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Kinetics and Mechanisms of the Axial Ligand Substitution Reaction of the Head-to-head 2-Pyridonato-bridged *cis*-Diammineplatinum(III) Dinuclear Complex

Nami Saeki, Yuji Hirano, Yasunari Sasamoto, Ichiro Sato, Tsuyoshi Toshida, Sousei Ito, Noriko Nakamura, Koji Ishihara,* and Kazuko Matsumoto*

Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 169-8555

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The following successive axial ligand substitution reactions of the head-to-head (HH) 2-pyridonato-bridged *cis*-diammineplatinum(III) dinuclear complex ($[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(H_2O)]^{4+}$) with halide ions X^- ($X^- = Cl^-$ and Br^-) to give monohalogeno and dihalogeno complexes were studied kinetically:

$$[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(H_2O)]^{4+} + X^- \xrightleftharpoons{k_{obs1}} [(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(X)]^{3+} + H_2O,$$

$$[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(X)]^{3+} + X^- \xrightleftharpoons{k_{obs2}} [(X)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(X)]^{2+} + H_2O.$$

The acid dissociation constant (K_{h1}) of the axial aqua ligand in the HH dimer and the formation constants ($K_1{}^X$ and $K_2{}^X$) of the monohalogeno and dihalogeno complexes were determined spectrophotometrically to be $-\log(K_{h1}/M) = 1.71 \pm 0.04$; $\log(K_1{}^{Cl}/M^{-1}) = 5.93 \pm 0.02$, $\log(K_2{}^{Cl}/M^{-1}) = 3.71 \pm 0.00$ for the reaction with Cl^-, and $\log(K_1{}^{Br}/M^{-1}) = 6.20 \pm 0.05$, $\log(K_2{}^{Br}/M^{-1}) = 4.55 \pm 0.01$ for the reaction with Br^-. The two platinum atoms are nonequivalent in the HH dimer, in which the first deprotonation occurs selectively to the water molecule on the $Pt(N_4)$ atom and the first nucleophilic substitution with X^- occurs preferentially to the $Pt(N_2O_2)$ atom, where the atoms in parentheses are the coordinating atoms. The first water substitution with X^- proceeds via two similar substitution paths, whereas the second substitution proceeds through two dissimilar paths: one is a simple substitution path and the other is via dissociation of the water molecule, providing a coordinatively unsaturated complex. These reaction paths are reasonably explained by the relative strength of the trans effect of the water, hydroxide, and halide ions in the monohalogeno complexes.

A substantial number of diplatinum(III) complexes having asymmetrical bridging ligands with different coordinating atoms, such as 2-pyrrolidonato-*N*,*O*, 2-pyridonato-*N*,*O*, or acetamidato-*N*,*O*, have been reported. These dinuclear complexes, having a metal–metal bonding between the two d^7 platinum atoms,[1–10] are formed by oxidation of the Pt(II, III) mixed-valent "platinum blues". The head-to-head (HH) dinuclear Pt^{III} complexes $[(X)Pt(NH_3)_2(\mu\text{-}N^\frown O)_2Pt(NH_3)_2(X)]^{n+}$ ($N^\frown O$ = amidate, $X = NO_3{}^-$, $NO_2{}^-$, H_2O, Cl^-, or alkyl, n = 2 or 4) have been reported to have various inorganic axial ligands and alkyl ligands.[11,12] The two platinum atoms in the HH dimer are not equivalent: one is coordinated by two amidate oxygen atoms and two ammine nitrogen atoms ($Pt(N_2O_2)$), whereas the other is by four nitrogen atoms ($Pt(N_4)$) (Chart 1).

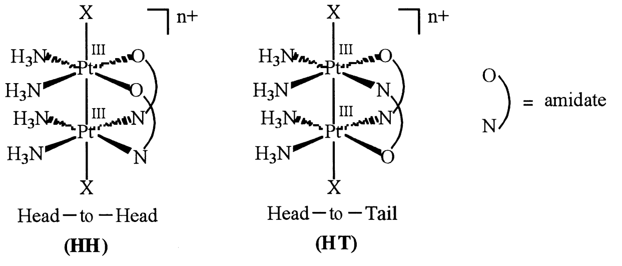


Chart 1.

A head-to-tail (HT) dimer having two equivalent Pt atoms can sometimes be obtained as an isomer of the HH dimer,[4] although HH and HT Pt(III) dimers do not isomerize in solution; the isomerization takes place at their reduced forms, HH and HT Pt(II) dimers. In our previous report, the kinetics of the following axial ligand substitution with halide ions in the HT dimer was reported:[13]

$$[H_2O\text{–}Pt(N_3O)\text{–}Pt(N_3O)\text{–}OH_2]^{4+} + X^- \rightleftarrows [H_2O\text{–}Pt(N_3O)\text{–}Pt(N_3O)\text{–}X]^{3+},$$

$$[H_2O\text{–}Pt(N_3O)\text{–}Pt(N_3O)\text{–}X]^{3+} + X^- \rightleftarrows [X\text{–}Pt(N_3O)\text{–}Pt(N_3O)\text{–}X]^{2+}.$$

The objective of the present study is to examine the same reaction on the HH isomer, and to clarify the difference in the reactivities of the $Pt(N_2O_2)$ and $Pt(N_4)$ atoms. The difference in the chemical properties between the two coordinatively different Pt^{III} atoms is especially the focus of interest, since the two atoms interact through the Pt–Pt bond.

Experimental

Reagents. *cis*-$[PtCl_2(NH_3)_2]$ (N. E. Chemcat) was purchased and used without purification. Reagent-grade 2-pyridone (Kanto

Chemical Co. Inc., Tokyo) was recrystallized once from benzene. Sodium chloride (99.99%, Kanto), sodium bromide (99.99%, Aldrich), and perchloric acid (60% UGR for trace analysis, Kanto) were used without further purification. Sodium perchlorate was prepared and purified according to the literature.[14] Head-to-head $[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(NO_3)]\ (NO_3)_3\bullet 2H_2O$ (HH isomer) was prepared according to the literature.[4]

Measurements. The ionic strength was maintained at 2.00 M (M = mol dm^{-3}) with perchloric acid and sodium perchlorate. All of the sample solutions were prepared by using twice-distilled water just before a measurement. Spectrophotometric measurements were performed with a rapid-scan/stopped-flow spectrophotometer (USP-500 (Unisoku Scientific Instruments, Osaka)) and three other spectrophotometers (UV-160A (Shimadzu, Kyoto), UV-2200 (Shimadzu), and UV-2400 (Shimadzu)). The NMR spectra were recorded on a JEOL Lambda 270 spectrometer, operating at 270 MHz for ^{1}H. The chemical-shift data are reported with reference to TMA (tetramethylammonium perchlorate, 3.190 ppm to TMS). The rate constants were measured by monitoring the absorbance change at 265 nm for the reaction of HH dimer with Cl^- and at 270 nm for the reaction with Br^- for k_{obs1}, and at 265 nm for the reaction of the HH dimer with Cl^- and at 256 or 260 nm for the reaction with Br^- for k_{obs2}, as a function of time after mixing solutions of the dimer and sodium halide. The acid dissociation constant (K_{h1}) of the HH dimer and the formation constants (K_1^X and K_2^X) of the monohalogeno and the dihalogeno complexes were determined spectrophotometrically under the following conditions: $C_{HH} = (5–6) \times 10^{-5}$ M, $[H^+] = 1.00 \times 10^{-3} - 0.501$ M for K_{h1}; $C_{HH} = 2.34 \times 10^{-5}$ M, $[H^+] = 1.27$ M, $C_{Cl^-} = 0–1.35 \times 10^{-2}$ M for K_1^{Cl} and K_2^{Cl}; $C_{HH} = 2 \times 10^{-5}$ M, $[H^+] = 1.27$ M, $C_{Br^-} = 0–9 \times 10^{-2}$ M for K_1^{Br} and K_2^{Br}.

An attempt to substitute the axial ligand with DMSO, Me_2S, DMF, and SCN^- in acidic aqueous solution resulted in decomposition of the dimers after axial ligand substitution.

Results and Discussion

The ^{1}H NMR spectra of the reaction solution were measured (Fig. 1). As $[Cl^-]$ in the aqueous HH solution was raised, a new peak of the bridging ligand appeared at $\delta = 8.50$, and another peak grew at $\delta = 8.55$ along with a decrease in the peak at $\delta = 8.50$. The peaks at $\delta = 8.50$ and 8.55 can be ascribed to the monochloro complex and the dichloro complex, respectively. The chloride ligand in the monochloro complex would be ligated to the $Pt(N_2O_2)$ in the HH dimer, based on the crystallographic results of the compound mentioned later.

Although the peaks of 4H and 6H in Fig. 1 shifted to a lower field, all other peaks remained when the acidity of the solution was lowered to $[D^+] = 0.05$ M. This result shows that there exists an acid dissociation equilibrium in the HH solution. From the above spectral change, it is concluded that only one monochloro complex is formed by substituting the diaqua complex and aquahydroxo complex; also, the monochloro complex further reacts with chloride to give the dichloro complex.

These results were almost the same as that for the reaction of the HT dimer with Cl^- in a previous study.[13]

Acid Dissociation Constant of the HH Dimer. X-ray crystallography shows[4] that one nitrate ion and one water molecule are coordinated at the axial positions of the HH-$[(H_2O)Pt(NH_3)_2(\mu\text{-}C_5H_4NO)_2Pt(NH_3)_2(NO_3)]^{3+}$ in the solid state. The axial nitrate ion would be completely replaced by H_2O or OH^- upon dissolution, since no spectral change was observed when sodium nitrate was added up to 0.020 M to an aqueous solution of the HH dimer (5.0×10^{-5} M). When the acidity of the solution was varied, the UV spectrum changed reversibly, and an isosbestic point was observed at 244 nm for the HH dimer (see Fig. S1). The HH dimer is stable in a strongly acidic aqueous solution, and no decomposition has been observed by acidification, at least for a couple of hours. The pH-dependent spectral change corresponds to deprotonation of the coordinated axial water molecule, as expressed from Eq. 1. Deprotonation takes place at the axial water molecule bound to the $Pt(N_4)$ atom, as detailed later. That is, the axial water molecule on the $Pt(N_4)$ is a stronger Brønsted acid than that on the $Pt(N_2O_2)$.

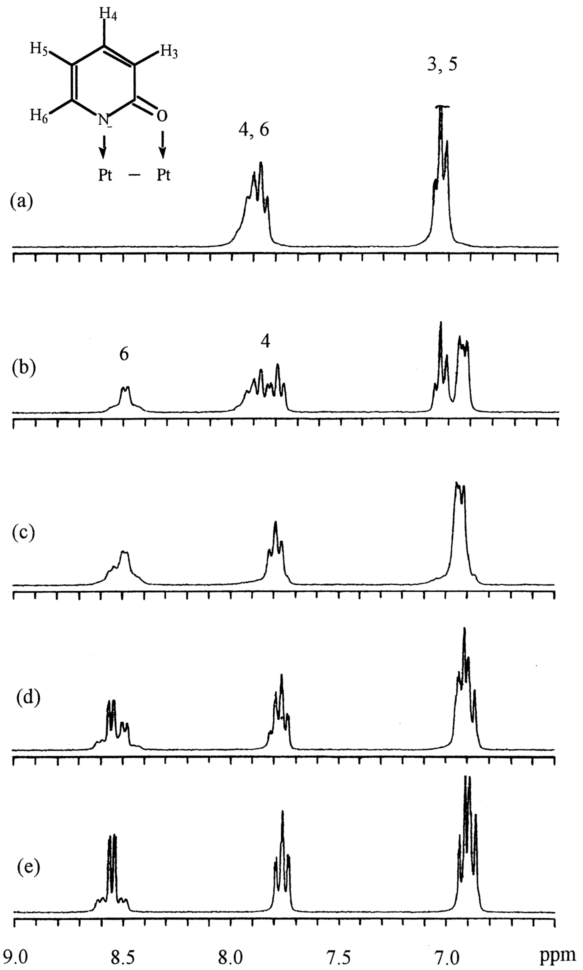
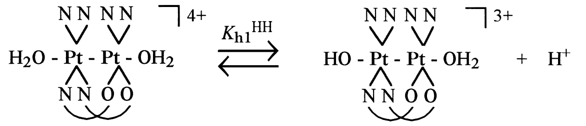


Fig. 1. The ^{1}H NMR spectra of the HH dimer in acidic D_2O solutions with various C_{Cl^-} at room temperature. $[DClO_4] = 1.3$ M, $[HH] = 1.7 \times 10^{-2}$ M, $[Cl^-]/[HT] =$ 0 (a), 0.5 (b), 1.0 (c), 1.5 (d), 2.0 (e).



$$H_2O\text{-}Pt\text{-}Pt\text{-}OH_2\ (4+) \underset{}{\overset{K_{h1}^{HH}}{\rightleftharpoons}} HO\text{-}Pt\text{-}Pt\text{-}OH_2\ (3+) + H^+ \quad (1)$$

$[H_2O–Pt(N_4)–Pt(N_2O_2)–OH_2]^{4+}$ $[HO–Pt(N_4)–Pt(N_2O_2)–OH_2]^{3+}$

Table 1. Equilibrium Constants for the Reactions of the HH- and HT-2-Pyridonato-Bridged *cis*-Diammineplatinum(III) Dimers with Halides, Determined at $I = 2.00$ M ($[H^+] = 1.27$ M) and 25 °C by Spectrophotometry

Complex	$-\log K_{h1}$ (M)	$\log K_1^{Cl}$ (M^{-1})	$\log K_2^{Cl}$ (M^{-1})	$\log K_1^{Br}$ (M^{-1})	$\log K_2^{Br}$ (M^{-1})
HH	1.71 ± 0.03	5.93 ± 0.02	3.71 ± 0.00	6.20 ± 0.05	4.55 ± 0.01
HT[a)]	1.98 ± 0.01	5.27 ± 0.02	3.83 ± 0.01	5.53 ± 0.03	4.44 ± 0.02
HH[b)]	3.02	5.23	3.60		
HT[c)]	3.49				

a) Ref. 13. b) For HH-2-pyrrolidonato-bridged *cis*-diammineplatinum(III) dimer.[18,27] c) For HT-1-methyluracilato-bridged *cis*-diammineplatinum(III) dimer.[8]

The apparent molar absorption coefficient (ε) is expressed as $\varepsilon = (\varepsilon_1 + \varepsilon_2 K_{h1}[H^+]^{-1})(1 + K_{h1}[H^+]^{-1})^{-1}$, where ε_1 and ε_2 are the molar absorption coefficients of the undissociated dimer (H_2O–$Pt(N_4)$–$Pt(N_2O_2)$–OH_2) and the deprotonated dimer (HO–$Pt(N_4)$–$Pt(N_2O_2)$–OH_2), respectively, and K_{h1} is the first acid dissociation constant of the diaqua complex. The ε values at 236, 254, 260, 270, and 280 nm were analyzed simultaneously as a function of $[H^+]$ using a non-linear least-squares fitting method. The K_{h1} values obtained at $I = 2.00$ M are as follows: $-\log(K_{h1}/M) = 1.73 \pm 0.02$ (20.0 °C), 1.71 ± 0.04 (25.0 °C), 1.53 ± 0.00 (35.0 °C). The value of K_{h1} for the HH dimer is significantly larger than that for the HT dimer (see Table 1). These values are ca. 1 order of magnitude larger than those of the related Pt(III) dimers with different bridging ligands: $-\log(K_{h1}/M) = 3.02$ for the 2-pyrrolidonato-bridged HH dimer,[15] and $-\log(K_{h1}/M) = 3.49$ for the 1-methyluracilato-bridged HT dimer.[8] This difference can be explained by the less donating 2-pyridonato ligand, compared to 2-pyrrolidonato and methyluracilato. Because of the weaker donation, the Pt(III) atom in the 2-pyridonato complex would be more electron-withdrawing.

Formation Constants of the Monohalogeno and Dihalogeno Complexes. The absorption spectra were measured at $I = 2.00$ M, $[H^+] = 1.27$ M, 25 °C, and various ratios of C_{X^-} ($X^- = Cl^-$ or Br^-) to fixed C_{HH}, as shown in Fig. 2. Two distinct isosbestic points were observed at 251 and 273 nm, and at 256 and 303 nm for the reactions with Cl^- and Br^-, respectively.

Although plots of the absorbance at the isosbestic point of the longer wavelength (273 and 303 nm) against C_{X^-}/C_{HH} showed a clear inflection point at $C_{X^-}/C_{HH} = 1$, another inflection point corresponding to $C_{X^-}/C_{HH} = 2$ was unclear, probably because of the smaller formation constant of the dihalogeno complex. The formation of the dichloro complex has been shown by X-ray crystallography for the dichloro-HH-2-pyrrolidonato-bridged dimer,[15] and the ^1H NMR spectra also confirmed it, as mentioned above.

The first substitution with X^- occurs selectively to one of the two nonequivalent Pt atoms, because only one monochloro complex is formed in the reaction of the HH dimer with Cl^-, as mentioned previously. 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, since the two Pt atoms in the HH dimer are not equivalent. For an HT dimer having equivalent Pt atoms, the experimental data were reasonably analyzed by postulating that the deprotonation and substitution reactions occur to different Pt atoms.[13] The results of X-ray crystallography on the related HH and HT dimers are summarized in Table 2, which, together with the ^1H NMR spectra, show that the axial position of the $Pt(N_2O_2)$ in the HH complexes is always occupied by a ligand with a stronger *trans* influence (**1**, **3**–**7** in Table 2)), which suggests that the first halide substitution occurs exclusively to the $Pt(N_2O_2)$ in the reaction of the HH-diaqua complex. In the HH complexes listed in Table 2, having axial ligands Cl^- or NO_3^- at the $Pt(N_2O_2)$, i.e., complexes **1** and **2**, the axial bond lengths are shorter for the $(N_4)Pt$–L_2 than for the $(N_2O_2)Pt$–L_1. This suggests that when complex **8** in this study is dissolved in water, the $(N_4)Pt$–OH_2 bond would be shorter than the $(N_2O_2)Pt$–OH_2 bond. That is, the $(N_2O_2)Pt$–OH_2 bond is weaker, and thus the Pt atom is more sensitive to substitution with halide ions, whereas the water molecule on the $Pt(N_4)$ is easier to deprotonate. In addition, the $Pt(N_2O_2)$ is sterically more open to an attack of X^- than the $Pt(N_4)$. These observations can explain why the first halide ion is incorporated pref-

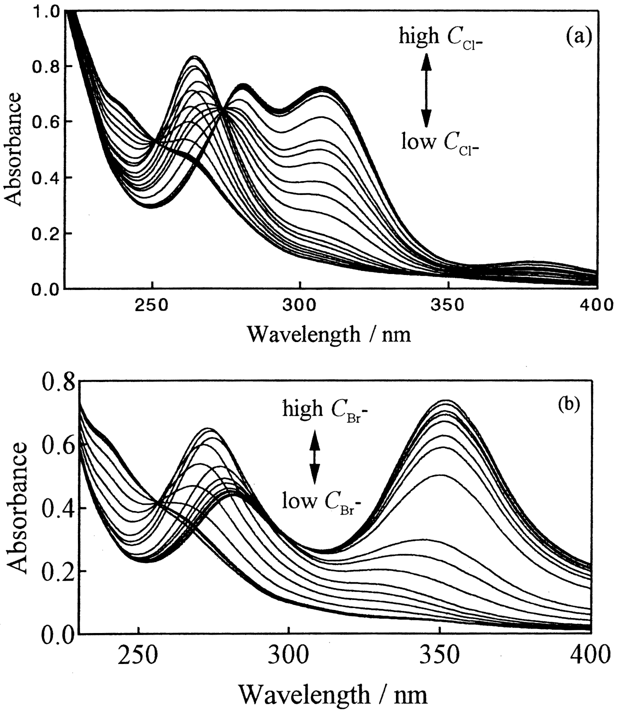


Fig. 2. The UV–visible spectra of the HH dimer in acidic aqueous solutions (a) with various chloride ion concentrations and (b) with various bromide ion concentrations at 25 °C and $I = 2.00$ M. $[H^+] = 1.27$ M; $C_{Cl^-} = 0$–1.35×10^{-2} M; $C_{Br^-} = 0$–8.0×10^{-2} M; $C_{HH}/M = 2.34 \times 10^{-5}$ (a), 2.48×10^{-5} (b).

Table 2. Axial Bond Distances (Å) of the HH- and HT-Dibridged *cis*-Diammineplatinum(III) Dinuclear Complexes

Complex	**1**[a]	**2**[a]	**3**[b]	**4**[c]	**5**[c]	**6**[d]	**7**[d]	**8**[e]	**9**[f]	**10**[g]
HH or HT	HH	HH	HH	HH	HH	HH	HH	HH	HT	HT
Bridging ligand	2-Pyrrolidonate	2-Pyrrolidonate	2-Pyrrolidonate	Pivalamidate	Pivalamidate	Pivalamidate	Pivalamidate	2-Pyridonate	2-Pyridonate	2-Pyridonate
X_1	Cl^-	Cl^-	NO_2^-	NO_2^-	$CH_3CO{-}CH_2^-$	$C_5H_9O^-$	$^-CH_2C{-}HO$	H_2O	NO_3^-	NO_2^-
$(N_2O_2)Pt{-}X_1$ or $(N_3O)Pt{-}X_1$	2.360(4)	2.455(4)	2.10(2)	2.086(8)	2.095(9)	2.11(1)	2.121(9)	2.122(6)	2.170(10)	2.172(10)
Pt–Pt	2.624(1)	2.6373(7)	2.644(1)	2.6091(4)	2.6892(6)	2.7486(8)	2.7106(7)	2.5401(5)	2.5486(8)	2.5759(7)
$(N_4)Pt{-}X_2$ or $(N_3O)Pt{-}X_2$	2.27(1)	2.392(4)	2.36(2)	2.281(5)	2.667(7)	2.92(1)	2.7498(8)	2.193(7)	2.165(10)	2.168(11)
X_2	NO_3^-	Cl^-	NO_3^-	NO_3^-	NO_3^-	NO_3^-	NO_3^-	NO_3^-	NO_3^-	NO_2^-

a) Ref. 27. b) Ref. 10. c) Ref. 22. d) Ref. 12. e) Ref. 28. f) Ref. 4. g) Refs. 5, 29.

erentially into the $Pt(N_2O_2)$.

$$[(H_2O)Pt(N_4){-}Pt(N_2O_2)(H_2O)]^{4+} + X^- \xrightleftharpoons{K_1^X} [(H_2O)Pt(N_4){-}Pt(N_2O_2)(X)]^{3+} + H_2O \quad (2)$$

$$[(H_2O)Pt(N_4){-}Pt(N_2O_2)(X)]^{3+} + X^- \xrightleftharpoons{K_2^X} [(X)Pt(N_4){-}Pt(N_2O_2)(X)]^{2+} + H_2O \quad (3)$$

The K_1^X and K_2^X values were obtained at $I = 2.00$ and 25 °C by simultaneously analyzing the absorbance at thirteen different wavelengths between 235 nm and 310 nm, and are given in Table 1 along with the K_{h1} values. In the determination of the K_2^{Br} value for the HH dimer, only a limited number of spectral data obtained for $C_{Br^-} < 4.0 \times 10^{-3}$ M were used, since the spectrum changed differently with a different isosbestic point at higher C_{Br^-}, probably due to a reduction of the Pt(III) dimer to the Pt(II) dimer by water.[16] Although the Pt(III) dimer is gradually reduced to the mixed-valent Pt blues and Pt(II) dimer complexes by water under a neutral condition, the Pt(III) oxidation state can be maintained under most of the present acidic conditions. The K_1^{Cl} and K_2^{Cl} values are comparable to those reported for the corresponding reactions of the HH-2-pyrrolidonato-bridged *cis*-diammineplatinum(III) dimer with Cl^-: $\log (K_1^{Cl}/M^{-1}) = 5.23$, $\log (K_2^{Cl}/M^{-1}) = 3.60$.[15]

Kinetics for the Formation of the Monohalogeno Complexes. Only reaction (2) was observed under the conditions $C_{HH} \gg C_{X^-}$ and $[H^+] = 0.10$–0.82 M, since the reaction of the HH dimer with X^- was first order and monophasic. The formation rate of the monohalogeno complex (Pt_2X) is given by the following equation, where $[X^-]$ is the concentration of the unreacted halide ion:

$$d[Pt_2X]/dt = k_{obs1}[X^-]. \quad (4)$$

The conditional first-order rate constant, k_{obs1}, was found to involve the dimer concentration and $[H^+]$. Since k_{obs1} was linearly dependent on C_{HH} at a given $[H^+]$, as shown in Fig. 3a, k_{obs1} is expressed by

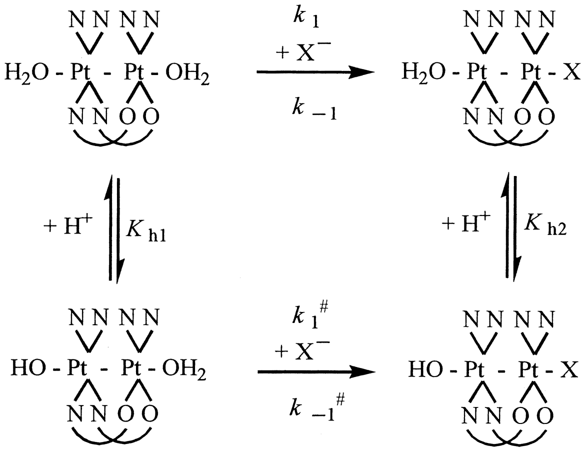
$$k_{obs1} = k_{f1}C_{HH}. \quad (5)$$

Under the present acidic conditions, Scheme 1, consisting of the two reaction paths, can be drawn as the reaction pathways, considering the K_{h1} value obtained in this study. For the reaction pathways in Scheme 1, the rate constant, k_{obs1}, is given by

$$k_{obs1} = \frac{k_1 + \dfrac{k_1^{\#}K_{h1}}{[H^+]}}{1 + \dfrac{K_{h1}}{[H^+]}} C_{HH}. \quad (6)$$

Combining Eq. 5 with Eq. 6 gives

$$\left(1 + \frac{K_{h1}}{[H^+]}\right)k_{f1} = k_1 + \frac{k_1^{\#}K_{h1}}{[H^+]} \quad (7)$$



Scheme 1.

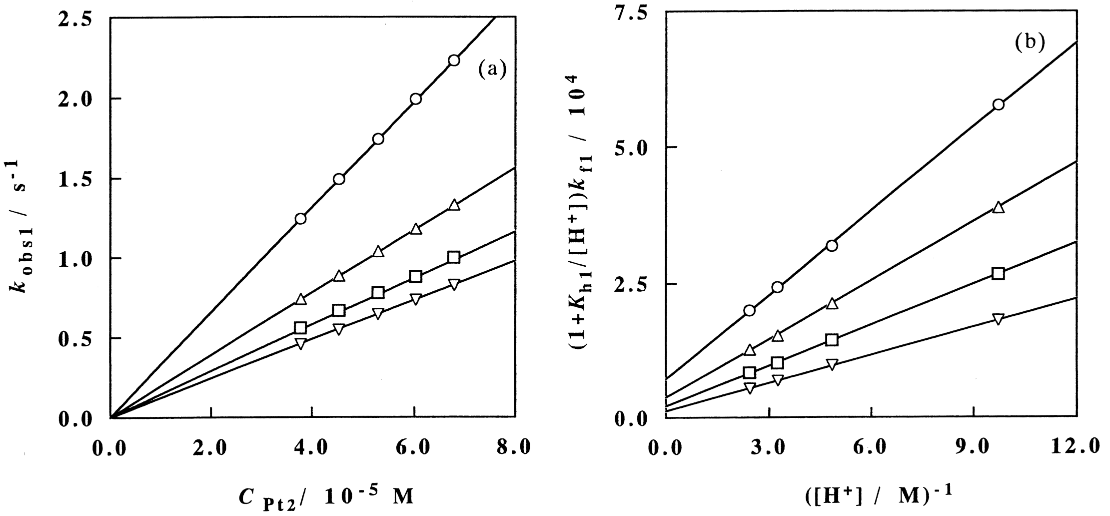


Fig. 3. (a) Dependence of k_{obs1} on C_{HH} for the reaction of the HH dimer with bromide ion in acidic aqueous solution at 20 ˚C and I = 2.00 M. $[H^+]$/M = 0.103 (○); 0.206 (△); 0.309 (□); 0.412(▽). C_{Br^-} = 8.75 × 10^{-7} M. (b) Plot of $(1 + K_{h1}/[H^+])k_{f1}$ against $1/[H^+]$ for the reaction of the HH dimer with bromide ion at 20 ˚C and I = 2.00 M. T/˚C= 25.0 (○); 20.0 (△); 15.0 (□); 10.6 (▽).

Table 3. Rate constants (25 ˚C) and Activation Parameters for the First Step of the Reactions of the HH and HT Dimers with Halides

Complex	Ligand	Path	k^{298}	$\Delta H^{\neq}$	$\Delta S^{\neq}$
			M^{-1} s^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
HH	Cl^-	k_1	3.1 × 10^3	64.1 ± 21.0	37 ± 72
		$k_1^{\#}$	4.6 × 10^5	38.7 ± 1.5	−6.8 ± 5.0
		k_2	550 ± 10		
		k_3	3.1 ± 0.3[b]		
		k_{-3}/k_4	(3.7 ± 0.5) × 10^{-3} [c]		
HT[a]	Cl^-	k_1	1.2 × 10^3 [d]	87.8 ± 21.0	108 ± 72[d]
		$k_1^{\#}$	3.3 × 10^5 [d]	11.9 ± 1.5	−99.5 ± 5.3[d]
		k_2	(2.49 ± 4) × 10^3		
		$k_2^{\#}K_{h2}$	115 ± 5[b]		
		k_{-2}	0.59 ± 0.38[b]		
HH	Br^-	k_1	7.2 × 10^3	85.6 ± 6.1	116 ± 1
		$k_1^{\#}$	2.4 × 10^5	29.1 ± 2.1	−44.5 ± 3.0
		k_2	450 ± 36		
		k_3	4.4 ± 0.8[b]		
		k_{-3}/k_4	(3.7 ± 0.8) × 10^{-3} [c]		
HT[a]	Br^-	k_1	3.3 × 10^3 [d]	79.7 ± 1.0	89.5 ± 3.0[d]
		$k_1^{\#}$	2.7 × 10^5 [d]	23.1 ± 0.7	−63.7 ± 2.0[d]
		k_2	—		
		k_3	3.7 ± 0.4[b]		
		k_{-3}/k_4	(1.4 ± 0.2) × 10^{-3} [c]		

a) Ref. 13. b) In s^{-1}. c) In M. d) Statistical factor was taken into account.[13]

The plots of $(1 + K_{h1}/[H^+])k_{f1}$ vs. $[H^+]^{-1}$ were linear, as shown in Fig. 3b.

The values of k_1 and $k_1^{\#}$ were obtained by applying a nonlinear least-squares fitting to Eq. 7, and are tabulated in Table 3, together with the related data of the HT dimer, obtained previously.[13]

Kinetic data were also analyzed according to an equation derived from a scheme involving ion pair-formation steps, since the effect of ion pairing should sometimes be considered, even in aqueous media, especially for such a highly charged complex as the present complexes (3+ or 4+). The result was quite unsatisfactory, so that the ion pairing effect is negligible in the present HH dimer reaction, as in the case of the HT dimer reaction, probably because k_{obs1} was measured at low C_{HH} (10^{-4} M > $C_{HH} \gg C_{X^-}$) and at a high ionic strength (2 M).

The rate constants for the substitution reactions on the many hexaaqua metal ions are smaller by 2–3 orders of magnitude than those on the corresponding pentaaquahydroxo metal ions.[17] The k_1 and $k_1^{\#}$ values for the HH and HT dimers in Ta-

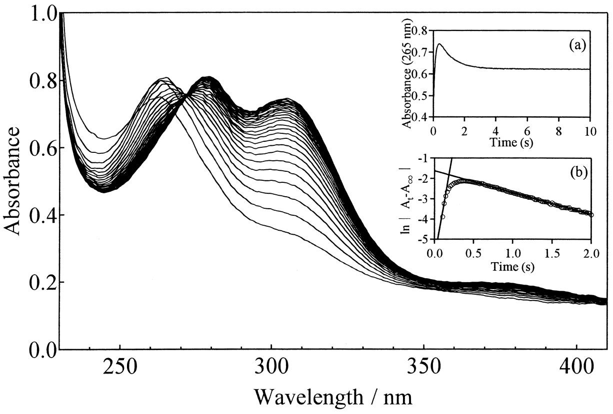


Fig. 4. The UV–visible spectra for the reaction of the HH dimer with chloride ion in acidic aqueous solution at 25 °C and I = 2.00 M. Measurement every 80 ms, C_{Cl^-} = 2.9 × 10^{-3} M, C_{HH} = 2.0 × 10^{-5} M. The inserted figure (a) shows the time dependence of the absorbance at 265 nm, and the semi-log plot (b) of the data in (a) show clearly that the reaction is biphasic.

ble 3 show that the same tendency holds, even through the metal-metal bond.

Table 3 shows that the k_1 values of the HH dimer are larger than those of the HT dimer for both the Cl^- and Br^- reactions. This may reflect the difference in the Pt–OH_2 bond strength in the diaqua complexes; the bond strength may be in the following order: (N_4)Pt–OH_2 > (N_3O)Pt–OH_2 > (N_2O_2)Pt–OH_2. A similar tendency is observed for the $k_1^{\#}$ values, but is less explicit. Interestingly, the k_1 values for the reactions of the HH and HT dimers with Br^- are larger than those with Cl^-; this trend is the same as that found for the reactions of mononuclear Pt(II) complexes, where the heavier halides with higher polarizability react faster.[18] On the other hand, the $k_1^{\#}$ values for reactions with Cl^- are larger than those with Br^-, which may reflect the decreased polarizabilities of the Pt(N_2O_2) in the HH dimer and the Pt(N_3O) in the HT dimer, due to deprotonation of the water molecules on the opposite axial sites. Consequently, it is concluded that the ligand substitution rates on the axial sites of the dimers are sensitive to the nature of the ligands on the opposite axial sites.

It is noteworthy, as stated previously,[13] that the rate constants, k_1 and $k_1^{\#}$, in Table 3 are larger than the rate constants for the following axial ligand substitution on the tetrabridged Pt(III) dinuclear complex (k_1 = 0.9 and 0.3 M^{-1} s^{-1}, k_2 = 0.8 and 0.4 M^{-1} s^{-1} for X = Cl^- and Br^-, respectively) (Eq. 8),[1] and are also larger than those for the direct substitution reaction on the square planar Pt(II) Werner-type complexes, as shown in Eq. 9, which are in the range of 1.3 M^{-1} s^{-1}–1.4 × 10^{-3} M^{-1} s^{-1}.[19] A linear relationship was observed between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (as shown in Fig. S2), which suggests that both the k_1 and $k_1^{\#}$ paths are via the same mechanism.[20,21]

$$\mathrm{Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2^{2-}} \underset{}{\overset{k_1}{\underset{}{\xrightleftharpoons{+X^-}}}} \mathrm{Pt_2(\mu\text{-}PO_4H)_4X(H_2O)^{3-}}$$

$$\overset{k_2}{\xrightleftharpoons{+X^-}} \mathrm{Pt_2(\mu\text{-}PO_4H)_4X_2^{4-}} \tag{8}$$

$$[\mathrm{Pt(dien)X_1}]^+ + \mathrm{X_2}^{n-} \rightarrow [\mathrm{Pt(dien)X_2}]^{(2-n)+} + \mathrm{X_1}^- \tag{9}$$

(X_1^- = Cl^-, Br^-, I^-, and N_3^-; X_2^{n-} = py, I^-, N_3^-, NO_2^-, and SCN^-)

Kinetics for the Formation of the Dihalogeno Complexes. Under the conditions $C_{HH} \ll C_{X^-}$ and $[H^+]$ = 0.11–1.3 M, the reaction was biphasic (see Fig. 4), and is expressed by $A_t = A_\infty + \alpha\exp(-k_{obs1}t) + \beta\exp(-k_{obs2}t)$, where A_t and A_∞ are the absorbances at time t and ∞, respectively, and α and β are composite parameters.[20] Only the rate constant for the slower reaction was calculated.

The formation rate of the dichlorocomplex (Pt_2X_2) is ex-

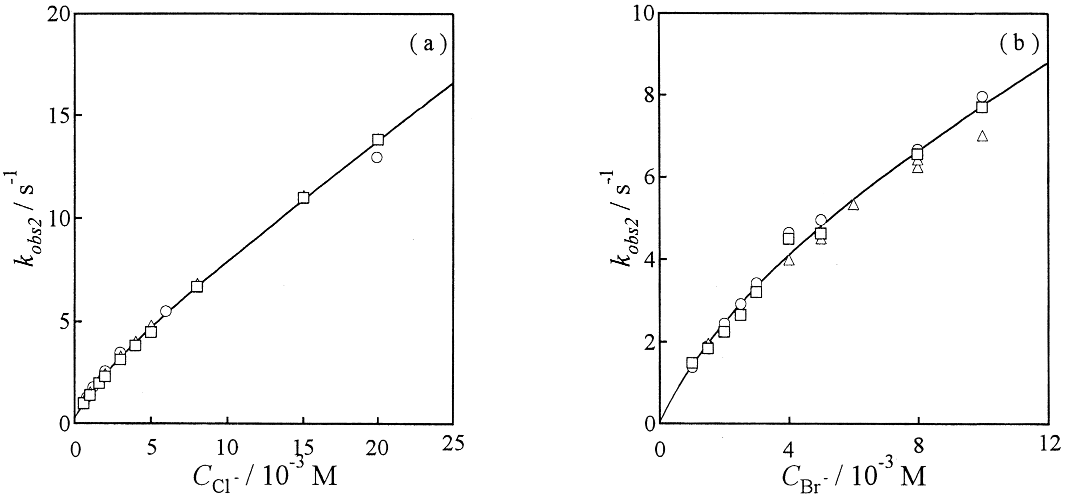
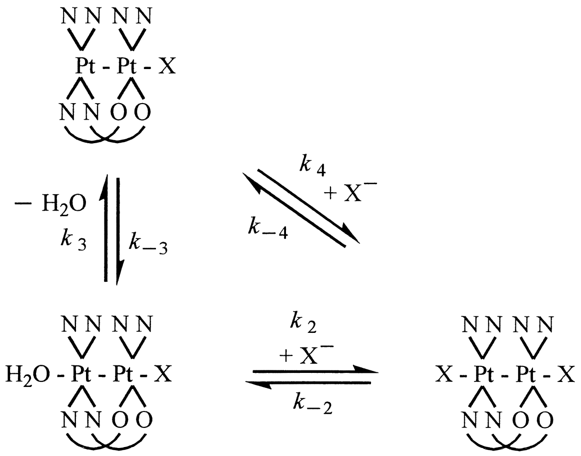


Fig. 5. Dependence of k_{obs2} on C_{X^-} in acidic aqueous solution at 25 °C and I = 2.00 M. (a) the reaction of the HH dimer with chloride ion, C_{HH} = 2.0 × 10^{-5} M, $[H^+]$/M = 0.805 (□), 0.403 (△), 0.106 (○); (b) the reaction of the HH dimer with bromide ion, C_{HH} = 6.0 × 10^{-5} M, $[H^+]$/M = 1.21 (□), 0.604 (△), 0.403 (○). The solid lines were drawn by applying a linear or a nonlinear least-squares fitting.



Scheme 2.

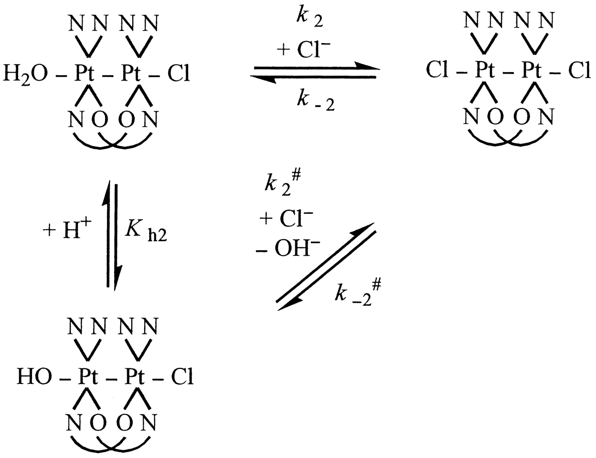
pressed by the following equation, where [HH] is the total concentration of the monohalogeno HH dimer:

$$d[Pt_2Cl_2]/dt = k_{obs2}[HHCl]. \quad (10)$$

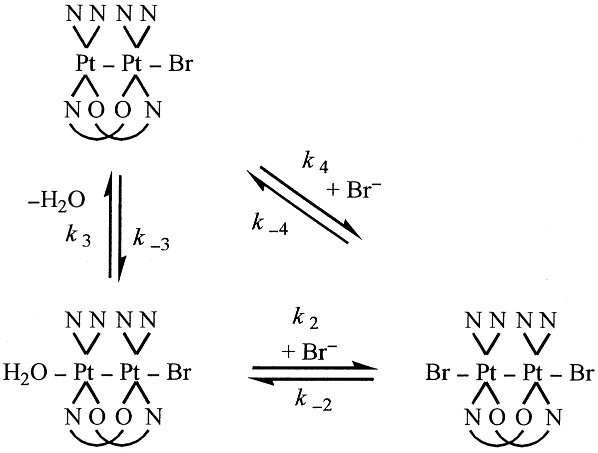
The rate constant of the second step, k_{obs2}, depends on C_{X^-} in a more complicated way than for k_{obs1}, and in a similar manner to that for the reaction of HT with Br^-.[13] It is also notable that k_{obs2} is almost independent of $[H^+]$ for both the Cl^- and Br^- reactions, as shown in Fig. 5.

The X-ray analysis data for several HH-dipivalamidato-bridged dinuclear complexes are tabulated in Table 2. Table 2 shows that the lengths of the Pt–Pt and the $(N_4)Pt–NO_3$ bonds vary drastically, depending on the axial ligands on the $Pt(N_2O_2)$. Virtually, there is no bond between the $Pt(N_4)$ and NO_3^- in complexes **5**–**7**, which suggests that the positive charge of the Pt atoms is extremely localized in these complexes, and is close to $L_1–Pt^{IV}(N_2O_2)–Pt^{II}(N_4)\cdots NO_3$, which is supported by the ^{195}Pt NMR chemical shifts.[12,22] In other words, a strong *trans* influence is operative, even through the Pt–Pt bond in these complexes. On the other hand, for non-Werner Pt(II) and Pt(IV) complexes, e.g., $Pt^{II}R_2S_2$ (R = Me, Ph; S = Me_2S, Me_2SO) and $Pt^{IV}Me_4(Me_2S)_2$, a dissociative mechanism has been proposed for the substitution reactions with water; this is because of the strong *trans* labilizing effect of Me and Ph groups.[23–26] The *trans* effect is also observed through the Pt–Pt bond for the present HH and HT dimers, as mentioned above. On the basis of these findings, it seems that the substitution reaction (Eq. 3) proceeds both through a direct path (k_2) and a dissociative path (k_3) via an intermediate having no ligand on the $Pt(N_4)$, as depicted in Scheme 2.

In Fig. 5, k_{obs2} increases linearly with $[X^-]$ at lower $[X^-]$; at higher $[X^-]$ it still increases linearly, but with a different slope. This can be reasonably explained if the steady-state approximation is applied to the monohalogeno dimer without an axial ligand at the opposite site in Scheme 2. Based on this assumption, Eq. 11 is obtained for Scheme 2, if the reverse reaction is negligible. The first term in Eq. 11 is related to the k_2 path, and the second is to the k_3 path. Equation 11 agrees well with the experimental data in Fig. 5. The values of the rate constants were estimated by applying a non-linear least-squares fitting to a modified equation derived from Eq. 11, and are listed in Table 3.



Scheme 3.



Scheme 4.

$$k_{obs2} = k_2[X^-] + \frac{k_3k_4[X^-]}{k_{-3}+k_4[X^-]} \quad (11)$$

The data in Fig. 5 were also analyzed by assuming a mechanism that involves ion-pair formation. However, because the fit was very poor, the ion-pair formation is negligible under the present conditions.

The difference in the equatorial donating atoms (N_4 or N_2O_2) in addition to the *trans* influence and/or the *trans* effect seems to determine the reaction paths. The increased *trans* influence and *trans* effect of X^- lengthen and labilize the H_2O–Pt bond in the aquahalogeno HH complexes, and promotes the dissociation of H_2O on the other Pt atom to produce monohalogeno dimers without an axial H_2O at the opposite site. The formation of the transient monohalogeno HH dimers without an opposite axial H_2O suggests that the aquahalogeno HH dimers have a more intense $Pt^{II}–Pt^{IV}–X$ character than the diaqua HH dimer. Although the involvement of such an electronic structure was previously suggested for alkyl–Pt^{III} dimer complexes,[12] the present study suggests that the same electron localization occurs even to non-alkyl Pt^{III} dimer complexes.

In our previous study on the ligand substitution reaction of the HT dimer with halide ions,[13] Schemes 3 and 4 were proposed for the HT–[H_2O–Pt–Pt–Cl] + Cl^- system and the HT–[H_2O–Pt–Pt–Br] + Br^- system, respectively. Scheme 3 involves the k_2 path in Scheme 2 and the $k_2^\#$ path in which the coordinated OH^- is replaced by X^-, and Scheme 4 is virtually the same as Scheme 2. The mechanistic difference in these systems was reasonably explained by the relative extent of the electron donor ability of Cl^- and Br^-. Because the more donating Br^- favors dissociation of the axial aqua ligand on the opposite Pt atom, the coordinatively unsaturated intermediate is involved in the mechanism (Scheme 4). The charge localization would be more pronounced in the aquahalogeno HH dimer compared with the aquahalogeno HT dimer because the two Pt atoms are not equivalent in the diaqua HH dimer, which shifts the mechanism of Scheme 3 to the dissociative mechanism of Scheme 4 (or Scheme 2). These mechanistic differences show how strongly the stability of the axial coordination is affected by the donor ability of the axial ligand on the opposite Pt atom.

Conclusion

The first deprotonation occurs to the water molecule on the $Pt(N_4)$ atom and the first nucleophilic substitution with X^- (X^- = Cl^- and Br^-) occurs to the $Pt(N_2O_2)$ atom. The formation of the HH dihalogeno complex from the aquahalogeno complex proceeds through two parallel paths: a simple substitution path and a path via dissociation of the water molecule. Mechanistic differences among the aquahalogeno HH dimer with X^- and the aquahalogeno HT dimer with X^- systems are reasonably explained by the relative extent of the electron donor ability of Cl^- and Br^- and the different charge delocalizations through Pt–Pt bonding in the aquahalogeno HH and HT dimers.

Supporting Data.

Numerical values of the observed k_0 under various conditions (Table SI–SIV)(in total 8 pages) and Figs. S1 and S2 are deposited as Document No. 74032 at the Office of the Editor of Bull. Chem. Soc. Jpn. and are also available from the author upon request.

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