NMR Study on Ru(II) Complexes Containing 2,2':6',2"-terpyridine

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The diamagnetic six-coordinate ruthenium polypyridyl complexes have been prepared and assigned. ^{1}H NMR spectral studies were used to unravel the ligand field strength and the basicity on the chemical shift to the particular proton of ligand L in $[(tpy)(L)Ru^{II}(X)]^{+/2+}$ (L=bpy, bqi, dmbpy, phen; X=Cl, CN, N_3, $NCCD_3$, NO_2, SCN) complexes.

Introduction

As a series of synthetic chemistry of polypyridyl complexes containing Ru and Os has evolved, the use of nuclear magnetic resonance spectrometers as a structural probe for the complexes has emerged.[1] Although X-ray crystallography has been successfully utilized for the determination of solid phase molecular and electronic structures, the questions of stereochemistry, fluxional behaviour, or substitution dynamics were best addressed through the application of multi-nuclear NMR instrument.[2] The NMR data have also proved valuable in understanding mechanistic pathways for the reaction containing Ru(IV) mono-oxo complexes.[3]

We now present the results of ^{1}H NMR spectral studies on polypyridyl Ru(II) complexes. Our results allow an assignment of each proton peak of precursor complexes and demonstrate that NMR techniques can provide a valuable insight for unravelling the underlying ligand field strength in the structural chemistry of six-coordinate ruthenium complexes containing higher oligopyridine.

Results and Discussion

$[Ru(tpy)(L)Cl]^+$ (tpy=2,2':2",6'-terpyridine, L=2,2'-bipyridine(bpy), 2,2'-biquinoline(bqi), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), and 1,10-phenanthroline(phen)) were prepared by reaction of the free ligand L with $Ru(tpy)Cl_3$ (eq. 1) using alternate procedures for obtaining similiar complexes.[4] Each ruthenium complex containing various ligands other than Cl was prepared by metathesis reaction with NaCN, NaN_3, $NaNO_2$, or NaSCN (eq. 2). The mono-aquo complex was obtained by the reaction of $[Ru(tpy)(L)Cl]^+$ with $AgClO_4$ in aqueous solution followed by precipitation with a saturated NH_4PF_6 solution. Each $[Ru\text{-}NCCH_3]^{2+}$ complex was prepared by dissolving corresponding ruthenium mono-aquo complex in acetonitrile.

$$Ru(tpy)Cl_3 + L=bpy,\ bqu,\ dmbpy,\ phen \xrightarrow[\text{reflux}]{EtOH/H_2O/NH_4PF_6} [Ru(tpy)(L)Cl](PF_6)_3 \quad (1)$$

$$[Ru(tpy)(L)Cl]^+ \xrightarrow[EtOH/H_2O,\ \text{reflux}]{X=NaCN,NaN_3,\ NaNO_2,\ NaSCN} [Ru(tpy)(L)(X)]^+ \quad (2)$$

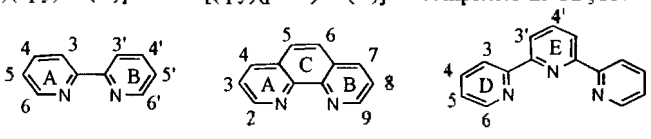
The ^{1}H NMR spectrum of each ruthenium complex prepared in CD_3CN solution showed 13 or 14 resonances, seven or eight from the bpy or phen moiety and six from the tpy ligand in the region 6.5-10.5 ppm. The ^{1}H chemical shift data and proton assignments for the complexes are summarized in Table 1. From previous studies of the ^{1}H NMR spectra of similiar complexes, each resonance can be assigned with the aid of a decoupling experiment and a COSY spectrum.[1,5]

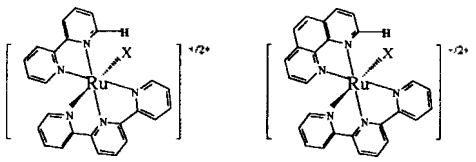
Table 1 shows the ^{1}H NMR spectroscopic data and the assignments for $[(tpy)(bpy)Ru(X)]^{+/2+}$ and $[(tpy)(phen)Ru(X)]^{+/2+}$. Because of similiar chemical environments in two complexes, it is not surprising to find out that the chemical shifts corresponding to the protons of rings D and E of the tpy fragment do not move greatly. Major differences are expected in the chemical shifts to the protons of the bpy and phen ligand. Each 6' positioned-proton ($H_{6'B}$) of ring B of the bpy ligand in $[(tpy)(bpy)Ru(X)]^{+/2+}$ and that to 9 positioned-proton (H_{9B}) of ring B of the phen ligand in $[(tpy)(phen)Ru(X)]^{+/2+}$ complex show a sole downfield chemical shift as a doublet of doublet. The proton $H_{6'B}$ of the bpy ligand and the proton H_{9B} of the phen ligand lie in the outer ring currents of tpy ligand from the molecular models and X-ray structral data.[1,3b,5] The resonance is shifted downfield accordingly.

Once again the doublet of doublet peak of $H_{6'A}$ and H_{9B} in each $[(tpy)(bpy)Ru(X)]^{+/2+}$ and $[(tpy)(bpy)Ru(X)]^{+/2+}$ complex shifted remarkably on changing ligand X in the Ru-X environment. Each $H_{6'A}$ and H_{9B} peak also provided a valuable diagnostic tool for detecting changes in X at the Ru-X coordination site.[3] Previous studies on the ^{1}H NMR spectra for $[(bpy)_2(py)Ru(X)]^{+/2+}$ (X=Cl, Br, NO, NO_2, OH_2 etc.) complexes showed that the chemical shift of one of 6 or 6' protons of the bipyridine appeared as an isolated doublet of doublet in the downfield in part of the spectrum, because it was out of ring current of the each bpy or py ligand.[7]

However, all the other protons of rings A and B of the bpy ligand and rings D and E of the tpy ligand were observed in the relatively upfield region from the chemical shift of the particular proton and little shifted on changing ligand X in the $[(tpy)(bpy)Ru(X)]^{+/2+}$ systems. Same results were obtained for those to all the other protons of rings A, B and C of the phen ligand and rings D and E of the tpy ligand in $[(tpy)(phen)Ru(X)]^{+/2+}$ ones.[6] This upfield shift is a result of the location of those protons in the bpy or phen or tpy inner ring currents for $[(tpy)(bpy)Ru(X)]^{+/2+}$ and $[(tpy)(phen)Ru(X)]^{+/2+}$ complexes. The chemical shifts to all the

Table 1. ^{1}H chemical shifts of $[(tpy)(bpy)Ru(X)]^{+/2+}$ and $[(tpy)(phen)Ru(X)]^{+/2+}$ complexes in CD_3CN





$[(tpy)(bpy)Ru(X)]^{+/2+}$ -X	3A	4A	5A	6A	3'B	4'B	5'B	**6'B**	3D	4D	5D	6D	3'E	4'E
Cl	8.32	7.66	6.96	7.31	8.60	8.25	7.92	**10.20**	8.38	7.86	7.30	7.64	8.48	8.10
N_3	8.31	7.63	6.96	7.28	8.60	8.29	7.95	**9.68**	8.40	7.92	7.31	7.69	8.53	8.12
SCN	8.30	7.70	6.99	7.25	8.59	8.30	8.00	**9.68**	8.40	7.92	7.32	7.68	8.51	8.20
$NCCD_3$	8.32	7.70	7.11	7.29	8.62	8.31	7.98	**9.60**	8.42	7.82	7.35	7.68	8.56	8.06
NO_2	8.34	7.78	7.05	7.26	8.56	8.24	7.94	**9.85**	8.34	7.90	7.32	7.72	8.46	8.15
CN	8.36	7.79	7.09	7.26	9.58	8.24	7.94	**10.09**	8.36	7.88	7.30	7.71	8.48	8.14

$[(tpy)(bpy)Ru(X)]^{+/2+}$ -X	2A	3A	4A	7B	8B	**9B**	5C	3D	4D	5D	6D	3'E	4'E
Cl	7.52	7.13	7.83	8.82	8.32	**10.43**	8.40	8.24	8.11	7.29	7.68	8.54	8.13
N_3	7.49	7.16	7.88	8.83	8.33	**9.97**	8.42	8.24	8.10	7.31	7.64	8.56	8.12
SCN	7.52	7.15	7.86	8.84	8.31	**10.20**	8.40	8.25	8.13	7.39	7.66	8.58	8.18
$NCCD_3$	7.55	7.22	7.97	8.90	8.35	**9.96**	8.44	8.32	8.15	7.42	7.65	8.62	8.18
NO_2	7.60	7.16	7.90	8.82	8.34	**10.26**	8.38	8.25	8.14	7.40	7.71	8.52	8.11
CN	7.56	7.15	7.88	8.79	8.31	**10.37**	8.38	8.26	8.14	7.44	7.65	8.52	8.80

other protons of ring A and B of the bpy ligand and rings D and E of the tpy ligand in the type of $[(tpy)(bpy)Ru(X)]^{+/2+}$ complexes showed slight shift by changing ligand X, same as those to all the other protons of rings A, B and C of the phen ligand and rings D and E of the tpy ligand in $[(tpy)(phen)Ru(X)]^{+/2+}$ ones.

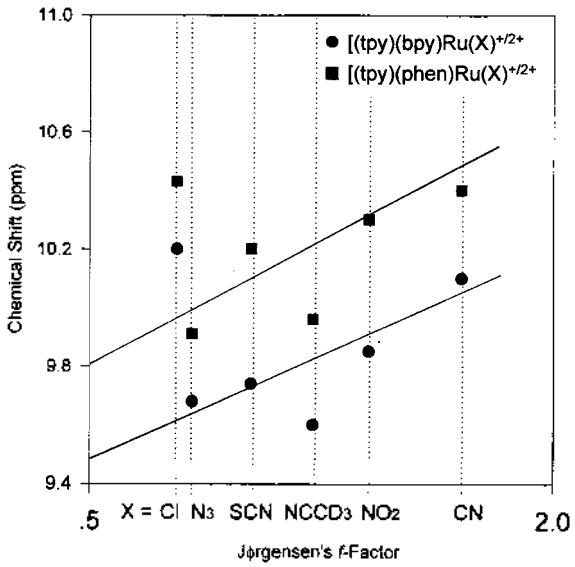


Figure 1. The ligand field strength vs the chemical shift to the particular proton of each ligand bpy and phen in $[(tpy)(bpy)Ru(X)]^{+/2+}$ and $[(tpy)(phen)Ru(X)]^{+/2+}$ (X=Cl, CN, N_3, $NCCD_3$, NO_2, SCN) complexes in CD_3CN; ● =$[(tpy)(bpy)Ru(X)]^{+/2+}$, ■ =$[(tpy)(phen)Ru(X)]^{+/2+}$.

It is quite interesting to examine the influence of ligand X in such Ru-X complexes from the ^{1}H NMR spectral data. Figure 1 presents the variation of ligand field strength[10] with the chemical shift of each $H_{6'B}$ and H_{9B} in the $[(tpy)(bpy)Ru(X)]^{+/2+}$ and $[(tpy)(phen)Ru(X)]^{+/2+}$ complexes.

With the exception of the $H_{6'B}$ and H_{9B} signal for each $[(tpy)(bpy)Ru(Cl)]^+$ and $[(tpy)(phen)Ru(Cl)]^+$ complex, the chemical shift to the particular proton uniformly increases as the ligand field strength increases upon substitution of the other ligand X for the chloride ligand in complexes. It is not surprising that the chemical shift of the proton $H_{6'B}$ and H_{9B} for each $[(tpy)(bpy)Ru(Cl)]^+$ and $[(tpy)(phen)Ru(Cl)]^+$ complex moves farthest downfield, because the particular proton of the bpy or phen moiety has a short intramolecular contact with the adjacent electronegative Cl atom as was discovered in the type of $[(tpy)(bpz)Ru(Cl)](PF_6)$ (bpz=2,2'-bipyrazine) complex.[1e] The particular proton of the bpy or phen ligand in each $[(tpy)(bpy)Ru(NCCD_3)]^{2+}$ and $[(tpy)(phen)Ru(NCCD_3)]^{2+}$ complex was deviated from the linear relationship, because of the presence of long and bulky acetonitrile moiety. The large downfield shift is due to less effective shielding by electron density *dxy* orbital (taking the z axis to lie along the Ru-X (X=CN, SCN).

To find out the effect of polyridyl ligand on the chemical shift to the proton such as $H_{6'B}$ and H_{9B}, other derivatives of

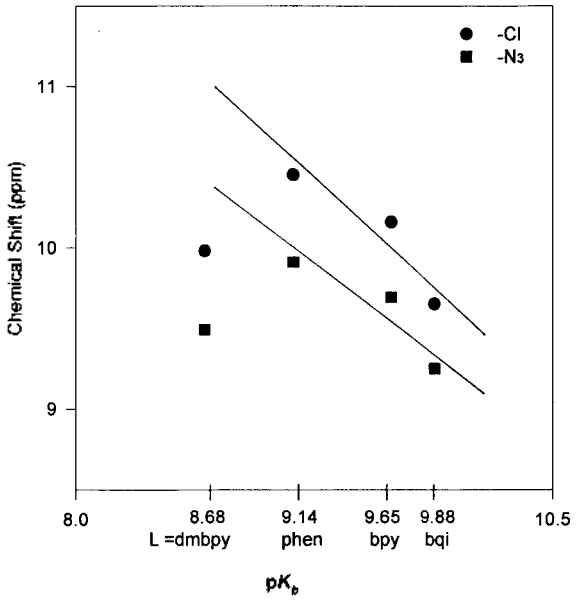


Figure 2. pK_b *vs* the chemical shift to the particular proton of each ligand L in $[(tpy)(L)Ru(X)]^+$ (L=bpy, dmbpy, bqi, phen; X= Cl, N_3) complexes in CD_3CN; ● =$[(tpy)(L)Ru(Cl)]^+$, ■ =$[(tpy)(L)Ru(N_3)]^+$.

ruthenium complexes, $[Ru(tpy)(L)X](PF_6)$ (L=bqi and dmbpy; X=Cl and N_3), were prepared (eq. 2). The relationship between pKb and the chemical shift to the particular proton in the ligand L which moves farthest downfield as a doublet of doublet for $[(tpy)(L)Ru(X)]^+$ (L=bpy, bqi, dmbpy, phen; X=Cl, N_3) complexes was plotted in Figure 2.

With the increasing basicity[11] of the ligand L in each ruthenium complex, the chemical shift increases. The plot indicates that the relationship partially reflects an electronic effect of the polypyridyl ligand on the electron density of the particular proton. It is instructive to note that the chemical shift to the particular proton of the dmbpy ligand containing dimethyl substituent in the complex shows an upfield shift. This upfield shift comes partly from a result of the steric effect, which must compete with the electronic effect of adjacent ligand X.

As a conclusion, these results clearly demonstrate that the ligand field strength and the basicity of the polypyridyl ligand adjacent to the central metal ion generally affect on the electronic environment of the partricular proton in the ligand for the diamagnetic six-coordinate ruthenium complexes, $[(tpy)(L)Ru(X)]^{+/2+}$ (L=bpy, bqi, dmbpy, phen; X= Cl, CN, N_3, $NCCD_3$, NO_2, SCN).

Experimental Details

$RuCl_3$, 2,2'-bipyridine(bpy), 2,2':6',2"-terpyridine(tpy), 1,10-phenanthroline(phen), 2,2'-biquinoline(bqi), activated alumina, and NH_4PF_6 were purchased from Aldrich Chemical Co. and used without further purification. The ligand 4,4'-dimethyl-bipyridine(dmbpy) was purchased from Reilly Tar Chemical Co. and recrystallized from hot acetone prior to use. Aceto-nitrile-d_3 (99.6% D, Aldrich Chemical Co.) were used as received.

Routine UV-visible spectra were recorded on a Hewlett-Packard 8452A Diode Array spectrophotometer using HP 89532A general scanning software. FT-IR spectra were obtained on a Bomen MB 100 FT-IR spectrophotometer as either on nujol mulls or in solutions using NaCl plates. ^1H NMR data were obtained in a Varian Model Gemini-200 FT-NMR spectrometer using CD_3CN as solvent. The chemical shift parameters were presented in parts per million (δ) downfield from internal reference tetramethylsilane (TMS). Elemental analyses were performed by analytical laboratory at Basic Science Institute of Korea.

Starting Materials. $[Ru(tpy)Cl_3]$, $[(tpy)(bpy)Ru(Cl)](PF_6)$, and $[(tpy)(phen)Ru(Cl)](PF_6)$ were prepared by previously described procedures.[8] Each $[(tpy)(bpy)Ru^{II}\text{-}NCCH_3]^{2+}$ and $[(tpy)(phen)Ru^{II}\text{-}NCCH_3]^{2+}$ were easily obtained by dissolving corresponding aqua complex in acetonitrile. They were confirmed by the change in max using UV-visible spectra and were also characterized by FT-IR spectroscopy, NMR spectrometer, and elemental analyses.[9]

Preparation of $[(tpy)(bpy)Ru(N_3)](PF_6)$. In a typical experiment, $[(tpy)(bpy)Ru(Cl)](Cl)$ (20 mg, 0.035 mmol) and NaN_3 (5 mg, 0.077 mmol) dissolved in 5 mL of ethanol and 5 mL of distilled water were heated at reflux under a stream of N_2 for 2h. After this period, the red pot contents were filtered hot and reduced to *ca.* half the original volume by rotary evaporation. To the filtrate was added an excess of saturated NH_4PF_6 solution which resulted in the formation of red precipitate. The product was washed with distilled water and dried under reduced pressure to give $[(tpy)(bpy)Ru(N_3)](PF_6)$. Yield: 319 mg (66%). Anal. Calcd for $C_{25}H_{19}F_6N_8PRu\cdot H_2O$: C, 43.17; H, 3.04; N, 16.11. Found: C, 43.88; H, 2.91; N, 16.32.

$[(tpy)(bpy)Ru(NO_2)](PF_6)$. The same procedure was utilized as was the preparation of $[(tpy)(bpy)Ru(N_3)](PF_6)$ except using $NaNO_2$ instead of NaN_3. Anal. Calcd for $C_{25}H_{19}F_6N_6O_2PRu\cdot H_2O$: C, 42.92; H, 3.03; N, 12.01. Found: C, 42.78; H, 2.96; N, 11.84.

$[(tpy)(bpy)Ru(CN)](PF_6)$. The same procedure was utilized as was for the preparation of $[(tpy)(bpy)Ru(N_3)](PF_6)$ except using NaCN instead of NaN_3. Anal. Calcd for $C_{26}H_{19}F_6N_6PRu\cdot H_2O$: C, 45.96; H, 3.12; N, 12.37. Found: C, 45.74; H, 3.07; N, 12.62.

$[(tpy)(bpy)Ru(SCN)](PF_6)$. The same procedure was utilized as was for the preparation of $[(tpy)(bpy)Ru(N_3)](PF_6)$ except using NaSCN instead of NaN_3. Anal. Calcd for $C_{26}H_{19}F_6N_6SPRu\cdot H_2O$: C, 43.89; H, 2.97; N, 11.81. Found: C, 44.02; H, 3.03; N, 11.65.

$[(tpy)(phen)Ru(N_3)](PF_6)$. The same procedure was utilized as was for the preparation of $[(tpy)(bpy)Ru(N_3)](PF_6)$ except using $[(tpy)(phen)Ru(Cl)](PF_6)$ for starting material. Anal. Calcd for $C_{27}H_{19}F_6N_8PRu\cdot H_2O$: C, 45.07; H, 2.94; N, 15.57. Found: C, 45.86; H, 3.10; N; 16.01.

$[(tpy)(phen)Ru(NO_2)](PF_6)$. The same procedure was utilized as was for the preparation of $[(tpy)(phen)Ru(N_3)](PF_6)$ except using $NaNO_2$ in place of NaN_3. Anal. Calcd for $C_{27}H_{19}F_6N_6O_2PRu\cdot 1.5H_2O$: C, 44.27; H, 3.02; N, 11.47. Found: C, 43.79; H, 2.95; N; 11.74.

$[(tpy)(phen)Ru(CN)](PF_6)$. The same procedure was utilized as was for the preparation of $[(tpy)(phen)Ru(N_3)](PF_6)$ except using NaCN in place of NaN_3. Anal. Calcd for $C_{28}H_{19}F_6N_6PRu\cdot H_2O$: C, 47.20; H, 3.11; N, 11.65. Found: C, 46.61; H, 2.99; N; 11.90.

$[(tpy)(phen)Ru(SCN)](PF_6)$. The same procedure was

utilized as was for the preparation of [(tpy)(phen)Ru(N_3)](PF_6) except using NaSCN in place of NaN_3. Anal. Calcd for $C_{28}H_{19}F_6N_7PRu\cdot H_2O$: C, 45.72; H, 2.88; N, 11.42. Found: C, 45.51; H, 2.76; N; 11.18.

Preparation of [(tpy)(bqi)Ru(Cl)](PF_6) complexes. To 20 mL of ethanol and 5 mL of distilled water was added 50 mg of Ru(tpy)Cl_3 (0.11 mmol) followed by 30 mg of 2,2'-biquinoline (0.12 mmol) and 25 mg of LiCl (0.59 mmol). 0.5 mL of Et_3N was then added and the reaction mixture was heated at reflux under a stream of N_2 for 2h. The pot contents were reduced to *ca.* one-third the original volume by rotary evaporation and stored in refrigerator overnight. To the cold solution was added an excess of saturated NH_4PF_6 solution which resulted in the formation of brownish red precipitate. The crude PF_6^- salt was dissolved in a minimum CH_3CN followed by elution on a 1×20 cm column of alumina; eluent was 1 : 1 toluene-acetonitrile. The second band was evaporated to dryness to give a crystalline product. Yield: 70 mg (80%). Anal. Calcd for $C_{33}H_{23}F_6N_5ClPRu\cdot H_2O$: C, 46.08; H, 3.19; N, 8.88. Found: C, 45.89; H, 3.09; N; 8.77.

[(tpy)(dmbpy)Ru(Cl)](PF_6). This complex was prepared identically as the preparation of [(tpy)(bqi)Ru(Cl)](PF_6) except using dmbpy as the ligand source. Anal. Calcd for $C_{27}H_{23}F_6N_5ClPRu\cdot H_2O$: C, 45.23; H, 3.51; N, 9.77. Found: C, 44.97; H, 3.45; N; 9.69.

Preparation of [(tpy)(bqi)Ru(N_3)](PF_6) complexes. In a typical experiment, [(tpy)(bqi)Ru(Cl)](PF_6) (35 mg, 0.045 mmol) and NaN_3 (30 mg, 0.46 mmol) were dissolved in 15 mL of ethanol and 15 mL of distilled water and heated at reflux for 2h. After this period, the pot contents were filtered hot and reduced to *ca.* half the original volume by rotary evaporation. To the filtrate was added an excess of saturated NH_4PF_6 solution, which resulted in the formation of red precipitate. The product was washed with distilled water followed by ether and then dried under reduced pressure to give [(tpy)(bqi)Ru(N_3)](PF_6). Yield: 29 mg (83%). Anal. Calcd for $C_{33}H_{23}F_6N_8PRu\cdot 1.5H_2O$: C, 49.26; H, 3.26; N, 13.93. Found: C, 48.97; H, 3.21; N; 13.72.

[(tpy)(dmbpy)Ru(N_3)](PF_6). This complex was prepared identically as for the preparation of [(tpy)(bqi)Ru(N_3)](PF_6) except using [(tpy)(dmbpy)Ru(Cl)](PF_6) as starting material. Anal. Calcd for $C_{27}H_{23}F_6N_8PRu\cdot 1.5H_2O$: C, 44.27; H, 3.58; N, 15.30. Found: C, 43.79; H, 3.25; N; 15.54.

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