

Fluxional dynamics of terpyridine ligand in $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$ complex

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Abstract

Herein, we report the fluxional dynamic behaviour of terpyridine ligand in $[\text{Ru}(\text{bpy-}d_8)(\eta^2\text{-tpy})]^{2+}$ **1**. Reaction of $\text{Ru}(\text{bpy-}d_8)_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with 2,2':6',2''-terpyridine in refluxing methanol afforded **1**. Complex **1** has been characterized by ^1H NMR spectroscopic analysis. Variable temperature ^1H NMR data reveals that the pendant pyridine ring of the tpy ligand in $[\text{Ru}(\text{bpy-}d_8)_2(\text{tpy})]^{2+}$ rotates which effects the adjacent ring protons. Moreover, protonation of **1** with trifluoroacetic acid (TFA) confirms that peripheral N on the pendant pyridyl ring of the tpy ligand affects the chemical shifts of protons on the tpy pendant pyridyl ring.

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Introduction

Morgan and Burstall in 1932 first isolated the 2,2':6',2''-terpyridine (tpy) ligand (Morgan *et al.*, 1932). Usually, the tpy ligand is chelated in a tridentate fashion when sufficient co-ordination sites are available on a metal ion. Still, there are some complexes where tpy appears as monodentate, bidentate or as a bridging ligand (Fig. 1).

The fluxional behaviour of tridentate tpy ligands was first reported in 1992 (Abel *et al.*, 1992). Temperature dependent ^1H NMR studies of the complexes *fac*- $[\text{ReBr}(\text{CO})_3(\eta^2\text{-tpy})]$, *cis*- $[\text{W}(\text{CO})_4(\eta^2\text{-tpy})]$ and *fac*- $[\text{PtClMe}_3(\eta^2\text{-tpy})]$ revealed a dynamic conformation process occurring on the NMR time scale in solution. Analysis of the temperature dependent ^1H NMR data revealed an intramolecular ligand exchange process where the tpy ligand is bound in a bidentate fashion. The two pyridyl rings of tpy ligand oscillates between two equivalent binding sites, through the formation of a seven coordinated transition state, as shown in Fig.2. This dynamic process was termed as the "tick-tock twist" mechanism (Abel *et al.*, 1992).

Fluxionality of tpy has also been studied in ruthenium dicarbonyl halide, $[\text{RuX}_2(\text{CO})_2(\text{tpy})]$ (X = Cl, Br or I) and

some metal tetracarbonyl complexes $[\text{M}(\text{CO})_4(\text{tpy})]$ (M = Cr, Mo, W). Unfortunately, the ruthenium based complexes react to form the thermodynamically stable tridentate ligand species under the conditions of the reported experiments. However, in light of the isoelectronic nature of the metals (M = Ru, Cr, Mo, W) and structural similarity, it has been concluded that the tick-tock twist mechanism is the most likely event functioning in these complexes (Abel *et al.*, 1994; Gelling *et al.*, 1998; Macartney and McAuley, 1979).

Chotali *et al.* (1995) and Pyo *et al.* (1999) studied a series of complexes containing bidentate tpy ligand with the general formula $[\text{Ru}(\text{L})_2(\eta^2\text{-tpy})]^{2+}$ [L = bpy or 1,10-phenanthroline] where the dynamic behavior of the tpy ligand was concluded to be a process analogous to the "ring wobbling".

Abel and co-workers reported a series of $[\text{Ru}(\text{bpy-}d_8)_2(\text{L})]^{2+}$ complexes where L is a 2-phenyl- or 2,9-diphenyl substituted phenanthroline ligand (Abel *et al.*, 1993). The use of $\text{bpy-}d_8$ instead of bpy significantly reduces the complexity of the ^1H NMR spectra as the replacement of bpy with $\text{bpy-}d_8$ renders the bpy proton signals NMR silent.

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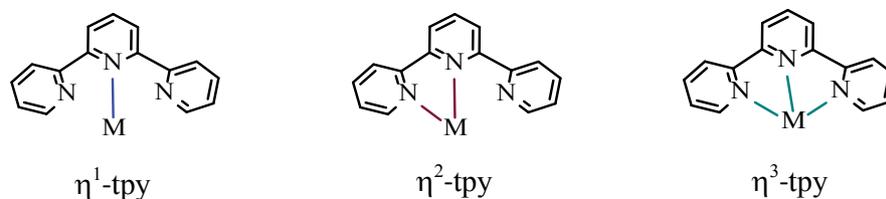


Fig. 1. Various bonding modes of terpyridine in metal complexes

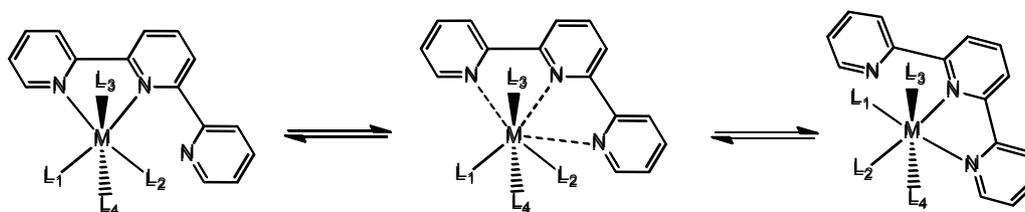


Fig. 2. "Tick-tock twist" mechanism.

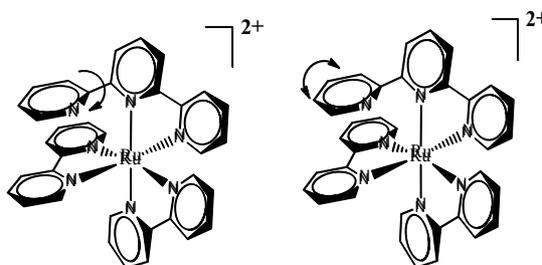


Fig. 3(a). Rotation and (b) Ring wobbling processes

Recently, tpy-based ruthenium polypyridyl complexes have received much attention as they exhibit important photochemical and electrochemical properties. The properties of tpy as an acceptor ligand in excited states have been characterized by resonance Raman, emission spectral fitting, temperature-dependent lifetimes and quantum yields. To address the excited states in bidentate tpy based complexes, it is a prerequisite to characterize the ground state properties. The purpose of our present study is to investigate the ground state dynamics and the fluxional behavior of tpy in a stable octahedral ruthenium polypyridyl complex, prior to studying the excited states of $[\text{Ru}(\text{bpy-d}_8)_2(\eta^2\text{-tpy})]^{2+}$. A previously published study with the $[\text{Ru}(\text{bpy})_2(\eta^2\text{-tpy})]^{2+}$ complex reported $^1\text{H NMR}$ spectra which were too complicated for the detailed evaluation of temperature dependent torsional and

other conformational changes (Chotali *et al.*, 1995; Pyo *et al.*, 1999). In this study $[\text{Ru}(\text{bpy-d}_8)_2(\eta^2\text{-tpy})]^{2+}$ has been used to obtain a simplified $^1\text{H NMR}$ spectrum. Thus, deuteration of the bpy assisted the interpretation of the fluxional dynamics of tpy as the proton signal due to the tpy ligand only appears in the $^1\text{H NMR}$ spectrum.

Materials and methods

All reagents purchased were used without further purification. Materials purchased for this work include: Pd/C (Strem Chemicals, 10%), py-d_8 (Sigma-Aldrich, 99 atom %D), $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (Sigma Aldrich), 2,2':6':2"-terpyridine (tpy) (Alfa Aesar, 97%), 2,2'-bipyridine (bpy) (Alfa Aesar, 98%), pyridine (Sigma-Aldrich, 99.5%), ammonium hexafluorophosphate (Alfa Aesar, 99.5%), tetra-n-butyl

ammonium bromide [TBA] (Sigma Aldrich, 98%), diethyl ether (ACP, 99.5%), chloroform (ACP, 99.8%), NaCO₃ (ACP, 99.5%), trifluoroacetic acid (Sigma Aldrich, 99%), tetrahydrofuran (Sigma Aldrich, >99.5%), acetonitrile (Burdick and Jackson 98.0%), dimethyl foramide (DMF).

Preparations

bpy-*d*₈ Pd/C (10%, 1.0 g) was heated in a 500 ml round bottom flask at 150 °C under vacuum for 1h. Pyridine-*d*₅ (4 ml, 0.05 mol) was added, and the slurry was heated to 140°C under nitrogen for three days. The excess pyridine-*d*₅ was removed by vacuum distillation. Then the residual solid was heated at refluxing temperature successively in 100 ml each of toluene, chloroform and 10% methanol in chloroform (volume of the solvents 300 ml), and then filtered while hot. The volatile fraction was removed under vacuum to give a brown solid (0.6 g). The solid was purified by flash chromatography (silica gel, 250 mesh; chloroform/MeOH (99% v/v 1%)). Yield: 0.450 g, 5.5%.

[Ru(bpy-*d*₈)₂Cl₂] In a 100 ml round bottom flask, RuCl₃·H₂O (0.1 g, 0.19 mmol), bpy-*d*₈ (0.147 g, 0.90 mmol), LiCl (0.7 g) and DMF (20 ml) were heated at reflux for 8 h. Then the reaction mixture was cooled at room temperature and 100 ml of acetone was added. The resultant solution was cooled at 0°C overnight. The solution was filtered to yield a red to red violet solution and a dark green-black micro-crystalline product was obtained. The solid was washed with six 25 ml portions of H₂O followed by three 25 ml portions of diethyl ether, and then dried in vacuo. Yield: 0.075 g, 75% (based on ruthenium).

[Ru(bpy-*d*₈)₂(η²-tpy)] (PF₆)₂ In a 100 ml round bottom flask, Ru(bpy-*d*₈)₂Cl₂·2H₂O (0.05 g, 0.1 mmol) and tpy were heated at reflux in 15 mL of methanol for 8 h. The colour of the solution changed from red to orange during this period. The solution was filtered, and the solvent was removed in vacuo. The product was redissolved in acetone and precipitated with aqueous NH₄PF₆ (0.5 g, 10 ml H₂O). The orange solid was collected by filtration and dried under vacuum. Yield: 0.075g, 80%.

Protonation of pendant pyridine

¹H NMR spectra were recorded for [Ru(bpy)₂(η²-tpy)] (2.49×10⁻⁵M), before and after the addition of two equivalents of TFA; [TFA] = 0.1 M in CH₃CN at 298 (±3) K, under 1 atm N₂.

Results and discussion

Deuteration of polypyridyl ligands is a powerful approach to simplify the complexity of ¹H NMR spectra to facilitate the characterization of complexes and possible dynamic conformational processes (Glazer *et al.*, 2005). In this work, the replacement of bpy with bpy-*d*₈ was made to render the bpy ligands NMR silent in the ¹H NMR of [Ru(bpy-*d*₈)₂(η²-tpy)]²⁺ derivatives.

At ambient temperature the ¹H NMR spectrum of the [Ru(bpy)₂(η²-tpy)]²⁺ complex in CD₃CN solution is exceedingly complicated because all the protons are non-equivalent giving rise to 27 peaks, all of which are coupled (Fig. 4).

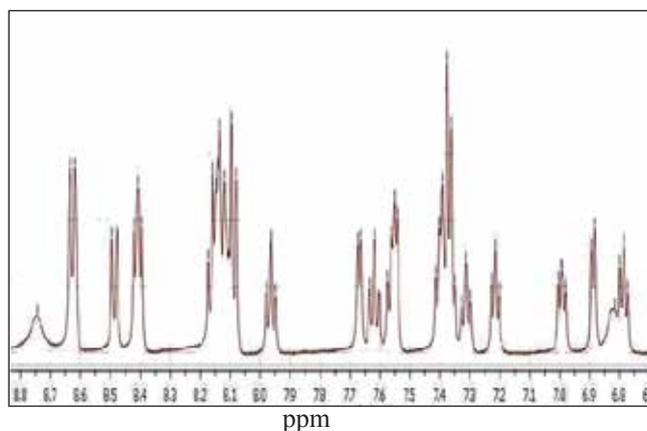


Fig. 4. 500 MHz ¹H NMR spectrum of [Ru(bpy)₂(η²-tpy)]²⁺ in CD₃CN at 298 K

Since the bpy ligands are deuterated, only the resonance associated with the tpy ligand are observed in the ¹H NMR spectrum of [Ru(bpy-*d*₈)₂(η²-tpy)]²⁺ together with small signals from bpy-*d*₈ impurities. Overlaid ¹H NMR spectra for [Ru(bpy)₂(η²-tpy)]²⁺ and [Ru(bpy-*d*₈)₂(η²-tpy)]²⁺ complexes are shown in Fig. 5. It is apparent that the tpy resonances are identical for the [Ru(bpy)₂(η²-tpy)]²⁺ and [Ru(bpy-*d*₈)₂(η²-tpy)]²⁺ complexes.

The ¹H NMR spectrum of [Ru(bpy-*d*₈)₂(η²-tpy)]²⁺ and assignments are shown in Fig. 6.

The ¹H NMR spectrum for [Ru(bpy-*d*₈)₂(η²-tpy)]²⁺ consists of one broad singlet, two doublets, two triplets, one doublet of doublets and one multiplet. The assignments were made by comparison to the [Ru(bpy)₂(η²-tpy)]²⁺ complex. The doublet at *d* 8.59 (*J* =

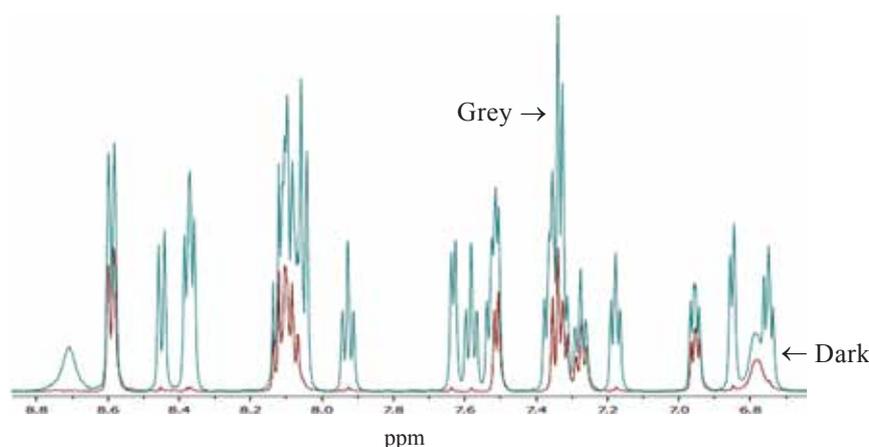


Fig. 5. Overlaid spectra of $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})][\text{PF}_6]_2$ (Dark) and $[\text{Ru}(\text{bpy})_2(\eta^2\text{-tpy})][\text{PF}_6]_2$ (Grey) in aromatic region

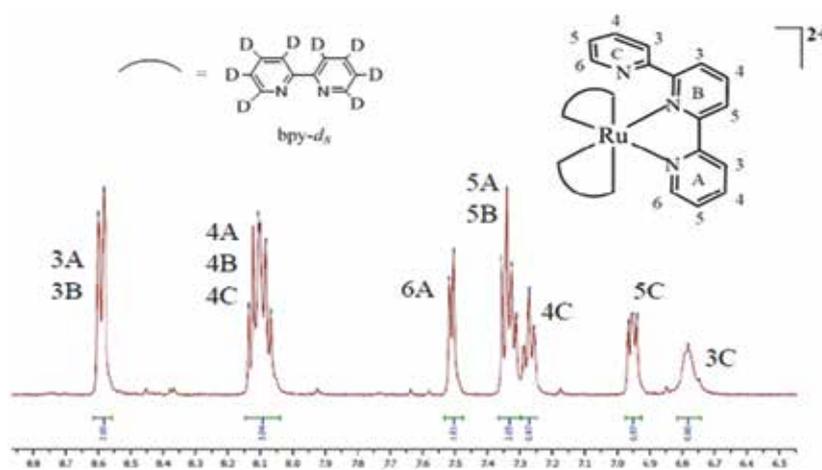


Fig. 6. 500 MHz ^1H NMR spectrum (aromatic region) of $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$ in CD_3CNat 298 K

10 Hz) is due to the 3A and 3B protons of the tpy ligand. Another doublet at d 7.51 ($J = 5$ Hz) is caused by the 6A proton of the tpy ligand. Triplets at d 7.27 ($J = 10$) and 6.95 ($J = 5$ Hz) can be attributed to the 4C and 5C protons, respectively. The multiplet at d 8.10 corresponds to the 4A, 4B and 6C protons. The doublet of doublets at d 7.33 can be assigned to the 5A and 5B protons. The broad singlet at d 6.78 is due to the 3C proton of the tpy ligand.

The ^1H NMR data are dynamic in the d 6.4 to 8.8 ppm region. Temperature dependent ^1H NMR spectra, recorded for $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})][\text{PF}_6]_2$ are shown in Fig. 7.

At room temperature the ^1H NMR the spectrum of $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$ shows one broad signal (d 6.78)

assigned to the 3C proton of tpy ligand which was shifted upfield at lower temperatures. Upon cooling to 0°C the width of this resonance increased where the resolution of the room temperature spectrum is consistent with a process which is rapid on the NMR time scale. At -20°C , the upfield signal is fully broadened, and is barely observable and there is a large upfield shift (d 6.66), together with significant changes in the positions and bandwidths of the resonances assigned to the 4C and 5C proton at d 7.27 and 6.95 ppm, respectively. These changes can be attributed to the wobbling (Fig.3) of the pendant pyridine ring of the tpy ligand at low temperature based on comparison with the $[\text{Ru}(\text{bpy-}d_8)_2(\text{phen-R})]$ systems (Abel *et al.*, 1993) where the rotation is almost restricted.

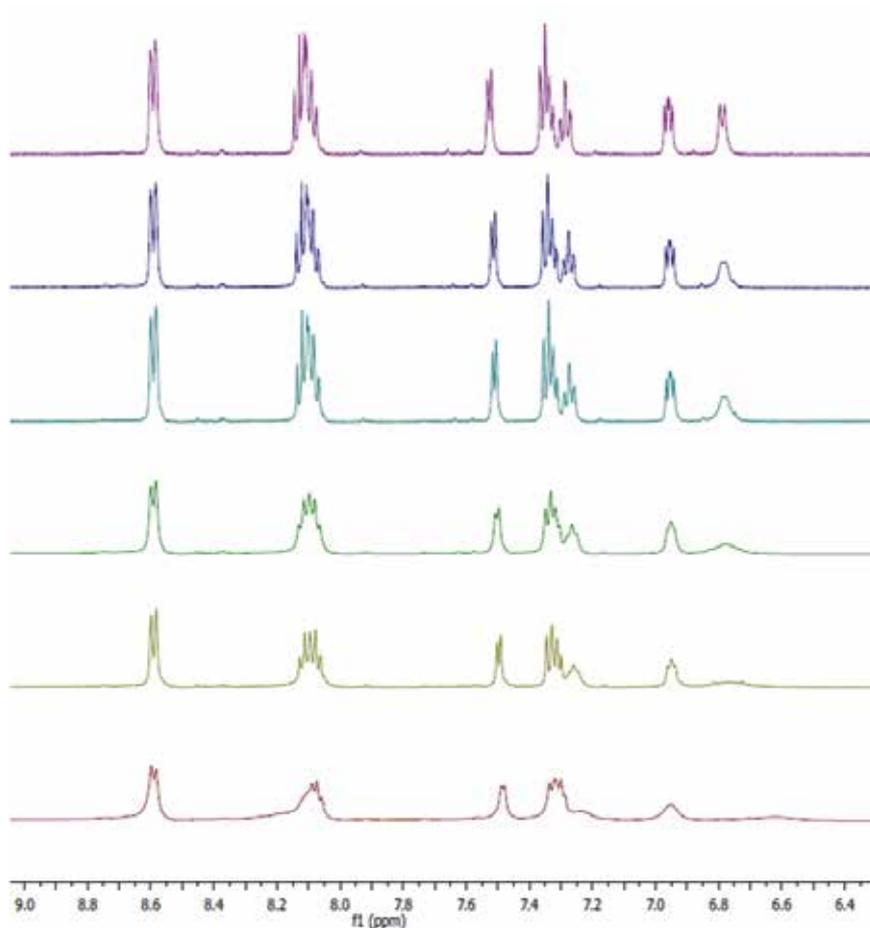


Fig. 7. Variable temperature ^1H NMR spectra of $[\text{Ru}(\text{bpy}-d_8)_2(\eta^2\text{-tpy})]^{2+}$ in CD_3CN over the temperature range 253-323 K

The 3C signal keeps broadening since the 3C proton moves far away from the 3B proton to which it is coupled. At $T = 253$ K, there exists a broad resonance at δ 6.66, that is barely noticeable and slightly shifted to upfield. This shift is caused by transient electron shielding of the 3C proton as it rotates close to the electron rich adjacent bpy moiety. The change in the 3C proton position affects the signals assigned to the 4C, 5C, 6C protons (Fig. 7). Increasing the temperature above 298 K, the signal intensity increases rapidly with temperature. At 323 K, the broad singlet due to 3C proton becomes a doublet. Pseudo triplets due to the 4C and 5C protons become sharp triplets and the intensity of other signals increases slightly which indicates free rotation of pendant pyridine on the NMR time scale. The broad signal at δ 6.78 which is assigned to the 3C proton, changes as the pyridine ring rotates from position A to B at high temperature (Fig. 8).

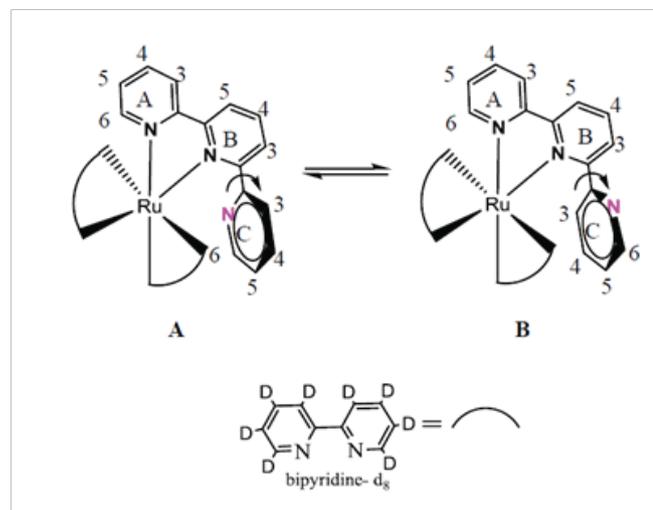


Fig. 8. Rotation of the pyridine ring

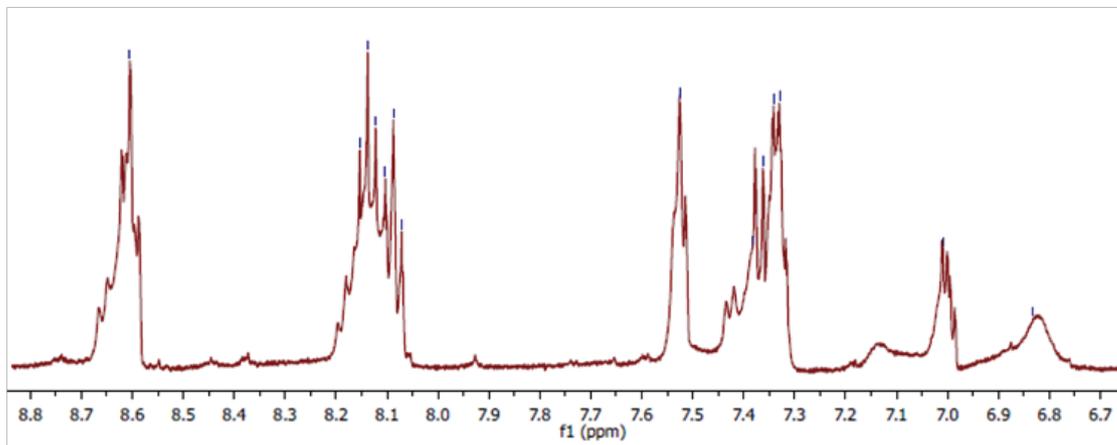


Fig. 9. ^1H NMR spectrum of protonated $[\text{Ru}(\text{bpy-d}_8)(\eta^2\text{-tpy})]^{2+}$

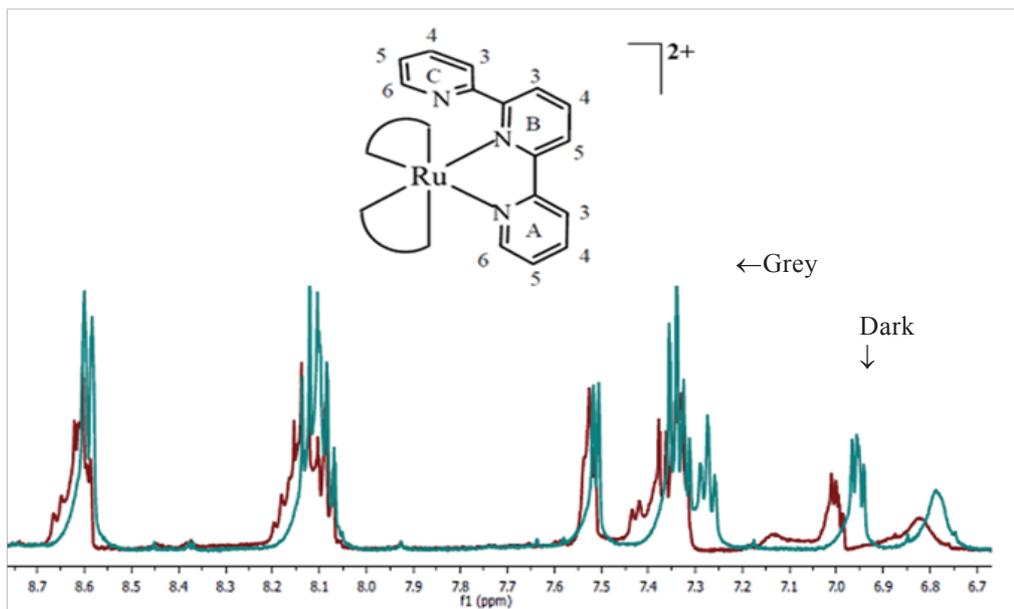


Fig. 10. Overlaid spectra of $[\text{Ru}(\text{bpy-d}_8)(\eta^2\text{-tpy})][\text{PF}_6]_2$ (Grey, before protonation) (Dark, after protonation) in the aromatic region in CD_3CN

For the exchange or tick-tock mechanism, the signals due to the central ring proton 4B that appear in the variable temperature ^1H NMR, would remain unaltered and the exchange dynamics between the ring A and C of the tpy ligand would change the proton signals those are due to

ring A and C. However, we did not observe any change in the signals for the 3A and 3B protons, even with the variation of temperature. This important observation suggests that the dynamics associated with this system do not follow the exchange or tick-tock mechanism (Abel *et*

al., 1994; Gelling *et al.*, 1998; Macartney and Mcauley, 1979). The data rather suggest that for $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$, the ligation remains constant and cleavage of Ru-N and bonds is not an important process in this family of complexes.

Excess trifluoroacetic acid (0.1M) was added to a CD_3CN solution of $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$. Fig. 9 shows the ^1H NMR spectrum of protonated $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$ with trifluoroacetic acid.

Protonation experiment of $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$ with trifluoroacetic acid (0.1M) in CD_3CN solution was performed and the ^1H NMR spectra were taken before and after the addition of TFA (Fig. 10). The ^1H NMR spectrum of $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})][\text{PF}_6]_2$ in CD_3CN shows signals for 11 protons as expected. However, five of the eleven protons shift to lower field (0.01- 0.1 ppm) with the addition of TFA. The changes in ^1H NMR spectrum are consistent with the formation of the cationic species, $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy-H})]^{3+}$. Four of the five protons correspond to the protons on the pendant pyridyl ring (3C-6C) and one to the 3B proton on the metal coordinated pyridyl ring of tpy.

Conclusion

The fluxional solution dynamics of the tpy ligand in the $[\text{Ru}(\text{bpy-}d_8)_2(\eta^2\text{-tpy})]^{2+}$ complex were studied by ^1H NMR spectroscopy. Variable temperature ^1H NMR data reveals that the pendant pyridine ring of the tpy ligand in $[\text{Ru}(\text{bpy-}d_8)_2(\text{tpy})]^{2+}$ rotates, rather than undergoing an exchange or "tick tock" twist mechanism. The ^1H NMR spectra illustrate that the protonation of the peripheral N on the pendant pyridyl ring of the tpy ligand affects the chemical shifts of protons on the tpy pendant pyridyl ring rather than the protons on the metal coordinated pyridyl ring of the tpy.

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