

Synthesis and Characterization of Tetraammineruthenium(II) Bound to the Bridging Ligand 2,3-Bis(2-pyridyl)pyrazine (dpp)

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The synthesis, electronic absorption spectra, electrochemistry, ^{13}C NMR spectra, and photochemistry of $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ and $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ are reported. The aqueous visible electronic absorption spectra show intense MLCT transitions occur at 454 and 545 nm for the monometallic complex and at 558 nm for the bimetallic complex. Cyclic voltammograms of $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ in $\text{CH}_3\text{CN}/0.1\text{ M TBAP}$ show a reversible couple at $E_{1/2} = +1.01\text{ V}$, and voltammograms of $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ show two couples at $E_{1/2}(1) = +0.90\text{ V}$ and $E_{1/2}(2) = +1.29\text{ V}$ vs NHE. The decrease in $E_{1/2}(1)$ for the bimetallic complex vs $E_{1/2}$ for the monometallic complex is interpreted as being due to the addition of σ -donating NH_3 ligands via the additional ruthenium center. The $\Delta E_{1/2}(2-1)$ value of 390 mV for the bimetallic complex indicates excellent metal-metal communication through the bridging ligand. Extended irradiation of the MLCT transitions of both complexes yields NH_3 release with wavelength-dependent $\Phi_{\text{max}} < 3 \times 10^{-4}$ for reactant loss.

Introduction

Several recent investigations have reported the preparation and characterization of mono- and bimetallic complexes bound to/through the bis-bidentate nitrogen aromatic bridging ligand 2,3-bis(2-pyridyl)pyrazine (dpp).¹⁻⁶ Highly absorbing photoinert transitions, long-lived emission, and favorable electrochemical characteristics of a relatively few ruthenium(II) polyazine complexes incorporating dpp have stimulated interest in the potential use of dpp-bridged complexes in photochemically initiated excited-state electron- and energy-transfer reactions.^{1,2}

Of critical importance in intramolecular energy-transfer processes is the ability of a bridging ligand (such as dpp, bpym, or pz) to facilitate electronic communication between the metal centers. Previous results of electronic absorption spectra and electrochemical studies of $\text{M}-\text{dpp}-\text{M}$ ($\text{M} = \text{Ru}(\text{II}), \text{Cr}(\text{0}), \text{Mo}(\text{0}), \text{W}(\text{0})$) complexes have suggested less M_d-M_d interaction occurs through dpp than through the previously studied bpym or pz bridging ligands.^{1,3-5} These previously studied dpp complexes, however, contain peripheral ligands, such as bpy, CO, or CN^- , which undergo competitive M_d-L_p back-bonding. Thus, the $\text{M}_d-\text{dpp}-\text{M}_d$ interaction is subjected to complex competitive π bonding throughout the molecular framework.

In order to more clearly evaluate the effectiveness of dpp as a bridging ligand in bimetallic complexes, we have prepared mono- and bimetallic dpp complexes with only σ -interacting peripheral ligands. We now wish to report the synthesis and characterization of the $[(\text{NH}_3)_4\text{Ru}(\text{dpp})](\text{ClO}_4)_2$ and $[(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4](\text{ClO}_4)_4$ complexes.

Experimental Section

Materials. Analytical reagent grade compounds were used for preparations described in this work. The dpp ligand was obtained from Aldrich Chemicals. Argon was deoxygenated by first passing it through a chromous solution and then passing it through a drying tube before use. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Synthesis. The syntheses of $[(\text{NH}_3)_4\text{Ru}(\text{dpp})](\text{ClO}_4)_2$ and $[(\text{NH}_3)_4\text{Ru}_2(\text{dpp})](\text{ClO}_4)_4$ required the reaction of the previously reported air-stable $[(\text{NH}_3)_5(\text{H}_2\text{O})\text{Ru}](\text{TFMS})_3$ ($\text{TFMS}^- = \text{trifluoromethanesulfonate}$) complex with dpp.⁷

$[(\text{NH}_3)_4\text{Ru}(\text{dpp})](\text{ClO}_4)_2$. A 0.11-g (1.69×10^{-4} mol) sample of $[(\text{NH}_3)_5(\text{H}_2\text{O})\text{Ru}](\text{TFMS})_3$ and 0.20 g (8.5×10^{-4} mol) of dpp were dissolved in 25 mL of anhydrous ethanol containing Zn(Hg) amalgam. The yellow mixture was warmed (50°C) and constantly stirred and deaerated with a continuous stream of argon passing over the solution for 2 h. The red solution that was formed was filtered by vacuum

filtration, solid NaClO_4 was added to precipitate the product, and the mixture was refrigerated overnight. The crude red precipitate was collected by filtration and then dissolved in a minimum of acetone, and the solution was eluted down an alumina column (2-cm diameter \times 10-cm length) with a solution of 1 g of $\text{NaClO}_4/100\text{ mL}$ of acetone. The red product, which quickly eluted, separated from the purple bimetallic complex and was collected and evaporated to dryness at room temperature. The dried product, which contained excess NaClO_4 , was washed with a minimum amount of cold H_2O , and the remaining solid was collected by vacuum filtration. The purified product was then washed with anhydrous ethanol and vacuum-dried. Yield: 0.0235 g (3.9×10^{-5} mol), 23%. Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_8\text{Cl}_2\text{O}_8\text{Ru}$: C, 27.91; H, 3.69; N, 18.59. Found: C, 27.89; H, 3.74; N, 18.54. Aqueous washes containing purified product were collected from several preparations and evaporated to dryness, and the solids were rewashed with cold H_2O to enhance the overall product recovery.

$[(\text{NH}_3)_4\text{Ru}_2(\text{dpp})](\text{ClO}_4)_4$. A 0.20-g (3.0×10^{-4} mol) sample of $[(\text{NH}_3)_5(\text{H}_2\text{O})\text{Ru}](\text{TFMS})_3$ and 0.033 g (1.4×10^{-4} mol) of dpp were dissolved in 25 mL of anhydrous ethanol containing Zn(Hg) amalgam. The yellow mixture was warmed (50°C) and constantly stirred and deaerated with a continuous stream of argon passing over the solution for 2 h. The violet solution that was formed was filtered by vacuum filtration, and solid NaClO_4 was added to precipitate the product. The crude violet precipitate was collected and then dissolved in 50 mL of water, solid NaClO_4 was added to reprecipitate the product, and the solution refrigerated for 6 h. The purified solid was separated from the red wash (which contained the more soluble monometallic complex) by vacuum filtration, washed with anhydrous ethanol, and vacuum-dried. Yield: 0.11 g (1.1×10^{-4} mol), 77%. Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{N}_{12}\text{Cl}_4\text{O}_{16}\text{Ru}_2 \cdot 3\text{H}_2\text{O}$: C, 16.41; H, 3.94; N, 16.40. Found: C, 16.40; H, 3.93; N, 16.18. **Caution!** Although no difficulty was encountered in the preparation of these complexes, perchlorate complexes in the presence of organic ligands are potentially explosive and should be handled with care. Under no circumstances were the entitled complexes evaporated to dryness by heating.

Instrumentation. Electronic absorption spectra were recorded on a Beckman Model 5240 spectrophotometer with matching quartz cells.

Cyclic voltammograms were recorded on a Bio Analytic Systems CV-1B cyclic voltammograph with a Hewlett-Packard 7044A XY recorder. The glassy-carbon working electrode (3.0-mm diameter) was polished prior to each scan. A Ag/AgCl (3 M KCl; nominally +0.20 V vs NHE) reference electrode was used. All potentials are reported vs NHE and are uncorrected for junction potentials. The potentials reported for oxidation couples $E_{1/2}$ are estimates obtained by averaging anodic and cathodic peak potentials, unless otherwise noted. Cyclic voltammograms were recorded in CH_3CN by using 0.1 M tetrabutylammonium perchlorate as the electrolyte and in H_2O by using 0.1 M KCl as the electrolyte.

Proton-decoupled ^{13}C NMR spectra were obtained on a Bruker Model WM-250 Fourier transform NMR spectrometer operating at 62.9 MHz. Samples were run in a 10.0-mm probe with acetone- d_6 as an internal lock and reference (δ 206.04 vs TMS).

Irradiation of samples was accomplished with a continuous-beam photolysis apparatus consisting of an Ealing universal arc source lamp with a 200-W high-pressure Hg lamp, a water-filled quartz cell (for removal of infrared radiation), a 1-in.-diameter Oriel Hg-line interference filter, and a thermostated cell compartment (constant-temperature circulating water bath operating at 21°C), all mounted on an Ealing optical railing. Intensities of the apparatus were measured by Reineckate ac-

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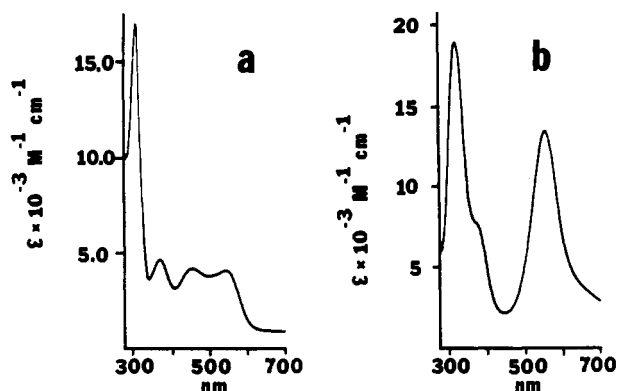


Figure 1. Aqueous electronic absorption spectra of (a) $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ and (b) $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$.

Table I. Electronic Absorption Data and Quantum Yields for Ruthenium(II) Complexes

complex ion	λ_{max} , nm	$10^{-3}\epsilon$, $\text{M}^{-1}\text{cm}^{-1}$	assgnt	$10^4\Phi$	ref
$(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$	545	4.5	MLCT	<1	a
	454	4.8	MLCT	1	
	368	5.0	MLCT	3	
$((\text{NH}_3)_4\text{Ru})_2(\text{dpp})^{4+}$	307	17	$\pi^* \leftarrow \pi$	<1	a
	558	19	MLCT	<1	
	368	9.8	MLCT	3	
$(\text{bpy})_2\text{Ru}(\text{dpp})^{2+}$	318	25	$\pi^* \leftarrow \pi$		
	480 (sh) ^b	10	MLCT		1
	430	12	MLCT		
$((\text{bpy})_2\text{Ru})_2(\text{dpp})^{4+}$	525	21	MLCT		1
	425	17	MLCT		
	330	26	MLCT		
$(\text{NH}_3)_4\text{Ru}(\text{bpym})^{2+}$	567	2.0	MLCT	<1	10
	402	8.4	MLCT		
	697	4.0	MLCT	<1	10
$((\text{NH}_3)_4\text{Ru})_2(\text{dpp})^{4+}$	424	18	MLCT		
	472		MLCT		13
	547		MLCT		13

^aThis work. ^bsh = shoulder.

tinometry at 577, 546, and 436 nm⁸ and ferrioxalate actinometry at 366 nm.⁹ The 5.0-mL solutions in 2.00 cm path length cells used for photolysis studies were prepared and then deoxygenated with dried argon gas prior to irradiation. All spectroscopic measurements were corrected for thermal reaction by use of a dark sample. Quantum yields were calculated as previously described.⁹

Emission spectra were recorded at Clemson University at room and liquid-nitrogen temperatures by using apparatus described elsewhere.²

Results

The aqueous electronic absorption spectra of $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ and $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ are dominated by intense absorptions in the visible region (Figure 1), typical of Ru(II) complexes bound to nitrogen aromatic heterocyclic ligands.^{1,2,10-15} The absorption spectrum of $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ (Figure 1a) consists of a set of transitions ($\epsilon \approx 5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) in the visible region of the spectrum that are similar in energy and absorptivity to those of previously reported monometallic Ru(II) complexes containing potential nitrogen heterocyclic bridging ligands (Table I). The aqueous electronic absorption spectrum of $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$

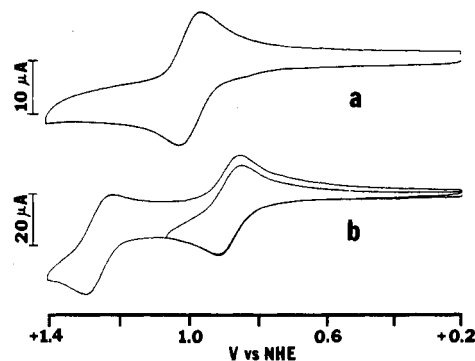


Figure 2. Cyclic voltammograms of (a) $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ and (b) $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ in 0.10 M TBAP/ CH_3CN at 100 mV/s.

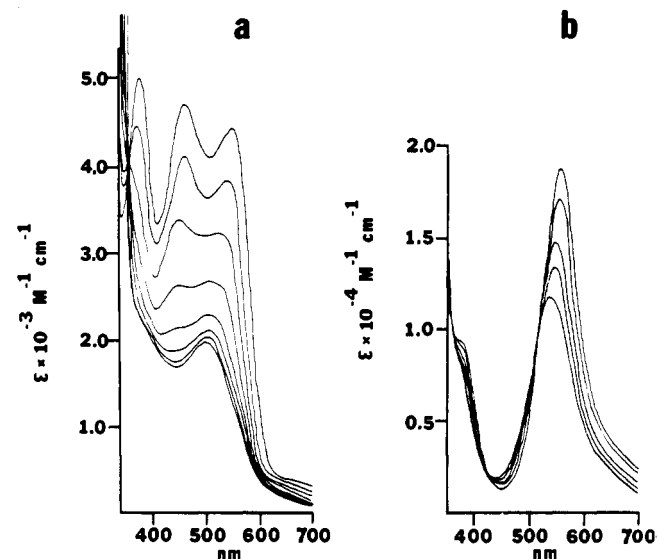


Figure 3. Aqueous electronic absorption spectral changes of (a) $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ upon 366-nm irradiation and (b) $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ upon 366-nm irradiation.

$(\text{NH}_3)_4^{4+}$ (Figure 1b) is distinctly different from that of the monometallic complex and consists of only a single absorption in the visible spectrum and higher energy near-UV transitions. The lowest energy transition of the bimetallic complex is shifted to longer wavelength vs that for the monometallic complex, and the change is consistent with those noted for similar mono- and bimetallic comparisons.^{1,6,10,11}

Deoxygenated, fluid room-temperature and frozen liquid-N₂ (77 K) samples of the $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ and $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ complexes were found to be nonemissive upon broad-band irradiation.

Cyclic voltammograms of deoxygenated solutions of $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ and $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ were recorded in $\text{CH}_3\text{CN}/0.10 \text{ M}$ tetrabutylammonium perchlorate. The cyclic voltammogram for the $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ complex (Figure 2) shows single anodic and cathodic waves for the Ru(II)/Ru(III) couple at $E_{1/2} = +1.01 \text{ V}$ vs NHE, with a peak to peak separation of 65 mV. Although the peak to peak separation is larger than the theoretical 59 mV for electrochemical reversibility, the equivalence of peak currents and reproducibility of the waves through several cycles indicate the one-electron oxidation of $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ is reversible. The $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ ion undergoes two one-electron anodic and cathodic waves associated with both Ru(II)/Ru(III) couples, at $E_{1/2}(1) = +0.90 \text{ V}$ and $E_{1/2}(2) = +1.29 \text{ V}$ vs NHE. The decrease in potential by 0.11 V of $E_{1/2}(1)$ for the bimetallic complex vs $E_{1/2}$ for the monometallic complex indicates Ru(II)_a-Ru(II)_b coupling occurs through the dpp bridging ligand. The less positive $E_{1/2}(1)$ for $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ vs $E_{1/2}$ for $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$ contrast with previous results for the $((\text{bpy})_2\text{Ru})_{1,2}(\text{dpp})^{2+,4+}$ complexes, in which the oxidation potentials of the mono- and

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Table II. Electrochemical^a Data for ((NH₃)₄Ru)_{1,2}(dpp)^{2+,4+} Complex Ions

complex	solvent	$E_{1/2}$, V ^b	$\Delta E_{1/2}$, mV ^c	$E_{1/2}(2)$, V ^b	$\Delta E_{1/2}$, mV ^c	$\Delta E_{1/2}(2-1)$, mV ^d	ref
(NH ₃) ₄ Ru(dpp) ²⁺	H ₂ O	0.86	62				
	CH ₃ CN	1.01	65				
((NH ₃) ₄ Ru) ₂ (dpp) ⁴⁺	H ₂ O	0.77	65	1.13	110	360	
	CH ₃ CN	0.90	65	1.29	85	390	
(bpy) ₂ Ru(dpp) ²⁺	CH ₃ CN	1.58	88				1
((bpy) ₂ Ru) ₂ (dpp) ⁴⁺	CH ₃ CN	1.57	95	1.76	95	190	1
(CN) ₄ Fe(dpp) ²⁺	H ₂ O	0.45 ^f	65				6
((CN) ₄ Fe) ₂ (dpp) ⁴⁺	H ₂ O	0.41	70	0.56	70	150	6
(NH ₃) ₄ Ru(bpym) ²⁺	H ₂ O	0.75 ^e					10
((NH ₃) ₄ Ru) ₂ (bpym) ⁴⁺	H ₂ O	0.83		1.02 ^e		190	10
(NH ₃) ₅ Ru(pz) ²⁺	H ₂ O	0.49 ^g					13
((NH ₃) ₅ Ru) ₂ (pz) ⁴⁺	H ₂ O	0.37		0.76		390	13

^a Aqueous solution cyclic voltammograms were run at 22 °C, 0.10 M KCl, and scan rate 100 mV/s. Acetonitrile solution cyclic voltammograms were run at 22 °C, 0.10 M tetrabutylammonium perchlorate, and scan rate 100 mV/s. ^b $E_{1/2}$ values were recorded vs a Ag/AgCl electrode (nominally +0.20 V vs NHE) and are reported vs NHE. ^c Peak to peak separations of anodic and cathodic waves. ^d Separation of Ru(III)/Ru(II) and Ru(III)/Ru(II) couples. ^e Potentials vs NHE. ^f Potentials vs SCE. ^g Potentials vs NHE.

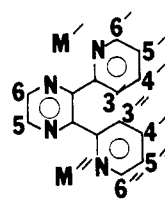
bimetallic species were identical, although this result is consistent with the trend noted for the ((NH₃)₅Ru)_{1,2}(pz)^{2+,4+} and ((CN)₄Fe)_{1,2}(dpp)^{2-,4-} complexes (Table II).

The ((NH₃)₄Ru)_{1,2}(dpp)^{2+,4+} complexes were irradiated in deoxygenated aqueous solutions to determine the potential use of dpp-bridged complexes as visibly absorbing photostable energy-transfer centers. Irradiation of (NH₃)₄Ru(dpp)²⁺ at 546 nm into the lowest energy MLCT transitions for 48 h produced no observable photoreaction. Extended irradiation of (NH₃)₄Ru(dpp)²⁺ at 436 and 366 nm into higher energy MLCT transitions resulted in a distinct change in the absorption spectrum of the irradiated solution (Figure 3). The observed changes upon 436- and 366-nm irradiation were identical, with an isosbestic point at 360 nm. Photolysis was continued until the primary photoreaction was complete, and absorbance values for the photoproduct were used to determine ϵ values at the necessary wavelengths for quantum yield (Φ) calculation. The quantum yields for (NH₃)₄Ru(dpp)²⁺ loss are $\Phi_{\max(436\text{nm})} = 0.0001$ and $\Phi_{\max(366\text{nm})} = 0.0003$ (Table I). Irradiation of (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺ at 577 nm into the lowest energy MLCT transition also produced no observable photoreaction, while irradiation at 366 nm produced a change in the absorption spectrum (Figure 3), with isosbestic points at 420 and 520 nm. The quantum yields for (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺ loss are $\Phi_{\max(577\text{nm})} = 0.0001$ and $\Phi_{\max(366\text{nm})} = 0.0003$. Extended irradiations resulted in secondary photolysis and the loss of the isosbestic points. Complete primary photoproduct formation of both mono- and bimetallic complexes produces more basic solution ($\Delta\text{pH} = 0.5$).

¹³C NMR spectra of dpp, (NH₃)₄Ru(dpp)²⁺, and (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺ were recorded in acetone-*d*₆ and are reported in Table III. Due to the limited solubilities of both complexes, extended accumulation of signal (30 000 scans) was required for satisfactory peak intensities. The bimetallic complex shows five signals, all shifted downfield from the free ligand positions except for C(4'), C(4''). The monometallic complex shows nine carbon signals, with the resonance at 125.83 ppm having a relative intensity of 2.

Discussion

The electronic absorption maxima and extinction coefficients in the UV-visible spectra of (NH₃)₄Ru(dpp)²⁺, (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺, and similar ruthenium(II) amine complex ions are summarized in Table I. On the basis of the intensity and energy of the transitions with analogous complexes, these are probably due to MLCT transitions.^{1,2,10-15} The highest energy absorption is most likely due to an intraligand $\pi \rightarrow \pi^*$ transition. The electronic transitions for (NH₃)₄Ru(dpp)²⁺ are similar, to those previously reported for (bpy)₂Ru(dpp)²⁺,¹ although at lower energy. This is the result of bpy π^* LUMO participation in π back-bonding with, and energy stabilization of, the Ru(II) d_{π} orbitals for (bpy)₂Ru(dpp)²⁺. No such Ru(II) d_{π} stabilization occurs as a result of interaction with the NH₃ ligands in (NH₃)₄Ru(dpp)²⁺, and therefore the MLCT transition is at lower energy.

Table III. ¹³C NMR Spectra of dpp and (NH₃)₄Ru(dpp)²⁺ and (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺ Complexes


complex ion	$\delta(^{13}\text{C})^a$				
	C(6), C(5)	C(6'), C(6'')	C(5'), C(5'')	C(4'), C(4'')	C(3'), C(3'')
dpp	148.49	143.30	123.66	137.11	124.61
Ru ₂ (dpp) ⁴⁺	154.79	147.26	126.50	133.97	128.59
Ru(dpp) ²⁺	154.35	148.82	125.83 ^b	138.93	126.92
	150.47	142.79	125.38	133.93	125.83 ^b

^a Chemical shift in acetone-*d*₆; δ 206.04 vs TMS. ^b Only one distinct signal observed at 125.83 ppm with a relative intensity of 2.

The lowest energy MLCT transition of (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺ is 13 nm (430 cm⁻¹) less than the lowest energy MLCT transition of (NH₃)₄Ru(dpp)²⁺. The shift to lower energy for the bimetallic vs monometallic lowest energy MLCT transition has previously been observed with a variety of nitrogen aromatic heterocyclic bridging ligands including pz,¹¹ bpym,¹⁰ dpq,¹⁵ and biim,¹⁶ as well as dpp. The lower energy bimetallic vs monometallic MLCT transition has been understood as being due to a combination of lowering of the bridging ligand π_{π^*} LUMO and formation of a metal-bridging ligand-metal d_{π} nonbonding molecular orbital.^{1,10,13} For the ((bpy)₂Ru)_{1,2}(dpp)^{2+,4+} complexes, with a shift to lower energy of 1600 cm⁻¹ (480 to 520 nm), electrochemical results show Ru(II) d_{π} orbitals to be energetically equivalent in the mono- and bimetallic complexes. That result indicates little or no coupling of the metal d_{π} orbitals through the dpp bridging ligand, and therefore the lower energy shift for the ((bpy)₂Ru)_{1,2}(dpp)^{2+,4+} complexes was primarily attributed to a lowering of the dpp π_{π^*} LUMO rather than Ru(II) d_{π} -metal d_{π} interaction. The suggested rationale for the limited metal d_{π} -metal d_{π} interaction is the nonplanar configuration of the dpp bridging ligand due to 3',3''-H,H steric repulsions, as demonstrated from the models of [(bpy)₂Ru(dpp)Ru(bpy)](PF₆)₄.

Electrochemical results for the ((NH₃)₄Ru)_{1,2}(dpp)^{2+,4+} complexes show coordination of the (NH₃)₄Ru²⁺ fragment on the (dpp)Ru(NH₃)₄²⁺ monometallic complex produces a decrease in the oxidation/reduction couples by 0.11 V (887 cm⁻¹). The less positive $E_{1/2}(1)$ for (NH₃)₄Ru(dpp)Ru(NH₃)₄⁴⁺ vs $E_{1/2}$ for (NH₃)₄Ru(dpp)²⁺ indicates formation of a Ru(II) d_{π} -dpp π_{π^*} -Ru(II) d_{π} nonbonding molecular orbital destabilized by 887 cm⁻¹ vs the monometallic Ru(II) d_{π} orbital. This result is highly significant

since it suggests substantial metal_{d_x}-metal_{d_x} electronic coupling occurs through the dpp bridging ligand, in the absence of ligands such as bpy or CO, which compete for π -electron density. The more effective Ru(II)_{d_x}-dpp_{p_x}-Ru(II)_{d_x} coupling may result from a radial extension of the d_x orbitals in the presence of σ -bonding peripheral ligands such as NH₃. This interpretation is supported by the fact that the potentials of the tetraammineruthenium couples are less positive than the analogous bis(bipyridine)ruthenium couples (Table II). Ru(II)-Ru(II) communication in $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ may also be enhanced by elimination of steric constraints in the analogous (bpy)₂ complex, allowing a more planar Ru(II)-dpp-Ru(II) geometry.

The net lowering of the $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ MLCT energy by 430 cm⁻¹ occurs because the bimetallic d_x levels are closer to the dpp p_x levels than in $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$. The fact that the bimetallic d_x orbitals are raised by 887 cm⁻¹ vs the monometallic d_x orbitals also suggests the dpp p_x LUMO is destabilized by the addition of the electron-donating NH₃ groups on the aromatic dpp ligand (through the Ru center).

The difference in $E_{1/2}(1)$ and $E_{1/2}(2)$ couples for bimetallic complexes has previously been interpreted as a measure of metal-metal communication through a bridging ligand.¹⁰⁻¹⁶ The $\Delta E_{1/2}(2-1)$ value of 0.39 V for $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ indicates substantially greater metal-metal interaction occurs through dpp as compared with similar ruthenium ammine-bridged complexes ($\Delta E_{1/2}(2-1) = 190 \text{ mV} - 50 \text{ mV}$), comparable to the interaction in the Creutz-Taube pyrazine-bridged bimetallic complex ($\Delta E_{1/2} = 390 \text{ mV}$).¹⁰⁻¹⁶

The $E_{1/2}(2-1)$ values of the bimetallic complex allow for the calculation of K_{com} according to the formula $\exp(\Delta E_{1/2}(2-1)/25.69)$, where $\Delta E_{1/2}$ is in millivolts and $T = 25^\circ\text{C}$, and the disproportionation equilibrium is described by $(\text{NH}_3)_4\text{Ru}_2(\text{dpp})^{4+} + ((\text{NH}_3)_4\text{Ru})_2(\text{dpp})^{6+} \rightarrow 2((\text{NH}_3)_4\text{Ru})_2(\text{dpp})^{5+}$. The aqueous $K_{\text{com}} = 1.2 \times 10^6$ is larger than the calculated value for the $((\text{bpy})_2\text{Ru})_2(\text{dpp})^{4+}$ bridged complex containing π -back-bonding ligands and the reported values for the analogous tetraammineruthenium bpm-bridged complex.^{1,6,10} The unusual stability of the dpp mixed-valence species has previously been studied in terms of the increased π acidity of the dpp bridging ligand in coordination with the oxidized M(III) metal center, electrostatic interaction of the metal centers, and the electronic delocalization effects through the conjugated 1,4-positions of the pyrazine dpp ring.⁶

The low quantum yields ($\Phi_{\text{max}} = 0.0001$) upon irradiation into the lowest energy MLCT transition are typical of ruthenium(II)

ammine complexes in which the MLCT state is the lowest lying excited state.¹⁷⁻¹⁹ It is this photostability that gives rise to the possible use of this type of complex as antennae fragments in energy-capture and energy-transfer reactions. Limited photo-reactivity upon extended-time higher energy irradiations produces a more basic solution ($\Delta\text{pH} = 0.5$), indicating photoaquation of NH₃ as a photoproduct. The photoproduct also retains a highly absorbing transition in the visible spectrum, which further suggests a photoaquation process in which the Ru(dpp) framework remains intact.

The assignment of signals for ¹³C NMR spectra of dpp, $(\text{NH}_3)_4\text{Ru}(\text{dpp})^{2+}$, and $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ is reported in Table III and is based on those previously reported for bpy and bpm.^{3,20-22} The assignment of signals for the symmetric $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ complex is based directly on the signals for dpp. The shielding of 4',4''-carbons has previously been noted in ruthenium amine centers bound to nitrogen heterocyclic ligands.²² The assignment of signals for carbons in the monometallic complex is based on the relative shifts of carbon signals derived from free ligand and bimetallic complex.

Conclusion

Electrochemical results show substantial Ru(II)-dpp-Ru(II) communication occurs for the $(\text{NH}_3)_4\text{Ru}(\text{dpp})\text{Ru}(\text{NH}_3)_4^{4+}$ complex as replacement of competitive π -back-bonding bpy ligands on Ru(II) centers with NH₃ increases electron communication through the Ru-dpp-Ru system. The $\Delta E_{1/2}(2-1)$ value indicates dpp affords enhanced metal-metal communication when compared with previously studied bridging ligands. Their electronic absorption spectra and photolability upon visible-region irradiation suggest that this class of dpp-bridged complexes may function effectively in energy-absorption and energy-transfer processes.

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