^{1}H-NMR Study of Ternary Platinum(II) Complexes with *N*-(1-Naphtyl)methyl-1,2-ethanediamine or *N*-(9-Anthrylmethyl)-1,2-ethanediamine and Bipyridine or Phenanthroline and Restricted Single Bond Rotation Due to Aromatic–Aromatic Ring Interaction

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^{1}H-NMR spectra of square-planar complexes with the formula $[Pt(L^1)(L^2)]X_2$ where L^1 is 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) and L^2 is *N*-(1-naphthyl)methyl-1,2-ethanediamine (Npen) or *N*-(9-anthryl)methyl-1,2-ethanediamine (Aten) indicate that the *N*-naphthylmethyl and *N*-anthrylmethyl groups are forced to adopt a pseudo axial disposition due to intramolecular repulsion of hydrogen atoms of the aromatic diimines. The aromatic–aromatic interactions in the *N*-arylmethyl-1,2-ethanediamine complexes and aromatic diimines caused them to undergo intramolecular stacking. ^{1}H-NMR spectra of these complexes showed a significant concentration and temperature dependence. The monomer–dimer equilibrium was estimated, based on the concentration dependency. Restricted single bond rotation was estimated from temperature dependency data. The rotation of the anthracene ring of the $[Pt(bpy)(Aten)]^{2+}$ complex showed an activation energy of *ca.* 38 kJ mol^{-1}, which is in good agreement with a mechanism involving successive rotations about single bonds with restriction by intramolecular aromatic–aromatic ring interactions.

Key words platinum(II) complex; NMR; aromatic compound; ternary complex

Aromatic π–π interactions have been a subject of extensive study because of its role in (i) the packing of aromatic molecules in the crystalline state, (ii) base-stacking interactions of DNA, (iii) three-dimensional structures of proteins, (iv) molecular recognition of pharmaceuticals by biological receptors or enzymes, and (v) template-directed synthesis.[1—8] Ternary complexes of platinum(II) or palladium(II) containing 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) and an amino acid bearing an aromatic side chain such as tyrosine and tryptophan have been reported to show aromatic π–π interactions.[9—13] The crystal structures of ternary complexes of platinum(II), bpy, and *N*-benzyl-1,2-ethanediamine (Been), *N*-(1-naphthylmethyl)-1,2-ethanediamine (Npen), or *N*-(9-anthrylmethyl)-1,2-ethanediamine (Aten) indicate that intramolecular aromatic π–π interactions occur in the cases of Npen and Aten complexes.[14] The structure of Been complexes in an aqueous solution was examined by ^{1}H-NMR spectroscopy and this cation has a structure in which the phenyl ring and bpy are partially stacked in aqueous solution although the phenyl and bpy rings participate in only intermolecular stacking in the crystalline state.[15]

In order to clarify the nature of the aromatic–aromatic interaction in various amino acids or proteins in solution as well as solid state, we used ternary platinum(II) complexes having two aromatic rings as a model compound.

The present paper describes the results of some detailed ^{1}H-NMR measurements of $[Pt(bpy)(Npen)]^{2+}$ and $[Pt(bpy)(Aten)]^{2+}$ along with $[Pt(phen)(Npen)]^{2+}$ and $[Pt(phen)(Aten)]^{2+}$. The aromatic π–π interactions became stronger as the ring size increased from pheny to naphthyl and anthryl groups. The characteristics of the intermolecular interactions between them and the restricted rotation about C_{ipso}–C–N–Pt (C_{ipso} denotes the ipso carbon of the aromatic ring; see Fig. 1) for $[Pt(bpy)(Aten)]^{2+}$ are delineated in this paper.

Results

Characterization of Platinum Complexes Figure 1 shows a scheme of the structure of the Pt(II) complexes used in this study and each ^{1}H is designated by the position shown in Fig. 1, such as H(B3) for hydrogen atom, which is bound to the 3 position of the bpy group.

The ^{1}H-NMR spectra of the aromatic regions of $[Pt(bpy)(Npen)]^{2+}$ and $[Pt(bpy)(Aten)]^{2+}$ were complicated but ^{1}H–^{1}H COSY spectra allowed the assignment of all the ^{1}H signals in these regions. The chemical shifts of these complexes showed a significant concentration dependence.

The concentration dependency of the chemical shifts of $[Pt(bpy)(Aten)]^{2+}$ (Figs. 2, 3) was much larger than those for $[Pt(bpy)(Npen)]^{2+}$ (data not shown). All the chemical shifts of the ternary complex moved to higher field with increase in the concentration of the platinum complex. This can be at-

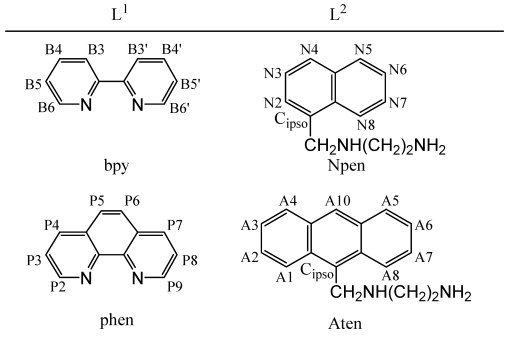

Fig. 1. Structures of the Pt(II) Complexes and the Numbering of Protons of the Ligands

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tributed to the aggregation of complexes but the present platinum complexes have positive charges of +2, and extensive aggregation is not plausible and was analyzed based on the equilibrium between monomer and dimmer, Eq. 1.

$$\text{monomer} + \text{monomer} \rightleftarrows \text{dimer} \quad (1)$$

If equilibrium, Eq. 1, is assumed, the observed chemical shift of each proton, δ_{obs}, can be expressed by the Hasselbach–Sanders equation, Eq. 2,

$$\delta_{obs} = \frac{c_t\delta_d + (\delta_m - \delta_d)\dfrac{\sqrt{1+8Kc_t}-1}{4K}}{c_t} \quad (2)$$

where, δ_m and δ_d are the chemical shifts for the monomer and the dimer respectively and c_t is the total concentration of the platinum complex. The H(B3′) and H(B6) of the bipyridine and H(A10) of the anthryl moiety were chosen to estimate the equilibrium constant, K, because the signals for these protons were isolated, not purturbed by temperature (see below), and strongly depended on the concentration. The equilibrium constant, K, derived from the chemical shift values for the three protons are 22(1), 13(1), and 23(2) M^{-1} for H(B3′), H(B6), and H(A10) protons. The average value of 19 M^{-1} was used to evaluate the δ_m and δ_d for each proton and the curves shown in the Figs. 2 and 3 are derived from Eq. 2 using the above estimated values. An analogous concentration dependency was observed for the dihydrochloride ligand, Aten·2HCl and the K value for this was estimated to be 7 M^{-1}(data not shown).

A similar concentration dependency was observed for a CD_3OD solution of [Pt(phen)(Aten)]Cl_2 and the dimerization constant was determined to be 5.8 M^{-1} at 30 °C.

The δ_m represents the chemical shift of the isolated platinum complex ion. The δ_m and δ_d values for $[Pt(bpy)(Aten)]^{2+}$ and $[Pt(phen)(Aten)]^{2+}$ complexes are listed in Table 1.

The presence of an aromatic ring causes upfield shifts in the proton signals in one of the pyridine rings and H(B5) and H(B6) are the most susceptible for the bpy complexes and H(P2) and H(P3) are the most susceptible for the phen complexes. The shift is increased with the increase of the size of the aromatic rings. These shifts can be attributed to the intramolecular stacking of the bipyridine and the aromatic rings.

The Upfield Shift Depended on the Ring Current Effect The protons bound to the half pyridyl ring of the coordinated bipyridine appear at higher field than those bound to the other half, as has been reported for $[Pt(bpy)(Been)]^{2+}$.[15] These up-field shifts are consistent with significant intramolecular aromatic–aromaric ring interactions, which is supported by the X-ray structures of these complexes.[14] Based on the X-ray crystal structure determination of [Pt(bpy)(Been)]$(NO_3)_2$, the upfield shift of each proton of the phen ring in $[Pt(phen)(Npen)]^{2+}$ and $[Pt(phen)(Aten)]^{2+}$ was

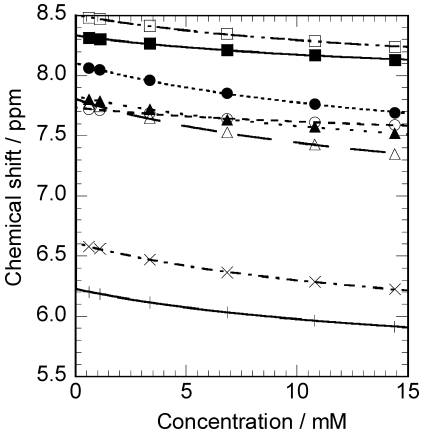

Fig. 2. Plots of Chemical Shifts for bpy Group of $[Pt(bpy)(Aten)]^{2+}$ *versus* Concentration

Key: △, H(B3); ▲, H(B4); +, H(B5); ×, H(B6); ●, H(B3′); ■, H(B4′); ○, H(B5′), □, H(B6′).

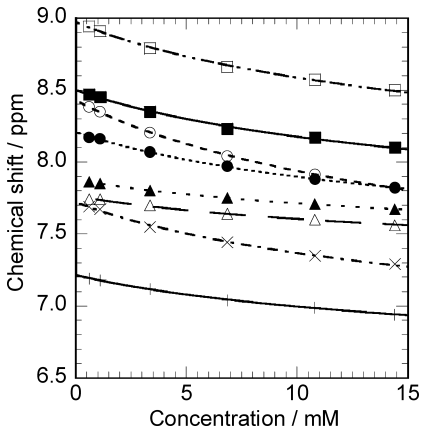

Fig. 3. Plots of Chemical Shifts for the Anthranyl Group of $[Pt(bpy)(Aten)]^{2+}$ *versus* Concentration

Key: ■, H(A1); ▲, H(A2); △, H(A3); ●, H(A4); ×, H(A5); +, H(A6,A7); □, H(A8); ○, H(A10).

Table 1. Estimated Chemical Shifts for Monomer (δ_m) and Dimer (δ_d) for the $[Pt(bpy)(Aten)]^{2+}$ and $[Pt(phen)(Aten)]^{2+}$ Complexes at 30 °C

$[Pt(bpy)(Aten)]^{2+}$						$[Pt(phen)(Aten)]^{2+}$					
Position	δ_m/ppm	δ_d[a]/ppm	Position	δ_m/ppm	δ_d[a]/ppm	Position	δ_m/ppm	δ_d[a]/ppm	Position	δ_m/ppm	δ_d[a]/ppm
H(B3)	7.80	6.20	H(A1)	8.50	7.07	H(P2)	6.81	6.08	H(A1)	8.66	7.71
H(B4)	7.80	6.71	H(A2)	7.88	7.16	H(P3)	6.63	5.01	H(A2)	7.94	7.15
H(B5)	6.23	5.12	H(A3)	7.76	7.06	H(P4)	8.52	6.74	H(A3)	7.77	7.06
H(B6)	6.61	5.24	H(A4)	8.21	6.84	H(P5)	8.04	6.45	H(A4)	8.26	6.95
H(B3′)	8.10	6.66	H(A5)	7.72	6.16	H(P6)	8.15	6.67	H(A5)	7.44	5.62
H(B4′)	8.33	7.63	H(A6, 7)	7.22	6.25	H(P7)	9.03	7.64	H(A6)	6.72	5.25
H(B5′)	7.73	7.22	H(A8)	8.97	7.27	H(P8)	8.17	7.11	H(A7)	6.92	5.47
H(B6′)	8.51	7.58	H(A10)	8.43	6.27	H(P9)	9.10	8.24	H(A8)	9.12	8.07
									H(A10)	8.43	6.37

a) Chemical sift at 57 mM.

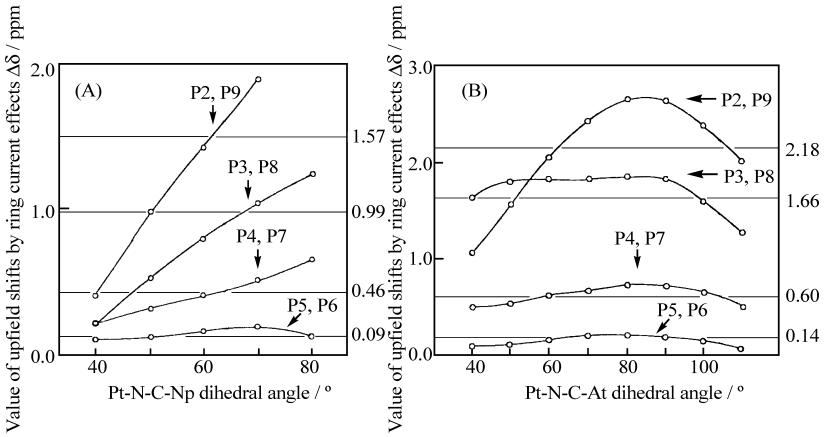

Fig. 4. Comparison of Value of Upfield Shifts between Experimental Data and Calculated Data

Experimental data are represented by horizontal lines. (A) $[Pt(phen)(Npen)]^{2+}$; (B) $[Pt(phen)(Aten)]^{2+}$.

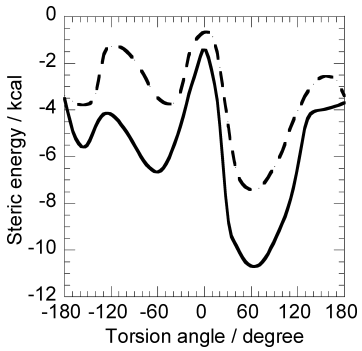

Fig. 5. Plots of Steric Energy *versus* Torsion Angle of Pt–N–C–Np for $[Pt(phen)(Npen)]^{2+}$ (---) and Pt–N–C–At (—) for $[Pt(phen)(Aten)]^{2+}$

calculated based on the method of Abraham with rotation about N–C bond from −180° to 180° in 10° steps and are shown in Fig. 4.[16]

When Pt–N–C–Np dihedral angles for $[Pt(phen)(Npen)]^{2+}$ is 60 degree, the up-field shift of calculated each proton of the phen ring is almost consistent with that of the experimental values. In $[Pt(phen)(Aten)]^{2+}$, similar results, except for H(P3) and H(P8) were observed at 60 degree of Pt–N–C–At dihedral angle.

Molecular Force Field Calculations As shown in Fig. 5, the molecular mechanics calculation for $[Pt(phen)(Npen)]^{2+}$ showed that the most stable form has a torsion angle of 60° and the next stable conformation is the anti conformer (torsion angle of −160°). The difference in steric energy between the two forms is 3.65 kcal mol^{-1}. $[Pt(phen)(Aten)]^{2+}$ showed an energy minima at 60° and the next stable conformer has a torsion angle of −60° with the energy difference between them being 4.02 kcal mol^{-1}.

Dimerization of the Platinum(II) Complexes In aqueous solutions, polyaromatic compounds are known to show upfield shifts due to aggregation.[17—19] However, the present platinum complexes bear positive charges of +2 and extensive aggregation is not plausible. Therefore, the concentration dependency was analyzed from the standpoint of monomer–dimer equilibrium.

The δ_d reflects the mode of the dimerization. All the proton signals moved to higher magnetic field on dimerization.

Table 2. *K* Values for the $[Pt(L^1)(L^2)]^{2+}$ Complex

L^2	L^1	
	bpy K/M^{-1}	phen K/M^{-1}
Aten	5.59	13.77
Npen	0.37	3.55
Been[a)]	0.20	2.09

a) Been, *N*-benzyl-1,2-ethanediamine.

The positions that moved significantly were H(N2), H(N4), H(N5), and H(N8) for the naphtylmethyl derivatives and H(A1), H(A4), H(A5), H(A8), and H(A10) for the anthrylmethyl derivative as well as the H(B6), H(B3), and H(B3′). From these results, the dimerization does not appear to involve a specific structure but occurs with tumbling of the monomers. The fact that both the bipyridine and aryl groups participate in the dimerization is noteworthy. In the crystal, the one-half of the bipyridine which is not included in intermolecular stacking, participates in the intermolecular stacking.[14] As shown in Table 2, the equilibrium constant for the dimerization, *K*, increased in the order L^2=Been<Npen<Aten.

Thermodynamics of the Dimerization of [Pt(bpy)(Aten)]$^{2+}$ The equilibrium constants were determined based on Eq. 2 at 5, 10, 15, 20, 25, 30, 35, and 40 °C. From these data, ln *K* was plotted against 1/*T*, and the following thermodynamic parameters are obtained: $\Delta H° = -21.1 \pm 1.0$ kJ mol^{-1}, $\Delta S° = -45.5 \pm 0.3$ J mol^{-1}K^{-1} and $\Delta G°_{298} = -7.5 \pm 1.1$ kJ mol^{-1}.

Temperature Dependency of ^{1}H-NMR Spectra of [Pt(bpy)(Aten)]Cl$_2$·2.5H$_2$O in D$_2$O and [Pt(phen)(Aten)]Cl$_2$·2H$_2$O in CD$_3$OD The spectral changes in the aromatic region of $[Pt(bpy)(Aten)]^{2+}$ and $[Pt(phen)(Aten)]^{2+}$ are reproduced in Figs. 6 and 7, respectively. For the bpy complex, at 40 °C, two types of signals with different behaviors are evident; narrow and broad signals at 40 °C. The assignment of the signals indicates that the signals with a narrow half-width correspond to the protons of the bpy moiety and H(A10) while the broad signals can be assigned to the remaining protons of the anthracene ring.

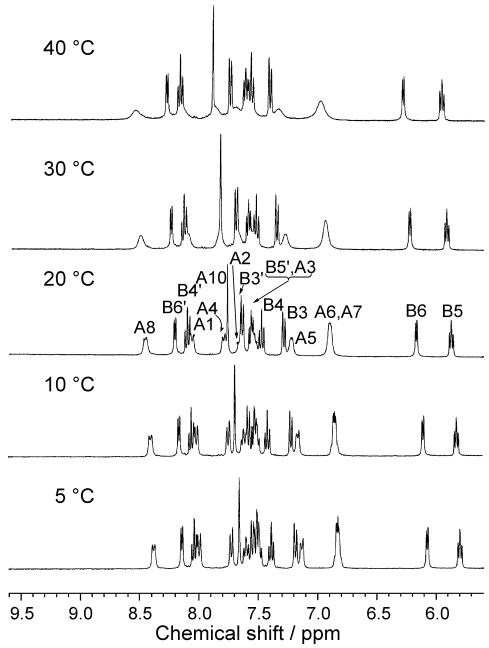

Fig. 6. Change in the Aromatic Region of ^{1}H-NMR Spectra of $[Pt(bpy)(Aten)]^{2+}$ in D_2O at 5 °C, 10 °C, 20 °C, 30 °C, and 40 °C from Bottom to Top

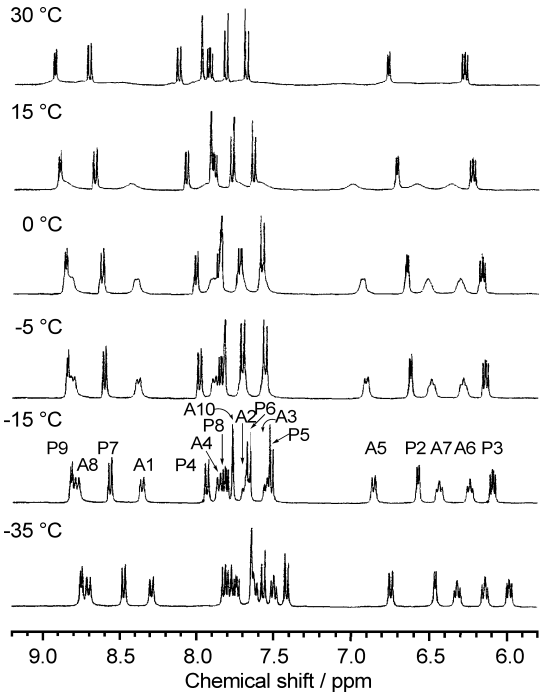

Fig. 7. Change in the Aromatic Region of ^{1}H-NMR Spectra of $[Pt(phen)(Aten)]^{2+}$ in CD_3OD at −35 °C, −15 °C, −5 °C, 0 °C, 15 °C and 30 °C from Bottom to Top

The equivalent protons, H(A1) and H(A8); H(A2) and H(A7); H(A3) and H(A6); and H(A4) and H(A5) appeared separately. When the temperature was lowered, these signals were narrowed and showed clear couplings with neighboring protons at 5 °C. The fact that the H(A10) signals are consistently narrow irrespective of the temperature, indicates that this broadening is caused by the rotation about the CH_2–C_{ipso} bond. The one-way rate constant for the two-sites model was obtained by the method described earlier using H(A8).[20] The $\Delta H^{\ddagger}=37\pm4\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger}=-92\pm13\,\mathrm{J\,mol^{-1}\,K^{-1}}$ were derived from the Eyring equation,

$$k=\kappa\cdot(k_B T/h)\cdot\exp(-\Delta H^{\ddagger}/RT)\cdot\exp(\Delta S^{\ddagger}/R) \quad (3)$$

where k is the rate constant, κ is the transmission coefficient, assumed to be 1.0, k_B is the Boltzmann constant.

An essentially similar temperature dependency was observed for $[Pt(phen)(Aten)]^{2+}$. Owing to the use of CD_3OD as solvent, all the signals were sharp at −35 °C and the anthracene signals, except for H(A10), were broadened.

Discussion

Intramolecular aromatic–aromatic ring interactions of ternary complexes with Pt(II), aromatic diamines such as bpy and phen, and *N*-arylmethylethanediamines (Been, Npen, and Aten) show an upfield shift for the ligand in ^{1}H-NMR spectra in aqueous (D_2O) solution as well as the solid state. The methylene of the arylmethyl group of *N*-arylethanediamine is forced to adopt an axial position because intramolecular repulsion between the arylmethyl and the aromatic rings does not allow the arylmethyl group to adopt an equatorial position.[21,22] In this study, we explored the consequence of ring enlargement of the arylmethyl group from benzyl to 1-naphthylmethyl and 9-anthrylmethyl group. Although the ^{1}H-NMR spectra of $[Pt(bpy)(Been)]^{2+}$ showed little concentration dependency,[15] those for $[Pt(bpy)(Npen)]^{2+}$ and $[Pt(bpy)(Aten)]^{2+}$ showed a significant concentration dependency. The concentration dependency can be accounted for by the monomer–dimer equillibrium. The dimerization constant, K, is dependent on the size of the aromatic ring. The dislocation of the ^{1}H chemical shift and its magnitude shows that dimerization occurs by stacking between bpy or phen of a platinum complex and the aromatic group of the other platinum complex. Though polyaromatic ring compounds aggregate in aqueous solution,[17—19] the positive charge of the $[Pt(bpy)(Aten)]^{2+}$ reduces this tendency for aggregation. These equilibrium constants have smaller values and the intramolecular stacking reduces extent of the intermolecular stacking. The concentration dependency of $[Pt(bpy)(Aten)]^{2+}$ was analyzed by assuming a monomer–dimer equilibrium. From the variation in the equilibrium constant K, the thermodynamic parameters ΔH° and ΔS° were calculated to be $-21.1\pm1.0\,\mathrm{kJ\,mol^{-1}}$ and $-45.5\pm0.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively. Both parameters have negative values and the association process is favored by a large enthalpy change in proceeding from the monomer to the dimer state.

The ^{1}H-NMR chemical shifts of the two pyridine halves of the bipyridine differ significantly and these were also dependent on both the concentration and temperature. The concentration dependency of the chemical shifts corresponds to intermolecular stacking in the solvent employed. The chemical shifts derived from the observed chemical shift by extrapolating to a concentration of 0, δ_m, correspond to the chemical shifts of the intrinsic monomer form. For both the bpy and phen complexes, the δ_m of H(B6), H(B5), H(P2), and H(P3) showed significant upfield shits as the result of changing the *N*-arylmethyl-1,2-ethanediamine. These upfield shifts can be accounted for by molecular force calculations and ring current effects[15] and were verified by X-ray crystallography,[14] The intramolecular π–π interaction is the driving

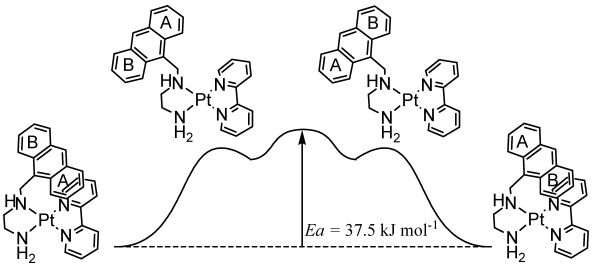

Fig. 8. Schematic Mechanism for the Successive Rotation about Single Bonds

force. Intramolecular π–π interactions have been reported for ternary complexes of platinum(II) or palladium(II), bpy or phen, and amino acids bearing an aromatic side chain, such as tyrosine, phenylalanine, and tryptophan. The present system has a unique feature: the alkyl group substituted at the nitrogen atom of the ethane-1,2-diamine is forced to adopt an axial disposition from the coexisting bpy due to the gauche structure of the 1,2-ethanediamine when a five-membered chelate ring is formed.

The temperature dependency of the ^{1}H-NMR spectra of [Pt(bpy)(Aten)]Cl_2 showed a broadening of the anthryl signals, except for the H(A10) signal. It is noteworthy that 7 out of 9 signals are independently observed at 5 °C. The shape of the signals become broad according to the order of the difference in chemical shift between exchangeable protons through rotation around the CH_2–C_{ipso} bond. These phenomena were analyzed by means of a two-site exchange model. The rate constant at 25 °C is estimated to be 27.1 s^{-1} and the activation parameters are 37.5 kJ mol^{-1} and -91 J mol^{-1} K^{-1} for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively for $[Pt(bpy)(Aten)]^{2+}$.

Although many examples of restricted rotation of a single bond are known,[23—33] this represents a new type of restricted rotation. A direct 180° rotation around CH_2–C_{ipso} must surmount a much higher activation enthalpy than the observed value. Another way to exchange the position of both the flanking ring of an anthracene ring involves two rotations: first, rotation around the N–CH_2 bond, followed by a second rotation around CH_2–C_{ipso} bond as shown in Fig. 8. The first rotation involves the aromatic ring sliding over the bpy ring. The agreement of the observed activation enthalpy and the calculated difference in steric energy between the anti and *syn*($-$) conformations clearly show that this exchange occurs. The rotation around N–CH_2 from $-60°$ (($-$)*syn*) to 0° (*anti*) requires energy, as estimated by a modified MM2 calculation. The rotation around C–C_{ipso} would occur with less energy cost than the first rotation.

$[Pt(phen)(Aten)]^{2+}$ also shows both the concentration and temperature dependences. Moreover, the up-filed shifts between two aromatic rings in $[Pt(phen)(Aten)]^{2+}$ were observed as found in that of $[Pt(bpy)(Aten)]^{2+}$, suggesting that $[Pt(phen)(Aten)]^{2+}$ may take nearly *syn*($-$) conformation as seen in $[Pt(bpy)(Aten)]^{2+}$. Further detail NMR study on solution behavior of $[Pt(bpy)(Aten)]^{2+}$ is underway.

Experimental

Materials [Pt(bpy)(Npen)]Cl_2, [Pt(bpy)(Npen)]$(NO_3)_2\cdot 2H_2O$, [Pt(bpy)(Aten)]$Cl_2\cdot 2H_2O$, and Aten·2HCl were prepared as reported previously.[14] Dichloro(phen)platinum(II) was prepared according to the method of Hall and Plowman.[34]

Synthesis. Preparation of [Pt(phen)(Npen)]$Cl_2\cdot 4H_2O$ To a suspension of [$PtCl_2$(phen)] (446.2 mg, 1 mmol) in 8 cm^3 of water, were added *N*-(1-naphthylmethyl)-1,2-ethanediamine hydrochloride (307.4 mg, 1.3 mmol) and sodium carbonate (126 mg, 1.5 mmol). The mixture was stirred under reflux until a yellow solution was obtained. A small amount of black precipitate was filtered off. Methanol (10 cm^3) was added to the filtrate, followed by the addition of sodium perchlorate (1.0 g). Separated precipitates were collected on a filter and washed with water. Yield, 466 mg (60.1%). The perchlorate salt was converted to the chloride salt by dissolving the salt (453.4 mg, 1.11 mmol) in boiling water (70 cm^3) followed by the addition of tetraphenylarsonium chloride (465.8 mg, 1.11 mmol) in 4 cm^3 of water. The mixture was filtered repeatedly until clear filtrate was obtained, which was then concentrated on a rotatory evaporator. Yield, 324.5 mg (45.2%). *Anal.* Calcd for $C_{29}H_{30}N_4Cl_2PtO_2$: C, 41.79; H, 4.49; N, 7.80. Found: C, 41.73; H, 3.82; N, 7.80. ^{1}H-NMR (D_2O) δ: 7.23 (H(N2), d), 7.15 (H(N3), t), 7.58 (H(N4), d), 6.86 (H(N5), d), 6.44 (H(N6), t), 6.55 (H(N7), t), 8.27 (H(N8), d).

Preparation of [Pt(phen)(Aten)]$Cl_2\cdot 2H_2O$ Aten·2HCl (98.1 mg, 0.303 mmol) was dissolved in 15 cm^3 of water followed by the addition of methanol (5 cm^3) and sodium carbonate (76.8 mg, 0.725 mmol). To this solution, [$PtCl_2$(phen)] (105.6 mg, 0.237 mmol) was added. The mixture was stirred at 80 °C for 20 min to give a clear solution. The solution was filtered and the filtrate concentrated to a volume of *ca.* 5 cm^3, which was then stored in the dark. The separated crystals were collected on a filter and washed with small amounts of cold water, ethanol, and ether successively. These crystals were recrystallized from 2 cm^3 of water. The crystals were collected and washed with small amounts of cold water, ethanol, and ether successively and dried at 45 °C *in vacuo*. Yield, 63.8 mg (37%). *Anal.* Calcd for $C_{29}H_{40}N_4Cl_2PtO_2$: C, 47.55; H, 4.13; N, 7.65. Found: C, 47.42; H, 3.70; N, 7.69.

Physical Measurements Absorption spectra were recorded on a Shimadzu UV 2200 spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL GX-400 spectrometer with D_2O as the solvent and sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (TSP) as an internal standard for [Pt(bpy)(Npen)]$(NO_3)_2\cdot 2H_2O$. For the measurement of [Pt(bpy)(Aten)]$Cl_2\cdot 2.5H_2O$ and Aten·2HCl·H_2O, the solvent and the internal reference were deuterium oxide and *tert*-buthanol (0.02%, 1.250 ppm). The concentration of the platinum complexes was determined using a molar absorption coefficient of 2.89×10^4 M^{-1} cm^{-1} at 320 nm after completion of the NMR measurements. [Pt(phen)(Aten)]$Cl_2\cdot 2H_2O$ was not sufficiently soluble in D_2O and, as a result, CD_3OD and TMS were used as a solvent and an internal standard.

Calculation of Molecular Mechanics and Anisotropic ^{1}H-NMR Chemical Shift A molecular-mechanics calculation was carried out using by a modified MM2 program[16] on an ACOS3700 Computer at the Okayama University Computer Center. The values of ^{1}H-NMR chemical shifts by ring current effects of the aromatic rings were calculated by the method of Abraham *et al.*[35,36] while varying the dihedral angle of the C–N (secondary) bond between 30 and 70°.

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References

1) Rebek J., Jr., *Angew. Chem., Int. Ed. Engl.*, **35**, 245—255 (1990).
2) Hunter C. A., *Chem. Soc. Rev.*, **23**, 101—109 (1994).
3) Leh F. K., Wolf W., *J. Pharm. Sci.*, **65**, 315—328 (1976).
4) Beaumont K. P., McAuliffe C. A., Cleare M. J., *Chem. Biol. Interact.*, **14**, 179—193 (1976).
5) Cleare M. J., Hoeschele J. D., *Bioinorg. Chem.*, **2**, 187—210 (1973).
6) Simon Z., Mracec M., Maurer A., Policec S., Dragulescu C., *Rev. Roum. Biochim.*, **14**, 117—125 (1977).
7) Brooks C. L., III, *Acc. Chem. Res.*, **35**, 447—454 (2002).
8) Yoshikawa M., Iwasaki H., Shinagawa H., *J. Biol. Chem.*, **276**, 10432—10436 (2001).
9) Masuda H., Sugimori T., Odani A., Yamaguchi O., *Inorg. Chim. Acta*, **180**, 73—79 (1991).
10) Aoki K., Yamazaki H., *J. Chem. Soc., Dalton Trans.*, **1987**, 2017—2021 (1987).
11) Yamauchi O., Tsujide K., Odani A., *J. Am. Chem. Soc.*, **107**, 659—666 (1985).
12) Yamauchi O., Odani A., *J. Am. Chem. Soc.*, **107**, 5938—5945 (1985).
13) Sugimori T., Masuda H., Ohata N., Koiwai K., Odani A., Yamauchi O., *Inorg. Chem.*, **36**, 576—583 (1997).
14) Goto M., Matsumoto T., Sumimoto M., Kurosaki H., *Bull. Chem. Soc.*

Jpn., **73**, 97—105 (2000).
15) Goto M., Sumimoto M., Matsumoto T., Iwasaki M., Tanaka Y., Kurosaki H., Yuto K., Yoshikawa Y., *Bull. Chem. Soc. Jpn.*, **73**, 1589—1598 (2000).
16) Yoshikawa Y., *J. Comput. Chem.*, **11**, 326—335 (1990).
17) Mitchell P. R., *J. Am. Chem. Soc.*, **102**, 1180—1181 (1980).
18) Ball R. G., Bowman N. J., Payne N. C., *Inorg. Chem.*, **15**, 1704—1708 (1976).
19) Mitchell P. R., *J. Chem. Soc., Dalton Trans.*, **1980**, 1079—1086 (1980).
20) Kuroda Y., Tanaka N., Goto M., Sakai T., *Inorg. Chem.*, **28**, 2163—2169 (1989).
21) Nakayama Y., Matsumoto K., Ooi S., Kuroya H., *Bull. Chem. Soc. Jpn.*, **50**, 2304—2309 (1977).
22) Bosnich B., Sullivan E. A., *Inorg. Chem.*, **14**, 2768—3007 (1975).
23) Nakamura M., Ōki M., *Bull. Chem. Soc. Jpn.*, **48**, 2106—2111 (1975).
24) Kawada Y., Iwamura H., *J. Am. Chem. Soc.*, **105**, 1449—1459 (1983).
25) Guenzi A., Johnson C. A., Cozzi F., Mislow K., *J. Am. Chem. Soc.*, **105**, 1438—1448 (1983).
26) Oki M., *Acc. Chem. Res.*, **23**, 351—356 (1990).
27) Fanizzi F. P., Lanfranchi M., Natile G., Tiripicchio A., *Inorg. Chem.*, **33**, 3331—3339 (1994).
28) Kelly T. R., Bowyer M. C., Bhaskar K. V., Bebbington D., Garcia A., Lang F., Kim M. H., Jette M. P., *J. Am. Chem. Soc.*, **116**, 3657—3658 (1994).
29) Rochon F. D., Gruia L. M., *Inorg. Chim. Acta*, **306**, 193—204 (2000).
30) Nakano Y., Sato S., *Bull. Chem. Soc. Jpn.*, **55**, 1683—1687 (1982).
31) Nakano Y., Sato S., *Inorg. Chem.*, **21**, 1315—1318 (1982).
32) Nakano Y., Yoshikawa Y., Hasegawa J., Asano T., Igarashi Y., Masuhara S., *J. Chem. Soc., Chem. Commun.*, **1987**, 1481—1482 (1987).
33) Nakano Y., Yoshikawa Y., Masuhara S., Sato S., *Bull. Chem. Soc. Jpn.*, **64**, 877—881 (1991).
34) Hall J. R., Plowman R. A., *Aust. J. Chem.*, **9**, 143—150 (1956).
35) Johnson C. E., Bovey F. A., *J. Chem. Phys.*, **29**, 1012—1014 (1958).
36) Abraham R. J., Fell S. C. M., Smith K. M., *Org. Magn. Reson.*, **9**, 367—373 (1977).