Preparation of Ternary Platinum(II) Complexes with *N*-(ω-Phenylalkyl)-1,2-ethanediamine and 2,2′-Dipyridine and the Effect of the Methylene Chain Length of the *N*-(ω-Phenylalkyl)-1,2-ethanediamine in the Complexes on Intermolecular Interactions with Various Arylsulfonates

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A series of ternary complexes comprised of platinum(II), 2,2′-dipyridine, and *N*-(ω-phenylalkyl)-1,2-ethanediamine was prepared by varying the number (*n*) of methylene chain carbons between the phenyl group and one of the amino groups of 1,2-ethanediamine. NMR measurements indicated that intramolecular stacking occurred for *n*=1 and intermolecular stacking occurred for *n*=3 for several of the aryl sulfonates.

Key words molecular recognition; platinum(II) complex; aromatic-aromatic interaction; aryl sulfonate

Aromatic-aromatic interactions are important in the three dimensional structures of biomolecules and supra molecules and such interaction have been investigated in several fields.[1,2] Metal complexes are good candidates for such studies, because several ligands are assembled by coordination of ligand donor atoms to a metal ion.[3—6] Platinum(II) complexes are of particular interest, because platinum(II) has a strong tendency to form a square-planar four-coordinated complex and the coordination bonds between the metal ion and ligand donor atoms are kinetically inert. The latter is the molecular basis for the action of cisplatin, widely used and effective antineoplasmic agent.[7,8]

In earlier studies, we reported on an NMR study of the intramolecular aromatic-aromatic interactions between the aryl group and 2,2′-dipyridine within (*N*-benzyl-1,2-ethanediamine)(2,2′-dipyridine)platinum(II), $[Pt(bpy)(Been)]^{2+}$, in which the equilibrium is shifted toward the *syn*-form in D_2O.[9,10]

A number of studies have reported on molecular recognition based on the stacking of an aromatic guest compound between the preformed aromatic planes of a host molecule.[11] The synthesis of platinum(II) complexes are relatively straightforward and can be extended to the preparation of ethanediamine derivatives with variable methylene chain lengths. In this study we report on an investigation of the effect of length between the two aromatic rings on intramolecular stacking. In addition, the possibility that these platinum(II) complexes and aryl sulfonates could form a sandwich structure where the aryl sulfonates are held by the aromatic ring and 2,2′-bipyridine in a platinum(II) complex were explored.

Experimental

Materials *N*-Benzyl-1,2-ethanediamine (Been), phenethyl chloride, 3-phenylpropyl bromide, 1,4-dioxane, disodium naphthalene-1,5-disulfonate sesquihydrate (Np-1,5-DS), disodium naphthalene-2,6-disulfonate (Np-2,6-DS), disodium naphthalene-2,7-disulfonate (Np-2,7-DS), disodium anthraquinone-2,6-disulfonate (Atq-2,6-DS), and disodium anthraquinone-2,7-disulfonate (Atq-2,7-DS) were purchased from Tokyo Kasei (Tokyo, Japan). 4-Phenyl-1-butanol was purchased from Janssen Chemical. 5-Phenyl-1-pentanol, deuterium oxide, dioxane-d_8, chloroform-*d* were purchased from Aldrich (Milwaukee, WI, U.S.A.). Methanol-d_4, sodium 3-(trimethylsilyl)-propionate-2,2,3,3-d_4 (TSP) were purchased from Merck (Darmstadt, Germany). Tetraphenylarsonium chloride was purchased from Dojindo Laboratories (Kumamoto, Japan). Sodium naphthalene-1-sulfonate hemihydrate (Np-1-S), and sodium naphthalene-2-sulfonate (Np-2-S) were obtained from Nakalai Tesque (Kyoto, Japan). Potassium tetrachloroplatinate(II), 2,2′-dipyridine(bpy), sodium perchlorate, nitric acid, 1,2-ethanediamine, sodium benzene sulfonate (BS), dichloromethane, benzene, thionyl chloride, 2-methyl-2-propanol (*tert*-BuOH), and disodium anthraquinone-1,5-disulfonate (Atq-1,5-DS) were purchased from Wako Pure Chemicals (Osaka, Japan). These were used as received.

$[Pt(bpy)Cl_2]$ was prepared according to the method described by Morgan and Burstall.[12] Np-1-S, Np-2-S, Np-1,5-DS were recrystallized from hot water after treatment with charcoal. *Anal.* Calcd for $NaC_{10}H_7SO_3 \cdot 0.5H_2O$(Np-1-S): C, 50.21; H, 3.37. Found: C, 49.90; H, 3.36. *Anal.* Calcd for $NaC_{10}H_7SO_3$(Np-2-S): C, 52.17; H, 3.07. Found: C, 52.21; H, 3.06. *Anal.* Calcd for $Na_2C_{10}H_6S_2O_6 \cdot 1.5H_2O$(Np-1,5-DS): C, 33.43; H, 2.52. Found: C, 33.09; H, 2.44.

Preparation of Ligands. 4-Phenylbutyl Chloride and 5-Phenylpentyl Chloride These compounds were prepared by treatment of the corresponding alcohols with thionyl chloride in dichlomethane. The residues, after the evaporation of dichloromethane and excess thionyl chloride, were used in the following procedures.

***N*-Phenylethyl-1,2-ethanediamine (Peen)** Anhydrous 1,2-ethanediamine (42.7 g, 711 mmol) was placed in a 100 ml flask equipped with a reflux condenser protected by a calcium chloride drying tube. At 0 °C, phenethyl chloride (12.5 g, 88.9 mmol) was added dropwise to the 1,2-ethanediamine with stirring over a 15 min period, followed by the addition of ethanol (20 ml). The reaction mixture was heated at reflux for 3 h. After

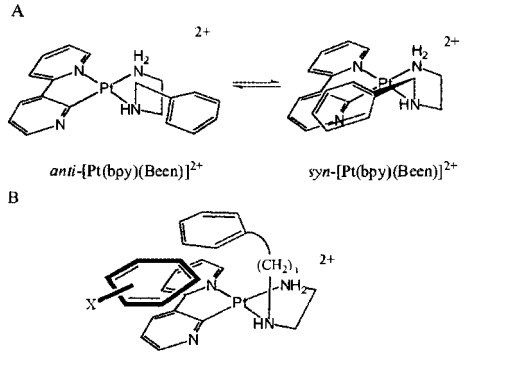

Fig. 1. Intramolecular Stacking of Aromatic Rings in $[Pt(bpy)(Been)]^{2+}$ (A) and Intermolecular Stacking between Host and Guest Molecules (B)

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cooling the reaction mixture, excess 1,2-ethanediamine was removed with a rotatory evaporator. Into the oily residue, an aqueous concentrated sodium hydroxide–sodium chloride solution (30 ml) was added and oily layer was separated and concentrated. The oily residue was distilled under reduced pressure and the fraction boiling at 116 °C at 7.5 mmHg was collected. Yield, 7.20 g (49.3%). ^{1}H-NMR ($CDCl_3$); δ: 7.29 (t, 2H, J=7.4 Hz, *m*-H), 7.21 (d, 2H, J=7.1 Hz, *o*-H), 7.20 (t, 1H, J=7.1 Hz, *p*-H).

***N*-(3-Phenylpropyl)-1,2-ethanediamine (Ppen)** This compound was prepared according to the method described above using 3-phenylpropyl bromide instead of phenethyl chloride. Yield, 7.14 g (63.8%). bp 133 °C/9.5 mmHg. ^{1}H-NMR ($CDCl_3$); δ: 7.27 (t, 2H, J=7.6 Hz, *m*-H), 7.19 (d, 2H, J=6.9 Hz, *o*-H), 7.18 (t, 1H, J=7.3 Hz, *p*-H).

***N*-(4-Phenylbutyl)-1,2-ethanediamine Dihydrochloride (Pben·2HCl)** Anhydrous 1,2-ethanediamine (22.4 g, 373 mmol) was placed in a 100 ml flask equipped with a reflux condenser protected by a calcium chloride drying tube. At 0 °C, 4-phenylbutyl chloride (6.30 g, 37.3 mmol) was added dropwise to 1,2-ethanediamine under stirring over a 15 min period, followed by the addition of ethanol (20 ml). The reaction mixture was heated at reflux for 5 h. After cooling the reaction mixture, 1,2-ethanediamine dihydrochloride separated as a white precipitate and the entire mixture was allowed to stand for 3 d in a refrigerator. The precipitates were removed by filtration and the filtrate was acidified to Congo red acidic with 1 M hydrochloric acid. This solution was washed with 30 ml of diethyl ether three times. The hydrochloric acid layer was concentrated on a rotatory evaporator. Methanol was added to the residue and the mixture was heated to reflux. After cooling the mixture, the separated precipitate was removed by filtration and the filtrate was concentrated. The remaining residue was recrystallized from ethanol. Yield, 4.02 g (44.1%). ^{1}H-NMR (D_2O); δ: 7.39 (t, 3H, J=8 Hz, *o*-H, *p*-H), 7.31 (dt, 2H, J=7 Hz, *m*-H). *Anal.* Calcd for $C_{12}H_{20}N_2\cdot 2HCl$: C, 54.34; H, 8.36; N, 10.56. Found: C; 54.06; H, 8.49; N, 10.80.

***N*-(5-Phenylpentyl)-1,2-ethanediamine Dihydrochloride (Pven·2HCl)** Anhydrous 1,2-ethanediamine (23.4 g, 390 mmol) was placed in a 100 ml flask equipped with a reflux condenser protected by a calcium chloride drying tube. After cooling the solution to 0 °C, 5-phenylpentyl chloride (7.02 g, 38.4 mmol) was added dropwise to 1,2-ethanediamine under stirring over a 15 min period, followed by the addition of ethanol (20 ml). The reaction mixture was heated to reflux for 5 h. After cooling the reaction mixture, excess 1,2-ethanediamine was distilled off. The resulting oily residue was treated with ethanol saturated with hydrogen chloride until Congo red test paper gave a blue color. The resulting white precipitate was removed by filtration. The addition of diethyl ether to the filtrate caused the separation of a brown precipitate. This was recrystallized from ethanol. Yield, 4.65 g (54.8%). ^{1}H-NMR (D_2O); δ: 7.38 (t, 2H, J=8 Hz, *m*-H), 7.31 (dt, 3H, J=7 Hz, *o*-H, *p*-H). *Anal.* Calcd for $C_{13}H_{22}N_2\cdot 2HCl$: C, 55.91; H, 8.66; N, 10.03. Found: C, 56.32; H, 8.85; N, 10.08.

Preparation of Pt(II) Complexes. *N*-Benzyl-1,2-ethanediamine(2,2′-dipyridine)platinum(II) Dichloride Tetrahydrate, [Pt(bpy)(Been)]$Cl_2\cdot 4H_2O$ (1) An aqueous solution of [Pt(bpy)(Been)]$(NO_3)_2$[9] was passed through a Dowex 1-X8 resin(chloride form). The eluted solution was concentrated on a rotatory evaporator and the resulting crystals were collected. Yield, 130 mg (77%). *Anal*. Calcd for [Pt($C_{10}H_8N_2$)($C_9H_{14}N_2$)]$Cl_2\cdot 4H_2O$: C, 35.41; H, 4.69; N, 8.69. Found: C, 35.83; H, 4.50; N, 8.62.

***N*-Phenylethyl-1,2-ethanediamine(2,2′-dipyridine)platinum(II) Dichloride Monohydrate, [Pt(bpy)(Peen)]$Cl_2\cdot H_2O$ (2)** A mixture of [Pt(bpy)Cl_2] (1.66 g, 3.93 mmol) and Peen (0.73 g, 4.44 mmol) in 20 ml of water was stirred at 80 °C for 1 h. Black precipitates were removed by filtration. The filtrate was concentrated to near dryness. The residue was dissolved in ethanol (10 ml) at 70 °C and diethyl ether was added until the solution became turbid. The mixture was allowed to stand in a refrigerator overnight. The resulting yellow crystals were collected on a filter and washed with diethyl ether. Yield, 1.98 g (83.4%). *Anal.* Calcd for [Pt($C_{10}H_8N_2$)($C_{10}H_{16}N_2$)]$Cl_2\cdot H_2O$: C, 39.74; H, 4.34; N, 9.27. Found: C, 39.20; H, 4.18; N, 9.27.

***N*-(3-Phenylpropyl)-1,2-ethanediamine(2,2′-dipyridine)platinum(II) Dichloride Dihydrate, [Pt(bpy)(Ppen)]$Cl_2\cdot 2H_2O$ (3)** A mixture of [Pt(bpy)Cl_2] (1.69 g, 4.00 mmol), Ppen (0.79 g, 4.43 mmol) in 10 ml of water was stirred at 80 °C for 1 h. The black precipitate was removed by filtration and the filtrate concentrated to near dryness. The residue was dissolved in water (12 ml) at 80 °C and the mixture was allowed to stand at room temperature overnight. The resulting yellow crystals were collected on a filter and successively washed with ethanol and diethyl ether. The crude product was recrystallized from water. Yield, 1.97 g (77.4%). *Anal.* Calcd for [Pt($C_{10}H_8N_2$)($C_{11}H_{18}N_2$)]$Cl_2\cdot 2H_2O$: C, 39.63; H, 4.75; N, 8.80. Found: C, 38.98; H, 4.71; N, 8.71.

***N*-(4-Phenylbutyl)-1,2-ethanediamine(2,2′-dipyridine)platinum(II) Dichloride Monohydrate, [Pt(bpy)(Pben)]$Cl_2\cdot H_2O$ (4)** A mixture of [Pt(bpy)Cl_2] (0.97 g, 2.29 mmol), Pben·2HCl (0.67 g, 2.52 mmol) and sodium carbonate (0.73 g, 6.86 mmol) in 10 ml of water was stirred at 80 °C for 1 h. The black precipitate was removed by filtration and the filtrate concentrated to near dryness. The yellow compounds in the residue were dissolved in ethanol (6 ml) at 70 °C and the mixture was filtered to remove the NaCl. The filtrate was allowed to stand in a refrigerator for 2 d. The resulting yellow crystals were collected on a filter and washed with diethyl ether. The crude product was recrystallized from water. Yield, 1.08 g (74.6%). *Anal.* Calcd for [Pt($C_{10}H_8N_2$)($C_{12}H_{20}N_2$)]$Cl_2\cdot H_2O$: C, 41.77; H, 4.78; N, 8.86. Found: C, 41.35; H, 4.91; N, 8.87.

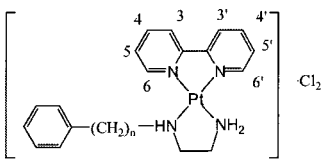
***N*-(5-Phenylpentyl)-1,2-ethanediamine(2,2′-dipyridine)platinum(II) Dichloride Monohydrate, [Pt(bpy)(Pven)]$Cl_2\cdot H_2O$ (5)** A mixture of [Pt(bpy)Cl_2] (1.27 g, 3.01 mmol), Pven·2HCl (0.92 g, 3.29 mmol) and sodium carbonate (0.95 g, 8.46 mmol) in 15 ml of water was stirred at 80 °C for 1 h. The black precipitate was removed by filtration. The filtrate was concentrated to near dryness. The yellow compounds in the residue were dissolved in ethanol (8 ml) at 70 °C and the mixture was filtered to remove NaCl. The filtrate was allowed to stand in a refrigerator for 2 d. The resulting yellow crystals were collected on a filter and washed with diethyl ether and the crude product recrystallized from water. Yield, 1.48 g (76.1%). *Anal.* Calcd for [Pt($C_{10}H_8N_2$)($C_{13}H_{22}N_2$)]$Cl_2\cdot H_2O$: C, 42.73; H, 4.98; N, 8.67. Found: C, 42.87; H, 4.68; N, 8.79.

General ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-GX400 and a JEOL JNM-EX270 spectrometer. ^{1}H-NMR measurements used TSP or *tert*-butanol (1.25 ppm) as internal standards for D_2O and 23% methanol-d_4-deuterium oxide solutions. Chloroform-*d* solutions were measured using TMS as an internal standard. ^{13}C-NMR measurements were done using dioxane as an internal standard (67.4 ppm). The ionic strength was maintained at I=0.2 M using sodium chloride. Electronic spectra were recorded with a Shimadzu UV-2200 spectrophotometer. Elemental analysis were carried out using a Yanaco CHN CORDER at Chemical Instrumental Analysis Center of Kumamoto University by Mrs. Kuniko Shiraki.

Results and Discussion

N-(ω-Phenylalkyl)-1,2-ethanediamines were prepared according to the method described by Linsker and Evans for the preparation of *N*-alkyl-1,2-ethanediamines.[13] All the platinum(II) complexes were prepared by the substitution of two chloro ligands of [Pt(bpy)Cl_2] with 1,2-ethanediamine derivatives at elevated temperature and were isolated as chloride salts. The structures of the platinum(II) complexes are shown schematically in Fig. 2. The UV spectra of these compounds share a common feature, *i.e.* two absorption maxima at 320 and 290 nm and one absorption maxima at around 240 nm. These correspond to the absorption of 2,2′-dipyridine.

The effect of the chain length between the phenyl group and the amine site of 1,2-ethanediamine on intramolecular stacking was evaluated by the chemical shift of the 2,2′-dipyridine portion of the complex. The chemical shifts of the



n		
1	[Pt(bpy)(Been)]$Cl_2\cdot 4H_2O$	**(1)**
2	[Pt(bpy)(Peen)]$Cl_2\cdot H_2O$	**(2)**
3	[Pt(bpy)(Ppen)]$Cl_2\cdot 2H_2O$	**(3)**
4	[Pt(bpy)(Pben)]$Cl_2\cdot H_2O$	**(4)**
5	[Pt(bpy)(Pven)]$Cl_2\cdot H_2O$	**(5)**

Fig. 2. Schematic Representation of the Platinum(II) Complexes

3,3′-, 4,4′-, 5,5′-, and 6,6′-protons of [Pt(bpy)(1,2-ethanediamine)]$^{2+}$ (**en**) were 8.43, 8.47, 7.81, and 8.64 ppm, respectively. Figure 3 shows the change in the chemical shift of proton signals of the platinum(II) complexes from those of **en**, $\delta-\delta_{en}$. The large up-field shifts observed at position 6 and 5 for complex **1** were caused by the ring current effect.[14,15] As the chain length became longer, this effect became smaller and at chain lengths of 4 and 5, the chemical shifts for these complexes were nearly equal to those of **en**. Thus, an intramolecular π–π aromatic interaction is significant in the case of **1**.

Intermolecular interactions between these platinum(II) complexes and several aromatic sulfonates shown in Fig. 4 were evaluated. ^{1}H-NMR spectra of an equimolar (1.6 mM) mixture of the platinum(II) complex (Host) and sodium aryl sulfonate (Guest) in 23% CD_3OD–D_2O were obtained at 30 °C. Figure 5 shows the aromatic region of spectra of a mixture of Np-2-S and **en** or platinum(II) complexes, **1**—**5**. The ^{1}H signals for Np-2-S are assigned as shown at the top of the Figure based on ^{1}H–^{1}H COSY data. The ^{1}H signals of the guest were shifted to higher field in the presence of the host.

In Fig. 6, the change in chemical shift for each ^{1}H signal of Np-2-S in the presence and absence of hosts, $\delta-\delta_{Np\text{-}2\text{-}S}$, is plotted against the length of the methylene chains, **1**—**5**. In the presence of hosts, the ^{1}H signals of the 8-, 5-, 3-positions of the guest are shifted significantly. These up-field shifts are dependent on the number of carbon atoms in the methylene chain and the largest up-field shift is observed for host **3**; the up-field shifts for which are 0.23, 0.25, 0.30 ppm for the 8-, 5-, and 3-positions. In the presence of host **4** or **5**, these up-field shifts are almost the same as those in the presence of **en** which have 2,2′-dipyridine rings accessible from both surfaces. On the other hand, host **1** caused the least up-field shifts, probably because the intramolecularly stacked phenyl

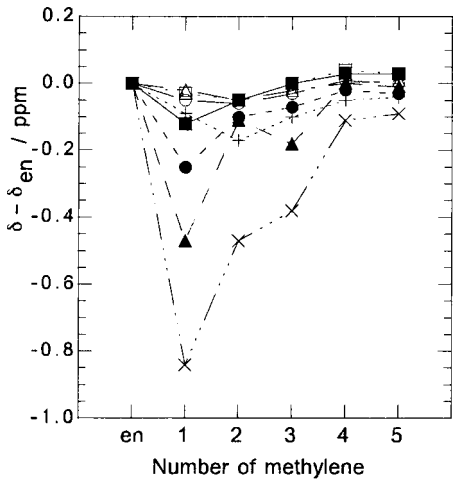


Fig. 3. Changes in Chemical Shifts for the 2,2′-Dipyridine Portions as a Fusnction of the Length of Methylene Bridge

3-, ■; 3′-; □; 4-; ●; 4′-, ○; 5-, ▲; 5′-, △; 6-, ×; 6′-, +.

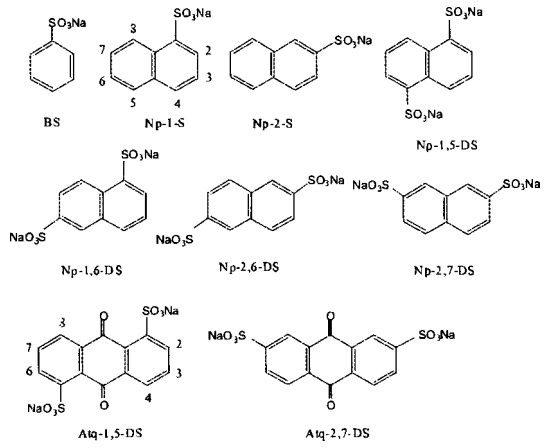


Fig. 4. Aryl Sulfonates and Their Abbreviations Used in This Study

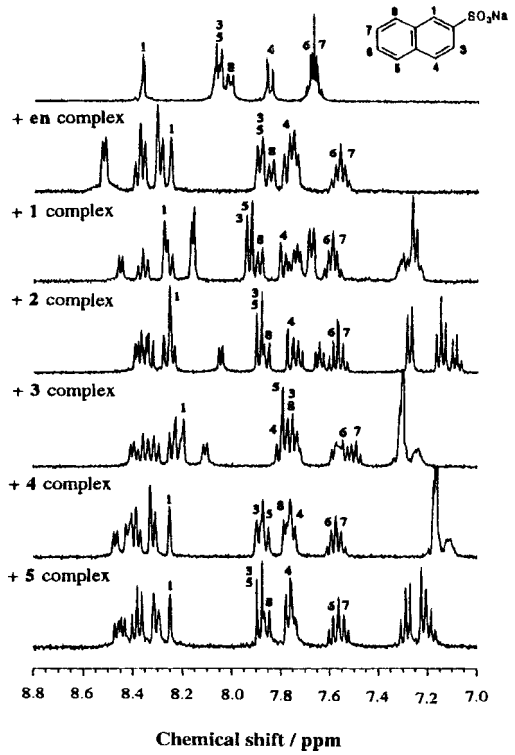


Fig. 5. Aromatic Region of ^{1}H-NMR Spectra of Equimolar (1.6 mM) Mixture of Pt(II) Complexes and Naphthalene-2-sulfonate in 23% CD_3OD–D_2O at 30 °C

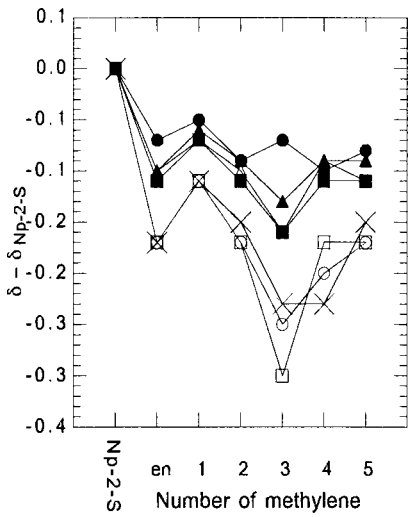


Fig. 6. Change in Chemical Shifts of Naphthalene-2-sulfonate in the Presence of Equimolar Amounts of Hosts

1-, —■—; 3-, —□—; 4-, —●—; 5-, —○—; 6-, —▲—; 7-, —△—; 8, —×—.

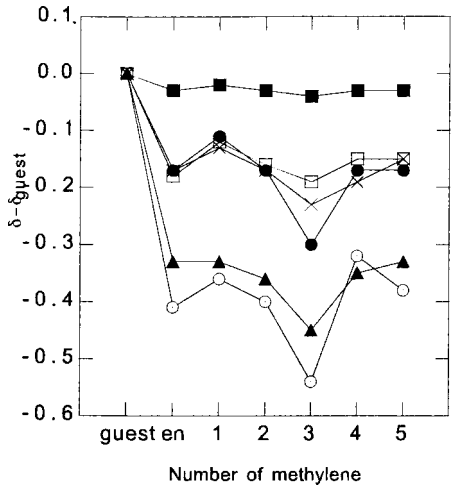


Fig. 7. Change in Chemical Shift of Aromatic Sulfonates in the Presence of an Equimolar Amount of Host

BS, *p*-, —■—; Np-1-S, 5-, —□—; Np-2-S, 3-, —●—; Np-1,6-DS, 4-, —○—; Np-2,7-DS, 1,8-, —▲—; Atq-1,5-DS, 3,7-, —×—.

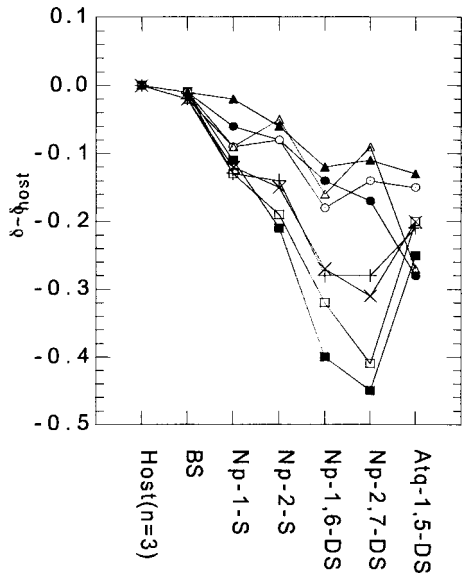


Fig. 8. Change in Chemical Shift of the Dipyridyl Portion of [Pt(bpy)(Ppen)]Cl_2 (**3**) in Equimolecular Mixture with Several Aromatic Sulfonates

3-, ■; 3′-; □; 4-; ●; 4′-, ○; 5-, ▲; 5′-, △; 6, ×; 6′, +.

rings cannot be used for intermolecular stacking. Thus, host **3** would be expected to accept an aryl sulfonate between the phenyl ring and the dipyridine moiety in the same molecule.

In order to confirm this assumption, the up-field shifts of several aryl sulfonates were measured, as described above. The differences in the chemical shifts of guests relative to those of the guest in the absence of the host were determined. The largest up-field-shifted signals for each guest are *p*-, for BS; 5-, Np-1-S; 3-, for Np-2-S; 4-, Np-1,6-DS; 1,8-, for Np-2.7-DS; 3,7-, for Atq-1,5-DS. The differences in chemical shifts are plotted against the chain length in Fig. 7. In each case, the maximum up-field shift was observed in the case of host **3**. The magnitude of the maximum shifts were dependent on the size of sulfonate aryl group: an increase in size led to up-field shifts. Both the number of the sulfonyl group and their position where it is substituted affect the magnitude of the up-field shift. This suggests that coulombic interactions contribute to some extent, to these host-guest interactions.

The effect of guest on the chemical shifts of ^{1}H signals of the bpy ring of host **3**, which showed the largest up-field shift among **1**—**5**, is shown in Fig. 8. The increase in the number of aromatic ring and sulfonate resulted in an increase in the up-field shift for host **3**. In the case of the Np-2,7-DS, the 6′-, 6-, 3′-, and 3-positioned ^{1}H showed up-field shifts of 0.28, 0.31, 0.41, and 0.45 ppm, respectively.

The chemical shifts of two host **en** and **3**, for each of which the concentration was maintained at 2 mM, were measured with varying concentrations of guests (0—40 mM) with I=0.2 M at 30 °C. The up-field shift increased with the concentration of guests, reaching a constant limiting value at higher concentrations. Figure 9 shows, the up-field shift of the 3-position ^{1}H signal of the bpy ring of **3** in the presence of several guest compared to hosts only ($\Delta\delta_{3\text{-H}}$). The binding constant, K, defined by Eq. 1 and the estimated limiting up-field shift for the host-guest complex, $\Delta\delta_{sat}$, was obtained as follows.[16] First, the primary K values and $\Delta\delta_{sat}$ values were estimated using Eq. 2 and data obtained under conditions of $[guest]_{total} \gg [host]_{total}$. Using these primary values, a non-linear least-squares method using the damping Gauss-Newton

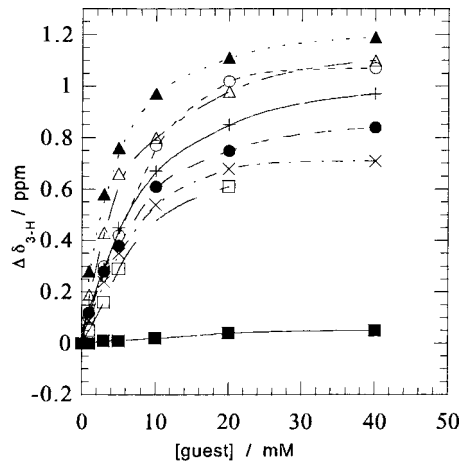


Fig. 9. Change in Chemical Shift of the 3-^{1}H Signal of the Dipyridine Portion of [Pt(bpy)(Ppen)]Cl_2 (**3**) with Varying Concentrations of Several Aromatic Sulfonates

BS, —■—; Np-1-S, —□—; Np-2-S, —●—; Np-1,5-DS, —○—; Np-2,6-DS, —▲—; Np-2,7-DS, —△—; Atq-1,5-DS, —×—; Atq-2,7-DS, —+—.

method was then employed to obtain the final values for K and $\Delta\delta_{sat}$ using all the experimental data with Eq. 3. The values of K and δ_{sat} are listed in Table 1.

$$\text{host} + \text{guest} \underset{}{\overset{K}{\rightleftarrows}} \text{host} * \text{guest} \tag{1}$$

$$\frac{1}{\Delta\delta_{obs}} = \frac{1}{\Delta\delta_{sat}} + \frac{1}{\Delta\delta_{sat} K [\text{guest}]_t} \tag{2}$$

$$\Delta\delta = \frac{\Delta\delta_{sat}}{2K[\text{host}]_t}\{K([\text{host}]_t + [\text{guest}]_t) + 1\} - \frac{\Delta\delta_{sat}}{2K[\text{host}]_t}\sqrt{K^2([\text{host}]_t - [\text{guest}]_t)^2 + 2K([\text{host}]_t + [\text{guest}]_t) + 1} \tag{3}$$

Table 1. Binding Constants (K) of Hosts **en** and **3** with Various Aryl Sulfonates and Estimated Shifts of the Aromatic 3-H Signal of Hosts in Associated Species ($\Delta\delta_{sat}$)

Guest	Host			
	en		**3**	
	K/M^{-1}	$\Delta\delta_{sat}$/ppm	K/M^{-1}	$\Delta\delta_{sat}$/ppm
BS	18±2	0.12±0.01	25±3	0.10±0.01
Np-1-S	42±1	1.19±0.03	79±5	1.04±0.04
Np-2-S	124±2	1.04±0.03	169±1	0.98±0.02
Np-1,5-DS	164±2	0.82±0.03	179±5	1.22±0.06
Np-2,6-DS	251±3	1.18±0.03	344±1	1.31±0.03
Np-2,7-DS	185±3	1.18±0.02	185±5	1.29±0.04
Atq-1,5-DS	—	—	186±2	0.84±0.03
Atq-2,7-DS	144±3	1.12±0.02	142±2	1.17±0.03

From these values, **3** acts as a stronger host than **en** in binding with most aromatic sulfonates, the binding constant increases with increasing size of the guest aromatic ring, disulfonates have a larger binding constant than monosulfonates for the naphthalene sulfonates but the position of the sulfonate group has a considerable effect on this, and the limiting shift in chemical shift is larger for **3** than **en** but the difference is not very large.

Several compounds have been reported to act as hosts for aromatic guests. Kuroda *et al.* reported that biporphyrins bind to pyrazine derivatives,[17] Kadish *et al.* reported that cofacial biscorroles and porphyrin-corroles bind with pyridine.[18] These compounds have been extensively explored for electron-transfer and the activation of small gaseous molecules such as O_2, H_2, and N_2.[19] Adams and Whitlock used [8.8](1,4)benzophanes, [8.8](2,6)- and [8.8](1,4)naphthalenophanes to capture naphtalene-2-sulfonate and 8-anilino-1-naphthalenesulfonic acid.[20] The hosts used either two metal coordinated macrocycles or organic compounds.

In the present work, ternary mono-metal complexes with the two aromatic rings (phenyl and dipyridine) separated by varying degrees were used and molecular recognition was demonstrated by the readily available platinum(II) complexes.

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