Nuclear Magnetic Resonance Studies on the Structure of Ruthenium(II) Complexes of Di-2-pyridylamine in DMSO Solution

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The complete assignments of the ^{1}H and ^{13}C NMR spectra of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—2) have been carried out on the basis of proton–proton coupling constants, H–H COSY, C–H COSY, and the aromatic ring-current effects of the ligand. The observed aromatic ring-current shifts of the assigned ^{1}H NMR signals were compared with the calculated ones by using a current-loop model. The flapping of the Hdpa ligands showed that the structures of $[Ru(bpy)_2(Hdpa)]^{2+}$, $[Ru(bpy)(Hdpa)_2]^{2+}$, and $[Ru(Hdpa)_3]^{2+}$ in solution have apparent C_2, C_2, and D_3 symmetries, respectively.

The ^{1}H and ^{13}C NMR spectra of $[Ru(bpy)_3]^{2+}$ (bpy= 2,2′-bipyridine) were reported and assigned by Lytle et al.[1] and Watts,[2] respectively. The ^{1}H NMR spectra of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (Hdpa=di-2-pyridylamine, n=0—2) were reported by DeArmond et al.[3] Their attention was mainly on the N–H protons of the Hdpa ligands, detailed assignment of other peaks and structures in solution was not described. Assignment of the ^{13}C NMR spectra for these complexes has not been reported.

The aromatic ring-current effect in ^{1}H NMR spectroscopy has been a useful probe for examining the geometry of a molecule or a molecular aggregate in solution.[4—10] Tachiyashiki and Yamatera reported a full calculation of the ^{1}H NMR aromatic ring-current shifts of the 1,10-phenanthroline (phen) protons in $[Co(phen)_m(en)_{3-m}]^{3+}$ (en=1,2-ethanediamine, m=1—3) based on the current-loop model.[11] Comparison of the experimental data with the calculated values showed that the current-loop calculation correctly predicted the upfield shifts of the NMR signals of protons in the neighborhood of aromatic ligands. The current-loop calculation is expected to provide useful information on the behavior of the series of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—3) in solution. A bpy ligand is planar and forms a five-membered chelate ring, whereas an Hdpa ligand is nonplanar and forms a six-membered ring. This conformation of the Hdpa ligand was observed in $[RuCl_2(Hdpa)_2]Cl$ by X-ray crystallography.[12]

The present work describes the complete assignment of the ^{1}H and ^{13}C NMR spectra of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—3) including the distinction of the pyridine rings on the basis of proton–proton coupling constants, H–H COSY, C–H COSY, and aromatic ring-current effects. The ^{1}H NMR aromatic ring-current shifts of each proton of the bpy and Hdpa ligands in $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—3) were calculated on the basis of the current-loop model.[11] The conformational structures of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—2) in solution are also discussed on the basis of the observed and calculated aromatic ring-current shifts of the ^{1}H NMR signals.

Experimental

Materials. The complexes, $[Ru(bpy)_3](ClO_4)_2$[13] and $[Ru(bpy)(Hdpa)_2](CF_3SO_3)_2$,[14] were prepared by literature methods. $[Ru(bpy)_2(Hdpa)](ClO_4)_2$ was prepared by refluxing an aqueous solution of $[RuCl_2(bpy)_2]Cl\cdot H_2O$[13] and a slight excess of Hdpa in the presence of sodium phosphinate for 4 h followed by precipitation with aqueous $NaClO_4$. The complexes were purified by Sp-Sephadex column chromatography.

$[Ru(Hdpa)_3](CF_3SO_3)_2$: To 150 cm^3 of an aqueous solution of Hdpa (1.35 mmol), *cis*-$[RuCl_2(Hdpa)_2]Cl\cdot H_2O$ (1.1 mmol) was added. The solution was refluxed for 4 h in the presence of sodium phosphinate (2 g). Upon addition of $NaClO_4$ to the reaction mixture, a yellow precipitate formed. For purification, the precipitate was charged on the top of an SP-Sephadex column (Na^+ form) and eluted with a 0.3 mol dm^{-3} NaCl solution. Fractions of yellow eluate were collected from which $[Ru(Hdpa)_3](CF_3SO_3)_2$ was precipitated upon the addition of $NaCF_3SO_3$. The product was washed with cold water and dried in vacuo. Yield 70%.

Measurements. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX-400 (400 MHz) spectrometer. The concentration of the samples was 0.025 mol dm^{-3} in DMSO-d_6 with TMS as the internal standard.

Method of Calculation.[11] The current-loop model,[16,17] developed to calculate the aromatic ring-current shifts of NMR signals of protons in the neighborhood of the benzene rings, was applied to metal complexes containing aromatic ligands. In this model, π-electrons of a six-membered aromatic ring were regarded as two loops with radii of 1.39 Å of the π-electron current on both sides of the plane of the aromatic ring with a spacing of 1.28 Å between the two loops. A computer program (written in BASIC[18]), which had been modified to calculate the aromatic ring-current shifts for ^{1}H NMR signals at an arbitrary place near aromatic rings, was used. For the calculation, the coordinates of the protons of bpy or Hdpa and of the centers of the aromatic rings of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—3) were estimated by assuming that the geometric parameters of the complexes were the same as those obtained for $[Ru(bpy)_3](PF_6)_2$[19] and $[RuCl_2(Hdpa)_2]Cl$[12] by X-ray crystallography.

Results and Discussion

Assignment of ^{1}H and ^{13}C NMR Signals. Figure 1 shows the numbering of the protons and carbons on the pyridine rings of bpy and Hdpa ligands. When there are several pyridine rings in different environments, the pyridine rings are numbered as R1, R2, and R3 to distinguish between them. The ^{1}H NMR spectra for the aromatic regions of the four complexes are shown in Fig. 2 (a—d).

$[Ru(bpy)_3]^{2+}$: The ^{1}H NMR spectrum of $[Ru(bpy)_3]^{2+}$ has been discussed in the literature.[1] The ^{1}H and ^{13}C chemical shifts and their assignments are as follows. ^{1}H NMR (DMSO-d_6) δ=7.54 (6H, t, J=7 Hz, H5), 7.74 (6H, d, J=5 Hz, H6), 8.18 (6H, t, J=8 Hz, H4), and 8.85 (6H, d, J=8 Hz, H3). ^{13}C NMR (DMSO-d_6) δ=124.35 (C3), 127.77 (C5), 137.80 (C4), 151.09 (C6), and 156.42 (C2). The present assignment of ^{1}H NMR signals agrees with the data reported in the literature.[1]

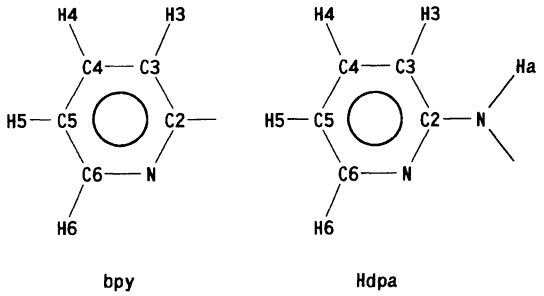

Fig. 1. The numbering of the protons and carbons on the pyridine rings of bpy and Hdpa.

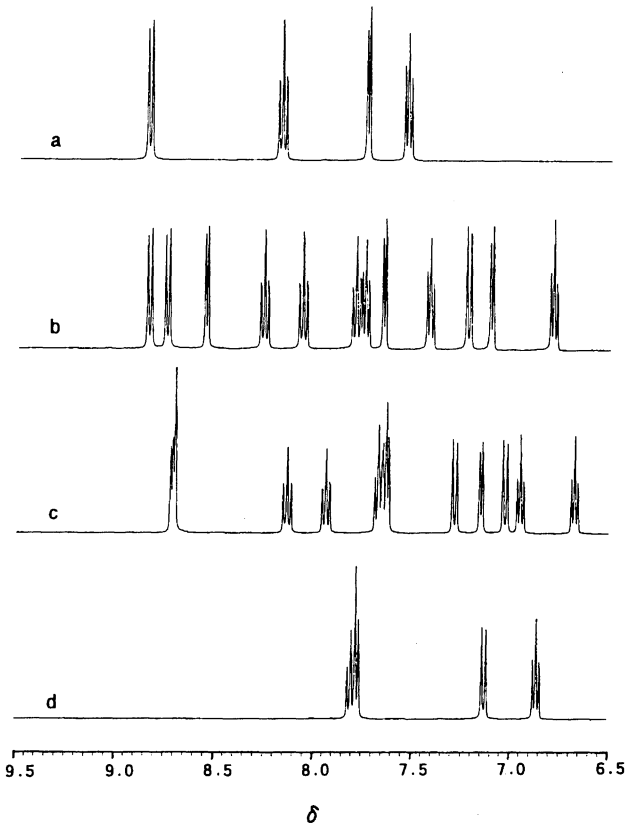

Fig. 2. ^{1}H NMR spectra for the aromatic region of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—3) in DMSO-d_6. a: $[Ru(bpy)_3]^{2+}$, b: $[Ru(bpy)_2(Hdpa)]^{2+}$, c: $[Ru(bpy)(Hdpa)_2]^{2+}$, d: $[Ru(Hdpa)_3]^{2+}$.

$[Ru(Hdpa)_3]^{2+}$: The ^{1}H NMR spectrum of $[Ru(Hdpa)_3]^{2+}$ contained four distinct resonances (two doublets and two triplets). The ^{13}C NMR spectrum of $[Ru(Hdpa)_3]^{2+}$ contained five signals. These spectra indicated that all pyridine moieties must be in the same magnetic environment and the complex has a D_3 symmetry as in the case of $[Ru(bpy)_3]^{2+}$. Since the Hdpa ligand, however, is nonplanar, the symmetry of $[Ru(Hdpa)_3]^{2+}$ would be C_3 even if the complex had highest symmetry, which means that the two pyridine moieties of an Hdpa ligand might not be equivalent due to the difference in the magnetic environment. The inconsistency between the assumed structure and the observed data on the ^{1}H and ^{13}C NMR spectra can be explained by rapid flapping of the Hdpa ligands, which may make the six pyridine moieties of $[Ru(Hdpa)_3]^{2+}$ equivalent and make the apparent symmetry of $[Ru(Hdpa)_3]^{2+}$ D_3. The possibility that the difference in the magnetic environment is not large enough to be observed in the chemical shift can be excluded throughout the series of complexes $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—2) as is discussed later in the section "Calculation of the Aromatic Ring-Current Effect".

Assignment of each set of the ^{1}H NMR signals was performed on the basis of the coupling constants and H–H COSY in the following way. A doublet at δ=7.13 (6H, J=8 Hz) was assigned to H3 by considering the multiplicity and the coupling constant. A triplet at δ=6.86 (6H, J=7 Hz), which did not couple with the H3 signal, was assigned to H5. A triplet and a doublet at δ=7.79 (12H) were assigned to H4 and H6, respectively. The assignment of the ^{1}H NMR signals of $[Ru(Hdpa)_3]^{2+}$ was different from the assignment by DeArmond et al., who did not describe the basis of his assignment in detail. The assignment of the ^{13}C NMR signals was performed by C–H COSY according to the assignment of the ^{1}H NMR signals. The ^{1}H and ^{13}C chemical shifts and their assignments are as follows. ^{1}H NMR (DMSO-d_6) δ=6.86 (6H, t, J=7 Hz, H5), 7.13 (6H, d, J=8 Hz, H3), 7.79 (6H, t, H4), 7.79 (6H, d, H6), and 10.67 (3H, s, Ha). ^{13}C NMR (DMSO-d_6) δ=114.59 (C3), 118.44 (C5), 138.44 (C4), 151.16 (C6), and 152.66 (C2).

$[Ru(bpy)_2(Hdpa)]^{2+}$: The ^{1}H NMR spectrum of $[Ru(bpy)_2(Hdpa)]^{2+}$ contained twelve distinct resonances (six doublets and six triplets), all of which had the same intensity. From H–H COSY, the twelve resonances could be classified into three groups (I, II, and III) which contained four resonances coupled with each other (two doublets and two triplets). The ^{13}C NMR spectrum of $[Ru(bpy)_2(Hdpa)]^{2+}$ contained fifteen sig-

nals which also could be classified into three groups based on C–H COSY. These spectra indicated that $[Ru(bpy)_2(Hdpa)]^{2+}$ should have a C_2 symmetry. This is explained by rapid flapping of the Hdpa ligand as was described in the case of $[Ru(Hdpa)_3]^{2+}$. The numbering of the pyridine rings of the ligands is shown in Fig. 3. In the apparent C_2 symmetry of $[Ru(bpy)_2(Hdpa)]^{2+}$, two pyridine rings of the Hdpa ligand (R1 and R1′) become equivalent to each other, and bpy2-R2 and bpy2-R3 become equivalent to bpy1-R2 and bpy1-R3, respectively.

The ^{1}H NMR signals within each group could be assigned to the appropriate proton based on the proton–proton coupling constants and H–H COSY. The ^{13}C NMR signals within each group also could be assigned by the combination of C–H COSY and assigned ^{1}H NMR signals. The ^{1}H and ^{13}C chemical shifts and their assignments within each group are as follows.

Group I, {^{1}H NMR (DMSO-d_6) δ=7.75 (2H, t, J=7 Hz, H5), 8.26 (2H, t, J=8 Hz, H4), 8.55 (2H, d, J=5 Hz, H6), and 8.84 (2H, d, J=8 Hz, H3). ^{13}C NMR (DMSO-d_6) 124.47 (C3), 127.18 (C5), 137.76 (C4), 152.19 (C6), and 156.88 (C2).};

Group II, {^{1}H NMR (DMSO-d_6) δ=7.42 (2H, t, J=7 Hz, H5), 7.65 (2H, d, J=5 Hz, H6), 8.06 (2H, t, J=8 Hz, H4), and 8.75 (2H, d, J=8 Hz, H3). ^{13}C NMR (DMSO-d_6) 124.34 (C3), 127.55 (C5), 137.38 (C4), 151.24 (C6), and 156.72 (C2).};

Group III, {^{1}H NMR (DMSO-d_6) δ=6.79 (2H, t, J=7 Hz, H5), 7.11 (2H, d, J=5 Hz, H6), 7.23 (2H, d, J=8 Hz, H3), and 7.79 (2H, t, J=8 Hz, H4). ^{13}C NMR (DMSO-d_6) 114.53 (C3), 118.98 (C5), 138.80 (C4), 149.48 (C6), and 153.07 (C2).}.

Figure 4-a shows the chemical shift patterns of Groups I, II, and III along with those of $[Ru(bpy)_3]^{2+}$ and $[Ru(Hdpa)_3]^{2+}$ (plots of the chemical shifts against the numbering of the protons). Judging by the similarity of the patterns with the homoleptic complexes, Group III can be assigned to R1 of the Hdpa ligand, while Groups I and II are assigned to either R2 or R3 of the bpy ligands. The distinct assignment of Groups I and II will be discussed later on the basis of the aromatic ring-current effect.

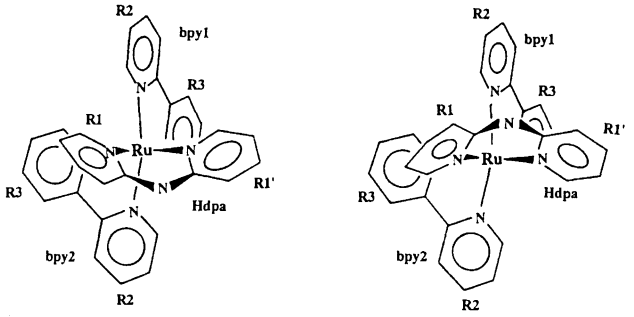

Fig. 3. The numbering of the pyridine rings and two cases due to the conformation of the Hdpa ligand in $[Ru(bpy)_2(Hdpa)]^{2+}$.

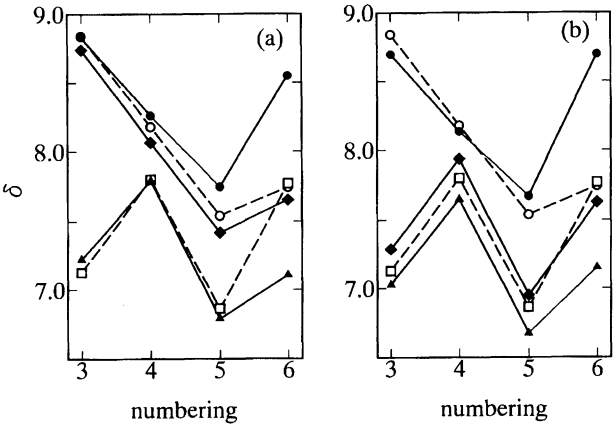

Fig. 4. The chemical shift patterns of $[Ru(bpy)_2(Hdpa)]^{2+}$ (a) and $[Ru(bpy)(Hdpa)_2]^{2+}$ (b). ○: $[Ru(bpy)_3]^{2+}$, □: $[Ru(Hdpa)_3]^{2+}$, ●: Group I, ◆: Group II, ▲: Group III.

$[Ru(bpy)(Hdpa)_2]^{2+}$: The ^{1}H NMR spectrum of $[Ru(bpy)(Hdpa)_2]^{2+}$ contained twelve distinct resonances (six doublets and six triplets). On the basis of H–H COSY, the twelve resonances could be classified into three groups (I, II, and III), and each group contained four resonances which coupled with each other. The ^{13}C NMR spectrum of $[Ru(bpy)(Hdpa)_2]^{2+}$ contained fifteen signals which also could be classified into three groups by C–H COSY. These spectra indicated that $[Ru(bpy)(Hdpa)_2]^{2+}$ should have C_2 symmetry as was described in the case of $[Ru(bpy)_2(Hdpa)]^{2+}$. In this case, to explain the spectra, $[Ru(bpy)(Hdpa)_2]^{2+}$ has an apparent C_2 symmetry by rapid flapping of the Hdpa ligands as was described in $[Ru(Hdpa)_3]^{2+}$. However, there is another possibility that a special combination of the conformations of the two Hdpa ligands will give $[Ru(bpy)(Hdpa)_2]^{2+}$ C_2 symmetry, which will be discussed later. The numbering of the pyridine rings of the ligands is shown in Fig. 5. In the apparent C_2 symmetry of $[Ru(bpy)(Hdpa)_2]^{2+}$, two pyridine rings of the bpy moiety (R1 and R1′) become equivalent, and Hdpa2-R2 and Hdpa2-R3 become equivalent to Hdpa1-R2 and Hdpa1-R3, respectively.

The ^{1}H NMR signals within each group could be assigned to the appropriate protons based on coupling constants and H–H COSY. Assignment of the ^{13}C NMR signals within each group also could be performed by C–H COSY. The ^{1}H and ^{13}C chemical shifts and their assignments within each group are as follows.

Group I, {^{1}H NMR (DMSO-d_6) δ=7.65 (2H, t, H5), 8.14 (2H, t, J=8 Hz, H4), 8.70 (2H, d, H3) and 8.70 (2H, d, H6). ^{13}C NMR (DMSO-d_6) δ=124.19 (C3), 126.93 (C5), 137.23 (C4), 153.31 (C6), and 157.40 (C2).};

Gruop II, {^{1}H NMR (DMSO-d_6) δ=6.95 (2H, t, J=7 Hz, H5), 7.29 (2H, d, J=8 Hz, H3), 7.65 (2H, d, H6), and 7.94 (2H, t, J=8 Hz, H4). ^{13}C NMR (DMSO-d_6) δ=114.31 (C3), 119.22 (C5), 138.86 (C4), 151.45 (C6), and 153.56 (C2).};

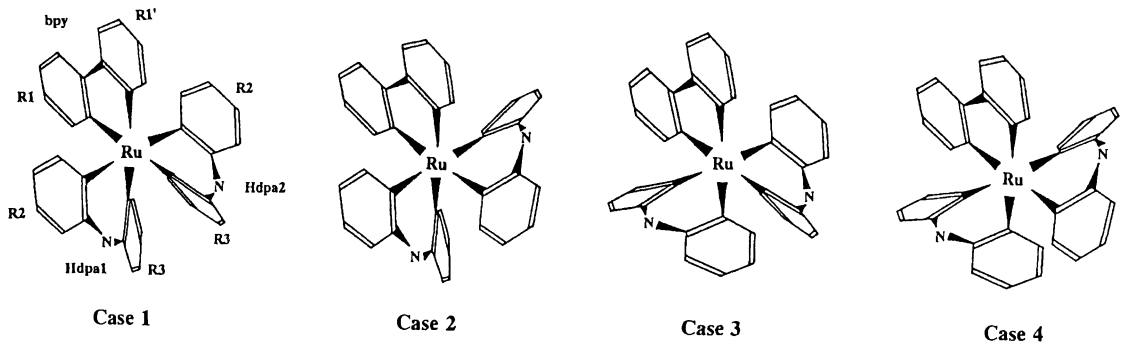

Fig. 5. The numbering of the pyridine rings and four cases due to the conformation of the Hdpa ligands in $[Ru(bpy)(Hdpa)_2]^{2+}$. The nitrogen atoms on the pyridine rings are omitted for simplicity.

Group III, {^{1}H NMR (DMSO-d_6) δ=6.67 (2H, t, J=7 Hz, H5), 7.03 (2H, d, J=8 Hz, H3), 7.15 (2H, d, J=5 Hz, H6), and 7.65 (2H, t, H4). ^{13}C NMR (DMSO-d_6) δ=114.08 (C3), 118.86 (C5), 138.53 (C4), 148.98 (C6), and 153.51 (C2).}.

Figure 4-b shows the chemical shift patterns of Groups I, II, and III along with those of $[Ru(bpy)_3]^{2+}$ and $[Ru(Hdpa)_3]^{2+}$. As in the case of $[Ru(bpy)_2(Hdpa)]^{2+}$, judging by the similarity of the patterns of the homoleptic complexes, Group I can be assigned to R1 of the bpy ligand, while Groups II and III are assigned to either R2 or R3 of the Hdpa ligands. The distinct assignment of Groups II and III will be discussed on the basis of the aromatic ring-current effect in the following section.

Calculation of the Aromatic Ring-Current Effect. **$[Ru(bpy)_3]^{2+}$:** The aromatic ring-current shifts of each proton signal of $[Ru(bpy)_3]^{2+}$ caused by the neighboring ligands were calculated. The calculated values (δ_{rc}) for the H3, H4, H5, and H6 protons, which were identical among the six pyridine moieties, were 0.06, −0.06, −0.25, and −0.80 ppm, respectively. Although there may be several effects on the chemical shift by coordination, the observed large upfield shift of the H6 proton (−0.97 ppm) from that of the free ligand can be explained mainly by the aromatic ring-current shift.

$[Ru(bpy)_2(Hdpa)]^{2+}$: For the calculation of the aromatic ring-current shifts of each proton signal of $[Ru(bpy)_2(Hdpa)]^{2+}$ caused by neighboring ligands, it is necessary to take the conformation of the Hdpa ligand into account. Due to the conformation of an Hdpa ligand, there exist two cases as shown in Fig. 3. Table 1 shows the calculated aromatic ring-current shifts (δ_{rc}) for the two cases (Case 1 and Case 2). For both cases, the calculated aromatic ring-current shifts of each proton were different enough among the six pyridine rings to distinguish the chemical shifts by measurement. Since Case 1 and Case 2 are equivalent in energy, the complex must exist as a mixture of equal quantities of Case 1 and Case 2 in solution. If the conformation of Hdpa were fixed, there would be six kinds of magnetic environments. This was inconsistent with the observed ^{1}H NMR spectrum which showed the existence of only three kinds of magnetic environments. Since the conformation of the Hdpa ligand was usually not fixed and the Hdpa ligand was rapidly flapping, the ^{1}H NMR spectrum of the complex should be observed as an average of the spectra of Case 1 and Case 2. That is, protons experience an averaged magnetic environment between Cases 1 and 2. In an averaged magnetic environment, Hdpa-R1 and R1′ become equivalent, and bpy2-R2 and bpy2-R3 become equivalent to bpy1-R2 and bpy1-R3, respectively. Consequently, there should exist three kinds of magnetic environments, which is consistent with the measured ^{1}H NMR spectrum.

Since the difference in the chemical shifts of the corresponding protons between R2 and R3 must arise from the aromatic ring-current effects of the other ligands (bpy and Hdpa), Groups I and II could be assigned to R2 and R3, respectively, with the aid of calculated aromatic ring-current shifts. The observed and calculated values for these differences were as follows. Obsd (Gruop II−Group I): H3, −0.09; H4, −0.20; H5, −0.33; H6, −0.90 ppm. Calcd (R3−R2)[20]: H3, −0.08; H4, −0.21; H5, −0.38; H6, −1.03 ppm. The calculated values for these differences are reasonably close to the observed values. Consequently, it is concluded that these differences arise mainly from the aromatic ring-current effects of the other ligands in the complex and the assignment for the rings is pertinent.

Furthermore, Table 2 shows the observed and calculated values of the shifts of each proton signal of bpy in $[Ru(bpy)_2(Hdpa)]^{2+}$ relative to the corresponding proton signals of bpy in $[Ru(bpy)_3]^{2+}$. The calculated values of the proton signals of both R2 and R3 are in good agreement with the observed values of Groups I and II, respectively. This also indicates that the comparison of the chemical shifts between the complexes supports the validity of the assignment.

$[Ru(bpy)(Hdpa)_2]^{2+}$: A combination of conformations of the two Hdpa ligands gives four cases as shown in Fig. 5, and the aromatic ring-current shifts (δ_{rc}) based on them were calculated. As was discussed in the section on $[Ru(bpy)_2(Hdpa)]^{2+}$, the flapping of the Hdpa ligands makes each proton of the complex experience an averaged magnetic environment among

Table 1. The Calculated Aromatic Ring-Current Shifts (δ_{rc}) of the Proton Signals of $[Ru(bpy)_2(Hdpa)]^{2+}$ in Case 1 and Case 2 in Fig. 3

		δ_{rc}/ppm				
Case 1	Case 2	H3	H4	H5	H6	Ha
Hdpa-R1	Hdpa-R1′	0.14	−0.08	−0.48	−0.69	0.18
-R1′	-R1	−0.16	−0.17	−0.20	0.33	—
bpy1-R2	bpy2-R2	−0.09	−0.01	0.02	−0.03	—
-R3	-R3	−0.14	−0.17	−0.27	−0.69	—
bpy2-R2	bpy1-R2	0.23	0.14	0.06	0.29	—
-R3	-R3	0.13	−0.10	−0.40	−1.10	—

Table 2. The Observed and Calculated Values of the Shifts of Each Proton Signal of bpy in $[Ru(bpy)_2(Hdpa)]^{2+}$ Relative to the Corresponding Proton Signals of bpy in $[Ru(bpy)_3]^{2+}$

	Group I=bpy-R2		Group II=bpy-R3	
Numbering	obsd/ppm	calcd/ppm	obsd/ppm	calcd/ppm
H3	−0.01	0.01	−0.10	−0.07
H4	0.08	0.13	−0.12	−0.08
H5	0.21	0.29	−0.12	−0.09
H6	0.81	0.93	−0.09	−0.10

Table 3. The Observed and Calculated Values of the Shift of Each Proton Signal of bpy and Hdpa in $[Ru(bpy)(Hdpa)_2]^{2+}$ Relative to the Corresponding Proton Signals of bpy in $[Ru(bpy)_3]^{2+}$ and Hdpa in $[Ru(bpy)_2(Hdpa)]^{2+}$, Respectively

	Obsd/ppm	Calcd/ppm		
Numbering		Case1	Case4	Avaraged Cases 1—4
(Group I)=(bpy-R1)[a]				
H3	−0.15	0.24	−0.35	−0.05
H4	−0.04	0.16	−0.07	0.04
H5	0.21	0.15	0.25	0.20
H6	1.00	0.78	0.88	0.84
(Group II)=(Hdpa-R3)[b]				
H3	0.06	−0.10	0.32	0.11
H4	0.15	−0.14	0.26	0.21
H5	0.16	0.24	0.19	0.36
H6	0.54	−0.30	−0.11	0.59
(Group III)=(Hdpa-R2)[b]				
H3	−0.20	−0.20	−0.16	−0.12
H4	−0.14	0.04	−0.11	−0.08
H5	−0.12	−0.14	−0.13	−0.10
H6	0.04	−0.82	−0.39	−0.20
Ha	−0.12	−0.95	0.08	−0.15

a) Obsd and calcd are relative to bpy in $[Ru(bpy)_3]^{2+}$. b) Obsd and calcd are relative to Hdpa in $[Ru(bpy)_2(Hdpa)]^{2+}$.

Cases 1—4. The calculated δ_{rc} based on this model[21] explained the ^{1}H NMR spectrum. For Cases 2 and 3, the calculation indicated that the aromatic ring-current shifts should be different among the six pyridine rings, which was not consistent with the ^{1}H NMR spectrum. On the other hand, for Cases 1 and 4 which have C_2 symmetry, the calculation showed that three kinds of magnetic environments existed and the pyridine rings were classified into three groups which was consistent with the ^{1}H NMR spectrum. Therefore, by considering the possibility that the flapping might be inhibited due to the crowdedness of ligands around the central ruthenium atom, the above three possible models, averaged Cases 1—4, Case 1, and Case 4, should be examined in more detail.

By assuming that Groups II and III were assigned to R3 and R2, respectively, the difference of the ^{1}H chemical shifts of bpy in $[Ru(bpy)(Hdpa)_2]^{2+}$ and those

in $[Ru(bpy)_3]^{2+}$ and the difference of the ^1H chemical shifts of Hdpa in the $[Ru(bpy)(Hdpa)_2]^{2+}$ and those in $[Ru(bpy)_2(Hdpa)]^{2+}$ were calculated for the averaged Cases 1—4, Case 1, and Case 4, and compared with the experimental data (Table 3). The calculated values for averaged Cases 1—4 are in best agreement with the observed values among these calculated values. This indicates that the averaged Cases 1—4 are in best agreement with the observed values among these calculated values. This indicates that the averaged Cases 1—4 with equal weight where Hdpa ligands are rapidly flapping in the same way as in $[Ru(bpy)_2(Hdpa)]^{2+}$ is the most pertinent model. The opposite assignment is quite impossible considering the signs of the differences.

$[Ru(Hdpa)_3]^{2+}$: A combination of conformations of the three Hdpa ligands in $[Ru(Hdpa)_3]^{2+}$ gives eight cases, and the aromatic ring-current shifts (δ_{rc}) for the eight cases were calculated. For six of the cases, the calculated aromatic ring-current shifts showed that their differences among the six pyridine rings should be big enough to be detectable. This was inconsistent with the observed ^1H NMR spectrum. Furthermore, for the other two cases, where the complex has C_3 symmetry, the calculation of the aromatic ring-current shifts showed that the ^1H NMR spectra should indicate the presence of two kinds of pyridine rings. This was also inconsistent with the observed ^1H NMR spectrum. As the Hdpa ligands are rapidly flapping in the same way as $[Ru(bpy)_2(Hdpa)]^{2+}$, each proton should experience an averaged magnetic environment among the eight cases. In an averaged magnetic environment,[21] there was only one kind of magnetic environment which could explain the observed ^1H NMR spectrum. The calculated aromatic ring-current shifts (δ_{rc}) in an averaged magnetic environment are as follows: H3, −0.02; H4, −0.03; H5, −0.08; H6, 0.22; Ha, −0.12 ppm.

The observed and calculated values of the shifts of the proton signals of Hdpa in $[Ru(Hdpa)_3]^{2+}$ relative to the corresponding proton signals of Hdpa in $[Ru(bpy)_2(Hdpa)]^{2+}$ were as follows. Obsd: H3, −0.10; H4, 0.00; H5, 0.07; H6, 0.68; Ha, −0.05 ppm. Calcd: H3, −0.01; H4, 0.10; H5, 0.26; H6, 0.40; Ha, −0.30 ppm. The agreement of the calculated values with the observed values was not as good as in the cases of either $[Ru(bpy)_2(Hdpa)]^{2+}$ or $[Ru(bpy)(Hdpa)_2]^{2+}$. The reason for the deviation may be that the structure of the model used in the calculation was somewhat different from the real situation of the complex in solution and/or that the difference of the energy among the eight cases cannot be disregarded for $[Ru(Hdpa)_3]^{2+}$ due to the crowdedness of the ligands around the ruthenium atom.

In conclusion, we have performed the complete assignment of the ^1H and ^{13}C NMR spectra of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ ($n=0$—2) including the distinction of the pyridine rings by the aid of an aromatic ring-current effect calculation, and the conformational structure of the complexes in solution was interpreted by the flapping of the Hdpa ligands. Flapping of the Hdpa ligands was also observed for *trans*-$[Ru(NO)(OH)(Hdpa)_2]^{2+}$.[22] The ^1H NMR spectrum of the complex at 130 °C was explained by the flapping of the Hdpa ligands. However, the steric interaction between the 6 (6′) protons of the Hdpa ligands in the trans position hindered the flapping of the Hdpa ligands at 30 °C, which caused the splitting of the ^1H NMR signals of the pyridine rings. On the other hand, in the measurement of the present complexes, $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ ($n=0$—2), at as low as −40 °C, the ^1H NMR spectra of the complexes did not show any appreciable change from the spectra at 30 °C. This observation indicates that there does not exist any hindrance of flapping of Hdpa ligand due to the crowdedness of ligands around the ruthenium atom.

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20) The calculated differences in the shifts were obtained based on the values in Table 1. For example, the average ring current shift of Case 1 and Case 2 for H3(R3) was calculated as $(-0.14+0.13)/2=-0.01$ and for H3(R2) as $(-0.09+0.23)/2=0.07$. Therefore, the difference in the shift of H3(R3-R2) was calculated as $-0.01-0.07=-0.08$.
21) Although the differences among the energies of each case are unknown, it was assumed that they would be small so that each case had a similar weight in the calculation. As will be seen later, this assumption was reasonably justified.
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