

## Photophysical and Photochemical Behavior of Nitro Complexes of Ruthenium(II)

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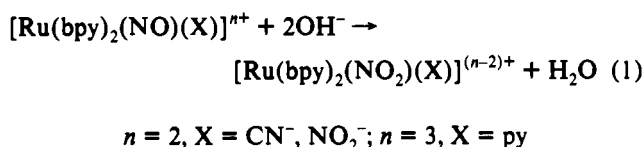
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### Introduction

For ruthenium(II) complexes of the type *cis*-Ru(bpy)<sub>2</sub>(X)-(Y), where bpy is 2,2'-bipyridine or a related polypyridyl ligand and X and Y are monodentate ligands, the properties of the Ru(II) → bpy, metal-to-ligand charge transfer (MLCT) excited states can be varied systematically by changing the nonchromophoric ligands<sup>1-3</sup> or the substituents on the polypyridyl ligands.<sup>1,2,4</sup> A complication is an instability toward ligand loss which occurs following MLCT excitation and thermally activated population of metal-centered, ligand field or dd states. Although this photochemistry has been used synthetically,<sup>5,6</sup> it is the major limitation to the potential use of the MLCT excited state of these complexes as luminescence probes and in driving photoinduced electron or energy transfer.

We report here the results of an initial investigation on the ground and excited state properties of the complexes *cis*-Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(X) (X = NO<sub>2</sub>, CN) and *cis*-[Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(py)]<sup>+</sup>, which contain the nitro ligand.<sup>7-10</sup> We were interested in investigating the excited state properties of these complexes given, (1) the extensive ground-state chemistry that exists for the nitro and related nitrosyl ligands,<sup>11</sup> (2) the possible existence of solvent dependent spectroscopic and photophysical properties which would allow the excited states to be used as probes for different environments, (3) the possible role of reversible NO<sub>2</sub><sup>-</sup> to NO<sup>+</sup> interconversion, eq 1, on excited state behavior (eq 1), and (4)



a continuing interest is establishing the electronic influence of different chromophoric and ancillary ligands on excited state

properties including their effect on the relative energies of MLCT and dd states.

### Experimental Section

**Materials.** The compounds and salts Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN),<sup>12</sup> [Ru(bpy)<sub>2</sub>(NO)(CN)](ClO<sub>4</sub>)<sub>2</sub>,<sup>12</sup> Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>,<sup>13</sup> [Ru(bpy)<sub>2</sub>(NO)(NO<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub>,<sup>13</sup> [Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(py)](PF<sub>6</sub>),<sup>14</sup> and [Ru(bpy)<sub>2</sub>(NO)(py)](PF<sub>6</sub>)<sub>3</sub>,<sup>13</sup> were prepared and purified according to literature procedures. The chloride salts [Ru(bpy)<sub>2</sub>(NO)(CN)](Cl)<sub>2</sub> and [Ru(bpy)<sub>2</sub>(NO)(NO<sub>2</sub>)](Cl)<sub>2</sub> were obtained by dropwise addition of a saturated CH<sub>3</sub>CN solution of [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]Cl to CH<sub>3</sub>CN solutions of the corresponding hexafluorophosphate salts. The precipitated chloride salts were filtered off, washed with ether and kept in a desiccator under vacuum. The solvento complexes [Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(H<sub>2</sub>O)]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CN)(H<sub>2</sub>O)]<sup>+</sup> were prepared by addition of solid [Ru(bpy)<sub>2</sub>(NO)(NO<sub>2</sub>)](Cl)<sub>2</sub> or [Ru(bpy)<sub>2</sub>(NO)(CN)](Cl)<sub>2</sub> to aqueous solutions containing stoichiometric amounts of NaN<sub>3</sub>.<sup>14</sup>

**Apparatus and Procedures.** Electrochemical measurements were performed in argon-deaerated CH<sub>3</sub>CN solutions with a Pt working, Pt-wire auxiliary and SSCE reference electrodes in a single compartment cell. The supporting electrolyte was [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>](PF<sub>6</sub>).

Electrochemical,<sup>12</sup> absorption,<sup>12</sup> emission,<sup>4,12</sup> lifetime,<sup>12</sup> and laser flash photolysis<sup>15</sup> measurements were performed as previously described. NMR spectra were obtained on a Bruker AC200/P 200 MHz FT-NMR spectrometer. Infrared spectra on solid samples were recorded in KBr pellets with a IFS88 Bruker FTIR spectrophotometer. FTIR spectra in aqueous solutions were obtained by using an Overhead ATR in conjunction with a ZnSe crystal. The measurements were made in sodium phosphate buffers at pH 4, 6, and 9.

Photochemical experiments were performed by irradiating samples at (0.3-0.6) × 10<sup>-4</sup> M with an Applied Photophysics irradiation system equipped with a 250-W xenon lamp. Potassium ferrioxalate was used as the standard for the actinometric measurements.<sup>16</sup>

The equilibrium constant (*K*<sub>1</sub>) for conversion of [Ru(bpy)<sub>2</sub>(NO)(CN)]<sup>2+</sup> to the corresponding nitro form (eq 1) was determined spectrophotometrically at 24.0 ± 0.3 °C by following previously reported procedures.<sup>17</sup> The spectral variations observed, in the pH range 2-8, occurred with the maintenance of isosbestic points at 234, 261, and 300 nm. The concentration of Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN) was calculated from absorbance measurements at 400 nm, where the nitrosyl complex does not absorb appreciably, and ε = 8500 M<sup>-1</sup> cm<sup>-1</sup> for the nitro complex. The value of *K*<sub>1</sub> obtained with this method was 1.0 (± 0.2) × 10<sup>18</sup> M<sup>-2</sup>.

### Results

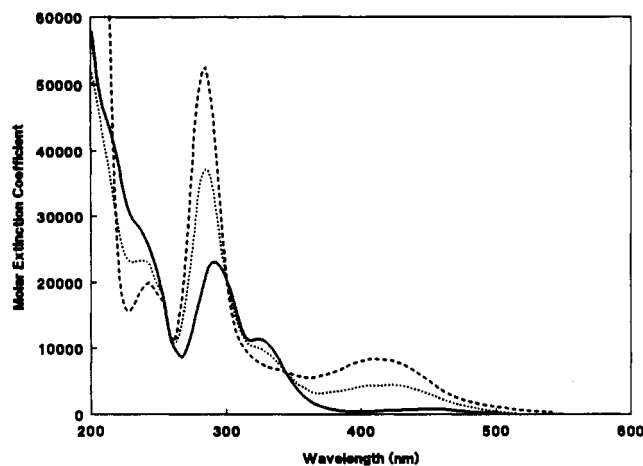
**Infrared Spectra.** The infrared spectra of [Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(py)](PF<sub>6</sub>),<sup>14</sup> Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>,<sup>13</sup> [Ru(bpy)<sub>2</sub>(NO)(py)](PF<sub>6</sub>)<sub>3</sub>,<sup>13</sup> and [Ru(bpy)<sub>2</sub>(NO)(NO<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub><sup>13</sup> have been reported elsewhere. In a KBr pellet containing Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN), bands for the symmetric and antisymmetric stretching modes for N-bonded nitrite appear at 1295 and 1333 cm<sup>-1</sup> and an intense cyanide band appears at 2078 cm<sup>-1</sup>. In the salt [Ru(bpy)<sub>2</sub>(NO)(CN)](ClO<sub>4</sub>)<sub>2</sub>, ν(NO) appeared at 1935 cm<sup>-1</sup>, which falls in the range 1890-1970 cm<sup>-1</sup> expected for bound NO<sup>+</sup>.<sup>11,18,19</sup> The band for the cyanide stretching mode appeared at 2153 cm<sup>-1</sup>, reduced in intensity by a factor of at least 10<sup>2</sup> relative to ν(CN) in Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN). This band was also observed at 2152 cm<sup>-1</sup> in FTIR reflectance spectra of an aqueous solution of [Ru(bpy)<sub>2</sub>(NO)(CN)](Cl)<sub>2</sub> at pH 4, together with the NO stretching band at 1944 cm<sup>-1</sup> (Figure S1).

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- (7) The cis configuration for these complexes can be established on the basis of their proton NMR spectra which are similar to those observed for analogous species belonging to C<sub>2</sub> and C<sub>1</sub> symmetry groups.<sup>8</sup> Trans isomers are expected to show a simpler pattern, constituted by two doublets and two triplets as for the 2,2'-bipyridine ligand.<sup>9,10</sup>
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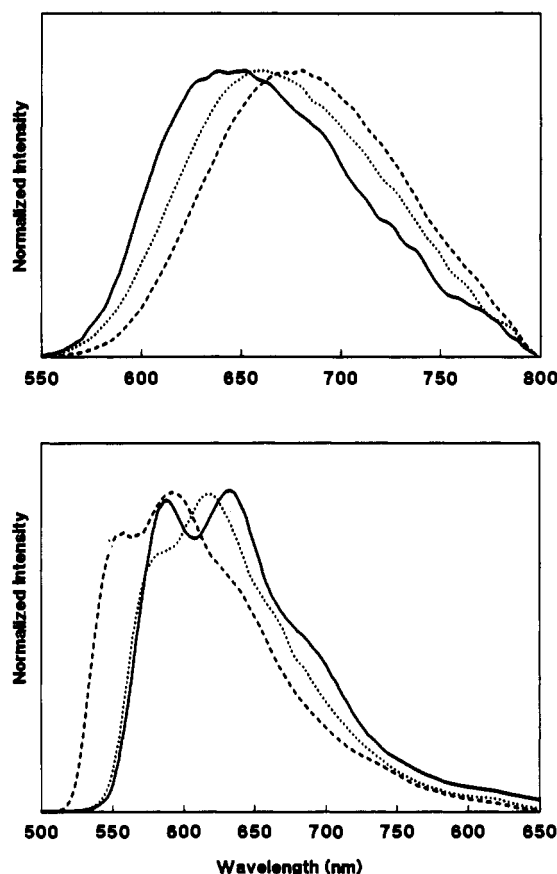


**Figure 1.** Electronic absorption spectra of equilibrated solutions containing  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})](\text{Cl})_2$  at pH 3 (continuous) pH 5 (dotted), and pH 7 (dashed).

**Electronic Spectra.** In Figure 1 are shown absorption spectra of solutions containing initially  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})](\text{Cl})_2$  at pH 3, 5, and 7. These solutions were allowed to equilibrate for 24 h before the spectra were recorded. The spectrum of the solution at pH 7 is coincident with that of  $\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{CN})$  as shown by the shift in the ligand-localized  $\pi \rightarrow \pi^*$  (bpy) band from 295 to 285 nm and the increase in the intensity and shift in the MLCT band initially at 325 (pH 3) to 405 nm (pH 7). The MLCT band for the nitrosyl complex at 325 nm may include contributions from both  $d\pi \rightarrow \pi^*$  (bpy) and  $d\pi \rightarrow \pi^*$  ( $\text{NO}^+$ ) transitions.<sup>20</sup> In the spectrum of  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})]^{2+}$ , an additional weak band appeared at 450 nm.

**Photophysical Properties and Photochemistry.** The complexes  $[\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{X})]$  ( $\text{X} = \text{Cl}^-, \text{Br}^-$ ) and  $[\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{L})]^+$  ( $\text{L} = \text{CH}_3\text{OH}, \text{CH}_3\text{COCH}_3, \text{H}_2\text{O}$ ) are nonemitting while those with  $\text{L} = \text{py}$  or  $\text{X} = \text{CN}^-$  or  $\text{NO}_2^-$  do emit. The emission maxima were solvent dependent and exhibited a pronounced solvatochromic behavior with the sensitivity decreasing in the order  $\text{NO}_2^- > \text{CN}^- > \text{py}$ . For example, in comparing  $\text{CH}_3\text{OH}$  to DMF as solvents, the emission maxima of the complexes undergo red shifts of the order of 0.98, 0.82, and  $0.67 \times 10^3 \text{ cm}^{-1}$ , respectively. Emission spectra, at room temperature in  $\text{CH}_3\text{OH}$  and at 77 K in 4:1 (v:v)  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ , are shown in Figure 2. The excitation spectra acquired at the emission maxima were found to match the visible absorption spectra for the three complexes. Emission quantum yields were measured at room temperature in deaerated  $\text{CH}_3\text{OH}$  solutions relative to emission from  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>21</sup> Relevant photophysical data are reported in Table I. No appreciable emission was observed for the nitrosyl complexes; as reported earlier for  $\text{Ru}(\text{bpy})_2(\text{NO})(\text{Cl})^{2+}$ ,<sup>20</sup> they undergo net photochemistry by a mechanism or mechanisms which were not investigated in detail. Irradiation of aqueous solutions containing  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})](\text{Cl})_2$  at 347 nm at pH 3 resulted in the formation of  $[\text{Ru}(\text{bpy})_2(\text{CN})(\text{H}_2\text{O})]^+$  (see below). During this conversion, spectral variations occurred with isosbestic points at 262, 299, and 348 nm (Figure S2). The quantum yield for the formation of the aqua complex was  $0.14 \pm 0.02$ .

The nitro complexes also underwent photosolvation upon MLCT excitation. The photochemistry of  $\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{CN})$  in water was studied in detail. The spectral variations in solutions containing this complex at pH 7 upon irradiation at 408 nm (Figure S3) show that the initial spectrum with  $\lambda_{\text{max}}$  (MLCT) at 405 nm is converted into a product spectrum with  $\lambda_{\text{max}}$  (MLCT) = 452 nm. Isosbestic points appeared at 282, 298, and 432 nm. From the absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{CN})(\text{H}_2\text{O})]^+$  ( $\lambda_{\text{max}}$  MLCT = 452 nm) and  $[\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{H}_2\text{O})]^+$  ( $\lambda_{\text{max}}$  MLCT



**Figure 2.** Relative emission spectra in methanol at room temperature (top) and at 77 K in 4:1 (v:v) ethanol/methanol (bottom) of  $[\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{py})](\text{PF}_6)_2$  (continuous),  $\text{Ru}(\text{bpy})_2(\text{CN})(\text{NO}_2)$  (dotted), and  $\text{Ru}(\text{bpy})_2(\text{NO}_2)_2$  (dashed). The apparent structure in the room temperature spectra is an artifact due to the weak emission intensities and low signal to noise ratio.

= 443 nm) photosubstitution appears to be dominated by loss of  $\text{NO}_2^-$ , with the appearance of isosbestic points suggesting a quantitative or near-quantitative formation of  $[\text{Ru}(\text{bpy})_2(\text{CN})(\text{H}_2\text{O})]^+$ .<sup>22</sup> Transient absorption measurements following 347-nm flash excitation of solutions  $(4-6) \times 10^{-4} \text{ M}$  in  $\text{Ru}(\text{bpy})_2(\text{NO}_2)(\text{CN})$  at pH 7 showed that a transient bleaching occurred followed by a positive, permanent absorption change in the 450–500-nm region. These changes occurred within the laser pulse (25 ns). From this observation for the loss of  $\text{NO}_2^-$  and aquation following MLCT excitation,  $k \geq 2 \times 10^7 \text{ s}^{-1}$ . In continuous irradiation experiments, the quantum yield of the photoreaction was  $0.12 \pm 0.02$ . Comparable photoinstabilities were observed for  $\text{Ru}(\text{bpy})_2(\text{NO}_2)_2$  and  $[\text{Ru}(\text{bpy})_2(\text{py})(\text{NO}_2)]^+$ , but in these cases the spectral changes with time were consistent with loss of both monodentate ligands on a competitive time scale, ultimately to give *cis*- $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ . These reactions were not followed quantitatively.

**Redox Properties.** The electrochemical behavior of  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})]^{2+}$  in  $\text{CH}_3\text{CN}$  solution is similar to that

(22) <sup>1</sup>H NMR spectroscopy has been proven to be the most valuable tool for determining the geometry of bis(bipyridine)-Ru(II) complexes. In the relatively dilute  $((0.3-0.6) \times 10^{-4} \text{ M}$  in complex in  $\text{H}_2\text{O}$ ) experimental condition used for the photochemical experiments; however, this technique cannot be used to follow the photoreaction directly. The maintenance of the *cis* configuration in the photochemically produced  $[\text{Ru}(\text{bpy})_2(\text{CN})(\text{H}_2\text{O})]^+$  complex is suggested by the coincidence of its absorption spectrum with that of thermally produced *cis* complex. Red shifts of the visible absorption of the order of 10–40 nm are observed from *cis* to *trans* isomers.<sup>9</sup> In addition, the product  $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})(\text{CN})]^+$  formed by photolysis of  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})]^{2+}$  in  $\text{CH}_3\text{CN}$  was shown to be the same as the product of the reaction between  $\text{N}_3^-$  and  $[\text{Ru}(\text{bpy})_2(\text{NO})(\text{CN})]^{2+}$  in  $\text{CH}_3\text{CN}$  by UV-visible measurements. The latter product has the *cis* geometry as shown by <sup>1</sup>H NMR.

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Table I. Photophysical Properties

complex	$\lambda_{em}(298\text{ K}),^{a,b}$ nm	$\Phi_{em}(298\text{ K})^a$	$\tau(298\text{ K}),^{a,c}$ ns	$10^{-4}k_r^{a,d}$ s <sup>-1</sup>	$\lambda_{em}(298\text{ K}),^{b,e}$ nm	$\lambda_{em}(77\text{ K}),^{b,e,f}$ nm	$\tau(77\text{ K}),^{e,g}$ $\mu\text{s}$
Ru(bpy) <sub>3</sub> <sup>2+</sup>	620	$4.5 \times 10^{-2}$ <sup>h</sup>	720	6.2	630	580 <sup>i</sup>	5.2 <sup>i</sup>
Ru(bpy) <sub>2</sub> (NO <sub>2</sub> )(py) <sup>+</sup>	645	$4.0 \times 10^{-4}$	7	5.7	655	590	3.8
Ru(bpy) <sub>2</sub> (NO <sub>2</sub> )(CN)	660	$1.8 \times 10^{-3}$	30	6.0	675	580	4.0
Ru(bpy) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	670	$1.1 \times 10^{-3}$	21	5.2	685	550	4.0

<sup>a</sup> CH<sub>3</sub>OH solution. <sup>b</sup>  $\pm 3$  nm. <sup>c</sup> Lifetime,  $\pm 2\%$ . <sup>d</sup> Calculated from  $\Phi = \eta k_r \tau$ , by assuming that the intersystem crossing efficiency,  $\eta$ , is 1. <sup>e</sup> 4:1 (v/v) C<sub>2</sub>H<sub>5</sub>OH-CH<sub>3</sub>OH solution. <sup>f</sup> Maximum of the vibronic component at higher energy. <sup>g</sup> Lifetime,  $\pm 1\%$ . <sup>h</sup> Data taken from ref 21. <sup>i</sup> Data taken from ref 2.

reported earlier for related nitrosyl complexes.<sup>20,23</sup> The complex undergoes a reversible one-electron reduction at +0.28 V vs SSCE and a second, irreversible reduction at -0.53 V. On the basis of previous observations, these processes correspond to the addition of electrons to redox orbitals that are largely localized on the nitrosyl ligand.<sup>20,23</sup> No oxidation processes were observed to the solvent limit (+2 V). In the corresponding nitro complex, Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN), a reversible Ru(III/II) oxidation wave was observed at +0.86 V vs SSCE.

## Discussion

The results of previous studies have shown that variations at the cis ligand in nitrosyl-bypyridyl complexes of ruthenium(II) can have a considerable influence on the properties of the coordinated nitrosyl.<sup>20,23</sup> In general, the ease of reduction of the NO<sup>+</sup> ligand is paralleled by an increase in the NO stretching frequency and in the equilibrium constant for eq 1.<sup>23</sup> These effects appear in [Ru(bpy)<sub>2</sub>(CN)(NO)]<sup>2+</sup> where they emphasize the importance of  $d\pi \rightarrow \pi^*$  mixing and of the competition for this mixing between ligands that are cis to one another in the coordination sphere.

The influence of the NO<sup>+</sup> ligand in withdrawing electron density from the metal is found in the shift of the MLCT (Ru  $\rightarrow$  bpy) bands in the nitrosyl complex to considerably higher energy (30 800 cm<sup>-1</sup> in [Ru(bpy)<sub>2</sub>(CN)(NO)]<sup>2+</sup>) compared to the corresponding nitro complex (24 700 cm<sup>-1</sup>) (Figure 1). There is also a considerable reduction in intensity of the  $\pi \rightarrow \pi^*$  (bpy) band following nitro-to-nitrosyl conversion (from  $\epsilon = 52\,500$  to  $\epsilon = 23\,000$  M<sup>-1</sup> cm<sup>-1</sup> in [Ru(bpy)<sub>2</sub>(NO)(CN)]<sup>2+</sup>) which resembles the changes that occur upon oxidation of [Ru<sup>II</sup>(bpy)<sub>2</sub>(py)(H<sub>2</sub>O)]<sup>2+</sup> ( $\lambda_{max} \pi \rightarrow \pi^* = 290$  nm,  $\epsilon = 57\,000$  M<sup>-1</sup> cm<sup>-1</sup>) to [Ru<sup>IV</sup>(bpy)<sub>2</sub>(py)O]<sup>2+</sup> ( $\lambda_{max} \pi \rightarrow \pi^* = 300$  nm,  $\epsilon = 23\,000$  M<sup>-1</sup> cm<sup>-1</sup>).<sup>24</sup> The influence of back-bonding to NO<sup>+</sup> is felt profoundly at the cis cyanide ligand as shown by the increase in energy and decrease in intensity for  $\nu(\text{CN})$  in [Ru(bpy)<sub>2</sub>(NO)(CN)]<sup>2+</sup> compared to Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN).<sup>25</sup> The increase in magnitude of the equilibrium constant for eq 1, [Ru(bpy)<sub>2</sub>(NO)(Cl)]<sup>2+</sup> ( $K_1 = 1.6 \times 10^9$  M<sup>-2</sup>)<sup>23</sup> to [Ru(bpy)<sub>2</sub>(NO)(CN)]<sup>2+</sup> ( $K_1 = 1 \times 10^{18}$  M<sup>-2</sup>), reflects the higher acidity of the NO group due, in part, to competitive back-bonding to the CN ligand. For [Ru(bpy)<sub>2</sub>(NO)(py)]<sup>+</sup>,  $K_1 = 1 \times 10^{20}$  M<sup>-2</sup>.<sup>23</sup>

The photophysical properties of the nitro complexes [Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(X)] (X = Cl, Br, CN, NO<sub>2</sub>) and [Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(L)]<sup>+</sup> (L = CH<sub>3</sub>OH, CH<sub>3</sub>COCH<sub>3</sub>, H<sub>2</sub>O, py) depend on the ligand field strength of the sixth ligand. The complexes containing the strong field ligands py, NO<sub>2</sub><sup>-</sup>, or CN<sup>-</sup> display observable emissions at room temperature in solution. Their lifetimes and emission quantum yields increase in the order CN<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > py. The existence of ligand-loss photochemistry demonstrates that dd states play a role in determining excited-state properties. With weak field ligands, the absence of discernible emissions is probably attributable to enhanced nonradiative decay because of the small excited to ground-state energy gaps and decay via dd states. In the ligand-loss

photochemistry of [Ru(bpy)<sub>2</sub>(NO)(CN)]<sup>2+</sup> and Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN), there is a selective loss of the nitrosyl or nitro ligands. This may be a consequence of the higher  $\sigma$ -donating ability of CN in the  $(d\pi)^5 d\sigma^*$ , dd excited states and the loss of  $d\pi-\pi^*$  back-bonding for the other two. In the laser flash photolysis experiments on Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN), we were unable to time-resolve the loss of the ligand. The spectral changes that were observed were consistent with MLCT excitation followed by rapid appearance of the aqua product.

Emission spectra at 77 K (Figure 2) are structured with the usual  $\nu(\text{bpy})$  vibronic progressions appearing at 1300–1400 cm<sup>-1</sup>. When compared to Ru(bpy)<sub>3</sub><sup>2+</sup>,<sup>26</sup> the relatively high intensities of the 0–1 and 0–2 components, compared to the 0–0 component, point to a relatively high degree of distortion at the bpy ligand in the MLCT excited states<sup>4</sup> most notably for Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>.

As is commonly observed, the MLCT emissions shift to the blue with the transition from the fluid to the glassy state.<sup>2</sup> The origin of the effect is that in the emission act the surrounding solvent dipoles are frozen in orientations appropriate to the electronic structure of the ground state.<sup>27</sup> This causes a blue shift relative to emission in fluid solution where the solvent dipole orientations are those appropriate to the electronic configurations of the equilibrated excited states. For the nitro complexes there is, in addition, an inversion in the order of the emission energies from py > CN > NO<sub>2</sub>, in fluid solution, to NO<sub>2</sub> > CN > py, at 77 K (Table I and Figure 2). The inversion in order and enhanced bpy distortion, especially for Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>, may arise, in part, from specific interactions (by H-bonding) with the low-temperature ethanol-methanol matrix.

The acid-base interconversion between Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)(CN) and [Ru(bpy)<sub>2</sub>(NO)(CN)]<sup>2+</sup> and the absence of emission from the latter provide the basis for an emission-based pH sensor in the range pH = 3–7. Although the results of initial experiments demonstrated a high sensitivity of the emission intensity to pH in this region, the photoinstability of the nitro complexes in the visible region precluded a quantitative study of the phenomenon.

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**Supplementary Material Available:** Infrared spectra of aqueous solutions of [Ru(bpy)<sub>2</sub>(NO)(CN)](Cl)<sub>2</sub> at pH 4, 6, and 9 (Figure S1), electronic absorption spectra of a solution of [Ru(bpy)<sub>2</sub>(NO)(CN)](Cl)<sub>2</sub> at pH 3 irradiated at 347 nm (Figure S2), and electronic absorption spectra of a solution of Ru(bpy)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> at pH 7, irradiated at 408 nm (Figure S3) (3 pages). Ordering information is given on any current masthead page.

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