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Ground and excited state structural isomers in *trans*-$[Ru(bpy)_2(L)_2](PF_6)_2$

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Abstract

Spectroscopic evidence is presented for different structural isomers of *trans*-$[Ru(bpy)_2(L_1)(L_1)]^{2+}$ (L_1 or L_2 = 4-Etpy (**1**), py-PTZ) in which bpy is planar or nonplanar compared to *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ or $[Ru(bpy)_3]^{2+}$ in which bpy is planar. The nonplanar form is dominant in the ground states in low temperature glasses. The two forms appear to be in a temperature dependent equilibrium in 4:1 (v/v) ethanol/methanol at higher temperatures. The nonplanar form is converted into the planar form in the MLCT excited state(s) of **1**.

Keywords: Trans-Ruthenium polypyridyl complexes; Structural isomers; Temperature dependence; MLCT excited states

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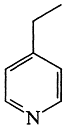
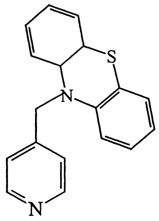
1. Introduction

Although the photophysics and photochemistry of $[M(bpy)_2(L)_2]^{2+}$ (bpy is 2,2′-bipyridine) complexes of Ru(II) and Os(II) have been well studied, the focus has been on *cis* isomers [1,2]. There is little information about the *trans* isomers. They are difficult to prepare and are photosensitive toward ligand loss [3–6]. The synthetic chemistry is evolving with procedures reported for the preparation of *trans*-based, chromophore-quencher complexes and assemblies [7–8].

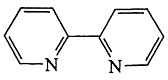
Fundamental details remain to be uncovered about the effect of the *cis-trans* geometry change on excited state electronic and molecular structure [9]. We report here, spectroscopic evidence for two different structural isomers of *trans*-$[Ru(bpy)_2(4\text{-}Etpy)_2]^{2+}$ (**1**; bpy is 2,2′-bipyridine; 4-Etpy is 4-ethylpyridine) and *trans*-$[Ru(bpy)_2(4\text{-}Etpy)(py\text{-}PTZ)]^{2+}$ (**2**; py-PTZ is 10-(4-picolyl)phenothiazine) in which bpy is planar or nonplanar compared to *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ or $[Ru(bpy)_3]^{2+}$ in which bpy is planar.[1] The ligands used in the study are illustrated below.



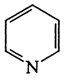
4-Etpy



py-PTZ



bpy



py

The absorption spectra of the *trans* complexes are dominated by low energy Ru(II) → bpy metal-to-ligand charge transfer (MLCT) bands at $\lambda_{max} = 485$ nm for *trans*-$[Ru(bpy)_2(4\text{-}Etpy)_2]^{2+}$ (**1**) in CH_3CN. Following MLCT excitation at room temperature, excited state decay of *trans*-$[Ru(bpy)_2(4\text{-}Etpy)_2]^{2+*}$ (**1***) and *trans*-$[Ru(bpy)_2(4\text{-}Etpy)(py\text{-}PTZ)]^{2+*}$ (**2***) is dominated by nonradiative pathways including thermally activated ligand loss through low-lying, highly reactive *dd* states [7,8]. In rigid 5:4 (v/v) propio/butyronitrile glasses at 77 K both excited states are intense emitters and photochemically stable. For **1**, $\phi_{em} = 0.22$, $\tau = 3.4\,\mu s$ ($k = 2.9 \times 10^5\,s^{-1}$), $\lambda_{max}^{em} = 606$ nm (16,500 cm^{-1}). For **2**, $\phi_{em} = 0.26$, $\tau = 3.4\,\mu s$ ($k = 2.9 \times 105\,s^{-1}$), $\lambda_{max}^{em} = 610$ nm (16,400 cm^{-1}). The stabilization of Ru(II) polypyridyl MLCT excited states in rigid media toward ligand loss is well known [10–12].

Emission and excitation spectra for *trans*-$[Ru(bpy)_2(4\text{-}Etpy)_2]^{2+}$ (**1**) and $[Ru(bpy)_3]^{2+}$ at 77 K in this glass are shown in Fig. 1. For *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ well defined vibronic progressions appear

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[1] Absorption, excitation and emission spectra for *trans*-$[Ru(bpy)_2(L)_2](PF_6)$ in 4/5 (v/v) propionitrile/butyronitrile have been reported previously at 77 K [7–9]. These results agree with the results reported here.

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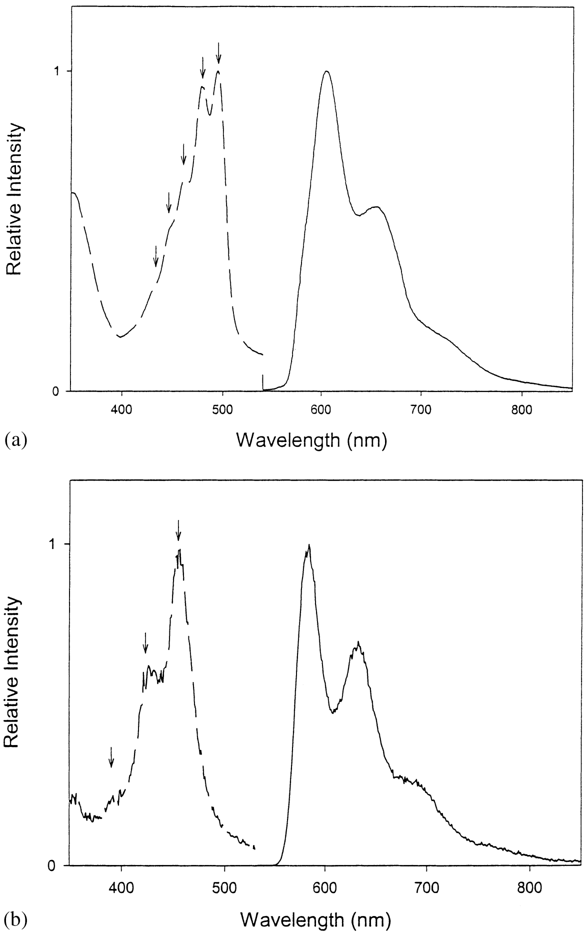


Fig. 1. (a). Excitation (- - -) and emission (—) spectra of *trans*-[Ru(bpy)$_2$(4-Etpy)$_2$](PF$_6$)$_2$ (**1**) at 77 K in a 5:4 (v/v) propio/butyronitrile glass. (b) Excitation (- - -) and emission (—) spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ at 77 K in a 4:1 (v/v) ethanol/methanol glass. The positions of the vibronic components are marked in the excitation spectra.

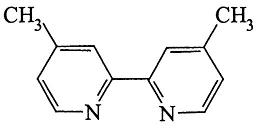
with spacings of ~1300 cm^{-1} which are characteristic of Ru(II) polypyridyl complexes [1,2,9]. The single vibronic component is the weighted average of a series of bipyridine ring stretching modes with quantum spacings between 1000 and 1610 cm^{-1} [13–16]. Its appearance in both excitation and emission spectra shows that the planar bpy structure in the ground state persists in the excited states.

By contrast, a ~1300 cm^{-1} vibronic component appears in the 77 K emission spectrum of **1** but the excitation spectrum is dominated by a progression at 660–670 cm^{-1}. Similarly in the low energy resonance Raman (RR) spectrum of **1** at 77 K obtained with 457.9 excitation, significant resonance enhancement occurs for bands at 202, 249, 370, 462, 645, 663, 735, 765, and 870 cm^{-1} with the intensity dominated by the band at 663 cm^{-1}. For [Ru(bpy)$_3$]$^{2+}$ in this region the spectrum includes significantly enhanced bands only at 668, 766, and 983 cm^{-1}. The 660–670 cm^{-1} progression in the excitation spectrum could be the result of overlapping 1300 cm^{-1} progressions, but it does coincide with the strongly enhanced band at 663 cm^{-1} in the RR.

The differences in excitation and RR spectra between the *cis* and *trans* isomers at 77 K can be explained by invoking a structural difference at bpy in the ground states. The bpy is planar in the *cis* isomers as evidenced by the ~1300 cm^{-1} vibronic progression in excitation and emission spectra. The bpy appears to be distorted in the *trans* isomers as shown by the 660–670 cm^{-1} progression in the excitation spectrum, the larger number of enhanced bands in the RR spectrum, and the dominance of the band at 663 cm^{-1} which is an inter-ring deformation mode.

The normal ~1300 cm^{-1} progression appears in the emission spectrum of **1*** suggesting that the structure at bpy in the emitting MLCT excited state of **1** is also planar. The excitation and RR spectra reflect the structure of bpy in the ground state. The emission spectrum reflects the bpy structure in the thermally equilibrated excited state.

There is precedence for a distorted bpy structure in certain *trans* complexes. In the crystal structure of *trans*-[Ru(4,4′-Me$_2$bpy)$_2$(py)$_2$][PF$_6$]$_2$, the bipyridine rings are in the octahedral plane but strained and bowed in a puckered configuration due to crossplanar repulsions between the 6 and 6′ hydrogen atoms [17]. This structure or one like it may resemble the structure of bpy in the *trans* isomer at low temperature. In *trans*-[Ru(phen)$_2$(py)$_2$][PF$_6$]$_2$ (phen is 1,10-phenanthroline) the individual phen ligands are planar but tilted by 16° from coplanarity due to in-plane H···H repulsions [18]. This structure may resemble the structure in the equilibrated excited state with bpy planar and the planar ligands tilted with respect to each other (planar-tilted). The driving force for planarity at bpy is the delocalization of the excited electron over both pyridyl ligands.



4, 4’-Me$_2$bpy

If this interpretation is correct, MLCT excitation of **1** at low temperature is followed by the sequence of events in Eq. (1). The structural isomers of the complex are labeled as nonplanar (at bpy) or planar (at bpy)-tilted (in the *trans* coordination plane). The initial excitation is a vertical Frank-Condon process to give an MLCT excited state or

$$\begin{aligned}&\mathrm{GS(nonplanar)}\xrightarrow{\text{(excitation)}\ h\nu}{}^{1}\mathrm{MLCT\ (nonplanar)}\\&\xrightarrow{\text{rapid}}{}^{3}\mathrm{MLCT(planar\text{-}tilted)}\xrightarrow{\text{(emission)}\ -h\nu'}\mathrm{GS\ (planar\text{-}tilted)}\\&\rightarrow \mathrm{GS\ (nonplanar)}\qquad(1)\end{aligned}$$

states largely singlet in character with retention of the nonplanar structure at bpy that exists in the ground state. Excitation is followed by rapid relaxation to the emitting thermally equilibrated triplet state or states [19–22] in which bpy is planar. Emission from this state is also a vertical process which gives the ground state but in the planar tilted structure of the excited state. Excited state decay is followed by isomerization of the complex to the form in which bpy is nonplanar.

An increase in Stoke's shift must have been predicted between absorption and emission for **1** compared to *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ for which the planar bpy structure is retained in both ground and excited states. Such comparisons are difficult because of the difference in patterns of absorption bands between isomers [4,5]. These are only apparent Stoke's shifts since the intense absorption bands result in states largely singlet in character, ^{1}MLCT, and emission occurs from states largely triplet in charcter, ^{3}MLCT.

The absorption spectrum of **2** in 4:1 (v/v) ethanol/methanol is temperature dependent,[2] but compared to $[Ru(bpy)_3]^{2+}$, in an unusual way (Fig. 2). At low temperature a prominent feature appears at 500 nm with vibronic progressions at 449, 463, 480, and 498 nm, an average spacing of 660–670 cm^{-1}. Upon warming to room temperature, this progression disappears and is replaced by the usual, broad MLCT absorption manifold with $\lambda_{max}^{abs} = 482$ nm at room temperature.

These observations are consistent with a temperature-dependent equilibrium in the ground state between isomers in which bpy is either planar or nonplanar. Assuming the nonplanar isomer to be the low temperature form, the relative contributions of the two to the absorption spectrum can be determined at intermediate temperatures by a linear least-squares analysis.[3] For the equilibrium in Eq. (3) this gives $K_{293} = 99$, $K_{170} = 0.16$,

$$\text{planar-tilted} \rightleftharpoons \text{nonplanar} \tag{3a}$$

$$k = \frac{\text{nonplanar}}{\text{planar-tilted}} \tag{3b}$$

$$\ln K = -\frac{\Delta H^\circ}{\mathrm{RT}} + \frac{\Delta S^\circ}{R} \tag{3c}$$

where $\Delta H^\circ = +15.3(\pm 0.7)$kJ/mol and $\Delta S^\circ = +75.6$ (± 3.6)J/mol K

There is probably an important contribution to the positive enthalpic change from H···H repulsion between bpys in the nonplanar isomer. Similarly, the positive ΔS° value must be largely due to a decrease in solvation of the nonplanar bpy isomer which is a less open structure. Solubility limitations precluded independent confirmation of the ground state equilibrium by ^{1}H-NMR measurements.

These observations provide evidence for the existence of a measurable temperature dependent equilibrium between isomers in which bpy is planar or nonplanar. In future experiments we hope to time resolve the nonplanar to planar transformation at low temperature by application of fast transient techniques.

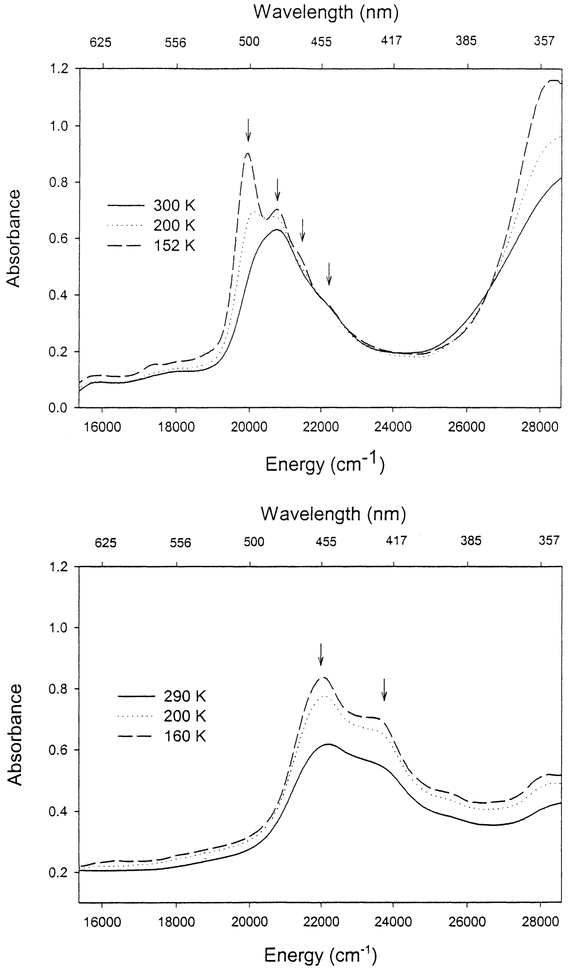


Fig. 2. (a) Absorption spectra of *trans*-$[Ru(bpy)_2(4\text{-Etpy})(py\text{-PTZ})]^{2+}$ (**2**) in 4:1 (v/v) ethanol/methanol at: (- - -) 152 K, (. . .) 200 K, (—) 300 K. The positions of the vibronic components are marked in the 152 K spectrum. (b) Absorption spectra of $[Ru(bpy)_3]^{2+}$ in 4:1 (v/v) ethanol/methanol at: (- - -) 160 K, (. . .) 200 K, (—) 290 K.

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[2] Intramolecular electron transfer quenching in $[Ru(bpy)_2(py)(py\text{-}PTZ)]^{2+}$ does not occur in the 77–180 K temperature range, and the complex is stable toward photodecomposition.

[3] In this analysis 152 and 300 K spectra were taken as the limiting forms and the contributions of the two to the intermediate spectra were calculated by using Grams software and a linear least-sequares analysis.

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