reaction path.
Equilibrium and kinetic studies on the axial water ligand substitution reaction of a hydrogenphosphato-bridged lantern-type platinum(III) binuclear complex with halide ions in acidic aqueous solution

Historically, two kinetic and mechanistic studies on the ligand substitution reactions with halide ions were carried out for a lantern-type complex with hydrogenphosphate bridging ligands in 1986 [47], and in 2003 [48]. Their results (mechanisms) are, however, inconsistent with each other for the same reaction system. Furthermore, the kinetic analyses in both reports are insufficient to clarify the detailed reaction mechanism. Thus, re-investigation was carried out on the axial water substitution reaction of the HPO$_4$-bridged lantern-type complex with halide and pseudo-halide ions (X$^-$/C$_0$ = Cl$^-$/C$_0$, Br$^-$/C$_0$, SCN$^-$/C$_0$) in acidic aqueous solution (Scheme 7) [32], and the detailed mechanisms were determined based on the mechanistic studies.

3. Equilibrium and kinetic studies on the axial water ligand substitution reaction of a hydrogenphosphato-bridged lantern-type platinum(III) binuclear complex with halide ions in acidic aqueous solution

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![Diagram](image-url)
information obtained from the amidato-bridged platinum(III) binuclear complexes [27–31].

3.1. Equilibrium analyses

According to the study on the axial ligand substitution reactions involving amidato-bridged cis-diammineplatinum(III) binuclear complexes, all of the diaqua Pt(III) dimers were found to be in an acid dissociation equilibrium in acidic aqueous solution [27–31]. However, the acid dissociation constant of \([\text{Pt}_2(\mu-\text{HPO}_4)_4(\text{OH}_2)_2]^{2-}\) was not determined in the earlier studies [47,48]. In our study, the acid dissociation constant of the complex was determined in acidic aqueous solution as well as the formation constants (independent of pH) of the monohalo and dihalo complexes. The latter constants were not determined previously except the conditional formation constants (depending on pH).

3.1.1. Acid dissociation constant of the diaqua complex

The UV–Vis spectra of the dimer at various \([\text{H}^+]/C_0\) (Fig. 6) show that the \([\text{H}_2\text{O}]\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH}_2)]^{2-}\) complex is also in an acid dissociation equilibrium with the aquahydroxo-complex, \([\text{H}_2\text{O}]\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH})]^{3^-}\) (Eq. (11)). The analysis of the data in Fig. 6 allows the estimate of the acid dissociation constant \((K_{h1})\) to be \(\log K_{h1} = 2.69 \pm 0.04\) at \(I = 1.0\ M\) and 25°C (Table 1).

\[\text{[(H}_2\text{O})\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH})]^{3^-} + \text{H}^+ \leftrightarrow \text{[(H}_2\text{O})\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH}_2)]^{2-}\] (11)

The value of \(K_{h1}\) indicates that ca. 67% of the complex exists as aquahydroxo-complex under the experimental conditions (pH = 3) in the earlier research [47]. In the report, only the conditional formation constants of the monohalo and dihalo complexes were determined.

3.1.2. Consecutive formation constants of the monohalo and dihalo complexes

The UV–Vis spectra of \([\text{H}_2\text{O}]\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH}_2)]^{2-}\) at various concentrations of halide ion \((X]/C_0; X]{/C_0 = \text{Cl}^- , \text{Br}^- )\) in acidic aqueous solution (pH = 1.0) at \(I = 1.0\ M\) show two distinct isosbestic points as \(C_X^-\) increases (Fig. 7), indicating stepwise substitution reactions. From simultaneous analysis of the UV–Vis spectra, the reaction processes are similar to those of the amidato-bridged dimer systems; consecutive formations of the aquahalo (Eq. (12)) and the dihalo complexes (Eq. (13)). The formation constants of the monohalo-\((K_X^1)\) and dihalo-complexes \((K_X^2)\) are listed in Table 2.

\[\text{[(H}_2\text{O})\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH}_2)]^{2-} + X^- \rightleftharpoons X\text{Pt}(\mu-\text{HPO}_4)_4\text{Pt}(\text{OH}_2)]^{3^-} + \text{H}_2\text{O}\] (12)
The “unconditional” \( K_1 \) and \( K_2 \) values determined here are very different from the conditional ones reported before [47]. The formation constants of the reaction with thiocyanate ion, however, could not be determined because the complex(es) decomposed [32].

The equilibrium constants for the reaction of the \( \text{HPO}_4^{2-} \)-bridged lantern dimer are smaller than those for the HH and HT amidato-bridged complexes (Table 2); in particular, the \( K_1 \) values for the lantern dimer are three orders of magnitude smaller than those of the amidato-bridged dimers. This means that the monohalo complexes in the amidato-bridged complex systems are much more stable than those of the \( \text{HPO}_4^{2-} \)-bridged lantern-type complex.

### 3.2. Kinetic analyses: 1-step kinetics for the formation of the monohalo and dihalo complexes

As mentioned above, two research groups performed the kinetic measurements on the axial water ligand substitution of \([\text{H}_2\text{O})\text{Pt}\text{[H}_\text{m}-\text{HPO}_4\text{]}_4\text{Pt}(\text{OH}_2)\text{]}_2\text{]}^{2-}\) in acidic aqueous solution under the conditions of \( C_\text{X} \gg C_\text{Pt} \), and \( \text{pH} = 3.29–1.55 \). However, the results were inconsistent with each other. El-Mehdawi et al. [47] concluded that the reaction proceeds successively in two steps (Eq. (14)), while Camadanli et al. [48] analyzed as one step reaction. 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 [46]. Therefore, the precise re-investigation of the system was carried out under similar conditions.

A single isosbestic point is observed in the time-resolved UV–Vis spectra for all the systems, as shown in Fig. 8. The absorption band assigned to the dihalo complex simultaneously increases with that of the monohalo complex, indicating that both complexes are in rapid equilibrium. These observations were also confirmed by time-resolved \( ^{31}\text{P} \) NMR measurements [32]. Under the pseudo first-order conditions (\( C_\text{X} \gg C_\text{Pt} \)), the kinetic traces are first order, so
that the rate equation is expressed as Eq. (15),
\[
\frac{d[PtX]}{dt} = k_{obs}[PtX] = \frac{d[PtX_2]}{dt} = k_{obs}[PtX_2],
\]
where \(k_{obs}\) is the conditional pseudo first-order rate constant, and \(PtX\) and \(PtX_2\) denote the monohalo and dihalo complexes, respectively. These observations indicate that the ligand substitution reaction of the diaqua complex proceeds in 1 step, and that the monohalo-species is in rapid equilibrium with the dihalo-species.

For the reactions with halide ions (X\(^-\) = Cl\(^-\), Br\(^-\)), the \(k_{obs}\) values depend on the concentration of the excess halide ion (C\(_X^-\)) 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 \([H^+]\) (Fig. 9a). The dependence of \(k_{obs}\) on the acidity indicates that the aquahydroxo-complex also reacts with halide ion to give the halo-hydroxo complex \([XPt(HPO_4)Pt(OH)]^4\). On the other hand, the values of \(k_{obs}\) deviate significantly from a straight line at low C\(_X^-\) (Fig. 9a, inset), because of the rapid equilibrium between the monohalo- and dihalo-complexes, as mentioned above. Thus, the reaction mechanism is proposed as shown in Scheme 8. Based on this scheme, \(k_{obs}\) is expressed as Eq. (16).

\[
k_{obs} = k_1 + (k_{h1}K_{h1}/[H^+]) = k_{-1} + (k_{h2}K_{h2}/[H^+]) + K_X^2 C_X^- \approx k_1 + (k_{h1}K_{h1}/[H^+]) + k_{-1} + (k_{h2}K_{h2}/[H^+]) \frac{1}{1 + (K_{h1}/[H^+])} + \frac{1}{1 + (K_{h2}/[H^+] + K_X^2 C_X^-)
\]

The simplification in Eq. (16) is reasonable because of the negligible contribution of \(K_{h2}/[H^+]\) under the present conditions of \([H^+]\gg K_{h2}\) and \(K_{h2} \ll K_{h1}\) [27–31]. The best-fit curves in Fig. 9a (solid line) based on Eq. (16) are consistent with the experimental data, even at low C\(_X^-\).

The rate constants in Eq. (16) are summarized in Table 5. The kinetics of the reaction with SCN\(^-\) was somewhat different from those with halide ions. The \(k_{obs}\) dependence on C\(_{SCN^-}\) is linear even at low C\(_{SCN^-}\), while the dependence
of $k_{\text{obs}}$ on $[H^+]$ is similar to that of the reaction with halide ions, as shown in Fig. 9b, although the UV–Vis spectral change is similar to those observed for halide ions, i.e., 1-step first-order kinetics. These effects on $k_{\text{obs}}$ are attributed to the negligible contributions of the reverse reactions (the $k_{-1}$ and $k^{\#}_{-1}$ values are negligibly small) as shown in the plots with zero intercepts (Fig. 9b). Therefore, Eq. (16) is simplified to Eq. (16').

$$
k_{\text{obs}} = \frac{k_1 + (k^{\#}_{-1}K_{H^+}/[H^+])}{1 + (K_{H^+}/[H^+])} C_{\text{SCN}^-}$$

(16')

The equation is valid as shown in the good fit of the experimental data with the calculated lines based on Eq. (16'). The rate constants ($k_1$ and $k^{\#}_{-1}$) in Eq. (16') obtained by a non-linear least squares fit are summarized in Table 5. The negligible reverse reactions in the kinetic analysis would be due to the higher coordination ability of SCN$^-$ compared to those of Cl$^-$ and Br$^-$. The $k_1$ value in the present lantern-type dimer systems in Table 5 scarcely depends on the nature of X$^-$, which is similar to those of the amidato-bridged dimers as mentioned in Section 2.2.1; the values are in the order of $\sim 10^{-1}$ M$^{-1}$ s$^{-1}$ for the reaction of the HPO$_4^{2-}$-bridged lantern dimer (Table 5), while those of the amidato-bridged dimers are in the order of $\sim 10^3$ M$^{-1}$ s$^{-1}$ (Table 4). This is in contrast to the large change in $k_1$ with different X$^-$ reported for the substitution reaction of [Pt(OH)$_2$]$_2$[X]$^-$, which indicates an associative interchange ($I_a$) mechanism; $k_1 = 6.7 \times 10^{-2}$ M$^{-1}$ s$^{-1}$ for the reaction with Cl$^-$, $5.3 \times 10^{-2}$ M$^{-1}$ s$^{-1}$ with Br$^-$, and 0.32 M$^{-1}$ s$^{-1}$ with SCN$^-$ [49–51]. Therefore, the first axial water ligand substitution ($k_1$ path) for both lantern-type and amidato-bridged Pt(III) binuclear complexes would proceed as a dissociative interchange ($I_d$) mechanism, which is due to the filled d$^7$ orbital of the d$^7$ Pt(III) centers [46,52].

### 4. Conclusion

All the HH and HT amidato-bridged cis-diammineplatinum(III) binuclear complexes reviewed here react with halide ions in a consecutive 2-step reaction, via the formation of a monohalo- (step 1) and then a dihalo-species (step 2), under the pseudo first-order conditions of $C_{X^-} \gg C_{Pt}$. In step 1, there are two parallel reaction pathways; the first is simple ligand substitution of the diaqua-complex, and the second is the water ligand substitution on the aquahydroxo-complex which is produced by deprotonation of the original diaqua complex. In step 2, one of the three reaction pathway types operates depending on the nature of the halide ion as well as the bridging ligand; (A) simple ligand substitution for the reactions of the HH $\alpha$-pyrrolidonato-bridged and HH pivalamidato-bridged complexes with Cl$^-$, (B) the path via a coordinatively unsaturated intermediate produced by dissociation of a H$_2$O molecule along with simple substitution, for the reactions of the HH and HT $\alpha$-pyridonato-bridged complex with Br$^-$, and (C) two parallel ligand substitution pathways on the aquahalo complex and on the halo-hydroxo complex, for the HT $\alpha$-pyridonato-bridged complex with Cl$^-$ and the HH pivalamidato-bridged complex with Br$^-$ (Scheme 6).

On the other hand, the axial water substitution reaction of the

![Scheme 8. The reaction mechanism of the hydrogenphosphato-bridged lantern dimer with X$^-$ in acidic aqueous solution.](image)

Table 5

| Type          | Bridging ligand | X$^-$   | Path | $k$           |
|---------------|-----------------|---------|------|---------------|
| Lanterrn      | Hydrogenphosphate | Cl$^-$ | $k_1$ | $0.136 \pm 0.004$ M$^{-1}$ s$^{-1}$ |
|               |                 | Br$^-$ | $k_1$ | $2.0 \pm 0.1$ M$^{-1}$ s$^{-1}$ |
|               |                 | SCN$^-$ | $k_1$ | $0.149 \pm 0.003$ M$^{-1}$ s$^{-1}$ |

$^a$Ref. [32]. Ionic strength was adjusted with sodium perchlorate and perchloric acid.

$^b$Statistical factor was taken into account.

$^c$Determined by using $k_{-1} = k_1/K_{H^+}$. $K_{H^+}/[H^+]$.
hydrogenphosphato-bridged lantern-type complex with halide and pseudo-halide ions proceeds via a one-step reaction kinetics. The rate-determining step is formation of the mono-substituted species, and consists of parallel reaction pathways similar to step 1 of the amidato-bridged systems. The di-substituted complex forms via a rapid equilibrium with the mono-substituted species (Scheme 8).

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